Reactivity of Alumosiloxanes for the Synthesis of new Metal Derivatives

Dissertation

Zur Erlangung des Grades
des Doktors der Naturwissenschaften
der Naturwissenschaftlich-Technischen Fakultät III
Chemie, Pharmazie, Bio- und Werkstoffwissenschaften
der Universität des Saarlandes

von
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Saarbrücken
2008

Tag des Kolloquiums:	03 April 2008
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Die vorliegende Arbeit entstand in der Zeit vom Februar 2004 bis September 2007 in der Anorganischen Chemie der Universität des Saarlandes in Saarbrücken unter Anleitung von Herrn Prof. Dr. Michael Veith.

Ich danke meinem verehrten Doktorvater, Herrn Prof. Dr. Michael Veith, recht herzlich für die interessante Themenstellung und großzügige Förderung dieser Arbeit. Seine hilfreichen Ratschläge und seine ständige Diskussionsbereitschaft während der Durchführung haben maßgeblich zum Gelingen der vorliegenden Arbeit beitragen.

Allen Mitarbeiterinnen und Mitarbeitern des Instituts für Anorganische Chemie, insbesondere dem AK Veith, die auf verschiedenste Weise zum Gelingen dieser Arbeit beigetragen haben, sei recht herzlich gedankt.

Herrn Dr. Volker Huch bin ich besonders dankbar für die Durchführung der Röntgenanalysen, für die wertvollen Ratschläge, die Diskussionsbereitschaft und auch für das gewissenhafte Korrekturlesen. Sein offenes Ohr und seine technische Versiertheit haben mir sehr geholfen.

Weiterhin danke ich Herrn Dr. Michael Zimmer für die Aufnahme der NMR-Spektren am 400MHz-Spektrometer.

Frau Helga Feuerhake gilt mein Dank für die Durchführung der Elementaranalysen.

Danke auch an den im Sommer 2007 verschiedenen Hans Conrad.

Für die gute Arbeitsatmosphäre bedanke ich mich herzlich bei meinen jetzigen und ehemaligen Kollegen von Labor 380, hier besonders bei Herrn Dr. Peter König, Frau Dr. Ina Hreleva, Herrn Dr. Thorsten Voigt, Herrn Dr. Yu Eung-Chul für ihre Freundschaft und Unterstützung in jeglicher Hinsicht.

Des Weiteren bedanke ich mich herzlich bei Frau Dipl. Lebensmittelchem. Dorothea Loytved und Frau Tatjana Kirs.

Herrn Dipl. Ing. Carsten Bubel bin ich dankbar für seinen Rückhalt und seine Unterstützung.

Ein besonderer Dank gilt meinen Freunden, die mir während dieser Arbeit Mut gemacht haben!

Je tient à remercier tout mes amis, de Saint-Dié des Vosges, de Strasbourg, de Saarbrücken et d´ailleurs…
Merci Carsten d´être là pour moi (et pour tout nos Wanawa !!)
Je remercie ma famille pour m´avoir soutenue.
Merci Eva, Antoine, Le bébé, Amadou.
Merci Raphaël.

Table of abbreviations

acac	Acetylacetonate or 2,4-pentanedionate
av.	average
Cp	cyclopentadienyl
ε	Extinction
Eq.	Equation
eq.	equivalent
Et	ethyl
et al.	and others (latin: et alii or et alteri)
*i*Pr	*iso*-propyl
IR	infrared
λ	wavelength
M	metal
Me	methyl
NMR	Nuclear Magnetic Resonance
Ph	phenyl
quasi	similar (latin: veluti in speculum)
*t*Bu	tertiary butyl
tert	tertiary
THF / thf	tetrahydrofuran / ~ as ligand
UV-Vis	Ultra Violet-Visible spectroscopy

Table of compounds

$[(Ph_2Si)_2O_3]_4[Al(OH)]_4$	*Ref. 9*	**1**
$[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$	*Ref. 14*	**2**
$[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2.\ 2Et_2O$	*sh2331*	**3**
$[(Ph_2Si)_2O_3]_4[Al(OLi)]_2\ [Al(OH)(LiOH)]_2.2Et_2O.\ 2THF$	*sh2448*	**4**
$[(Ph_2Si)_2O_3]_4[Al(OLi)]_2\ [Al(OH)(LiOH)]_2.4Et_2O.\ 4THF$	*sh2228*	**4a**
$[(Ph_2Si)_2O_3]_4[Al(OTl)]_2[Al(OH)(TlOEt)]_2.\ 2Et_2O$	-	**5**
$Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.3HO^tBu$	*sh2351*	**6**
$[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$	*sh2387*	**7**
$[(Ph_2Si)_2O_3]_4[Al(OLi)]_4.6THF$	*sh2282*	**8**
$[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.2Et_2O$	*sh2221*	**9**
$[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$	*sh2457*	**10**
$[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2Et_2O$	*sh2475*	**11**
$Al[\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Li(THF)_2\}]$	*sh2252*	**12**
$[Ni\ (H_2O)_2\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Al(acac)_2\}_2].OEt_2$	*sh2436*	**13**
$Co(H_2O)_2\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Al(acac)_2\}_2].OEt_2$	*sh2513*	**14**
$[Mg\ (H_2O)_2\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Al(acac)_2\}_2].OEt_2$	*sh2473*	**15**
$Mg\ (Et_2O)[\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Mg(OEt_2)Br\}_2]$	*sh2205*	**16**

Die vorliegende Arbeit befasst sich mit der Untersuchung der unterschiedlichen Reaktionsfähigkeit des erstmalig 1997 von Veith et al. synthetisierten Polyalumosilxans (tetrakis (μ_2-hydroxo)-(μ_2-tetraphenyldisilanoxy diolato)- Aluminium) $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) bei der Veränderung dieser bekannten Verbindung durch die Einführung von Alkali-, Hauptgruppen- oder Übergangsmetallen.

Im ersten Teil der Arbeit wird die Einbindung von Metallalkoxid und -hydroxid in **1** beschrieben, die zu einer Vergrößerung des zentralen Ringes von **1** führt. Im Rahmen der Untersuchung der Reaktivität des Alumopolysiloxans **1** wurde auch die Synthese einer Verbindung mit einer zentral angeordneten Li_3O_4Al-Gruppe vorgenommen. Ebenso wurde die Reaktivität von **1** durch die Reaktion mit einer sterisch abgeschirmten Lithium-Verbindung untersucht.

Der zweite Teil der Arbeit beinhaltet die Synthese neuartiger Komplexe von **1** mit Zinn(II), Nickel(II) und Eisen(III).
Die Reaktion von **1** mit einem Diazasilastannetidin führt zu einer Verbindung mit einer tetranuklearen Sn(II)-Einheit. Metallkomplexe mit Nickel(II) und Eisen(III) wurden durch die Einführung von Bis-(acetylaceton)-Nickel(II) bzw. Tris-(acetylaceton)-Eisen(III) in **1** erhalten, wobei ein Ligandenaustausch zu beobachten ist.

Der dritte und letzte Teil beschäftigt sich mit der Herstellung neuer aluminiumhaltiger Hetero-Metallasiloxankomplexe mit Li, Ni, Co und Mg durch die Reaktion von **1** mit Metall(II)-bisacetylaceton-dihydrat oder Grignard-Verbindungen.

The subject of this work is the study of the reactivity of the polyalumosiloxane (tetrakis (μ_2-hydroxo)-(μ_2-tetraphenyldisilanoxy diolato)- aluminium) $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) synthesized in 1997 by Veith *et al.*. The aim of the work is to modify this well-known compound by the introduction of alkaline-, main group- or transition-metals.

The first part deals with the insertion of metal alkoxide or hydroxide into **1** and the substitution of hydrogen of the central $Al_4(OH)_4$-ring by the corresponding metals involving an enlargement of the central ring of **1**. Still within the scope of the research, the synthesis of a new compound containing a cubic central arrangement of Li_3O_4Al was performed.
Furthermore, the reactivity of **1** towards a sterically encumbered lithium compound has been studied.
The second part includes the synthesis of new complex derivatives of **1** containing tin(II), nickel(II) and iron(III).
The reaction between **1** and Diazasilastannetidine leads to a compound containing a tetra-nuclear Sn(II) entity. In addition, nickel(II) and iron(II) complexes have been obtained by the introduction of Bis-(acetylacetonato) nickel(II) and Tris-(acetylacetonato) iron(III) into **1** including ligands redistribution.
The last part is devoted to the design of new aluminium hetero-metallasiloxane complexes containing Li, Ni, Co and Mg atoms resulting from the reaction of **1** with Bisacetylacetone dihydrate metal (II) or Grignard reagent.

1. Introduction and aim of the work

1.1. Aluminosilicates

Aluminosilicates are part of a wide variety of naturally occurring minerals. They contain the Al-O-Si unit as the basic fragment. Examples of aluminosilicates are feldspars like gismondine $[CaAl_2Si_2O_8(H_2O)]n$, cancrinite $[Na_6Al_6Si_6O_{24}(CaCO_3)(H_2O)]n$ or sodalite $Na_8[AlSiO_4]_6Cl_2$.

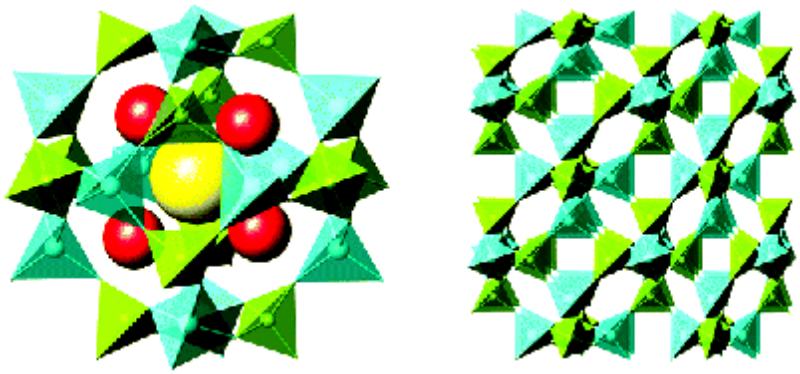
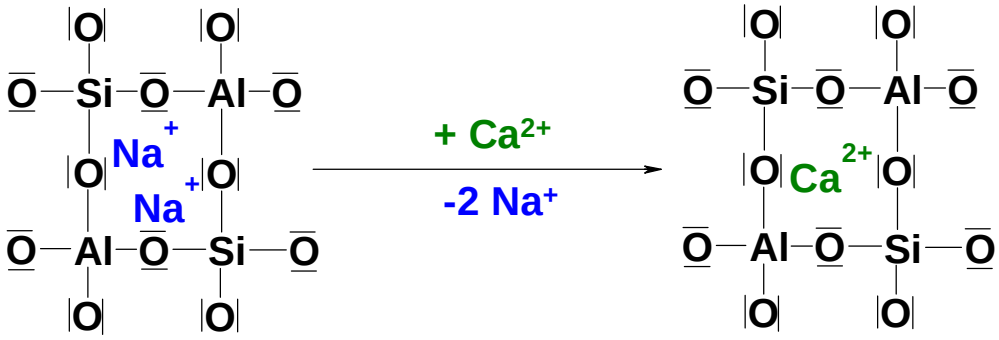


Figure 1: The sodalite structure: $Na_8[AlSiO_4]_6Cl_2$.

The linking of alternate SiO_4 (green) and AlO_4 (blue) tetrahedra forms a body centered arrangement of framework cages, right. Each cage contains a central anion (yellow) surrounded tetrahedrally by cations (red), left; the cations also interact strongly with three framework oxygen atoms to produce a distorted tetrahedral environment for these ions [1].

Mobile and readily exchangeable (Scheme 1) cations neutralize the negative charges due to the AlO_4^- units.



Scheme 1: Representation of a ionic exchange in aluminosilicates.

Many synthetic and natural zeolites are built upon the same construction principle. Zeolites are three-dimensional crystalline networks of edge-linked, oxygen-sharing AlO_4^- and SiO_4 tetrahedra that contain 5-13 Å wide pore systems [2, 3].

The regular dimensions of channels and voids make it possible to implement well-defined nanowires and cluster assemblies with narrow size distributions [4]. Furthermore, zeolites are insulators with band gaps around 5 eV, making them excellent supports for optically active host guest materials [5, 6]. The more than 60 topologically distinct framework types offer a large variety of one, two, and three-dimensional pore systems.

The Brönsted acidic sites have been the subject of several experimental and theoretical investigations because of their importance for understanding the catalytic activity of these materials. In general, the activity of zeolites is rationalized in terms of the acidity of Si(OH)Al hydroxyl group [7].
Catalysts with transition metal cations, such as Co, Cu, Ni, Fe, Ag, coordinated to the cationic sites of zeolites attract a lot of attention. They exhibit high activity in NO decomposition (Cu) as well as in selective catalytic reduction of NO with low paraffin [8, 9], and in selective activation of ethane or propane (Co) in their ammoxidation to corresponding nitriles [10, 11]. They are often prepared by exchanging part of the original guest ions in the zeolite against ions of the desired metal. Usually, these metal ions are introduced in their complexed form. The ligands are subsequently destroyed by heating, the so-called "calcination step", and naked metal ions are formed.
The catalytic sites are represented by metal ions that are coordinated in a ligand field of oxygen arrangement. These sites are able to carry extraframework ligands and hence form the reaction centers in the course of catalytic transformations [12].

Additionally, among zeolites which are composed of three-dimensional networks of SiO_4 and AlO_4 tetrahedra, there is a large variation of their composition which can be modified and used for many applications. There are several types of synthetic zeolites formed by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates. One of the important processes to carry out zeolite synthesis is sol-gel processing [5].

Alumopolysiloxanes are considered as molecular counterpart of aluminosilicates. Molecular aluminosiloxanes, which function as model substances for zeolites, are known. The first structural report [13] of an alumo-polysiloxane was reported in 1968 by Bonamico *et al.*. The molecule $(Me_2SiO)_4(OAlBr_2)(AlBr)$ consists of a $Si_4Al_2O_6$ 12-membered ring which is spiro-cyclically bridged by an Al-Br unit. (Figure 2)

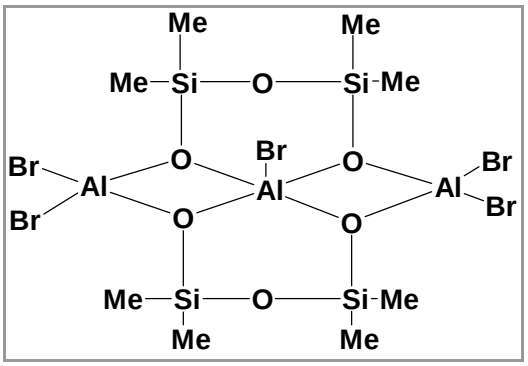
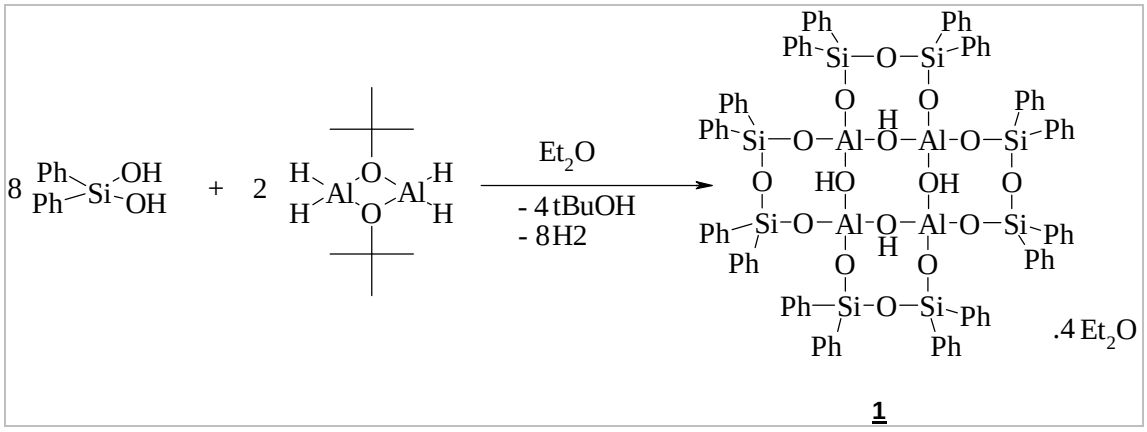


Figure 2 : Representation of $(Me_2SiO)_4(OAlBr_2)(AlBr)$.

Alumopolysiloxane $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ reported [14] in 1997 by Veith *et al.* has also a aluminosilicate framework. The molecular structure can be derived from a 24-membered $Si_8Al_4O_{12}$ cycle which is polycyclic. The compound $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ has a polycyclic framework consisting of Al, Si, and O atoms; the silicon atoms bear phenyl groups as organic ligands. The structure contains a central Al_4O_4 ring. The Loewenstein rule (according to which the AlO_4 tetrahedra in such compounds are always separated by silicon atoms) is applicable to this molecular aluminum/silicon-oxygen compound [15]. No similar structure has until now been detected in natural aluminosilicates.

1.2. Polyalumosiloxane $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (1) and it's derivatives

Polyalumosiloxane (tetrakis (μ_2-hydroxo)-(μ_2-tetraphenyldisilanoxy diolato)- aluminium) $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) is formed by the reaction of $Ph_2Si(OH)_2$ with *tert*-butoxyalane [16] in diethyl-ether as solvent.



Eq. 1: Synthesis of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (1).

Treatment of tert-butoxyaluminium [16a-b] hydride with four molecules of diphenylsilandiol [17] leads to $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) in acceptable yields. The disilanolate ligands ($OSi(Ph_2)OSi(Ph_2)O$) in a μ_2-bridging present in the molecule can be attributed to the condensation of $Ph_2Si(OH)_2$ monomers.

Compound **1** is an isolated aluminopolysiloxane, which crystallizes with four molecules of diethyl-ether. There is an $Al_4(OH)_4$, eight-membered ring in the center of the structure; the Al(OH)Al edges are spanned by four disiloxane bridges [18]. This results in an arrangement of five eight-membered rings and the molecule has approximately S_4, point symmetry. The annulated rings form an average angle of 131.5° (O-Al….Al) with the central four-membered Al_4-ring.

The S_4 symmetry is disrupted because only three of the four molecules of diethyl ether are coordinated through their oxygen atoms to the hydrogen atoms of the central OH groups in the $Al_4(OH)_4$, unit. The fourth diethyl-ether molecule acts only as a space filler in the *Van der Waals* lattice. The coordination of the ether molecules is an indirect evidence of the presence of OH groups in the central eight-membered ring; the O-O distances of the O- H….O bridges lie in the range of 2.60-2.70 Å, and indicate strong hydrogen bonding. The Al-O-A1 bridges are virtually symmetrical (Al-O bond lengths of 1.787(3)-1.814(3) Å).

Only three of the four ether molecules are directly coordinated to the $Al_4(OH)_4$, unit because there is not enough space for another ether molecule to approach the free OH group. Evidently coordination of the fourth diethyl-ether molecule would require distortion of the $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ polycycle. (Figure 3, left).

During the formation of **1**, there is formation of *tert*-butanol molecules which can also be coordinated through their oxygen atom to a hydrogen atom of the $Al_4(OH)_4$ unit. One *tert*-butanol molecule is accepted in the Lewis acid-base $Al_4(OH)_4$ core because of the steric requirement of the donor guest molecule and the congestion of **1**. Thus, similarly to the etherate compound, only two of the three diethyl-ether molecules are directly coordinated through their oxygen atoms to the hydrogen atoms of **1**. The third diethyl-ether molecule serves to optimize the crystal packing of **1**. (Figure 3, right)

In the case of triethylamine only two molecules react with **1**.$4Et_2O$ with complete substitution or loss of the ether molecules to form the amine adduct. Amines as well as ethers and alcohols serve as acceptor for the protons of **1**.

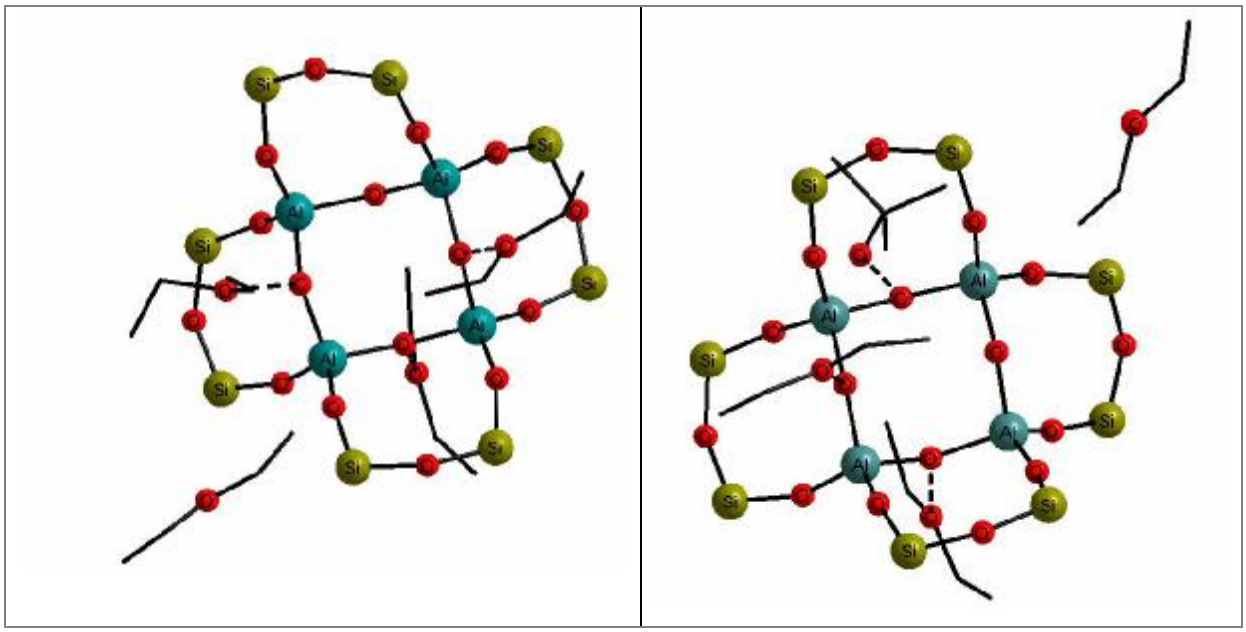


Figure 3: Representation of the crystal structures of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O$ (left) and of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4.3Et_2O.HOtBu$ (right). The phenyl groups of Ph_2Si atoms are omitted for clarity.

Research efforts have been focused on the synthesis of compounds derivates from $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) using the acidic character of the hydrogen from the OH groups, the four protons in this compound can easily be replaced by electropositive elements [19] like lithium (Eq.2) using bases such PhLi.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} + 4PhLi \xrightarrow[-4PhH]{Et_2O} \underset{\mathbf{2}.4Et_2O}{[(Ph_2Si)_2O_3]_4[Al(OLi)]_4.4Et_2O}$$

Eq. 2: Synthesis of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (2).

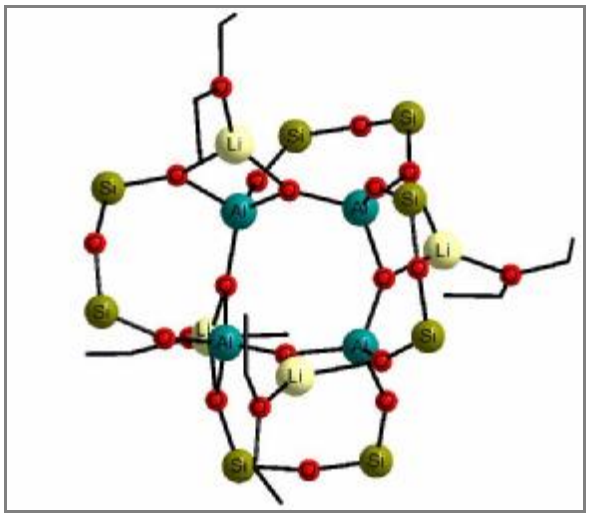


Figure 4: Representation of the structure of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (2)

(Phenyl groups of the Ph_2Si are no represented for clarity.)

Compound **2** has the same central cyclic structural unit as **1**, but has supplementary four AlO_2Li rings. Each lithium atom is additionally connected to a diethyl ether ligand molecule, so that approximately trigonal-planar LiO_3 units are formed. Alternatively, the inner unit can also be described as consisting of four AlO_4 tetrahedra connected through common vertices with one edge of each tetrahedron being bridged by a lithium atom.
The similarity to lithium aluminium silicates is also reflected by the formula $[\{Ph_2SiO\}_8][\{LiAlO_2\}_4].4OEt_2$. The point symmetry of the molecule in the crystal is C_2; however, the deviation from S_4 (compound **1**) symmetry is only slight.

In recent time, it has been shown that one and two metals of the group 14 (Sn, Ge, Pb) can also be coordinated [20] in the structure of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**). (Eq.3, 4).

Two hydrogen atoms of the central eight-membered ring of **1** are replaced by one Sn or Ge metal atom [21]. These compounds have the same cyclic Al_4O_4 structural unit surrounded by four disilanolate ligands as **1**.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} + 2MCp_2 \xrightarrow[-4Et_2O\ -MCp_2]{Dioxan} [(Ph_2Si)_2O_3]_4[Al_4(OH)_2O_2]M.2C_4H_8O_2$$

Eq. 3: Synthesis of $[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2M$. (M=Sn, Pb).

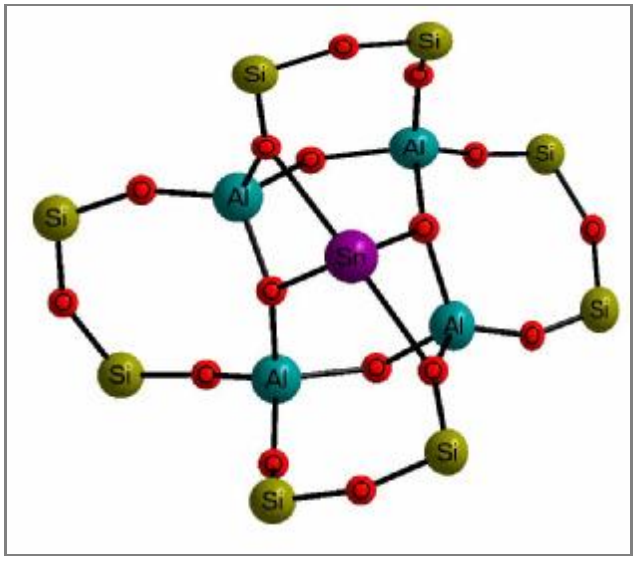


Figure 5 : Representation of the structure of $[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2Sn$.
(The phenyl groups on the Si atoms are omitted for clarity.)

All the hydrogen atoms can be replaced by two metal atoms [20]. Practically, the use of the dimer $[(^tBuO)_2Sn]_2$ [22] in presence of **1** in THF as solvent leads to a derivative of compound **1**, performing a coordination with two tin metals.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} + [(^tBuO)_2Sn]_2 \xrightarrow[-4\,^tBuOH]{THF} [(Ph_2Si)_2O_3]_4[AlO]_4Sn_2.2THF$$

Eq. 4 : Synthesis of $[(Ph_2Si)_2O_3]_4(AlO)_4Sn_2$.

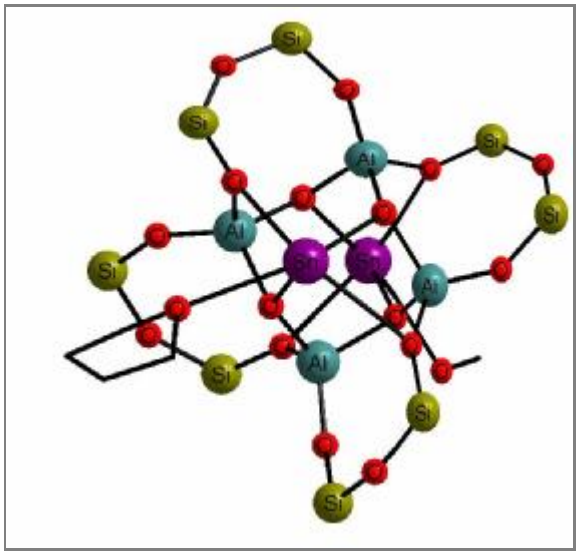


Figure 6 : Representation of the structure of $[(Ph_2Si)_2O_3]_4(AlO)_4Sn_2$.
(The phenyl groups on the Si atoms are omitted for clarity.)

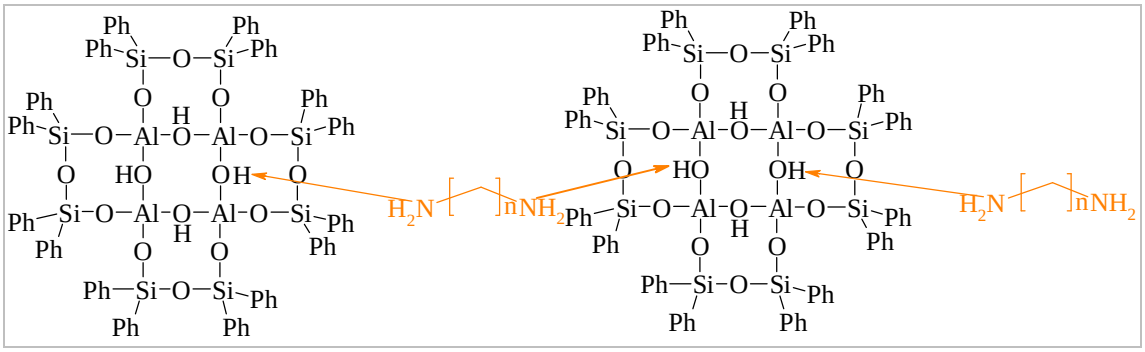
Currently, investigations reporting reactions of substitution of the hydrogen atoms from the OH groups of compound **1** by sodium atoms have been also described [23].

The reaction of four equivalents NaCp with the etherate compound $[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O$, leads to $[(Ph_2Si)_2O_3]_4[Al(ONa)]_4$. As with the Li derivative, all four hydrogen atoms of the central eight-membered ring of **1** are replaced in $[(Ph_2Si)_2O_3]_4[Al(ONa)]_4$. The Al-O-Si skeleton of **1** is disturbed only little by the introduction of sodium atoms. The compound has the same cyclic Al_4O_4 structural unit as **1**, completed by four AlO_2Na four-membered rings.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} + 4NaCp \xrightarrow[\substack{-2C_5H_5\\-4Et_2O}]{THF} [(Ph_2Si)_2O_3)_4[Al(ONa)]_4.4THF$$

Eq. 5: Synthesis of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_4$.

Study of the coordination of di-hapto bases such poly methylene diamines ($_2$HN-(CH$_2$)n-NH$_2$) on **1** have also been explored [21,24]. These reactions using the acidic character of the protons from the OH groups lead to intramolecular loops or to intermolecular aggregations of molecules (Scheme 2).

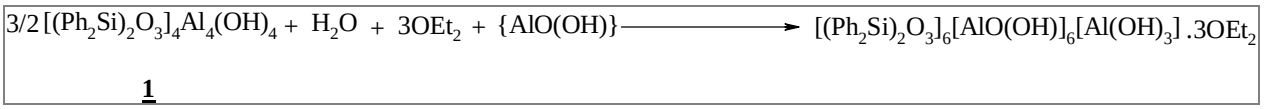


Scheme 2 : Representation of the intermolecular connection of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ via diamine $H_2N(CH_2)_nNH_2$.

The studies have already been focused on the reactivity of **1** toward water or ammonia [24, 25].

Actually, small bases such water or ammonia can be introduced inside $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) leading to the formation of new structures (Figure 7).

The reactivity consists of a basic effect on the aluminium Lewis acid. The reaction between **1** and a limited amount of water leads to $[(Ph_2Si)_2O_3]_6[Al_6(OH)_3][Al(OH)_6].3OEt_2$ (Eq. 6).



Eq. 6 : Reaction of 1 with water leading to $[(Ph_2Si)_2O_3]_6[Al_6(OH)_3][Al(OH)_6].3OEt_2$.

This compound is a polycycle containing an inner $[Al(OH)_6]^{3-}$ octahedron linked to three double tetrahedral $[Al_2O_2(OH)]^+$ cations connected by six disilanolate ligands.

Similar rearrangement of **1** is observed when water is replaced by ammonia molecules, the compound obtained, $\{[Ph_2SiO)_{12}[Al_5O_7(OH)][Al(OH)_2(NH_3)_2].OEt_2\}^-$, is a polycyclic arrangement of AlO_4 tetrahedra which contains an octahedrally coordinated aluminium atom (two nitrogen atoms and four oxygen atoms forming the coordination polyhedron). (Figure 7)

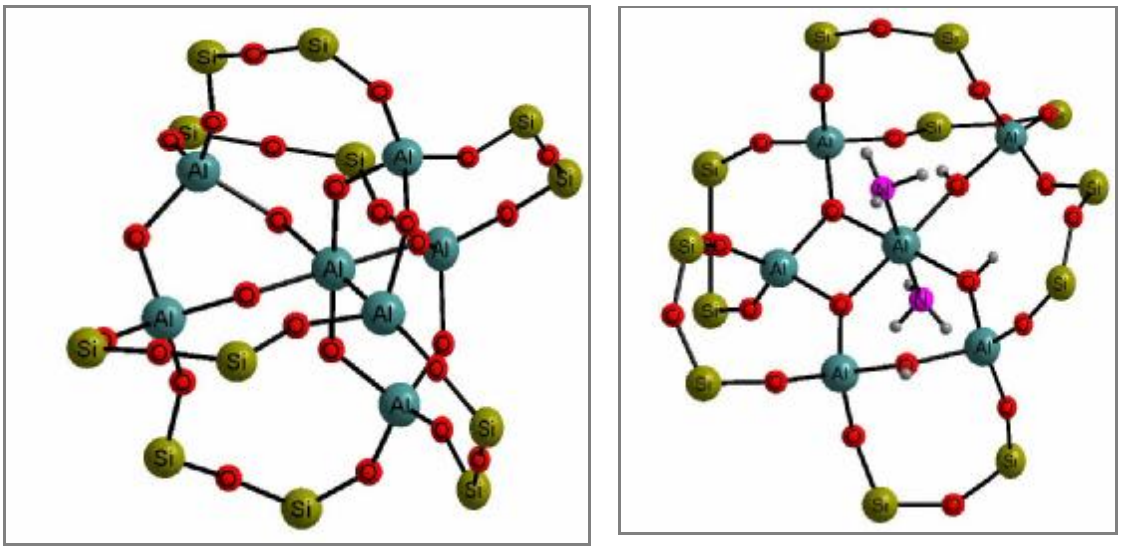


Figure 7 : Representation of the structures of $[(Ph_2Si)_2O_3]_6[Al_6(OH)_3][Al(OH)_6].3OEt_2$ (left) and $\{[Ph_2SiO)_{12}[Al_5O_7(OH)][Al(OH)_2(NH_3)_2].OEt_2\}^-$ (right).

(The phenyl groups on the Si atoms are omitted for clarity.)

The reaction of the alumopolysiloxane **1** toward hexamethyldisilazane was also studied [26] and leads to the triple ionic $[Ph_2SiO]_8[AlO_2]_2[AlO(O\text{-}SiMe_3)]_2[NH_4 \cdot THF]_2 \cdot 2$ THF and in the presence of pyridine to $[Ph_2SiO]_8[AlO_{1.5}]_4 \cdot 2py \cdot 1.5\ C_7H_8$.(Figure 8).

These compounds present new types of molecular structures with a central four-membered Al_2O_2-ring, on which the further aluminium atoms are attached via oxygen atoms.

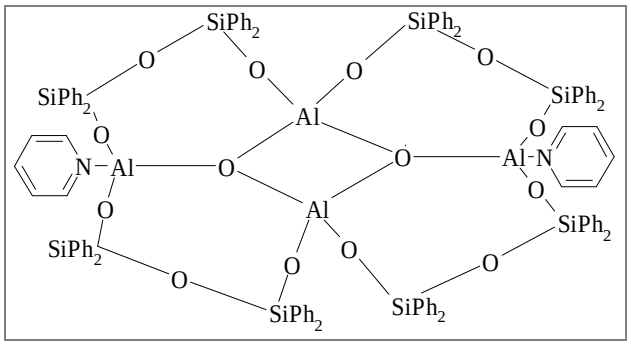


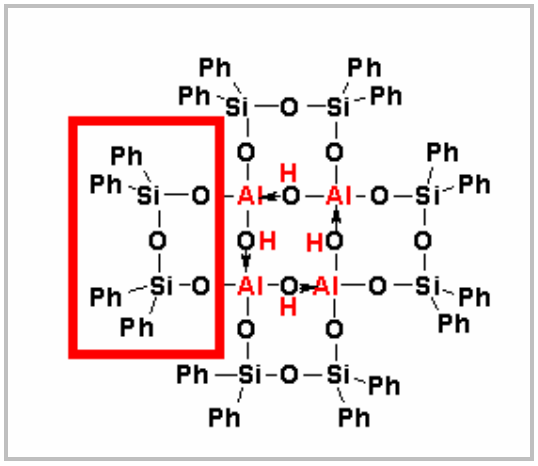
Figure 8 : Representation of $[Ph_2SiO]_8[AlO_{1.5}]_4 \cdot 2py$

In the previous researches, the structure of adducts of **1** with different organic bases functioning as electrons donors versus the protons of the hydroxide groups and ranging from monobasic ethers and amines to di-basic diamines was studied. Molecular pseudo-alumosilicates containing metals were also reported.

The different sites of reactivity involved during these researches are summarized in the scheme **1**.

Compound $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (1) holds three relevant sites of reactivity:

- Very acidic hydrogen atoms.



Scheme 1 : Reactivity sites of 1 (red).

- Al atom is a Lewis acid and particularly a strong acid because the Al^{3+} ions are considered to be small and hard, according with the HSBA [27] (Hard and Soft Base and Acid) theory.

- Disilanolate ligands are able to make some coordination [18] with a large variety of metal atoms.

1.3. Aim of the work

The subject of this work is the study of the different reactivities of the polyalumosiloxane $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ synthesized in 1997 by Veith *et al.*. The aim of the work is to modify the well-known compound by introduction of alkaline metals, main group's metals, or transition metals. Thus, the reactivity varies according to the type of the reagent used. The essence of the work will be the control and understanding of the modification process and the design of new complexes.

The introduction of metals in this polyalumosiloxane can induce an enlargement of the molecule, different rearrangements and the synthesis of new types of metallasiloxane or hetero-metallasiloxane. These three directions will be studied in details.

2. Enlargement of a eight-membered ring to a twelve-membered ring

Substitutions of the four hydrogen atoms from the OH groups of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) by electropositive elements of group I such as lithium [19] or sodium [23] inside the core **1** have previously been realized (see introduction). These compounds have the same cyclic Al_4O_4 core surrounded by four disilanolate ligands as in **1**.

During the attempt to coordinate some metals [28] into $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**), modifications of the core $Al_4(OH)_4$ can occur. In fact, some alkoxide or hydroxide groups can be inserted involving an enlargement of the central ring. The use of sodium ethoxid, thallium ethoxid and lithium hydroxid was fruitful: unusual compounds, derivatives of **1**, with twelve-membered rings are synthesized (Reaction scheme 1). The reactivity varies depending on different components; therefore other alterations of **1** were studied in order to understand the reactivity of this alumopolysiloxane.

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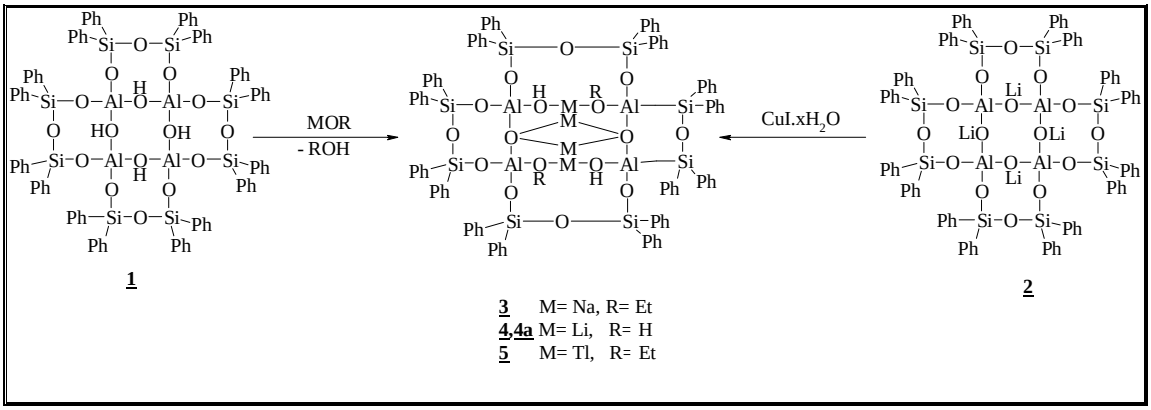


Reaction Scheme 1: Reaction between alumoxane compounds 1 and 2 with metal atoms.

2.1. Synthesis of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2.\ 2Et_2O$ (3)

Compound $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2.\ 2Et_2O$ **3** is obtained by the reaction of sodium ethoxid (NaOEt) and $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) (with the stoichiometry 4/1 respectively) in diethyl-ether with elimination of two molecules of ethanol. The compound can be easily purified by re-crystallization, on standing at +4°C, from the solvent to give colorless crystals with a yield of 66%.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} \xrightarrow[-2\ EtOH]{\begin{array}{c}4\ NaOEt\\ Et_2O\end{array}} \underset{\mathbf{3}}{[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2.2\ Et_2O}$$

Equation 1: Synthesis of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2.\ 2Et_2O$ (3)

The reaction seems to be initiated by the insertion of two NaOEt molecules inside the central eight-membered ring of **1**. The $Al_4(OH)_4$ center of **1** turns into a twelve-membered ring ([-Al-O-Al-O-Na-O]$_2$) containing four aluminium atoms and two sodium atoms.

Simultaneously, or in a second step, substitutions of the acidic OH-groups occur as well. In fact, the hydrogen atoms of two hydroxide groups from **1** are substituted by sodium atoms with elimination of two ethanol molecules. This leads to the formation of a Na_2O_2 four-membered ring inside the twelve-membered ring.

The ^{29}Si-NMR spectra of a solution of **3** in d^6-benzene display two distinct signals at -46.24ppm and at -42.51ppm. They clearly confirm the presence of two types of silicon atoms which is consistent with the loss of symmetry for the free molecule **1** (almost D_{2d}).

The ^{1}H-NMR spectrum of the same solution shows multiplets signals for the phenyl groups between 7.15ppm and 8.16ppm. The signals for the CH_3 protons from the NaOEt (triplet at 0.58ppm, 6H) are distinct from the signal of the two diethyl-ether molecules coordinated to the sodium atoms (triplet at 1.07ppm, 12H).

2.1.1. Crystal structure determination of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ (3)

A crystal of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ (**3**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a triclinic crystal system [126]. The R-value is 6.41%. In table 1 are reported the crystal data and the structure refinement for the compound and in table 2 are reported some selected bond lengths and angles of interest.

Table 1 : Crystal data and structure refinement for sh2331.

Identification code	sh2331	
Empirical formula	$C_{108}\ H_{112}\ Al_4\ Na_4\ O_{20}\ Si_8$	
Formula weight	2154.58	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 13.301(3) Å	α= 109.99(3)°.

	b = 16.131(3) Å	β= 107.01(3)°.
	c = 16.227(3) Å	γ = 91.57(3)°.
Volume	3097.1(11) $Å^3$	
Z	1	
Density (calculated)	1.155 Mg/m^3	
Absorption coefficient	0.188 mm^{-1}	
F(000)	1128	
Crystal size	0.15 x 0.3 x 0.4 mm^3	
Theta range for data collection	2.25 to 24.12°.	
Index ranges	-15<=h<=15, -18<=k<=18, -18<=l<=18	
Reflections collected	26584	
Independent reflections	9103 [R(int) = 0.0385]	
Completeness to theta = 24.12°	92.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9103 / 0 / 676	
Goodness-of-fit on F^2	1.743	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1874	
R indices (all data)	R1 = 0.0786, wR2 = 0.1955	
Largest diff. peak and hole	0.838 and -0.369 $e.Å^{-3}$	

Table 2 : Selected bond lengths [Å] and angles [°] for sh2331.

Al(1)-O(4)	1.733(3)	Na(1)-O(1)	2.410(3)
Al(1)-O(1)	1.735(3)	Na(1)-O(1)´	2.411(3)
Al(1)-O(9)	1.765(2)	Na(1)-O(2)	2.596(3)
Al(1)-O(3)	1.768(3)	Na(1)-O(7)	2.743(3)
Al(1)-Na(2)	3.114(2)	Na(1)-O(3)´	2.779(4)
Al(1)-Na(1)´	3.253(2)	Na(2)-O(2)´	2.314(3)
Al(2)-O(6)	1.721(3)	Na(2)-O(10)	2.319(4)
Al(2)-O(1)	1.734(2)	Na(2)-O(3)	2.336(4)
Al(2)-O(7)´	1.757(3)	Na(2)-O(9)	2.480(3)
Al(2)-O(2)	1.764(3)		

O(4)-Al(1)-O(1)	115.7(1)	O(6)-Al(2)-O(1)	117.7(1)
O(4)-Al(1)-O(9)	110.5(1)	O(6)-Al(2)-O(7)´	110.2(1)
O(1)-Al(1)-O(9)	109.6(1)	O(1)-Al(2)-O(7)´	105.2(1)
O(4)-Al(1)-O(3)	116.0(2)	O(6)-Al(2)-O(2)	112.5(1)
O(1)-Al(1)-O(3)	104.1(2)	O(1)-Al(2)-O(2)	105.6(1)
O(9)-Al(1)-O(3)	99.80(1)	O(7)´-Al(2)-O(2)	105.1(2)

2.1.2. Crystal structure description of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ (3)

$[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ (**3**) (Figure 9) crystallizes in the triclinic system in the centrosymmetric space group $P\bar{1}$. The compound has a Na_2O_2 four-membered ring core surrounded by a 12-membered ring containing two sodium atoms and spanned by four disilanolate ligands.

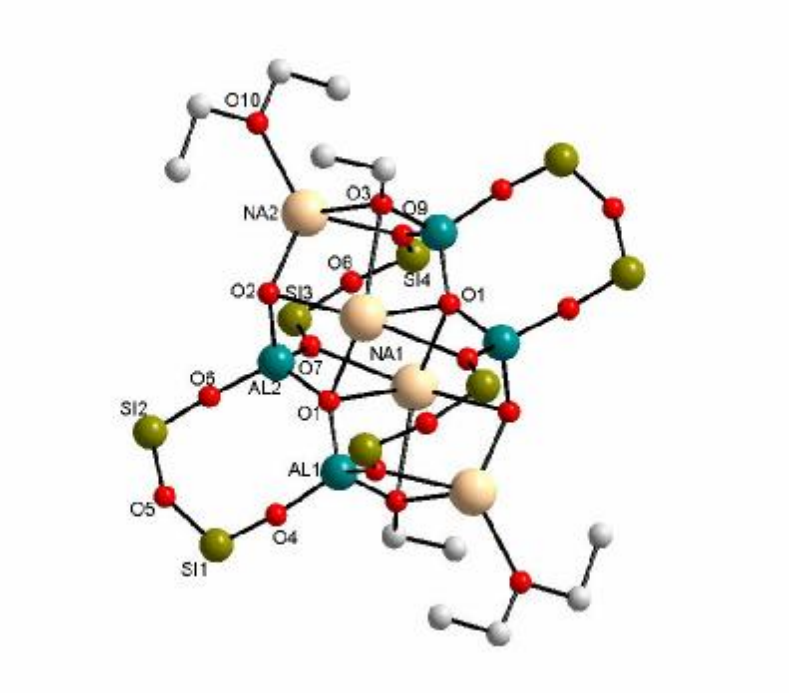


Figure 9: **Structure of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$**
(Phenyl groups of the Ph_2Si are no represented for clarity.)
Unlabeled atoms are related to those shown by a crystallographic symmetry between Na(1) and Na(1)´.

The central Na_2O_2 (Figure 10) is situated inside the main twelve-membered cycle which is composed of $[-O(1)-Al(1)-O(3)-Na(2)-O(2)-Al(2)-]_2$ (Figure 11). Most of the Al-O bond length are between 1.729(1)Å and 1.739(1)Å. Due to the ethyl subsituents on O(2) and the hydrogen atoms on O(3), the Al(2)-O(2) and Al(1)-O(3) bond lengths are somewhat elongated (1.7671(5)Å and 1.7683(4)Å).

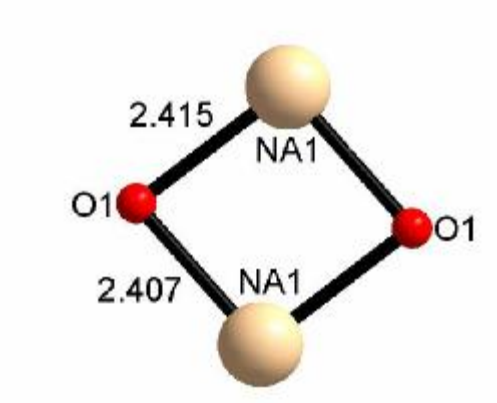


Figure 10: Distances (Å) Na-O bond of the Na_2O_2 core

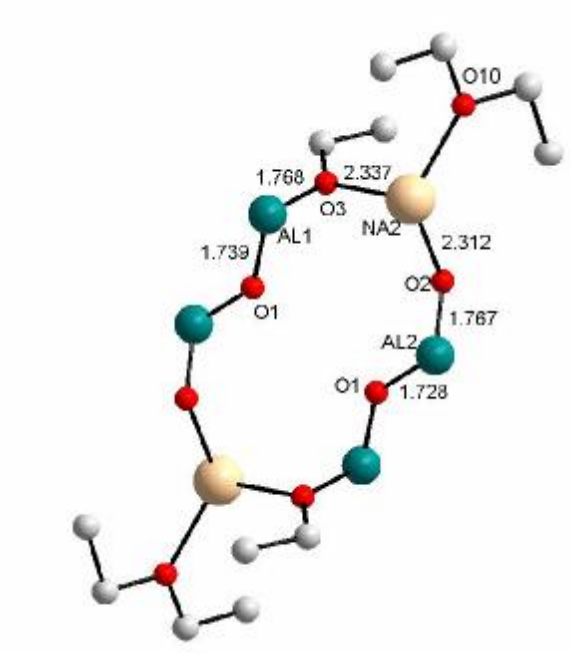


Figure 11: Distances (Å) Na-O and Al-O bonds of the "12-membered ring"

The sodium atoms Na(1) are penta-coordinated by five oxygen atoms (Figure 12). The Na(1)-O bond length vary from 2,41(3)Å to 2,779(4)Å. The longer length corresponds to the distance from the oxygen O(7) inherent to the ethoxide group inserted and the shorter agrees with the oxygen O(1) from the core Na_2O_2. The oxygen atoms around the Na(1) atom show a very distorted trigonal bipyramidal arrangement. Atoms O(1), O(3), and O(1´) form the trigonal plan and share angles of 92,98(1)°, 125,48(1)° and 63,84(1)°.

The sodium atoms Na(2) are tetra-coordinated surrounded by oxygen atoms (Figure 12), one of them belongs to the coordinated diethyl-ether O(10) with a bond length of 2.319(4)Å. The Na-O distances range from 2,314(3)Å to 2,480(3)Å. The shorter distance correspond to the distance Na(2)-O(2)H(-Al)

and the longer displays a coordination with one oxygen atom from a disilanolate ligand O(9). The (O-Na-O) bond angles at Na(2) vary from 68,167(2)° to 122,826(2)°.

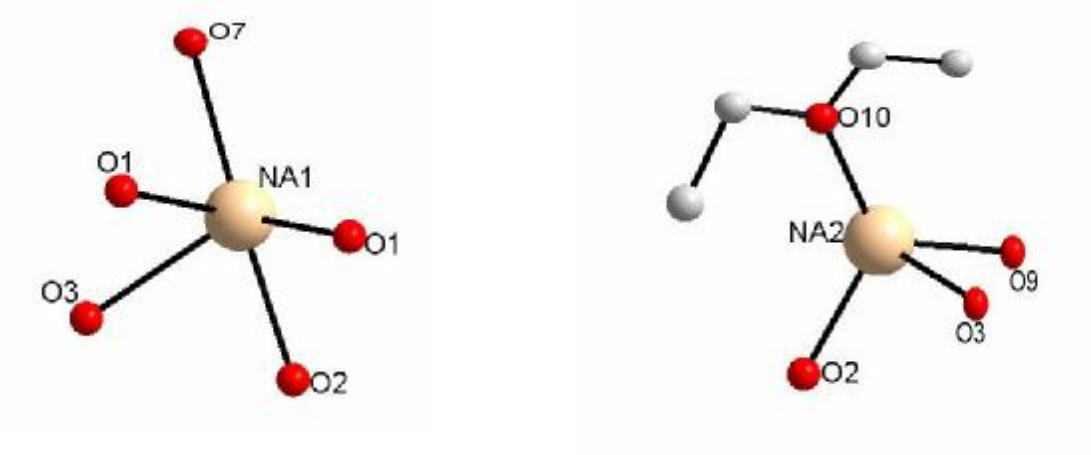


Figure 12 : Penta-coordination and tetra-coordination environment around Na(1) and Na(2).

Four disilanolate ligands [18] are present in the structure, two of them are bridging a Al-O-Al link and the two other bridge a longer chain Al-O(H)-Na-O(Et)-Al. Nevertheless, the Si-O bond lengths are, as in **1**, about 1.6Å. Consequently, the "up and down" conformation of the four siloxane groups of **1** is replaced by a conformation where two disilanolate bridges are in approximately the same plan as the 12-membered ring and the two others opposite ligands are up and down of this plan. The Al-O(Si) distances range from 1.721(3)Å to 1.733(3)Å. These distances are close to those [14] observed in **1**.

2.2. Synthesis of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (4)

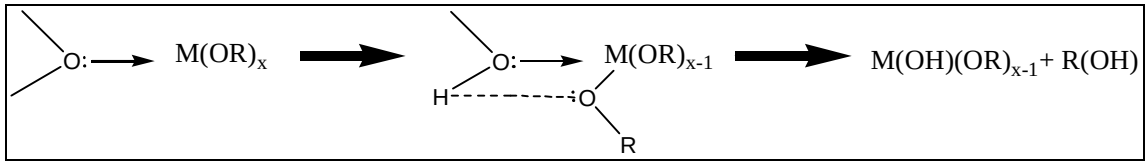
The reactivity of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) towards water molecules was already studied [24] (see introduction), and leads to unusual compounds issue of the re-arrangement of **1** (see introduction). It was then interesting to study the behavior of compound **2** towards water. The reagent $CuI.xH_2O$ was used in order to have a limited quantity of water.

The reaction between compound $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (**2**) with copper iodide hydrate ($CuI.xH_2O$) (in a *ratio* 1/4) in THF was realized. Colorless crystals were obtained by re-crystallization in diethyl-ether, after filtration of the residual $CuI.(x-2)H_2O$, with a yield of 25%.
The structure determination (described in chapter 2.2.1) revealed the formation of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF.

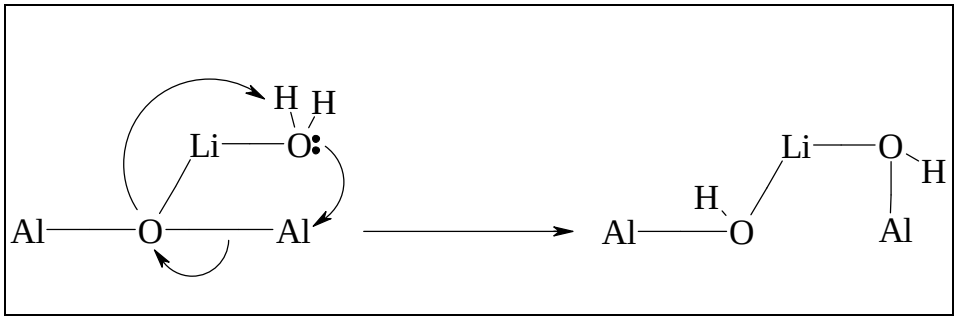
$$\underset{\mathbf{2}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OLi)_4.4Et_2O} \xrightarrow[THF]{CuI.xH_2O} \underset{\mathbf{4}}{[(Ph_2Si)_2O_3]_4[Al(OLi)]_2[Al(OH)(LiOH)]_2}.\ 2THF.2\ Et_2O$$

Equation 2: Synthesis of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (4)

It seems clear that the water introduced by the copper salt is responsible for the most probable intermediate formation of LiOH. More remarkable is the fact that a similar [Al-O-Al-O-Li-O] assembly was build very reminiscent to the formation of the corresponding sodium ring in **3**.
From the general properties of metal alkoxides [29], a proposal for the mechanism of the reaction can be given. In fact, metal alkoxides are in most cases water sensitive, an effect which is used in the so called sol/gel process [30, 31, 32], and which leads to meta-stable products as the metal hydroxide or more commonly the hydrated metal oxide. Under carefully controlled conditions intermediate products called hydroxyl-metal alkoxides M (OH) $(OR)_x$ are formed. The initial step involves the coordination of a water molecule through oxygen to the metal, addressed as nucleophilic process[33]. (Scheme 3)
One of the protons of the water molecule interacts with the oxygen of an alkoxide group through hydrogen bonding and, following an electronic rearrangement, a molecule of alcohol is expelled.
In the case of the formation of **4** "hydrolysis" is carried out by $CuI.xH_2O$ which can be considered as a water reservoir [34]. The electronic rearrangement leads to the re-protonation of one oxygen atom connected to the aluminium atom. (Scheme 4)



Scheme 3: Proton transfert from the water molecule to the metal alkoxide.

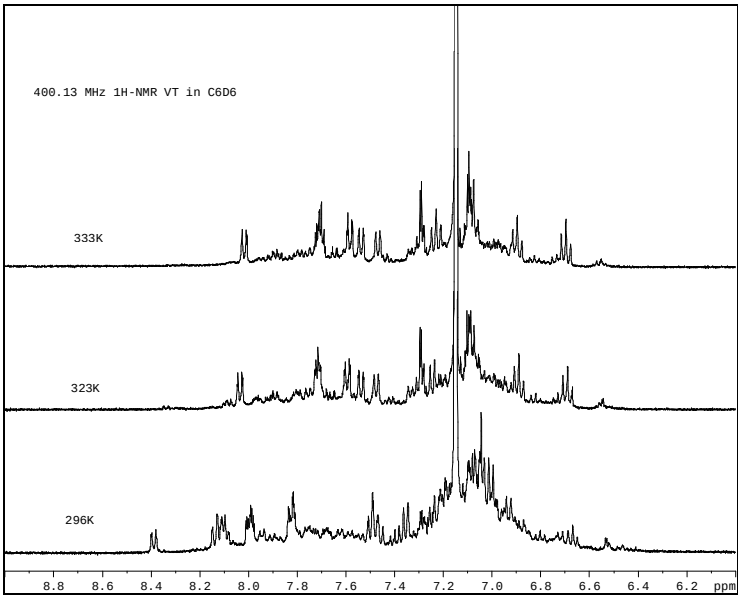


Scheme 4: Proposed reaction pathway for the rearrangement of 2 during the reaction with H_2O molecules

The ^{29}Si-NMR spectrum of a solution of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (**4**) in C_6D_6 shows two signals at -42.98ppm and -45.80ppm corresponding to the two silicon atoms environments.

Due to the weak intensity of the signal for the phenyl groups on the silicon atom the ^{1}H-NMR monitoring has been made at 400MHz in C_6D_6 and at different temperatures in order to have a better resolution of these phenyl groups signals present between 7.51ppm and 7.96ppm.

The resolution of these signals is slightly better at a higher temperature (333K), which revealed a dynamic movement of the hydrogen atoms from the OH groups which are not engaged with solvent molecules (Chap.2.2.1.1., Figure 13). These protons exchange is apparently faster with a higher temperature and lead to a better resolved ^{1}H-NMR spectrum.



Graph 1 : ^{1}H-NMR spectrum of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (4) at 296, 323, 333K (signals of the phenyl groups)

The ^{13}C-NMR spectrum displays signals at 128.28ppm, 134.99ppm and at 134.88ppm corresponding to the phenyl groups of compound **4**.

2.2.1. Crystal structure determination of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (4)

Crystals of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (**4**) and $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.4Et_2O$. 4THF (**4a**) were isolated from diethyl-ether at +4°C. The R-value is 3.96% for **4** and 6.11% for **4a**. In table 3 are reported the crystal data and the structure refinement for the compound and in table 4 and 5 are reported some selected bond lengths and angles of interest [126].

Table 3: Crystal data and structure refinement for sh2448 and 2228.

Identification code	sh2448 **4**	sh2228 **4a**
Empirical formula	$C_{112}\ H_{120}\ Al_4\ Li_4\ O_{22}\ Si_8$	$C1_{28}\ H_{156}\ Al_4\ Li_4\ O_{26}\ Si_8$
Formula weight	2178.48	2470.93
Temperature	103(2) K	103(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions	a = 16.6098(5) Å α= 90°. b = 15.9235(5) Å β= 99.507(2) °. c = 21.5637(7) Å γ = 90°.	a = 15.020(3) Å α = 99.056(8)°. b = 15.044(2) Å β = 107.354(6)°. c = 16.263(3) Å γ = 105.404(8)°.
Volume	5625.0(3) $Å^3$	3267.8(10) $Å^3$
Z	2	1
Density (calculated)	1.286 Mg/m^3	1.256 Mg/m^3
Absorption coefficient	0.195 mm^{-1}	0.178 mm^{-1}
F(000)	2288	1308
Crystal size	0.2x 0.4 x 0.45 mm3	0.3 x 0.45 x 0.5 mm^3
Theta range for data collection	1.44 to 28.49°.	1.36 to 26.45°.
Index ranges	-22<=h<=22, -21<=k<=21, -28<=l<=28	-18<=h<=18, -18<=k<=18, -20<=l<=19
Reflections collected	67465	64590
Independent reflections	to theta = 28.49° 14058 [R(int) = 0.0434]	to theta = 26.45° 13321 [R(int) = 0.0443]
Completeness	98.6 %	98.8 %
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14058 / 0 / 686	13321 / 0 / 770

Goodness-of-fit on F^2	1.012	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0996	R1 = 0.0611, wR2 = 0.1644
R indices (all data)	R1 = 0.0578, wR2 = 0.1100	R1 = 0.0736, wR2 = 0.1738
Largest diff. peak and hole	1.063 and -0.353 e.Å^{-3}	0.714 and -0.566 e.Å^{-3}

Table 4: Selected bond lengths [Å] and angles [°] for sh2448

Al(1)-O(4)	1.720(1)	Si(1)-O(4)	1.594(1)
Al(1)-O(1)	1.745(1)	Si(1)-O(5)	1.638(1)
Al(1)-O(9)´	1.754(1)	Si(2)-O(6)	1.600(1)
Al(1)-O(3)	1.774(1)	Si(2)-O(5)	1.634(1)
Al(2)-O(6)	1.720(1)	Si(3)-O(7)	1.619(1)
Al(2)-O(1)	1.749(1)	Si(3)-O(8)	1.631(1)
Al(2)-O(7)	1.759(1)	Si(4)-O(9)	1.605(1)
Al(2)-O(2)	1.762(1)	Si(4)-O(8)	1.636(1)

O(4)-Al(1)-O(1)	115.86(6)	O(6)-Al(2)-O(7)	111.54(6)
O(4)-Al(1)-O(9)´	110.77(6)	O(1)-Al(2)-O(7)	99.80(5)
O(1)-Al(1)-O(9)´	102.90(6)	O(6)-Al(2)-O(2)	109.04(6)
O(4)-Al(1)-O(3)	110.77(6)	O(1)-Al(2)-O(2)	108.85(6)
O(1)-Al(1)-O(3)	106.16(6)	O(7)-Al(2)-O(2)	109.08(6)
O(6)-Al(2)-O(1)	118.02(6)		

Table 5: Selected bond lengths [Å] and angles [°] for sh2228

Al(1)-O(4)	1.709(2)	Si(1)-O(4)	1.586(2)
Al(1)-O(2)	1.730(2)	Si(1)-O(5)	1.623(2)
Al(1)-O(9)´	1.755(2)	Si(2)-O(6)	1.586(2)
Al(1)-O(1)	1.761(2)	Si(2)-O(5)	1.626(2)
Al(1)-Li(1)	2.740(5)	Si(3)-O(7)	1.606(2)
Al(2)-O(6)	1.710(2)	Si(3)-O(8)	1.627(2)

Al(2)-O(2)	1.736(2)	Si(4)-O(9)	1.600(2)
Al(2)-O(7)	1.741(2)	Si(4)-O(8)	1.625(2)
Al(2)-O(3)	1.761(2)		

O(4)-Al(1)-O(2)	115.00(1)	O(6)-Al(2)-O(2)	118.40(1)
O(4)-Al(1)-O(9)´	110.50(1)	O(6)-Al(2)-O(7)	110.90(1)
O(2)-Al(1)-O(9)´	101.40(1)	O(2)-Al(2)-O(7)	99.70(1)
O(4)-Al(1)-O(1)	111.90(1)	O(6)-Al(2)-O(3)	109.00(1)
O(2)-Al(1)-O(1)	108.20(1)	O(2)-Al(2)-O(3)	108.30(1)
O(9)´-Al(1)-O(1)	109.20(1)	O(7)-Al(2)-O(3)	110.10(1)

2.2.2. Crystal structure description of $(Ph_2SiO)_8(AlO)_2(AlOH)_2Li_2(LiOH)_2.2\ Et_2O.\ 2THF$ (4)

Compound **4** crystallizes in the monoclinic system in space group $P2_1/n$ with two thf molecules and two diethyl-ether molecules per unit.(Compound **4a** crystallizes in the triclinic system $P\bar{1}$ with four thf molecules and four diethyl-ether molecules).

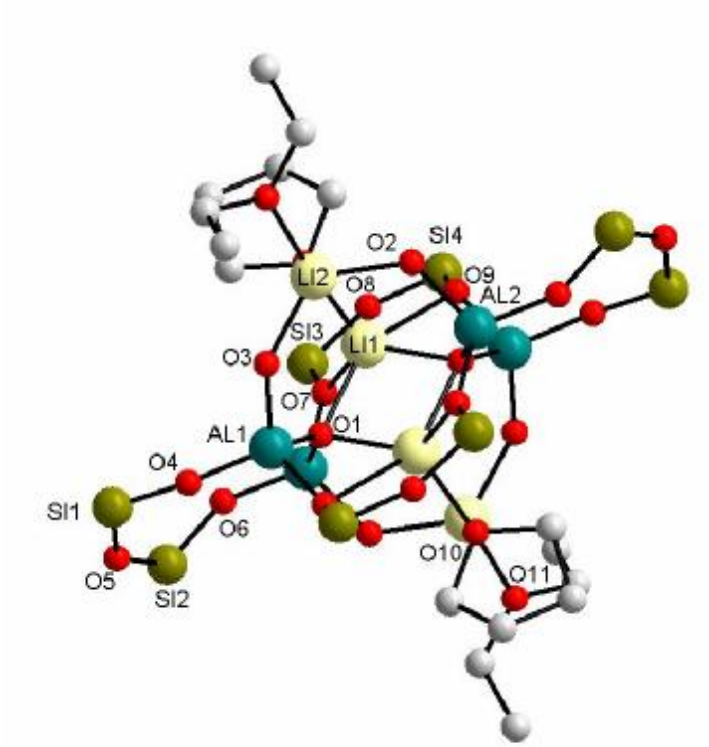


Figure 13: Structure of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2\ [Al(OH)(LiOH)]_2.2Et_2O.\ 2THF$
(Phenyl groups of the Ph_2Si are no represented for clarity.)
Unlabeled atoms are related to those shown by a crystallographic symmetry between Li(1) and Li´.

Similarly to $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2.\ 2Et_2O$ (**3**) an inner Li_2O_2 ring is formed together with the twelve-membered ring built of AlOLi units, spanned by four disilanolate ligands. (Figures 14, 15, 16)

The Li(1) atoms are penta-coordinated by oxygen atoms. Tetra-coordination is observed for the Li(2) atoms which participate in the twelve-membered ring.

The Li-O bond length range from 1,883(3)Å to to 2,530 (3)Å depending on their coordination numbers and the nature of boundary (covalent versus donor bonds). The penta-coordinated lithium atoms are surrounded by a very distorted trigonal bipyramidal oxygen atoms arrangement (O(9)-Li(1)-O(1) = 148,227(4) °). (figure15).

As usual in the trigonal bipyramids one finds shorter Li(1)-O distances in the plane compared with the "axial" oxygen atoms O(9) and O(1) (2,530(1)Å and 2,085(3)Å respectively). The tetra-coordinated of Li(2) atoms are surrounded by oxygen atoms which are present in a distorted tetrahedral fashion with bond length ranging from 1,883(3)Å to 2,065(3)Å. (figure15). In comparison to **3** in **4** two donor molecules interact with Li(2) preventing Li(2) to interact as Na(2) with the Al-O skeleton. The Al(2)-O(1) and Al(1)-O(1), Al(1)-O(3) and Al(2)-O(2) bond lengths are comparable to those found in the Al_4O_4 ring of **2** [19] .

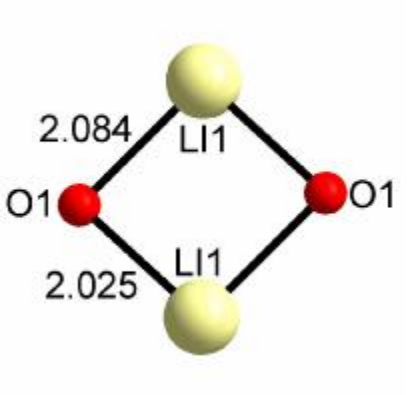


Figure 14: Distances (Å) Li-O bond of the Li_2O_2 core (average).

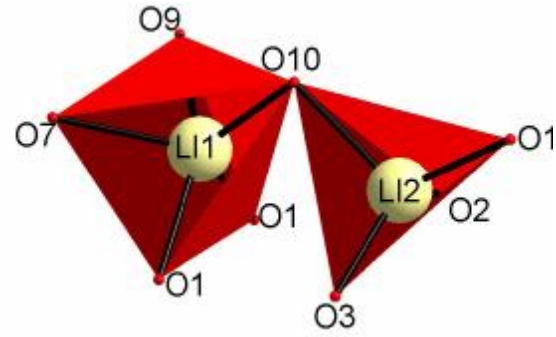


Figure 15: Environments around the lithium ions.

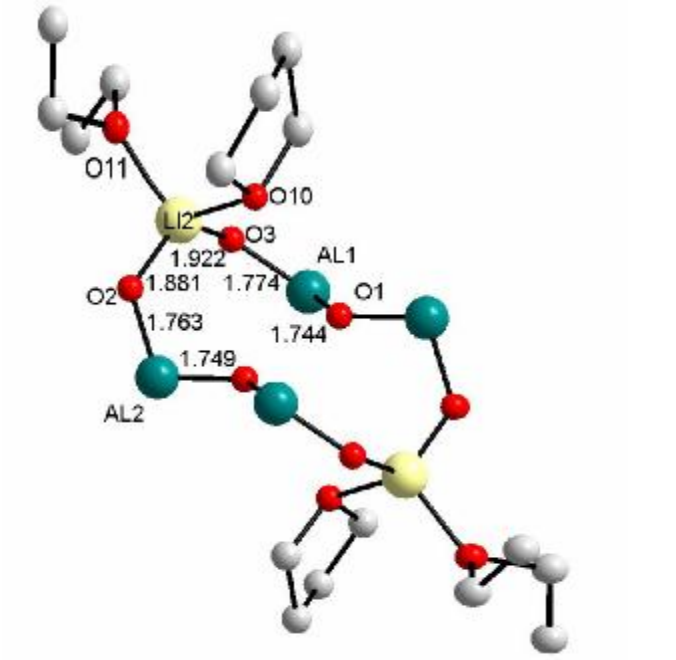


Figure 16: Distances (Å) of Li-O and Al-O bonds of the "12-membered ring" (average).

Four disilanolate ligands are present in the structure, two of them are briging a Al-O-Al link and the two other bridge a longer chain Al-O(H)-Li-O(H)-Al. Nevertheless, the Si-O bond lengths are, as in **1**, about 1.6Å.

Consequently, the "up and down" conformation of the four siloxane groups of **1** is replaced by a conformation where two disilanolate bridges are in approximately the same plan as the 12-membered ring and the two others opposite ligands are up and down of this plan as in **3**. The Al-O(Si) distances range from 1.720(1)Å to 1.759(1)Å. These distances are close to those observed in **1** [14].

The space group and some distances for compounds **3**, **4** and **4a** are reported for comparison.

Compounds	Space group	Al-O(Al)	Al-O(M)	Al-O(Si)
3	triclinic	1.728-1.739	1.767-1.768	1.721-1.733
4	monoclinic	1.744-1.749	1.763-1.774	1.720-1.759
4a	triclinic	1.746-1.750	1.761-1.774	1.721-1.751

Table 6: Space groups and distances in $(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ (3), $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF (4) and $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2[Al(OH)(LiOH)]_2.4Et_2O$. 4THF (4a).

*** Bond distances and angles are average values.**

The Al-O(Si) and Al-O(M) are close in the three compounds. On the other hand the Al-O-(Al) distance seems to be shorter in compound **3** where the NaOEt is inserted inside the Al_4O_4 ring.

2.3. Synthesis of $[(Ph_2Si)_2O_3]_4[Al(OTl)]_2[Al(OH)(TlOEt)]_2.2Et_2O$ (5)

Thallium, when compared with the remainder of the group 13 elements, shows a pronounced preference for the oxidation state +I. This has been attributed to the effect of the "inert electron pair" introduced by Sidgwick [35, 36] and since then generally used in introductory textbooks to explain the tendency of the heavier main-group elements to adopt oxidation numbers that are 2 less than the respective group number.
Moreover, Tl might be regarded as a counterpart alkali metal because Tl chemistry parallels that of the alkali metals [37].

Attempt to make such reaction was realized according to the previously established procedure (Equation 1). Four equivalents of thallium ethoxid (TlOEt) were allowed to react with $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) in diethyl-ether; the mixture was stirred 16 hours and became a clear solution. On standing at +4°C, a white solid precipitated from the clear solution, it was filtrated and dried under vacuum to give a yield of 55%.

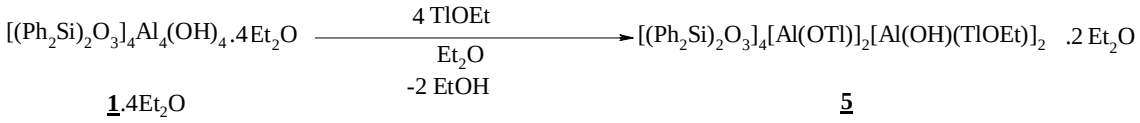
The NMR monitoring of the resulting compound seem to confirm the formation of $[(Ph_2Si)_2O_3]_4[Al(OTl)]_2[Al(OH)(TlOEt)]_2$.
In fact, the ^{29}Si NMR spectrum of **5** realized in d^6-benzene shows two characteristic signals at -41.4 and -46.13ppm corresponding to the silicon atoms in two different environments as in **3**.

The ^{1}H-NMR spectra of compound **5** in d^6-benzene show the signal corresponding to the phenyl groups and prove the presence of diethyl-ether as coordinative solvents. In fact, a triplet signal which integrates for 12 protons is present at 1.10ppm corresponding to the CH_3 of the diethyl-ether molecules. The signal for the CH_3 group from the TlOEt is situated at 0.98ppm, with an integration of 6 protons, indicating the presence of two TlOEt groups. The signal for the CH_2 group from the ethyl susbstituent is indistinct from the CH_2 group from the solvent molecule (quartet signal at 3.27ppm with an integration of 12 hydrogen atoms).
The ^{13}C-NMR spectrum displays signal at 134.97ppm, 135.12ppm and 135.82ppm agreeing with the phenyl groups and at 14.48ppm and 25.23ppm and for the ethyl group.

Furthermore, electron ionization (EI) and fast atom bombardment (FAB) mass spectrometric techniques have been used allowing analyze of compound **5** with high molecular mass [38]. This soft method is appropriate for inorganic compounds, containing complexes of metals.

Thallium involves more than one polyisotopic metal atom, Tl has two stable isotopes: ^{203}Tl (30 %) and ^{205}Tl (70%). the value (2880g.mol^{-1}) has been calculated for a multiple of the most abundant isotope. The more intense peaks observed correspond to the calculated molecular weight of compound $[(Ph_2Si)_2O_3]_4[Al(O^{205}Tl)]_2[Al(OH)(^{205}TlOEt)]_2$ (**5**).

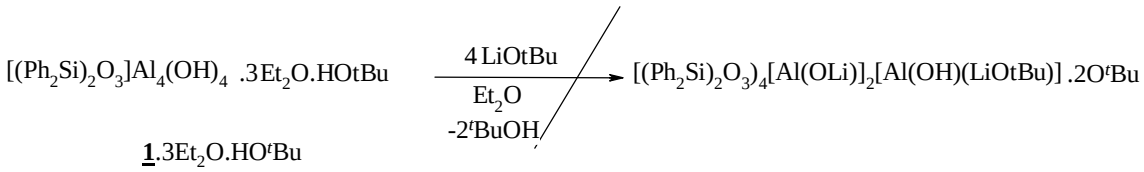
Therefore, it is well-defined that TlOEt reacts in the same way as NaOEt with **1**. Two TlOEt molecules are inserted in the central ring to give a twelve-membered central ring. Moreover, two hydrogen atoms from the hydroxide groups from **1** are also substituted by two thallium atoms.



Equation 3: Synthesis of $[(Ph_2Si)_2O_3]_4[Al(OTl)]_2[Al(OH)(TlOEt)]_2.2Et_2O$ (5).

2.4. Reaction between 1 and Lithium *tert*-butoxide

According to the previous studies (Chap. 2.2.1), an attempt of insertion of more congestioned group was realized. Compound **1**.3Et_2O.O^{t}Bu was allowed to react with four equivalents of lithium *tert*-butoxide (LiO^{t}Bu) in diethyl-ether. After 16 hours under stirring, the resulting compound crystallized easily from the solution after concentration of the solvent, as well-formed white crystals with a yield of 63%.



Equation 4 : Reaction between 1 and LiO^{t}Bu.

An attempted synthesis of an analogous Li compound to compound **4** with *tert*-butoxid (Equation 4) takes a very different course (Equation 5).

The structure determination described in chapter 2.4.1 revealed an unexpected structure, with the formula $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (**6**).

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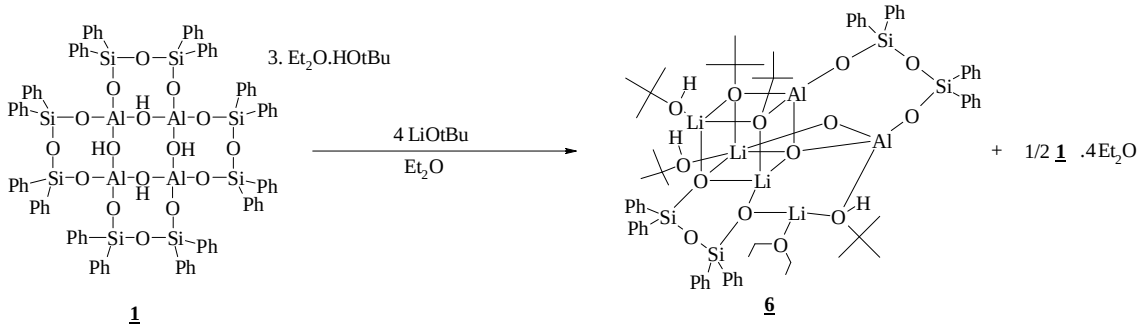
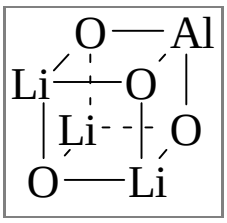


Equation 5: Synthesis of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6).

The use of a *tert*-butoxid group [39] as reagent, dramatically changes the type of product obtained. Actually, the reaction between four equivalents of lithium *tert*-butoxide and compound **1** leads to a decomposition of the initial skeleton. O^{t}Bu group is sterically hindered and involve a reorganization of the atoms. In the vast majority of lithiated organic compounds, lithium is found to be in a four-coordinate environment. Tertiary butoxides of alkali metals are known to be associated and to crystallize in a cubic system [40, 41]. The aggregates of alkali metals are formed by mutual coordination of oxygen and metal atoms. This coordination leads to the formation of a square block [42, 43, 44] formed by coordination of four oxygen atoms, three lithium ions and one aluminium atom.



Scheme 5: Li_3AlO_4 cube of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6).

The ^{29}Si-NMR spectrum of compound **6** in d^6-benzene displays two signals at -43.57ppm and -58.23ppm corresponding to the two different disilanolate ligands.

The ^{1}H NMR spectrum of **6** in d^6-benzene shows multiplets for the phenyl groups on the silicon atoms between 7.8ppm and 8ppm. Three signals representing the three different types of ($C(CH_3)$) groups are noticeable. The signal for the two terminal O^tBu groups from Li-O^tBu are present at 1.36ppm, the signal corresponding to the Li-O(H)^{t}Bu group are present at 1.24ppm and the O^tbu (Al-O(H)^{t}Bu-Li) signal is situated at 1.29ppm.

2.4.1. Crystal structure determination of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6)

A crystal of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$) (**6**) was isolated from diethyl-ether at room temperature after concentration of the solvent. From the determination and the refinement of the unit cell dimensions arose a triclinic crystal system [126]. The R-value is 4.86%. In table 7 are reported the crystal data and the structure refinement for the compound and in table 8 are reported some selected bond lengths and angles of interest.

Table 7: Crystal data and structure refinement for sh2351.

Identification code	sh2351	
Empirical formula	C_{72} H_{96} Al_2 Li_4 O_{13} Si_4	
Formula weight	1363.57	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 13.1163(6) Å	α= 99.551(2)°.
	b = 13.5950(5) Å	β= 94.242(2)°.
	c = 22.6717(9) Å	γ= 93.741(2)°.

Volume	3963.4(3) $Å^3$
Z	2
Density (calculated)	1.143 Mg/m^3
Absorption coefficient	0.152 mm^{-1}
F(000)	1452
Crystal size	0.25 x 0.3 x 0.55 mm^3
Theta range for data collection	1.52 to 26.27°.
Index ranges	-16<=h<=16, -16<=k<=16, -28<=l<=28
Reflections collected	74333
Independent reflections	15943 [R(int) = 0.0367]
Completeness to theta = 26.27°	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15943 / 0 / 897
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1283
R indices (all data)	R1 = 0.0676, wR2 = 0.1426
Largest diff. peak and hole	1.036 and -0.325 $e.Å^{-3}$

Table 8: Bond lengths [Å] and angles [°] for sh2351.

Al(1)-O(4)	1.714(2)	O(5)-Li(2)	1.940(4)
Al(1)-O(1)	1.739(2)	O(5)-Li(4)	1.942(4)
Al(1)-O(9)	1.781(2)	O(7)-Li(4)	1.831(4)
Al(1)-O(8)	1.791(2)	O(7)-Li(3)	1.832(4)
Al(2)-O(2)	1.725(2)	O(8)-Li(1)	2.057(4)
Al(2)-O(11)	1.746(2)	O(8)-Li(2)	2.125(4)
Al(2)-O(1)	1.764(2)	O(9)-Li(1)	2.059(4)
Al(2)-O(13)	1.771(2)	O(9)-Li(4)	2.082(4)
O(1)-Li(4)	2.064(4)	O(10)-Li(1)	1.947(4)
O(1)-Li(2)	2.197(4)	O(11)-Li(3)	1.941(4)
O(1)-Li(3)	2.297(4)	O(12)-Li(3)	1.989(4)
O(5)-Li(1)	1.905(4)	O(13)-Li(2)	1.932(4)

O(4)-Al(1)-O(1)	118.07(8)	O(2)-Al(2)-O(11)	113.84(8)
O(4)-Al(1)-O(9)	118.07(8)	O(2)-Al(2)-O(1)	114.06(8)
O(1)-Al(1)-O(9)	100.29(7)	O(11)-Al(2)-O(1)	100.13(7)
O(4)-Al(1)-O(8)	119.18(8)	O(2)-Al(2)-O(13)	111.25(8)
O(1)-Al(1)-O(8)	101.76(7)	O(11)-Al(2)-O(13)	118.25(8)
O(9)-Al(1)-O(8)	95.430(7)	O(1)-Al(2)-O(13)	97.670(7)
O(4)-Al(1)-Li(4)	147.10(1)	O(2)-Al(2)-Li(2)	124.50(1)
O(8)-Al(1)-Li(4)	93.700(1)	O(11)-Al(2)-Li(2)	121.40(1)
O(4)-Al(1)-Li(1)	142.70(1)	O(1)-Al(2)-Li(2)	53.100(1)
O(1)-Al(1)-Li(1)	99.200(1)	O(13)-Al(2)-Li(2)	44.550(9)
O(9)-Al(1)-Li(1)	48.160(9)	O(2)-Al(2)-Li(3)	129.20(1)
O(4)-Al(1)-Li(2)	147.10(1)	O(11)-Al(2)-Li(3)	44.200(1)
		O(1)-Al(2)-Li(3)	55.890(9)
		O(13)-Al(2)-Li(3)	119.30(1)

2.4.2. Crystal structure description of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6)

Compound **6** crystallizes in the triclinic space group $P\bar{1}$ with one diethyl-ether molecule and one *tert*-butanol group per unit cell. The core of the structure is representing by a cubane built of $AlLi_3O_4$ units by mutual coordination of oxygen and metal atoms, supplemented by one lithium, one aluminium atoms and two disilanolate ligands.

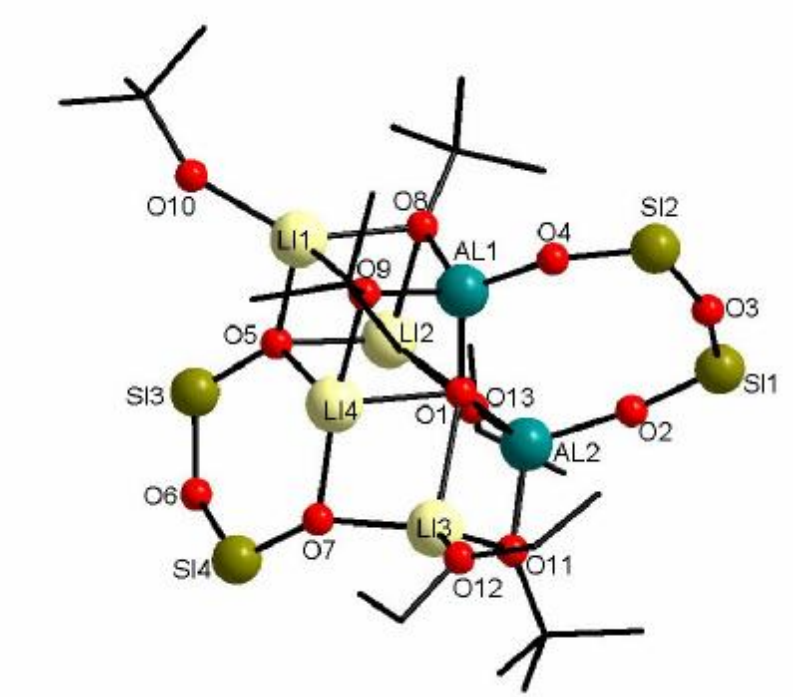


Figure 17: Representation of the crystal structure of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6) (Phenyl groups are not represented and carbon atoms are unlabelled for clarity)

The three tetra-coordinated Li ions of the cube geometry include Li-O bonds lengths from 1,905(4)Å to 2,197(4)Å. The aluminium atom Al(1)is surrounded by three oxygen atoms from the cube and makes a fourth coordination with one oxygen atom from the disilanolate ligand.

The Al(1)-O(1), Al(1)-O(8) and Al(1)-O(9) bond lengths inner the cube have values of 1,739(2)Å, 1.781(2) and 1,791(2)Å respectively. The two longer distances correspond to the distances from oxygen atoms which are a part of *tert*-butoxy groups [45]. The angles values of the cubic tetramer vary from 75,421(2)Å to 101,902(3)Å. This subject a distortion in the cube geometry adopted.

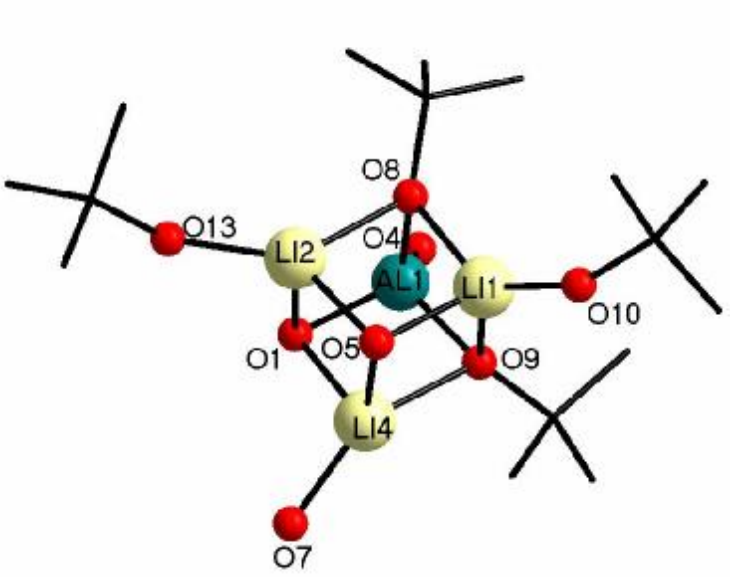


Figure 18: View of the cubic (Li_3AlO_4) of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6).

Li(2) ion and O(1) atom share a side with the four-membered ring [O(1)-Al(2)-O(13)-Li(2)], which has Al(2)-O(1) and Al(2)-O(13) bond lengths of 1,764(2)Å and 1,771(2)Å respectively. These distances values are reminiscent of the Al-O bond length in **2**.

Li(4) ion and O(1) atom from the cube take part to the formation of the four membered ring [Li(4)-O(1)-O(7)-Li(3)].

Two disilanolates ligands are present in the structure, one is coordinated to Al(1) and Al(2) by its oxygen atoms in the same μ_2- coordination mode as in **1** ,forming a 8-membered ring . The Al(1)-O(1) and Al(2)-O(1) bond lengths have values of 1.739(2)Å and 1.764(2)Å and Al(1)-O(4)-Si and Al(2)-O(2)-Si bond lengths of 1.714(2)Å and 1.725(2)Å.

The other disilanolate ligand chelates Li(1), Li(3) and Li(4) ions in a μ_4- chelate bridging [46] coordination mode forming a 6-membered ring system(O_3Si_2Li).The Li-O(Si) distances vary from 1.831(4)Å to 1.942(4)Å. The Si-O bond lengths in the disilanolate ligands present in the structure are all about 1.6Å.

2.5. Reaction between 1 and Potassium hydroxide

Reaction of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) with small amounts of water was previously carried out [24] (see introduction, Eq.6). Water molecules can also be formed in the "pot". The use of a metal hydroxide often involves the formation of water molecules. Therefore, reaction of **1** with water can occur when metal hydroxides are used.

The reaction of **1** with four equivalents of potassium hydroxide (KOH) in diethyl-ether leads to compound $[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$ (**7**). It crystallized after a few days from diethyl-ether after concentration of the solvent which became viscous. The yield was not calculated because of the difficulty to separate the crystals from the gel formed.

$$\underset{\textbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4OEt_2} \xrightarrow[Et_2O]{4KOH} \underset{\textbf{7}}{[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2} + \underset{\text{decomposition products}}{[\ .....]}$$

Equation 6: Reaction of 1 with potassium hydrosxide.

The reaction of **1**.$4Et_2O$ with metal hydroxide leads to the formation of water in the medium:

$$\textbf{1}.4Et_2O + 4KOH \longrightarrow H_2O + 4K^+[\textbf{1}]^{4-}$$

Thus the coordination [47] of K can not occur in the same way as the addition of NaOEt or the intramolecular insertion of LiOH (chap.2.1 and Chap.2.2). In this case, the formation of water is not controlled. Alumopolysiloxane **1** is hydrolyzed [48] , this reaction leads to decomposition products and can be compared to the beginning of a sol-gel process. Compound **7** was isolated from this hydrolysis. The other products (as gel), insoluble in polar or non-polar solvents, are certainly the result of an oligomerization.

2.5.1. Crystal structure determination of $[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$ (7)

From the crystalline gel formed, one crystal was isolated for identification of the structure as shown in Figure 19. The final refinement of the structure was not successful because of the poor quality of the isolated crystals. Therefore, a brief overview of the structure was realized. In figure 19, the structure represented corresponds to an approximation of the atoms position.

2.5.2. Crystal structure description of $[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$ (7)

Compound 7 is composed by a central eight-membered ring $Al_2O_4Si_2$.The crystallographic inversion center is located in the center of this ring.

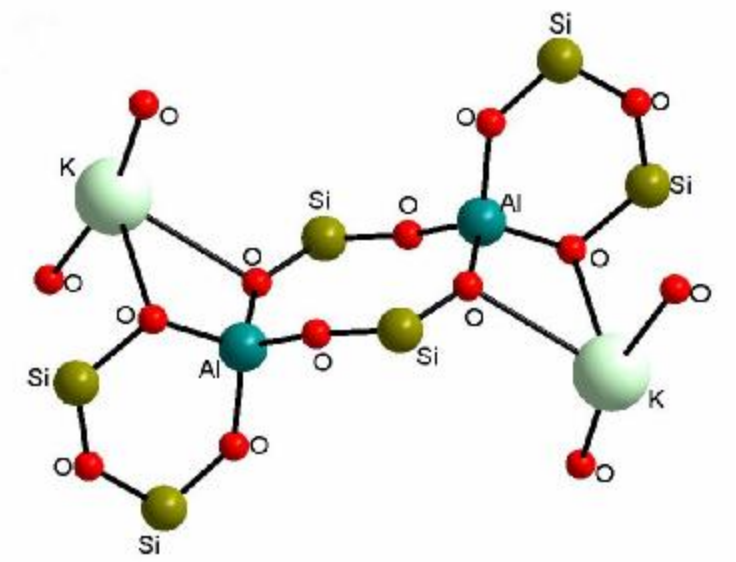


Figure 19: Representation of the crystal structure of $[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$. (Phenyl groups of the Ph_2Si are no represented for clarity.)

The aluminium atoms are tetra-coordinated with a trigonal pyramidal geometry. These atoms are chelated by a disilanolate ligand and form a six-membered ring with this ligand. The potassium atoms are coordinated to an oxygen atom from the disilanolate ligand and one from the core of the structure. These form a $AlKO_2$ four-membered ring.

2.6. Reaction between 1 and $LiN[Si(Me_3)]_2$

The interaction between $LiN(SiMe_3)_2$ [49, 50] and compound $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) in THF for 16 hours as solvent leads to $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ (**8**) with a yield of 56% . The compound is separated from the amine formed by re-crystallization from diethyl-ether to give colorless crystals.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} + 4LiN(SiMe_3)_2 \xrightarrow[-4HN(SiMe_3)_2]{THF} \underset{-4Et_2O}{[(Ph_2Si)_2O_3]_4[Al(OLi)]_4.6THF}$$

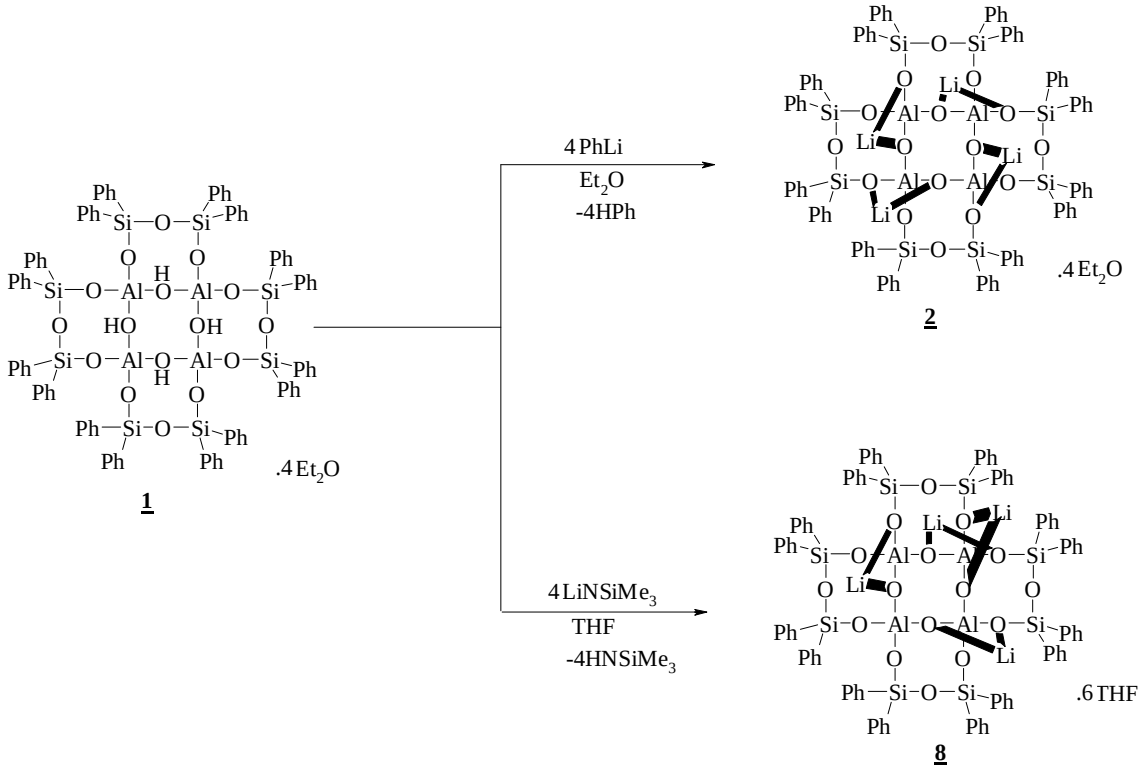
Equation 7: Reaction between 1 and $LiNSiMe_3$.

The ^{1}H- and ^{13}C-NMR monitoring of the reaction revealed that the displacement of the amido ligands is almost complete, the free amine $HN(SiMe_3)_2$ is the by-product. The ^{1}H-NMR and ^{13}C-NMR solution spectra of compound **8** in d^6-benzene support the formation of an identical product as **2**, except for the coordinative solvents (thf) represented by signals at 1.35ppm and 3.35pm in the ^{1}H-NMR and at 25.58ppm and 67.76ppm in the ^{13}C-NMR..

The ^{1}H-NMR spectra displays signals between 7.91 and 8ppm for 48 of the phenyl protons and between 7.69 and 7.79ppm for the other 32 protons. In the ^{13}C-NMR, the phenyl group signals are shifted at 128.29ppm and at 135.98ppm.

The study of the ^{29}Si-NMR where four signals are distinct (-40.31, -42.15, -43.17, -44.50ppm) permit to assume that silicon atoms are situated in four different environments on the compound **8** whereas the ^{29}Si-NMR of compound **2** shows only one signal at -45.93ppm.

The structure determination of **8** (Chapter 2.6.1) confirms that compound **8** has the same central cyclic structural unit as $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ **(2)** supplemented by four AlO_2Li rings [19].
In compound **2,** each lithium atoms is additionally connected to a diethyl ether ligand molecule, so that approximately trigonal-planar LiO_3 units are formed.
In compound **8**, two pairs of lithium ions are connected via a THF molecule and each lithium atoms are coordinated to a THF molecule forming trigonal pyramidal LiO_4 units.



Equation 8: Reaction between 1 and PhLi [19] and between 1 and $LiNSiMe_3$.

The use of a lithium compound, containing a sterically encumbered group, induces a change in the symmetry of compound **8** comparing with the symmetry of compound **2** (Equation 8). This is due to the different approach of the subsistent, comparing with the phenyl lithium which has a "flat" conformation (plan). Indeed, the lithium atoms make coordination with oxygen atoms of two disilanolates ligands in contrast with **2** where the four disilanolate ligands are involved. The symmetry ceases.

2.6.1. Crystal structure determination of $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ (**8**)

A crystal of $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ (**8**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 6.86%. In table 9 are reported the crystal data and the structure refinement for the compound and in table 10 are reported some selected bond lengths and angles of interest.

Table 9: Crystal data and structure refinement for sh2282.

Identification code	sh2282	
Empirical formula	$C_{120}\ H_{128}\ Al_4\ Li_4\ O_{22}\ Si_8$	
Formula weight	2410.83	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.549(2) Å	α = 90°.
	b = 26.057(2) Å	β = 95.766(5)°.
	c = 22.4635(19) Å	γ = 90°.
Volume	12549.3(19) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	5088	
Crystal size	0.2 x 0.3 x 0.45 mm^3	
Theta range for data collection	1.23 to 24.48°.	
Index ranges	-24<=h<=24, -28<=k<=30, -26<=l<=26	
Reflections collected	33070	
Independent reflections	10235 [R(int) = 0.0988]	
Completeness to theta = 24.48°	98.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10235 / 0 / 729	
Goodness-of-fit on F^2	1.296	
Final R indices [I>2sigma(I)]	R1 = 0.0686, wR2 = 0.1793	

R indices (all data)	R1 = 0.1327, wR2 = 0.2019
Largest diff. peak and hole	1.724 and -0.784 e.Å^{-3}

Table 10: Bond lengths [Å] and angles [°] for sh2282.

Al(1)-O(1)´	1.735(4)	Si(2)-O(5)	1.605(4)
Al(1)-O(1)	1.735(4)	Si(2)-O(4)´	1.637(4)
Al(1)-O(3)	1.758(4)	Si(3)-O(8)	1.611(4)
Al(1)-O(3)´	1.758(4)	Si(3)-O(7)	1.637(4)
Al(2)-O(2)´	1.733(4)	Si(4)-O(6)	1.605(4)
Al(2)-O(1)	1.739(4)	Si(4)-O(7)	1.644(4)
Al(2)-O(5)	1.752(3)	Li(1)-O(2)	1.878(9)
Al(2)-O(6)	1.789(4)	Li(1)-O(9)	1.934(9)
Al(3)-O(2)	1.743(4)	Li(1)-O(8)	2.03(1)
Al(3)-O(2)´	1.743(4)	Li(1)-O(10)	2.10(1)
Al(3)-O(8)	1.768(4)	Li(2)-O(1)	1.89(1)
Al(3)-O(8)´	1.768(4)	Li(2)-O(11)	1.93(1)
Si(1)-O(3)	1.588(4)	Li(2)-O(6)	2.05(1)
Si(1)-O(4)	1.636(4)	Li(2)-O(10)	2.10(1)

O(2)-Al(3)-O(2)´	120.0(3)	O(1)´-Al(1)-O(3)´	107.7(2)
O(2)-Al(3)-O(8)	97.7(1)	O(1)-Al(1)-O(3)´	110.2(2)
O(2)´-Al(3)-O(8)	113.5(2)	O(3)-Al(1)-O(3)´	106.9(3)
O(2)-Al(3)-O(8)´	113.5(2)	O(2)´-Al(2)-O(1)	112.4(2)
O(2)´-Al(3)-O(8)´	97.7(1)	O(2)´-Al(2)-O(5)	111.0(2)
O(8)-Al(3)-O(8)´	115.6(3)	O(1)-Al(2)-O(5)	113.3(2)
O(1)´-Al(1)-O(1)	113.8(3)	O(2)´-Al(2)-O(6)	110.4(2)
O(1)´-Al(1)-O(3)	110.2(2)	O(1)-Al(2)-O(6)	98.1(2)
O(1)-Al(1)-O(3)	107.7(2)	O(5)-Al(2)-O(6)	111.0(2)

2.6.2. Crystal structure description of $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ (8)

Compound **8** crystallizes monoclinic in space group C2/c. $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ has the same Al_4O_4 central cyclic structural unit surrounded by four disilanolate ligands as in **2**.

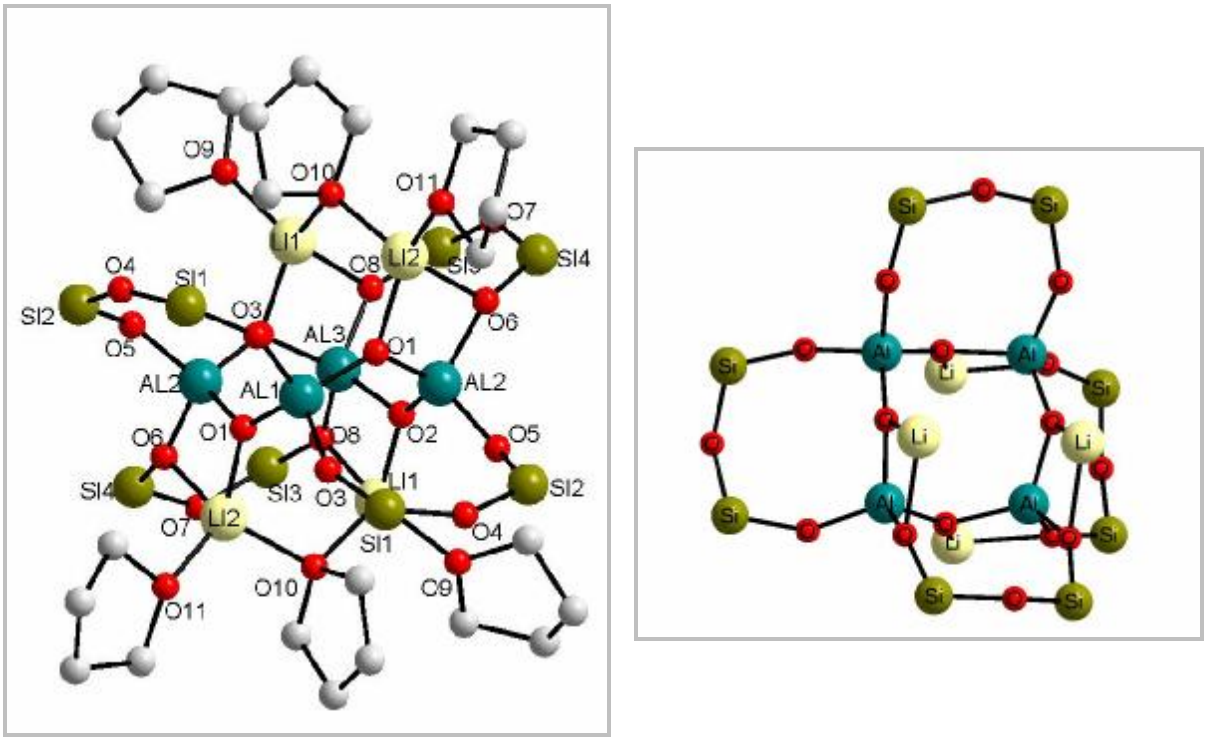


Figure 20: Representation of the crystal structure of $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ (8) (left) and of 8 without the solvent molecules ($[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4$, right)
(Phenyl groups of the Ph_2Si are no represented for clarity.)

The Al-O bond lengths in the core of the structure vary from 1.733(4)Å to 1.743(4)Å. The compound is supplemented by four LiO_2Al rings. Alternatively, the inner unit can also be described as consisting of four AlO_4 tetrahedra connected through common vertices with one edge of each tetrahedron being bridged by a lithium atom. Each lithium atoms make coordination with one THF molecule and are also bridged through another THF molecule. The four lithium ions are in a trigonal pyramidal sphere including Li-O bond length from 1.86(1) Å to 1.9384(2) Å.

The lithium atoms make a fourth coordination with oxygen atoms from two disilanolate ligands with bond lengths of 2.0519(1) Å and 2.0774(1)Å . The four disilanolate ligands have Si-O bond lengths about 1.6Å and Al-O-Si distances about 1.7Å, close to those in **2**.

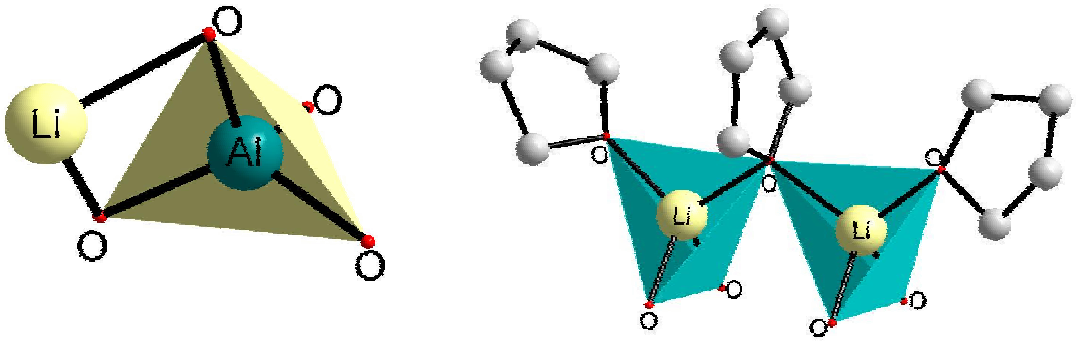


Figure 21: Environments around the aluminium atoms and the lithium ions.

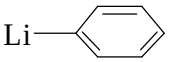
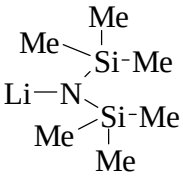
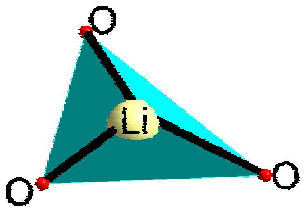
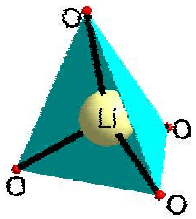
Compound	**2**	**8**
Reagents **Distances (Å) in the final product**		
Li-O(-Al)	1.8686(1)-1.8843(1)	1.8436(3)-1.8522(2)
Li-O(-Si)	2.0519(1)-2.0774(1)	2.0273(4)-1.9542(4)
Al-O(-Al)	1.7344(1)-1.7452(1) 1.7348(1)-1.7384(1)	1.7344(1)-1.7197(5) 1.7292(4)-1.7273(5)
units	LiO_3 	LiO_4 
Units geometry	Trigonal planar	Trigonal pyramidal

Table 11: Crystallographic values for compounds 2 and 8.

Compound **2** is composed [19] of LiO_3 units in a trigonal planar geometry, whereas the new synthesized compound **8** has LiO_4 units in trigonal pyramidal geometry induced by the higher number of coordinative solvent molecules (THF). However, the distances for structure **8** are very close to those in **2** (Table 11).

2.7. Discussion

The reactivity of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) in the presence of NaOEt, LiOH ,TlOEt, LiO^tBu, KOH and $LiN(SiMe_3)_2$ reagents is depending on following factors:

- **Lewis acid-base interaction :**

The ionic chemistry of aluminium is relatively unexplored because of the ease with which Al^{3+} complexes undergo hydrolysis in aqueous solution. With an ionic radius of 0,53A, Al^{3+} is generally considered to be a very hard acid [51].

Apart from the acidic hydrogen atoms of the OH groups in $(Ph_2SiO)_8[AlO(OH)]_4$ (**1**), the aluminium atoms act as Lewis acids and are very reactive in presence of hard base such as water formed during the reaction of **1** with potassium hydroxide. Organoaluminium compounds react violently with water yielding only to decomposition products:

$$R_3Al + 3H_2O \rightarrow Al(OH)_3 + 3RH$$

The use of Cu(I) has permitted the "water softening" [52, 53] during the intra-molecular hydrolysis [54-57] of compound **2** because of the ability of Cu(I) to coordinate water molecules. This method has permitted to obtain compound **4** and **4a** without decomposition of the main structure.
This concept was introduced by Razuaev [58] with the now widely used method of alumoxane synthesis. The reactions of organoaluminium compounds with water of copper sulphate pentahydrate were carried out in order to have a slow hydrolysis. The reaction proceeded according to the equation:

$$8AlR_3 + CuSO_4.5H_2O \rightarrow 4\ R_2Al\text{-}O\text{-}AlR_2 + CuSO_4.H_2O + 8RH$$

- **The structure of tertiary butoxides of alkali metals:**

Lithium alkoxides are known to be associated in solutions [59-63]. They form aggregates which crystallize in cubes. The association of Li_2O_2 and $LiAlO_2$ four-membered rings leads to a cubane geometry with two different metal atoms. The tendency of such compounds to form cube partially induce the rearrangement of compound **1**. The initial skeleton of **1** can not be conserved due to the stress generated by the cubane formed.

- **The steric congestion of the reagent** :

The molecular structure of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) looks like two baskets which are fused together by a common $Al_4(OH)_4$ bottom, two of the hydroxyl groups are pointing toward the upper basket part whereas the other two are pointing in opposite directions within the second basket [24]. This conformation can hinder the access of bulky reagent to one or more side of the compound (figure 22).

This induces the formation of non-symmetric compound (**8**) during the substitution of the four hydrogen atoms by lithium ions by the use of the bulky $LiN(SiMe_3)_2$ reagent. (The use [19] of the flattened phenyl group leads to the symmetric compound **2**).
Only two disilanolate ligands of **1** are involved in this reaction because of the steric requirement of the amine group. Consequently, the position of the Li ions depends on the reagent used.

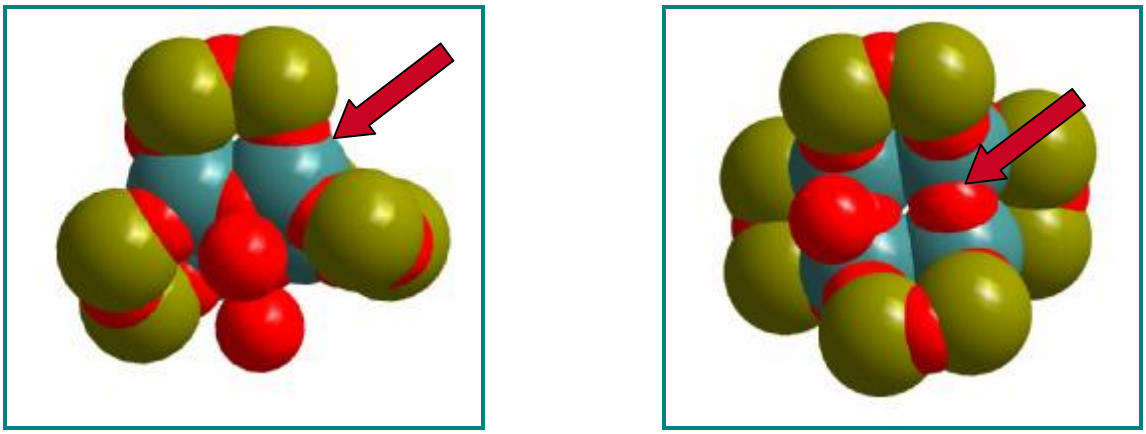


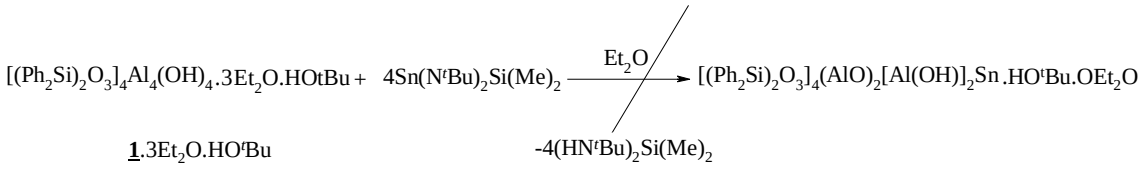
Figure 22: Views of 1 (space-filling), the basket conformation of 1 hinders the approach of an sterically encumbered group such N $(SiMe_3)_2$. The arrows correspond to the approach of the reagent, (green=silicon atoms; blue=aluminium; red=oxygen atoms)

3. Introduction of metal atoms with a sensitive alteration of the core of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**)

Substitution of the protons from the OH groups in $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) by metal atoms using the hydrogen acidic character has already been described [19, 20, 23] (see introduction).These reactions, leading to compounds derivates of **1** with one or two metal atoms (Sn, Ge, Pb) occurred by the use of metal amide, metal cyclopentadienyl or metal *tert*-butoxide. It has been demonstrated that some difficulty appeared by the use of amide compound. It was then interesting to follow the research in this direction. Attempts to make substitution were also completed with transition metal acetylacetonate (Ni and Fe) in order to enlarge the metal's pallet coordinated on $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**).

3.1. Reaction between 1 and Veith-stannylene

A previous study showed that reaction was observed between $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) and bis(amido)stannylene $Sn[N(SiMe_3)_2]$, leading to $[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2Sn$ [20]. Our attempts to make such substitution were realized according to the previously established procedure in order to improve the poor yield obtained. The progressive addition of 1,3-di-*tert*-butyl-2,2-dimethyl-1,3,2,4λ^2-diazasilastannetidine (Veith stannylene) [64, 65] (4 *eq.)* to a diethyl-ether suspension of **1**.$3Et_2O.HO^tBu$ even at room temperature resulted in a rapid formation of a yellow solution. The solution, which certainly contained the amine formed during the reaction, was evaporated, and the solid obtained was dissolved in pure diethyl-ether. This solution was kept at +4°C for a few months to give colorless crystals with a yield of 10%.



Equation 9: Supposed reaction between 1 and $Sn(N^tBu)_2Si(Me)_2$ (Veith sannylene).

The ^1H- and ^{13}C-NMR monitoring of the reaction revealed that the displacement of the amido ligands is almost complete, the free amine $(HN^tBu)_2Si(Me)_2$ is the byproduct and the ^{119}Sn-NMR revealed the formation of two new resonances at -206.37ppm and -545.93ppm indicative of three and four-coordinated tin atoms [66].

The ^1H-NMR spectrum exhibits one broad singlet at 0.91ppm arising from *tert*-butoxy groups, and signals corresponding to the phenyl groups between 7.76ppm and 8.17ppm.

The ^{13}C-NMR displays distinct peaks for the two *tert*-butoxide groups shifted at 32.98ppm and 30.11ppmm.

And finally, the structure determination (Chap.3.1.1) revealed an unusual tetra-nuclear tin compound [67, 68].

$$[(Ph_2Si)_2O_3]_4Al_4(OH)_4 .3\,Et_2O.HOtBu + 4Sn(N^tBu)_2Si(Me)_2 \xrightarrow[-4(HN^tBu)_2Si(Me)_2]{Et_2O} [(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2 .O^tBu.2OEt_2$$

1.3Et$_2$O.HO^{t}Bu — **9**

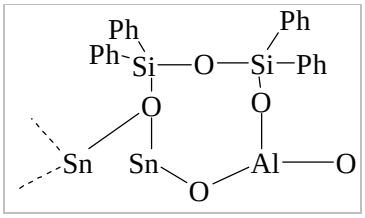
Equation 10: Synthesis of [(SnO)$_4$(OtBu)][(Ph$_2$Si)$_2$O$_3$]$_4$Al$_4$(OH)$_2$.O^{t}Bu.2Et$_2$O (9).

This reaction depends greatly on the solvent molecules coordinated on **1**; the use of **1**.HO^{t}bu.3OEt$_2$ (1.1 Introduction) is required. (Equation 10)

The reaction leading to **9** can be understood as being initiated by a proton transfer from the hydroxyl group of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ to the nitrogen atoms resulting to the formation of the free amine molecules, and to a coordination of the oxygen atom of the O^{t}Bu group of **1** to the Sn metal leading to an Sn-O^{t}Bu bond [69].

The assemblies of Sn-O bond [69] lead to the formation of $\{Sn_2O_2\}$ four-membered rings and result in the formation of a heterocubane where three Sn metal atoms are connected through a *tert*-butanolat group.

Two tin atoms are also chelated by a disilanolate ligand, with the formation a rare metallastannoxane eight-membered ring $(Ph_2SiO)_2\,O_2AlSn$ [70, 111, 117].



Scheme 6 : Coordination mode of disilanolate ligand around the tin atoms: μ$_3$-chelate bridging

The conversion into the desired product by using **1**.4OEt$_2$ did not occur. This problem is not overcome with the addition of small amount of ^{t}BuOH in the reaction mixture. Practically the reaction was performed in diethyl-ether with the right equivalent of ^{t}BuOH. But after filtration of the side products, the compound crystallized from the resulting solution to give $[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2Sn$ (analyzed by X-Ray structure determination).

$$[(Ph_2Si)_2O_3]_4Al_4(OH)_4 .4Et_2O + 4Sn(N^tBu)_2Si(Me)_2 \xrightarrow[Et_2O]{2^tBuOH} [(Ph_2Si)_2O_3]_4[Al(OH)]_2(AlO)_2Sn$$

1.4Et$_2$O

-(HN^{t}Bu)$_2$Si(Me)$_2$
-3Sn(N^{t}Bu)$_2$Si(Me)$_2$
-2^{t}BuOH

Equation 11 : Formation of $[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2Sn$.

It seems clear that the alcohol has first reacted with the stannylene to give the dimeric $[Sn(O^tBu)_2]_2$[71]. The reaction consisted of the interaction of the dimer with **1.4Et$_2$O** to give $[(Ph_2Si)_2O_3]_4Al_4(OH)_2O_2Sn$ [20].

3.1.1. Crystal structure determination of $[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.2Et_2O$ (9)

Crystals of $[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.2Et_2O$ (**9**) were obtained from a concentrated diethyl-ether solution placed at +4°C. From the determination and the refinement of the unit cell dimensions arose a triclinic crystal system [126]. The R-value is 10.44 %. This high value is due to the poor quality of the measured crystal. This complex shows disorders. It mainly concerns the "periphery" of the molecule (the organic part of the complex); whereas the different measured electron densities corresponding to the metallic core of the molecule can be unambiguously assigned. Thus, one can assume that the central metallic part of the complex matches with the reality. In table 12 are reported the crystal data and the structure refinement for the compound and in table 13 are reported some selected bond lengths and angles of interest.

Table 12: Crystal data and structure refinement for sh2221.

Identification code	sh2221	
Empirical formula	$C_{112}H_{119}Al_4O_{22}Si_8Sn_4$	
Formula weight	2624.47	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 14.6812(16) Å	α= 93.027(6)°.
	b = 15.3722(16) Å	β= 96.038(6)°.
	c = 29.148(3) Å	γ = 116.457(5)°.

Volume	5819.8(11) $Å^3$
Z	2
Density (calculated)	1.498 Mg/m^3
Absorption coefficient	1.028 mm^{-1}
F(000)	2662
Crystal size	0.55 x 0.4 x 0.2 mm^3
Theta range for data collection	1.49 to 27.10°.
Index ranges	-18<=h<=18, -19<=k<=19, -37<=l<=37
Reflections collected	112902
Independent reflections	25545 [R(int) = 0.0587]
Completeness to theta = 27.10°	99.4 %
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	25545 / 0 / 1341
Goodness-of-fit on F^2	2.867
Final R indices [I>2sigma(I)]	R1 = 0.1044, wR2 = 0.2892
R indices (all data)	R1 = 0.1339, wR2 = 0.3078
Largest diff. peak and hole	4.836 and -3.382 $e.Å^{-3}$

Table 13 : Selected bond lengths [Å] and angles [°] for sh2221.

Sn(1)-O(6)	2.101(6)	Sn(4)-O(4)	2.081(6)
Sn(1)-O(5)	2.110(6)	Sn(4)-O(6)	2.099(6)
Sn(1)-O(19)	2.279(6)	Sn(4)-O(7)	2.235(7)
Sn(1)-O(7)	2.516(6)	Al(1)-O(2)	1.790(6)
Sn(2)-O(5)	2.113(6)	Al(1)-O(1)	1.793(6)
Sn(2)-O(2)	2.118(6)	Al(2)-O(1)	1.775(6)
Sn(2)-O(19)	2.125(6)	Al(3)-O(3)	1.754(7)
Sn(3)-O(5)	2.079(6)	Al(3)-O(1)	1.830(6)
Sn(3)-O(4)	2.103(6)	Al(4)-O(3)	1.738(6)
Sn(3)-O(7)	2.283(7)	Al(4)-O(2)	1.776(6)

O(6)-Sn(1)-O(5)	86.3(2)	Sn(3)-O(5)-Sn(1)	113.1(3)
O(5)-Sn(1)-O(19)	74.2(2)	Sn(3)-O(5)-Sn(2)	134.7(3)

O(6)-Sn(1)-O(7)	73.2(2)	Sn(1)-O(5)-Sn(2)	106.8(3)
O(5)-Sn(1)-O(7)	73.8(2)	Sn(4)-O(6)-Sn(1)	112.5(3)
O(5)-Sn(3)-O(4)	92.6(2)	Sn(4)-O(7)-Sn(3)	98.6(2)
O(4)-Sn(3)-O(7)	74.8(2)	Sn(4)-O(7)-Sn(1)	94.4(2)
O(4)-Sn(4)-O(6)	90.6(2)	Sn(3)-O(7)-Sn(1)	93.3(2)
Sn(4)-O(4)-Sn(3)	110.0(3)		

3.1.2. Crystal structure description of $[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.2Et_2O$ (**9**)

Compound $[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.2Et_2O$ (**9**) crystallizes in a triclinic system with a space group of $P\bar{1}$ with two Et_2O molecules per formula units, which do not interact with the acidic center but serve to optimize the crystal packing and with one O^tBu group which interacts with a hydrogen atom of the complex. Compound **9** consists of a central Sn_4O_4 unit supplemented by four aluminium atoms surrounded by four disilanolate ligands.

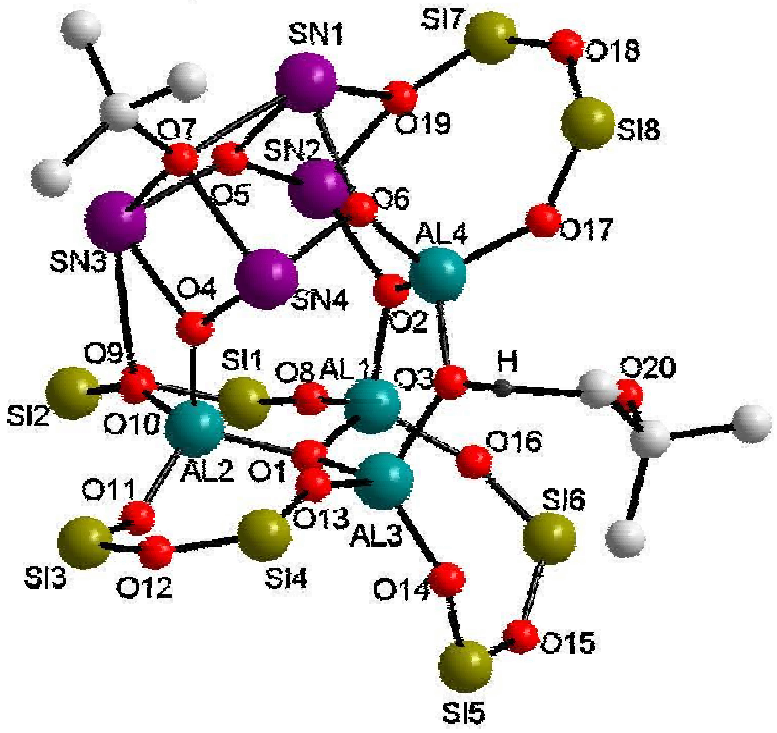


Figure 23: Representation of $[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.2Et_2O$ (9) (Phenyl groups of the Ph_2Si are no represented for clarity.)

Three of the tin atoms (Sn(1), Sn(3), and Sn(4)) are bridged by a terminal O^{t}Bu group (O(7)). The value of the Sn(1)-O(7) bond (2. 516(6)Å) is remarkably elongated compared with the Sn(3)-O(7) and Sn(4)-O(7) bond lengths (2. 283(7) Å and 2. 235(7) Å respectively). These Sn-O^{t}Bu bond lengths are relatively longer as the Sn-O^{t}bu (bridge) distances reported by Fjeldberg *et al.* [68] in the molecular model of [Sn(μ-O^{t}Bu)(O^{t}Bu)]$_2$ (2.16Å).This could reflect the presence of some stress in the distorted heterocubane {Sn_3O_4} formed by the O(7), O(5), O(4), O(6) atoms and Sn(1), Sn(3) and Sn(4) metal atoms. The angles in this heterocubane range from 73.2(2) ° to 112.5(3) °.

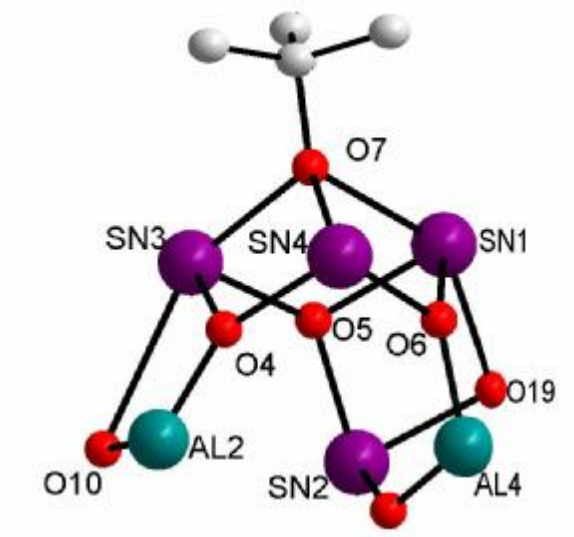
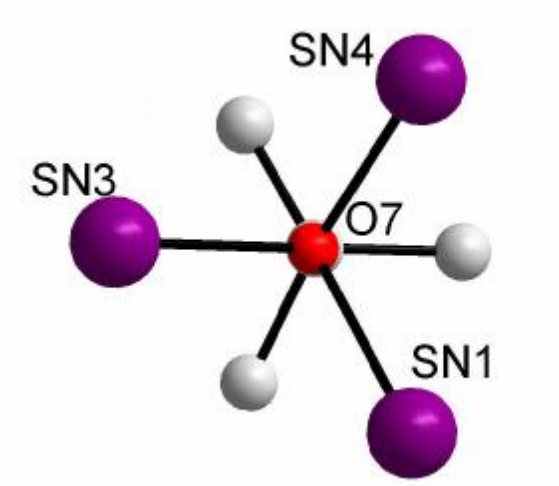


Figure 24: Representation of the coordination environment around the tin atoms.



Sn(3)-O(7)-Sn(4) = 98.6(2)°
Sn(4)-O(7)-Sn(1) = 94.4(2)°
Sn(1)-O(7)-Sn(3) = 93.3(2)°

Figure 25: Angles between the Sn atoms connected through O^{t}Bu group.

As depicted in Figure 24, the structure of **9** is formed of tin (II) tetra-nuclear species which involve two types of shapes for the tin (II) hybrids (Scheme 7). Both independent Sn atoms exhibit the typical one-sided coordination towards oxygen atoms due to the stereo-activity of their ns^2 lone pair [72].

:Sn	:Sn
sp^{3}d hybridizing for Sn(1) and Sn(3) atoms	**sp^3 hybridizing for Sn(2) and Sn(4) atoms**

Scheme 7: Hybridizing for Sn atoms.

The highest Sn-O bond length of the structure is the Sn(3)-O(10) with 2.8657(3)Å. Sn(3) makes a fourth coordination with the O(10) oxygen atom from the disilanolate ligand. The Sn-O bond lengths are all greater than those of related compounds [68].

Three of the disilanolate ligands are, as in **1**, in a μ_2–bridging system, chelating aluminium atoms (Al(2), Al(3), and Al(1)). The fourth disilanolate ligand bridge Al(4), Sn(1) and Sn(2) with Sn-O(19)-Si bond length of 2.279(6)Å and 2.125(6) Å. The Si-O lengths of the ($OSi(Ph_2)OSi(Ph_2)O$) bridge are all about 1.6Å. Al(1), Al(2), and Al(3) atoms form a six-membered ring (Al_3O_3) including Al-O bond lengths from 1.738(6)Å to 1.83(6)Å and angles from 102.9(3)° to 131.1(4)°.

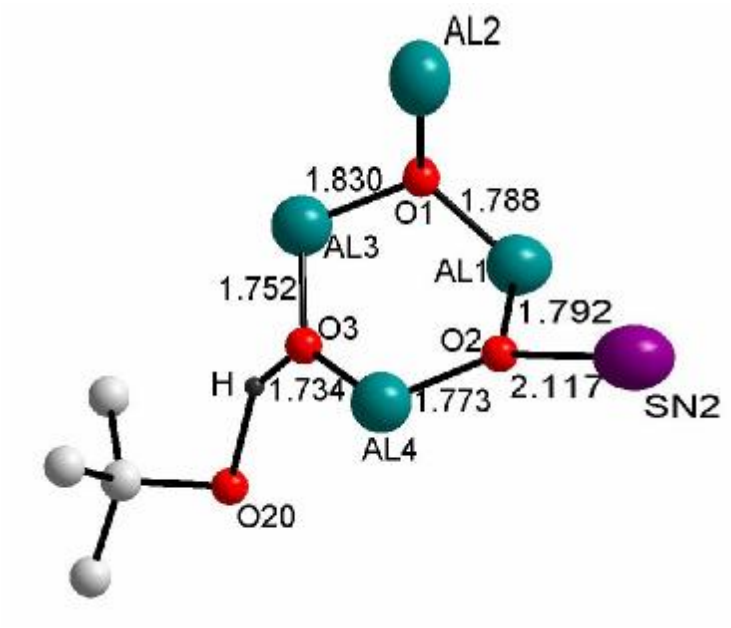


Figure 26: Representation of the configuration of the aluminium atoms in the six-membered ring (Al_3O_3).

The coordination of the ether molecules is an indirect evidence of the presence of OH groups in the six-membered ring.

The O(3)-H….O(20) hydrogen bridge of 2.6197(2) is at same range of the hydrogen bridge for **1**.O^{t}Bu.3OEt_2.where the O-O distances of the O- H . . O bridges lie in the range of 2.60-2.70 Å, which indicates strong hydrogen bonding [19].

3.2. Reaction between 1 and bis(acetylacetonato)nickel (II)

Attempts to carry on substitution of the protons from the OH groups of **1** by metal atoms were performed, using metal acetylacetonate complexes. These formers probably react in the same way as metal *tert*-butoxide [20]. Reaction of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) with two equivalents of nickel acetylacetonate $Ni(acac)_2$) (freshly sublimated at 50°C under reduced pressure [73-76]) was carried out in toluene at room temperature. Green crystalline solids were isolated from diethyl-ether in acceptable yields (30%).

$$2\,Ni(acac)_2 + [(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O \xrightarrow[-4Hacac]{Toluol} [(Ph_2Si)_2O_3]_4(AlO)_4Ni_2$$

1.$4Et_2O$

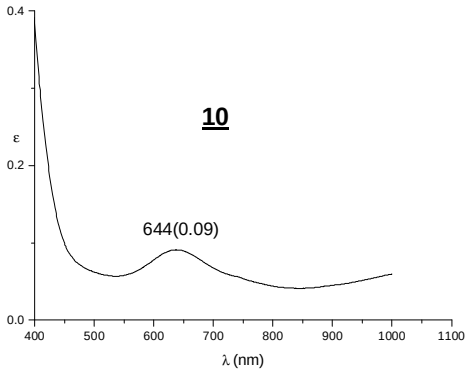
Equation 12: Supposed reaction between 1 and $Ni(acac)_2$.

The reaction was performed in a non-polar solvent and did not occur in coordinating solvents such diethyl ether even under refluxing conditions because of the ability of $Ni(acac)_2$ to make coordination with other neutral or anionic ligands such diethyl-ether [73].

The signals corresponding to the acetylacetone ligands [77] have not been detected by the NMR study of the resulting solution. That revealed that the displacement of these ligands did not occur as described in reaction 12.

From a qualitative point of view, the comparison of the recorded spectrum (Graph 2) with other previous reports dealing with nickel(II) complexes allows to form the assumption that the compound obtained is octahedrally surrounded.

Ni (II) has the $3d^8$ electronical configuration; the complex is high spin having trans-octahedral stereochemistry. The ^3F ground term is split in an octahedral field giving rise to the triplet terms with three main bands expected [73].



Graph 2 : $^3A_{2g}$ à $3T_{1g}$ (F) transition of 10

The UV-Vis. spectral study of the solutions of the compound in toluene has shown very distinct band at *v*2=644nm corresponding to the $^3A_{2g}$ à $3T_{1g}$ (F). The $^3A_{2g}$ à $^3T_{2g}$ (*v*1) transition is not visible because situated after 1000nm, and the third $^3A_{2g}$ à $^3T_{1g}$ (P) (*v*3) is obscured by the intense charge transfer bands.

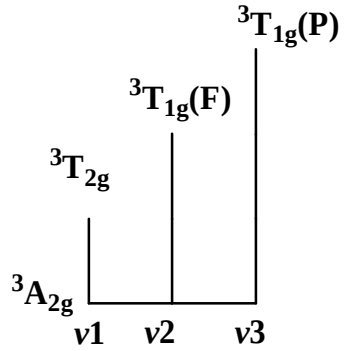
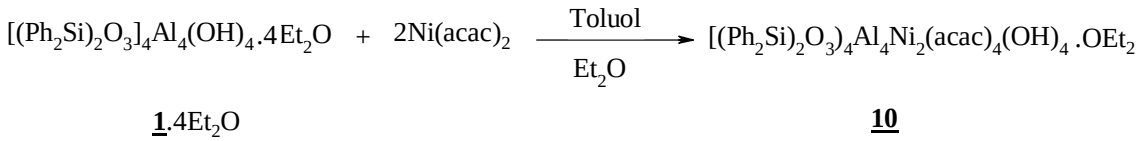


Figure 27 : Interpretation of the electronic absorption spectra.

The initial assumption that the central nickel atom displays an octahedral environment is confirmed in chapter 3.2.2 by the considerations about the molecular crystal structure which revealed a unusual nickel compound: $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$ (**10**).



Equation 13.Synthesis of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$ (10)

The two equivalents of $Ni(acac)_2$ are integrally introduced with a rearrangement of the central eight-membered ring of **1**. Actually, in order to preserve their hexa-coordination environment and their +II oxidation state, the nickel atoms make coordination with oxygen atoms of the disilanolate ligands in a μ_3-chelate bridging system and also with the oxygen atom from hydroxide group of compound **1**.

Those generate the cleavage of three Al-O bonds. The free β-ketoenolate ligands in the reaction medium make coordination with the aluminium atoms, which conserve in this manner a +III oxidation state. Three aluminium ions are such coordinated. One nickel atom preserves an acetylacetonate as ligand. Due to the small difference in term of Lewis acidity between Ni(II) and Al(III) [78], there is an exchange of ligands, then the nickel atom forms a nickel hydroxide.

3.2.1. Crystal structure determination of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$(10)

A crystal of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$ **(10)** was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 7.79%. In table **14** are reported the crystal data and the structure refinement for the compound and in table **15** are reported some selected bond lengths and angles of interest.

Table 14: Crystal data and structure refinement for sh2447.

Identification code	sh2457
Empirical formula	$C_{120}\ H_{122}\ Al_4\ Ni_2\ O_{25}\ Si_8$
Formula weight	2414.24
Temperature	103(2) K

Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 15.4483(12) Å	α= 81.191(2)°.
	b = 15.7031(13) Å	β= 87.024(2)°.
	c = 27.469(2) Å	γ = 66.646(2)°.
Volume	6045.2(9) $Å^3$	
Z	2	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.490 mm^{-1}	
F(000)	2524	
Crystal size	0.44 x 0.2 x 0.07 mm^3	
Theta range for data collection	1.43 to 28.44°.	
Index ranges	-20<=h<=20, -20<=k<=20, -36<=l<=36	
Reflections collected	123107	
Independent reflections	29553 [R(int) = 0.1187]	
Completeness to theta = 28.44°	97.1 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29553 / 5 / 1469	
Goodness-of-fit on F^2	1.252	
Final R indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.1763	
R indices (all data)	R1 = 0.2002, wR2 = 0.2131	
Largest diff. peak and hole	1.242 and -1.487 $e.Å^{-3}$	

Table 15: Selected bond lengths [Å] and angles [°] for sh2457.

Ni(1)-O(16)	1.970(4)	Al(1)-O(4)	1.783(4)
Ni(1)-O(17)	1.990(3)	Al(1)-O(1)	1.964(4)
Ni(1)-O(2)	2.033(4)	Al(2)-O(7)	1.788(4)
Ni(1)-O(4)	2.073(3)	Al(2)-O(6)	1.795(4)
Ni(1)-O(6)	2.120(3)	Al(2)-O(2)	1.889(4)
Ni(1)-O(1)	2.133(4)	Al(3)-O(10)	1.748(4)
Ni(2)-O(3)	2.009(3)	Al(3)-O(3)	1.792(3)
Ni(2)-O(9)	2.017(3)	Al(3)-O(9)	1.868(4)
Ni(2)-O(2)	2.036(4)	Al(4)-O(13)	1.704(3)
Ni(2)-O(17)	2.083(3)	Al(4)-O(12)	1.717(4)
Ni(2)-O(7)	2.131(3)	Al(4)-O(3)	1.728(3)
Ni(2)-O(22)	2.149(4)	Al(4)-O(1)	1.874(4)

O(2)-Ni(1)-O(4)	95.6 (1)	O(15)-Al(1)-O(4)	111.7 (2)
O(2)-Ni(1)-O(6)	74.8(1)	O(15)-Al(1)-O(1)	92.6(2)
O(4)-Ni(1)-O(6)	94.8 (1)	O(4)-Al(1)-O(1)	85.6(2)
O(2)-Ni(1)-O(1)	91.1 (2)	O(7)-Al(2)-O(6)	118.0 (2)
O(4)-Ni(1)-O(1)	74.6(1)	O(7)-Al(2)-O(2)	86.1(2)
O(6)-Ni(1)-O(1)	161.6 (2)	O(6)-Al(2)-O(2)	86.4(2)

3.2.2. Crystal structure description of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$ (**10**)

Compound **10** crystallizes in a triclinic system with a space group of $P\bar{1}$ with one molecule diethyl-ether per formula unit. Four disilanolate ligands ($OSi(Ph_2)OSi(Ph_2)O$) are present in the molecule. Three aluminium atoms are bonded to one acetylacetonate groups (per aluminium atom) through its two oxygen atoms.

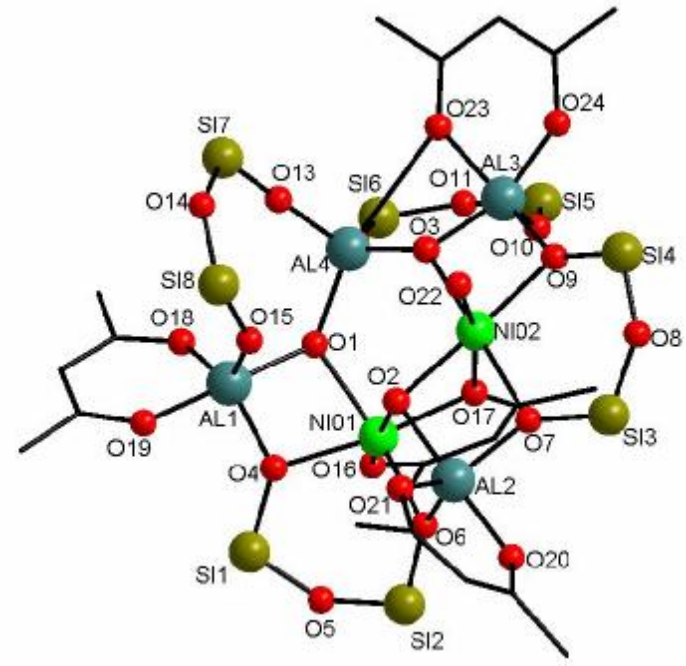


Figure 28: Representation of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$ (10)

The Al-O bond length inner the core of the structure built from $Al_4Ni_2(OH)_4$ span a range from 1,8239(1)Å to 1,9323(2)Á.

The fourth aluminium atom Al(4) is coordinated *via* one oxygen atom to an acetylacetonate ligand (which bridges Al(3)) with a great bond length Al(4)-O(23) of 2, 8309(2)Å. By that means, the four aluminium atoms of the structure are five coordinated and conserve their +III oxidation degree.

The O(1)-H hydroxide group between Al(1) and Al(4) and O(3)-H between Al(4) and Al(3) are still present as in **1**, but the distances values Al-O(-Al) are elongated (from 1,728(3)Å to 1,964(4)Å) compared with the Al-O(-Al) bond length in **1**. This difference reflects the stress inside the centre of the structure.

The two nickel atoms have the same stereo chemical environment as in the complex $Ni(acac)_2$, namely an octahedral coordination.

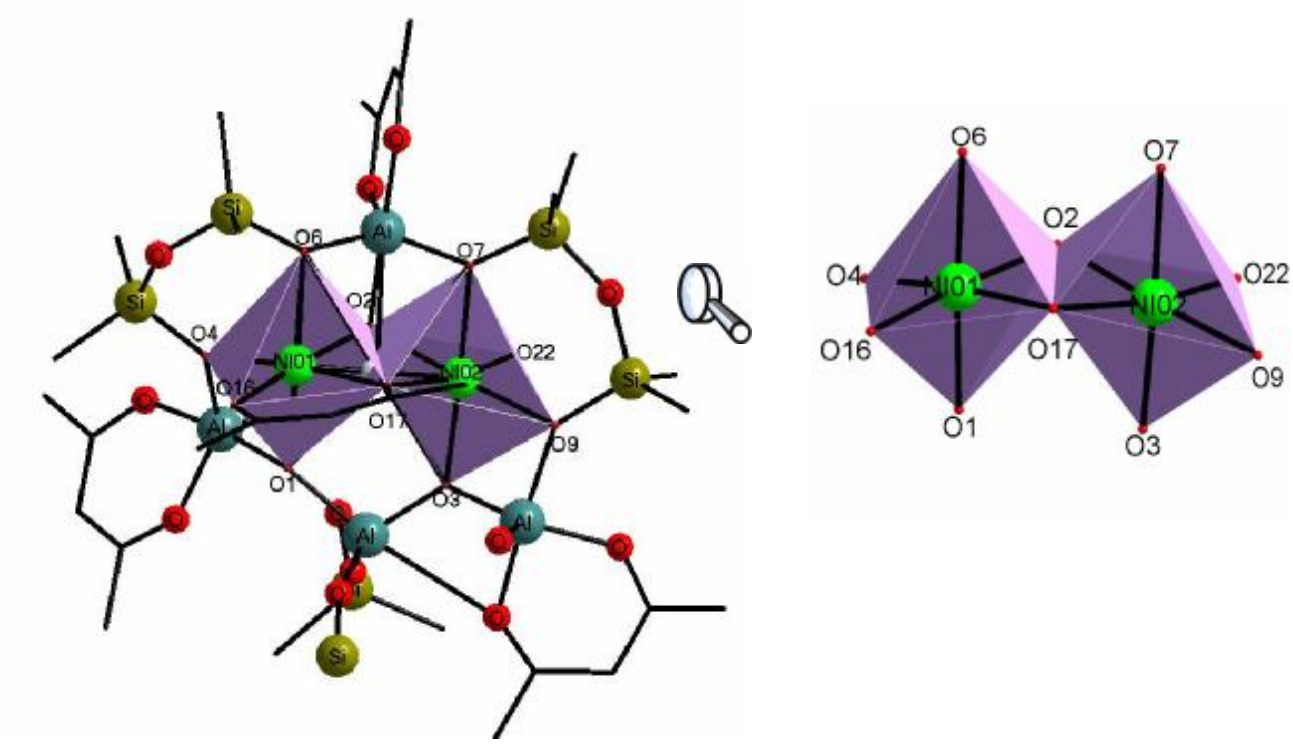


Figure 29: Representation of the core of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$ (10)

The first Nickel atom Ni(1) is surrounded by an actylacetonate ligand with a Ni(1)-O(16) bond length of 1, 970(4)Å and Ni(1)-O(17) bond length of 1, 990(3)Å close to those reported by Bullen *et al.* for the trimeric$[Ni(acac)_2]_3$ [76].

This metal atom is also chelated in a μ_3-bridging system by a disilanolate ligand with Ni(1)-O(4) and Ni(1)-O(6) bond length of 2, 073(3)Å and 2,120(3)Å respectively. These four oxygen atoms (O(17), O(16), O(4), and O(2)-(H)) belong to the square plane of the bipyramidal geometry form with the nickel atom as centre. The two opposite tops of the bipyramid are composed by O(1)-(H) with a distance of 2,133(4)Å and by O(6) with a distance of 2, 120(3)Å.

The second nickel atom Ni(2) is chelated by a disilanolate ligand in a μ_3-bridging system with a Ni(2)-O(9) bond length of 2,017(3)Å and a Ni(2)-O(7) bond length of 2,131(3)Å this nickel atom is also coordinated to one oxygen atom O(17) from the acetylacetonate ligand which bridge Ni(1) metal with a distance of 2,0841(1)Å. Ni(2) share an oxygen atom O(2) from a hydroxide group with Ni(1) (Ni(2)-O(2)= 2,0309(1)Å) and is bonded to O(3) from a hydroxide group between Al(4) and Al(3) (Ni(2)-O(3)= 2,0091(1) Å). The last coordination is made with a hydroxide group Ni-O(22)-H with a bond length of 2, 1503(1)Å.

3.3. Reaction between 1 and ferric acetylacetonate

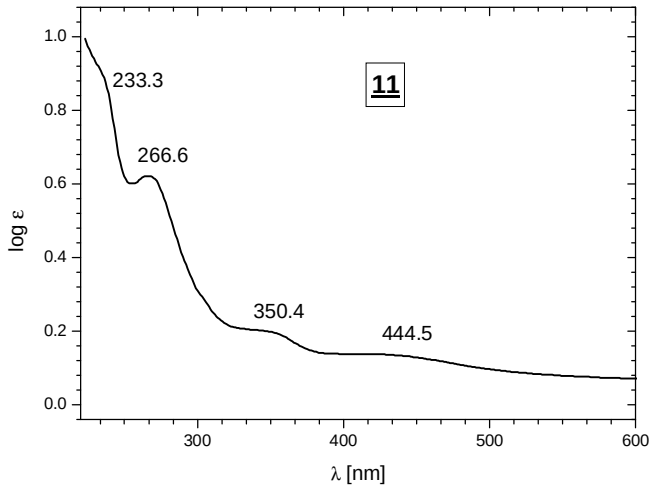
Attempts to make substitution of the hydrogen of the OH groups of **1** by iron atom were also realized. Reactions between $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ **1** and n equivalents (n= 1-3) of iron (III) acetylacetonate $Fe(acac)_3$ [79] in diethyl-ether as solvent were performed. The compound obtained was re-crystallized at +4°C from diethyl-ether to give 43% of red large crystals.

$$2\,Fe(acac)_3 + [(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O \xrightarrow[-6Hacac]{Et_2O} [(Ph_2Si)_2O_3]_4(AlO)_4Fe_2$$

$$\mathbf{1}.4Et_2O$$

Equation 14: Supposed reaction between 1 and $Fe(acac)_3$.

All of the transitions from the ground $6A^1(^6S)$ state to the excited ligand field states are, in principle, both spin- and parity-forbidden so that the ligand field bands in the spectra of complexes of Fe^{3+} are very weak [79, 80]. In binuclear inorganic complexes, these transitions become allowed through the magnetic coupling of electronic spins of next-nearest neighbor Fe^{3+} cations in the crystal structure (Figure 27). If two Fe^{3+} are strongly coupled, one must consider the spectroscopic selection rules for the Fe^{3+}-Fe^{3+} pairs and not those for individual Fe^{3+} centers. Thus, the spectrum (Graph 3) is not well resolved and complicated by the presence of transitions resulting from the simultaneous excitation of magnetically coupled Fe^{3+} cations (Shugar *et al.*, 1972) [81], from the ligand to metal charge transfer, or from the Fe^{3+} ligand field.



Graph 3 : UV-Visible spectra of compound (11).

The structure determination (chap.3.3.1) revealed the formation of an unexpected compound. $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (**11**) was the result of the reaction between $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) and $[Fe(acac)_3]$.

The resulting product persists with variations in reaction conditions like time, temperature, dilution, or solvent. Variation in reaction stoichiometry from the ideal stoichiometric precursor metal compound requirement (based on **1**: 1/1) does not alter the course of the reaction. Therefore, it is clear that for this case contrary that for the formation of **10** with $Ni(acac)_2$, the observed reaction pathways are highly selective for specific reagent pair. The result of this reaction is due to the target metal center Fe^{3+}.

The presence of a metal with the same oxidation degree as the aluminium ion and with a *quasi* similar Lewis acidity induces a competition between the two metal atoms. In fact, the disilanolate ligands tend to chelate also the iron metals. There is certainly formation of tris-(2,4-pentanedionato)aluminum(III) ($Al(acac)_3$) as second product because of the tendency of these metals to make ligands exchange The side product was deducted from the stoichiometry.

$$\underset{\mathbf{1}.4Et_2O}{[(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O} + 2Fe(acac)_3 \xrightarrow[\begin{array}{l}-Al(acac)_3\\ -Al(acac)[O_3(Ph_2Si)_2].OEt_2\end{array}]{Et_2O} \underset{\mathbf{11}}{[(Ph_2Si)_2O_3)_3O(OH)Al_2(acac)[Fe(acac)]_2.2OEt_2}$$

Equation 15: Synthesis of $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (11).

3.3.1. Crystal structure determination of $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (11)

A crystal of $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]2.2OEt_2$ **(11)** was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 7.6%. In table 16 are reported the crystal data and the structure refinement for the compound and in table 17 are reported some selected bond lengths and angles of interest.

Table 16: Crystal data and structure refinement for sh2475.

Identification code	sh2475	
Empirical formula	$C_{87} H_{81} Al_2 Fe_2 O_{17} Si_6 \cdot 2 C_4 H_{10} O$	
Formula weight	1880.96	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 18.2234(13) Å	α= 90°.
	b = 15.2964(9) Å	β= 100.696(3)°.
	c = 37.322(2) Å	γ = 90°.
Volume	10222.8(12) $Å^3$	
Z	4	
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.433 mm^{-1}	
F(000)	3940	
Crystal size	0.4 x 0.2 x 0.11 mm^3	
Theta range for data collection	1.11 to 28.36°.	
Index ranges	-24<=h<=22, -20<=k<=16, +48<=l<=49	
Reflections collected	85869	
Independent reflections	25406 [R(int) = 0.0919]	
Completeness to theta = 28.36°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25406 / 0 / 1109	
Goodness-of-fit on F^2	1.185	
Final R indices [I>2sigma(I)]	R1 = 0.0760, wR2 = 0.1711	

R indices (all data)	R1 = 0.1752, wR2 = 0.2024
Largest diff. peak and hole	1.045 and -1.193 e.Å^{-3}

Table 17 : Selected bond lengths [Å] and angles [°] for sh2475.

Fe(1)-O(8)	1.937(3)	Fe(2)-O(7)	2.007(3)
Fe(1)-O(1)	1.955(3)	Al(2)-O(6)	1.827(3)
Fe(1)-O(2)	1.983(3)	Al(2)-O(16)	1.831(3)
Fe(1)-O(1)	1.955(3)	Al(2)-O(12)	1.855(3)
Fe(1)-O(7)	2.000(3)	Al(2)-O(15)	1.884(3)
Fe(1)-O(15)	2.043(3)	Al(2)-O(5)	1.888(3)
Fe(1)-O(16)	2.120(3)	Al(1)-O(13)	1.713(3)
Fe(2)-O(9)	1.808(3)	Al(1)-O(11)	1.717(3)
Fe(2)-O(8)	1.900(3)	Al(1)-O(8)	1.756(3)
Fe(2)-O(4)	1.929(3)	Al(1)-O(12)	1.826(3)
Fe(2)-O(3)	1.976(3)		

O(1)-Fe(1)-O(2)	87.5(1)	O(2)-Fe(1)-O(7)	92.8(1)
O(8)-Fe(1)-O(7)	79.2(1)	O(8)-Fe(2)-O(7)	79.9(1)
O(4)-Fe(2)-O(3)	87.3(1)	O(16)-Al(2)-O(15)	86.5(1)
O(2)-Fe(1)-O(15)	98.5(1)	O(6)-Al(2)-O(5)	88.9(1)
O(8)-Fe(1)-O(15)	89.6(1)		

3.3.2. Crystal structure description of $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (11)

$[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (**11**) crystallizes monoclinic in a P21/n space group with two diethyl-ether molecules. The structure exhibits two iron metals and two aluminium atoms and contains two disilanolate ligands and three acetyacetonate groups.

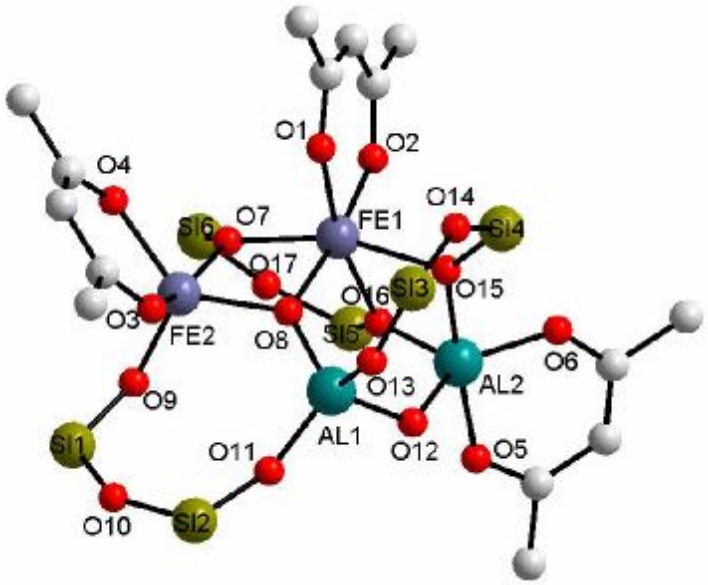


Figure 30: Representation of $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (11).

Al(1) is tetra-coordinated, as in **1**, connected to the another Al(2) atom through O(12) oxygen atom. The observed Al(1)-O(12) bond length has a value of 1.826(3)Å and the mean Al(1)-O (Si) of 1.71Å, those are close to those in **1**.

The Al(2) atom is penta-coordinated by two silanolate oxygen atoms and by an acetylacetonate ligand, where the Al-O distances (1.827(3)Å and 1.888(3)Å) are similar to those observed in $Al(acac)_3$. (Figure 31)

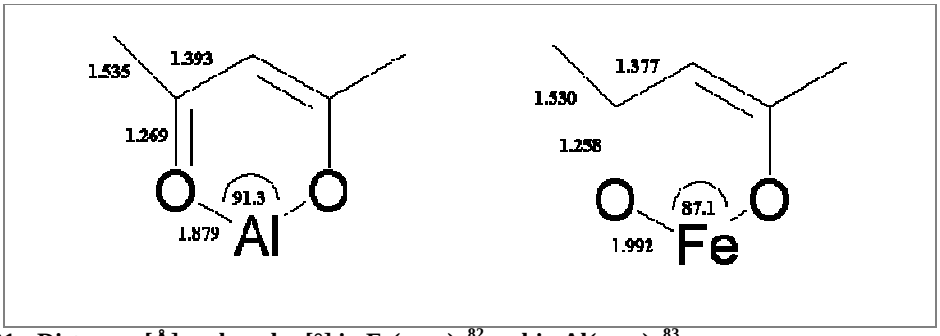


Figure 31 : Distances [Å] and angles [°] in $Fe(acac)_3$ [82] and in $Al(acac)_3$ [83].

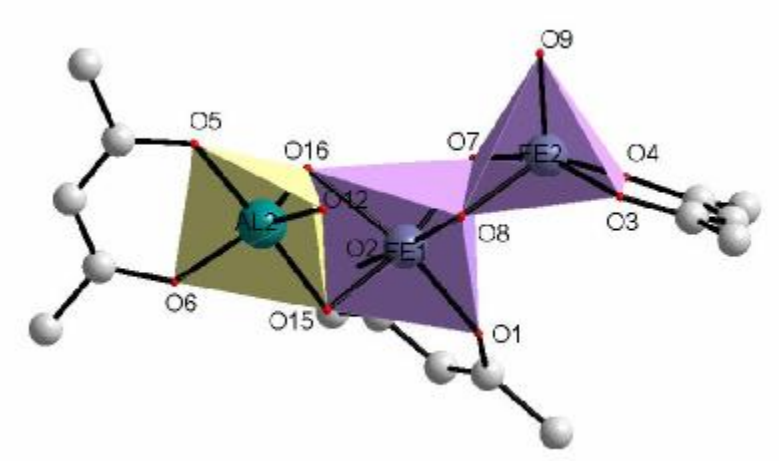


Figure 32: Environment of the iron and aluminium atoms surrounded by acetylacetonate ligands.

Each iron atoms are surrounded by an acetylacetonate group. The iron Fe(1) is hexa-coordinated in distorted square bypiramidal geometry. The square plan is formed by (O(7), O(8), O(15), O(2)) with Fe-O distances varying from 1.900(3)Å to 2.043(3)Å. The angles in this plane span a range from 79.2(1)Å to 98.5(1)Å. (sum of angles= 360°) The axial oxygen atoms are situated at 1.955(3)Å for O(1) and 2.120(3)Å for O(16).The iron atom Fe(2) is penta-coordinated in a square pyramidal geometry. The square plane is formed by O(3) and O(4) from the acetyacetonate ligand and by O(8) and O(7) with distances varying from 1.9(3)Å to 2.007(3) Å. The axial oxygen is situated at 1.808(3)Å. Due its higher coordination degree, Fe(1) is surrounded by Fe-O bond lengths longer as around Fe(2).

$\sum M-O/n$	M=Al	M=Fe
n= 4	1.753	
n= 5	1.857	1.92
n= 6		2

Table 18 : $\sum M-O/n$ for M= Al and Fe with different coordination numbers (n=4, 5, 6).

As expected, the M-O distances are higher with the increase of the coordination's sphere. In table, the sum of the M-O distances ($\sum M-O$) divided by the number of ligands (n) are reported for the penta- and hexa-coordinated iron ant the tetra- and penta-coordinated aluminium atom.

The mean length bond for the iron-oxygen bond Fe-O(acac) (1.9Å) are close to the values quoted by Iball *et al.*[82, 83]. (Figure 28)

Three ($OSi(Ph_2)OSi(Ph_2)O$) ligand are present in the structure with Si-O bond length about 1.6 Å . One of these ligands chelates Fe(2) and Al(1) in a μ_2-coordination system forming a eight-membered ring. The Fe(2)-O(Si) and Al(1)-O(Si) bond lengths have values of 1.808(3) Å and 1.717(3) Å respectively.

The second disilanolate ligand, in a μ_3-coordination system, connects Al(1), Al(2) and Fe(1). The Fe(2)-O(Si), Fe(3)-O(Si) and Al(2)-O(Si) bond lengths have values of 1.713(3) Å ,1.884(3) Å and 2.043(3)Å respectively.

The third disilanolate ligand chelates Fe(2), Fe(3) and Al(2). The Al(2)-O(Si), Fe(2)-O(Si) and Fe(1)-O(Si) bond lengths have values of 1.831 (3) Å , 2.007(3) Å and 2.120(3) Å respectively.

3.4. Discussion

The reactivity of **1** in front of metallic reagents is depending of two following things.

- The solvent coordinated on **1**, which can have an effect in the reaction. In fact, Sn(II) metal tends to make easily [Sn-O] entity. The presence of O^{t}Bu group which is more available to the approach of a congestioned group such the "Veith" stannylene, permit to form the new tetra-nuclear compound **9** allowing the connection of three of the Sn atoms with the formation of a heterocubane.

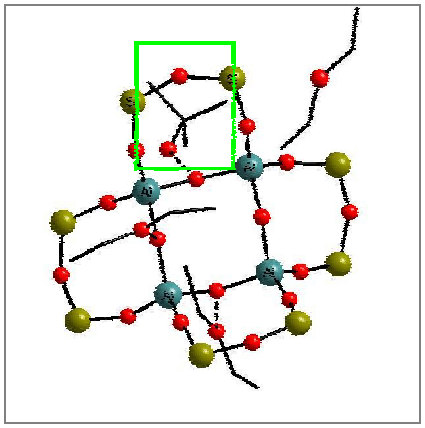
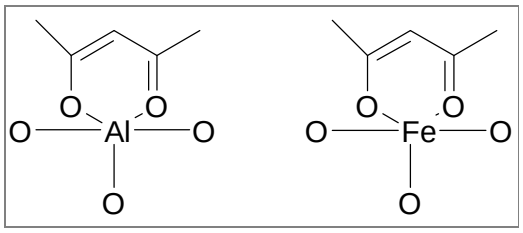


Figure 33 : Structure representation of 1.3OEt$_2$.O^{t}Bu.

- The metal used affects the reactivity of **1**. The choice of a metal with virtually similar acid-base proprieties induces some ligand exchange. The reactions associated with the ligand redistribution according to Equation 15 can be explained by much smaller difference in Lewis acidity and basicity between Al(III) and Fe(III) than Ni(II).

In the case of compound **10**, the coordination number of the aluminium atom is preserved by the coordination with acetylacetonate ligand. In the reaction leading to compound **11**, there is a competition between Al(III) and Fe(III) metals. Fe(III) atom tends to compete with the aluminium atoms for the ketoenolate ligands.



Scheme 2 : Environment around Al(2) and Fe(2).

Both aluminium and iron atoms, have the same environment, specifically two oxygen atoms from the acetylacetonate ligand and three other oxygen atoms.

4. Contraction of an eight-membered ring to four–membered rings

Reactivity of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) toward water molecules was already studied [24] (see introduction) and leads to a polycyclic rearrangement of **1** which contains an octahedral coordinated aluminium atom. In this reaction, water is formally trapped by one of the [AlO(OH)] units and by the rearrangement of the whole molecule.

$$3/2\,[(Ph_2Si)_2O_3]_4Al_4(OH)_4 + H_2O + 3OEt_2 + \{AlO(OH)\} \longrightarrow [(Ph_2Si)_2O_3]_6[AlO(OH)]_6[Al(OH)_3].3OEt_2$$

1

Equation 16 : Reaction [24] of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (1) with water.

The approach of small bases such as water is then accomplished leading to original structure. Thus, it was interesting to check how compound $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (**2**) reacts with water and if the Li atoms of the molecule interfere in this reactivity. This purpose was studied in chapter 2.2 by the reaction between $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (**2**) and hydrated copper iodide where the water molecules were introduce through the Cu(I), this former permits to the water to be softly approached to the aluminium atoms.

The research presented in this chapter, is focused to the understanding and the control of the formation of metallasiloxane compounds derivatives from $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**).The first metallasiloxane obtained during the reaction of **2** with water molecules induces a strategy for the synthesis of new type of metallasiloxane [84] compounds with nickel, cobalt or magnesium atoms.

4.1. Synthesis of $Al[\{(OPh_2Si)_2O\}_2$-μ-$\{Li(THF)_2\}]$

The unexpected compound issue from the reaction of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (**2**) with water molecules is a rare metallasiloxane [85, 86] of aluminium and lithium atoms, it was confirmed by the structure determination (Chap. 4.1.1).

A simple strategy for the synthesis of $Al[\{(OPh_2Si)_2O\}_2$-μ-$\{Li(THF)_2\}]$ (**12**) from the compound $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (**2**) was then explored.

Compound **12** is formed during the reaction between **2** and four equivalents of water in THF as solvent. After 16 hours, the clear solution is evaporated and the resulting white powder was dissolved in diethyl-ether. A small amount of side-products was precipitating. White clear crystals suitable for structure determination were obtained in diethyl-ether after the filtration of the side-products with a yield of 56%.

$$[(Ph_2Si)_2O_3]_4Al_4(OLi)_4.4Et_2O \;+\; 4\ H_2O \xrightarrow[-\,2\,[(Al(OH)_4]^-\ Li^+\ (H_2O)_3]{THF/Et_2O} 2\ Al[O(OPh_2Si)]_2Li(THF)_2$$

2.4Et$_2$O — **12**

Equation 17: Synthesis of Al[{(OPh$_2$Si)$_2$O}$_2$-μ-{Li(THF)$_2$}] (12).

Only one signal was observed at -34ppm in the ambient-temperature ^{29}Si NMR spectrum (in d^6-benzene), suggesting that the magnetically distinct Si environments of the solid-state structure were equilibrated in solution. The equilibration may be accomplished by intramolecular lithium ion mobility. The small quantity obtained has not permitted further investigations such ^{7}Li NMR studies at variable temperatures [87 a, b].

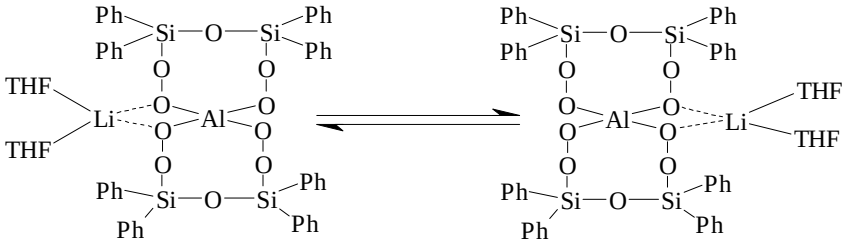


Figure 34 : Possible exchange process for compound 12.

In the ^{1}H-NMR, two multiplets are situated between 7.23ppm to 7.96ppm for 20 protons, and between 8.02 and 8.56ppm for the 20 others hydrogen atoms.

The ^{13}C-NMR spectrum displays signals at 132.43ppm and at 129.7ppm for the phenyl groups from the disilanolate ligands.

According to the structure determination (Chapt.4.1.1), compound **12** is composed by one aluminium atom and one lithium ion connected through oxygen atoms from the disilanolate ligands. The lithium ion is coordinated with further two THF molecules.

The presence of a strong base such water which can access to the aluminium atom induces the formation of an aggregate of compound **2**. Contrary to the previous reaction of **1** with water [24], the presence of Li atom permits the formation of an unusual hetero-metallasiloxane of Li and aluminium. One suggestion to the formation of side-products ($AlLiO_7H_{10}$) is that water molecules form, with the aluminium atom and lithium ion, two molecules of $[Al(OH)_4]^-Li^+\ (H_2O)_3]$. These fragments precipitate in diethyl ether and are filtrated. These molecules were deducted from the stoichiometry; the elemental analysis has confirmed the absence of any carbon rest.

4.1.1. Crystal structure determination of Al[{(OPh$_2$Si)$_2$O}$_2$-μ-{Li(THF)$_2$}] (**12**)

A crystal of Al[{(OPh$_2$Si)$_2$O}$_2$-μ-{Li(THF)$_2$}] (**12**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 3.99%. In table 19 are reported the crystal data and the structure refinement for the compound and in table 20 are reported some selected bond lengths and angles of interest.

Table 19: Crystal data and structure refinement for sh2252.

Identification code	sh2252	
Empirical formula	C_{56} H_{56} Al Li O_8 Si_4	
Formula weight	1003.29	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 16.5739(8) Å	α= 90°.
	b = 13.1460(5) Å	β= 95.248(4)°.
	c = 24.1491(17) Å	γ = 90°.
Volume	5239.6(5) Å^3	
Z	4	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.184 mm^{-1}	
F(000)	2112	
Crystal size	0.2 x 0.45 x 0.55 mm^3	
Theta range for data collection	1.69 to 30.29°.	
Index ranges	-23<=h<=23, -18<=k<=18, -34<=l<=34	
Reflections collected	66625	
Independent reflections	7813 [R(int) = 0.0304]	
Completeness to theta = 30.29°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7813 / 0 / 317	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1087	
R indices (all data)	R1 = 0.0477, wR2 = 0.1160	
Largest diff. peak and hole	0.833 and -0.589 e.Å^{-3}	

Table 20 : Selected bond lengths [Å] and angles [°] for sh2252.

Al-O(3)´	1.7295(9)	Si(2)-O(3)	1.611(1)
Al-O(3)	1.7296(9)	Si(2)-O(2)	1.648(1)
Al-O(1)	1.7648(9)	Li(1)-O(4)´	1.896(2)
Al-O(1)´	1.7648(9)	Li(1)-O(4)	1.897(2)
Si(1)-O(1)	1.6222(9)	Li(1)-O(1)	2.027(3)
Si(1)-O(2)	1.6445(9)	Li(1)-O(1)´	2.027(3)

O(1)-Al-O(1)´	97.480(6)	O(4)´-Li(1)-O(1)	111.18(5)
O(1)-Si(1)-O(2)	109.78(5)	O(4)-Li(1)-O(1)	118.28(6)
O(3)-Si(2)-O(2)	109.46(5)	O(4)´-Li(1)-O(1)´	118.28(6)
Al-O(1)-Li(1)	90.380(7)	O(4)-Li(1)-O(1)´	111.19(5)
O(4)´-Li(1)-O(4)	112.90(2)	O(1)-Li(1)-O(1)´	81.800(1)

4.1.2. Crystal structure description of Al[{$(OPh_2Si)_2O$}$_2$-μ-{$Li(THF)_2$}] (12)

Compound **12** crystallizes monoclinic in a I 2/a space group. The aluminium atom and the lithium ion are bridged by two disilanolate ligands in a μ_2 coordination system resulting in the formation of a $AlLiO_2$ four-membered ring. The coordination of the lithium atom is completed by two THF molecules. The molecule has C_2, point symmetry.

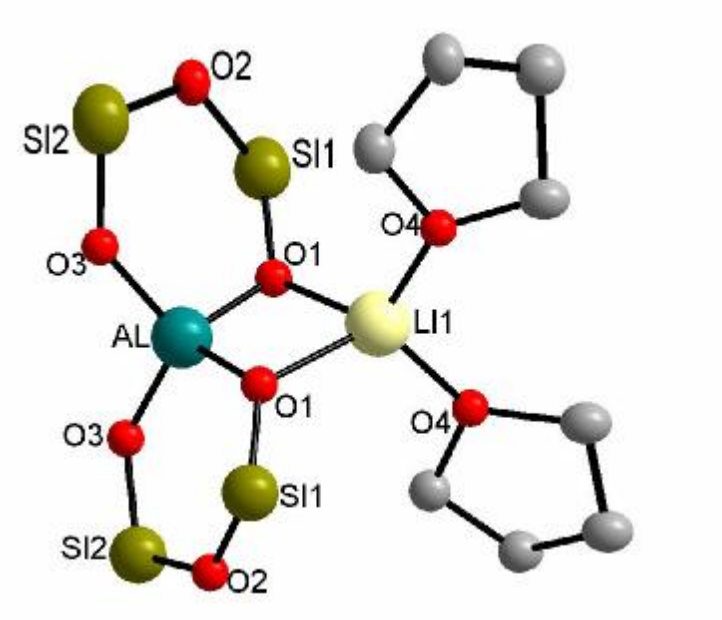


Figure 35: Representation of Al[{$(OPh_2Si)_2O$}$_2$-μ-{$Li(THF)_2$}] (12). (Phenyl groups of the Ph_2Si are omitted for clarity.)

The aluminium metal is tetra-coordinated by the four oxygen atoms of the silanolate ligands with angles varying from 81.77(2)° to 97.479(2)° . The bond lengths Al-O(Si) have values of 1.7296(1)Å and 1.7648(1)Å close to those [19] in **2**. The former distance corresponds to the Al-O(Li) bond. The lithium ion makes two coordination bonds with THF molecules with bond length Li-O of 1.8965(1) Å. The Si-O bond lengths in the disilanolate ligands present in the structure are all about 1.6Å.

4.2. Synthesis of $[Ni(H_2O)_2\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Al(acac)_2\}_2].OEt_2$ (13)

The precedent reaction showed clearly that the presence of a limited amount of water in presence of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) coordinated to lithium leads to metallasiloxane compounds. It was then interesting to perform reactions including water molecules in a controlled amount. An interesting approach was to use transition metals complexes with water as ligand. These complexes can then be regarded as water source.

The reaction of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) with nickel(II) acetyacetonate hydrate (diaquobisacetylacetonatonickel) $Ni(acac)_2(H_2O)_2$ [73] in toluene/diethyl-ether was then realized. The water molecules of $Ni(acac)_2(H_2O)_2$ are readily replaced by other neutral or anionic ligands. Alcohols are able to displace water molecules. Water molecules are certainly replaced by diethyl-ether and this replacement leads to the presence of water in the reaction medium. That implies an hydrolysis of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**).

The structure determination of **13** revealed that the reaction leads to the complex $[Ni(H_2O)_2\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Al(acac)_2\}_2].OEt_2$ with a yield of 30%. The complex crystallizes easily from diethyl-ether to give green crystals. The composition of the side-product obtained by evaporation of the remaining solution is deducted from the stoichiometry and was characterized by elemental analysis.

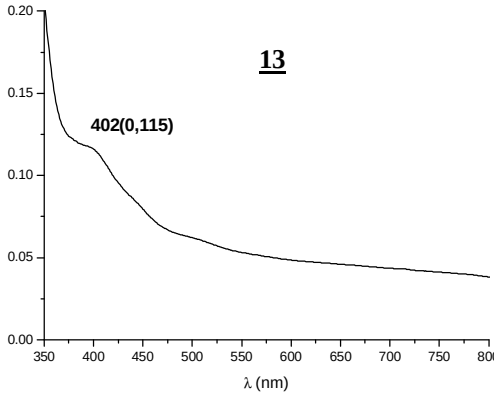
$$2\ Ni(acac)_2(H_2O)_2 + [(Ph_2Si)_2O_3]_4Al_4(OH)_4.4OEt_2 \xrightarrow[Et_2O]{Toluol} Ni(H_2O)_2[O(OPh_2Si)_2]_2Al_2(acac)_4.OEt_2$$

1.$4Et_2O$ → **13** + $Ni(H_2O)_2(OH)_4Al_2[O(OPh_2Si)_2]_2$

Equation 18: Synthesis of $[Ni(H_2O)_2\{(OPh_2Si)_2O\}_2\text{-}\mu\text{-}\{Al(acac)_2\}_2].OEt_2$ (13).

The initial structure **1** is decomposed to form a new type of aggregate which contains two $NiAlO_2$ four-membered rings. Each aluminium atoms is surrounded by two acetylacetonate groups.

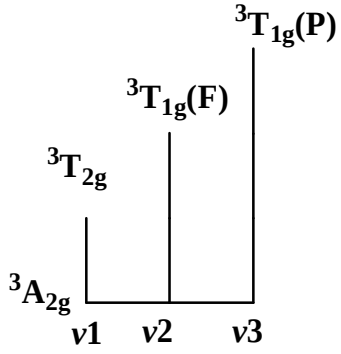
The molecular structure shows that the octahedral structure of Ni (II) acetylacetonate is preserved thanks to the water molecules coordinated on the central nickel atom. NMR spectroscopy was not carried out because of the paramagnetism of Ni (II) in octahedral environment [73].



Graph 4: $^3A_{2g}$ à $3T_{1g}$ (F) transition of [Ni $(H_2O)_2$\{$(OPh_2Si)_2O$\}$_2$-μ-\{$Al(acac)_2$\}$_2$].OEt_2.

The UV-Vis. spectral study of the solutions of **13** in toluene confirmed the octahedral environment and has shown a very distinct band at *v*2=402nm corresponding to the $^3A_{2g}$ à $3T_{1g}$ (F). The $^3A_{2g}$ à $^3T_{2g}$ (*v*1) transition is not visible because situated after 1000nm, and the third $^3A_{2g}$ à $^3T_{1g}$ (P) (*v*3) is obscured by the intense charge transfer bands [88].

Ni (II) has the $3d^8$ electronical configuration; the complex is high spin having trans-octahedral stereochemistry. The ^3F ground term is split in an octahedral field giving rise to the triplet terms with three main bands expected [89].



Scheme 8: Interpretation of the electronic absorption spectra.

4.2.1. Crystal structure determination of Ni $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (13)

A crystal of [Ni $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (**13**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 4.82%. In table 21 are reported the crystal data and the structure refinement for the compound and in table 22 are reported some selected bond lengths and angles of interest.

Table 21 : Crystal data and structure refinement for 2436.

Identification code	sh2436	
Empirical formula	$C_{72}\ H_{80}\ Al_2\ Ni\ O_{17}\ Si_4$	
Formula weight	1442.39	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.338(4) Å	α= 90°.
	b = 11.588(2) Å	β= 107.036(16)°.
	c = 25.489(4) Å	γ = 90°.
Volume	7155.5(19) $Å^3$	
Z	4	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	0.430 mm^{-1}	
F(000)	3032	
Crystal size	0.37 x 0.26 x 0.08 mm^3	
Theta range for data collection	1.67 to 36.53°.	
Index ranges	+42<=h<=42, -19<=k<=19, +42<=l<=42	
Reflections collected	150271	
Independent reflections	17379 [R(int) = 0.0786]	
Completeness to theta = 36.53°	98.7 %	
Absorption correction	Numerical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17379 / 0 / 444	

Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1174
R indices (all data)	R1 = 0.0878, wR2 = 0.1364
Largest diff. peak and hole	0.739 and -0.772 e.$Å^{-3}$

Table 22 : Selected bond lengths [Å] and angles [°] for sh2436.

Ni-O(4)	2.052(2)	Al(1)-O(1)	1.850(1)
Ni-O(2)´	2.053(1)	Al(1)-O(2)	1.853(1)
Ni-O(2)	2.053(1)	Al(1)-O(5)	1.902(1)
Ni-O(1)	2.059(1)	Al(1)-O(8)	1.909(1)
Ni-O(1)´	2.059(1)	Al(1)-O(7)	1.909(1)
Ni-O(3)	2.096(2)	Al(1)-O(6)	1.913(1)

O(4)-Ni-O(2)´	91.82(3)	O(2)´-Ni-O(1)´	76.77(4)
O(4)-Ni-O(2)	91.82(3)	O(2)-Ni-O(1)´	103.27(4)
O(2)´-Ni-O(2)	176.35(6)	O(1)-Ni-O(1)´	178.70(5)
O(4)-Ni-O(1)	89.35(3)	O(4)-Ni-O(3)	180.00(1)
O(2)´-Ni-O(1)	103.27(4)	O(2)´-Ni-O(3)	88.18(3)
O(2)-Ni-O(1)	76.77(4)	O(2)-Ni-O(3)	88.18(3)
O(4)-Ni-O(1)´	89.35(3)	O(1)-Ni-O(3)	90.65(3)
		O(1)´-Ni-O(3)	90.65(3)

4.2.2. Crystal structure description of Ni $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (13)

Compound **13** crystallizes in a monoclinic system with a space group of C 2/c with one molecule of Et_2O per formula unit. The Et_2O molecule does not interact with the acidic centers of the molecule but serve to optimize the crystal packing. Compound **13** (Figure 36) is formed by a central nickel metal surrounded by two water molecules and by two disilanolate ligands in a μ_3 coordination system forming two NiO_2Al four-membered rings. The aluminium atoms on each side from the nickel atom are surrounded by two acetyacetonate groups. [Ni $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (**13**) has C_2, point symmetry as compounds **14** and **15** (described in the following chapters). These entire compounds are iso-structural.

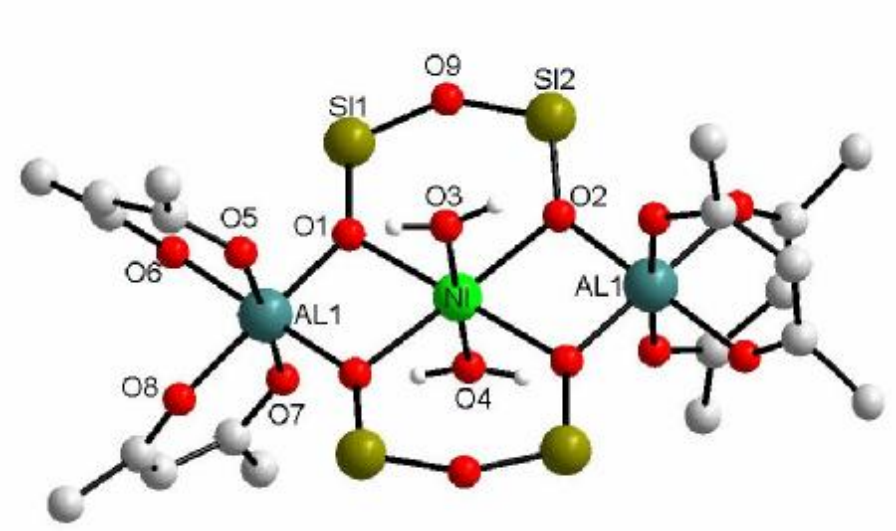


Figure 36: Representation of the crystal structure of Ni $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (13) (Phenyl groups of the Ph_2Si are omitted for clarity.)

The central nickel atom, surrounded by two disilanolate ligands and by two molecules of water, is in square-bipyramidal geometry. Atoms O(1), O(1)´, O(2), and O(2)´ constitute the square plane with angles varying from 76.774(8)° to 103.269(5) °. The axial water molecules are located 2.0523(3) Å and 2.0961(3) Å away from the nickel atom, and make angles of 88.241(6) ° and 89.669(6) ° from the square plane.

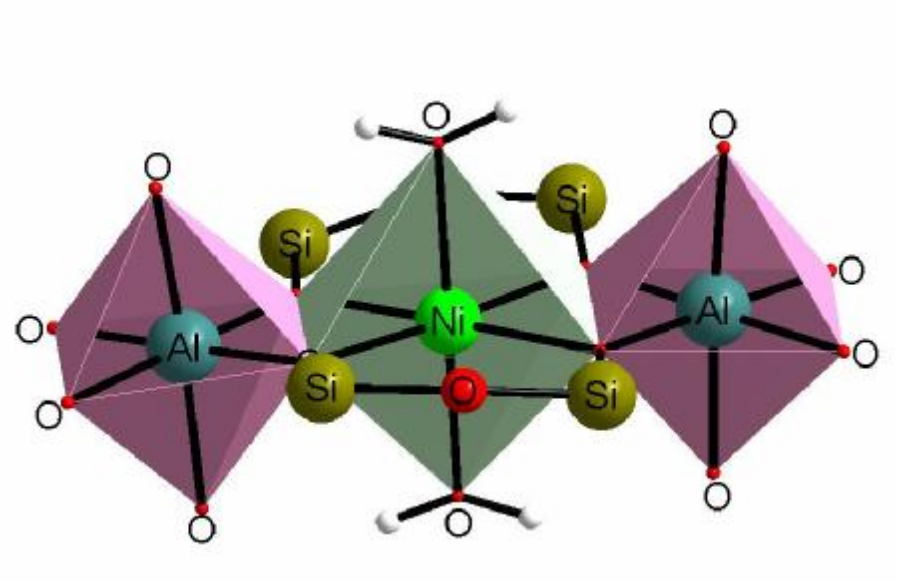


Figure 37 : Square bipyramidal arrangement around Ni and Al atoms.

The disilanolate ligand oxygen atoms coordinated to the nickel atom with 2.0533(3)Å and 2.0593(4)Å bond length, also bridge two aluminium atoms on either side of the square plane, resulting in the formation of two four-membered $NiAlO_2$ rings. The Ni-O bond length (2.0533(3) Å and 2.0593(4) Å) are close to those in $Ni(acac)_2(H_2O)_2$ (2.05 Å) [90].

The aluminium atoms are surrounded by two acetylacetonate groups in a spirocyclic fashion. These aluminium atoms are in a square bipyramidal arrangement [78]. The square plane is formed by O(1) and O(2) atoms from the disilanolate ligands situated at 1.85Å from the aluminium atom , and by O(6) and O(8) atoms from the acetyacetonate groups (1.9 Å). The axial oxygen atoms are also situated at 1.9 Å from the aluminium metal atom, these distances are close to those found in the complex $Al(acac)_3$ [83]. The oxygen atoms around the aluminium ion form angles varying from 87.199(10) ° to 92.765(6) °.

4.3. Synthesis of $Co(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2].Et_2O$ (14)

Repeated attempts to achieve a hydrolysis reaction with formation of a hetero-metallasiloxane as previously were realized with cobalt instead of nickel.

$[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) was allowed to react with cobalt acetylacetonate hydrate $Co(acac)_2(H_2O)_2$ [92] in toluene. After 16 hours under vigorous stirring, the compound was obtained by re-crystallization in diethyl-ether, 40% of pink crystals were isolated by standing at +4° for few days.

$$2\,Co(acac)_2(H_2O)_2 + [(Ph_2Si)_2O_3]_4Al_4(OH)_4\,.4OEt_2 \xrightarrow[Et_2O]{\text{Toluol}} Co(H_2O)_2[O(OPh_2Si)_2]_2Al_2(acac)_4\,.OEt_2$$

1.$4Et_2O$

14

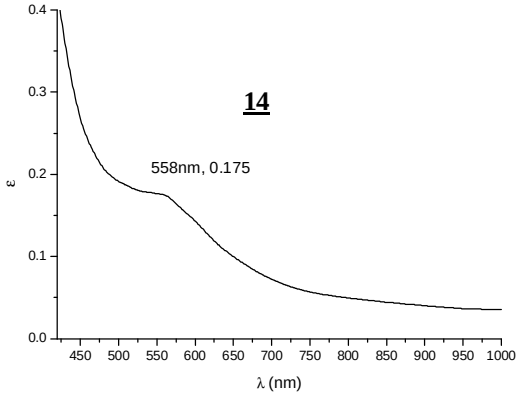
+

$Co(H_2O)_2(OH)_4Al_2[O(OPh_2Si)_2]_2$

Equation 19: Synthesis of $Co(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2].Et_2O$ (14).

In the solid state, $Co(acac)_2$ is tetrameric [93], the metal atoms are in a pseudo-octahedral geometry with bridging and non bridging acetylacetonate units present in the structure. In coordinating solvents, the solvent fills the two available sites around the four coordinate $Co(acac)_2$. The dihydrate $Co(acac)_2(H_2O)_2$ has the trans-octahedral structure.

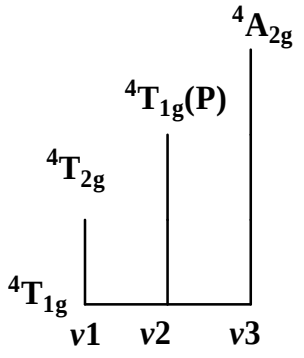
From a qualitative point of view, the comparison of the recorded spectrum (Graph.5) with other previous reports dealing with cobalt(II) complexes [94-95] allows to form the assumption that the cobalt in compound **14** stay in an octahedral environment.



Graph 5: $^4T_{1g}$ à $^4T_{1g}$ (P) transition of $[Co\,(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2].OEt_2$.

The UV-Vis. spectral study of the solutions of compound **14** in toluene confirmed the octahedral environment The Co^{2+} ion has the $3d^7$ electronic configuration which in octahedral fields gives rise to high spin $t^2g^5\,eg^2$. The ground term arising is ^4T_1g.

In general, with this type of six-coordinate cobalt (II) compounds, it can be seen that the spectra consist of a band in the near infrared which is assigned to the lowest energy transition $^4T_{1g} \rightarrow {}^4T_{2g}$ (v1 not observed for **14**) and a band in the visible near (v2 at 558nm) which is assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition. The $^4T_{1g} \rightarrow {}^4A_{2g}$ (*v*3) is frequently not observed [92].



Scheme 3 : Interpretation of the electronic absorption spectra.

The structure determination (Chapt.4.3.1) confirms that this geometry environment is conserved in the hetero-metallic complex [96] formed where the Co metal is surrounded by two water molecules and the Al atoms by two acetylacetonate groups in a hexa-coordination environment.

4.3.1. Crystal structure determination of $Co(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2].Et_2O$ (14)

A crystal of [Co $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (**14**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 3.12%. In table 23 are reported the crystal data and the structure refinement for the compound and in table 24 are reported some selected bond lengths and angles of interest.

Table 23 : Crystal data and structure refinement for sh2513.

Identification code	sh2513	
Empirical formula	$C_{72}\ H_{82}\ Al_2\ Co\ O_{17}\ Si_4$	
Formula weight	1444.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.364(3) Å	α= 90°.
	b = 11.551(1) Å	β= 108.132(8)°.
	c = 25.647(3) Å	γ = 90°.

Volume	7140.8(12) $Å^3$
Z	4
Density (calculated)	1.344 Mg/m^3
Absorption coefficient	0.400 mm^{-1}
F(000)	3036
Crystal size	0.35 x 0.5 x 0.65 mm^3
Theta range for data collection	1.67 to 24.61°.
Index ranges	-29<=h<=29, -13<=k<=13, -30<=l<=29
Reflections collected	57380
Independent reflections	6007 [R(int) = 0.0352]
Completeness to theta = 24.61°	99.7 %
Absorption correction	Multi scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6007 / 0 / 588
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0794
R indices (all data)	R1 = 0.0392, wR2 = 0.0846
Largest diff. peak and hole	0.386 and -0.233 $e.Å^{-3}$

Table 24 : Selected bond lengths [Å] and angles [°] for sh2513.

Al-O(1)	1.845(1)	Al-O(5)	1.919(1)
Al-O(2)	1.857(1)	Co-O(10)	2.062(2)
Al-O(4)	1.905(1)	Co-O(2)	2.084(1)
Al-O(7)	1.906(1)	Co-O(1)	2.096(1)
Al-O(6)	1.911(1)	Co-O(9)	2.140(2)

O(1)-Al-O(2)	87.43(6)	O(2)-Co-O(1)´	104.68(5)
O(10)-Co-O(2)´	94.21(4)	O(2)´-Co-O(9)	85.79(4)
O(10)-Co-O(2)	94.21(4)	O(2)-Co-O(9)	85.79(4)
O(10)-Co-O(1)	88.94(3)	O(1)-Co-O(9)	91.06(3)
O(2)-Co-O(1)	75.47(5)	O(1)´-Co-O(9)	91.06(3)

4.3.2. Crystal structure description of $Co(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2].Et_2O$ (14)

14 crystallizes as **13** in a monoclinic system with a space group of C 2/c with one molecule of Et_2O per formula unit. These two compounds are iso-structural. The Et_2O molecule does not interact with the acidic centers of the molecule but serves to optimize the crystal packing. Compound **13** is formed by a central cobalt metal surrounded by two water molecules and by two disilanolate ligands in a μ_3 coordination system forming two CoO_2Al four-membered rings. The aluminium atoms on each side from the nickel atom are surrounded by two acetylacetonate groups. [Co $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (**14**) has C_2, point symmetry as compounds **13** and **15**.

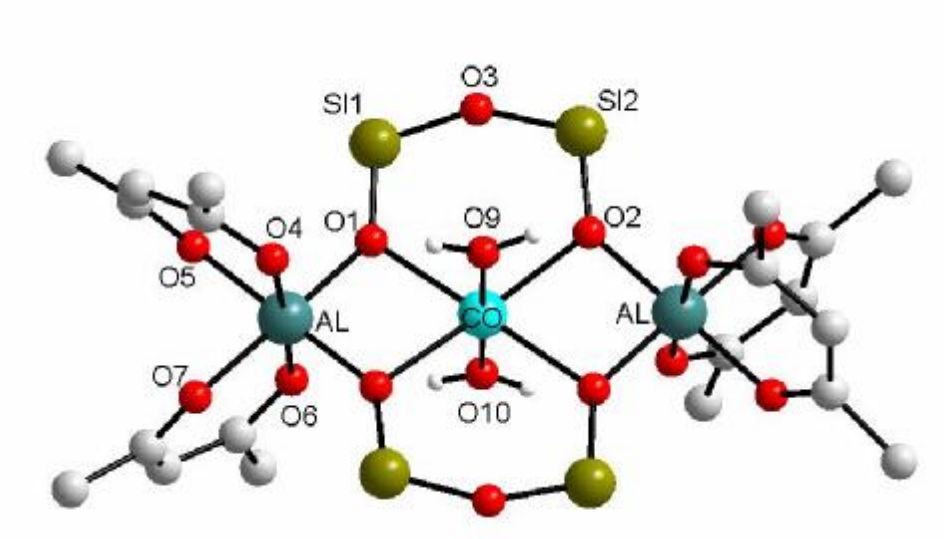


Figure 38: Representation of the crystal structure of [Co $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$] (Phenyl groups of the Ph_2Si are no represented for clarity).

The cobalt atom, surrounded by two disilanolate ligands and by two molecules of water, is in square-bipyramidal geometry. Atoms O(1), O(1´), O(2), and O(2´) constitute the square plane with angles varying from 75.47(5)° to 104.68(5) °. The axial water subsistent are located 2.062(2) Å and 2.14(2) Å away from the nickel atom, these bond distances are close to those in $Co(acac)_2(H_2O)_2$ [97] (2.1Å). The water molecules make angles of 91.06(3) ° and 94.21(4) ° from the square plane.

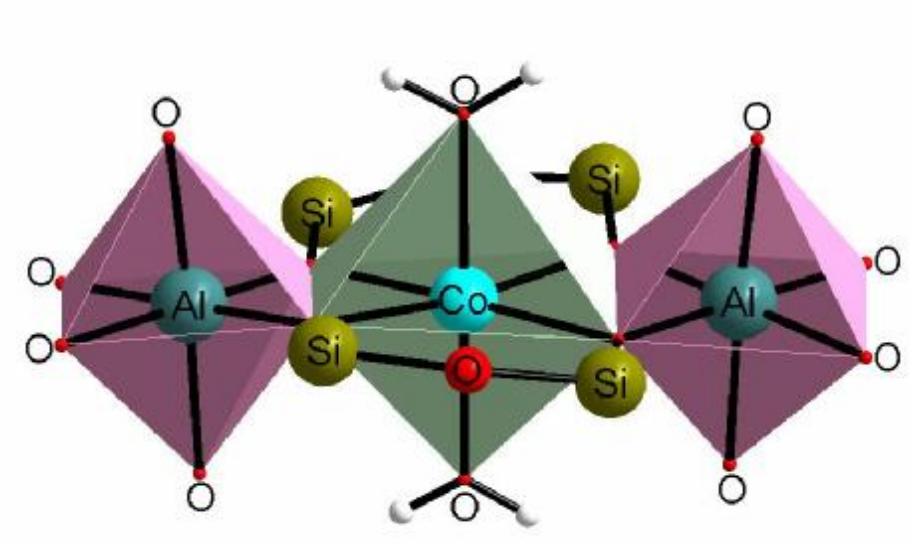


Figure 39: Square bipyramidal arrangement around Co and Al atoms.

The aluminium atoms are surrounded by two acetylacetonate groups in a spirocyclic fashion. These aluminium atoms are in a square bipyramidal arrangement. The square plane is formed by O(1) and O(2) atoms from the disilanolate ligands situated at 1.845(1)Å and 1.857(1)Å from the aluminium atom , and by O(5) and O(7) atoms from the acetyacetonate groups (1.919(1)Å and 1.906(1)Å). The axial oxygen atoms are also situated at 1.9 Å (av.) from the metal atom [98]. The Al-O(acac) bond lengths are very close to those observed in the related heterometallic complex $[CoAl_2(acac)_4(O^iPr)_4]$ synthesized by Kessler *et al.* [99].

4.4. Synthesis of [Mg $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (15)

Motevalli *et al.* [100] have synthesized in 1994 the magnesiasiloxane $[(py)_2Li]_2$-μ-$Mg[\{Ph_2SiO\}_2O][\{Ph_2SiO\}_3O]$ isolated from the reaction between $MgCl_2$-2THF and the dilithium salt $[(Ph_2SiOLi.THF)_2O]$. This was the first example of a molecular magnesium siloxide compound to be characterized. The molecular structure of this compound shows the presence of a six- and an eight-membered spirocyclic siloxane ring.

Repeated attempts to achieve an hydrolysis reaction with formation of a metallasiloxane with the same degree of oligomerisation (six-membered ring) as compound **13** and **14** was achieved with the use of $Mg(acac)_2(H_2O)_2$.

Compound **15** is obtained by interaction between $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) and magnesium acetylacetonate hydrate $Mg(acac)_2(H_2O)_2$ [101]. After 20min refluxing in toluene as solvent, the compound was obtained by re-crystallization in diethyl-ether, 20% of clear white crystals were isolated by standing at +4°C for few months.

$$2\,Mg(acac)_2(H_2O)_2 + [(Ph_2Si)_2O_3]_4Al_4(OH)_4.4OEt_2 \xrightarrow[Et_2O]{Toluol} Mg(H_2O)_2[O(OPh_2Si)_2]_2Al_2(acac)_4.OEt_2$$

1.$4Et_2O$ → **15** + $Mg(H_2O)_2(OH)_4Al_2[O(OPh_2Si)_2]_2$

Equation 20: Synthesis of [Mg $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$.

The NMR monitoring permits to conclude that the reactivity of **1** toward $Mg(acac)_2(H_2O)_2$ is clearly the same as for M $(acac)_2(H_2O)_2$ (M=Ni, Co).

In fact, the ^{29}Si NMR CP/MAS spectrum shows one signal at -39.29ppm corresponding to the silicon atoms that confirm the symmetry center on the magnesium atom. In the ^{1}H-NMR spectrum of **15** in d^6-benzene, the phenyl group are represented by multiplets between 7.02 and 7.64ppm. The signals for the acac ligands coordinated on the aluminium atom [102] are situated at 2.10ppm (singlet for CH_3 integrating for 24 protons), and at 4.65ppm (singlet for CH group integrating for four protons).

The ^{13}C-NMR spectrum displays signals at 135.25ppm and at 129.32ppm corresponding to the phenyl groups. The sp^2 carbon of acac ligand has a signal shifted at 25.23ppm and the CH_3 signal is situated at 30.05ppm.

These NMR study provides the formation of the magnesiasiloxane [Mg $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$.

Magnesium exhibits rich coordination chemistry, ranging from mononuclear to polymeric species with linear two to ten coordinate Mg atoms. The structure determination (Chapt.4.4.1) revealed that this compound is composed by two MgO_2Al four-membered rings connected via the oxygen atoms of the disilanolate ligands. The central magnesium is six-coordinated and has two water ligands in the axial position.

4.4.1. Crystal structure determination of [Mg $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (15)

A crystal of [Mg $(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2$].$OEt_2$ (**15**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a monoclinic crystal system [126]. The R-value is 5.9%. In table 25 are reported the crystal data and the structure refinement for the compound and in table 26 are reported some selected bond lengths and angles of interest.

Table 25 : Crystal data and structure refinement for 2473

Identification code	sh2473	
Empirical formula	$C_{72}\ H_{81}\ Al_2\ Mg\ O_{17}\ Si_4$	
Formula weight	1409.00	
Temperature	169(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.473(1) Å	α= 90°.
	b = 11.5789(6) Å	β= 108.069(2)°.
	c = 25.807(1) Å	γ= 90°.
Volume	7236.3(6) $Å^3$	
Z	4	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	2972	
Crystal size	0.33 x 0.25 x 0.1 mm^3	
Theta range for data collection	1.66 to 28.28°.	

Index ranges	-32<=h<=33, -15<=k<=11, -33<=l<=34
Reflections collected	26444
Independent reflections	8681 [R(int) = 0.0427]
Completeness to theta = 28.28°	96.4 %
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8681 / 0 / 445
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1323
R indices (all data)	R1 = 0.0893, wR2 = 0.1476
Largest diff. peak and hole	0.734 and -0.905 e.Å^{-3}

Table 26: Bond lengths [Å] and angles [°] for sh2473.

Al-O(1)	1.856(2)	Mg-O(9)	2.032(4)
Al-O(2)	1.862(2)	Mg-O(2)´	2.050(1)
Al-O(4)	1.896(2)	Mg-O(2)	2.050(1)
Al-O(6)	1.904(2)	Mg-O(1)´	2.052(2)
Al-O(5)	1.913(2)	Mg-O(1)	2.052(1)
Al-O(7)	1.916(2)	Mg-O(10)	2.274(6)

O(1)-Al-O(2)	86.23(7)	O(9)-Mg-O(2)	98.19(6)
O(1)-Al-O(4)	94.07(8)	O(2)´-Mg-O(2)	163.6 (1)
O(2)-Al-O(4)	90.94(8)	O(9)-Mg-O(1)´	92.28(6)
O(1)-Al-O(6)	178.89(8)	O(2)´-Mg-O(1)´	76.56(6)
O(2)-Al-O(6)	93.91(8)	O(2)-Mg-O(1)´	102.77(6)
O(4)-Al-O(6)	87.03(8)	O(9)-Mg-O(1)	92.28(6)
O(1)-Al-O(5)	92.12(7)	O(2)´-Mg-O(1)	102.77(6)
O(2)-Al-O(5)	178.28(8)	O(2)-Mg-O(1)	76.56(6)
O(4)-Al-O(5)	89.67(8)	O(1)´-Mg-O(1)	175.4(1)
O(6)-Al-O(5)	87.73(8)	O(9)-Mg-O(10)	180.000(2)
O(1)-Al-O(7)	89.60(7)	O(2)´-Mg-O(10)	81.81(6)
O(2)-Al-O(7)	91.50(8)	O(2)-Mg-O(10)	81.81(6)
O(4)-Al-O(7)	175.72(8)	O(1)´-Mg-O(10)	87.72(6)
O(6)-Al-O(7)	89.29(8)	O(1)-Mg-O(10)	87.72(6)
O(5)-Al-O(7)	87.99(8)	O(9)-Mg-O(2)´	98.19(6)

4.4.2. Crystal structure description of [Mg $(H_2O)_2${$(OPh_2Si)_2O$}$_2$-μ-{$Al(acac)_2$}$_2$].OEt_2 (15)

Compound **15** (Figure 40) crystallizes, as **13** and **14**, monoclinic in a C 2/c space group with one diethyl-ether molecule per formula units. [$Mg(H_2O)_2${$(OPh_2Si)_2O$}$_2$-μ-{$Al(acac)_2$}$_2$].OEt_2 (**15**) has C_2, point symmetry.

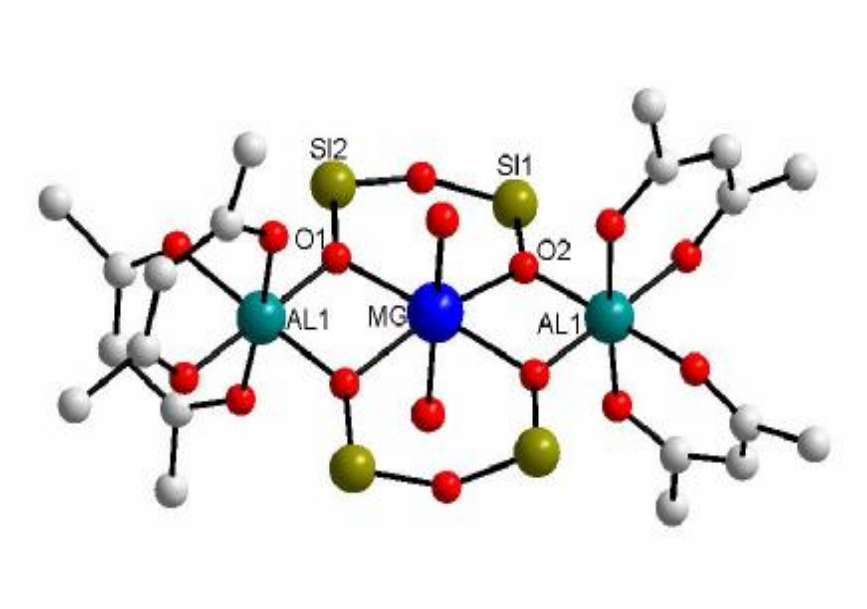


Figure 40: Representation of the crystal structure of [Mg $(H_2O)_2${$(OPh_2Si)_2O$}$_2$-μ-{$Al(acac)_2$}$_2$].OEt_2 (15).

Compound **15** is iso-structural with the compounds **13** and **14**. Both show the same crystal space group and are isotypic. In table 27, their space groups and unit cell dimensions are reported for comparison.

	Symmetry/Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Ni (13)	C_2/Monoclinic	25.338	11.588	25.489	90	107.036	90
Co (14)	C_2/Monoclinic	25.364	11.551	25.647	90	108.132	90
Mg (15)	C_2/Monoclinic	25.473	11.579	25.807	90	108.069	90

Table 27 : Space groups and unit cell dimensions of compounds [M $(H_2O)_2${$(OPh_2Si)_2O$}$_2$-μ-{$Al(acac)_2$}$_2$].OEt_2; M=Ni (13), Co (14), Mg (15).

The central magnesium metal in compound **15** is surrounded by two disilanolate ligands and has two axial water molecules in square bipyramidal geometry.

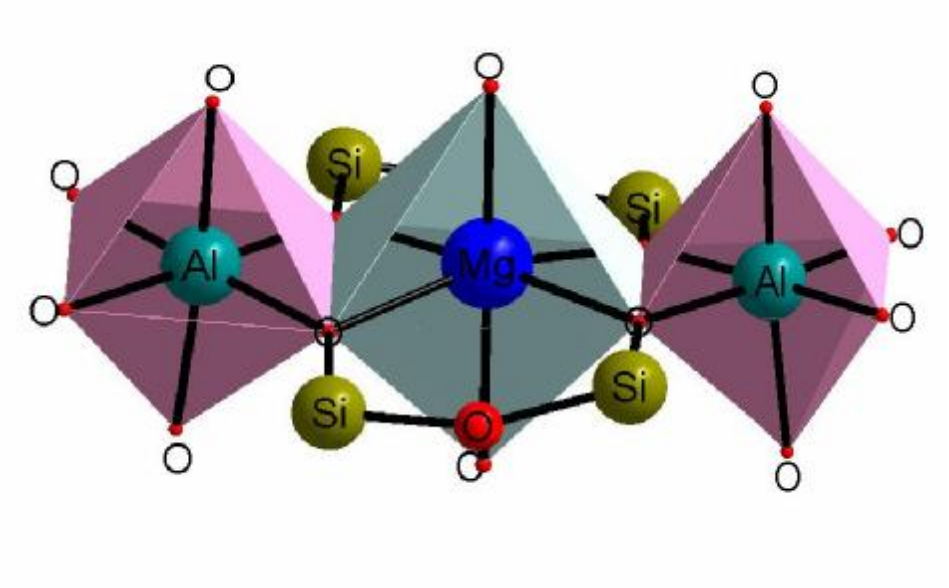


Figure 41 : Square bipyramidal arrangement around Mg and Al atoms.

The axial water molecules are located 2.032(4)Å and 2.274(6)Å away from the magnesium atom and make angles of 87.691(2)° and 92.309(2)° from the square plane constituted by O(1), O(2), O(1)´ and O(2)´. The Mg-O(-Al) distances (2.052(1)Å and 2.05(1) Å) are close to those reported for $Mg(acac)_2(H_2O)_2$ [103].

4.5. Synthesis of $Mg(Et_2O)[\{(OPh_2Si)_2O\}_2$-μ-$\{Mg(OEt_2)Br\}_2]$ (16)

Surprisingly, a similar metallasiloxane compound was obtained during the attempt to substitute metals such magnesium on **1** by using Grignard reagent [104]. The reaction between $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) and Grignard reagent such *tert*-butyl magnesium bromide leads to an unusual magnesiasiloxane compound which was confirmed by structure determination. The metallasiloxane $Mg(Et_2O)[\{(OPh_2Si)_2O\}_2$-μ-$\{Mg(OEt_2)Br\}_2]$ **16** was prepared by the reaction of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) with four equivalents of *tert*-butyl magnesium bromide freshly prepared in diethyl-ether. The complex crystallizes easily in the same solvent to give colorless crystals with a yield of 70%.

$$4\ {}^{t}BuMgBr + [(Ph_2Si)_2O_3]_4Al_4(OH)_4.4Et_2O \xrightarrow[-{}^{t}BuMgBr]{Et_2O} Mg(OEt_2)[O(OPh_2Si)_2]_2[Mg(OEt_2)Br]_2$$

1.$4Et_2O$ — **16**

$$- (AlO)_4[O(OPh_2Si)_2]_2Br(OtBu)_3$$

Equation 21: Synthesis of $Mg(Et_2O)[\{(OPh_2Si)_2O\}_2$-μ-$\{Mg(OEt_2)Br\}_2]$ (16)

The NMR monitoring of the resulting solution revealed the presence of *tert*-butyl magnesium as by-product. The ^{29}SiNMR CP/MAS spectrum of compound **16** shows one signal at -36.49ppm corresponding to the silicon atoms of the disilanolate ligands. The compound, insoluble in benzene, must be dissolved in THF-C_6D_6 (3/4-1/4) for the ^{1}H and ^{13}C-NMR.The signals for the phenyl groups of these silicon atoms are situated between 7.25ppm and 8.24ppm in the ^{1}H-NMR spectrun and at 135.16ppm in the ^{13}C-NMR spectrum.

$Mg(Et_2O)[\{(OPh_2Si)_2O\}_2$-μ-$\{Mg(OEt_2)Br\}_2]$ **16** is composed by three magnesium atoms connected by two disilanolate ligands, the two external magnesium atoms are also bonded to two bromine elements.

The reactivity of $BrMg^{t}Bu$ is governed by a carbonionic character of the organic groups and the electro deficient character of the metal atom [105, 106, 107]. Consequently, these metallic compounds have a basic reactivity.

It seems clear that the presence of Grignard reagent leads to a division of the components of **1**, and thus the formation of free disilanolate $(^{-}OSiPh_2)_2O_3$.

4.5.1. Crystal structure determination $Mg(Et_2O)[\{(OPh_2Si)_2O\}$-μ-$\{Mg(OEt_2)Br\}_2]$ (16)

A crystal of $Mg(Et_2O)[\{(OPh_2Si)_2O\}$-μ-$\{Mg(OEt_2)Br\}_2]$ (**16**) was isolated from diethyl-ether at +4°C. From the determination and the refinement of the unit cell dimensions arose a triclinic crystal system [126]. The R-value is 4.66%. In table 28 are reported the crystal data and the structure refinement for the compound and in table 29 are reported some selected bond lengths and angles of interest.

Table 28: Crystal data and structure refinement for sh2205.

Identification code	sh2205	
Empirical formula	$C_{60}\ H_{70}\ Br_2\ Mg_3\ O_9\ Si_4$	
Formula weight	1280.27	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.7405(9) Å	α= 90°
	b = 11.4100(4) Å	β= 108.749(2)°.
	c = 24.9847(9) Å	γ= 90°.
Volume	6408.7(4) $Å^3$	
Z	4	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	1.421 mm^{-1}	
F(000)	2656	
Crystal size	0.15 x 0.4 x 0.55 mm^3	
Theta range for data collection	1.81 to 28.93°.	
Index ranges	-32<=h<=32, -15<=k<=15, -33<=l<=33	
Reflections collected	37334	
Independent reflections	8434 [R(int) = 0.0802]	
Completeness to theta = 28.93°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8434 / 0 / 360	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1111	
R indices (all data)	R1 = 0.0810, wR2 = 0.1246	
Largest diff. peak and hole	0.866 and -1.151 e.$Å^{-3}$	

Table 29: Selected bond lengths [Å] and angles [°] for sh2205.

Br(1)-Mg(2)	2.4228(9)	Mg(1)-O(2)´	2.071(2)
Mg(1)-O(3)´	2.0353(16)	Mg(2)-O(3)´	1.932(2)
Mg(1)-O(3)	2.0354(16)	Mg(2)-O(2)	1.945(2)
Mg(1)-O(5)	2.049(3)	Mg(2)-O(4)	2.011(2)
Mg(1)-O(2)	2.0707(18)	O(3)-Mg(2)´	1.9321(19)

O(3)´-Mg(1)-O(3)	157.15(12)	O(3)-Mg(1)-O(2)´	80.70(7)
O(3)´-Mg(1)-O(5)	101.42(6)	O(5)-Mg(1)-O(2)´	103.95(6)
O(3)-Mg(1)-O(5)	101.42(6)	O(2)-Mg(1)-O(2)´	152.09(12)
O(3)´-Mg(1)-O(2)	80.70(7)	O(3)´-Mg(2)-O(2)	86.60(8)
O(3)-Mg(1)-O(2)	93.79(7)	O(3)´-Mg(2)-O(4)	108.67(9)
O(5)-Mg(1)-O(2)	103.95(6)	O(2)-Mg(2)-O(4)	113.05(9)
O(3)´-Mg(1)-O(2)´	93.79(7)		

4.5.2. Crystal structure description of $Mg(Et_2O)[\{(OPh_2Si)_2O\}_2$-μ-$\{Mg(OEt_2)Br\}_2]$ (16)

The magnesium trinuclear complex crystallizes in a monoclinic with a space group of C2/c. The Mg atoms are bridged by two disilanolate ligands in a μ_3 coordination system, and their coordination is completed by two terminal Br and three diethyl ether ligands.

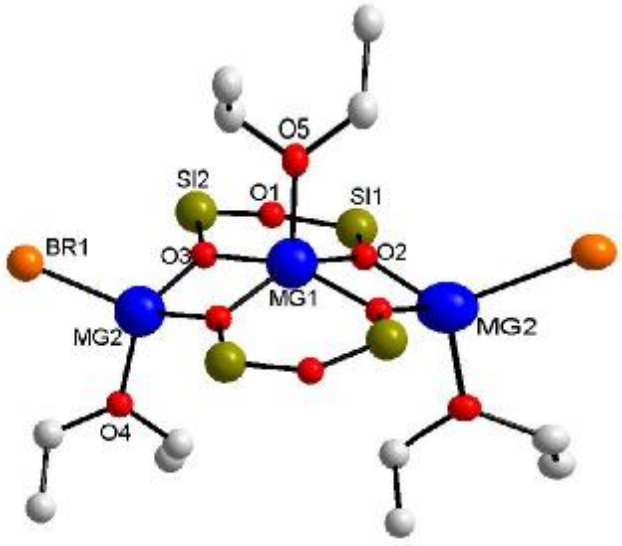


Figure 42: A view of 16, showing the atom-labeling scheme.
(Phenyl groups on the Si atoms have been omitted for clarity.)

Mg(1) atom is surrounded by one diethyl ether molecule and by four oxygen atoms from the disilanolate ligands. These ligands also bridge two magnesium atoms on either side from the square plane (O2, O2´, O3, O3´), resulting in the formation of two four-membered Mg_2O_2 rings. The central magnesium atom Mg(1) lies 0,45Å above the rectangular plane formed by the four oxygen atoms of the disilanolate ligands. This five-coordinated Mg atom have a square pyramidal coordination sphere with an axial diethyl ether molecule located at 2, 049(3) Å.

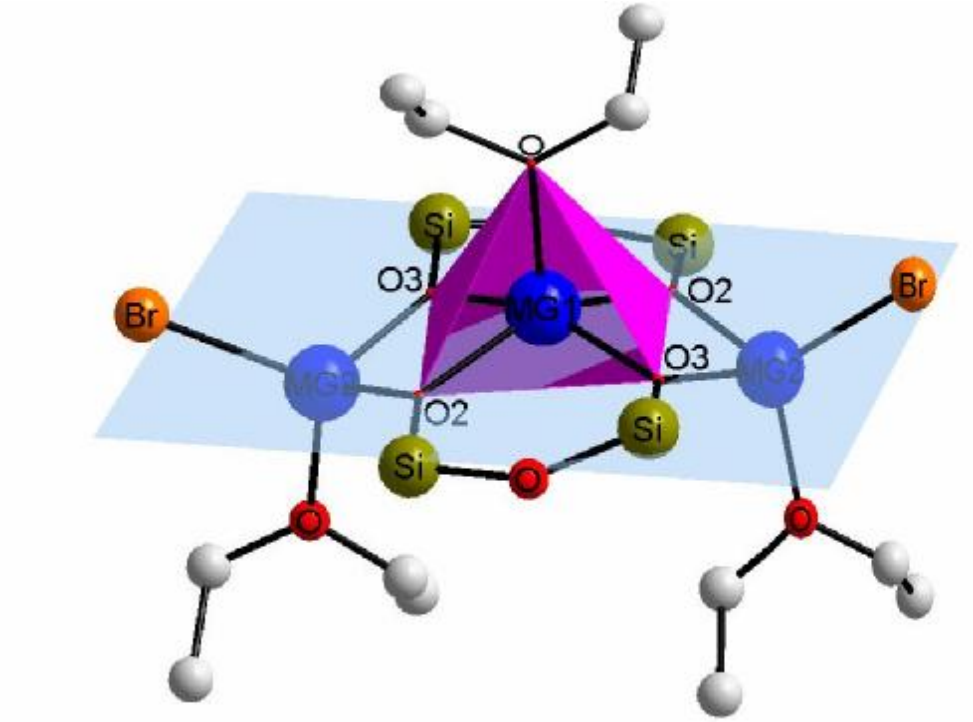


Figure 43: A drawing of the square plane (O(2), O(3), O(2)´, O(3)´) and of the central Mg atom square-pyramidal coordination sphere.

The external Mg(2) atoms are four-coordinated with a terminal diethyl ether ligand and also a terminal Br atom. These Mg(2) atoms exhibit a trigonal-pyramidal coordination sphere. The equatorial coordination sites are occupied by a terminal diethyl ether ligand and by two μ_2-OSi atoms. The top of the pyramidal geometry is occupied by a Br ligand. The angles between the equatorial ligands range from 86,60(8) ° to113, 05(9) ° (sum of angles 308,36°). The Mg- μ_2OSi are in the order Mg(1)- μ_2OSi [2, 0372(1)-2, 0710(1) Å] > Mg(2)- μ_2-OSi [1, 932(2)-1, 945(2) Å], so that bonds to the Mg(1) atom are longer than to the Mg(2) atom which has a smaller coordination sphere.

4.6. Discussion

Different literatures [84, 108-124] dealing with metallasiloxane have already described similar systems but to the best of our knowledge, this kind of metallasiloxane (Table 30) has never been evidenced with water and siloxane as ligands and aluminium as metal. Nevertheless, considerations about the chemical proprieties of the metal used (Al, Ni, Co, Mg) could provide an explanation for these unusual systems.

The aluminium atom (group 13) is very reactive in presence of water molecules [51, 54-57]. The reason can be understood when Pearson´s Hard and Soft Acids and Bases principle is considered. In terms of Pearson´s hard-soft classification [27] of Lewis acids and bases, aluminium is a hard acid and water is a hard base. Consequently, this interaction is particularly favored.

Table 30 : Metallasiloxanes synthesized*.

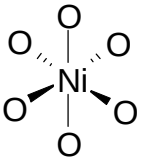
Compd.	Color	Yield(%)	Si (ppm)	M/ M´	M-O(Si) (Å)	Si-O(M)(Å)	Si-O-M(°)
12	white	60	-34	Al/Li	1.76- 1.72	1.61-1.62	125.6- 131.6
13	green	30	para	Ni/Al	2.05	1.62	125.6- 126.4
14	pink	40	para	Co/Al	2.08- 2.09	1.61	124.3- 124.4
15	white	20	-39.3	Mg/Al	2.04	1.62	127.1- 126.9
16	white	70	-36.5	Mg/Mg	2.03- 2.07	1.61	128.5- 132.6

*** Bond distances and angles are average values.**

The reactivity of Al ion toward strong bases is the key element in the formation of the disilanolate derivatives of Li, Ni, Co and Mg. The decomposition of the initial compound $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) is the first step. Then, the formation of heterometallic complexes can occur due to the Lewis Acid-Base interaction. Exploiting the difference between two or several metal atoms in electronegativity; permits to consider one metal center as a stronger acceptor of the electron density and the alkoxide or other ligands at the other as a better donor of it [78].

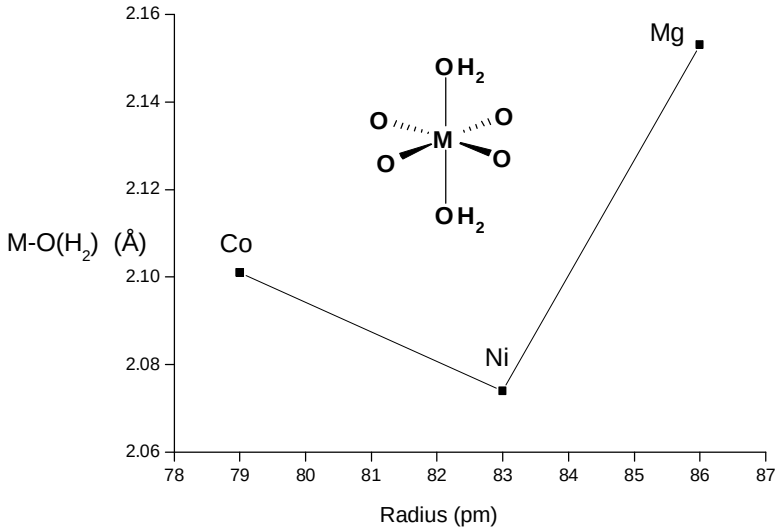
These complexes are very stable, the explanation is that the combination of softer acid- softer base and harder acid-harder base leads to a high stability. Mixing of a complex of harder acid-softer base type with that of softer acid-harder base type will provide a trend to ligand exchange and facilitates the aggregation leading to the heterometallic derivatives.

Table 31 : crystallographic and spectroscopic values for Ni(acac)$_2$, 12, 13, 14, 15, 16 are reported for comparison.

M central	n (nm)	Space Group	Geometry of central M	M-μ$_2$-O	M-O(S)*	Core
Ni(acac)$_2$ (H$_2$O)$_2$**	479	Monoclinic P21/c	Trans-octahedral	2,01 2,02	2,14	
12		Monoclinic I2/a	Tetra-coordinated	2,02	1,89	**Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen.**

***S= solvent coordinated on the metal atom. * Bond distances are average values.**

The evolution of the metal-ligand (M-OH$_2$) distance in compounds **13**, **14** and **15** can be explained by two following factors:



Graph 6 : Distance metal-ligand (H$_2$O) internuclear distance(Å) compared with the metal radius (pm).

In the case of transition metals,

The total energy splitting Δ is termed the crystal field stabilization energy. May be estimated from

$$\Delta \approx \frac{\langle r^2 \rangle}{R^5}$$

Where *r* is the radius of the d orbital and R is the metal-ligand (H$_2$O) internuclear distance.

We know that: $\Delta_{Ni^{2+}} < \Delta_{Co^{2+}}$

$r_{Co} < r_{Ni}$

Then: $\boxed{\Rightarrow R_{Co} > R_{Ni}}$

As, the ionic radius decreases, we might expect a systematic decrease of the distances between the metal and the water molecules. An examination of Graph.6 shows that this is not the case.
The distance Mg-OH_2 doesn't follow the established tendency of the transition metals. This effect can be explained as follows: Alfred and Rochow suggest a scale of electronegativity based upon the electrostatic force of attraction between the nucleus and the valence electrons.

The force of attraction χ is given by: $c = \frac{Z_{eff} e^2}{r_{cov}^2}$

Where

- r is the distance between the electron and the nucleus (covalent radius)
- e is the charge on an electron
- eZ_{eff} is the charge effective at the electron due to the nucleus and its surrounding electrons

Then, it is well defined that the metallasiloxane (**13**, **14**) formed by transition metals (nickel and cobalt) have distances, from the metal to the oxygen from the water ligand, which are smaller with the increase of the radius of the metal atom. The distance in the magnesiasiloxane **15** doesn't follow this rule. The lack of d-orbitals in magnesium atom permits to explain the tendency by the electrostatic force of attraction between the nucleus and the valence electrons.

.

5. Summary and outlook

In this work, the reactivity of polyalumosiloxane $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**) is studied. In this purpose, new compounds derivatives have been synthesized and characterized.

They can be divided in three groups according with the reactivity of **1**. The first group consists of the synthesis of compounds $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ (**3**), $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O.2THF$ (**4**), $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2[Al(OH)(LiOH)]_2.4Et_2O.4THF$ (**4a**), and $[(Ph_2Si)_2O_3]_4[Al(OTl)]_2$ $[Al(OH)(TlOEt)]_2.2Et_2O$ (**5**) with introduction of sodium ethoxid, lithium hydroxide or thallium ethoxid in the core of **1**, **Fig.a**. involving an enlargement of the central ring $Al_4(OH)_4$.
Despite the lack of crystallographic evidences for compound **5**, it appears almost sure that the introduction of TlOEt is performed as for NaOEt.

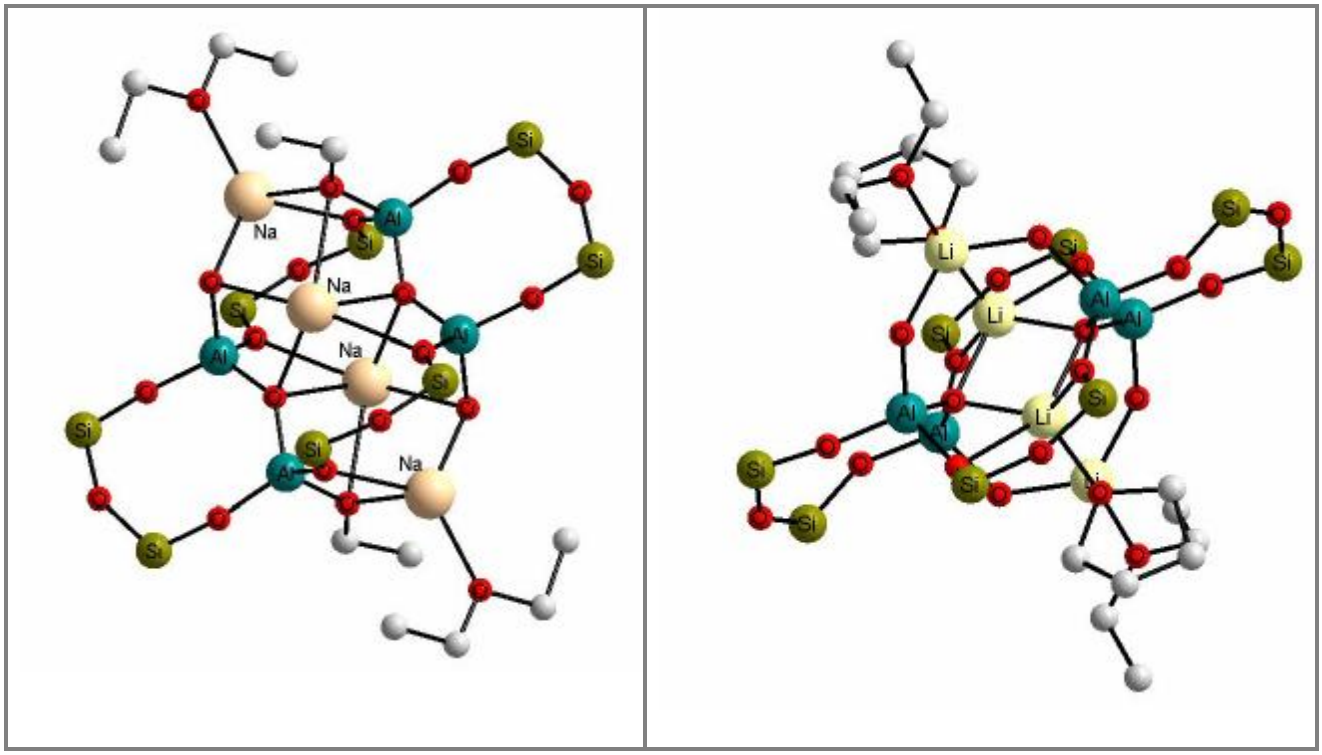


Fig. a : Representation of compounds 3 $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2$. $2Et_2O$ and 4 $[(Ph_2Si)_2O_3]_4[Al(OLi)]_2$ $[Al(OH)(LiOH)]_2.2Et_2O$. 2THF

Compound **3**, **4**, **4a** and **5** conserve the initial skeleton of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ (**1**), only the original eight-membered core is enlarged with the inserting of metal ethoxide (**3**,**5**) or metal hydroxide (**4**,**4a**) leading to the formation of a central $([\text{-Al-O-Al-O-M-O}]_2)$ twelve-membered ring containing four

aluminium atoms and two metal atoms (M= Na, Li or Tl). Simultaneously, substitutions of the acidic OH-groups occur as well, leading to the formation of a M_2O_2 four-membered ring inside the twelve-membered ring.

Compounds **4** and **4a** are resulting of the presence of small amount of water with compound $[(Ph_2Si)_2O_3]_4Al_4(OLi)_4$ (**2**), this procedure require a water "softening" to be achieve, in particular the use of hydrated copper iodide which permits a soft approach of the acidic Al atoms.

The investigation of the reaction leading to decomposition products among compound $[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$ (**7**), where **1** is hydrolyzed; confirms the necessity of a soft access of water to the poly-alumosiloxane (**1**).

The reactivity of **1** is not only dependent on the acidic sites but also on the congested conformation of **1** which prevents the approach of sterically encumbered reagents.

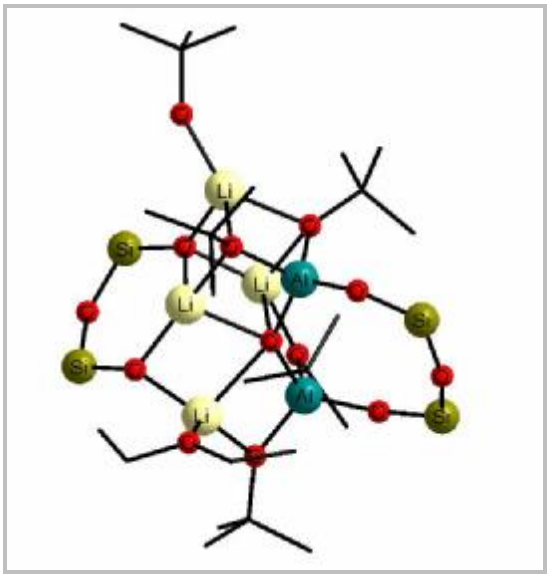


Fig. b : Compound 6

$Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.3HO^tBu$

The reaction of alumosiloxane **1** toward polymeric compounds such LiO^tBu requires a reorganization of the molecule and leads to the new compound **6** containing an unusual cubane consisted of two different metal atoms ($AlLi_3O_4$), **Fig.b**.

However, the use of sterically encumbered compound such $LiN[Si(Me)_3]$ leading to compound **8** **(Fig.c)** denotes the relevance of the reagent's bulk in the reactivity of **1**.

This compound differs from the previously reported homologue $[(Ph_2Si)_2O_3]_4Al_4(OLi)_4$ (**2**) because of its symmetry.

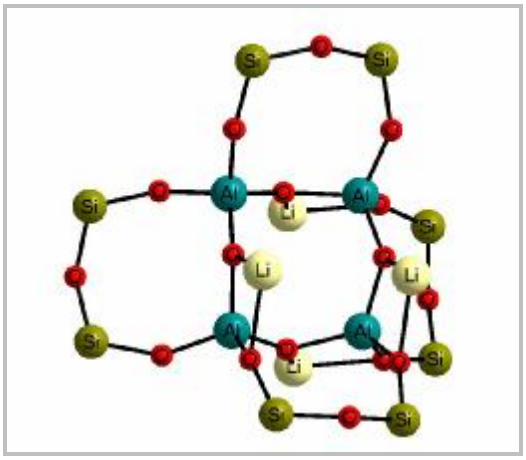


Fig. c : Compound 8 $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4.6THF$

The second group consists of the compounds which have been subjected to an alteration of the initial skeleton of $[(Ph_2Si)_2O_3]_4Al_4(OH)_4$ **1**. (**9**, **10** and **11**)

Actually, in the case of the synthesis of compound **9** **(Fig.d)**, the solvent molecules coordinated on **1** are involved. The reactivity of **1** depends greatly on the donor molecule accepted on the central $Al_4(OH)_4$ ring of **1**. Compound **9** is a new tetra nuclear Sn compound containing aluminium and disilanolate components. It was obtained with the support of ^{t}BuOH coordinated on **1,** allowing the formation of [Sn-O] units.

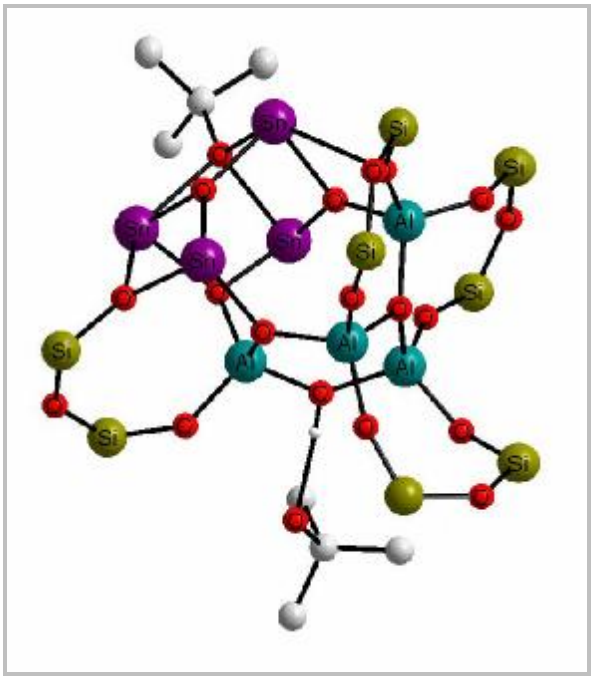


Fig. d :Compound 9
$[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.Et_2O$

The metal involved in the reactions leading to **10** **(Fig.e)** and **11** **(Fig.f)**, play considerable roles due to their Lewis acidity (Ni(II) and Fe(III)). These reactions are associated to β-ketoenolate ligand or disilanolate ligand redistribution between the aluminium atoms and the metal atoms used.

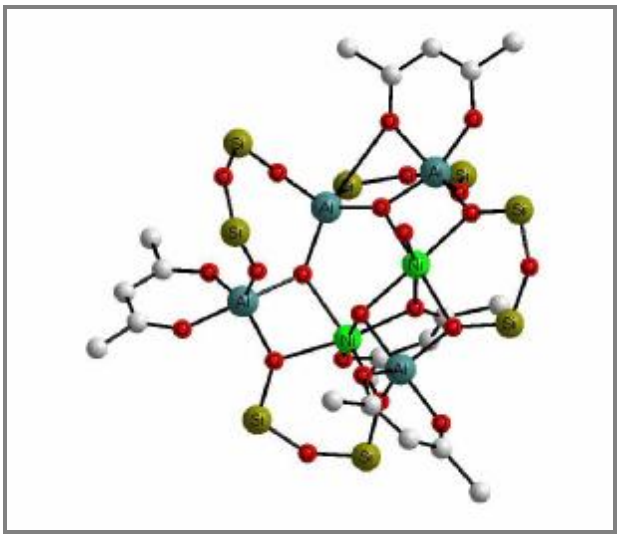


Fig. e : Representation of compound 10
$[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4$

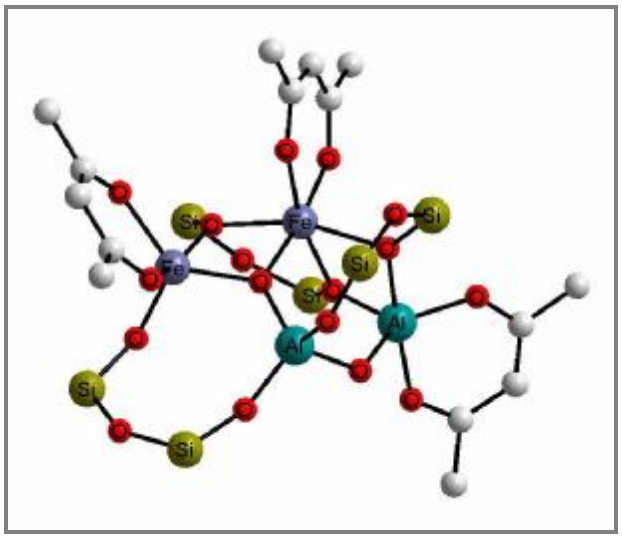


Fig. f : Representation of compound 11
$[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2$

The third group consists of compound **12**, **13**, **14**, **15**, **16**. The synthesis of news type of metallasiloxane involving Li, Al, Ni, Co, and Mg atoms have been completed. The condensation of **1** by the soft introduction of water (as ligand in $M(acac)_2(H_2O)_2$)) leads to the formation of a collection of new complexes.

It was then clear, that the system, even in the formation of **12** **(Fig.g)**, has a trend toward formation of metallasiloxane, but needs additional strong base, H_2O or Grignard reagent **(Fig. i)** to be provided.

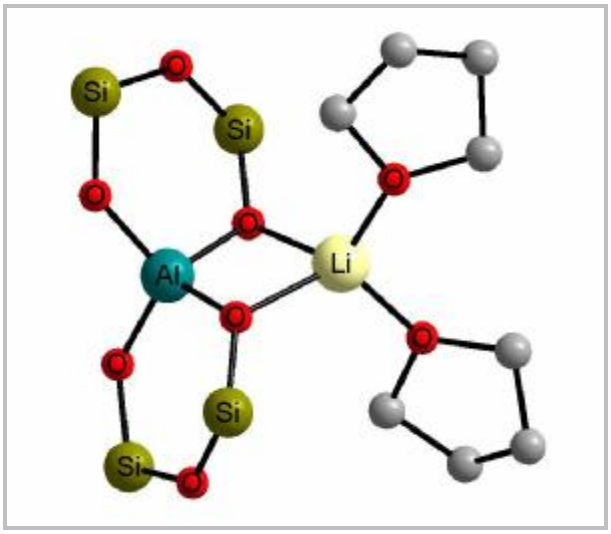


Fig. g : Al/Li metallasiloxane: compound 12
$Al[\{(OPh_2Si)_2O\}_2$-μ-$\{Li(THF)_2\}]$

New hetero-metallasiloxane complexes with water molecules as ligands on the metallic center (Ni, Co, Mg) have been synthesized **(Fig.h)**. Metallasiloxane compounds can be regarded as models of metals on the silica surfaces.

The presence of a metal in the siloxane framework often results in high thermal stability and improved catalytic and conducting properties. Moreover, the metallasiloxanes can be considered as precursors for silicon polymers containing metal centers in the polymer backbone [123].

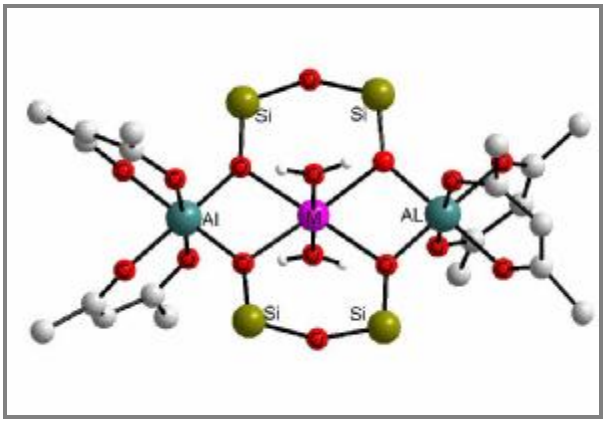


Fig. h : M/Al hetero-metallasiloxane,
$[M(H_2O)_2\{(OPh_2Si)_2O\}_2$-μ-$\{Al(acac)_2\}_2]$
M= Ni (13), Co (14), Mg (15).

The transition metal complexes anchored on silica surfaces are known to catalyze a variety of organic transformations [124].

The exploration of the true structure and nature of the surface species formed on oxide supports from transition metal complexes is one of the most important goals in present catalysis research.

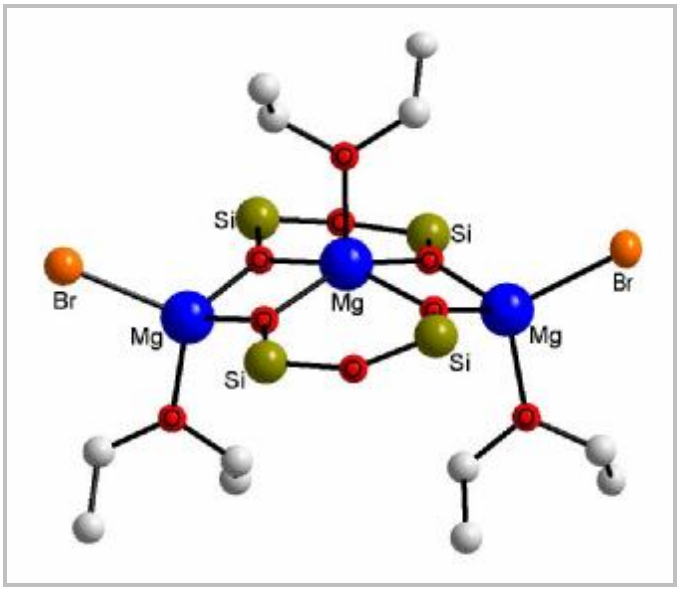


Fig. i : Representation of compound 16

Mg (Et_2O)[{($OPh_2Si)_2O$}$_2$-μ-{$Mg(OEt_2)Br$}$_2$]

One of the most efficient methods of exploration of this problem is the preparation of model compounds which could be isolated and structurally characterized.

All the metallasiloxanes formed have been isolated and characterized by structure determination and also by UV-Visible for **14** and **13** and by NMR spectroscopy for compounds **12**, **15**, and **16**.

They constitute potential precursors of interest. Actually, complexes of this type have already proven their quality as single source molecular precursors for MO-CVD.

Further investigations on a potential catalytic activity of these metallasiloxane complexes may also constitute an interesting field of research

6. Experimental part

6.1. General techniques

All reactions were carried out under inert dinitrogen atmosphere in a modified "Stockschen vacuum apparatus". The necessary vacuum was obtained with a rotary vane pump of the Vacuumbrand company (model R75, 5.4 m^3/h, $4x10^{+4}$ mbar). The solvents (THF, diethyl-ether, toluene, benzene) were distilled from sodium and kept under nitrogen.

6.2. Elemental analysis

Analytical data were measured on an all-automatic CHN-900 Elemental Analyzer from LECO *Corporation*, by Mss. Helga Feuerhake (Anorganische Chemie, Saarbrücken). Calculations of theoretical molar masses were done with relative atomic masses IUPAC 2001.

6.3. Spectroscopic methods

6.3.1. Nuclear Magnetic Resonance (NMR)

The NMR spectra were recorded on Bruker 200 NMR ACF and ACP spectrometers. Samples were prepared with appropriate solvent and approximately 5 Vol.% C_6D_6 used as lock solvent. Chemical shifts are given according to the δ-scale in ppm. The reference corresponds to the signal of benzene ($\delta(^1H, C_6D_5H)$ = 7.15 ppm, $\delta(^{13}C)$ = 128.0 ppm). To characterize the spin multiplicity, abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

The abbreviations m-C, o-C and p-C correspond to meta, orto or para positions of the carbon atoms on the phenyl groups.

Core	Measurement frequency (MHz)
^1H	200.1
^{13}C	50.3
^{29}Si	39.7
^{119}Sn	74.6

Table 32: Measurement frequency used for NMR samples.

6.3.2. Ultraviolet-Visible

The electronic transition spectra were measured in liquid media on a SP8-100 spectrometer from Pye Unicam.

6.3.3. Crystallographic analysis

X-Ray crystallography was performed with a STOE IPDS diffractometer with Kα radiation (λ = 0.71073 Δ). Structures were solved by direct methods and refined by full-matrix least-square methods on F^2 with SHELX-97 [125]. Hydrogen atoms were refined as rigid groups with the attached carbon atoms. Drawings were made with Diamond 3.1.

6.4. Synthesis of the starting materials

The following compounds were obtained, synthesized or purified according to well-established procedures. Excepting elemental analyses, which were not systematically proceeding, they were fully characterized.

1	*Ref.14*
2	*Ref.19*
NaOEt	*Aldrich*
$CuI.4H_2O$	*Fluka*
TlOEt	*Aldrich*
KOH	Fluka (dried under vacuum before use)
$LiN[Si(Me)_3]_2$	*Ref.49, 50*
$Sn(NtBu)_2SiMe_2$	*Ref.64, 65*
$Ni(acac)_2$	$Ni(acac)_2(H_2O)_2$ freshly sublimated at 50°C under vacuum *Ref.* 73-76
$Fe(acac)_3$	*Fluka*
$Ni(acac)_2(H_2O)_2$	*Merck*
$Co(acac)_2(H_2O)_2$	*Merck*
$Mg(acac)_2(H_2O)_2$	$Mg(acac)_2$ was prepared by refluxing magnesium metal with acetylacetone. The slurry and solvent were transferred to a new flask, the solvent was removed by decantation and the crystals were washed with boiling toluene and evaporated to dryness, repeated twice.
^tBuMgBr	*Ref.104*

Table 33: Bibliographical references or source of the starting materials.

6.5. Synthesis of $[(Ph_2Si)_2O_3]_4[Al(ONa)]_2[Al(OH)(NaOEt)]_2 . 2Et_2O$ (3)

Na(OEt) (0.1g, 1.432mmol) was slowly added to a suspension of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) (0.76g, 0.358mmol) in 10ml of diethyl ether. The mixture was stirred 16hours and became a colorless solution which was placed for one day at +4°C; well formed white crystals were isolated from the solution. (0.427g, 66% based on **1**).

Characterization:

Formula: $C_{100}H_{92}Al_4Na_4O_{18}Si_8(OC_4H_{10})_2$

Molecular weight (calculated): 2154.58g.mol^{-1}

^{1}H-NMR(C_6D_6,200.1MHz): δ (ppm) = 6.66 – 7.10 (m, 48H, Ph)
7.73 – 8.06 (m, 32H, Ph)
3.13(q, 12H, -C**H**$_2$-CH$_3$, Et_2O)
1.0027 (t, 6H, Et_2O)
0.58(t, 6H, -CH$_2$-C**H**$_3$)

^{13}C{^{1}H}-NMR(C_6D_6, 50.3MHz): δ (ppm) =
14.32 (s,2C, -CH$_2$-**C**H$_3$)
15.50(s, 2C, Et_2O)
23.08(s,2C,-**C**H$_2$-CH$_3$)
65.84(s, 6C, Et_2O)
128.20(s, m-Ph)
134.73(s, o-C, Ph)
134.82(s, o-C, Ph)
135.14(s, p-C, Ph)

^{29}Si-NMR (C_6D_6, 39.7MHz): δ (ppm) = -42.51 (s, 4Si, **Si**Ph$_2$)
-46.24 (s, 4Si, **Si**Ph$_2$).

Elemental analysis:

%	C	H	N
Calculated	60.2	5.2	-
Found	59.6	4.9	-

6.6. Synthesis of $(Ph_2SiO)_8(AlO)_2(AlOH)_2Li_2(LiOH)_2.2\ Et_2O.\ 2THF$ (4)

$CuI.xH_2O$ (0.03g, 0.21mmol) was slowly added to a solution of $[(Ph_2Si)_2O_3]_4[Al(OLi)]_4$ (**2**) (0.1g, 0.05 mmol) in 10ml of THF. The mixture was stirred for 16 hours and then filtrated from the fully $CuI.(x-2)H_2O$. The solvent was removed under reduced pressure and the residue was dissolved in 10 ml of diethyl-ether with the formation of a solid at the bottom of the flask. The clear supernatant solution was kept at +4°C and clear white crystals were isolated. (0.03g, 25% based on **1**).

Characterization:

Formula: $C_{96}H_{84}Al_4Li_4O_{18}Si_8(OC_4H_8)_2(OC_4H_{10})_2$

Molecular weight (calculated): M= 2177.46g.mol^{-1}

^{1}H-NMR(C_6D_6,200.1MHz):	δ (ppm) =	7.69– 7.96 (m, 48H, Ph)
		7.51 – 7.54 (m, 32H, Ph)
		3.26(q, 12H, -C**H**$_2$-CH_3, Et_2O)
		3.15(THF)
		1.18 (THF)
		1.06(t, 6H, Et_2O)
^{13}C{ ^{1}H}-NMR(C_6D_6, 50.3MHz):	δ (ppm) =	
		15.52(s, -**C**H_2-CH_3, Et_2O)
		30.16(THF)
		65.41(s, -CH_2-**C**H_3, Et_2O)
		128.28(s, m-C, Ph)
		134.99(s, o-C, Ph)
		134.88(s, p-C, Ph)
^{29}Si-NMR(C_6D_6, 39.7MHz) :	δ (ppm) =	-42.98 (s, 4Si, **Si**Ph_2)
		-45.80 (s, 4Si, **Si**Ph_2)

Elemental analysis:

%	C	H	N
Calculated	61.7	5.5	-
Found	59.4	5.1	-

6.7. Synthesis of $[(Ph_2Si)_2O_3]_4[Al(OTl)]_2[Al(OH)(TlOEt)]_2.2Et_2O$ (5)

A solution of 0.14ml (2mmol) of $TlOC_2H_5$ in 5ml of diethyl-ether was slowly added to a suspension of 0.1g of $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) (0.5mmol) in 10ml of diethyl-ether. The suspension became immediately a clear solution. After one hour under stirring, a solid appeared at the bottom of the flask. The mixture was filtrated after 16 hours under stirring and the residue was dried under vacuum to give a white solid. (0.8g, 55% based on **1**)

Characterization:

Formula: $C_{100}H_{92}Al_4Tl_4O_{18}Si_8(OC_4H_{10})_2$

Molecular weight (calculated): M= 2879.18g.mol^{-1}

^{1}H-NMR (C_6D_6,200.1MHz):	δ (ppm) =	8.15-8.18 (m, 48H, SiPh2)
		7.93 – 7.97 (m, 32H, $SiPh_2$
		3.27(q, 12H, -C**H**$_2$-CH_3, Et_2O)
		1.10 (t, 6H, Et_2O)
		0.98(t, 6H, -C**H**$_3$)
^{13}C{ ^{1}H}-NMR(C_6D_6, 50.3MHz):	δ (ppm) =	
		14.48 (s,2C, -CH_2-**C**H_3)
		15.74(s, 2C, Et_2O)
		25.23(s,2C,-**C**H_2-CH_3)
		65.56(s, 6C, Et_2O)
		134.97(s, m-C, Ph)
		135.12(s, o-C, Ph)
		135.82(s, p-C, Ph)
^{29}Si-NMR (C_6D_6, 39.7MHz):	δ (ppm) =	-41.40 (s, 4Si, **Si**Ph2)
		-46.13 (s, 4Si, **Si**Ph2)

Elemental analysis:

%	C	H	N
Calculated	43.3	3.8	-
Found	43.1	3.2	-

6.8. Synthesis of $Li_4Al_2(O^tBu)_2O_2[(SiPh_2)_2O_3]_2.OEt_2.3HO^tBu$ (6)

$Li(O^tBu)$ (0.07g, 0.89mmol) was slowly added to a suspension of **1**.$3OEt_2.O^tBu$ (0.5g, 0.23mmol) in 10ml of diethyl-ether. The mixture was stirred for 16 hours and then, became a colorless solution. The solution was concentrated under reduced pressure until white clear, well-developed crystals appeared. (0.2g, 63% based on **1**).

Characterization:

Formula: $C_{68}H_{86}Al_2Li_4O_{12}Si_4(OC_4H_{10})$

Molecular weight (calculated): M= 1363.57g.mol^{-1}

^{1}H-NMR(C_6D_6,200.1MHz):	δ (ppm) =	7.85 – 8.02 (m, 40H, $SiPh_2$)
		3.25(q, 4H, Et_2O)
		1.36(s, 18H, -CH_3)
		1.24(s, 9H, -CH_3)
		1.29(s, 18H, -CH_3)
		1.11 (t, 6H, Et_2O)
^{13}C{ ^{1}H}-NMR(C_6D_6, 50.3MHz):	δ (ppm) =	
		15.51(s, Et_2O)
		30.99(s,-CH_3)
		33.10(s, -CH_3)
		65.84(s,Et_2O)
		128.28(s, Ph)
		135.04 (s, Ph)
^{29}Si-NMR (C_6D_6, 39.7MHz):	δ (ppm) =	- 43.57(s, 4Si, **Si**Ph2)
		- 58.23(s, 4Si, **Si**Ph2)

Elemental analysis:

%	C	H	N
Calculated	62.7	6.9	-
Found	60.6	6.3	-

6.9. Synthesis of $[(Ph_2Si)_2O_3]_2(Ph_2SiO_2Al)_2[K(OEt_2)_2]_2$ (7)

0.09 g of KOH (1.6mmol) is added to a suspension of 0.65g of **1** in 10ml of diethyl-ether. The white suspension, after 16hours under vigorous stirring, became light yellow. The mixture was filtrated and the clear solution obtained was placed on standing at room temperature to give, after 4days, a crystalline gel which was not soluble.

The compound was not separated from the gel obtained and no yield was calculated. Only one crystal was separated from the gel for the structure determination.

6.10. Synthesis of $[(Ph_2Si)_2O_3]_4[AlO(OLi)]_4.6THF$ (8)

$LiN(SiMe_3)_2$ (0.15g, 0.92mmol) was added to a stirred solution of compound $[(Ph_2Si)_2O_3]_4[Al(OH)]_4$ (**1**) (0.5g, 0.23mmol) in 10ml thf. After 16 hours, about one third of the solvent was removed and the solution was placed at +4°C, well-formed white crystals were isolated. (0.29g, 56% based on **1**).

Characterization:

Formula: $C_{96}H_{80}Al_4Si_8Li_4O_{16}(OC_4H_8)_6$

Molecular weight (calculated): 2410.83g.mol^{-1}

^{1}H-NMR(C_6D_6):	δ (ppm) =	7.91 – 8.00 (m, 48H, $SiPh_2$)
		7.69 – 7.79 (m, 32H, $SiPh_2$)
		3.35(thf)
		1.35 (thf)
$^{13}C\{^1H\}$-NMR(C_6D_6, 50.3MHz):	δ (ppm) =	25.58(thf)
		67.76(thf)
		128.29(s, Ph)
		135.98(s, Ph)
^{29}Si-NMR (C_6D_6, 39.7MHz):	δ (ppm)=	-40.31 (s, 2Si, **Si**Ph_2)
		-42.15 (s, 2Si, **Si**Ph_2)
		-43.17 (s, 2Si, **Si**Ph_2)
		-44.50 (s, 2Si, **Si**Ph_2)

Elemental analysis:

%	C	H	N
Calculated	63.1	5.6	-
Found	63.9	5.2	-

6.11. Synthesis $[(SnO)_4(OtBu)][(Ph_2Si)_2O_3]_4Al_4(OH)_2.O^tBu.Et_2O$ (**9**)

$Sn(N^tBu)_2SiMe$ (0.281g, 0.9mmol) in 5ml of diethyl-ether was slowly added to an suspension of $(Ph_2SiO)_8$ $[Al(O)(OH)]_4.O^tBu.3OEt_2$ (**1**.$O^tBu.3OEt_2$) (0.5g, 0.23mmol) in 10ml of diethyl-ether. The mixture became immediately a yellow pale solution. The volatiles were removed under reduced pressure. The white residue was re-dissolved in 5ml of diethyl-ether. Then, the solution was placed at +4°C for several months. 0.06g of **9** (10%) was isolated as well formed white crystals.

Characterization:

Color of the compound: clear white.

Formula: $C_{112}H_{119}Al_4O_{22}Si_8Sn_4$

Molecular weight (calculated): 2624.47g.mol^{-1}

^{1}H-NMR(C_6D_6,200.1MHz):	δ (ppm) =	7.93 – 8.17 (m, 48H, $SiPh_2$)
		7.76 – 7.82 (m, 32H, $SiPh_2$)
		1.29-1.35(m, $C(C\mathbf{H}_3)_3$, Et_2O)
		0.91 (s, 9H, $C(C\mathbf{H}_3)_3$)
^{13}C-NMR(C_6D_6):	δ (ppm) =	14.32(s, Et_2O)
		30.11(s, $\mathbf{C}(CH_3)_3$)
		32.98(s, -$\mathbf{C}H_3$)
		128.28(s, Ph)
		135.11(s, Ph)
		135.30 (s, Ph)
^{119}Sn-NMR(C_6D_6, 74.6 MHz) :	δ (ppm) =	-206.37
		-545.93

Elemental analysis:

%	C	H	N
Calculated	51.2	4.5	0
Found	49.3	4.0	0.4

6.12. Synthesis of $[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$(**10**)

A solution of $Ni(acac)_2$ (0.18g, 0.72mmol) in 5ml of toluene was slowly added to a stirred solution of **1** (0,72g; 0,36mmol) in 10ml of toluene. The mixture turned instantaneously from white to green.
After 5 minutes refluxing and one night under vigorous stirring, the solution was concentrated under reduced pressure. 5ml of Et_2O was added. The solution was kept at +4 °C over several days and pale green needles were isolated. (0.265g, 30% based on **1**)

Characterization:

Color of the compound: green.
Formula: $C_{120}\ H_{122}\ Al_4\ Ni_2\ O_{25}\ Si_8$
Molecular weight (calculated): M= 2414.24.mol^{-1}

$[(Ph_2Si)_2O_3]_4Al_4Ni_2(acac)_4(OH)_4.OEt_2$
UV-Vis,λ /nm (ε /$dm^3\ mol^{-1}\ cm^{-1}$): 644(0.09)

Elemental analysis:

%	C	H	Ni
Calculated	59.7	5	4.8
Found	57.1	4.6	4.9

6.13. Synthesis of $[(Ph_2Si)_2O_3]_3O(OH)(acac)Al_2[Fe(acac)]_2.2OEt_2$ (11)

0.1g (0.28mmol) of $Fe(C_5H_7O_2)_3$ in 5ml of diethyl-ether was added to a 15ml diethyl-ether suspension of **1** (0.3g, 0.85mmol). The solution turned instantaneously from white to dark red with the formation of a solid at the bottom of the flask. The mixture, after 16hours under stirring, was filtrated. In vacuum about one third of the solvent was removed from the filtrate. On standing at +4°C, red purple crystals were precipitated. The supernatant solution was removed and the solid dried in vacuum. (0.2g, 43% based on **1**).

Characterization:

Formula: $C_{87}H_{81}Al_2Fe_2O_{17}Si_6.2(C_4H_{10}O)$
Molecular weight (calculated): M= 1880, 96.mol-1

$[(Ph_2Si)_2O_3]_3(AlO)_2(acac)[Fe(acac)]_2$:
UV-Vis: λ/nm(ε/dm^{3}Mol^{-1}cm^{-1}):

266.6(16.5)
350.4(5.5)
444.5(4)

6.14. Synthesis of $Al[\{(OPh_2Si)_2O\}_2$-μ-$\{Li(THF)_2\}]$ (12)

A volume of $3.35.10^{-3}$ml of distillated water was added to a solution of **2** (0.1g, 4.6.10-5mol) in 10ml of THF. After 16hours under stirring, the solvent was removed under reduced pressure and the white residue was re-dissolved in diethyl-ether with the formation of a solid at the bottom of the flask.
The supernatant solution was placed at room temperature for few months to give light white crystals. (0.03g, 56% based on **2**).

Characterization:

Color of the compound: clear white.
Formula: $C_{48}H_{40}AlLiO_6Si_4(OC_4H_8)_2$
Molecular weight (calculated): M= 1002.76g.mol^{-1}

^{1}H-NMR(C_6D_6): δ (ppm) = 7.23 – 7.96 (m, 20H, $SiPh_2$)
8.02 – 8.56 (m, 20H, $SiPh_2$)
3.32(s, 4H, THF)
1.56 (s, 4H, THF)

^{13}C-NMR(C_6D_6): δ (ppm) = 132.43 (s, Ph)
129.4 (s, Ph)
67.34 (THF)
25.43 (THF)

^{29}Si-NMR (C_6D_6, 39.7MHz): δ (ppm) = -34 (**Si**Ph_2)

Elemental analysis:

%	C	H	N
Calculated	57.5	4.2	-
Found	56.2	3.9	-

6.15. Synthesis of [Ni $(H_2O)_2${$(OPh_2Si)_2O$}$_2$-μ-{$Al(acac)_2$}$_2$].OEt_2 (13)

$Ni(acac)_2(H_2O)_2$ (0.14g, 0.54mmol) was slowly added to a suspension of **1** (0.584, 0.27mmol) in 10ml of Et_2O. The mixture turned instantaneously from white to green.

After one night under stirring, the reaction mixture was filtrated. The resulting green solid (side-product) was dried under reduced pressure. In vacuum, about one third of the solvent was removed from the filtrate. On standing at +4°C, light green crystals were precipitated. The supernatant solution was removed and the solid dried in vacuum. (0,11g, 30% based on **1**).

Characterization:

Color of the compound: green.

Formula: $C_{68}H_{72}Al_2NiO_{16}Si_4(OC_4H_{10})$

Molecular weight (calculated): M= 1247.69g.mol^{-1}

$[Ni(OPh_2SiO)_2Al_2(acac)_4(H_2O)_2]$:

UV-Vis,λ /nm (ε /dm^3 mol^{-1} cm^{-1}): 402(0.115).

Elemental analysis:

%	C	H	Ni
Calculated	69.2	6.6	4.7
Found	67.7	6.2	5.3

Characterization of the side product:

Color of the compound: green.

Formula: $C_{48}H_{48}Al_2NiO_{12}Si_4$

Molecular weight (calculated): M=1041.51.mol^{-1}

$[Ni(H_2O)_2Al_2(OPh_2SiO)_2(OH)_4]$:

UV-Vis,λ /nm (ε /dm^3 mol^{-1} cm^{-1}): 458(0.15).

Elemental analysis for the side product:

%	C	H	Ni
Calculated	55	4.6	5.2
Found	54.1	4.4	5.5

6.16. Synthesis of $Co(H_2O)_2\{(OPh_2Si)_2O\}$-μ-$\{Al(acac)_2\}_2].Et_2O$ (14)

$Co(acac)_2(H_2O)_2$ (0.142g,0.55mmol) was added to a solution of **1** in 10ml toluene. The solution turned instantaneously pink. The solution was then allowed to react under refluxing during 30min.
The solvent was removed under reduced pressure and the residue was washed with hexane to extract the side-product and dissolved in 5ml diethyl-ether. The solution was slowly re-concentrated under reduced pressure until a solid starts to form at the glass wall. The solution was kept at +4 °C and after one night, well-developed pink crystals were isolated. (0.2g, 40% based on **1**).

Characterization:

Color of the compound: pink.
Formula: $C_{68}H_{72}Al_2CoO_{16}Si_4(OC_4H_{10})$
Molecular weight (calculated): M=1444.63 $g.mol^{-1}$

$[Co(OPh_2SiO)_2Al_2(acac)_4(H_2O)_2]$:
UV-Vis,λ /nm (ε /dm^3 mol^{-1} cm^{-1}): 558(0.175).

Elemental analysis:

%	C	H	Co
Calculated	59.8	5.6	4
Found	58.2	5.2	3.59

6.17. Synthesis of [Mg $(H_2O)_2\{(OPh_2Si)_2O\}$-μ-$\{Al(acac)_2\}_2].OEt_2$ (15)

$Mg(acac)_2(H_2O)_2$ (0.08g, 0.29mmol) was added to a solution of **1** (0.3g, 0.14mmol) in 10ml toluene. The solution was allowed to reflux for 20min. After 16hours under vigorous stirring, the solvent was removed under reduced pressure. The white residue was dissolved in 5 ml diethyl-ether. After few months on standing at +4°C, light white crystals were precipitated. (0.03g, 20% based on **1**).

Characterization:

Color of the compound: white clear.
Formula: $C_{68}H_{72}Al_2MgO_{16}Si_4(OC_4H_{10})$
Molecular weight (calculated): 1409.00$g.mol^{-1}$

^{1}H-NMR(C_6D_6,200.1MHz):	δ (ppm) =	7.02 -8.64(m, 40H,Ph)
		4.65(s, 24H, -C**H**$_3$(acac))
		2.10(s, 4H, C**H**(acac))
^{13}C{ ^{1}H}-NMR(C_6D_6, 50.3MHz):	δ (ppm) =	
		135.04 (s, Ph)
		30.05 (s, -**C**H$_3$)
		29.32 (s, **C**H)
		25.23 (s, -**C**(CH$_3$)
^{29}Si-NMR (C_6D_6, 39.7MHz):	δ (ppm)=	-39.29 (s, 4Si, **Si**Ph$_2$)

6.18. Synthesis of $Mg(Et_2O)[\{(OPh_2Si)_2O\}$-μ-$\{Mg(OEt_2)Br\}_2]$ (16)

1.032ml (4 *eq.*) of a solution of tert-butylmagnesium bromide (c = 0.89mol.L-1), freshly prepared according to the established procedure [104], was slowly added to a suspension of **1** (0.5g, 0.23mmol) in 10 ml of diethyl-ether. The suspension became instantaneously a clear solution. After 16 hours under stirring, a white solid was formed and was filtrated. The filtrate was kept at +4°C over 3 days and well-developed, light white crystals were isolated. (1.6g, 60% based on **1**).

Characterization:

Color of the compound: white clear.
Formula: $C_{48}H_{40}Br_2Mg_3O_6Si_4(OC_4H_{10})_3$
Molecular weight (calculated): M= 1280.27.mol^{-1}

The compound, insoluble in benzene (C_6D_6), has been dissolved in THF-C_6D_6 (3/4-1/4).

^{1}H-NMR(C_6D_6,200.1MHz):	δ (ppm) =	7.25- 8.24(m, 40H,Ph)
		3.32(m, THF)
		3.13(q, Et_2O)
		1.35(m, THF)
		1.22(t, Et_2O)

$^{13}C\{^{1}H\}$-NMR(C_6D_6, 50.3MHz): δ (ppm) =

135.16 (s, Ph)

67.94 (s, THF)

30.35 (s, ^{t}Bu) rest of ^{t}BuMgBr

25.75 (s, THF)

15.75 (s, Et_2O)

^{29}Si-NMR CP/MAS δ (ppm) = -36.49 (s, 4Si, **Si**Ph_2)

Elemental analysis:

%	C	H	Mg
Calculated	56.3	5.4	5.6
Found	55.1	5.2	6.7

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(126) From the structural refinement and determination, the space groups of the compound was determined by E-statistic and proved in further refinements. Each atom except the hydrogen atoms, were anisotropically refined. Hydrogen atoms were treated as rigid groups with the adjacent carbon atoms in ideal positions.

8. Appendix: additional information on the X-ray crystal structures

8.1. Compound 3

Table 1. Crystal data and structure refinement for sh2331.

Identification code	sh2331	
Empirical formula	$C_{108}\ H_{110}\ Al_4\ Na_4\ O_{20}\ Si_8$	
Formula weight	2152.56	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.301(3) Å	α= 109.99(3)°.
	b = 16.131(3) Å	β= 107.01(3)°.
	c = 16.227(3) Å	γ = 91.57(3)°.
Volume	3097.1(11) $Å^3$	
Z	1	
Density (calculated)	1.154 Mg/m^3	
Absorption coefficient	0.188 mm^{-1}	
F(000)	1126	
Crystal size	0.15 x 0.3 x 0.4 mm^3	
Theta range for data collection	2.25 to 24.12°.	
Index ranges	-15<=h<=15, -18<=k<=18, -18<=l<=18	
Reflections collected	26584	
Independent reflections	9103 [R(int) = 0.0385]	
Completeness to theta = 24.12°	92.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9103 / 0 / 668	
Goodness-of-fit on F^2	1.858	
Final R indices [I>2sigma(I)]	R1 = 0.0678, wR2 = 0.1991	
R indices (all data)	R1 = 0.0826, wR2 = 0.2080	
Largest diff. peak and hole	0.940 and -0.359 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2331. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	561(1)	9967(1)	1924(1)	38(1)
Al(2)	1288(1)	11493(1)	1258(1)	41(1)
Si(1)	1940(1)	11249(1)	4034(1)	41(1)
Si(2)	2923(1)	12566(1)	3343(1)	41(1)
Si(3)	62(1)	7091(1)	-677(1)	51(1)
Si(4)	1540(1)	8176(1)	1265(1)	46(1)
Na(1)	1069(1)	9608(1)	-232(1)	54(1)
Na(2)	-1275(1)	8378(1)	823(1)	57(1)
O(1)	734(2)	10470(2)	1176(2)	45(1)
O(2)	2000(2)	11245(2)	459(2)	61(1)
O(3)	-821(2)	9891(3)	1748(3)	64(1)
O(4)	1380(2)	10456(2)	3062(2)	46(1)
O(5)	2743(2)	11989(2)	3958(2)	48(1)
O(6)	2042(2)	12223(2)	2338(2)	50(1)
O(7)	-208(2)	8023(2)	-787(2)	64(1)
O(8)	1003(2)	7300(2)	315(2)	60(1)
O(9)	678(2)	8825(1)	1474(2)	42(1)
C(1)	888(4)	11814(3)	4488(3)	60(1)
C(2)	91(5)	11320(6)	4612(5)	106(2)
C(3)	-697(6)	11762(9)	4953(7)	138(4)
C(4)	-740(8)	12620(9)	5125(6)	142(4)
C(5)	19(8)	13093(6)	5012(6)	132(3)
C(6)	832(6)	12696(4)	4702(5)	95(2)
C(7)	2807(4)	10848(3)	4912(3)	57(1)
C(8A)	2322(9)	10214(8)	5151(9)	78(1)
C(9A)	2869(10)	10001(8)	5907(9)	78(1)
C(10A)	3975(10)	10476(8)	6418(9)	78(1)
C(11A)	4291(9)	11137(7)	6310(8)	78(1)
C(12A)	3699(9)	11407(7)	5603(8)	78(1)
C(8B)	2686(10)	10740(8)	5617(9)	78(1)
C(9B)	3474(11)	10418(9)	6299(10)	78(1)
C(10B)	4410(10)	10240(8)	6078(9)	78(1)
C(11B)	4592(9)	10291(7)	5370(8)	78(1)
C(12B)	3850(9)	10551(7)	4759(9)	78(1)
C(13)	4290(3)	12457(2)	3237(3)	44(1)
C(14)	5058(3)	12122(3)	3767(3)	58(1)
C(15)	6053(4)	12040(4)	3652(4)	75(1)
C(16)	6301(4)	12301(3)	3006(4)	76(2)
C(17)	5562(5)	12629(4)	2470(5)	85(2)
C(18)	4568(4)	12709(3)	2586(4)	69(1)
C(19)	2865(3)	13761(2)	3986(3)	49(1)
C(20)	1960(5)	14151(3)	3735(4)	87(2)
C(21)	1895(6)	15024(4)	4256(5)	106(2)
C(22)	2715(6)	15516(3)	5023(5)	95(2)
C(23)	3595(5)	15142(4)	5290(5)	113(3)
C(24)	3677(4)	14284(3)	4772(4)	90(2)
C(25)	537(4)	6423(3)	-1634(3)	64(1)
C(26)	917(5)	6814(5)	-2179(5)	98(2)
C(27)	1262(6)	6274(7)	-2914(5)	129(3)
C(28)	1223(8)	5380(8)	-3110(7)	147(4)

C(29)	838(8)	4983(6)	-2615(7)	131(3)
C(30)	489(5)	5488(3)	-1891(4)	86(2)
C(31)	-1091(4)	6412(3)	-648(3)	57(1)
C(32)	-2070(4)	6211(3)	-1325(4)	78(2)
C(33)	-2928(5)	5689(4)	-1332(6)	109(2)
C(34)	-2826(6)	5331(6)	-665(7)	124(3)
C(35)	-1857(8)	5520(7)	13(6)	139(3)
C(36)	-994(5)	6036(5)	19(5)	103(2)
C(37A)	2011(5)	7728(4)	2246(4)	38(2)
C(38A)	1905(6)	6825(5)	2087(5)	61(2)
C(39A)	2279(7)	6511(5)	2811(6)	70(2)
C(40A)	2804(7)	7086(5)	3681(6)	63(2)
C(37B)	2276(11)	7786(8)	2104(9)	32(3)
C(38B)	2381(12)	6886(9)	1963(10)	45(3)
C(39B)	2799(13)	6599(10)	2718(11)	56(4)
C(40B)	3159(14)	7188(11)	3629(12)	54(4)
C(41)	2925(4)	8018(3)	3844(4)	69(1)
C(42)	2501(4)	8326(3)	3128(3)	59(1)
C(43)	2636(3)	8789(3)	1067(3)	52(1)
C(44)	2894(4)	8468(4)	239(4)	80(2)
C(45)	3685(5)	8926(5)	106(5)	110(2)
C(46)	4246(5)	9730(5)	771(5)	103(2)
C(47)	4007(4)	10073(4)	1574(4)	71(1)
C(48)	3216(3)	9610(3)	1720(3)	52(1)
C(49A)	-1407(7)	10414(8)	2216(8)	77(4)
C(50A)	-2588(10)	10183(10)	1856(11)	101(6)
C(49B)	-1470(80)	9990(30)	2330(40)	480(80)
C(50B)	-1710(50)	10860(40)	2200(40)	350(40)
O(10)	-2294(4)	7774(4)	1474(4)	119(2)
C(51)	-1883(11)	7592(9)	2269(8)	181(5)
C(52)	-718(11)	7829(10)	2606(8)	210(7)
C(53)	-3445(8)	7492(9)	1103(9)	181(5)
C(54)	-3833(8)	7719(10)	206(9)	194(5)
Q(1)	5634(11)	5860(9)	2164(10)	99(4)
Q(2)	6138(13)	4612(12)	1265(13)	120(5)
Q(3)	5999(14)	5112(12)	2085(14)	131(5)
Q(4)	6147(18)	3973(16)	557(18)	163(7)

Table 3. Bond lengths [Å] and angles [°] for sh2331.

Al(1)-O(4)	1.732(3)	Si(1)-O(5)	1.641(3)
Al(1)-O(1)	1.735(3)	Si(1)-C(7)	1.868(4)
Al(1)-O(9)	1.765(2)	Si(1)-C(1)	1.883(5)
Al(1)-O(3)	1.769(3)	Si(2)-O(6)	1.602(3)
Al(1)-Na(2)	3.114(2)	Si(2)-O(5)	1.637(3)
Al(1)-Na(1)#1	3.255(2)	Si(2)-C(19)	1.868(4)
Al(2)-O(6)	1.720(3)	Si(2)-C(13)	1.883(4)
Al(2)-O(1)	1.736(2)	Si(3)-O(7)	1.612(3)
Al(2)-O(7)#1	1.756(3)	Si(3)-O(8)	1.643(3)
Al(2)-O(2)	1.766(3)	Si(3)-C(25)	1.854(5)
Al(2)-Na(1)	3.113(2)	Si(3)-C(31)	1.881(5)
Al(2)-Na(1)#1	3.221(2)	Si(4)-O(9)	1.604(3)
Al(2)-Na(2)#1	3.448(2)	Si(4)-O(8)	1.641(3)
Si(1)-O(4)	1.601(3)		

Si(4)-C(37B)	1.746(13)	C(22)-C(23)	1.357(9)
Si(4)-C(43)	1.903(5)	C(23)-C(24)	1.378(8)
Si(4)-C(37A)	1.918(6)	C(25)-C(30)	1.414(7)
Na(1)-O(1)	2.409(3)	C(25)-C(26)	1.436(8)
Na(1)-O(1)#1	2.412(3)	C(26)-C(27)	1.424(11)
Na(1)-O(2)	2.598(3)	C(27)-C(28)	1.361(13)
Na(1)-O(7)	2.743(3)	C(28)-C(29)	1.376(13)
Na(1)-O(3)#1	2.779(5)	C(29)-C(30)	1.395(10)
Na(1)-Al(2)#1	3.221(2)	C(31)-C(32)	1.381(7)
Na(1)-Al(1)#1	3.254(2)	C(31)-C(36)	1.389(7)
Na(1)-Na(1)#1	3.324(3)	C(32)-C(33)	1.394(8)
Na(1)-Na(2)#1	3.713(2)	C(33)-C(34)	1.368(10)
Na(2)-O(2)#1	2.314(4)	C(34)-C(35)	1.373(11)
Na(2)-O(10)	2.318(5)	C(35)-C(36)	1.395(10)
Na(2)-O(3)	2.336(4)	C(37A)-C(42)	1.371(7)
Na(2)-O(9)	2.482(3)	C(37A)-C(38A)	1.384(9)
Na(2)-C(49B)	2.98(7)	C(38A)-C(39A)	1.402(10)
Na(2)-Al(2)#1	3.448(2)	C(39A)-C(40A)	1.354(11)
Na(2)-Na(1)#1	3.713(2)	C(40A)-C(41)	1.431(9)
O(1)-Na(1)#1	2.412(3)	C(37B)-C(38B)	1.408(18)
O(2)-Na(2)#1	2.314(4)	C(37B)-C(42)	1.520(15)
O(3)-C(49A)	1.357(10)	C(38B)-C(39B)	1.42(2)
O(3)-C(49B)	1.43(10)	C(39B)-C(40B)	1.38(2)
O(3)-Na(1)#1	2.779(5)	C(40B)-C(41)	1.335(16)
O(7)-Al(2)#1	1.756(3)	C(41)-C(42)	1.393(7)
C(1)-C(6)	1.354(7)	C(43)-C(48)	1.407(6)
C(1)-C(2)	1.410(8)	C(43)-C(44)	1.412(7)
C(2)-C(3)	1.423(11)	C(44)-C(45)	1.376(8)
C(3)-C(4)	1.321(13)	C(45)-C(46)	1.386(9)
C(4)-C(5)	1.340(13)	C(46)-C(47)	1.366(8)
C(5)-C(6)	1.402(10)	C(47)-C(48)	1.395(6)
C(7)-C(8B)	1.267(13)	C(49A)-C(50A)	1.493(19)
C(7)-C(12A)	1.396(12)	C(49B)-C(50B)	1.51(9)
C(7)-C(8A)	1.411(12)	O(10)-C(51)	1.380(11)
C(7)-C(12B)	1.540(12)	O(10)-C(53)	1.465(10)
C(8A)-C(9A)	1.391(16)	C(51)-C(52)	1.475(15)
C(9A)-C(10A)	1.493(17)	C(53)-C(54)	1.566(15)
C(10A)-C(11A)	1.221(14)	Q(1)-Q(3)	1.29(2)
C(11A)-C(12A)	1.400(15)	Q(2)-Q(4)	1.26(3)
C(8B)-C(9B)	1.529(18)	Q(2)-Q(3)	1.37(2)
C(9B)-C(10B)	1.404(18)	O(4)-Al(1)-O(1)	115.70(13)
C(10B)-C(11B)	1.269(16)	O(4)-Al(1)-O(9)	110.48(13)
C(11B)-C(12B)	1.366(16)	O(1)-Al(1)-O(9)	109.47(14)
C(11B)-C(11B)#2	1.88(2)	O(4)-Al(1)-O(3)	116.01(17)
C(13)-C(14)	1.382(6)	O(1)-Al(1)-O(3)	104.01(17)
C(13)-C(18)	1.391(6)	O(9)-Al(1)-O(3)	99.84(16)
C(14)-C(15)	1.392(7)	O(4)-Al(1)-Na(2)	135.73(11)
C(15)-C(16)	1.371(8)	O(1)-Al(1)-Na(2)	108.54(10)
C(16)-C(17)	1.359(8)	O(9)-Al(1)-Na(2)	52.74(9)
C(17)-C(18)	1.393(8)	O(3)-Al(1)-Na(2)	48.00(13)
C(19)-C(24)	1.384(6)	O(4)-Al(1)-Na(1)#1	143.18(10)
C(19)-C(20)	1.392(7)	O(1)-Al(1)-Na(1)#1	46.41(9)
C(20)-C(21)	1.393(7)	O(9)-Al(1)-Na(1)#1	106.24(10)
C(21)-C(22)	1.361(9)	O(3)-Al(1)-Na(1)#1	58.60(14)

Na(2)-Al(1)-Na(1)#1	71.29(6)	O(1)#1-Na(1)-O(2)	109.27(11)
O(6)-Al(2)-O(1)	117.63(14)	O(1)-Na(1)-O(7)	102.08(12)
O(6)-Al(2)-O(7)#1	110.07(14)	O(1)#1-Na(1)-O(7)	64.69(9)
O(1)-Al(2)-O(7)#1	105.10(14)	O(2)-Na(1)-O(7)	168.34(12)
O(6)-Al(2)-O(2)	112.39(15)	O(1)-Na(1)-O(3)#1	125.51(11)
O(1)-Al(2)-O(2)	105.52(14)	O(1)#1-Na(1)-O(3)#1	63.83(10)
O(7)#1-Al(2)-O(2)	105.19(17)	O(2)-Na(1)-O(3)#1	74.93(12)
O(6)-Al(2)-Na(1)	144.50(11)	O(7)-Na(1)-O(3)#1	109.04(12)
O(1)-Al(2)-Na(1)	50.32(10)	O(1)-Na(1)-Al(2)	33.69(6)
O(7)#1-Al(2)-Na(1)	105.42(11)	O(1)#1-Na(1)-Al(2)	98.10(9)
O(2)-Al(2)-Na(1)	56.55(10)	O(2)-Na(1)-Al(2)	34.55(8)
O(6)-Al(2)-Na(1)#1	138.84(12)	O(7)-Na(1)-Al(2)	134.28(10)
O(1)-Al(2)-Na(1)#1	47.39(10)	O(3)#1-Na(1)-Al(2)	98.16(10)
O(7)#1-Al(2)-Na(1)#1	58.36(10)	O(1)-Na(1)-Al(2)#1	95.34(9)
O(2)-Al(2)-Na(1)#1	108.76(11)	O(1)#1-Na(1)-Al(2)#1	31.99(6)
Na(1)-Al(2)-Na(1)#1	63.28(6)	O(2)-Na(1)-Al(2)#1	139.24(9)
O(6)-Al(2)-Na(2)#1	125.75(11)	O(7)-Na(1)-Al(2)#1	33.03(6)
O(1)-Al(2)-Na(2)#1	114.71(11)	O(3)#1-Na(1)-Al(2)#1	88.11(9)
O(7)#1-Al(2)-Na(2)#1	67.64(13)	Al(2)-Na(1)-Al(2)#1	116.72(6)
O(2)-Al(2)-Na(2)#1	37.55(11)	O(1)-Na(1)-Al(1)#1	107.83(8)
Na(1)-Al(2)-Na(2)#1	68.72(5)	O(1)#1-Na(1)-Al(1)#1	31.41(7)
Na(1)#1-Al(2)-Na(2)#1	88.53(6)	O(2)-Na(1)-Al(1)#1	89.30(9)
O(4)-Si(1)-O(5)	112.63(15)	O(7)-Na(1)-Al(1)#1	88.98(8)
O(4)-Si(1)-C(7)	112.31(18)	O(3)#1-Na(1)-Al(1)#1	32.92(7)
O(5)-Si(1)-C(7)	104.11(17)	Al(2)-Na(1)-Al(1)#1	95.39(6)
O(4)-Si(1)-C(1)	109.16(18)	Al(2)#1-Na(1)-Al(1)#1	59.94(4)
O(5)-Si(1)-C(1)	109.33(19)	O(1)-Na(1)-Na(1)#1	46.45(8)
C(7)-Si(1)-C(1)	109.2(2)	O(1)#1-Na(1)-Na(1)#1	46.37(8)
O(6)-Si(2)-O(5)	111.63(14)	O(2)-Na(1)-Na(1)#1	87.86(10)
O(6)-Si(2)-C(19)	110.03(17)	O(7)-Na(1)-Na(1)#1	80.88(9)
O(5)-Si(2)-C(19)	108.15(18)	O(3)#1-Na(1)-Na(1)#1	95.79(10)
O(6)-Si(2)-C(13)	110.44(18)	Al(2)-Na(1)-Na(1)#1	59.95(6)
O(5)-Si(2)-C(13)	107.63(16)	Al(2)#1-Na(1)-Na(1)#1	56.77(5)
C(19)-Si(2)-C(13)	108.87(17)	Al(1)#1-Na(1)-Na(1)#1	66.59(6)
O(7)-Si(3)-O(8)	108.71(14)	O(1)-Na(1)-Na(2)#1	91.01(8)
O(7)-Si(3)-C(25)	109.6(2)	O(1)#1-Na(1)-Na(2)#1	78.87(8)
O(8)-Si(3)-C(25)	109.16(19)	O(2)-Na(1)-Na(2)#1	38.09(8)
O(7)-Si(3)-C(31)	113.71(19)	O(7)-Na(1)-Na(2)#1	141.57(9)
O(8)-Si(3)-C(31)	106.13(19)	O(3)#1-Na(1)-Na(2)#1	38.93(9)
C(25)-Si(3)-C(31)	109.4(2)	Al(2)-Na(1)-Na(2)#1	59.91(5)
O(9)-Si(4)-O(8)	110.86(15)	Al(2)#1-Na(1)-Na(2)#1	110.67(6)
O(9)-Si(4)-C(37B)	120.5(5)	Al(1)#1-Na(1)-Na(2)#1	52.60(5)
O(8)-Si(4)-C(37B)	106.8(4)	Na(1)#1-Na(1)-Na(2)#1	82.68(7)
O(9)-Si(4)-C(43)	109.30(15)	O(2)#1-Na(2)-O(10)	123.10(18)
O(8)-Si(4)-C(43)	106.97(19)	O(2)#1-Na(2)-O(3)	89.52(14)
C(37B)-Si(4)-C(43)	101.3(5)	O(10)-Na(2)-O(3)	105.84(18)
O(9)-Si(4)-C(37A)	108.8(2)	O(2)#1-Na(2)-O(9)	111.62(11)
O(8)-Si(4)-C(37A)	105.9(2)	O(10)-Na(2)-O(9)	125.07(18)
C(37B)-Si(4)-C(37A)	14.6(5)	O(3)-Na(2)-O(9)	68.22(11)
C(43)-Si(4)-C(37A)	115.0(2)	O(2)#1-Na(2)-C(49B)	100.8(12)
O(1)-Na(1)-O(1)#1	92.82(10)	O(10)-Na(2)-C(49B)	78.3(14)
O(1)-Na(1)-O(2)	67.55(10)	O(3)-Na(2)-C(49B)	28.0(15)

O(9)-Na(2)-C(49B)	87.9(18)	C(4)-C(5)-C(6)	121.7(9)
O(2)#1-Na(2)-Al(1)	98.31(9)	C(1)-C(6)-C(5)	122.1(7)
O(10)-Na(2)-Al(1)	124.99(17)	C(8B)-C(7)-C(12A)	79.8(8)
O(3)-Na(2)-Al(1)	34.26(8)	C(8B)-C(7)-C(8A)	39.8(6)
O(9)-Na(2)-Al(1)	34.48(6)	C(12A)-C(7)-C(8A)	115.7(8)
C(49B)-Na(2)-Al(1)	58.1(18)	C(8B)-C(7)-C(12B)	111.7(8)
O(2)#1-Na(2)-Al(2)#1	27.72(8)	C(12A)-C(7)-C(12B)	67.9(7)
O(10)-Na(2)-Al(2)#1	141.70(16)	C(8A)-C(7)-C(12B)	108.7(7)
O(3)-Na(2)-Al(2)#1	99.02(12)	C(8B)-C(7)-Si(1)	131.8(7)
O(9)-Na(2)-Al(2)#1	90.98(9)	C(12A)-C(7)-Si(1)	120.2(5)
C(49B)-Na(2)-Al(2)#1	119.8(11)	C(8A)-C(7)-Si(1)	117.4(6)
Al(1)-Na(2)-Al(2)#1	91.60(6)	C(12B)-C(7)-Si(1)	116.4(5)
O(2)#1-Na(2)-Na(1)#1	43.84(8)	C(9A)-C(8A)-C(7)	120.5(10)
O(10)-Na(2)-Na(1)#1	137.88(16)	C(8A)-C(9A)-C(10A)	115.5(11)
O(3)-Na(2)-Na(1)#1	48.38(11)	C(11A)-C(10A)-C(9A)	121.6(12)
O(9)-Na(2)-Na(1)#1	80.55(7)	C(10A)-C(11A)-C(12A)	121.7(12)
C(49B)-Na(2)-Na(1)#1	69.2(11)	C(7)-C(12A)-C(11A)	120.1(9)
Al(1)-Na(2)-Na(1)#1	56.12(4)	C(7)-C(8B)-C(9B)	126.8(11)
Al(2)#1-Na(2)-Na(1)#1	51.37(5)	C(10B)-C(9B)-C(8B)	112.9(11)
Al(1)-O(1)-Al(2)	137.51(16)	C(11B)-C(10B)-C(9B)	125.3(13)
Al(1)-O(1)-Na(1)	120.41(12)	C(10B)-C(11B)-C(12B)	119.9(12)
Al(2)-O(1)-Na(1)	96.00(13)	C(10B)-C(11B)-C(11B)#2	134.8(13)
Al(1)-O(1)-Na(1)#1	102.18(13)	C(12B)-C(11B)-C(11B)#2	101.0(11)
Al(2)-O(1)-Na(1)#1	100.62(12)	C(11B)-C(12B)-C(7)	123.1(10)
Na(1)-O(1)-Na(1)#1	87.18(10)	C(14)-C(13)-C(18)	116.2(4)
Al(2)-O(2)-Na(2)#1	114.72(16)	C(14)-C(13)-Si(2)	123.9(3)
Al(2)-O(2)-Na(1)	88.90(12)	C(18)-C(13)-Si(2)	119.9(3)
Na(2)#1-O(2)-Na(1)	98.07(12)	C(13)-C(14)-C(15)	121.8(5)
C(49A)-O(3)-C(49B)	32(2)	C(16)-C(15)-C(14)	120.3(5)
C(49A)-O(3)-Al(1)	132.1(5)	C(17)-C(16)-C(15)	119.5(5)
C(49B)-O(3)-Al(1)	136(3)	C(16)-C(17)-C(18)	120.0(5)
C(49A)-O(3)-Na(2)	127.0(6)	C(13)-C(18)-C(17)	122.2(5)
C(49B)-O(3)-Na(2)	101.9(16)	C(24)-C(19)-C(20)	116.5(4)
Al(1)-O(3)-Na(2)	97.74(16)	C(24)-C(19)-Si(2)	122.2(4)
C(49A)-O(3)-Na(1)#1	103.6(7)	C(20)-C(19)-Si(2)	121.2(3)
C(49B)-O(3)-Na(1)#1	129(3)	C(19)-C(20)-C(21)	120.9(5)
Al(1)-O(3)-Na(1)#1	88.49(15)	C(22)-C(21)-C(20)	120.7(6)
Na(2)-O(3)-Na(1)#1	92.69(14)	C(23)-C(22)-C(21)	119.3(5)
Si(1)-O(4)-Al(1)	156.48(18)	C(22)-C(23)-C(24)	120.5(6)
Si(2)-O(5)-Si(1)	145.79(18)	C(23)-C(24)-C(19)	122.1(6)
Si(2)-O(6)-Al(2)	158.55(18)	C(30)-C(25)-C(26)	116.8(5)
Si(3)-O(7)-Al(2)#1	140.28(19)	C(30)-C(25)-Si(3)	121.0(4)
Si(3)-O(7)-Na(1)	131.10(16)	C(26)-C(25)-Si(3)	122.2(4)
Al(2)#1-O(7)-Na(1)	88.61(11)	C(27)-C(26)-C(25)	120.2(7)
Si(4)-O(8)-Si(3)	136.05(17)	C(28)-C(27)-C(26)	120.0(8)
Si(4)-O(9)-Al(1)	141.08(16)	C(27)-C(28)-C(29)	121.0(8)
Si(4)-O(9)-Na(2)	124.97(13)	C(28)-C(29)-C(30)	120.7(8)
Al(1)-O(9)-Na(2)	92.78(12)	C(29)-C(30)-C(25)	121.1(7)
C(6)-C(1)-C(2)	116.0(5)	C(32)-C(31)-C(36)	115.8(5)
C(6)-C(1)-Si(1)	123.4(4)	C(32)-C(31)-Si(3)	121.8(4)
C(2)-C(1)-Si(1)	120.5(4)	C(36)-C(31)-Si(3)	122.3(4)
C(1)-C(2)-C(3)	119.4(8)	C(31)-C(32)-C(33)	122.8(5)
C(4)-C(3)-C(2)	122.4(9)	C(34)-C(33)-C(32)	120.8(6)
C(3)-C(4)-C(5)	118.2(8)		

C(33)-C(34)-C(35)	117.3(7)	C(41)-C(42)-C(37B)	125.1(6)
C(34)-C(35)-C(36)	122.1(7)	C(48)-C(43)-C(44)	115.5(4)
C(31)-C(36)-C(35)	121.1(6)	C(48)-C(43)-Si(4)	122.2(3)
C(42)-C(37A)-C(38A)	119.4(6)	C(44)-C(43)-Si(4)	122.3(3)
C(42)-C(37A)-Si(4)	118.3(4)	C(45)-C(44)-C(43)	121.4(5)
C(38A)-C(37A)-Si(4)	122.3(5)	C(44)-C(45)-C(46)	121.5(6)
C(37A)-C(38A)-C(39A)	121.3(7)	C(47)-C(46)-C(45)	119.0(6)
C(40A)-C(39A)-C(38A)	120.4(7)	C(46)-C(47)-C(48)	119.9(5)
C(39A)-C(40A)-C(41)	118.3(7)	C(47)-C(48)-C(43)	122.7(4)
C(38B)-C(37B)-C(42)	110.5(11)	O(3)-C(49A)-C(50A)	118.8(9)
C(38B)-C(37B)-Si(4)	125.2(10)	O(3)-C(49B)-C(50B)	89(4)
C(42)-C(37B)-Si(4)	120.4(8)	O(3)-C(49B)-Na(2)	50.1(17)
C(37B)-C(38B)-C(39B)	121.6(13)	C(50B)-C(49B)-Na(2)	123(4)
C(40B)-C(39B)-C(38B)	122.3(14)	C(51)-O(10)-C(53)	109.4(8)
C(41)-C(40B)-C(39B)	120.0(14)	C(51)-O(10)-Na(2)	124.0(6)
C(40B)-C(41)-C(42)	118.4(9)	C(53)-O(10)-Na(2)	126.5(6)
C(40B)-C(41)-C(40A)	22.0(7)	O(10)-C(51)-C(52)	109.0(8)
C(42)-C(41)-C(40A)	120.8(5)	O(10)-C(53)-C(54)	105.6(7)
C(37A)-C(42)-C(41)	119.7(4)	Q(4)-Q(2)-Q(3)	163(2)
C(37A)-C(42)-C(37B)	18.9(5)	Q(1)-Q(3)-Q(2)	119.2(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z #2 -x+1,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2331. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	38(1)	28(1)	38(1)	8(1)	5(1)	5(1)
Al(2)	46(1)	26(1)	37(1)	10(1)	-4(1)	1(1)
Si(1)	44(1)	39(1)	32(1)	10(1)	4(1)	3(1)
Si(2)	46(1)	28(1)	35(1)	7(1)	-2(1)	-1(1)
Si(3)	60(1)	29(1)	41(1)	7(1)	-8(1)	9(1)
Si(4)	51(1)	29(1)	39(1)	6(1)	-5(1)	10(1)
Na(1)	46(1)	47(1)	54(1)	6(1)	6(1)	12(1)
Na(2)	53(1)	55(1)	55(1)	18(1)	9(1)	-7(1)
O(1)	57(2)	28(1)	36(2)	9(1)	1(1)	0(1)
O(2)	56(2)	66(2)	50(2)	18(2)	7(1)	-5(1)
O(3)	41(2)	69(2)	63(3)	2(2)	13(2)	10(1)
O(4)	52(2)	37(1)	37(2)	9(1)	6(1)	0(1)
O(5)	49(2)	41(1)	44(2)	15(1)	3(1)	0(1)
O(6)	55(2)	33(1)	43(2)	10(1)	-8(1)	-2(1)
O(7)	69(2)	34(1)	60(2)	13(1)	-18(2)	8(1)
O(8)	74(2)	30(1)	44(2)	3(1)	-15(1)	15(1)
O(9)	43(1)	29(1)	45(2)	10(1)	2(1)	3(1)
C(1)	56(3)	82(3)	29(3)	10(2)	5(2)	13(2)
C(2)	70(4)	145(6)	117(6)	48(5)	49(4)	22(4)
C(3)	75(5)	248(12)	133(8)	96(8)	60(5)	48(6)
C(4)	122(7)	227(12)	108(7)	67(7)	67(6)	100(8)
C(5)	149(7)	139(7)	125(8)	38(5)	78(6)	86(6)
C(6)	118(5)	77(4)	96(5)	18(3)	59(4)	37(3)
C(7)	63(3)	58(2)	44(3)	26(2)	0(2)	-3(2)
C(13)	50(2)	30(2)	41(2)	8(2)	5(2)	-3(2)
C(14)	54(3)	68(3)	44(3)	20(2)	6(2)	7(2)
C(15)	52(3)	95(4)	69(4)	25(3)	10(2)	17(2)

C(16)	62(3)	67(3)	88(4)	10(3)	32(3)	0(2)
C(17)	105(4)	75(3)	101(5)	42(3)	58(4)	17(3)
C(18)	83(3)	63(3)	73(4)	36(3)	28(3)	19(2)
C(19)	56(2)	32(2)	45(3)	5(2)	6(2)	-1(2)
C(20)	93(4)	50(3)	75(4)	2(2)	-10(3)	25(3)
C(21)	131(6)	60(3)	98(5)	9(3)	15(4)	46(4)
C(22)	134(6)	40(3)	95(5)	-1(3)	47(4)	6(3)
C(23)	91(4)	62(3)	111(6)	-38(3)	9(4)	-10(3)
C(24)	65(3)	60(3)	90(5)	-15(3)	-5(3)	1(2)
C(25)	59(3)	66(3)	44(3)	11(2)	-3(2)	-2(2)
C(26)	94(4)	95(4)	77(5)	16(4)	9(3)	-32(3)
C(27)	120(6)	169(8)	74(6)	7(5)	43(4)	-41(6)
C(28)	147(8)	149(8)	123(8)	-3(6)	73(7)	9(6)
C(29)	174(8)	101(5)	118(7)	18(5)	69(6)	62(5)
C(30)	119(5)	62(3)	73(4)	15(3)	32(3)	35(3)
C(31)	73(3)	40(2)	47(3)	11(2)	8(2)	14(2)
C(32)	72(3)	64(3)	94(4)	46(3)	2(3)	0(2)
C(33)	78(4)	99(4)	151(7)	76(5)	3(4)	-4(3)
C(34)	101(5)	148(7)	144(8)	85(6)	34(5)	0(5)
C(35)	148(8)	188(9)	94(7)	84(6)	24(5)	-24(6)
C(36)	95(4)	140(6)	72(5)	59(4)	3(3)	-5(4)
C(41)	78(3)	67(3)	47(3)	17(2)	3(2)	4(2)
C(42)	68(3)	46(2)	53(3)	15(2)	10(2)	5(2)
C(43)	47(2)	56(2)	40(3)	9(2)	4(2)	21(2)
C(44)	57(3)	96(4)	51(4)	-11(3)	13(2)	10(3)
C(45)	87(4)	157(6)	61(5)	-4(4)	40(3)	-1(4)
C(46)	72(4)	151(6)	72(5)	18(4)	32(3)	-16(4)
C(47)	64(3)	82(3)	55(4)	15(3)	15(2)	0(2)
C(48)	51(2)	56(2)	42(3)	12(2)	11(2)	6(2)
C(49A)	36(6)	70(7)	78(7)	-33(6)	23(4)	7(4)
C(50A)	68(9)	123(10)	116(12)	31(8)	48(7)	44(7)
C(49B)	880(170)	90(20)	200(50)	20(30)	-180(80)	-130(50)
C(50B)	440(80)	210(50)	580(100)	150(50)	430(80)	110(50)
O(10)	132(4)	134(4)	121(5)	64(3)	65(3)	8(3)
C(51)	223(13)	233(13)	126(10)	103(9)	71(9)	4(10)
C(52)	184(11)	312(18)	152(11)	156(12)	4(8)	-41(11)
C(53)	106(7)	265(14)	191(12)	94(11)	65(7)	-19(8)
C(54)	120(8)	273(15)	181(13)	102(12)	16(8)	16(8)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sh2331.

	x	y	z	U(eq)
H(2)	80	10703	4470	127
H(3)	-1207	11432	5059	166
H(4)	-1287	12892	5323	170
H(5)	7	13706	5144	158
H(6)	1354	13054	4641	114
H(8A)	1624	9934	4796	94
H(9A)	2563	9586	6085	94
H(10A)	4440	10261	6833	94
H(11A)	4948	11474	6713	94
H(12A)	3902	11965	5593	94

H(8B)	2045	10872	5732	94
H(9B)	3346	10347	6813	94
H(10B)	4945	10069	6487	94
H(11B)	5236	10150	5266	94
H(12B)	3982	10548	4220	94
H(14)	4905	11944	4217	69
H(15)	6557	11803	4018	90
H(16)	6976	12254	2936	91
H(17)	5723	12803	2020	102
H(18)	4068	12940	2211	83
H(20)	1387	13821	3206	104
H(21)	1278	15276	4075	127
H(22)	2672	16108	5365	113
H(23)	4154	15471	5831	135
H(24)	4305	14047	4959	108
H(26)	938	7430	-2049	118
H(27)	1518	6534	-3265	155
H(28)	1463	5030	-3591	177
H(29)	808	4363	-2767	158
H(30)	219	5203	-1567	103
H(32)	-2163	6436	-1802	94
H(33)	-3584	5582	-1801	130
H(34)	-3397	4971	-671	148
H(35)	-1772	5294	488	166
H(36)	-336	6131	483	123
H(38A)	1576	6415	1481	74
H(39A)	2164	5898	2692	83
H(40A)	3082	6878	4165	76
H(38B)	2169	6463	1355	54
H(39B)	2832	5989	2594	67
H(40B)	3570	7002	4096	65
H(41)	3294	8428	4441	83
H(42)	2552	8941	3248	70
H(44)	2519	7931	-231	96
H(45)	3847	8688	-447	132
H(46)	4784	10034	669	124
H(47)	4376	10621	2028	85
H(48)	3064	9857	2278	63
H(49A)	-1236	11023	2251	92
H(49B)	-1167	10425	2851	92
H(50A)	-2896	10608	2264	151
H(50B)	-2782	9588	1829	151
H(50C)	-2853	10203	1240	151
H(49C)	-1084	10063	2965	580
H(49D)	-2097	9534	2063	580
H(50D)	-2100	11166	2606	520
H(50E)	-2136	10738	1560	520
H(50F)	-1051	11233	2345	520
H(51A)	-2071	6958	2137	217
H(51B)	-2183	7937	2744	217
H(52A)	-422	7696	3161	315
H(52B)	-538	8460	2748	315
H(52C)	-428	7487	2132	315
H(53A)	-3788	7814	1553	217
H(53B)	-3608	6851	954	217

H(54A)	-4594	7538	-79	291
H(54B)	-3475	7404	-226	291
H(54C)	-3671	8355	367	291

8.2. Compound 4

Table 1. Crystal data and structure refinement for sh2448.

Identification code	sh2448	
Empirical formula	C_{112} H_{120} Al_4 Li_4 O_{22} Si_8	
Formula weight	2178.48	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 16.6098(5) Å	α= 90°.
	b = 15.9235(5) Å	β= 99.507(2)°.
	c = 21.5637(7) Å	γ = 90°.
Volume	5625.0(3) $Å^3$	
Z	2	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	2288	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.44 to 28.49°.	
Index ranges	-22<=h<=22, -21<=k<=21, -28<=l<=28	
Reflections collected	67465	
Independent reflections	14058 [R(int) = 0.0434]	
Completeness to theta = 28.49°	98.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14058 / 0 / 686	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0996	
R indices (all data)	R1 = 0.0578, wR2 = 0.1100	
Largest diff. peak and hole	1.063 and -0.353 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2448. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	125(1)	328(1)	-1276(1)	12(1)
Al(2)	1431(1)	678(1)	-68(1)	12(1)
Si(1)	1288(1)	1488(1)	-2035(1)	15(1)
Si(2)	2693(1)	1317(1)	-943(1)	14(1)
Si(3)	1502(1)	1976(1)	1041(1)	13(1)
Si(4)	372(1)	1386(1)	1949(1)	13(1)
Li(1)	59(2)	-793(2)	-279(2)	19(1)
Li(2)	1588(2)	-992(2)	790(1)	19(1)
O(1)	478(1)	358(1)	-468(1)	13(1)
O(2)	1976(1)	-213(1)	252(1)	17(1)
O(3)	-888(1)	721(1)	-1386(1)	18(1)
O(4)	702(1)	866(1)	-1738(1)	18(1)
O(5)	2232(1)	1452(1)	-1666(1)	20(1)
O(6)	2043(1)	1263(1)	-473(1)	15(1)
O(7)	1120(1)	1261(1)	544(1)	14(1)
O(8)	1045(1)	1942(1)	1654(1)	16(1)
O(9)	-116(1)	750(1)	1444(1)	17(1)
O(10)	871(1)	-1670(1)	90(1)	16(1)
O(11)	2514(1)	-1686(1)	1187(1)	24(1)
C(1)	1364(1)	1160(1)	-2858(1)	17(1)
C(2)	1121(1)	1667(1)	-3384(1)	20(1)
C(3)	1226(1)	1413(1)	-3984(1)	26(1)
C(4)	1567(1)	638(1)	-4070(1)	31(1)
C(5)	1807(1)	117(1)	-3557(1)	30(1)
C(6)	1704(1)	377(1)	-2960(1)	23(1)
C(7)	930(1)	2600(1)	-1995(1)	20(1)
C(8)	1407(1)	3287(1)	-2111(1)	30(1)
C(9)	1144(1)	4108(1)	-2045(1)	36(1)
C(10)	410(2)	4259(1)	-1851(1)	35(1)
C(11)	-74(2)	3593(1)	-1732(1)	34(1)
C(12)	181(1)	2776(1)	-1810(1)	26(1)
C(13)	3413(1)	2204(1)	-711(1)	15(1)
C(14)	3730(1)	2698(1)	-1152(1)	23(1)
C(15)	4279(1)	3342(1)	-966(1)	28(1)
C(16)	4519(1)	3517(1)	-337(1)	25(1)
C(17)	4218(1)	3039(1)	111(1)	25(1)
C(18)	3677(1)	2386(1)	-74(1)	21(1)
C(19)	3273(1)	304(1)	-918(1)	19(1)
C(20)	4120(1)	272(1)	-759(1)	32(1)
C(21)	4536(1)	-493(2)	-709(1)	39(1)
C(22)	4105(1)	-1242(1)	-819(1)	34(1)
C(23)	3273(1)	-1214(1)	-1010(1)	33(1)
C(24)	2865(1)	-452(1)	-1060(1)	29(1)
C(25)	1355(1)	3043(1)	678(1)	16(1)
C(26)	1000(1)	3724(1)	944(1)	20(1)
C(27)	917(1)	4503(1)	643(1)	27(1)
C(28)	1187(1)	4613(1)	72(1)	28(1)
C(29)	1546(1)	3949(1)	-200(1)	26(1)
C(30)	1627(1)	3175(1)	103(1)	21(1)
C(31)	2618(1)	1824(1)	1314(1)	15(1)

C(32)	2978(1)	1024(1)	1378(1)	20(1)
C(33)	3811(1)	931(1)	1583(1)	26(1)
C(34)	4301(1)	1628(1)	1740(1)	25(1)
C(35)	3960(1)	2422(1)	1693(1)	23(1)
C(36)	3130(1)	2518(1)	1478(1)	19(1)
C(37)	938(1)	807(1)	2643(1)	17(1)
C(38)	1793(1)	834(1)	2805(1)	23(1)
C(39)	2195(1)	400(1)	3329(1)	32(1)
C(40)	1752(1)	-60(1)	3703(1)	35(1)
C(41)	911(1)	-101(1)	3551(1)	32(1)
C(42)	510(1)	326(1)	3022(1)	24(1)
C(43)	-342(1)	2185(1)	2185(1)	15(1)
C(44)	-1190(1)	2121(1)	2033(1)	20(1)
C(45)	-1693(1)	2784(1)	2144(1)	28(1)
C(46)	-1361(1)	3513(1)	2424(1)	30(1)
C(47)	-526(1)	3586(1)	2595(1)	31(1)
C(48)	-24(1)	2930(1)	2470(1)	25(1)
C(49)	1364(1)	-2006(1)	-354(1)	19(1)
C(50)	1062(1)	-2893(1)	-485(1)	30(1)
C(51)	866(1)	-3165(1)	156(1)	29(1)
C(52)	531(1)	-2371(1)	403(1)	21(1)
C(53)	2576(1)	-1908(1)	1842(1)	27(1)
C(54)	2851(1)	-1179(1)	2272(1)	33(1)
C(55)	3281(1)	-1733(2)	960(1)	32(1)
C(56)	3502(2)	-2615(2)	800(1)	49(1)

Table 3. Bond lengths [Å] and angles [°] for sh2448.

Al(1)-O(4)	1.7204(12)	Si(4)-C(37)	1.8732(17)
Al(1)-O(1)	1.7450(12)	Li(1)-O(10)	2.012(3)
Al(1)-O(9)#1	1.7539(12)	Li(1)-O(1)	2.026(3)
Al(1)-O(3)	1.7740(13)	Li(1)-O(7)#1	2.085(3)
Al(1)-Li(1)	2.810(3)	Li(1)-O(1)#1	2.085(3)
Al(2)-O(6)	1.7199(12)	Li(1)-O(9)#1	2.530(3)
Al(2)-O(1)	1.7491(12)	Li(1)-Al(2)#1	2.707(3)
Al(2)-O(7)	1.7586(12)	Li(1)-Li(1)#1	2.819(6)
Al(2)-O(2)	1.7620(13)	Li(1)-Li(2)	3.151(4)
Al(2)-Li(1)#1	2.707(3)	Li(2)-O(2)	1.883(3)
Al(2)-Li(2)	3.225(3)	Li(2)-O(3)#1	1.918(3)
Al(2)-Li(1)	3.248(3)	Li(2)-O(11)	1.972(3)
Si(1)-O(4)	1.5939(12)	Li(2)-O(10)	2.065(3)
Si(1)-O(5)	1.6380(12)	O(1)-Li(1)#1	2.085(3)
Si(1)-C(1)	1.8739(17)	O(3)-Li(2)#1	1.918(3)
Si(1)-C(7)	1.8740(18)	O(7)-Li(1)#1	2.085(3)
Si(2)-O(6)	1.6002(12)	O(9)-Al(1)#1	1.7540(12)
Si(2)-O(5)	1.6338(13)	O(9)-Li(1)#1	2.530(3)
Si(2)-C(13)	1.8643(17)	O(10)-C(49)	1.4603(19)
Si(2)-C(19)	1.8747(18)	O(10)-C(52)	1.465(2)
Si(3)-O(7)	1.6192(12)	O(11)-C(55)	1.440(2)
Si(3)-O(8)	1.6308(12)	O(11)-C(53)	1.443(2)
Si(3)-C(31)	1.8663(16)	C(1)-C(2)	1.397(2)
Si(3)-C(25)	1.8688(17)	C(1)-C(6)	1.401(2)
Si(4)-O(9)	1.6052(12)	C(2)-C(3)	1.395(3)
Si(4)-O(8)	1.6362(12)	C(3)-C(4)	1.381(3)
Si(4)-C(43)	1.8655(17)	C(4)-C(5)	1.388(3)

C(5)-C(6)	1.389(3)
C(7)-C(12)	1.397(3)
C(7)-C(8)	1.398(3)
C(8)-C(9)	1.394(3)
C(9)-C(10)	1.372(3)
C(10)-C(11)	1.381(3)
C(11)-C(12)	1.388(3)
C(13)-C(14)	1.401(2)
C(13)-C(18)	1.402(2)
C(14)-C(15)	1.387(3)
C(15)-C(16)	1.378(3)
C(16)-C(17)	1.385(3)
C(17)-C(18)	1.389(2)
C(19)-C(24)	1.390(3)
C(19)-C(20)	1.394(3)
C(20)-C(21)	1.395(3)
C(21)-C(22)	1.390(3)
C(22)-C(23)	1.376(3)
C(23)-C(24)	1.385(3)
C(25)-C(26)	1.400(2)
C(25)-C(30)	1.405(2)
C(26)-C(27)	1.397(3)
C(27)-C(28)	1.388(3)
C(28)-C(29)	1.391(3)
C(29)-C(30)	1.390(2)
C(31)-C(36)	1.403(2)
C(31)-C(32)	1.405(2)
C(32)-C(33)	1.390(2)
C(33)-C(34)	1.384(3)
C(34)-C(35)	1.383(3)
C(35)-C(36)	1.389(2)
C(37)-C(42)	1.398(2)
C(37)-C(38)	1.404(2)
C(38)-C(39)	1.398(3)
C(39)-C(40)	1.386(3)
C(40)-C(41)	1.383(3)
C(41)-C(42)	1.398(3)
C(43)-C(44)	1.396(2)
C(43)-C(48)	1.399(2)
C(44)-C(45)	1.390(3)
C(45)-C(46)	1.381(3)
C(46)-C(47)	1.379(3)
C(47)-C(48)	1.392(3)
C(49)-C(50)	1.510(3)
C(50)-C(51)	1.535(3)
C(51)-C(52)	1.512(3)
C(53)-C(54)	1.510(3)
C(55)-C(56)	1.506(3)
O(4)-Al(1)-O(1)	115.86(6)
O(4)-Al(1)-O(9)#1	110.77(6)
O(1)-Al(1)-O(9)#1	102.90(6)
O(4)-Al(1)-O(3)	110.77(6)
O(1)-Al(1)-O(3)	106.16(6)
O(9)#1-Al(1)-O(3)	110.00(6)
O(4)-Al(1)-Li(1)	148.72(7)
O(1)-Al(1)-Li(1)	45.80(7)
O(9)#1-Al(1)-Li(1)	62.37(7)
O(3)-Al(1)-Li(1)	99.79(7)
O(6)-Al(2)-O(1)	118.02(6)
O(6)-Al(2)-O(7)	111.54(6)
O(1)-Al(2)-O(7)	99.80(5)
O(6)-Al(2)-O(2)	109.04(6)
O(1)-Al(2)-O(2)	108.85(6)
O(7)-Al(2)-O(2)	109.08(6)
O(6)-Al(2)-Li(1)#1	138.43(8)
O(1)-Al(2)-Li(1)#1	50.37(7)
O(7)-Al(2)-Li(1)#1	50.36(7)
O(2)-Al(2)-Li(1)#1	112.35(8)
O(6)-Al(2)-Li(2)	137.66(7)
O(1)-Al(2)-Li(2)	91.34(6)
O(7)-Al(2)-Li(2)	90.62(7)
O(2)-Al(2)-Li(2)	28.79(7)
Li(1)#1-Al(2)-Li(2)	83.57(8)
O(6)-Al(2)-Li(1)	141.18(7)
O(1)-Al(2)-Li(1)	33.24(6)
O(7)-Al(2)-Li(1)	101.53(7)
O(2)-Al(2)-Li(1)	77.12(7)
Li(1)#1-Al(2)-Li(1)	55.62(10)
Li(2)-Al(2)-Li(1)	58.25(7)
O(4)-Si(1)-O(5)	112.41(6)
O(4)-Si(1)-C(1)	110.43(7)
O(5)-Si(1)-C(1)	103.97(7)
O(4)-Si(1)-C(7)	110.42(7)
O(5)-Si(1)-C(7)	107.16(7)
C(1)-Si(1)-C(7)	112.27(8)
O(6)-Si(2)-O(5)	110.61(6)
O(6)-Si(2)-C(13)	109.95(7)
O(5)-Si(2)-C(13)	109.60(7)
O(6)-Si(2)-C(19)	109.40(7)
O(5)-Si(2)-C(19)	107.35(7)
C(13)-Si(2)-C(19)	109.90(8)
O(7)-Si(3)-O(8)	109.19(6)
O(7)-Si(3)-C(31)	112.20(7)
O(8)-Si(3)-C(31)	108.09(7)
O(7)-Si(3)-C(25)	110.68(7)
O(8)-Si(3)-C(25)	108.85(7)
C(31)-Si(3)-C(25)	107.74(7)
O(9)-Si(4)-O(8)	112.21(6)
O(9)-Si(4)-C(43)	110.03(7)
O(8)-Si(4)-C(43)	104.08(7)
O(9)-Si(4)-C(37)	111.22(7)
O(8)-Si(4)-C(37)	106.96(7)
C(43)-Si(4)-C(37)	112.11(7)
O(10)-Li(1)-O(1)	118.52(15)
O(10)-Li(1)-O(7)#1	113.48(14)
O(1)-Li(1)-O(7)#1	127.34(15)
O(10)-Li(1)-O(1)#1	105.59(14)
O(1)-Li(1)-O(1)#1	93.42(13)
O(7)#1-Li(1)-O(1)#1	80.09(11)

O(10)-Li(1)-O(9)#1	106.24(13)	Al(1)-O(1)-Li(1)	96.08(10)
O(1)-Li(1)-O(9)#1	72.87(10)	Al(2)-O(1)-Li(1)	118.52(10)
O(7)#1-Li(1)-O(9)#1	85.70(11)	Al(1)-O(1)-Li(1)#1	131.66(10)
O(1)#1-Li(1)-O(9)#1	148.11(14)	Al(2)-O(1)-Li(1)#1	89.39(9)
O(10)-Li(1)-Al(2)#1	121.40(13)	Li(1)-O(1)-Li(1)#1	86.58(13)
O(1)-Li(1)-Al(2)#1	110.76(12)	Al(2)-O(2)-Li(2)	124.43(11)
O(7)#1-Li(1)-Al(2)#1	40.50(6)	Al(1)-O(3)-Li(2)#1	131.02(11)
O(1)#1-Li(1)-Al(2)#1	40.24(6)	Si(1)-O(4)-Al(1)	167.74(9)
O(9)#1-Li(1)-Al(2)#1	117.26(11)	Si(2)-O(5)-Si(1)	136.80(8)
O(10)-Li(1)-Al(1)	129.46(13)	Si(2)-O(6)-Al(2)	150.26(8)
O(1)-Li(1)-Al(1)	38.13(6)	Si(3)-O(7)-Al(2)	137.35(7)
O(7)#1-Li(1)-Al(1)	99.84(11)	Si(3)-O(7)-Li(1)#1	132.86(11)
O(1)#1-Li(1)-Al(1)	117.11(12)	Al(2)-O(7)-Li(1)#1	89.14(10)
O(9)#1-Li(1)-Al(1)	37.89(5)	Si(3)-O(8)-Si(4)	140.67(8)
Al(2)#1-Li(1)-Al(1)	108.74(10)	Si(4)-O(9)-Al(1)#1	138.08(8)
O(10)-Li(1)-Li(1)#1	122.82(19)	Si(4)-O(9)-Li(1)#1	124.00(9)
O(1)-Li(1)-Li(1)#1	47.59(9)	Al(1)#1-O(9)-Li(1)#1	79.74(8)
O(7)#1-Li(1)-Li(1)#1	107.98(16)	C(49)-O(10)-C(52)	108.85(12)
O(1)#1-Li(1)-Li(1)#1	45.84(9)	C(49)-O(10)-Li(1)	113.95(13)
O(9)#1-Li(1)-Li(1)#1	114.60(16)	C(52)-O(10)-Li(1)	115.30(13)
Al(2)#1-Li(1)-Li(1)#1	71.95(12)	C(49)-O(10)-Li(2)	110.68(12)
Al(1)-Li(1)-Li(1)#1	76.81(12)	C(52)-O(10)-Li(2)	106.33(13)
O(10)-Li(1)-Li(2)	40.01(8)	Li(1)-O(10)-Li(2)	101.20(13)
O(1)-Li(1)-Li(2)	88.62(11)	C(55)-O(11)-C(53)	113.32(14)
O(7)#1-Li(1)-Li(2)	140.48(14)	C(55)-O(11)-Li(2)	123.51(14)
O(1)#1-Li(1)-Li(2)	82.17(11)	C(53)-O(11)-Li(2)	119.13(14)
O(9)#1-Li(1)-Li(2)	124.86(12)	C(2)-C(1)-C(6)	117.17(16)
Al(2)#1-Li(1)-Li(2)	117.87(12)	C(2)-C(1)-Si(1)	123.52(14)
Al(1)-Li(1)-Li(2)	119.67(11)	C(6)-C(1)-Si(1)	119.28(13)
Li(1)#1-Li(1)-Li(2)	83.22(14)	C(3)-C(2)-C(1)	121.48(17)
O(10)-Li(1)-Al(2)	92.07(10)	C(4)-C(3)-C(2)	120.04(18)
O(1)-Li(1)-Al(2)	28.24(5)	C(3)-C(4)-C(5)	119.77(18)
O(7)#1-Li(1)-Al(2)	154.39(13)	C(4)-C(5)-C(6)	119.88(19)
O(1)#1-Li(1)-Al(2)	91.81(10)	C(5)-C(6)-C(1)	121.65(18)
O(9)#1-Li(1)-Al(2)	88.83(9)	C(12)-C(7)-C(8)	116.88(17)
Al(2)#1-Li(1)-Al(2)	124.38(10)	C(12)-C(7)-Si(1)	120.44(14)
Al(1)-Li(1)-Al(2)	62.23(6)	C(8)-C(7)-Si(1)	122.59(14)
Li(1)#1-Li(1)-Al(2)	52.42(9)	C(9)-C(8)-C(7)	121.31(19)
Li(2)-Li(1)-Al(2)	60.52(8)	C(10)-C(9)-C(8)	120.3(2)
O(2)-Li(2)-O(3)#1	124.84(17)	C(9)-C(10)-C(11)	119.7(2)
O(2)-Li(2)-O(11)	108.31(15)	C(10)-C(11)-C(12)	120.0(2)
O(3)#1-Li(2)-O(11)	110.53(15)	C(11)-C(12)-C(7)	121.77(19)
O(2)-Li(2)-O(10)	96.28(14)	C(14)-C(13)-C(18)	117.15(15)
O(3)#1-Li(2)-O(10)	105.50(14)	C(14)-C(13)-Si(2)	122.67(13)
O(11)-Li(2)-O(10)	109.79(15)	C(18)-C(13)-Si(2)	120.16(13)
O(2)-Li(2)-Li(1)	78.47(11)	C(15)-C(14)-C(13)	121.51(17)
O(3)#1-Li(2)-Li(1)	87.91(12)	C(16)-C(15)-C(14)	120.15(18)
O(11)-Li(2)-Li(1)	148.31(15)	C(15)-C(16)-C(17)	119.79(17)
O(10)-Li(2)-Li(1)	38.78(8)	C(16)-C(17)-C(18)	120.11(18)
O(2)-Li(2)-Al(2)	26.78(6)	C(17)-C(18)-C(13)	121.28(17)
O(3)#1-Li(2)-Al(2)	101.43(12)	C(24)-C(19)-C(20)	117.23(17)
O(11)-Li(2)-Al(2)	133.99(13)	C(24)-C(19)-Si(2)	120.65(13)
O(10)-Li(2)-Al(2)	91.72(10)	C(20)-C(19)-Si(2)	122.12(14)
Li(1)-Li(2)-Al(2)	61.23(7)	C(19)-C(20)-C(21)	121.20(19)
Al(1)-O(1)-Al(2)	128.94(7)		

C(22)-C(21)-C(20)	120.10(19)	C(35)-C(36)-C(31)	121.59(16)
C(23)-C(22)-C(21)	119.05(19)	C(42)-C(37)-C(38)	117.56(16)
C(22)-C(23)-C(24)	120.41(19)	C(42)-C(37)-Si(4)	120.00(13)
C(23)-C(24)-C(19)	121.80(18)	C(38)-C(37)-Si(4)	122.44(13)
C(26)-C(25)-C(30)	117.69(16)	C(39)-C(38)-C(37)	120.90(18)
C(26)-C(25)-Si(3)	124.55(13)	C(40)-C(39)-C(38)	120.20(19)
C(30)-C(25)-Si(3)	117.76(13)	C(41)-C(40)-C(39)	119.98(18)
C(27)-C(26)-C(25)	120.78(17)	C(40)-C(41)-C(42)	119.74(19)
C(28)-C(27)-C(26)	120.28(17)	C(41)-C(42)-C(37)	121.61(18)
C(27)-C(28)-C(29)	120.04(18)	C(44)-C(43)-C(48)	117.26(15)
C(30)-C(29)-C(28)	119.43(18)	C(44)-C(43)-Si(4)	123.32(13)
C(29)-C(30)-C(25)	121.78(17)	C(48)-C(43)-Si(4)	119.07(12)
C(36)-C(31)-C(32)	117.42(15)	C(45)-C(44)-C(43)	121.04(17)
C(36)-C(31)-Si(3)	120.39(13)	C(46)-C(45)-C(44)	120.38(17)
C(32)-C(31)-Si(3)	122.17(13)	C(47)-C(46)-C(45)	119.94(17)
C(33)-C(32)-C(31)	120.81(16)	C(46)-C(47)-C(48)	119.56(19)
C(34)-C(33)-C(32)	120.46(17)	C(47)-C(48)-C(43)	121.76(17)
C(35)-C(34)-C(33)	119.87(16)	O(10)-C(49)-C(50)	105.12(14)
C(34)-C(35)-C(36)	119.82(17)	C(49)-C(50)-C(51)	102.03(15)
		C(52)-C(51)-C(50)	103.10(15)
		O(10)-C(52)-C(51)	106.44(14)
		O(11)-C(53)-C(54)	112.25(16)
		O(11)-C(55)-C(56)	112.87(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2448. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	11(1)	11(1)	14(1)	0(1)	2(1)	-1(1)
Al(2)	11(1)	10(1)	13(1)	-1(1)	2(1)	0(1)
Si(1)	13(1)	16(1)	15(1)	2(1)	2(1)	-2(1)
Si(2)	12(1)	14(1)	15(1)	-1(1)	2(1)	-1(1)
Si(3)	12(1)	12(1)	14(1)	-2(1)	2(1)	0(1)
Si(4)	12(1)	12(1)	15(1)	-2(1)	2(1)	0(1)
Li(1)	15(1)	15(1)	28(2)	3(1)	3(1)	0(1)
Li(2)	17(1)	19(2)	20(1)	1(1)	3(1)	2(1)
O(1)	12(1)	12(1)	14(1)	0(1)	2(1)	-1(1)
O(2)	14(1)	15(1)	21(1)	2(1)	5(1)	3(1)
O(3)	14(1)	21(1)	18(1)	-1(1)	1(1)	3(1)
O(4)	15(1)	21(1)	18(1)	4(1)	3(1)	-3(1)
O(5)	14(1)	28(1)	16(1)	2(1)	2(1)	-3(1)
O(6)	15(1)	15(1)	18(1)	0(1)	4(1)	-2(1)
O(7)	13(1)	13(1)	15(1)	-2(1)	3(1)	0(1)
O(8)	16(1)	15(1)	18(1)	-4(1)	5(1)	-2(1)
O(9)	17(1)	12(1)	20(1)	-3(1)	-1(1)	0(1)
O(10)	17(1)	13(1)	19(1)	1(1)	6(1)	1(1)
O(11)	20(1)	29(1)	23(1)	5(1)	3(1)	10(1)
C(1)	13(1)	20(1)	17(1)	1(1)	1(1)	-4(1)
C(2)	17(1)	22(1)	20(1)	2(1)	2(1)	-1(1)
C(3)	25(1)	36(1)	17(1)	3(1)	1(1)	1(1)
C(4)	30(1)	41(1)	21(1)	-11(1)	4(1)	-1(1)
C(5)	30(1)	27(1)	33(1)	-9(1)	5(1)	3(1)
C(6)	23(1)	21(1)	24(1)	2(1)	1(1)	0(1)
C(7)	24(1)	18(1)	16(1)	1(1)	1(1)	-1(1)
C(8)	25(1)	24(1)	41(1)	3(1)	1(1)	-4(1)
C(9)	39(1)	20(1)	46(1)	2(1)	-4(1)	-8(1)
C(10)	54(1)	20(1)	27(1)	-2(1)	1(1)	5(1)
C(11)	49(1)	27(1)	31(1)	3(1)	18(1)	11(1)
C(12)	35(1)	24(1)	23(1)	4(1)	12(1)	3(1)
C(13)	13(1)	14(1)	19(1)	0(1)	3(1)	0(1)
C(14)	23(1)	27(1)	20(1)	2(1)	3(1)	-6(1)
C(15)	26(1)	27(1)	31(1)	9(1)	5(1)	-8(1)
C(16)	21(1)	18(1)	35(1)	0(1)	0(1)	-7(1)
C(17)	24(1)	25(1)	25(1)	-4(1)	2(1)	-6(1)
C(18)	21(1)	23(1)	20(1)	0(1)	5(1)	-5(1)
C(19)	16(1)	20(1)	20(1)	-3(1)	4(1)	1(1)
C(20)	25(1)	28(1)	41(1)	-6(1)	1(1)	2(1)
C(21)	27(1)	39(1)	47(1)	-10(1)	-2(1)	10(1)
C(22)	35(1)	23(1)	43(1)	-7(1)	5(1)	10(1)
C(23)	38(1)	21(1)	41(1)	-8(1)	4(1)	0(1)
C(24)	23(1)	26(1)	36(1)	-4(1)	2(1)	1(1)
C(25)	14(1)	13(1)	19(1)	-1(1)	-2(1)	0(1)
C(26)	21(1)	19(1)	20(1)	-4(1)	0(1)	2(1)
C(27)	31(1)	16(1)	31(1)	-6(1)	0(1)	6(1)
C(28)	35(1)	15(1)	31(1)	3(1)	-2(1)	3(1)
C(29)	32(1)	20(1)	25(1)	3(1)	5(1)	0(1)
C(30)	24(1)	15(1)	24(1)	-1(1)	5(1)	1(1)
C(31)	14(1)	18(1)	13(1)	0(1)	3(1)	0(1)
C(32)	18(1)	19(1)	23(1)	-1(1)	0(1)	-1(1)

C(33)	21(1)	24(1)	31(1)	1(1)	-2(1)	6(1)
C(34)	15(1)	32(1)	27(1)	2(1)	-2(1)	1(1)
C(35)	19(1)	25(1)	25(1)	0(1)	1(1)	-6(1)
C(36)	19(1)	17(1)	21(1)	0(1)	3(1)	-2(1)
C(37)	19(1)	13(1)	17(1)	-4(1)	1(1)	3(1)
C(38)	20(1)	22(1)	25(1)	-1(1)	0(1)	3(1)
C(39)	28(1)	30(1)	34(1)	-3(1)	-8(1)	9(1)
C(40)	50(1)	24(1)	25(1)	3(1)	-8(1)	12(1)
C(41)	48(1)	22(1)	25(1)	5(1)	5(1)	0(1)
C(42)	27(1)	21(1)	22(1)	0(1)	3(1)	0(1)
C(43)	15(1)	15(1)	16(1)	1(1)	4(1)	2(1)
C(44)	16(1)	27(1)	18(1)	-2(1)	4(1)	0(1)
C(45)	17(1)	42(1)	25(1)	4(1)	6(1)	10(1)
C(46)	32(1)	24(1)	36(1)	7(1)	18(1)	14(1)
C(47)	35(1)	16(1)	47(1)	-6(1)	21(1)	-1(1)
C(48)	18(1)	21(1)	37(1)	-7(1)	9(1)	-1(1)
C(49)	20(1)	19(1)	19(1)	-1(1)	6(1)	4(1)
C(50)	39(1)	21(1)	31(1)	-7(1)	11(1)	-1(1)
C(51)	37(1)	15(1)	35(1)	3(1)	8(1)	2(1)
C(52)	25(1)	15(1)	24(1)	3(1)	8(1)	-3(1)
C(53)	26(1)	28(1)	27(1)	10(1)	3(1)	7(1)
C(54)	30(1)	40(1)	26(1)	1(1)	-1(1)	12(1)
C(55)	23(1)	46(1)	29(1)	11(1)	7(1)	14(1)
C(56)	47(1)	59(2)	44(1)	3(1)	13(1)	32(1)

8.3. Compound 4a

Table 1. Crystal data and structure refinement for sh2228.

Identification code	sh2228	
Empirical formula	$C_{128}\ H_{156}\ Al_4\ Li_4\ O_{26}\ Si_8$	
Formula weight	2470.93	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.020(3) Å	α= 99.056(8)°.
	b = 15.044(2) Å	β= 107.354(6)°.
	c = 16.263(3) Å	γ = 105.404(8)°.
Volume	3267.8(10) $Å^3$	
Z	1	
Density (calculated)	1.256 Mg/m^3	
Absorption coefficient	0.178 mm^{-1}	
F(000)	1308	
Crystal size	0.3 x 0.45 x 0.5 mm^3	
Theta range for data collection	1.36 to 26.45°.	
Index ranges	-18<=h<=18, -18<=k<=18, -20<=l<=19	
Reflections collected	64590	
Independent reflections	13321 [R(int) = 0.0443]	
Completeness to theta = 26.45°	98.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13321 / 0 / 770	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1644	
R indices (all data)	R1 = 0.0736, wR2 = 0.1738	
Largest diff. peak and hole	0.714 and -0.566 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2228. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	4245(1)	-961(1)	8233(1)	15(1)
Al(2)	3380(1)	392(1)	9176(1)	16(1)
Li(1)	4628(4)	-982(4)	9985(3)	21(1)
Li(2)	6647(4)	264(4)	9001(4)	26(1)
Si(1)	2718(1)	-879(1)	6370(1)	18(1)
Si(2)	1530(1)	-202(1)	7362(1)	19(1)
Si(3)	4193(1)	2643(1)	9907(1)	18(1)
Si(4)	5822(1)	3030(1)	11687(1)	17(1)
O(1)	5439(2)	-616(2)	8181(1)	23(1)
O(2)	4244(1)	-165(1)	9124(1)	16(1)
O(3)	2776(2)	-76(2)	9868(2)	23(1)
O(4)	3354(2)	-1103(2)	7234(1)	22(1)
O(5)	1776(2)	-624(2)	6503(1)	22(1)
O(6)	2511(2)	356(2)	8200(1)	24(1)
O(7)	4170(2)	1555(1)	9714(1)	19(1)
O(8)	5094(2)	3250(1)	10839(1)	19(1)
O(9)	5966(2)	2022(1)	11422(1)	20(1)
O(10)	3710(2)	-1453(2)	10626(1)	23(1)
C(1)	2226(2)	-1970(2)	5432(2)	20(1)
C(2)	1498(2)	-2770(2)	5425(2)	30(1)
C(3)	1184(3)	-3615(3)	4780(2)	39(1)
C(4)	1579(3)	-3678(3)	4123(2)	40(1)
C(5)	2287(3)	-2897(3)	4107(2)	36(1)
C(6)	2607(2)	-2049(2)	4754(2)	28(1)
C(7)	3461(3)	151(2)	6090(2)	29(1)
C(8)	3059(3)	847(3)	5815(2)	41(1)
C(9)	3604(4)	1629(3)	5629(3)	56(1)
C(10)	4556(4)	1739(3)	5724(3)	64(2)
C(11)	4977(3)	1071(4)	5980(3)	68(2)
C(12)	4422(3)	263(4)	6158(3)	49(1)
C(13)	750(3)	-1239(3)	7606(2)	33(1)
C(14)	-221(4)	-1371(5)	7489(5)	98(3)
C(15)	-797(5)	-2161(7)	7646(8)	152(5)
C(16)	-405(4)	-2837(5)	7922(6)	107(3)
C(17)	547(3)	-2711(3)	8063(3)	52(1)
C(18)	1123(3)	-1920(2)	7911(2)	35(1)
C(19)	807(2)	596(2)	7050(2)	24(1)
C(20)	891(2)	1389(2)	7668(2)	28(1)
C(21)	312(2)	1955(2)	7446(2)	32(1)
C(22)	-359(3)	1739(3)	6601(3)	42(1)
C(23)	-454(4)	957(3)	5977(3)	60(1)
C(24)	115(3)	391(3)	6196(2)	44(1)
C(25)	4421(2)	3248(2)	9041(2)	22(1)
C(26)	3811(3)	2857(2)	8147(2)	31(1)
C(27)	3935(3)	3335(3)	7506(2)	40(1)
C(28)	4678(3)	4208(3)	7746(2)	39(1)
C(29)	5288(3)	4600(2)	8620(2)	32(1)
C(30)	5157(2)	4125(2)	9262(2)	24(1)
C(31)	3003(2)	2726(2)	9982(2)	24(1)
C(32)	2655(3)	3440(2)	9697(2)	30(1)

C(33)	1781(3)	3524(3)	9746(3)	40(1)
C(34)	1238(3)	2908(3)	10091(3)	50(1)
C(35)	1564(3)	2196(3)	10381(3)	49(1)
C(36)	2437(3)	2110(2)	10325(3)	35(1)
C(37)	5245(2)	3012(2)	12557(2)	21(1)
C(38)	4326(2)	3110(2)	12413(2)	29(1)
C(39)	3855(3)	2986(3)	13020(3)	39(1)
C(40)	4303(3)	2762(3)	13787(3)	45(1)
C(41)	5231(4)	2684(3)	13958(3)	50(1)
C(42)	5699(3)	2813(3)	13352(2)	37(1)
C(43)	7026(2)	4002(2)	12096(2)	23(1)
C(44)	7124(2)	4893(2)	11933(2)	28(1)
C(45)	8021(3)	5631(3)	12296(3)	38(1)
C(46)	8837(3)	5484(3)	12823(3)	43(1)
C(47)	8767(3)	4602(3)	12991(3)	49(1)
C(48)	7869(3)	3869(2)	12627(3)	38(1)
C(49)	2814(2)	-2231(2)	10049(2)	31(1)
C(50)	2924(3)	-3101(3)	10360(3)	41(1)
C(51)	3470(3)	-2687(3)	11358(3)	43(1)
C(52)	4186(3)	-1751(2)	11409(2)	30(1)
O(13)	7587(2)	570(2)	8358(2)	43(1)
C(61)	7255(4)	644(4)	7470(3)	60(1)
C(62)	7242(7)	-115(5)	6793(5)	119(3)
C(63)	8629(4)	835(7)	8694(6)	118(3)
C(64)	9058(6)	407(9)	9179(9)	196(7)
O(11)	1903(3)	5494(4)	2214(2)	88(2)
C(53)	2607(3)	5071(3)	2318(4)	54(1)
C(54)	3330(6)	5337(7)	3195(4)	137(4)
C(55)	1205(3)	5316(3)	1410(3)	53(1)
C(56)	564(6)	5881(7)	1358(4)	122(3)
O(12)	7516(3)	6536(2)	4823(2)	66(1)
C(57)	7026(4)	5567(4)	4545(4)	63(1)
C(58)	6023(4)	5371(4)	4572(3)	61(1)
C(59)	8559(5)	6758(5)	4930(6)	92(2)
C(60)	8932(6)	7761(6)	5003(8)	147(4)

Table 3. Bond lengths [Å] and angles [°] for sh2228.

Al(1)-O(4)	1.709(2)	Li(1)-Li(2)#1	3.159(8)
Al(1)-O(2)	1.730(2)	Li(2)-O(1)	1.884(6)
Al(1)-O(9)#1	1.755(2)	Li(2)-O(3)#1	1.886(6)
Al(1)-O(1)	1.761(2)	Li(2)-O(13)	1.997(6)
Al(1)-Li(1)	2.740(5)	Li(2)-O(10)#1	2.053(6)
Al(2)-O(6)	1.710(2)	Li(2)-Li(1)#1	3.159(8)
Al(2)-O(2)	1.736(2)	Si(1)-O(4)	1.586(2)
Al(2)-O(7)	1.741(2)	Si(1)-O(5)	1.623(2)
Al(2)-O(3)	1.761(2)	Si(1)-C(1)	1.861(3)
Al(2)-Li(1)#1	2.716(5)	Si(1)-C(7)	1.862(3)
Li(1)-O(10)	2.017(5)	Si(2)-O(6)	1.586(2)
Li(1)-O(2)#1	2.035(5)	Si(2)-O(5)	1.626(2)
Li(1)-O(2)	2.059(5)	Si(2)-C(19)	1.853(3)
Li(1)-O(7)#1	2.162(5)	Si(2)-C(13)	1.863(4)
Li(1)-O(9)#1	2.321(5)	Si(3)-O(7)	1.606(2)
Li(1)-Al(2)#1	2.716(5)	Si(3)-O(8)	1.627(2)
Li(1)-Li(1)#1	2.854(10)	Si(3)-C(25)	1.859(3)

Si(3)-C(31)	1.863(3)	C(43)-C(44)	1.386(4)
Si(4)-O(9)	1.600(2)	C(43)-C(48)	1.387(5)
Si(4)-O(8)	1.625(2)	C(44)-C(45)	1.386(5)
Si(4)-C(43)	1.850(3)	C(45)-C(46)	1.365(5)
Si(4)-C(37)	1.866(3)	C(46)-C(47)	1.379(5)
O(2)-Li(1)#1	2.035(5)	C(47)-C(48)	1.383(5)
O(3)-Li(2)#1	1.886(6)	C(49)-C(50)	1.507(5)
O(7)-Li(1)#1	2.162(5)	C(50)-C(51)	1.521(6)
O(9)-Al(1)#1	1.755(2)	C(51)-C(52)	1.501(5)
O(9)-Li(1)#1	2.321(5)	O(13)-C(63)	1.412(6)
O(10)-C(49)	1.458(4)	O(13)-C(61)	1.413(5)
O(10)-C(52)	1.462(4)	C(61)-C(62)	1.448(8)
O(10)-Li(2)#1	2.053(6)	C(63)-C(64)	1.236(10)
C(1)-C(6)	1.390(4)	O(11)-C(55)	1.344(5)
C(1)-C(2)	1.390(5)	O(11)-C(53)	1.355(5)
C(2)-C(3)	1.380(5)	C(53)-C(54)	1.428(8)
C(3)-C(4)	1.370(6)	C(55)-C(56)	1.437(7)
C(4)-C(5)	1.368(6)	O(12)-C(57)	1.377(6)
C(5)-C(6)	1.384(5)	O(12)-C(59)	1.463(7)
C(7)-C(12)	1.376(5)	C(57)-C(58)	1.473(7)
C(7)-C(8)	1.408(5)	C(59)-C(60)	1.436(10)
C(8)-C(9)	1.375(5)		
C(9)-C(10)	1.353(8)	O(4)-Al(1)-O(2)	114.98(10)
C(10)-C(11)	1.376(8)	O(4)-Al(1)-O(9)#1	110.52(11)
C(11)-C(12)	1.404(6)	O(2)-Al(1)-O(9)#1	101.41(10)
C(13)-C(14)	1.367(6)	O(4)-Al(1)-O(1)	111.90(11)
C(13)-C(18)	1.382(5)	O(2)-Al(1)-O(1)	108.24(10)
C(14)-C(15)	1.381(8)	O(9)#1-Al(1)-O(1)	109.21(10)
C(15)-C(16)	1.372(10)	O(4)-Al(1)-Li(1)	145.68(13)
C(16)-C(17)	1.334(7)	O(2)-Al(1)-Li(1)	48.67(12)
C(17)-C(18)	1.377(5)	O(9)#1-Al(1)-Li(1)	57.28(12)
C(19)-C(20)	1.384(5)	O(1)-Al(1)-Li(1)	102.36(13)
C(19)-C(24)	1.392(4)	O(6)-Al(2)-O(2)	118.42(10)
C(20)-C(21)	1.384(4)	O(6)-Al(2)-O(7)	110.89(11)
C(21)-C(22)	1.367(5)	O(2)-Al(2)-O(7)	99.69(10)
C(22)-C(23)	1.373(6)	O(6)-Al(2)-O(3)	109.01(12)
C(23)-C(24)	1.371(5)	O(2)-Al(2)-O(3)	108.29(10)
C(25)-C(30)	1.389(4)	O(7)-Al(2)-O(3)	110.11(11)
C(25)-C(26)	1.396(4)	O(6)-Al(2)-Li(1)#1	140.55(14)
C(26)-C(27)	1.385(5)	O(2)-Al(2)-Li(1)#1	48.51(13)
C(27)-C(28)	1.387(6)	O(7)-Al(2)-Li(1)#1	52.70(13)
C(28)-C(29)	1.371(5)	O(3)-Al(2)-Li(1)#1	110.41(13)
C(29)-C(30)	1.386(4)	O(10)-Li(1)-O(2)#1	106.3(2)
C(31)-C(36)	1.386(5)	O(10)-Li(1)-O(2)	117.9(3)
C(31)-C(32)	1.397(4)	O(2)#1-Li(1)-O(2)	91.6(2)
C(32)-C(33)	1.375(5)	O(10)-Li(1)-O(7)#1	110.2(2)
C(33)-C(34)	1.368(6)	O(2)#1-Li(1)-O(7)#1	78.50(18)
C(34)-C(35)	1.382(6)	O(2)-Li(1)-O(7)#1	131.6(3)
C(35)-C(36)	1.379(5)	O(10)-Li(1)-O(9)#1	108.0(2)
C(37)-C(38)	1.382(4)	O(2)#1-Li(1)-O(9)#1	145.5(3)
C(37)-C(42)	1.389(4)	O(2)-Li(1)-O(9)#1	75.74(17)
C(38)-C(39)	1.383(5)	O(7)#1-Li(1)-O(9)#1	86.2(2)
C(39)-C(40)	1.370(6)	O(10)-Li(1)-Al(2)#1	120.8(2)
C(40)-C(41)	1.378(6)	O(2)#1-Li(1)-Al(2)#1	39.71(10)
C(41)-C(42)	1.380(5)	O(2)-Li(1)-Al(2)#1	110.7(2)

O(7)#1-Li(1)-Al(2)#1	39.83(10)	O(8)-Si(4)-C(37)	107.67(13)
O(9)#1-Li(1)-Al(2)#1	115.0(2)	C(43)-Si(4)-C(37)	110.84(14)
O(10)-Li(1)-Al(1)	130.8(2)	Al(1)-O(1)-Li(2)	131.3(2)
O(2)#1-Li(1)-Al(1)	114.9(2)	Al(1)-O(2)-Al(2)	129.15(11)
O(2)-Li(1)-Al(1)	39.12(10)	Al(1)-O(2)-Li(1)#1	129.23(19)
O(7)#1-Li(1)-Al(1)	103.5(2)	Al(2)-O(2)-Li(1)#1	91.78(17)
O(9)#1-Li(1)-Al(1)	39.50(9)	Al(1)-O(2)-Li(1)	92.22(17)
Al(2)#1-Li(1)-Al(1)	108.05(17)	Al(2)-O(2)-Li(1)	121.27(18)
O(10)-Li(1)-Li(1)#1	122.5(3)	Li(1)#1-O(2)-Li(1)	88.4(2)
O(2)#1-Li(1)-Li(1)#1	46.15(15)	Al(2)-O(3)-Li(2)#1	127.9(2)
O(2)-Li(1)-Li(1)#1	45.47(15)	Si(1)-O(4)-Al(1)	161.44(15)
O(7)#1-Li(1)-Li(1)#1	109.7(3)	Si(1)-O(5)-Si(2)	134.48(13)
O(9)#1-Li(1)-Li(1)#1	114.2(3)	Si(2)-O(6)-Al(2)	150.86(15)
Al(2)#1-Li(1)-Li(1)#1	72.91(19)	Si(3)-O(7)-Al(2)	142.40(14)
Al(1)-Li(1)-Li(1)#1	74.94(19)	Si(3)-O(7)-Li(1)#1	129.94(18)
O(10)-Li(1)-Li(2)#1	39.49(15)	Al(2)-O(7)-Li(1)#1	87.47(16)
O(2)#1-Li(1)-Li(2)#1	83.8(2)	Si(4)-O(8)-Si(3)	137.57(13)
O(2)-Li(1)-Li(2)#1	87.2(2)	Si(4)-O(9)-Al(1)#1	136.07(13)
O(7)#1-Li(1)-Li(2)#1	137.1(2)	Si(4)-O(9)-Li(1)#1	127.79(16)
O(9)#1-Li(1)-Li(2)#1	126.5(2)	Al(1)#1-O(9)-Li(1)#1	83.22(15)
Al(2)#1-Li(1)-Li(2)#1	118.43(19)	C(49)-O(10)-C(52)	108.9(2)
Al(1)-Li(1)-Li(2)#1	119.39(19)	C(49)-O(10)-Li(1)	112.9(2)
Li(1)#1-Li(1)-Li(2)#1	83.5(2)	C(52)-O(10)-Li(1)	112.9(2)
O(1)-Li(2)-O(3)#1	120.8(3)	C(49)-O(10)-Li(2)#1	109.5(2)
O(1)-Li(2)-O(13)	108.3(3)	C(52)-O(10)-Li(2)#1	110.7(2)
O(3)#1-Li(2)-O(13)	113.7(3)	Li(1)-O(10)-Li(2)#1	101.8(2)
O(1)-Li(2)-O(10)#1	103.6(3)	C(6)-C(1)-C(2)	117.4(3)
O(3)#1-Li(2)-O(10)#1	99.8(3)	C(6)-C(1)-Si(1)	122.5(2)
O(13)-Li(2)-O(10)#1	109.1(3)	C(2)-C(1)-Si(1)	120.0(2)
O(1)-Li(2)-Li(1)#1	86.2(2)	C(3)-C(2)-C(1)	121.2(3)
O(3)#1-Li(2)-Li(1)#1	79.7(2)	C(4)-C(3)-C(2)	120.3(4)
O(13)-Li(2)-Li(1)#1	147.8(3)	C(5)-C(4)-C(3)	119.8(3)
O(10)#1-Li(2)-Li(1)#1	38.67(14)	C(4)-C(5)-C(6)	120.1(3)
O(4)-Si(1)-O(5)	111.50(11)	C(5)-C(6)-C(1)	121.2(3)
O(4)-Si(1)-C(1)	108.17(12)	C(12)-C(7)-C(8)	118.1(3)
O(5)-Si(1)-C(1)	107.41(12)	C(12)-C(7)-Si(1)	121.1(3)
O(4)-Si(1)-C(7)	111.71(14)	C(8)-C(7)-Si(1)	120.8(3)
O(5)-Si(1)-C(7)	107.38(14)	C(9)-C(8)-C(7)	121.8(4)
C(1)-Si(1)-C(7)	110.60(14)	C(10)-C(9)-C(8)	119.1(5)
O(6)-Si(2)-O(5)	111.41(12)	C(9)-C(10)-C(11)	121.1(4)
O(6)-Si(2)-C(19)	110.69(13)	C(10)-C(11)-C(12)	120.1(5)
O(5)-Si(2)-C(19)	108.24(13)	C(7)-C(12)-C(11)	119.7(5)
O(6)-Si(2)-C(13)	110.55(14)	C(14)-C(13)-C(18)	116.5(4)
O(5)-Si(2)-C(13)	106.84(15)	C(14)-C(13)-Si(2)	122.0(3)
C(19)-Si(2)-C(13)	108.99(15)	C(18)-C(13)-Si(2)	121.5(3)
O(7)-Si(3)-O(8)	108.79(11)	C(13)-C(14)-C(15)	121.2(5)
O(7)-Si(3)-C(25)	113.77(12)	C(16)-C(15)-C(14)	120.4(5)
O(8)-Si(3)-C(25)	106.34(13)	C(17)-C(16)-C(15)	119.4(5)
O(7)-Si(3)-C(31)	111.28(13)	C(16)-C(17)-C(18)	120.1(5)
O(8)-Si(3)-C(31)	109.65(12)	C(17)-C(18)-C(13)	122.3(4)
C(25)-Si(3)-C(31)	106.85(14)	C(20)-C(19)-C(24)	117.2(3)
O(9)-Si(4)-O(8)	111.71(11)	C(20)-C(19)-Si(2)	121.5(2)
O(9)-Si(4)-C(43)	110.16(13)	C(24)-C(19)-Si(2)	121.2(3)
O(8)-Si(4)-C(43)	107.48(12)	C(21)-C(20)-C(19)	121.5(3)
O(9)-Si(4)-C(37)	108.97(12)	C(22)-C(21)-C(20)	120.1(3)

C(21)-C(22)-C(23)	119.5(3)	C(39)-C(40)-C(41)	119.6(4)
C(24)-C(23)-C(22)	120.5(3)	C(40)-C(41)-C(42)	120.3(4)
C(23)-C(24)-C(19)	121.3(3)	C(41)-C(42)-C(37)	121.0(3)
C(30)-C(25)-C(26)	117.8(3)	C(44)-C(43)-C(48)	117.3(3)
C(30)-C(25)-Si(3)	121.6(2)	C(44)-C(43)-Si(4)	122.6(2)
C(26)-C(25)-Si(3)	120.4(2)	C(48)-C(43)-Si(4)	120.0(2)
C(27)-C(26)-C(25)	120.7(3)	C(45)-C(44)-C(43)	121.7(3)
C(26)-C(27)-C(28)	120.2(3)	C(46)-C(45)-C(44)	119.8(3)
C(29)-C(28)-C(27)	119.9(3)	C(45)-C(46)-C(47)	119.9(3)
C(28)-C(29)-C(30)	120.0(3)	C(46)-C(47)-C(48)	119.9(3)
C(29)-C(30)-C(25)	121.5(3)	C(47)-C(48)-C(43)	121.3(3)
C(36)-C(31)-C(32)	117.3(3)	O(10)-C(49)-C(50)	105.0(3)
C(36)-C(31)-Si(3)	122.7(2)	C(49)-C(50)-C(51)	102.1(3)
C(32)-C(31)-Si(3)	120.0(3)	C(52)-C(51)-C(50)	102.6(3)
C(33)-C(32)-C(31)	121.4(3)	O(10)-C(52)-C(51)	105.9(3)
C(34)-C(33)-C(32)	120.1(3)	C(63)-O(13)-C(61)	110.0(5)
C(33)-C(34)-C(35)	119.9(4)	C(63)-O(13)-Li(2)	128.7(4)
C(36)-C(35)-C(34)	119.9(4)	C(61)-O(13)-Li(2)	121.0(3)
C(35)-C(36)-C(31)	121.4(3)	O(13)-C(61)-C(62)	116.4(5)
C(38)-C(37)-C(42)	117.5(3)	C(64)-C(63)-O(13)	121.7(8)
C(38)-C(37)-Si(4)	122.1(2)	C(55)-O(11)-C(53)	120.4(4)
C(42)-C(37)-Si(4)	120.2(2)	O(11)-C(53)-C(54)	115.5(4)
C(37)-C(38)-C(39)	121.7(3)	O(11)-C(55)-C(56)	115.5(5)
C(40)-C(39)-C(38)	119.8(4)	C(57)-O(12)-C(59)	111.3(4)
		O(12)-C(57)-C(58)	109.4(4)
		C(60)-C(59)-O(12)	106.4(6)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2228. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	16(1)	15(1)	13(1)	3(1)	1(1)	7(1)
Al(2)	17(1)	14(1)	13(1)	1(1)	-1(1)	8(1)
Li(1)	18(2)	22(2)	19(2)	7(2)	1(2)	5(2)
Li(2)	21(2)	28(3)	26(3)	8(2)	5(2)	7(2)
Si(1)	18(1)	21(1)	12(1)	4(1)	2(1)	8(1)
Si(2)	17(1)	23(1)	15(1)	4(1)	1(1)	11(1)
Si(3)	23(1)	14(1)	14(1)	2(1)	2(1)	8(1)
Si(4)	23(1)	14(1)	14(1)	3(1)	3(1)	8(1)
O(1)	20(1)	24(1)	24(1)	4(1)	6(1)	7(1)
O(2)	18(1)	14(1)	13(1)	1(1)	-1(1)	7(1)
O(3)	17(1)	24(1)	23(1)	5(1)	3(1)	6(1)
O(4)	23(1)	27(1)	14(1)	4(1)	1(1)	12(1)
O(5)	21(1)	27(1)	13(1)	2(1)	0(1)	12(1)
O(6)	25(1)	26(1)	17(1)	1(1)	-3(1)	15(1)
O(7)	23(1)	14(1)	17(1)	2(1)	3(1)	7(1)
O(8)	25(1)	13(1)	16(1)	2(1)	3(1)	8(1)
O(9)	26(1)	17(1)	19(1)	6(1)	8(1)	11(1)
O(10)	24(1)	21(1)	23(1)	7(1)	5(1)	7(1)
C(1)	19(1)	24(1)	13(1)	2(1)	-2(1)	12(1)
C(2)	30(2)	31(2)	22(2)	2(1)	4(1)	7(1)
C(3)	38(2)	31(2)	31(2)	-1(2)	-2(2)	5(2)
C(4)	42(2)	37(2)	28(2)	-8(2)	-4(2)	22(2)
C(5)	40(2)	45(2)	22(2)	-2(2)	5(2)	25(2)
C(6)	27(2)	35(2)	22(2)	5(1)	6(1)	15(1)
C(7)	36(2)	29(2)	16(1)	4(1)	8(1)	3(1)
C(8)	67(3)	28(2)	34(2)	10(2)	27(2)	14(2)
C(9)	92(4)	33(2)	39(2)	11(2)	31(2)	8(2)
C(10)	84(4)	52(3)	28(2)	12(2)	13(2)	-16(3)
C(11)	36(2)	109(4)	39(2)	30(3)	9(2)	-10(3)
C(12)	31(2)	75(3)	33(2)	27(2)	9(2)	4(2)
C(13)	27(2)	41(2)	36(2)	17(2)	14(2)	12(2)
C(14)	43(3)	120(5)	180(7)	107(5)	60(4)	41(3)
C(15)	44(3)	192(9)	280(12)	180(10)	77(5)	43(4)
C(16)	55(3)	120(6)	165(7)	104(6)	50(4)	11(3)
C(17)	52(3)	45(2)	52(3)	25(2)	12(2)	3(2)
C(18)	31(2)	30(2)	38(2)	12(2)	6(2)	5(1)
C(19)	21(2)	28(2)	21(2)	5(1)	0(1)	14(1)
C(20)	26(2)	30(2)	24(2)	4(1)	0(1)	13(1)
C(21)	29(2)	26(2)	37(2)	3(1)	5(2)	14(1)
C(22)	35(2)	36(2)	46(2)	4(2)	-7(2)	24(2)
C(23)	63(3)	55(3)	37(2)	-8(2)	-25(2)	41(2)
C(24)	49(2)	46(2)	26(2)	-4(2)	-9(2)	33(2)
C(25)	33(2)	19(1)	16(1)	5(1)	5(1)	15(1)
C(26)	45(2)	23(2)	19(2)	2(1)	4(1)	13(1)
C(27)	61(2)	38(2)	17(2)	7(1)	6(2)	22(2)
C(28)	64(3)	36(2)	26(2)	17(2)	19(2)	25(2)
C(29)	48(2)	24(2)	32(2)	11(1)	18(2)	17(2)
C(30)	33(2)	21(1)	20(1)	5(1)	8(1)	14(1)
C(31)	25(2)	22(1)	19(1)	-2(1)	2(1)	10(1)
C(32)	32(2)	29(2)	24(2)	2(1)	1(1)	17(1)
C(33)	38(2)	41(2)	40(2)	4(2)	4(2)	26(2)

C(34)	35(2)	52(2)	63(3)	2(2)	17(2)	25(2)
C(35)	44(2)	41(2)	71(3)	13(2)	31(2)	16(2)
C(36)	37(2)	29(2)	44(2)	9(2)	18(2)	18(2)
C(37)	30(2)	18(1)	18(1)	3(1)	9(1)	11(1)
C(38)	31(2)	34(2)	23(2)	6(1)	8(1)	13(1)
C(39)	33(2)	49(2)	37(2)	10(2)	15(2)	14(2)
C(40)	59(3)	53(2)	41(2)	21(2)	32(2)	25(2)
C(41)	77(3)	71(3)	35(2)	31(2)	32(2)	52(3)
C(42)	50(2)	51(2)	23(2)	14(2)	14(2)	35(2)
C(43)	26(2)	21(1)	21(2)	5(1)	5(1)	8(1)
C(44)	28(2)	24(2)	23(2)	6(1)	-1(1)	6(1)
C(45)	35(2)	25(2)	40(2)	12(2)	0(2)	2(1)
C(46)	28(2)	32(2)	47(2)	7(2)	-5(2)	-2(2)
C(47)	30(2)	37(2)	59(3)	12(2)	-12(2)	8(2)
C(48)	31(2)	23(2)	47(2)	9(2)	-4(2)	8(1)
C(49)	24(2)	24(2)	36(2)	4(1)	8(1)	2(1)
C(50)	48(2)	24(2)	51(2)	9(2)	22(2)	6(2)
C(51)	63(3)	35(2)	49(2)	24(2)	35(2)	21(2)
C(52)	41(2)	33(2)	27(2)	15(1)	15(2)	20(2)
O(13)	26(1)	60(2)	44(2)	18(1)	13(1)	14(1)
C(61)	68(3)	75(3)	45(3)	15(2)	35(2)	20(3)
C(62)	202(9)	79(5)	94(5)	9(4)	99(6)	29(5)
C(63)	41(3)	179(9)	132(7)	57(6)	18(4)	41(4)
C(64)	68(5)	244(13)	326(17)	207(14)	58(8)	69(7)
O(11)	101(3)	159(4)	34(2)	10(2)	16(2)	108(3)
C(53)	39(2)	48(2)	77(3)	16(2)	18(2)	20(2)
C(54)	142(7)	238(10)	61(4)	6(5)	6(4)	162(8)
C(55)	42(2)	57(3)	60(3)	21(2)	14(2)	18(2)
C(56)	125(6)	219(9)	58(4)	24(5)	17(4)	142(7)
O(12)	60(2)	58(2)	65(2)	14(2)	13(2)	5(2)
C(57)	72(3)	60(3)	62(3)	11(2)	33(3)	23(3)
C(58)	68(3)	52(3)	56(3)	8(2)	27(3)	6(2)
C(59)	79(4)	82(4)	132(6)	38(4)	54(4)	29(3)
C(60)	84(5)	104(6)	231(12)	38(7)	41(7)	18(5)

8.4. Compound 6

Table 1. Crystal data and structure refinement for sh2351.

Identification code	sh2351	
Empirical formula	$C_{72}\ H_{96}\ Al_2\ Li_4\ O_{13}\ Si_4$	
Formula weight	1363.57	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.1163(6) Å	α= 99.551(2)°.
	b = 13.5950(5) Å	β= 94.242(2)°.
	c = 22.6717(9) Å	γ = 93.741(2)°.
Volume	3963.4(3) $Å^3$	
Z	2	
Density (calculated)	1.143 Mg/m^3	
Absorption coefficient	0.152 mm^{-1}	
F(000)	1452	
Crystal size	0.25 x 0.3 x 0.55 mm^3	
Theta range for data collection	1.52 to 26.27°.	
Index ranges	-16<=h<=16, -16<=k<=16, -28<=l<=28	
Reflections collected	74333	
Independent reflections	15943 [R(int) = 0.0367]	
Completeness to theta = 26.27°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15943 / 0 / 897	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1283	
R indices (all data)	R1 = 0.0676, wR2 = 0.1426	
Largest diff. peak and hole	1.036 and -0.325 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2351. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	1946(1)	1835(1)	1853(1)	18(1)
Al(2)	1763(1)	3691(1)	2913(1)	17(1)
Si(1)	584(1)	4748(1)	1886(1)	22(1)
Si(2)	347(1)	2698(1)	954(1)	21(1)
Si(3)	4433(1)	1228(1)	3501(1)	21(1)
Si(4)	2497(1)	1087(1)	4179(1)	22(1)
O(1)	1820(1)	2429(1)	2582(1)	18(1)
O(2)	1215(1)	4417(1)	2439(1)	25(1)
O(3)	232(1)	3792(1)	1350(1)	25(1)
O(4)	1048(1)	2003(1)	1298(1)	23(1)
O(5)	3799(1)	1408(1)	2897(1)	20(1)
O(6)	3719(1)	1257(1)	4063(1)	29(1)
O(7)	1771(1)	1231(1)	3613(1)	21(1)
O(8)	3274(1)	2136(1)	1777(1)	22(1)
O(9)	2101(1)	592(1)	1979(1)	20(1)
O(10)	4716(1)	-111(1)	1958(1)	37(1)
O(11)	1051(1)	3539(1)	3517(1)	19(1)
O(12)	-460(1)	1290(1)	3172(1)	28(1)
O(13)	3100(1)	4007(1)	3060(1)	22(1)
Li(1)	3674(3)	845(3)	2065(2)	25(1)
Li(2)	3497(3)	2708(3)	2712(2)	25(1)
Li(3)	886(3)	2087(3)	3352(2)	26(1)
Li(4)	2320(3)	1183(3)	2891(2)	22(1)
C(1)	-622(2)	5335(2)	2102(1)	28(1)
C(2)	-1574(2)	4787(2)	2034(1)	40(1)
C(3)	-2462(3)	5232(3)	2202(2)	56(1)
C(4)	-2415(3)	6232(3)	2444(1)	57(1)
C(5)	-1484(3)	6792(3)	2520(1)	52(1)
C(6)	-598(2)	6342(2)	2350(1)	39(1)
C(7)	1400(2)	5663(2)	1556(1)	25(1)
C(8)	1000(2)	6110(2)	1083(1)	29(1)
C(9)	1625(2)	6690(2)	784(1)	34(1)
C(10)	2667(2)	6843(2)	959(1)	40(1)
C(11)	3075(2)	6434(2)	1436(1)	41(1)
C(12)	2442(2)	5850(2)	1730(1)	30(1)
C(13)	-981(2)	2080(2)	756(1)	26(1)
C(14)	-1186(2)	1040(2)	636(1)	31(1)
C(15)	-2168(2)	600(2)	453(1)	41(1)
C(16)	-2972(2)	1192(3)	389(1)	47(1)
C(17)	-2797(2)	2224(3)	504(1)	43(1)
C(18)	-1809(2)	2664(2)	684(1)	33(1)
C(19)	914(2)	2864(2)	236(1)	24(1)
C(20)	1002(2)	2030(2)	-202(1)	34(1)
C(21)	1435(2)	2120(2)	-734(1)	41(1)
C(22)	1783(2)	3051(3)	-842(1)	44(1)
C(23)	1700(2)	3884(2)	-417(1)	44(1)
C(24)	1271(2)	3793(2)	117(1)	34(1)
C(25)	5506(2)	2224(2)	3731(1)	30(1)
C(26)	6036(2)	2600(2)	3299(1)	38(1)
C(27)	6801(2)	3400(2)	3463(2)	51(1)

C(28)	7016(2)	3805(2)	4063(2)	47(1)
C(29)	6525(2)	3431(2)	4502(2)	49(1)
C(30)	5780(2)	2643(2)	4337(1)	40(1)
C(31)	4952(2)	-40(2)	3408(1)	22(1)
C(32)	5970(2)	-200(2)	3570(1)	30(1)
C(33)	6291(2)	-1157(2)	3567(1)	37(1)
C(34)	5601(2)	-1984(2)	3387(1)	37(1)
C(35)	4590(2)	-1856(2)	3215(1)	40(1)
C(36)	4272(2)	-899(2)	3234(1)	33(1)
C(37)	2199(2)	-228(2)	4332(1)	31(1)
C(38)	2475(2)	-522(2)	4879(1)	41(1)
C(39)	2231(3)	-1485(2)	4980(1)	49(1)
C(40)	1698(3)	-2189(2)	4527(1)	46(1)
C(41)	1417(2)	-1928(2)	3985(1)	43(1)
C(42)	1651(2)	-947(2)	3897(1)	35(1)
C(43)	2371(2)	1999(2)	4885(1)	23(1)
C(44)	3134(2)	2768(2)	5104(1)	27(1)
C(45)	3039(2)	3461(2)	5618(1)	29(1)
C(46)	2166(2)	3398(2)	5929(1)	31(1)
C(47)	1402(2)	2640(2)	5725(1)	30(1)
C(48)	1504(2)	1954(2)	5210(1)	27(1)
C(49)	1493(2)	-333(2)	1744(1)	23(1)
C(50)	1560(2)	-565(2)	1065(1)	30(1)
C(51)	389(2)	-214(2)	1891(1)	34(1)
C(52)	1940(2)	-1148(2)	2048(1)	29(1)
C(53)	5494(2)	-575(2)	1613(1)	32(1)
C(54)	5125(2)	-589(2)	960(1)	43(1)
C(55)	5594(3)	-1619(2)	1743(2)	59(1)
C(56)	6495(2)	62(3)	1789(1)	53(1)
C(57)	3783(2)	2583(2)	1334(1)	26(1)
C(58)	3549(2)	1910(2)	721(1)	40(1)
C(59)	4930(2)	2678(2)	1526(1)	37(1)
C(60)	3402(2)	3612(2)	1318(1)	35(1)
C(61)	3707(2)	4866(2)	3396(1)	23(1)
C(62)	4618(2)	5073(2)	3039(1)	31(1)
C(63)	3069(2)	5771(2)	3483(1)	28(1)
C(64)	4089(2)	4617(2)	4001(1)	30(1)
C(65)	532(2)	4099(2)	3979(1)	21(1)
C(66)	18(2)	4949(2)	3742(1)	29(1)
C(67)	1298(2)	4507(2)	4519(1)	26(1)
C(68)	-270(2)	3375(2)	4171(1)	28(1)
C(69)	-689(2)	670(2)	3614(1)	40(1)
C(70)	-972(3)	-398(2)	3358(2)	56(1)
C(71)	-1334(2)	1407(2)	2784(1)	34(1)
C(72)	-1080(2)	2205(2)	2425(1)	34(1)
C(73)	5446(6)	5623(7)	685(4)	67(2)
C(74)	5267(8)	5108(9)	346(5)	86(3)
C(75)	5546(14)	6216(14)	493(8)	96(5)
C(75B)	5787(7)	5466(7)	1126(4)	81(2)
C(74B)	5159(7)	4377(8)	218(5)	84(3)

Table 3. Bond lengths [Å] and angles [°] for sh2351.

Al(1)-O(4)	1.7143(16)	O(12)-C(69)	1.447(3)
Al(1)-O(1)	1.7385(15)	O(12)-Li(3)	1.989(4)
Al(1)-O(9)	1.7812(16)	O(13)-C(61)	1.440(3)
Al(1)-O(8)	1.7909(16)	O(13)-Li(2)	1.932(4)
Al(1)-Li(4)	2.672(4)	Li(1)-Li(4)	2.680(5)
Al(1)-Li(1)	2.763(4)	Li(1)-Li(2)	2.741(5)
Al(1)-Li(2)	2.769(4)	Li(2)-Li(4)	2.608(5)
Al(2)-O(2)	1.7254(16)	Li(3)-Li(4)	2.512(5)
Al(2)-O(11)	1.7459(15)	C(1)-C(6)	1.389(4)
Al(2)-O(1)	1.7644(15)	C(1)-C(2)	1.396(4)
Al(2)-O(13)	1.7709(16)	C(2)-C(3)	1.396(4)
Al(2)-Li(2)	2.742(4)	C(3)-C(4)	1.375(5)
Al(2)-Li(3)	2.762(4)	C(4)-C(5)	1.380(5)
Si(1)-O(2)	1.5946(16)	C(5)-C(6)	1.398(4)
Si(1)-O(3)	1.6407(16)	C(7)-C(12)	1.389(3)
Si(1)-C(7)	1.872(2)	C(7)-C(8)	1.404(3)
Si(1)-C(1)	1.877(3)	C(8)-C(9)	1.388(4)
Si(2)-O(4)	1.6115(16)	C(9)-C(10)	1.387(4)
Si(2)-O(3)	1.6267(16)	C(10)-C(11)	1.385(4)
Si(2)-C(13)	1.874(2)	C(11)-C(12)	1.392(4)
Si(2)-C(19)	1.878(2)	C(13)-C(14)	1.399(4)
Si(3)-O(5)	1.6112(16)	C(13)-C(18)	1.403(4)
Si(3)-O(6)	1.6334(17)	C(14)-C(15)	1.389(4)
Si(3)-C(25)	1.868(2)	C(15)-C(16)	1.382(5)
Si(3)-C(31)	1.880(2)	C(16)-C(17)	1.384(5)
Si(3)-Li(4)	2.996(4)	C(17)-C(18)	1.394(4)
Si(3)-Li(2)	3.153(4)	C(19)-C(24)	1.394(3)
Si(4)-O(7)	1.5858(15)	C(19)-C(20)	1.396(3)
Si(4)-O(6)	1.6507(17)	C(20)-C(21)	1.390(4)
Si(4)-C(43)	1.881(2)	C(21)-C(22)	1.383(4)
Si(4)-C(37)	1.899(3)	C(22)-C(23)	1.376(4)
Si(4)-Li(4)	2.937(4)	C(23)-C(24)	1.391(4)
O(1)-Li(4)	2.064(4)	C(25)-C(26)	1.387(4)
O(1)-Li(2)	2.197(4)	C(25)-C(30)	1.409(4)
O(1)-Li(3)	2.297(4)	C(26)-C(27)	1.413(4)
O(5)-Li(1)	1.905(4)	C(27)-C(28)	1.380(5)
O(5)-Li(2)	1.940(4)	C(28)-C(29)	1.374(5)
O(5)-Li(4)	1.942(4)	C(29)-C(30)	1.385(4)
O(7)-Li(4)	1.831(4)	C(31)-C(32)	1.399(3)
O(7)-Li(3)	1.832(4)	C(31)-C(36)	1.404(3)
O(8)-C(57)	1.440(3)	C(32)-C(33)	1.393(4)
O(8)-Li(1)	2.057(4)	C(33)-C(34)	1.382(4)
O(8)-Li(2)	2.125(4)	C(34)-C(35)	1.385(4)
O(9)-C(49)	1.444(3)	C(35)-C(36)	1.388(4)
O(9)-Li(1)	2.059(4)	C(37)-C(42)	1.388(4)
O(9)-Li(4)	2.082(4)	C(37)-C(38)	1.395(3)
O(10)-C(53)	1.446(3)	C(38)-C(39)	1.386(4)
O(10)-Li(1)	1.947(4)	C(39)-C(40)	1.393(4)
O(11)-C(65)	1.431(2)	C(40)-C(41)	1.365(4)
O(11)-Li(3)	1.941(4)	C(41)-C(42)	1.398(4)
O(12)-C(71)	1.427(3)	C(43)-C(44)	1.400(3)

C(43)-C(48)	1.402(3)	Li(1)-Al(1)-Li(2)	59.40(11)
C(44)-C(45)	1.391(3)	O(2)-Al(2)-O(11)	113.84(8)
C(45)-C(46)	1.392(4)	O(2)-Al(2)-O(1)	114.06(8)
C(46)-C(47)	1.385(4)	O(11)-Al(2)-O(1)	100.13(7)
C(47)-C(48)	1.390(3)	O(2)-Al(2)-O(13)	111.25(8)
C(49)-C(51)	1.522(3)	O(11)-Al(2)-O(13)	118.25(8)
C(49)-C(52)	1.525(3)	O(1)-Al(2)-O(13)	97.67(7)
C(49)-C(50)	1.528(3)	O(2)-Al(2)-Li(2)	124.50(10)
C(53)-C(55)	1.509(4)	O(11)-Al(2)-Li(2)	121.45(10)
C(53)-C(56)	1.515(4)	O(1)-Al(2)-Li(2)	53.14(9)
C(53)-C(54)	1.518(4)	O(13)-Al(2)-Li(2)	44.55(9)
C(57)-C(60)	1.521(3)	O(2)-Al(2)-Li(3)	129.18(10)
C(57)-C(59)	1.525(3)	O(11)-Al(2)-Li(3)	44.25(10)
C(57)-C(58)	1.530(3)	O(1)-Al(2)-Li(3)	55.89(9)
C(61)-C(64)	1.524(3)	O(13)-Al(2)-Li(3)	119.30(10)
C(61)-C(63)	1.526(3)	Li(2)-Al(2)-Li(3)	90.63(12)
C(61)-C(62)	1.528(3)	O(2)-Si(1)-O(3)	111.64(8)
C(65)-C(66)	1.528(3)	O(2)-Si(1)-C(7)	109.86(10)
C(65)-C(67)	1.528(3)	O(3)-Si(1)-C(7)	107.34(9)
C(65)-C(68)	1.529(3)	O(2)-Si(1)-C(1)	112.73(9)
C(69)-C(70)	1.483(4)	O(3)-Si(1)-C(1)	106.44(10)
C(71)-C(72)	1.496(4)	C(7)-Si(1)-C(1)	108.61(11)
C(73)-C(74)	0.954(11)	O(4)-Si(2)-O(3)	113.49(8)
C(73)-C(75)	0.985(18)	O(4)-Si(2)-C(13)	110.18(10)
C(73)-C(75B)	1.124(11)	O(3)-Si(2)-C(13)	106.81(10)
C(73)-C(74B)	1.842(13)	O(4)-Si(2)-C(19)	108.95(9)
C(74)-C(74B)	0.985(12)	O(3)-Si(2)-C(19)	109.32(10)
C(74)-C(75)	1.50(2)	C(13)-Si(2)-C(19)	107.95(10)
C(74)-C(74)#1	1.64(2)	O(5)-Si(3)-O(6)	112.24(8)
C(74)-C(74B)#1	1.636(13)	O(5)-Si(3)-C(25)	110.25(10)
C(74)-C(75B)	1.823(14)	O(6)-Si(3)-C(25)	107.31(11)
C(75)-C(74B)#1	1.83(2)	O(5)-Si(3)-C(31)	111.94(9)
C(75)-C(75B)	1.91(2)	O(6)-Si(3)-C(31)	104.99(10)
C(74B)-C(74)#1	1.636(13)	C(25)-Si(3)-C(31)	109.89(10)
C(74B)-C(75)#1	1.83(2)	O(5)-Si(3)-Li(4)	36.08(9)
O(4)-Al(1)-O(1)	118.07(8)	O(6)-Si(3)-Li(4)	77.91(9)
O(4)-Al(1)-O(9)	118.07(8)	C(25)-Si(3)-Li(4)	133.97(11)
O(1)-Al(1)-O(9)	100.29(7)	C(31)-Si(3)-Li(4)	112.63(10)
O(4)-Al(1)-O(8)	119.18(8)	O(5)-Si(3)-Li(2)	30.29(9)
O(1)-Al(1)-O(8)	101.76(7)	O(6)-Si(3)-Li(2)	105.12(10)
O(9)-Al(1)-O(8)	95.43(7)	C(25)-Si(3)-Li(2)	85.66(11)
O(4)-Al(1)-Li(4)	147.05(10)	C(31)-Si(3)-Li(2)	139.75(10)
O(1)-Al(1)-Li(4)	50.57(10)	Li(4)-Si(3)-Li(2)	50.10(10)
O(9)-Al(1)-Li(4)	51.11(9)	O(7)-Si(4)-O(6)	111.48(8)
O(8)-Al(1)-Li(4)	93.70(10)	O(7)-Si(4)-C(43)	115.13(9)
O(4)-Al(1)-Li(1)	142.71(10)	O(6)-Si(4)-C(43)	103.56(10)
O(1)-Al(1)-Li(1)	99.20(10)	O(7)-Si(4)-C(37)	108.06(10)
O(9)-Al(1)-Li(1)	48.16(9)	O(6)-Si(4)-C(37)	110.12(10)
O(8)-Al(1)-Li(1)	48.11(10)	C(43)-Si(4)-C(37)	108.39(10)
Li(4)-Al(1)-Li(1)	59.06(11)	O(7)-Si(4)-Li(4)	33.27(9)
O(4)-Al(1)-Li(2)	147.06(10)	O(6)-Si(4)-Li(4)	79.59(9)
O(1)-Al(1)-Li(2)	52.48(9)	C(43)-Si(4)-Li(4)	134.95(10)
O(9)-Al(1)-Li(2)	94.79(10)	C(37)-Si(4)-Li(4)	112.48(11)
O(8)-Al(1)-Li(2)	50.10(10)	Al(1)-O(1)-Al(2)	133.42(9)
Li(4)-Al(1)-Li(2)	57.24(11)	Al(1)-O(1)-Li(4)	88.85(12)

Al(2)-O(1)-Li(4)	134.05(13)	O(8)-Li(1)-Li(2)	50.12(12)
Al(1)-O(1)-Li(2)	88.64(12)	O(9)-Li(1)-Li(2)	89.55(16)
Al(2)-O(1)-Li(2)	86.87(12)	Li(4)-Li(1)-Li(2)	57.49(14)
Li(4)-O(1)-Li(2)	75.39(15)	O(5)-Li(1)-Al(1)	91.99(15)
Al(1)-O(1)-Li(3)	135.23(12)	O(10)-Li(1)-Al(1)	160.9(2)
Al(2)-O(1)-Li(3)	84.62(11)	O(8)-Li(1)-Al(1)	40.39(8)
Li(4)-O(1)-Li(3)	70.11(15)	O(9)-Li(1)-Al(1)	40.12(8)
Li(2)-O(1)-Li(3)	121.08(15)	Li(4)-Li(1)-Al(1)	58.78(11)
Si(1)-O(2)-Al(2)	161.93(11)	Li(2)-Li(1)-Al(1)	60.41(11)
Si(2)-O(3)-Si(1)	154.64(11)	O(13)-Li(2)-O(5)	143.2(2)
Si(2)-O(4)-Al(1)	152.06(10)	O(13)-Li(2)-O(8)	122.8(2)
Si(3)-O(5)-Li(1)	137.43(15)	O(5)-Li(2)-O(8)	91.97(17)
Si(3)-O(5)-Li(2)	124.95(14)	O(13)-Li(2)-O(1)	79.99(15)
Li(1)-O(5)-Li(2)	90.93(18)	O(5)-Li(2)-O(1)	97.41(17)
Si(3)-O(5)-Li(4)	114.67(13)	O(8)-Li(2)-O(1)	78.62(14)
Li(1)-O(5)-Li(4)	88.31(17)	O(13)-Li(2)-Li(4)	115.5(2)
Li(2)-O(5)-Li(4)	84.39(17)	O(5)-Li(2)-Li(4)	47.83(13)
Si(3)-O(6)-Si(4)	138.99(10)	O(8)-Li(2)-Li(4)	88.19(16)
Si(4)-O(7)-Li(4)	118.36(14)	O(1)-Li(2)-Li(4)	49.99(12)
Si(4)-O(7)-Li(3)	142.18(16)	O(13)-Li(2)-Li(1)	167.6(2)
Li(4)-O(7)-Li(3)	86.61(18)	O(5)-Li(2)-Li(1)	44.02(12)
C(57)-O(8)-Al(1)	131.90(14)	O(8)-Li(2)-Li(1)	48.00(12)
C(57)-O(8)-Li(1)	124.27(17)	O(1)-Li(2)-Li(1)	89.29(15)
Al(1)-O(8)-Li(1)	91.50(13)	Li(4)-Li(2)-Li(1)	60.08(14)
C(57)-O(8)-Li(2)	123.19(17)	O(13)-Li(2)-Al(2)	40.02(9)
Al(1)-O(8)-Li(2)	89.60(12)	O(5)-Li(2)-Al(2)	127.90(18)
Li(1)-O(8)-Li(2)	81.89(16)	O(8)-Li(2)-Al(2)	102.39(15)
C(49)-O(9)-Al(1)	130.62(13)	O(1)-Li(2)-Al(2)	39.99(7)
C(49)-O(9)-Li(1)	128.03(17)	Li(4)-Li(2)-Al(2)	82.45(14)
Al(1)-O(9)-Li(1)	91.72(13)	Li(1)-Li(2)-Al(2)	128.88(16)
C(49)-O(9)-Li(4)	123.04(16)	O(13)-Li(2)-Al(1)	107.47(16)
Al(1)-O(9)-Li(4)	87.14(12)	O(5)-Li(2)-Al(1)	91.04(14)
Li(1)-O(9)-Li(4)	80.64(16)	O(8)-Li(2)-Al(1)	40.29(8)
C(53)-O(10)-Li(1)	150.5(2)	O(1)-Li(2)-Al(1)	38.88(7)
C(65)-O(11)-Al(2)	141.43(14)	Li(4)-Li(2)-Al(1)	59.51(11)
C(65)-O(11)-Li(3)	121.13(18)	Li(1)-Li(2)-Al(1)	60.18(11)
Al(2)-O(11)-Li(3)	96.88(14)	Al(2)-Li(2)-Al(1)	71.44(10)
C(71)-O(12)-C(69)	113.34(19)	O(13)-Li(2)-Si(3)	122.31(17)
C(71)-O(12)-Li(3)	130.62(19)	O(5)-Li(2)-Si(3)	24.76(7)
C(69)-O(12)-Li(3)	113.83(18)	O(8)-Li(2)-Si(3)	114.78(15)
C(61)-O(13)-Al(2)	133.61(14)	O(1)-Li(2)-Si(3)	110.19(15)
C(61)-O(13)-Li(2)	130.40(17)	Li(4)-Li(2)-Si(3)	61.83(12)
Al(2)-O(13)-Li(2)	95.44(13)	Li(1)-Li(2)-Si(3)	67.16(12)
O(5)-Li(1)-O(10)	106.2(2)	Al(2)-Li(2)-Si(3)	125.79(14)
O(5)-Li(1)-O(8)	95.12(18)	Al(1)-Li(2)-Si(3)	114.47(13)
O(10)-Li(1)-O(8)	139.7(2)	O(7)-Li(3)-O(11)	126.6(2)
O(5)-Li(1)-O(9)	96.45(17)	O(7)-Li(3)-O(12)	105.0(2)
O(10)-Li(1)-O(9)	129.4(2)	O(11)-Li(3)-O(12)	124.3(2)
O(8)-Li(1)-O(9)	79.87(15)	O(7)-Li(3)-O(1)	95.19(17)
O(5)-Li(1)-Li(4)	46.41(12)	O(11)-Li(3)-O(1)	78.37(15)
O(10)-Li(1)-Li(4)	131.6(2)	O(12)-Li(3)-O(1)	120.11(19)
O(8)-Li(1)-Li(4)	87.65(16)	O(7)-Li(3)-Li(4)	46.67(13)
O(9)-Li(1)-Li(4)	50.06(12)	O(11)-Li(3)-Li(4)	117.5(2)
O(5)-Li(1)-Li(2)	45.06(12)	O(12)-Li(3)-Li(4)	112.65(19)
O(10)-Li(1)-Li(2)	137.7(2)	O(1)-Li(3)-Li(4)	50.60(12)

O(7)-Li(3)-Al(2)	116.27(18)	C(3)-C(4)-C(5)	119.5(3)
O(11)-Li(3)-Al(2)	38.87(9)	C(4)-C(5)-C(6)	120.0(3)
O(12)-Li(3)-Al(2)	133.57(18)	C(1)-C(6)-C(5)	121.8(3)
O(1)-Li(3)-Al(2)	39.50(7)	C(12)-C(7)-C(8)	117.5(2)
Li(4)-Li(3)-Al(2)	83.79(14)	C(12)-C(7)-Si(1)	121.32(18)
O(7)-Li(4)-O(5)	118.0(2)	C(8)-C(7)-Si(1)	120.86(19)
O(7)-Li(4)-O(1)	103.64(19)	C(9)-C(8)-C(7)	121.5(2)
O(5)-Li(4)-O(1)	101.96(17)	C(10)-C(9)-C(8)	119.6(2)
O(7)-Li(4)-O(9)	144.5(2)	C(11)-C(10)-C(9)	120.0(3)
O(5)-Li(4)-O(9)	94.56(16)	C(10)-C(11)-C(12)	119.9(3)
O(1)-Li(4)-O(9)	81.33(14)	C(7)-C(12)-C(11)	121.5(2)
O(7)-Li(4)-Li(3)	46.72(13)	C(14)-C(13)-C(18)	117.3(2)
O(5)-Li(4)-Li(3)	137.2(2)	C(14)-C(13)-Si(2)	122.73(19)
O(1)-Li(4)-Li(3)	59.29(14)	C(18)-C(13)-Si(2)	119.84(19)
O(9)-Li(4)-Li(3)	117.14(19)	C(15)-C(14)-C(13)	121.6(3)
O(7)-Li(4)-Li(2)	119.0(2)	C(16)-C(15)-C(14)	120.0(3)
O(5)-Li(4)-Li(2)	47.78(12)	C(15)-C(16)-C(17)	120.0(3)
O(1)-Li(4)-Li(2)	54.62(13)	C(16)-C(17)-C(18)	119.9(3)
O(9)-Li(4)-Li(2)	92.80(16)	C(17)-C(18)-C(13)	121.2(3)
Li(3)-Li(4)-Li(2)	99.68(18)	C(24)-C(19)-C(20)	117.2(2)
O(7)-Li(4)-Al(1)	138.75(19)	C(24)-C(19)-Si(2)	123.04(18)
O(5)-Li(4)-Al(1)	93.97(15)	C(20)-C(19)-Si(2)	119.78(19)
O(1)-Li(4)-Al(1)	40.58(8)	C(21)-C(20)-C(19)	121.5(3)
O(9)-Li(4)-Al(1)	41.75(8)	C(22)-C(21)-C(20)	120.1(3)
Li(3)-Li(4)-Al(1)	92.21(15)	C(23)-C(22)-C(21)	119.4(2)
Li(2)-Li(4)-Al(1)	63.26(12)	C(22)-C(23)-C(24)	120.4(3)
O(7)-Li(4)-Li(1)	158.8(2)	C(23)-C(24)-C(19)	121.4(3)
O(5)-Li(4)-Li(1)	45.28(12)	C(26)-C(25)-C(30)	117.8(2)
O(1)-Li(4)-Li(1)	93.88(16)	C(26)-C(25)-Si(3)	120.2(2)
O(9)-Li(4)-Li(1)	49.30(12)	C(30)-C(25)-Si(3)	122.0(2)
Li(3)-Li(4)-Li(1)	153.0(2)	C(25)-C(26)-C(27)	120.9(3)
Li(2)-Li(4)-Li(1)	62.43(15)	C(28)-C(27)-C(26)	119.0(3)
Al(1)-Li(4)-Li(1)	62.16(12)	C(29)-C(28)-C(27)	121.6(3)
O(7)-Li(4)-Si(4)	28.37(8)	C(28)-C(29)-C(30)	119.0(3)
O(5)-Li(4)-Si(4)	91.07(14)	C(29)-C(30)-C(25)	121.7(3)
O(1)-Li(4)-Si(4)	121.09(16)	C(32)-C(31)-C(36)	116.4(2)
O(9)-Li(4)-Si(4)	155.16(18)	C(32)-C(31)-Si(3)	123.82(18)
Li(3)-Li(4)-Si(4)	72.35(13)	C(36)-C(31)-Si(3)	119.29(17)
Li(2)-Li(4)-Si(4)	108.69(15)	C(33)-C(32)-C(31)	121.9(2)
Al(1)-Li(4)-Si(4)	161.66(16)	C(34)-C(33)-C(32)	120.0(2)
Li(1)-Li(4)-Si(4)	130.80(16)	C(33)-C(34)-C(35)	119.7(2)
O(7)-Li(4)-Si(3)	90.33(14)	C(34)-C(35)-C(36)	119.8(2)
O(5)-Li(4)-Si(3)	29.25(7)	C(35)-C(36)-C(31)	122.1(2)
O(1)-Li(4)-Si(3)	120.69(16)	C(42)-C(37)-C(38)	116.3(2)
O(9)-Li(4)-Si(3)	117.72(16)	C(42)-C(37)-Si(4)	120.33(19)
Li(3)-Li(4)-Si(3)	124.13(16)	C(38)-C(37)-Si(4)	123.3(2)
Li(2)-Li(4)-Si(3)	68.07(12)	C(39)-C(38)-C(37)	121.9(3)
Al(1)-Li(4)-Si(3)	123.03(13)	C(38)-C(39)-C(40)	119.9(3)
Li(1)-Li(4)-Si(3)	70.30(12)	C(41)-C(40)-C(39)	119.8(3)
Si(4)-Li(4)-Si(3)	62.45(7)	C(40)-C(41)-C(42)	119.4(3)
C(6)-C(1)-C(2)	116.8(2)	C(37)-C(42)-C(41)	122.7(3)
C(6)-C(1)-Si(1)	120.9(2)	C(44)-C(43)-C(48)	117.0(2)
C(2)-C(1)-Si(1)	122.3(2)	C(44)-C(43)-Si(4)	121.17(17)
C(3)-C(2)-C(1)	121.7(3)	C(48)-C(43)-Si(4)	121.83(18)
C(4)-C(3)-C(2)	120.1(3)	C(45)-C(44)-C(43)	121.7(2)

C(44)-C(45)-C(46)	119.8(2)	C(74)-C(73)-C(75)	101.6(16)
C(47)-C(46)-C(45)	119.7(2)	C(74)-C(73)-C(75B)	122.6(13)
C(46)-C(47)-C(48)	120.0(2)	C(75)-C(73)-C(75B)	130.3(16)
C(47)-C(48)-C(43)	121.8(2)	C(74)-C(73)-C(74B)	18.6(8)
O(9)-C(49)-C(51)	108.90(18)	C(75)-C(73)-C(74B)	119.8(14)
O(9)-C(49)-C(52)	107.37(18)	C(75B)-C(73)-C(74B)	104.4(8)
C(51)-C(49)-C(52)	110.3(2)	C(73)-C(74)-C(74B)	143.5(16)
O(9)-C(49)-C(50)	108.47(18)	C(73)-C(74)-C(75)	40.0(10)
C(51)-C(49)-C(50)	110.9(2)	C(74B)-C(74)-C(75)	172.7(14)
C(52)-C(49)-C(50)	110.72(19)	C(73)-C(74)-C(74)#1	143.2(15)
O(10)-C(53)-C(55)	109.6(2)	C(74B)-C(74)-C(74)#1	72.3(11)
O(10)-C(53)-C(56)	108.0(2)	C(75)-C(74)-C(74)#1	106.0(12)
C(55)-C(53)-C(56)	110.6(3)	C(73)-C(74)-C(74B)#1	108.6(13)
O(10)-C(53)-C(54)	105.4(2)	C(74B)-C(74)-C(74B)#1	107.3(11)
C(55)-C(53)-C(54)	111.5(3)	C(75)-C(74)-C(74B)#1	71.3(10)
C(56)-C(53)-C(54)	111.5(2)	C(74)#1-C(74)-C(74B)#1	35.0(5)
O(8)-C(57)-C(60)	108.99(18)	C(73)-C(74)-C(75B)	31.3(7)
O(8)-C(57)-C(59)	107.15(19)	C(74B)-C(74)-C(75B)	112.7(11)
C(60)-C(57)-C(59)	110.2(2)	C(75)-C(74)-C(75B)	69.5(9)
O(8)-C(57)-C(58)	109.09(19)	C(74)#1-C(74)-C(75B)	174.0(12)
C(60)-C(57)-C(58)	110.4(2)	C(74B)#1-C(74)-C(75B)	139.8(10)
C(59)-C(57)-C(58)	110.9(2)	C(73)-C(75)-C(74)	38.5(9)
O(13)-C(61)-C(64)	108.50(18)	C(73)-C(75)-C(74B)#1	94.1(14)
O(13)-C(61)-C(63)	110.28(18)	C(74)-C(75)-C(74B)#1	57.8(8)
C(64)-C(61)-C(63)	110.47(19)	C(73)-C(75)-C(75B)	26.6(9)
O(13)-C(61)-C(62)	107.47(18)	C(74)-C(75)-C(75B)	63.2(9)
C(64)-C(61)-C(62)	109.9(2)	C(74B)#1-C(75)-C(75B)	120.4(11)
C(63)-C(61)-C(62)	110.18(19)	C(73)-C(75B)-C(74)	26.2(6)
O(11)-C(65)-C(66)	110.12(17)	C(73)-C(75B)-C(75)	23.1(8)
O(11)-C(65)-C(67)	109.48(17)	C(74)-C(75B)-C(75)	47.3(7)
C(66)-C(65)-C(67)	110.82(19)	C(74)-C(74B)-C(74)#1	72.7(11)
O(11)-C(65)-C(68)	107.29(18)	C(74)-C(74B)-C(75)#1	123.2(13)
C(66)-C(65)-C(68)	110.45(19)	C(74)#1-C(74B)-C(75)#1	51.0(8)
C(67)-C(65)-C(68)	108.60(19)	C(74)-C(74B)-C(73)	17.9(8)
O(12)-C(69)-C(70)	114.2(2)	C(74)#1-C(74B)-C(73)	90.4(8)
O(12)-C(71)-C(72)	109.7(2)	C(75)#1-C(74B)-C(73)	140.0(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2351. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	21(1)	17(1)	14(1)	2(1)	2(1)	2(1)
Al(2)	20(1)	16(1)	15(1)	2(1)	2(1)	2(1)
Si(1)	30(1)	21(1)	17(1)	5(1)	2(1)	6(1)
Si(2)	25(1)	23(1)	15(1)	3(1)	1(1)	2(1)
Si(3)	17(1)	23(1)	21(1)	0(1)	0(1)	4(1)
Si(4)	27(1)	25(1)	17(1)	5(1)	3(1)	9(1)
O(1)	20(1)	16(1)	16(1)	2(1)	2(1)	2(1)
O(2)	34(1)	21(1)	20(1)	5(1)	0(1)	6(1)
O(3)	30(1)	24(1)	20(1)	4(1)	2(1)	5(1)
O(4)	28(1)	23(1)	17(1)	2(1)	0(1)	3(1)

O(5)	19(1)	19(1)	21(1)	2(1)	4(1)	3(1)
O(6)	24(1)	43(1)	20(1)	2(1)	1(1)	11(1)
O(7)	22(1)	23(1)	19(1)	6(1)	4(1)	3(1)
O(8)	24(1)	25(1)	20(1)	7(1)	7(1)	1(1)
O(9)	23(1)	16(1)	21(1)	1(1)	0(1)	-1(1)
O(10)	35(1)	43(1)	36(1)	5(1)	10(1)	16(1)
O(11)	23(1)	19(1)	17(1)	2(1)	5(1)	6(1)
O(12)	23(1)	30(1)	30(1)	6(1)	2(1)	-2(1)
O(13)	21(1)	17(1)	27(1)	0(1)	2(1)	-2(1)
Li(1)	25(2)	26(2)	25(2)	4(2)	4(2)	3(2)
Li(2)	25(2)	21(2)	29(2)	4(2)	3(2)	2(2)
Li(3)	26(2)	22(2)	28(2)	4(2)	1(2)	4(2)
Li(4)	22(2)	25(2)	20(2)	4(2)	1(1)	1(2)
C(1)	40(1)	30(1)	17(1)	9(1)	5(1)	14(1)
C(2)	41(2)	45(2)	41(2)	16(1)	14(1)	14(1)
C(3)	43(2)	72(2)	62(2)	24(2)	25(2)	21(2)
C(4)	60(2)	82(3)	41(2)	23(2)	25(2)	42(2)
C(5)	86(3)	50(2)	25(1)	6(1)	12(2)	41(2)
C(6)	57(2)	37(2)	24(1)	4(1)	4(1)	18(1)
C(7)	36(1)	18(1)	20(1)	2(1)	3(1)	5(1)
C(8)	42(1)	22(1)	22(1)	3(1)	1(1)	5(1)
C(9)	59(2)	22(1)	22(1)	7(1)	6(1)	7(1)
C(10)	56(2)	28(1)	41(2)	9(1)	20(1)	1(1)
C(11)	36(2)	36(2)	52(2)	10(1)	8(1)	2(1)
C(12)	36(1)	26(1)	31(1)	7(1)	3(1)	8(1)
C(13)	28(1)	35(1)	14(1)	6(1)	2(1)	0(1)
C(14)	36(1)	36(1)	20(1)	4(1)	2(1)	-3(1)
C(15)	44(2)	50(2)	26(1)	3(1)	3(1)	-16(1)
C(16)	33(2)	78(2)	27(1)	15(1)	2(1)	-20(2)
C(17)	28(1)	80(2)	28(1)	22(1)	5(1)	7(1)
C(18)	30(1)	47(2)	23(1)	12(1)	5(1)	5(1)
C(19)	24(1)	32(1)	17(1)	4(1)	0(1)	5(1)
C(20)	35(1)	40(2)	23(1)	-1(1)	2(1)	-4(1)
C(21)	35(1)	62(2)	21(1)	-9(1)	3(1)	-2(1)
C(22)	34(2)	78(2)	21(1)	13(1)	9(1)	3(1)
C(23)	50(2)	50(2)	38(2)	20(1)	14(1)	5(1)
C(24)	43(2)	34(1)	26(1)	9(1)	9(1)	6(1)
C(25)	19(1)	24(1)	44(1)	-2(1)	-4(1)	6(1)
C(26)	27(1)	26(1)	59(2)	6(1)	-3(1)	4(1)
C(27)	29(1)	36(2)	92(3)	23(2)	5(2)	5(1)
C(28)	31(2)	22(1)	82(2)	-1(1)	-14(2)	3(1)
C(29)	34(2)	38(2)	63(2)	-14(2)	-13(1)	8(1)
C(30)	27(1)	41(2)	47(2)	-7(1)	-6(1)	9(1)
C(31)	23(1)	24(1)	19(1)	5(1)	4(1)	4(1)
C(32)	26(1)	31(1)	32(1)	2(1)	-2(1)	5(1)
C(33)	31(1)	39(2)	40(2)	8(1)	-2(1)	14(1)
C(34)	47(2)	27(1)	40(2)	12(1)	6(1)	12(1)
C(35)	40(2)	28(1)	53(2)	12(1)	5(1)	-2(1)
C(36)	26(1)	30(1)	43(2)	9(1)	2(1)	1(1)
C(37)	40(1)	32(1)	25(1)	10(1)	9(1)	14(1)
C(38)	58(2)	35(2)	33(1)	8(1)	1(1)	15(1)
C(39)	74(2)	41(2)	40(2)	18(1)	9(2)	21(2)
C(40)	59(2)	33(2)	52(2)	14(1)	17(2)	9(1)
C(41)	50(2)	33(2)	45(2)	6(1)	12(1)	-2(1)
C(42)	40(2)	33(1)	36(1)	11(1)	10(1)	1(1)

C(43)	27(1)	25(1)	19(1)	7(1)	1(1)	9(1)
C(44)	26(1)	29(1)	27(1)	6(1)	4(1)	8(1)
C(45)	31(1)	28(1)	27(1)	4(1)	-3(1)	7(1)
C(46)	44(2)	30(1)	19(1)	3(1)	1(1)	15(1)
C(47)	36(1)	33(1)	25(1)	10(1)	12(1)	12(1)
C(48)	30(1)	25(1)	27(1)	8(1)	4(1)	6(1)
C(49)	27(1)	17(1)	22(1)	-1(1)	2(1)	-2(1)
C(50)	43(2)	23(1)	22(1)	-1(1)	1(1)	3(1)
C(51)	29(1)	35(1)	35(1)	0(1)	4(1)	-5(1)
C(52)	41(1)	19(1)	25(1)	3(1)	0(1)	-1(1)
C(53)	29(1)	36(1)	32(1)	2(1)	8(1)	8(1)
C(54)	40(2)	51(2)	37(2)	1(1)	7(1)	5(1)
C(55)	68(2)	45(2)	71(2)	15(2)	24(2)	22(2)
C(56)	36(2)	77(2)	43(2)	6(2)	2(1)	-7(2)
C(57)	30(1)	28(1)	24(1)	8(1)	11(1)	2(1)
C(58)	50(2)	47(2)	23(1)	4(1)	14(1)	9(1)
C(59)	30(1)	44(2)	43(2)	16(1)	14(1)	3(1)
C(60)	37(1)	30(1)	41(2)	15(1)	9(1)	1(1)
C(61)	24(1)	18(1)	26(1)	-1(1)	0(1)	-2(1)
C(62)	25(1)	28(1)	36(1)	2(1)	4(1)	-5(1)
C(63)	32(1)	20(1)	31(1)	2(1)	1(1)	0(1)
C(64)	32(1)	28(1)	28(1)	0(1)	-2(1)	2(1)
C(65)	24(1)	22(1)	17(1)	0(1)	5(1)	8(1)
C(66)	34(1)	28(1)	25(1)	3(1)	5(1)	14(1)
C(67)	30(1)	29(1)	18(1)	-2(1)	2(1)	5(1)
C(68)	29(1)	31(1)	25(1)	1(1)	9(1)	6(1)
C(69)	34(1)	50(2)	38(2)	17(1)	5(1)	-5(1)
C(70)	54(2)	51(2)	68(2)	28(2)	4(2)	-10(2)
C(71)	23(1)	36(1)	43(2)	7(1)	-2(1)	2(1)
C(72)	31(1)	40(2)	31(1)	5(1)	-1(1)	5(1)

8.5. Compound 8

Table 1. Crystal data and structure refinement for sh2282.

Identification code	sh2282	
Empirical formula	$C_{128}H_{144}Al_4Li_4O_{23}Si_8$	
Formula weight	2410.83	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.549(2) Å	α= 90°.
	b = 26.057(2) Å	β= 95.766(5)°.
	c = 22.4635(19) Å	γ = 90°.
Volume	12549.3(19) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	5088	
Crystal size	0.2 x 0.3 x 0.45 mm^3	
Theta range for data collection	1.23 to 24.48°.	
Index ranges	-24<=h<=24, -28<=k<=30, -26<=l<=26	
Reflections collected	33070	
Independent reflections	10235 [R(int) = 0.0988]	
Completeness to theta = 24.48°	98.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10235 / 0 / 729	
Goodness-of-fit on F^2	1.296	
Final R indices [I>2sigma(I)]	R1 = 0.0686, wR2 = 0.1793	
R indices (all data)	R1 = 0.1327, wR2 = 0.2019	
Largest diff. peak and hole	1.724 and -0.784 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2282. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	5000	3501(1)	2500	14(1)
Al(2)	5938(1)	2665(1)	2132(1)	15(1)
Al(3)	5000	1845(1)	2500	15(1)
Si(1)	3828(1)	4220(1)	2018(1)	18(1)
Si(2)	7099(1)	3411(1)	2498(1)	17(1)
Si(3)	5243(1)	1144(1)	1367(1)	17(1)
Si(4)	6119(1)	1973(1)	958(1)	17(1)
Li(1)	4159(4)	1959(4)	1614(4)	21(2)
Li(2)	5203(4)	2922(4)	1189(4)	24(2)
O(1)	5371(2)	3137(1)	1994(2)	17(1)
O(2)	4296(1)	2180(1)	2413(2)	16(1)
O(3)	4460(2)	3902(1)	2088(2)	17(1)
O(4)	3220(2)	3882(2)	2159(2)	21(1)
O(5)	6668(1)	2909(1)	2410(2)	17(1)
O(6)	5950(2)	2438(1)	1381(2)	18(1)
O(7)	5585(2)	1520(1)	916(2)	19(1)
O(8)	4894(2)	1483(1)	1832(2)	18(1)
O(9)	3332(2)	1717(2)	1337(2)	29(1)
O(10)	4338(2)	2548(2)	1015(2)	20(1)
O(11)	5322(2)	3408(2)	561(2)	25(1)
C(1)	3871(2)	4784(2)	2531(2)	20(1)
C(2)	3419(2)	5172(2)	2498(3)	23(1)
C(3)	3420(3)	5557(2)	2921(3)	28(2)
C(4)	3879(3)	5573(2)	3396(3)	28(2)
C(5)	4346(3)	5198(2)	3442(3)	32(2)
C(6)	4345(2)	4813(2)	3015(3)	26(2)
C(7)	3669(2)	4415(2)	1212(2)	18(1)
C(8)	3071(2)	4543(2)	947(2)	25(1)
C(9)	2971(3)	4656(2)	343(3)	29(2)
C(10)	3461(3)	4659(2)	-13(3)	26(2)
C(11)	4056(3)	4535(2)	238(3)	29(2)
C(12)	4155(3)	4417(2)	843(3)	25(1)
C(13)	7831(2)	3247(2)	2992(3)	24(1)
C(14)	7929(3)	3422(2)	3577(3)	32(2)
C(15)	8466(4)	3308(3)	3944(3)	54(2)
C(16)	8921(3)	3022(4)	3732(4)	74(3)
C(17)	8849(3)	2837(5)	3149(4)	112(5)
C(18)	8289(3)	2941(4)	2789(3)	77(3)
C(19)	7315(2)	3663(2)	1761(2)	19(1)
C(20)	7278(2)	4192(2)	1637(2)	22(1)
C(21)	7452(2)	4392(2)	1103(3)	25(1)
C(22)	7668(3)	4068(2)	682(2)	25(2)
C(23)	7708(2)	3545(2)	791(2)	25(1)
C(24)	7532(2)	3344(2)	1324(2)	22(1)
C(25)	4664(2)	759(2)	877(2)	20(1)
C(26)	4554(2)	838(2)	265(2)	22(1)
C(27)	4141(3)	539(3)	-96(3)	33(2)
C(28)	3838(3)	141(3)	150(3)	35(2)
C(29)	3935(3)	42(3)	761(3)	44(2)
C(30)	4338(3)	354(3)	1114(3)	35(2)

C(31)	5827(2)	687(2)	1749(2)	21(1)
C(32)	5952(3)	230(2)	1460(3)	34(2)
C(33)	6391(3)	-119(3)	1712(3)	43(2)
C(34)	6699(3)	-22(3)	2268(3)	37(2)
C(35)	6582(3)	421(3)	2560(3)	40(2)
C(36)	6151(3)	774(3)	2307(3)	34(2)
C(37)	6889(2)	1672(2)	1217(2)	19(1)
C(38)	7076(2)	1235(2)	916(3)	25(1)
C(39)	7650(3)	996(2)	1068(3)	28(2)
C(40)	8048(3)	1195(3)	1540(3)	29(2)
C(41)	7872(2)	1625(3)	1844(3)	29(2)
C(42)	7300(2)	1866(2)	1687(2)	21(1)
C(43)	6148(2)	2200(2)	173(2)	19(1)
C(44)	6587(2)	2567(2)	42(2)	19(1)
C(45)	6633(2)	2732(2)	-540(2)	23(1)
C(46)	6231(2)	2530(2)	-1007(3)	27(2)
C(47)	5796(3)	2170(3)	-888(3)	29(2)
C(48)	5758(2)	2005(2)	-308(2)	24(1)
C(49)	3074(3)	1405(3)	836(3)	44(2)
C(50)	2396(3)	1330(3)	911(3)	42(2)
C(51)	2248(3)	1762(3)	1331(3)	34(2)
C(52)	2856(2)	1815(3)	1735(3)	27(2)
C(53)	4220(2)	2383(2)	391(2)	22(1)
C(54)	3672(3)	2690(3)	118(3)	45(2)
C(55)	3500(5)	3030(4)	567(3)	106(5)
C(56)	3886(2)	2961(2)	1119(3)	27(2)
C(57)	5222(3)	3442(3)	-84(2)	30(2)
C(58)	5649(3)	3872(3)	-268(3)	36(2)
C(59)	5850(3)	4150(3)	316(3)	45(2)
C(60)	5854(3)	3725(2)	768(3)	32(2)
O(12)	9833	2087	2199	50
C(61)	9833	2087	2199	50
C(63)	10000	1214(6)	2500	92(4)
C(62)	9909(4)	1571(4)	1951(4)	69(2)
C(64)	4804(5)	8557(5)	2211(5)	50(3)
C(65)	4658(7)	9069(6)	2073(6)	72(4)
O(13)	5000	9387(9)	2500	110(7)

Table 3. Bond lengths [Å] and angles [°] for sh2282.

Al(1)-O(1)#1	1.735(4)	Si(1)-O(4)	1.636(4)
Al(1)-O(1)	1.735(4)	Si(1)-C(1)	1.864(6)
Al(1)-O(3)	1.758(4)	Si(1)-C(7)	1.879(5)
Al(1)-O(3)#1	1.758(4)	Si(2)-O(5)	1.605(4)
Al(2)-O(2)#1	1.733(4)	Si(2)-O(4)#1	1.637(4)
Al(2)-O(1)	1.739(4)	Si(2)-C(19)	1.882(6)
Al(2)-O(5)	1.752(3)	Si(2)-C(13)	1.884(5)
Al(2)-O(6)	1.789(4)	Si(3)-O(8)	1.611(4)
Al(2)-Li(2)	2.601(9)	Si(3)-O(7)	1.637(4)
Al(3)-O(2)	1.743(4)	Si(3)-C(25)	1.870(5)
Al(3)-O(2)#1	1.743(4)	Si(3)-C(31)	1.876(6)
Al(3)-O(8)	1.768(4)	Si(4)-O(6)	1.605(4)
Al(3)-O(8)#1	1.768(4)	Si(4)-O(7)	1.644(4)
Al(3)-Li(1)	2.571(8)	Si(4)-C(43)	1.866(6)
Al(3)-Li(1)#1	2.571(8)	Si(4)-C(37)	1.874(5)
Si(1)-O(3)	1.588(4)	Li(1)-O(2)	1.878(9)

Li(1)-O(9)	1.934(9)	C(39)-C(40)	1.396(8)
Li(1)-O(8)	2.032(10)	C(40)-C(41)	1.385(9)
Li(1)-O(10)	2.102(10)	C(41)-C(42)	1.398(7)
Li(2)-O(1)	1.892(10)	C(43)-C(44)	1.397(8)
Li(2)-O(11)	1.933(10)	C(43)-C(48)	1.397(7)
Li(2)-O(6)	2.054(10)	C(44)-C(45)	1.389(7)
Li(2)-O(10)	2.104(10)	C(45)-C(46)	1.394(7)
Li(2)-C(60)	2.741(12)	C(46)-C(47)	1.372(8)
O(2)-Al(2)#1	1.733(4)	C(47)-C(48)	1.384(8)
O(4)-Si(2)#1	1.637(4)	C(49)-C(50)	1.500(8)
O(9)-C(52)	1.450(6)	C(50)-C(51)	1.523(9)
O(9)-C(49)	1.451(7)	C(51)-C(52)	1.524(7)
O(10)-C(53)	1.464(6)	C(53)-C(54)	1.506(8)
O(10)-C(56)	1.484(6)	C(54)-C(55)	1.419(10)
O(11)-C(57)	1.446(6)	C(55)-C(56)	1.433(8)
O(11)-C(60)	1.450(6)	C(57)-C(58)	1.533(8)
C(1)-C(2)	1.401(8)	C(58)-C(59)	1.523(9)
C(1)-C(6)	1.418(7)	C(59)-C(60)	1.503(9)
C(2)-C(3)	1.381(8)	O(12)-C(61)#2	1.46567(12)
C(3)-C(4)	1.382(8)	O(12)-O(12)#2	1.46567(12)
C(4)-C(5)	1.397(8)	O(12)-C(62)	1.469(9)
C(5)-C(6)	1.388(8)	C(61)-C(61)#2	1.46567(12)
C(7)-C(12)	1.400(8)	C(61)-O(12)#2	1.46567(12)
C(7)-C(8)	1.403(7)	C(61)-C(62)	1.469(9)
C(8)-C(9)	1.383(8)	C(63)-C(62)	1.543(12)
C(9)-C(10)	1.389(8)	C(63)-C(62)#2	1.543(12)
C(10)-C(11)	1.385(8)	C(64)-C(65)	1.398(19)
C(11)-C(12)	1.387(8)	C(64)-C(64)#1	1.48(2)
C(13)-C(18)	1.382(9)	C(65)-O(13)	1.417(18)
C(13)-C(14)	1.389(8)	O(13)-C(65)#1	1.417(18)
C(14)-C(15)	1.384(8)	O(1)#1-Al(1)-O(1)	113.8(3)
C(15)-C(16)	1.355(12)	O(1)#1-Al(1)-O(3)	110.23(16)
C(16)-C(17)	1.388(12)	O(1)-Al(1)-O(3)	107.70(16)
C(17)-C(18)	1.411(9)	O(1)#1-Al(1)-O(3)#1	107.70(16)
C(19)-C(24)	1.402(8)	O(1)-Al(1)-O(3)#1	110.23(16)
C(19)-C(20)	1.407(8)	O(3)-Al(1)-O(3)#1	106.9(3)
C(20)-C(21)	1.394(8)	O(2)#1-Al(2)-O(1)	112.37(18)
C(21)-C(22)	1.382(8)	O(2)#1-Al(2)-O(5)	110.96(17)
C(22)-C(23)	1.386(8)	O(1)-Al(2)-O(5)	113.33(19)
C(23)-C(24)	1.394(8)	O(2)#1-Al(2)-O(6)	110.37(19)
C(25)-C(26)	1.387(7)	O(1)-Al(2)-O(6)	98.15(17)
C(25)-C(30)	1.404(8)	O(5)-Al(2)-O(6)	111.03(17)
C(26)-C(27)	1.381(8)	O(2)#1-Al(2)-Li(2)	118.6(2)
C(27)-C(28)	1.371(9)	O(1)-Al(2)-Li(2)	46.7(2)
C(28)-C(29)	1.392(9)	O(5)-Al(2)-Li(2)	130.4(3)
C(29)-C(30)	1.381(8)	O(6)-Al(2)-Li(2)	51.9(2)
C(31)-C(36)	1.392(7)	O(2)-Al(3)-O(2)#1	120.0(3)
C(31)-C(32)	1.394(8)	O(2)-Al(3)-O(8)	97.70(15)
C(32)-C(33)	1.390(8)	O(2)#1-Al(3)-O(8)	113.54(16)
C(33)-C(34)	1.376(9)	O(2)-Al(3)-O(8)#1	113.55(16)
C(34)-C(35)	1.365(9)	O(2)#1-Al(3)-O(8)#1	97.70(15)
C(35)-C(36)	1.387(8)	O(8)-Al(3)-O(8)#1	115.6(3)
C(37)-C(42)	1.401(7)	O(2)-Al(3)-Li(1)	46.9(2)
C(37)-C(38)	1.405(8)	O(2)#1-Al(3)-Li(1)	124.5(3)
C(38)-C(39)	1.395(8)	O(8)-Al(3)-Li(1)	51.9(2)

O(8)#1-Al(3)-Li(1)	137.8(2)	Al(2)-Li(2)-C(60)	100.8(3)
O(2)-Al(3)-Li(1)#1	124.5(3)	Al(1)-O(1)-Al(2)	129.1(2)
O(2)#1-Al(3)-Li(1)#1	46.9(2)	Al(1)-O(1)-Li(2)	137.0(3)
O(8)-Al(3)-Li(1)#1	137.8(2)	Al(2)-O(1)-Li(2)	91.4(3)
O(8)#1-Al(3)-Li(1)#1	51.9(2)	Al(2)#1-O(2)-Al(3)	126.8(2)
Li(1)-Al(3)-Li(1)#1	166.7(5)	Al(2)#1-O(2)-Li(1)	139.4(4)
O(3)-Si(1)-O(4)	113.4(2)	Al(3)-O(2)-Li(1)	90.4(3)
O(3)-Si(1)-C(1)	111.1(2)	Si(1)-O(3)-Al(1)	151.5(2)
O(4)-Si(1)-C(1)	107.2(2)	Si(1)-O(4)-Si(2)#1	151.3(2)
O(3)-Si(1)-C(7)	108.0(2)	Si(2)-O(5)-Al(2)	145.8(2)
O(4)-Si(1)-C(7)	105.1(2)	Si(4)-O(6)-Al(2)	146.4(2)
C(1)-Si(1)-C(7)	112.0(3)	Si(4)-O(6)-Li(2)	123.9(3)
O(5)-Si(2)-O(4)#1	113.85(19)	Al(2)-O(6)-Li(2)	84.9(3)
O(5)-Si(2)-C(19)	111.6(2)	Si(3)-O(7)-Si(4)	138.6(2)
O(4)#1-Si(2)-C(19)	107.7(2)	Si(3)-O(8)-Al(3)	144.4(2)
O(5)-Si(2)-C(13)	109.1(2)	Si(3)-O(8)-Li(1)	125.6(3)
O(4)#1-Si(2)-C(13)	105.0(2)	Al(3)-O(8)-Li(1)	84.9(3)
C(19)-Si(2)-C(13)	109.3(2)	C(52)-O(9)-C(49)	109.7(4)
O(8)-Si(3)-O(7)	109.9(2)	C(52)-O(9)-Li(1)	115.5(4)
O(8)-Si(3)-C(25)	110.4(2)	C(49)-O(9)-Li(1)	134.5(4)
O(7)-Si(3)-C(25)	105.8(2)	C(53)-O(10)-C(56)	108.0(4)
O(8)-Si(3)-C(31)	112.8(2)	C(53)-O(10)-Li(1)	111.9(4)
O(7)-Si(3)-C(31)	109.9(2)	C(56)-O(10)-Li(1)	105.2(4)
C(25)-Si(3)-C(31)	107.8(3)	C(53)-O(10)-Li(2)	112.3(4)
O(6)-Si(4)-O(7)	112.13(19)	C(56)-O(10)-Li(2)	102.6(4)
O(6)-Si(4)-C(43)	110.6(2)	Li(1)-O(10)-Li(2)	115.8(4)
O(7)-Si(4)-C(43)	105.3(2)	C(57)-O(11)-C(60)	108.6(4)
O(6)-Si(4)-C(37)	112.2(2)	C(57)-O(11)-Li(2)	138.9(5)
O(7)-Si(4)-C(37)	108.0(2)	C(60)-O(11)-Li(2)	107.4(4)
C(43)-Si(4)-C(37)	108.2(2)	C(2)-C(1)-C(6)	116.4(5)
O(2)-Li(1)-O(9)	117.3(5)	C(2)-C(1)-Si(1)	123.1(4)
O(2)-Li(1)-O(8)	85.0(4)	C(6)-C(1)-Si(1)	120.3(4)
O(9)-Li(1)-O(8)	123.2(5)	C(3)-C(2)-C(1)	122.4(5)
O(2)-Li(1)-O(10)	111.5(5)	C(2)-C(3)-C(4)	120.2(5)
O(9)-Li(1)-O(10)	104.8(4)	C(3)-C(4)-C(5)	119.4(6)
O(8)-Li(1)-O(10)	114.3(4)	C(6)-C(5)-C(4)	120.3(5)
O(2)-Li(1)-Al(3)	42.7(2)	C(5)-C(6)-C(1)	121.2(5)
O(9)-Li(1)-Al(3)	140.0(5)	C(12)-C(7)-C(8)	117.2(5)
O(8)-Li(1)-Al(3)	43.22(19)	C(12)-C(7)-Si(1)	119.8(4)
O(10)-Li(1)-Al(3)	114.8(4)	C(8)-C(7)-Si(1)	122.9(4)
O(1)-Li(2)-O(11)	118.4(5)	C(9)-C(8)-C(7)	120.9(5)
O(1)-Li(2)-O(6)	84.9(4)	C(8)-C(9)-C(10)	120.9(5)
O(11)-Li(2)-O(6)	113.4(5)	C(11)-C(10)-C(9)	119.3(5)
O(1)-Li(2)-O(10)	113.3(5)	C(10)-C(11)-C(12)	119.8(6)
O(11)-Li(2)-O(10)	110.4(4)	C(11)-C(12)-C(7)	122.0(5)
O(6)-Li(2)-O(10)	114.6(5)	C(18)-C(13)-C(14)	117.2(6)
O(1)-Li(2)-Al(2)	42.0(2)	C(18)-C(13)-Si(2)	121.3(5)
O(11)-Li(2)-Al(2)	130.4(4)	C(14)-C(13)-Si(2)	121.5(5)
O(6)-Li(2)-Al(2)	43.2(2)	C(15)-C(14)-C(13)	122.1(7)
O(10)-Li(2)-Al(2)	119.2(4)	C(16)-C(15)-C(14)	120.0(7)
O(1)-Li(2)-C(60)	92.7(4)	C(15)-C(16)-C(17)	120.4(7)
O(11)-Li(2)-C(60)	30.3(2)	C(16)-C(17)-C(18)	118.9(8)
O(6)-Li(2)-C(60)	97.1(4)	C(13)-C(18)-C(17)	121.3(8)
O(10)-Li(2)-C(60)	139.8(4)	C(24)-C(19)-C(20)	117.3(5)

C(24)-C(19)-Si(2)	122.5(5)	C(48)-C(43)-Si(4)	122.7(4)
C(20)-C(19)-Si(2)	120.2(4)	C(45)-C(44)-C(43)	121.7(5)
C(21)-C(20)-C(19)	121.5(5)	C(44)-C(45)-C(46)	119.6(5)
C(22)-C(21)-C(20)	119.9(6)	C(47)-C(46)-C(45)	119.8(5)
C(21)-C(22)-C(23)	119.9(6)	C(46)-C(47)-C(48)	120.2(5)
C(22)-C(23)-C(24)	120.3(6)	C(47)-C(48)-C(43)	121.8(5)
C(23)-C(24)-C(19)	121.2(6)	O(9)-C(49)-C(50)	106.8(5)
C(26)-C(25)-C(30)	116.4(5)	C(49)-C(50)-C(51)	103.9(5)
C(26)-C(25)-Si(3)	122.9(4)	C(50)-C(51)-C(52)	102.4(5)
C(30)-C(25)-Si(3)	120.6(4)	O(9)-C(52)-C(51)	103.7(4)
C(27)-C(26)-C(25)	122.3(6)	O(10)-C(53)-C(54)	106.7(5)
C(28)-C(27)-C(26)	119.7(6)	C(55)-C(54)-C(53)	106.9(5)
C(27)-C(28)-C(29)	120.4(6)	C(54)-C(55)-C(56)	111.5(6)
C(30)-C(29)-C(28)	118.8(6)	C(55)-C(56)-O(10)	106.7(5)
C(29)-C(30)-C(25)	122.3(6)	O(11)-C(57)-C(58)	106.4(5)
C(36)-C(31)-C(32)	117.1(5)	C(59)-C(58)-C(57)	104.0(5)
C(36)-C(31)-Si(3)	124.1(5)	C(60)-C(59)-C(58)	102.4(6)
C(32)-C(31)-Si(3)	118.8(4)	O(11)-C(60)-C(59)	104.7(4)
C(33)-C(32)-C(31)	121.6(6)	O(11)-C(60)-Li(2)	42.3(3)
C(34)-C(33)-C(32)	119.7(6)	C(59)-C(60)-Li(2)	145.9(4)
C(35)-C(34)-C(33)	119.7(6)	C(61)#2-O(12)-O(12)#2	0.0
C(34)-C(35)-C(36)	120.8(6)	C(61)#2-O(12)-C(62)	106.7(3)
C(35)-C(36)-C(31)	121.0(6)	O(12)#2-O(12)-C(62)	106.7(3)
C(42)-C(37)-C(38)	117.6(5)	C(61)#2-C(61)-O(12)#2	0.0
C(42)-C(37)-Si(4)	123.8(4)	C(61)#2-C(61)-C(62)	106.7(3)
C(38)-C(37)-Si(4)	118.6(4)	O(12)#2-C(61)-C(62)	106.7(3)
C(39)-C(38)-C(37)	122.3(5)	C(62)-C(63)-C(62)#2	105.7(12)
C(38)-C(39)-C(40)	118.8(6)	C(61)-C(62)-O(12)	0.0
C(41)-C(40)-C(39)	119.8(5)	C(61)-C(62)-C(63)	105.0(7)
C(40)-C(41)-C(42)	121.1(6)	O(12)-C(62)-C(63)	105.0(7)
C(41)-C(42)-C(37)	120.3(6)	C(65)-C(64)-C(64)#1	107.0(8)
C(44)-C(43)-C(48)	117.0(5)	C(64)-C(65)-O(13)	108.5(14)
C(44)-C(43)-Si(4)	120.3(4)	C(65)-O(13)-C(65)#1	108(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x+2,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2282. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	12(1)	16(1)	15(1)	0	3(1)	0
Al(2)	12(1)	17(1)	16(1)	0(1)	3(1)	0(1)
Al(3)	13(1)	17(1)	15(1)	0	4(1)	0
Si(1)	15(1)	20(1)	19(1)	2(1)	4(1)	3(1)
Si(2)	12(1)	20(1)	19(1)	-1(1)	4(1)	-1(1)
Si(3)	15(1)	18(1)	17(1)	-3(1)	4(1)	0(1)
Si(4)	16(1)	18(1)	16(1)	0(1)	5(1)	-1(1)
Li(1)	21(5)	24(6)	17(5)	-6(4)	1(4)	-1(4)
Li(2)	22(5)	27(6)	25(5)	-1(5)	7(4)	1(4)
O(1)	15(2)	22(2)	15(2)	0(2)	2(2)	2(2)
O(2)	14(2)	21(2)	14(2)	0(2)	2(2)	-2(2)
O(3)	16(2)	18(2)	18(2)	1(2)	5(2)	1(2)

O(4)	17(2)	23(2)	22(2)	3(2)	1(2)	1(2)
O(5)	12(2)	19(2)	20(2)	-1(2)	3(2)	-1(2)
O(6)	15(2)	19(2)	19(2)	2(2)	5(2)	-1(2)
O(7)	21(2)	20(2)	15(2)	0(2)	5(2)	-1(2)
O(8)	17(2)	19(2)	18(2)	-3(2)	3(2)	0(2)
O(9)	20(2)	41(3)	25(2)	-8(2)	5(2)	-11(2)
O(10)	19(2)	23(2)	19(2)	-3(2)	3(2)	4(2)
O(11)	28(2)	26(3)	23(2)	5(2)	5(2)	-6(2)
C(1)	21(3)	17(4)	23(3)	4(3)	9(2)	1(2)
C(2)	24(3)	19(4)	25(3)	3(3)	5(3)	4(3)
C(3)	27(3)	22(4)	35(4)	2(3)	10(3)	11(3)
C(4)	39(4)	21(4)	25(3)	-5(3)	9(3)	2(3)
C(5)	32(3)	33(4)	29(4)	-5(3)	-3(3)	1(3)
C(6)	22(3)	25(4)	32(4)	-2(3)	7(3)	3(3)
C(7)	19(3)	14(3)	21(3)	4(3)	4(2)	1(2)
C(8)	20(3)	29(4)	24(3)	1(3)	2(3)	0(3)
C(9)	23(3)	37(4)	26(4)	-1(3)	-8(3)	3(3)
C(10)	37(4)	24(4)	18(3)	6(3)	1(3)	-3(3)
C(11)	33(3)	31(4)	25(3)	3(3)	8(3)	-2(3)
C(12)	22(3)	26(4)	27(3)	1(3)	1(3)	0(3)
C(13)	19(3)	27(4)	26(3)	2(3)	3(3)	-4(3)
C(14)	42(4)	27(4)	25(4)	4(3)	-8(3)	-2(3)
C(15)	62(5)	47(5)	45(5)	15(4)	-25(4)	-19(4)
C(16)	27(4)	132(9)	59(6)	61(6)	-13(4)	-14(5)
C(17)	36(5)	247(15)	57(6)	46(7)	18(4)	77(7)
C(18)	40(4)	156(10)	35(4)	7(5)	7(3)	62(5)
C(19)	8(2)	26(4)	22(3)	-3(3)	-1(2)	-2(2)
C(20)	18(3)	27(4)	21(3)	-4(3)	7(2)	-1(3)
C(21)	20(3)	22(4)	33(4)	1(3)	8(3)	1(3)
C(22)	29(3)	31(4)	17(3)	1(3)	6(3)	-4(3)
C(23)	26(3)	27(4)	22(3)	-5(3)	11(3)	1(3)
C(24)	22(3)	19(4)	26(3)	-3(3)	6(3)	2(3)
C(25)	16(3)	23(4)	22(3)	1(3)	4(2)	1(2)
C(26)	23(3)	20(4)	23(3)	-3(3)	7(3)	-1(3)
C(27)	40(4)	32(4)	25(3)	-7(3)	-4(3)	2(3)
C(28)	26(3)	38(5)	40(4)	-16(3)	-2(3)	-7(3)
C(29)	35(4)	48(5)	48(5)	-13(4)	8(3)	-24(3)
C(30)	33(3)	43(5)	28(4)	-3(3)	4(3)	-13(3)
C(31)	19(3)	25(4)	21(3)	-1(3)	7(2)	-3(3)
C(32)	37(4)	29(4)	35(4)	-9(3)	-6(3)	6(3)
C(33)	44(4)	30(5)	53(5)	-5(4)	-8(4)	15(3)
C(34)	32(3)	42(5)	35(4)	9(4)	-8(3)	9(3)
C(35)	36(4)	59(5)	23(4)	-9(4)	-4(3)	15(4)
C(36)	28(3)	40(5)	34(4)	-14(3)	-1(3)	11(3)
C(37)	17(3)	25(4)	17(3)	6(3)	10(2)	-2(2)
C(38)	24(3)	26(4)	26(3)	-5(3)	7(3)	1(3)
C(39)	28(3)	24(4)	33(4)	0(3)	14(3)	8(3)
C(40)	23(3)	35(4)	31(4)	12(3)	11(3)	6(3)
C(41)	20(3)	46(5)	22(3)	8(3)	5(3)	1(3)
C(42)	20(3)	25(4)	18(3)	-1(3)	6(2)	3(3)
C(43)	18(3)	21(4)	20(3)	0(3)	6(2)	2(2)
C(44)	15(3)	21(4)	23(3)	-1(3)	4(2)	1(2)
C(45)	23(3)	24(4)	23(3)	5(3)	7(3)	3(3)
C(46)	26(3)	36(4)	18(3)	-1(3)	6(3)	7(3)
C(47)	21(3)	47(5)	19(3)	4(3)	-1(3)	-8(3)

C(48)	20(3)	32(4)	22(3)	2(3)	5(2)	-10(3)
C(49)	34(4)	62(6)	36(4)	-23(4)	8(3)	-16(3)
C(50)	31(4)	51(5)	44(4)	-14(4)	0(3)	-10(3)
C(51)	22(3)	39(5)	40(4)	-5(3)	3(3)	-2(3)
C(52)	21(3)	36(4)	25(3)	-4(3)	6(3)	-2(3)
C(53)	25(3)	25(4)	16(3)	-1(3)	7(2)	0(3)
C(54)	45(4)	57(5)	30(4)	-7(4)	-11(3)	20(4)
C(55)	127(8)	142(10)	39(5)	-41(6)	-39(5)	111(8)
C(56)	24(3)	27(4)	29(3)	-5(3)	4(3)	8(3)
C(57)	32(3)	35(4)	23(3)	3(3)	3(3)	3(3)
C(58)	42(4)	34(5)	33(4)	8(3)	16(3)	4(3)
C(59)	40(4)	43(5)	50(5)	15(4)	1(3)	-15(3)
C(60)	25(3)	33(4)	36(4)	-2(3)	-5(3)	-5(3)

8.6. Compound 9

Table 1. Crystal data and structure refinement for sh2221.

Identification code	sh2221	
Empirical formula	C_{112} H_{119} Al_4 O_{22} Si_8 Sn_4	
Formula weight	2624.47	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.6812(16) Å	α= 93.027(6)°.
	b = 15.3722(16) Å	β= 96.038(6)°.
	c = 29.148(3) Å	γ = 116.457(5)°.
Volume	5819.8(11) $Å^3$	
Z	2	
Density (calculated)	1.498 Mg/m^3	
Absorption coefficient	1.028 mm^{-1}	
F(000)	2662	
Crystal size	0.55 x 0.4 x 0.2 mm^3	
Theta range for data collection	1.49 to 27.10°.	
Index ranges	-18<=h<=18, -19<=k<=19, -37<=l<=37	
Reflections collected	112902	
Independent reflections	25545 [R(int) = 0.0587]	
Completeness to theta = 27.10°	99.4 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25545 / 0 / 1341	
Goodness-of-fit on F^2	2.867	
Final R indices [I>2sigma(I)]	R1 = 0.1044, wR2 = 0.2892	
R indices (all data)	R1 = 0.1339, wR2 = 0.3078	
Largest diff. peak and hole	4.836 and -3.382 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2221. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	9521(1)	12928(1)	7612(1)	23(1)
Sn(2)	10687(1)	11612(1)	8041(1)	24(1)
Sn(3)	10067(1)	11694(1)	6725(1)	27(1)
Sn(4)	7557(1)	11025(1)	6856(1)	25(1)
Al(1)	8992(2)	9282(2)	7880(1)	20(1)
Al(2)	8694(2)	9391(2)	6806(1)	23(1)
Al(3)	6884(2)	8630(2)	7354(1)	19(1)
Al(4)	8057(2)	10702(2)	7959(1)	21(1)
Si(1)	11237(2)	9329(2)	7808(1)	29(1)
Si(2)	11079(2)	9774(2)	6807(1)	33(1)
Si(3)	7386(3)	8459(2)	5838(1)	36(1)
Si(4)	5622(2)	8386(2)	6329(1)	32(1)
Si(5)	6209(2)	6497(2)	7648(1)	24(1)
Si(6)	7667(2)	7607(2)	8516(1)	27(1)
Si(7)	10189(2)	13017(2)	8832(1)	32(1)
Si(8)	7875(2)	12109(2)	8727(1)	28(1)
O(1)	8222(4)	8906(4)	7319(2)	18(1)
O(2)	9161(4)	10499(4)	8015(2)	19(1)
O(3)	7006(4)	9589(4)	7749(2)	22(1)
O(4)	8633(5)	10516(4)	6772(2)	23(1)
O(5)	10332(5)	12153(4)	7431(2)	23(1)
O(6)	8222(5)	11557(4)	7550(2)	22(1)
O(7)	8965(5)	12367(5)	6758(2)	30(2)
O(8)	10191(5)	9351(5)	7885(2)	31(2)
O(9)	11599(5)	9733(5)	7314(2)	34(2)
O(10)	10022(5)	9840(5)	6848(2)	31(2)
O(11)	8071(6)	8571(5)	6325(2)	32(2)
O(12)	6241(6)	8335(7)	5906(2)	51(2)
O(13)	6385(5)	8777(5)	6817(2)	31(2)
O(14)	6196(4)	7489(5)	7522(2)	25(1)
O(15)	6895(5)	6650(5)	8154(2)	35(2)
O(16)	8313(5)	8535(5)	8270(2)	32(2)
O(17)	7780(4)	11122(5)	8466(2)	22(1)
O(18)	9063(5)	12897(5)	8926(2)	35(2)
O(19)	10073(5)	12531(5)	8293(2)	26(1)
O(20)	5759(6)	9230(8)	8367(3)	59(2)
O(21)	5585(12)	4050(13)	9607(6)	126(6)
O(22)	7051(14)	3567(10)	5306(7)	129(6)
C(1)	12302(8)	10194(8)	8271(4)	38(2)
C(2)	12155(11)	10184(13)	8730(5)	68(4)
C(3)	12878(12)	10872(14)	9077(5)	75(5)
C(4)	13786(10)	11627(12)	8958(6)	75(5)
C(5)	13932(10)	11647(9)	8500(5)	53(3)
C(6)	13188(8)	10939(9)	8162(5)	44(3)
C(7)	11068(8)	8058(8)	7789(4)	41(3)
C(8)	10551(17)	7449(12)	8117(7)	97(7)
C(9)	10440(20)	6491(13)	8099(8)	112(8)
C(10)	10791(15)	6138(11)	7791(7)	82(5)
C(11)	11333(11)	6719(10)	7473(5)	54(3)
C(12)	11465(10)	7658(9)	7476(4)	45(3)

C(13)	10899(8)	8684(8)	6416(3)	33(2)
C(14)	9946(11)	7903(9)	6271(5)	60(4)
C(15)	9863(13)	7074(10)	6000(6)	79(5)
C(16)	10733(13)	7071(10)	5869(6)	67(4)
C(17)	11672(10)	7823(10)	6014(4)	50(3)
C(18)	11762(9)	8639(9)	6281(4)	42(3)
C(19)	12008(9)	10916(9)	6594(5)	47(3)
C(20)	12035(13)	11010(11)	6129(6)	70(5)
C(21A)	12830(20)	11950(20)	6059(10)	41(2)
C(22A)	13510(20)	12690(20)	6417(11)	41(2)
C(23A)	13450(20)	12600(20)	6861(10)	41(2)
C(21B)	12470(17)	11766(16)	5867(8)	41(2)
C(22B)	13197(17)	12605(16)	6183(7)	41(2)
C(23B)	13231(17)	12585(16)	6654(8)	41(2)
C(24)	12684(10)	11731(9)	6903(6)	67(4)
C(25)	8015(10)	9533(8)	5515(3)	39(3)
C(26)	7476(12)	9824(10)	5186(4)	55(4)
C(27)	8006(15)	10584(10)	4929(4)	68(5)
C(28)	9041(12)	11085(10)	4986(4)	56(4)
C(29)	9601(12)	10824(9)	5308(5)	58(4)
C(30)	9115(10)	10052(8)	5578(4)	45(3)
C(31)	7227(14)	7362(9)	5471(4)	64(4)
C(32A)	6300(20)	6580(20)	5242(10)	68(3)
C(33A)	6140(30)	5660(20)	4982(10)	68(3)
C(34A)	7270(30)	5780(30)	4917(10)	68(3)
C(35A)	8130(20)	6630(20)	5002(10)	68(3)
C(36A)	8220(30)	7440(20)	5307(10)	68(3)
C(32B)	7080(30)	6540(30)	5675(11)	68(3)
C(33B)	6870(30)	5680(30)	5430(10)	68(3)
C(34B)	6740(30)	5730(30)	4922(12)	68(3)
C(35B)	7420(30)	6600(30)	4771(11)	68(3)
C(36B)	7580(30)	7410(30)	5056(11)	68(3)
C(37)	5106(9)	9265(8)	6206(4)	47(3)
C(38)	4775(11)	9637(11)	6544(7)	77(5)
C(39)	4431(12)	10373(14)	6464(13)	153(15)
C(40)	4450(20)	10720(20)	6096(16)	190(20)
C(41)	4760(20)	10320(30)	5732(12)	192(19)
C(42)	5058(15)	9601(19)	5790(8)	119(9)
C(43)	4539(8)	7147(8)	6324(3)	37(2)
C(44)	4641(10)	6302(9)	6217(5)	51(3)
C(45)	3846(13)	5392(11)	6194(5)	72(4)
C(46)	2872(10)	5256(9)	6266(4)	52(3)
C(47)	2746(9)	6064(10)	6384(4)	50(3)
C(48)	3579(9)	7002(9)	6417(4)	39(2)
C(49)	4887(7)	5546(7)	7679(3)	27(2)
C(50)	4729(8)	4746(8)	7932(4)	40(3)
C(51)	3734(9)	3985(9)	7937(4)	51(3)
C(52)	2898(8)	4024(8)	7688(4)	42(3)
C(53)	3014(8)	4801(8)	7435(3)	36(2)
C(54)	4020(7)	5548(8)	7440(3)	33(2)
C(55)	6794(9)	6030(8)	7229(4)	39(2)
C(56)	6197(12)	5328(11)	6859(4)	58(3)
C(57)	6680(20)	5030(13)	6533(7)	115(10)
C(58)	7660(20)	5402(15)	6556(9)	118(10)
C(59)	8294(14)	6079(14)	6944(8)	89(7)

C(60)	7864(11)	6391(11)	7272(5)	61(4)
C(61)	6888(8)	7888(8)	8908(3)	34(2)
C(62)	5983(9)	7158(10)	9020(4)	49(3)
C(63)	5462(11)	7328(15)	9342(5)	73(5)
C(64)	5803(16)	8240(20)	9565(5)	94(7)
C(65)	6667(17)	9019(16)	9455(5)	84(6)
C(66)	7228(11)	8840(10)	9130(4)	55(3)
C(67)	8541(8)	7258(8)	8887(3)	33(2)
C(68)	8271(10)	6303(9)	8963(4)	49(3)
C(69)	8894(12)	6093(11)	9276(5)	63(4)
C(70)	9803(12)	6835(11)	9526(5)	65(4)
C(71)	10057(10)	7763(10)	9459(4)	54(3)
C(72)	9450(9)	7999(9)	9138(4)	45(3)
C(73)	10635(9)	12353(8)	9228(3)	40(3)
C(74)	10063(10)	11370(9)	9240(3)	48(3)
C(75)	10347(13)	10852(11)	9532(4)	65(4)
C(76)	11275(13)	11319(13)	9830(4)	71(5)
C(77)	11868(11)	12270(14)	9827(5)	77(5)
C(78)	11534(11)	12814(12)	9530(4)	60(4)
C(79)	11085(8)	14355(8)	8890(4)	44(3)
C(80)	10906(14)	15025(13)	9121(9)	140(12)
C(81)	11618(19)	16020(15)	9176(14)	240(20)
C(82)	12463(17)	16334(13)	8967(11)	150(12)
C(83)	12640(10)	15659(10)	8715(5)	64(4)
C(84)	11957(9)	14684(9)	8676(4)	48(3)
C(85)	7186(8)	11785(7)	9243(3)	30(2)
C(86)	6122(8)	11404(10)	9205(4)	43(3)
C(87)	5615(10)	11085(10)	9586(4)	50(3)
C(88)	6174(10)	11141(10)	10000(4)	48(3)
C(89)	7194(10)	11499(9)	10049(4)	46(3)
C(90)	7709(9)	11812(9)	9669(4)	43(3)
C(91)	7375(9)	12738(8)	8315(3)	36(2)
C(92)	6546(9)	12205(9)	7958(4)	42(3)
C(93)	6169(14)	12665(12)	7639(5)	69(4)
C(94)	6659(17)	13666(13)	7678(5)	81(6)
C(95)	7440(20)	14201(12)	8014(6)	104(8)
C(96)	7805(14)	13751(10)	8336(4)	67(4)
C(97)	8863(8)	13021(6)	6397(3)	24(2)
C(98)	8062(13)	13292(11)	6528(5)	66(4)
C(99)	9918(12)	13916(9)	6462(5)	66(4)
C(100)	8571(13)	12453(10)	5929(4)	57(4)
C(101)	4610(8)	8820(9)	8191(4)	36(2)
C(102)	4057(10)	8840(12)	8596(5)	62(4)
C(103)	4482(10)	9495(12)	7850(5)	66(4)
C(104)	4255(10)	7810(10)	7969(5)	64(4)
C(105)	6607(19)	4270(20)	9601(15)	203(19)
C(106)	7030(30)	3940(40)	9964(18)	390(50)
C(107)	5250(20)	4470(20)	9301(12)	171(14)
C(108)	4230(20)	4320(30)	9374(13)	190(16)
C(109)	7600(30)	3580(20)	4947(6)	138(13)
C(110)	8670(20)	4480(20)	5082(10)	150(12)
C(111)	6040(20)	2860(20)	5172(13)	192(18)
C(112)	5350(40)	2810(20)	5413(15)	290(40)

Table 3. Bond lengths [Å] and angles [°] for sh2221.

Sn(1)-O(6)	2.101(6)	Si(6)-C(61)	1.861(11)
Sn(1)-O(5)	2.110(6)	Si(6)-C(67)	1.867(10)
Sn(1)-O(19)	2.279(6)	Si(7)-O(18)	1.635(8)
Sn(1)-O(7)	2.516(6)	Si(7)-O(19)	1.663(7)
Sn(2)-O(5)	2.113(6)	Si(7)-C(73)	1.834(11)
Sn(2)-O(2)	2.118(6)	Si(7)-C(79)	1.871(11)
Sn(2)-O(19)	2.125(6)	Si(8)-O(17)	1.603(7)
Sn(3)-O(5)	2.079(6)	Si(8)-O(18)	1.636(7)
Sn(3)-O(4)	2.103(6)	Si(8)-C(91)	1.865(11)
Sn(3)-O(7)	2.283(7)	Si(8)-C(85)	1.869(9)
Sn(4)-O(4)	2.081(6)	O(7)-C(97)	1.533(10)
Sn(4)-O(6)	2.099(6)	O(20)-C(101)	1.530(12)
Sn(4)-O(7)	2.235(7)	O(21)-C(107)	1.30(3)
Al(1)-O(8)	1.715(7)	O(21)-C(105)	1.39(3)
Al(1)-O(16)	1.720(7)	O(22)-C(111)	1.39(3)
Al(1)-O(2)	1.790(6)	O(22)-C(109)	1.38(3)
Al(1)-O(1)	1.793(6)	C(1)-C(6)	1.379(16)
Al(2)-O(11)	1.704(7)	C(1)-C(2)	1.379(18)
Al(2)-O(10)	1.742(7)	C(2)-C(3)	1.39(2)
Al(2)-O(1)	1.775(6)	C(3)-C(4)	1.42(2)
Al(2)-O(4)	1.777(7)	C(4)-C(5)	1.38(2)
Al(3)-O(14)	1.718(7)	C(5)-C(6)	1.397(16)
Al(3)-O(13)	1.725(6)	C(7)-C(12)	1.389(17)
Al(3)-O(3)	1.754(7)	C(7)-C(8)	1.408(19)
Al(3)-O(1)	1.830(6)	C(8)-C(9)	1.40(2)
Al(4)-O(3)	1.738(6)	C(9)-C(10)	1.29(3)
Al(4)-O(17)	1.738(6)	C(10)-C(11)	1.38(2)
Al(4)-O(6)	1.776(6)	C(11)-C(12)	1.367(17)
Al(4)-O(2)	1.776(6)	C(13)-C(14)	1.379(16)
Si(1)-O(8)	1.588(7)	C(13)-C(18)	1.394(15)
Si(1)-O(9)	1.644(7)	C(14)-C(15)	1.414(18)
Si(1)-C(7)	1.853(12)	C(15)-C(16)	1.37(2)
Si(1)-C(1)	1.884(11)	C(16)-C(17)	1.35(2)
Si(2)-O(9)	1.610(7)	C(17)-C(18)	1.387(18)
Si(2)-O(10)	1.615(7)	C(19)-C(20)	1.372(19)
Si(2)-C(19)	1.868(11)	C(19)-C(24)	1.40(2)
Si(2)-C(13)	1.876(11)	C(20)-C(21B)	1.37(2)
Si(3)-O(11)	1.607(7)	C(20)-C(21A)	1.44(3)
Si(3)-O(12)	1.640(10)	C(21A)-C(22A)	1.42(4)
Si(3)-C(25)	1.858(10)	C(22A)-C(23A)	1.32(4)
Si(3)-C(31)	1.857(14)	C(23A)-C(24)	1.34(3)
Si(4)-O(13)	1.618(6)	C(21B)-C(22B)	1.45(3)
Si(4)-O(12)	1.625(9)	C(22B)-C(23B)	1.37(3)
Si(4)-C(37)	1.852(13)	C(23B)-C(24)	1.48(2)
Si(4)-C(43)	1.858(11)	C(25)-C(26)	1.395(18)
Si(5)-O(14)	1.595(7)	C(25)-C(30)	1.432(18)
Si(5)-O(15)	1.638(6)	C(26)-C(27)	1.391(16)
Si(5)-C(55)	1.850(11)	C(27)-C(28)	1.35(2)
Si(5)-C(49)	1.853(10)	C(28)-C(29)	1.37(2)
Si(6)-O(16)	1.579(7)	C(29)-C(30)	1.413(16)
Si(6)-O(15)	1.630(7)	C(31)-C(36B)	1.36(3)

C(31)-C(32B)	1.36(4)	C(80)-C(81)	1.40(2)
C(31)-C(32A)	1.41(3)	C(81)-C(82)	1.34(3)
C(31)-C(36A)	1.53(4)	C(82)-C(83)	1.37(3)
C(32A)-C(33A)	1.48(4)	C(83)-C(84)	1.373(18)
C(33A)-C(34A)	1.61(5)	C(85)-C(90)	1.378(14)
C(34A)-C(35A)	1.34(4)	C(85)-C(86)	1.391(15)
C(35A)-C(36A)	1.44(4)	C(86)-C(87)	1.391(15)
C(32B)-C(33B)	1.36(5)	C(87)-C(88)	1.361(17)
C(33B)-C(34B)	1.48(4)	C(88)-C(89)	1.333(18)
C(34B)-C(35B)	1.39(5)	C(89)-C(90)	1.392(15)
C(35B)-C(36B)	1.37(5)	C(91)-C(96)	1.390(16)
C(37)-C(42)	1.349(19)	C(91)-C(92)	1.411(16)
C(37)-C(38)	1.35(2)	C(92)-C(93)	1.407(17)
C(38)-C(39)	1.45(3)	C(93)-C(94)	1.37(2)
C(39)-C(40)	1.22(5)	C(94)-C(95)	1.34(3)
C(40)-C(41)	1.40(5)	C(95)-C(96)	1.40(2)
C(41)-C(42)	1.38(4)	C(97)-C(98)	1.490(17)
C(43)-C(48)	1.385(16)	C(97)-C(100)	1.492(14)
C(43)-C(44)	1.396(17)	C(97)-C(99)	1.530(16)
C(44)-C(45)	1.357(19)	C(101)-C(104)	1.485(18)
C(45)-C(46)	1.39(2)	C(101)-C(102)	1.506(15)
C(46)-C(47)	1.37(2)	C(101)-C(103)	1.531(17)
C(47)-C(48)	1.405(16)	C(105)-C(106)	1.40(4)
C(49)-C(54)	1.386(14)	C(107)-C(108)	1.45(4)
C(49)-C(50)	1.410(13)	C(109)-C(110)	1.56(4)
C(50)-C(51)	1.410(15)	C(111)-C(112)	1.28(5)
C(51)-C(52)	1.385(17)		
C(52)-C(53)	1.393(16)	O(6)-Sn(1)-O(5)	86.3(2)
C(53)-C(54)	1.408(14)	O(6)-Sn(1)-O(19)	87.0(2)
C(55)-C(56)	1.389(18)	O(5)-Sn(1)-O(19)	74.2(2)
C(55)-C(60)	1.402(18)	O(6)-Sn(1)-O(7)	73.2(2)
C(56)-C(57)	1.41(2)	O(5)-Sn(1)-O(7)	73.8(2)
C(57)-C(58)	1.29(4)	O(19)-Sn(1)-O(7)	143.2(2)
C(58)-C(59)	1.42(3)	O(5)-Sn(2)-O(2)	93.4(2)
C(59)-C(60)	1.37(2)	O(5)-Sn(2)-O(19)	77.5(2)
C(61)-C(62)	1.390(16)	O(2)-Sn(2)-O(19)	83.5(2)
C(61)-C(66)	1.412(17)	O(5)-Sn(3)-O(4)	92.6(2)
C(62)-C(63)	1.355(19)	O(5)-Sn(3)-O(7)	79.6(2)
C(63)-C(64)	1.36(3)	O(4)-Sn(3)-O(7)	74.8(2)
C(64)-C(65)	1.39(3)	O(4)-Sn(4)-O(6)	90.6(2)
C(65)-C(66)	1.41(2)	O(4)-Sn(4)-O(7)	76.3(2)
C(67)-C(68)	1.377(16)	O(6)-Sn(4)-O(7)	79.5(2)
C(67)-C(72)	1.403(14)	O(8)-Al(1)-O(16)	112.5(4)
C(68)-C(69)	1.374(17)	O(8)-Al(1)-O(2)	107.3(3)
C(69)-C(70)	1.40(2)	O(16)-Al(1)-O(2)	110.3(3)
C(70)-C(71)	1.34(2)	O(8)-Al(1)-O(1)	114.0(3)
C(71)-C(72)	1.395(16)	O(16)-Al(1)-O(1)	109.0(3)
C(73)-C(74)	1.367(16)	O(2)-Al(1)-O(1)	103.2(3)
C(73)-C(78)	1.370(16)	O(11)-Al(2)-O(10)	111.5(4)
C(74)-C(75)	1.350(18)	O(11)-Al(2)-O(1)	111.9(3)
C(75)-C(76)	1.39(2)	O(10)-Al(2)-O(1)	112.2(3)
C(76)-C(77)	1.33(2)	O(11)-Al(2)-O(4)	113.5(3)
C(77)-C(78)	1.43(2)	O(10)-Al(2)-O(4)	98.5(3)
C(79)-C(80)	1.34(2)	O(1)-Al(2)-O(4)	108.6(3)
C(79)-C(84)	1.381(16)	O(14)-Al(3)-O(13)	113.3(3)

O(14)-Al(3)-O(3)	113.8(3)	O(17)-Si(8)-C(91)	110.1(4)
O(13)-Al(3)-O(3)	107.5(3)	O(18)-Si(8)-C(91)	106.1(5)
O(14)-Al(3)-O(1)	112.1(3)	O(17)-Si(8)-C(85)	107.9(4)
O(13)-Al(3)-O(1)	106.5(3)	O(18)-Si(8)-C(85)	106.2(4)
O(3)-Al(3)-O(1)	102.9(3)	C(91)-Si(8)-C(85)	113.6(5)
O(3)-Al(4)-O(17)	107.0(3)	Al(2)-O(1)-Al(1)	123.3(3)
O(3)-Al(4)-O(6)	109.8(3)	Al(2)-O(1)-Al(3)	115.5(3)
O(17)-Al(4)-O(6)	108.8(3)	Al(1)-O(1)-Al(3)	111.9(3)
O(3)-Al(4)-O(2)	107.2(3)	Al(4)-O(2)-Al(1)	118.5(3)
O(17)-Al(4)-O(2)	116.3(3)	Al(4)-O(2)-Sn(2)	124.4(3)
O(6)-Al(4)-O(2)	107.7(3)	Al(1)-O(2)-Sn(2)	114.8(3)
O(8)-Si(1)-O(9)	111.3(4)	Al(4)-O(3)-Al(3)	131.1(4)
O(8)-Si(1)-C(7)	110.1(5)	Al(2)-O(4)-Sn(4)	136.6(3)
O(9)-Si(1)-C(7)	107.5(5)	Al(2)-O(4)-Sn(3)	112.8(3)
O(8)-Si(1)-C(1)	109.6(4)	Sn(4)-O(4)-Sn(3)	110.0(3)
O(9)-Si(1)-C(1)	105.2(5)	Sn(3)-O(5)-Sn(1)	113.1(3)
C(7)-Si(1)-C(1)	113.0(5)	Sn(3)-O(5)-Sn(2)	134.7(3)
O(9)-Si(2)-O(10)	109.5(4)	Sn(1)-O(5)-Sn(2)	106.8(3)
O(9)-Si(2)-C(19)	106.4(5)	Al(4)-O(6)-Sn(4)	118.5(3)
O(10)-Si(2)-C(19)	109.1(5)	Al(4)-O(6)-Sn(1)	122.9(3)
O(9)-Si(2)-C(13)	108.6(4)	Sn(4)-O(6)-Sn(1)	112.5(3)
O(10)-Si(2)-C(13)	113.5(4)	C(97)-O(7)-Sn(4)	118.4(5)
C(19)-Si(2)-C(13)	109.5(5)	C(97)-O(7)-Sn(3)	121.9(5)
O(11)-Si(3)-O(12)	111.9(4)	Sn(4)-O(7)-Sn(3)	98.6(2)
O(11)-Si(3)-C(25)	111.4(5)	C(97)-O(7)-Sn(1)	123.7(5)
O(12)-Si(3)-C(25)	108.2(5)	Sn(4)-O(7)-Sn(1)	94.4(2)
O(11)-Si(3)-C(31)	109.4(6)	Sn(3)-O(7)-Sn(1)	93.3(2)
O(12)-Si(3)-C(31)	108.3(7)	Si(1)-O(8)-Al(1)	171.0(5)
C(25)-Si(3)-C(31)	107.5(5)	Si(2)-O(9)-Si(1)	138.4(4)
O(13)-Si(4)-O(12)	110.8(4)	Si(2)-O(10)-Al(2)	155.6(5)
O(13)-Si(4)-C(37)	108.6(5)	Si(3)-O(11)-Al(2)	140.1(5)
O(12)-Si(4)-C(37)	107.5(6)	Si(4)-O(12)-Si(3)	138.3(5)
O(13)-Si(4)-C(43)	113.2(4)	Si(4)-O(13)-Al(3)	153.7(5)
O(12)-Si(4)-C(43)	107.2(5)	Si(5)-O(14)-Al(3)	146.1(4)
C(37)-Si(4)-C(43)	109.5(5)	Si(6)-O(15)-Si(5)	133.8(5)
O(14)-Si(5)-O(15)	111.5(4)	Si(6)-O(16)-Al(1)	162.9(5)
O(14)-Si(5)-C(55)	112.7(4)	Si(8)-O(17)-Al(4)	140.4(4)
O(15)-Si(5)-C(55)	105.4(5)	Si(7)-O(18)-Si(8)	134.5(5)
O(14)-Si(5)-C(49)	110.4(4)	Si(7)-O(19)-Sn(2)	129.3(4)
O(15)-Si(5)-C(49)	107.3(4)	Si(7)-O(19)-Sn(1)	128.9(4)
C(55)-Si(5)-C(49)	109.3(5)	Sn(2)-O(19)-Sn(1)	100.6(2)
O(16)-Si(6)-O(15)	113.7(4)	C(107)-O(21)-C(105)	113(2)
O(16)-Si(6)-C(61)	110.1(5)	C(111)-O(22)-C(109)	108(3)
O(15)-Si(6)-C(61)	108.3(4)	C(6)-C(1)-C(2)	117.5(11)
O(16)-Si(6)-C(67)	110.3(4)	C(6)-C(1)-Si(1)	121.8(9)
O(15)-Si(6)-C(67)	107.4(4)	C(2)-C(1)-Si(1)	120.2(9)
C(61)-Si(6)-C(67)	106.7(4)	C(1)-C(2)-C(3)	122.1(15)
O(18)-Si(7)-O(19)	108.2(3)	C(2)-C(3)-C(4)	119.6(15)
O(18)-Si(7)-C(73)	110.9(5)	C(5)-C(4)-C(3)	118.6(13)
O(19)-Si(7)-C(73)	107.9(5)	C(4)-C(5)-C(6)	120.0(13)
O(18)-Si(7)-C(79)	107.5(5)	C(1)-C(6)-C(5)	122.2(13)
O(19)-Si(7)-C(79)	109.4(4)	C(12)-C(7)-C(8)	115.8(12)
C(73)-Si(7)-C(79)	112.9(5)	C(12)-C(7)-Si(1)	123.8(9)
O(17)-Si(8)-O(18)	113.0(4)	C(8)-C(7)-Si(1)	120.4(10)
		C(9)-C(8)-C(7)	119.4(16)

C(10)-C(9)-C(8)	122.7(17)	C(34B)-C(35B)-C(36B)	113(3)
C(9)-C(10)-C(11)	119.9(15)	C(31)-C(36B)-C(35B)	123(3)
C(12)-C(11)-C(10)	119.8(13)	C(42)-C(37)-C(38)	115.3(17)
C(11)-C(12)-C(7)	122.4(13)	C(42)-C(37)-Si(4)	124.1(15)
C(14)-C(13)-C(18)	118.6(11)	C(38)-C(37)-Si(4)	120.6(11)
C(14)-C(13)-Si(2)	122.4(9)	C(37)-C(38)-C(39)	122(2)
C(18)-C(13)-Si(2)	119.0(9)	C(40)-C(39)-C(38)	123(3)
C(13)-C(14)-C(15)	119.9(13)	C(39)-C(40)-C(41)	117(2)
C(16)-C(15)-C(14)	119.4(14)	C(42)-C(41)-C(40)	122(2)
C(17)-C(16)-C(15)	121.2(14)	C(37)-C(42)-C(41)	121(3)
C(16)-C(17)-C(18)	119.8(12)	C(48)-C(43)-C(44)	115.9(10)
C(17)-C(18)-C(13)	121.0(12)	C(48)-C(43)-Si(4)	122.4(9)
C(20)-C(19)-C(24)	116.8(12)	C(44)-C(43)-Si(4)	121.7(9)
C(20)-C(19)-Si(2)	122.0(11)	C(45)-C(44)-C(43)	122.4(13)
C(24)-C(19)-Si(2)	121.2(10)	C(44)-C(45)-C(46)	121.3(15)
C(21B)-C(20)-C(19)	135.9(18)	C(47)-C(46)-C(45)	118.1(12)
C(21B)-C(20)-C(21A)	27.7(11)	C(46)-C(47)-C(48)	120.2(12)
C(19)-C(20)-C(21A)	110.8(19)	C(43)-C(48)-C(47)	122.0(12)
C(22A)-C(21A)-C(20)	125(2)	C(54)-C(49)-C(50)	116.8(9)
C(23A)-C(22A)-C(21A)	123(3)	C(54)-C(49)-Si(5)	122.9(7)
C(22A)-C(23A)-C(24)	108(3)	C(50)-C(49)-Si(5)	120.2(8)
C(20)-C(21B)-C(22B)	107.0(19)	C(51)-C(50)-C(49)	121.2(10)
C(23B)-C(22B)-C(21B)	121(2)	C(52)-C(51)-C(50)	119.3(10)
C(22B)-C(23B)-C(24)	127(2)	C(51)-C(52)-C(53)	121.6(10)
C(23A)-C(24)-C(19)	134.9(19)	C(52)-C(53)-C(54)	117.2(10)
C(23A)-C(24)-C(23B)	26.0(12)	C(49)-C(54)-C(53)	123.8(10)
C(19)-C(24)-C(23B)	111.2(16)	C(56)-C(55)-C(60)	117.9(12)
C(26)-C(25)-C(30)	117.5(10)	C(56)-C(55)-Si(5)	121.6(10)
C(26)-C(25)-Si(3)	123.4(10)	C(60)-C(55)-Si(5)	120.6(10)
C(30)-C(25)-Si(3)	118.9(9)	C(55)-C(56)-C(57)	119.8(17)
C(27)-C(26)-C(25)	120.1(14)	C(58)-C(57)-C(56)	122(2)
C(28)-C(27)-C(26)	123.2(15)	C(57)-C(58)-C(59)	119.2(16)
C(27)-C(28)-C(29)	118.5(11)	C(60)-C(59)-C(58)	120.4(17)
C(28)-C(29)-C(30)	121.4(13)	C(59)-C(60)-C(55)	120.1(17)
C(29)-C(30)-C(25)	119.3(13)	C(62)-C(61)-C(66)	117.0(12)
C(36B)-C(31)-C(32B)	115(2)	C(62)-C(61)-Si(6)	121.5(9)
C(36B)-C(31)-C(32A)	86(2)	C(66)-C(61)-Si(6)	121.4(9)
C(32B)-C(31)-C(32A)	72(2)	C(63)-C(62)-C(61)	122.4(14)
C(36B)-C(31)-C(36A)	44.3(17)	C(62)-C(63)-C(64)	120.7(16)
C(32B)-C(31)-C(36A)	92(2)	C(63)-C(64)-C(65)	120.4(15)
C(32A)-C(31)-C(36A)	116(2)	C(64)-C(65)-C(66)	119.0(17)
C(36B)-C(31)-Si(3)	123.0(17)	C(65)-C(66)-C(61)	120.3(15)
C(32B)-C(31)-Si(3)	118.7(16)	C(68)-C(67)-C(72)	118.5(10)
C(32A)-C(31)-Si(3)	127.9(18)	C(68)-C(67)-Si(6)	122.2(8)
C(36A)-C(31)-Si(3)	114.8(15)	C(72)-C(67)-Si(6)	118.9(9)
C(31)-C(32A)-C(33A)	129(3)	C(69)-C(68)-C(67)	120.0(12)
C(32A)-C(33A)-C(34A)	106(3)	C(68)-C(69)-C(70)	121.4(13)
C(35A)-C(34A)-C(33A)	124(3)	C(71)-C(70)-C(69)	118.7(12)
C(34A)-C(35A)-C(36A)	122(3)	C(70)-C(71)-C(72)	121.3(12)
C(35A)-C(36A)-C(31)	118(3)	C(71)-C(72)-C(67)	120.1(11)
C(31)-C(32B)-C(33B)	123(3)	C(74)-C(73)-C(78)	117.1(11)
C(32B)-C(33B)-C(34B)	112(3)	C(74)-C(73)-Si(7)	120.8(8)
C(35B)-C(34B)-C(33B)	116(3)	C(78)-C(73)-Si(7)	122.1(10)

C(75)-C(74)-C(73)	123.1(12)	C(80)-C(79)-Si(7)	122.7(11)
C(74)-C(75)-C(76)	119.7(14)	C(84)-C(79)-Si(7)	119.6(9)
C(77)-C(76)-C(75)	119.7(13)	C(79)-C(80)-C(81)	121.3(16)
C(76)-C(77)-C(78)	119.8(13)	C(82)-C(81)-C(80)	120.6(18)
C(73)-C(78)-C(77)	120.5(14)	C(81)-C(82)-C(83)	118.7(16)
C(80)-C(79)-C(84)	117.7(12)		
C(82)-C(83)-C(84)	120.2(15)	C(98)-C(97)-C(100)	112.8(11)
C(83)-C(84)-C(79)	121.4(13)	C(98)-C(97)-C(99)	110.8(11)
C(90)-C(85)-C(86)	117.4(9)	C(100)-C(97)-C(99)	113.8(10)
C(90)-C(85)-Si(8)	120.4(8)	C(98)-C(97)-O(7)	105.9(8)
C(86)-C(85)-Si(8)	121.9(7)	C(100)-C(97)-O(7)	108.1(7)
C(87)-C(86)-C(85)	121.0(10)	C(99)-C(97)-O(7)	104.6(8)
C(88)-C(87)-C(86)	118.9(12)	C(104)-C(101)-C(102)	112.0(11)
C(89)-C(88)-C(87)	121.7(10)	C(104)-C(101)-O(20)	107.1(9)
C(88)-C(89)-C(90)	119.8(11)	C(102)-C(101)-O(20)	108.9(9)
C(85)-C(90)-C(89)	121.1(11)	C(104)-C(101)-C(103)	112.5(12)
C(96)-C(91)-C(92)	116.2(11)	C(102)-C(101)-C(103)	108.7(11)
C(96)-C(91)-Si(8)	122.4(10)	O(20)-C(101)-C(103)	107.5(9)
C(92)-C(91)-Si(8)	121.4(8)	O(21)-C(105)-C(106)	114(3)
C(93)-C(92)-C(91)	122.4(13)	O(21)-C(107)-C(108)	109(3)
C(94)-C(93)-C(92)	117.4(15)	O(22)-C(109)-C(110)	105.7(19)
C(95)-C(94)-C(93)	122.3(14)	C(112)-C(111)-O(22)	120(4)
C(94)-C(95)-C(96)	120.6(15)		
C(95)-C(96)-C(91)	121.1(15)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2221. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	25(1)	15(1)	29(1)	4(1)	4(1)	9(1)
Sn(2)	15(1)	16(1)	38(1)	5(1)	3(1)	5(1)
Sn(3)	30(1)	20(1)	33(1)	8(1)	13(1)	10(1)
Sn(4)	25(1)	23(1)	30(1)	4(1)	1(1)	13(1)
Al(1)	17(1)	13(1)	28(1)	3(1)	1(1)	5(1)
Al(2)	23(1)	20(1)	28(1)	3(1)	7(1)	11(1)
Al(3)	15(1)	15(1)	26(1)	4(1)	1(1)	4(1)
Al(4)	19(1)	17(1)	28(1)	7(1)	6(1)	8(1)
Si(1)	18(1)	22(1)	50(2)	1(1)	1(1)	12(1)
Si(2)	27(1)	23(1)	52(2)	8(1)	16(1)	12(1)
Si(3)	52(2)	23(1)	25(1)	2(1)	9(1)	10(1)
Si(4)	28(1)	31(2)	28(1)	7(1)	-3(1)	7(1)
Si(5)	18(1)	17(1)	31(1)	6(1)	4(1)	3(1)
Si(6)	22(1)	22(1)	30(1)	9(1)	1(1)	5(1)
Si(7)	28(1)	26(1)	28(1)	-8(1)	2(1)	2(1)
Si(8)	27(1)	25(1)	27(1)	0(1)	6(1)	9(1)
O(1)	19(3)	14(3)	22(3)	8(2)	1(2)	8(2)
O(2)	15(3)	10(3)	28(3)	7(2)	2(2)	4(2)
O(3)	15(3)	21(3)	30(3)	9(2)	11(2)	4(2)
O(4)	26(3)	19(3)	28(3)	8(2)	8(2)	13(3)
O(5)	19(3)	14(3)	32(3)	5(2)	8(2)	3(2)
O(6)	22(3)	18(3)	29(3)	5(2)	2(2)	13(3)
O(7)	44(4)	25(4)	33(3)	13(3)	12(3)	22(3)
O(8)	17(3)	39(4)	41(4)	2(3)	0(2)	17(3)
O(9)	24(3)	33(4)	48(4)	3(3)	8(3)	16(3)
O(10)	30(4)	28(4)	40(4)	12(3)	12(3)	15(3)
O(11)	40(4)	19(3)	36(4)	6(3)	13(3)	11(3)
O(12)	41(4)	65(6)	28(4)	19(4)	4(3)	6(4)
O(13)	21(3)	37(4)	29(3)	7(3)	-3(2)	9(3)
O(14)	15(3)	19(3)	32(3)	1(2)	1(2)	2(2)
O(15)	29(4)	27(4)	34(3)	13(3)	-5(3)	0(3)
O(16)	23(3)	25(4)	35(3)	9(3)	0(3)	-2(3)
O(17)	21(3)	26(3)	23(3)	4(2)	6(2)	14(3)
O(18)	28(4)	27(4)	41(4)	-7(3)	9(3)	5(3)
O(19)	22(3)	20(3)	33(3)	-2(2)	1(2)	10(3)
O(20)	34(5)	78(7)	59(5)	5(5)	6(4)	21(5)
O(21)	80(10)	136(15)	144(13)	54(11)	-6(9)	33(10)
O(22)	122(13)	55(8)	198(17)	3(9)	-18(12)	39(9)
C(1)	21(5)	33(6)	57(6)	2(5)	1(4)	13(4)
C(2)	39(7)	99(13)	66(9)	9(8)	-5(6)	33(8)
C(3)	51(9)	94(13)	69(9)	-18(8)	-9(7)	28(9)
C(4)	31(7)	68(11)	101(12)	-23(9)	-17(7)	11(7)
C(5)	35(6)	36(7)	83(9)	2(6)	-5(6)	14(5)
C(6)	22(5)	35(6)	75(8)	-4(5)	-8(5)	16(5)
C(7)	27(5)	34(6)	60(7)	4(5)	1(4)	13(5)
C(8)	137(18)	46(9)	135(16)	27(10)	86(14)	49(11)
C(9)	170(20)	43(10)	152(18)	47(11)	82(17)	53(13)
C(10)	94(13)	34(8)	133(15)	4(9)	20(11)	40(9)
C(11)	62(8)	46(8)	65(8)	-13(6)	-11(6)	41(7)
C(12)	52(7)	35(6)	52(6)	-2(5)	-6(5)	26(6)
C(13)	31(5)	30(5)	42(5)	12(4)	16(4)	13(4)

C(14)	49(7)	32(7)	97(10)	-2(6)	40(7)	12(6)
C(15)	68(10)	29(7)	127(14)	-13(8)	48(9)	5(7)
C(16)	77(11)	33(7)	94(11)	2(7)	35(8)	23(7)
C(17)	59(8)	62(9)	53(7)	21(6)	31(6)	44(7)
C(18)	47(7)	47(7)	47(6)	20(5)	24(5)	28(6)
C(19)	40(6)	30(6)	82(8)	21(6)	33(6)	19(5)
C(20)	78(10)	47(8)	106(11)	32(8)	68(9)	34(8)
C(24)	38(7)	21(6)	145(14)	17(7)	46(8)	9(5)
C(25)	77(8)	25(5)	24(5)	5(4)	25(5)	27(6)
C(26)	81(10)	44(7)	36(6)	15(5)	23(6)	20(7)
C(27)	127(15)	40(7)	39(6)	23(5)	23(7)	34(9)
C(28)	82(10)	40(7)	46(7)	20(5)	36(7)	21(7)
C(29)	67(9)	31(6)	65(8)	6(6)	35(7)	6(6)
C(30)	64(8)	30(6)	43(6)	10(5)	29(5)	18(6)
C(31)	118(13)	31(7)	38(6)	7(5)	11(7)	29(8)
C(37)	32(6)	27(6)	62(7)	9(5)	-18(5)	1(5)
C(38)	49(8)	44(8)	118(13)	-29(8)	-40(8)	18(7)
C(39)	27(8)	41(10)	360(40)	-60(17)	-44(15)	17(8)
C(40)	110(20)	92(19)	420(60)	130(30)	70(30)	80(18)
C(41)	170(30)	260(40)	270(40)	210(40)	110(30)	170(30)
C(42)	91(14)	170(20)	133(17)	113(17)	31(12)	83(16)
C(43)	38(6)	34(6)	30(5)	2(4)	-3(4)	11(5)
C(44)	44(7)	38(7)	74(8)	5(6)	19(6)	20(6)
C(45)	77(11)	33(7)	91(11)	3(7)	23(8)	9(7)
C(46)	51(7)	33(7)	56(7)	10(5)	10(5)	3(6)
C(47)	31(6)	64(9)	40(6)	20(6)	6(4)	7(6)
C(48)	41(6)	37(6)	41(6)	5(4)	6(4)	18(5)
C(49)	32(5)	17(4)	30(5)	4(3)	10(4)	8(4)
C(50)	24(5)	25(5)	65(7)	17(5)	5(4)	6(4)
C(51)	37(6)	28(6)	76(8)	23(6)	10(5)	1(5)
C(52)	23(5)	33(6)	53(6)	7(5)	8(4)	-2(4)
C(53)	25(5)	39(6)	41(5)	4(4)	4(4)	11(4)
C(54)	23(5)	30(5)	40(5)	1(4)	4(4)	6(4)
C(55)	52(7)	21(5)	53(6)	17(4)	27(5)	20(5)
C(56)	75(10)	53(8)	53(7)	1(6)	23(6)	33(8)
C(57)	200(30)	44(10)	113(15)	8(9)	100(17)	45(14)
C(58)	180(20)	56(12)	160(20)	28(13)	130(20)	64(15)
C(59)	78(11)	73(12)	171(18)	69(13)	87(12)	62(10)
C(60)	59(8)	59(9)	92(10)	37(8)	35(7)	42(8)
C(61)	32(5)	35(6)	37(5)	7(4)	-1(4)	17(5)
C(62)	33(6)	52(8)	62(7)	16(6)	9(5)	17(6)
C(63)	41(8)	112(15)	60(9)	4(9)	14(6)	29(9)
C(64)	94(14)	190(30)	50(9)	20(12)	17(9)	108(17)
C(65)	124(17)	107(15)	59(9)	-16(9)	-15(9)	95(14)
C(66)	61(8)	51(8)	63(8)	3(6)	1(6)	36(7)
C(67)	30(5)	42(6)	25(4)	10(4)	1(4)	16(5)
C(68)	56(7)	44(7)	49(7)	1(5)	-10(5)	27(6)
C(69)	78(10)	44(8)	70(9)	9(6)	-9(7)	35(8)
C(70)	81(10)	67(10)	57(8)	2(7)	-21(7)	50(9)
C(71)	46(7)	58(8)	54(7)	-7(6)	-21(5)	28(6)
C(72)	36(6)	39(6)	50(6)	5(5)	-11(5)	13(5)
C(73)	46(6)	30(6)	34(5)	6(4)	-1(4)	8(5)
C(74)	69(8)	42(7)	27(5)	4(4)	-4(5)	23(6)
C(75)	93(11)	56(9)	34(6)	16(6)	3(6)	26(8)
C(76)	77(10)	87(12)	49(7)	34(8)	-3(7)	39(9)

C(77)	46(8)	108(14)	54(8)	32(8)	-8(6)	15(9)
C(78)	54(8)	69(9)	46(7)	19(6)	-6(6)	19(7)
C(79)	28(5)	24(5)	62(7)	-14(5)	7(5)	-2(4)
C(80)	65(11)	53(11)	250(30)	-80(14)	80(15)	-25(9)
C(81)	104(18)	40(11)	510(60)	-120(20)	140(30)	-21(12)
C(82)	74(14)	22(8)	320(40)	-20(14)	51(19)	-6(9)
C(83)	36(7)	43(8)	98(11)	12(7)	20(7)	2(6)
C(84)	40(6)	43(7)	43(6)	0(5)	9(5)	3(5)
C(85)	34(5)	31(5)	27(4)	4(4)	11(4)	15(4)
C(86)	31(6)	57(8)	40(6)	8(5)	10(4)	19(5)
C(87)	45(7)	68(9)	42(6)	12(6)	18(5)	26(6)
C(88)	52(7)	56(8)	39(6)	16(5)	20(5)	24(6)
C(89)	59(8)	50(7)	31(5)	6(5)	8(5)	26(6)
C(90)	45(6)	53(7)	36(5)	13(5)	11(4)	24(6)
C(91)	49(6)	24(5)	40(5)	4(4)	15(4)	19(5)
C(92)	38(6)	43(7)	52(6)	15(5)	5(5)	23(5)
C(93)	98(12)	75(11)	55(8)	21(7)	5(7)	58(10)
C(94)	154(18)	76(11)	55(9)	29(8)	24(10)	87(13)
C(95)	220(30)	39(9)	69(10)	19(8)	29(13)	67(13)
C(96)	116(13)	33(7)	47(7)	5(5)	9(7)	32(8)
C(97)	47(6)	9(4)	27(4)	4(3)	10(4)	21(4)
C(98)	99(12)	55(9)	75(9)	28(7)	29(8)	58(9)
C(99)	81(10)	30(7)	73(9)	34(6)	14(7)	10(7)
C(100)	103(11)	48(8)	33(6)	5(5)	-2(6)	47(8)
C(101)	23(5)	46(6)	52(6)	15(5)	16(4)	24(5)
C(102)	34(7)	76(10)	75(9)	21(7)	29(6)	20(7)
C(103)	34(7)	79(11)	96(10)	39(9)	20(6)	31(7)
C(104)	29(6)	52(9)	102(11)	-2(7)	17(6)	10(6)
C(105)	60(14)	140(30)	390(50)	120(30)	0(20)	28(16)
C(106)	190(40)	410(80)	500(90)	310(70)	-90(50)	90(50)
C(107)	160(30)	120(20)	250(40)	120(20)	40(30)	80(20)
C(108)	80(18)	170(30)	340(50)	90(30)	50(20)	70(20)
C(109)	260(40)	210(30)	41(9)	19(13)	32(14)	190(30)
C(110)	120(20)	140(30)	200(30)	30(20)	70(20)	60(20)
C(111)	120(30)	110(20)	210(30)	10(20)	-50(20)	-50(20)
C(112)	350(70)	47(15)	390(60)	-30(20)	270(60)	-30(30)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for sh2221.

	x	y	z	U(eq)
H(3)	6391	9482	7868	27
H(2)	11540	9690	8812	82
H(3A)	12764	10836	9392	91
H(4)	14284	12109	9191	89
H(5)	14540	12143	8413	64
H(6)	13295	10972	7846	53
H(8)	10279	7683	8349	116
H(9)	10092	6088	8323	134
H(10)	10676	5478	7783	99
H(11)	11615	6468	7253	65
H(12)	11842	8050	7255	54
H(14)	9345	7923	6353	72

H(15)	9212	6523	5910	95
H(16)	10673	6529	5672	80
H(17)	12269	7794	5933	59
H(18)	12423	9176	6374	51
H(20)	11590	10520	5887	83
H(21A)	12902	12092	5748	50
H(22A)	14024	13274	6331	50
H(23A)	13886	13083	7110	50
H(21B)	12323	11743	5540	50
H(22B)	13656	13176	6063	50
H(23B)	13652	13188	6841	50
H(24)	12573	11644	7216	80
H(26)	6745	9502	5137	66
H(27)	7620	10759	4703	82
H(28)	9376	11606	4807	67
H(29)	10331	11169	5350	70
H(30)	9513	9880	5799	54
H(32A)	5701	6662	5257	82
H(33A)	5502	5110	4874	82
H(34A)	7321	5212	4812	82
H(35A)	8708	6699	4856	82
H(36A)	8858	7995	5403	82
H(32B)	7121	6572	6004	82
H(33B)	6804	5114	5567	82
H(34B)	6232	5205	4713	82
H(35B)	7729	6626	4500	82
H(36B)	7968	8034	4959	82
H(38)	4768	9411	6841	93
H(39)	4178	10594	6709	183
H(40)	4272	11238	6057	224
H(41)	4757	10561	5437	230
H(42)	5235	9335	5533	143
H(44)	5291	6366	6157	61
H(45)	3958	4838	6128	87
H(46)	2310	4619	6234	63
H(47)	2093	5990	6443	60
H(48)	3480	7554	6507	47
H(50)	5303	4719	8101	48
H(51)	3638	3451	8110	61
H(52)	2229	3507	7690	50
H(53)	2438	4825	7265	44
H(54)	4109	6085	7271	40
H(56)	5469	5049	6826	70
H(57)	6259	4537	6286	138
H(58)	7960	5226	6317	142
H(59)	9019	6317	6978	106
H(60)	8292	6853	7528	73
H(62)	5721	6515	8866	59
H(63)	4853	6806	9412	87
H(64)	5445	8344	9799	112
H(65)	6878	9663	9595	101
H(66)	7837	9363	9061	67
H(68)	7654	5790	8800	59
H(69)	8704	5431	9323	76
H(70)	10231	6680	9739	78

H(71)	10661	8273	9633	65
H(72)	9654	8663	9089	53
H(74)	9437	11036	9033	58
H(75)	9916	10173	9533	77
H(76)	11482	10958	10034	85
H(77)	12511	12588	10023	93
H(78)	11940	13501	9542	72
H(80)	10285	14824	9251	168
H(81)	11501	16475	9363	283
H(82)	12930	17011	8993	180
H(83)	13237	15867	8566	76
H(84)	12087	14225	8499	57
H(86)	5737	11360	8914	51
H(87)	4889	10832	9558	60
H(88)	5829	10918	10260	58
H(89)	7568	11541	10343	55
H(90)	8434	12048	9704	52
H(92)	6231	11511	7932	51
H(93)	5597	12296	7406	82
H(94)	6439	13991	7457	97
H(95)	7740	14895	8035	125
H(96)	8360	14143	8572	80
H(98A)	7803	13523	6261	98
H(98B)	8361	13813	6788	98
H(98C)	7494	12719	6620	98
H(99A)	10442	13712	6402	99
H(99B)	10078	14231	6782	99
H(99C)	9910	14380	6246	99
H(10A)	7935	11848	5924	86
H(10B)	9122	12293	5860	86
H(10C)	8465	12845	5694	86
H(10D)	3313	8471	8499	92
H(10E)	4234	9518	8703	92
H(10F)	4266	8542	8849	92
H(10G)	4752	9418	7565	99
H(10H)	4861	10175	7991	99
H(10I)	3752	9323	7775	99
H(10J)	4335	7403	8202	96
H(10K)	4666	7824	7723	96
H(10L)	3529	7537	7835	96
H(10M)	7016	4986	9613	243
H(10N)	6667	3972	9303	243
H(10O)	7414	4482	10211	583
H(10P)	7491	3706	9849	583
H(10Q)	6475	3408	10087	583
H(10R)	5229	4185	8984	206
H(10S)	5729	5177	9332	206
H(10T)	3757	3621	9323	284
H(10U)	3999	4667	9155	284
H(10V)	4257	4576	9693	284
H(10W)	7246	3639	4650	165
H(10$)	7673	2969	4912	165
H(11A)	8594	5085	5077	225
H(11B)	9129	4484	4860	225
H(11C)	8970	4455	5394	225

H(11D)	5829	2952	4852	230
H(11E)	6047	2217	5156	230
H(11F)	5277	3411	5411	432
H(11G)	5535	2715	5733	432
H(11H)	4691	2251	5279	432

8.7. Compound 10

Table 1. Crystal data and structure refinement for sh2457.

Identification code	sh2457	
Empirical formula	C_{120} H_{122} Al_4 Ni_2 O_{25} Si_8	
Formula weight	2414.24	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.4483(12) Å	α= 81.191(2)°.
	b = 15.7031(13) Å	β= 87.024(2)°.
	c = 27.469(2) Å	γ = 66.646(2)°.
Volume	6045.2(9) $Å^3$	
Z	2	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.490 mm^{-1}	
F(000)	2524	
Crystal size	0.44 x 0.2 x 0.07 mm^3	
Theta range for data collection	1.43 to 28.44°.	
Index ranges	-20<=h<=20, -20<=k<=20, -36<=l<=36	
Reflections collected	123107	
Independent reflections	29553 [R(int) = 0.1187]	
Completeness to theta = 28.44°	97.1 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29553 / 5 / 1469	
Goodness-of-fit on F^2	1.252	
Final R indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.1763	
R indices (all data)	R1 = 0.2002, wR2 = 0.2131	
Largest diff. peak and hole	1.242 and -1.487 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2457. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	3142(1)	1520(1)	2760(1)	24(1)
Ni(2)	2352(1)	3482(1)	3058(1)	28(1)
Al(1)	2804(1)	1819(1)	1674(1)	27(1)
Al(2)	1381(1)	2161(1)	3337(1)	29(1)
Al(3)	3573(1)	4488(1)	2865(1)	26(1)
Al(4)	3713(1)	3311(1)	2041(1)	24(1)
Si(1)	2790(1)	-70(1)	2283(1)	27(1)
Si(2)	2624(1)	-82(1)	3399(1)	28(1)
Si(3)	1233(1)	3508(1)	4121(1)	28(1)
Si(4)	2033(1)	5035(1)	3748(1)	30(1)
Si(5)	5729(1)	3457(1)	3135(1)	29(1)
Si(6)	6005(1)	2600(1)	2162(1)	29(1)
Si(7)	2722(1)	4464(1)	984(1)	28(1)
Si(8)	1144(1)	3778(1)	1304(1)	31(1)
O(1)	3538(3)	2185(3)	2102(1)	28(1)
O(2)	1882(3)	2626(3)	2766(1)	27(1)
O(3)	3108(2)	3879(2)	2522(1)	23(1)
O(4)	2792(2)	985(2)	2191(1)	26(1)
O(5)	2953(3)	-464(2)	2871(1)	29(1)
O(6)	2328(2)	1050(2)	3295(1)	27(1)
O(7)	1615(2)	2986(2)	3634(1)	27(1)
O(8)	1539(3)	4402(3)	4069(1)	35(1)
O(9)	2685(2)	4425(2)	3342(1)	27(1)
O(10)	4622(3)	3725(2)	3170(1)	29(1)
O(11)	6215(3)	2951(2)	2651(1)	31(1)
O(12)	4921(3)	2797(2)	2082(1)	31(1)
O(13)	3326(2)	3858(2)	1462(1)	29(1)
O(14)	1715(3)	4350(2)	980(1)	31(1)
O(15)	1833(2)	2876(2)	1668(1)	29(1)
O(16)	4415(3)	513(2)	2816(1)	29(1)
O(17)	3464(2)	2187(2)	3237(1)	26(1)
O(18)	3824(3)	1614(2)	1269(1)	35(1)
O(19)	2280(3)	1321(2)	1248(1)	35(1)
O(20)	932(3)	1686(3)	3918(1)	37(1)
O(21)	280(3)	2450(3)	3024(1)	39(1)
O(22)	1046(3)	4607(3)	2804(2)	54(1)
O(23)	4127(3)	4817(2)	2255(1)	32(1)
O(24)	3251(3)	5710(2)	2982(1)	32(1)
O(25)	1247(7)	412(6)	9269(2)	150(3)
C(1)	1641(4)	0(4)	2074(2)	35(1)
C(2)	835(4)	833(5)	2030(2)	42(2)
C(3)	-14(5)	880(5)	1874(2)	53(2)
C(4)	-82(5)	81(5)	1734(2)	55(2)
C(5)	672(6)	-727(6)	1784(3)	65(2)
C(6)	1527(5)	-799(5)	1960(2)	50(2)
C(7)	3803(4)	-874(4)	1965(2)	34(1)
C(8)	3722(5)	-1054(4)	1490(2)	52(2)
C(9)	4532(6)	-1608(5)	1240(2)	70(2)
C(10)	5395(5)	-1990(5)	1475(3)	60(2)
C(11)	5487(5)	-1837(5)	1952(3)	56(2)

C(12)	4691(4)	-1285(4)	2190(2)	44(2)
C(13)	3612(4)	-631(4)	3848(2)	33(1)
C(14)	3662(5)	-179(5)	4239(2)	47(2)
C(15)	4350(5)	-608(5)	4603(2)	56(2)
C(16)	5013(5)	-1476(5)	4577(2)	51(2)
C(17)	5013(5)	-1936(5)	4191(2)	54(2)
C(18)	4319(4)	-1516(4)	3827(2)	40(2)
C(19)	1660(4)	-445(4)	3632(2)	31(1)
C(20)	1748(5)	-1047(4)	4074(2)	42(2)
C(21)	1044(6)	-1382(5)	4236(2)	54(2)
C(22)	234(6)	-1091(5)	3958(3)	57(2)
C(23)	119(5)	-506(5)	3531(3)	57(2)
C(24)	821(5)	-185(4)	3364(2)	49(2)
C(25)	1794(4)	2800(4)	4725(2)	34(1)
C(26)	1955(5)	3280(5)	5071(2)	47(2)
C(27)	2377(6)	2811(6)	5527(2)	64(2)
C(28)	2637(5)	1862(6)	5626(3)	65(2)
C(29)	2487(5)	1375(5)	5297(2)	56(2)
C(30)	2049(5)	1856(4)	4837(2)	44(2)
C(31)	-63(4)	3919(4)	4147(2)	32(1)
C(32)	-543(5)	3792(4)	4584(2)	44(2)
C(33)	-1507(5)	4084(5)	4595(2)	57(2)
C(34)	-2043(5)	4538(5)	4171(2)	59(2)
C(35)	-1598(5)	4691(5)	3737(2)	54(2)
C(36)	-631(5)	4389(4)	3723(2)	44(2)
C(37)	1024(4)	6113(4)	3466(2)	40(2)
C(38)	174(5)	6379(5)	3730(3)	63(2)
C(39)	-627(6)	7135(6)	3535(4)	82(3)
C(40)	-603(7)	7610(5)	3075(4)	79(3)
C(41)	203(5)	7380(5)	2817(3)	63(2)
C(42)	1004(5)	6631(4)	3011(2)	47(2)
C(43)	2738(4)	5304(4)	4180(2)	37(2)
C(44)	2715(5)	6205(4)	4177(2)	48(2)
C(45)	3246(5)	6393(5)	4499(3)	54(2)
C(46)	3799(5)	5695(5)	4849(3)	61(2)
C(47)	3843(4)	4777(5)	4877(2)	47(2)
C(48)	3329(4)	4592(4)	4533(2)	43(2)
C(49)	5922(4)	4568(4)	3115(2)	36(1)
C(50)	6406(4)	4910(4)	2751(2)	45(2)
C(51)	6447(5)	5787(5)	2737(3)	55(2)
C(52)	6013(5)	6316(5)	3112(3)	55(2)
C(53)	5549(5)	5997(5)	3471(3)	55(2)
C(54)	5487(5)	5143(4)	3480(2)	44(2)
C(55)	6377(4)	2584(4)	3674(2)	34(1)
C(56A)	6556(9)	2820(8)	4100(4)	34(2)
C(57A)	7080(9)	2129(8)	4489(4)	39(2)
C(56B)	6055(10)	2752(9)	4185(4)	34(2)
C(57B)	6486(10)	2144(9)	4571(5)	39(2)
C(58)	7370(6)	1248(5)	4464(3)	70(2)
C(59)	7410(5)	989(5)	4005(2)	64(2)
C(60)	6922(5)	1673(4)	3625(2)	57(2)
C(61)	6484(4)	3173(4)	1639(2)	32(1)
C(62)	7192(5)	3453(5)	1683(2)	55(2)
C(63)	7552(5)	3919(6)	1288(2)	63(2)
C(64)	7171(5)	4061(5)	831(2)	56(2)C(65)

C(66)	6106(5)	3345(4)	1158(2)	44(2)
C(67)	6683(4)	1306(4)	2184(2)	34(1)
C(68)	7561(4)	830(4)	2399(2)	42(2)
C(69)	8086(5)	-132(5)	2361(3)	55(2)
C(70)	7721(5)	-584(5)	2101(3)	59(2)
C(71)	6837(5)	-124(5)	1884(2)	55(2)
C(72)	6326(4)	809(4)	1923(2)	39(2)
C(73)	2490(4)	5715(4)	992(2)	32(1)
C(74)	2604(4)	6307(4)	578(2)	40(2)
C(75)	2472(5)	7234(4)	607(2)	53(2)
C(76)	2238(6)	7568(5)	1050(3)	72(3)
C(77)	2133(5)	6986(4)	1466(2)	56(2)
C(78)	2268(5)	6090(4)	1433(2)	45(2)
C(79)	3333(5)	4071(4)	403(2)	38(2)
C(80)	2929(6)	3668(5)	92(2)	58(2)
C(81)	3415(7)	3378(6)	-346(3)	78(3)
C(82)	4227(6)	3486(5)	-471(2)	60(2)
C(83)	4625(5)	3848(5)	-170(2)	54(2)
C(84)	4163(5)	4150(4)	268(2)	43(2)
C(85)	515(4)	3437(4)	862(2)	42(2)
C(86)	352(5)	3855(5)	376(2)	61(2)
C(87)	-196(6)	3624(6)	57(3)	86(3)
C(88)	-562(6)	2978(5)	240(3)	77(3)
C(89)	-435(6)	2570(5)	717(3)	76(3)
C(90)	93(5)	2804(5)	1025(3)	60(2)
C(91)	257(4)	4615(4)	1676(2)	34(1)
C(92A)	113(6)	5565(5)	1620(3)	41(2)
C(93A)	-576(6)	6187(6)	1897(3)	50(2)
C(92B)	530(30)	4890(20)	2057(12)	53(9)
C(93B)	-140(40)	5520(30)	2344(18)	97(15)
C(94)	-1111(5)	5864(5)	2233(2)	53(2)
C(95A)	-1003(6)	4955(6)	2289(3)	43(2)
C(96A)	-335(5)	4332(5)	2027(2)	34(2)
C(95B)	-1300(30)	5540(30)	1820(16)	81(13)
C(96B)	-670(30)	5040(20)	1481(13)	58(10)
C(97)	4105(4)	2295(4)	3980(2)	34(1)
C(98)	4170(4)	1802(4)	3549(2)	31(1)
C(99)	4910(4)	973(4)	3507(2)	32(1)
C(100)	5022(4)	395(4)	3144(2)	32(1)
C(101)	5939(4)	-453(4)	3133(2)	45(2)
C(102)	4875(5)	1359(5)	612(2)	56(2)
C(103)	3968(5)	1372(4)	836(2)	40(2)
C(104)	3366(5)	1124(4)	596(2)	48(2)
C(105)	2531(5)	1099(4)	818(2)	42(2)
C(106)	1884(5)	809(5)	558(2)	64(2)
C(107)	-1283(5)	2715(5)	2837(3)	69(2)
C(108)	-519(5)	2394(4)	3208(3)	45(2)
C(109)	-599(5)	2036(5)	3677(2)	50(2)
C(110)	119(5)	1672(4)	4019(2)	44(2)
C(111)	-1(5)	1209(5)	4531(2)	60(2)
C(112)	4743(5)	5562(4)	1592(2)	48(2)
C(113)	4263(4)	5552(4)	2080(2)	36(1)
C(114)	3989(4)	6333(4)	2327(2)	40(2)
C(115)	3495(4)	6385(4)	2758(2)	37(2)
C(116)	3172(5)	7232(4)	3009(2)	49(2)

C(117)	1314(9)	-511(7)	9490(4)	120(4)
C(118)	2233(8)	-1145(7)	9317(4)	128(4)
C(119)	279(7)	1440(20)	9291(7)	430(20)
C(120)	1260(30)	1786(17)	9152(6)	660(40)

Table 3. Bond lengths [Å] and angles [°] for sh2457.

Ni(1)-O(16)	1.970(4)	Si(6)-O(12)	1.598(4)
Ni(1)-O(17)	1.990(3)	Si(6)-O(11)	1.623(4)
Ni(1)-O(2)	2.033(4)	Si(6)-C(61)	1.854(6)
Ni(1)-O(4)	2.073(3)	Si(6)-C(67)	1.873(6)
Ni(1)-O(6)	2.120(3)	Si(7)-O(13)	1.594(3)
Ni(1)-O(1)	2.133(4)	Si(7)-O(14)	1.634(4)
Ni(1)-Al(2)	2.9662(18)	Si(7)-C(73)	1.857(6)
Ni(1)-Al(1)	2.9892(16)	Si(7)-C(79)	1.870(6)
Ni(2)-O(3)	2.009(3)	Si(8)-O(15)	1.619(4)
Ni(2)-O(9)	2.017(3)	Si(8)-O(14)	1.637(4)
Ni(2)-O(2)	2.036(4)	Si(8)-C(85)	1.853(6)
Ni(2)-O(17)	2.083(3)	Si(8)-C(91)	1.868(6)
Ni(2)-O(7)	2.131(3)	O(16)-C(100)	1.274(6)
Ni(2)-O(22)	2.149(4)	O(17)-C(98)	1.306(6)
Ni(2)-Al(3)	2.8882(18)	O(18)-C(103)	1.286(6)
Ni(2)-Al(2)	2.9999(18)	O(19)-C(105)	1.278(6)
Al(1)-O(15)	1.740(4)	O(20)-C(110)	1.280(7)
Al(1)-O(4)	1.783(4)	O(21)-C(108)	1.341(7)
Al(1)-O(18)	1.829(4)	O(23)-C(113)	1.272(6)
Al(1)-O(19)	1.875(4)	O(24)-C(115)	1.319(6)
Al(1)-O(1)	1.964(4)	O(25)-C(117)	1.449(11)
Al(2)-O(7)	1.788(4)	O(25)-C(119)	1.718(19)
Al(2)-O(6)	1.795(4)	C(1)-C(2)	1.397(8)
Al(2)-O(21)	1.805(4)	C(1)-C(6)	1.415(8)
Al(2)-O(20)	1.875(4)	C(2)-C(3)	1.372(9)
Al(2)-O(2)	1.889(4)	C(3)-C(4)	1.409(9)
Al(3)-O(10)	1.748(4)	C(4)-C(5)	1.333(9)
Al(3)-O(3)	1.792(3)	C(5)-C(6)	1.387(9)
Al(3)-O(24)	1.856(4)	C(7)-C(12)	1.394(8)
Al(3)-O(9)	1.868(4)	C(7)-C(8)	1.398(8)
Al(3)-O(23)	1.934(4)	C(8)-C(9)	1.423(9)
Al(4)-O(13)	1.704(3)	C(9)-C(10)	1.374(10)
Al(4)-O(12)	1.717(4)	C(10)-C(11)	1.392(9)
Al(4)-O(3)	1.728(3)	C(11)-C(12)	1.390(8)
Al(4)-O(1)	1.874(4)	C(13)-C(18)	1.394(8)
Si(1)-O(5)	1.633(4)	C(13)-C(14)	1.396(7)
Si(1)-O(4)	1.637(4)	C(14)-C(15)	1.385(9)
Si(1)-C(1)	1.851(6)	C(15)-C(16)	1.352(9)
Si(1)-C(7)	1.854(6)	C(16)-C(17)	1.371(8)
Si(2)-O(6)	1.631(4)	C(17)-C(18)	1.390(8)
Si(2)-O(5)	1.633(4)	C(19)-C(20)	1.395(8)
Si(2)-C(19)	1.848(6)	C(19)-C(24)	1.406(8)
Si(2)-C(13)	1.851(6)	C(20)-C(21)	1.410(9)
Si(3)-O(8)	1.635(4)	C(21)-C(22)	1.377(10)
Si(3)-O(7)	1.638(3)	C(22)-C(23)	1.346(9)
Si(3)-C(31)	1.846(6)	C(23)-C(24)	1.397(9)
Si(3)-C(25)	1.886(6)	C(25)-C(30)	1.363(8)
Si(4)-O(8)	1.616(4)	C(25)-C(26)	1.388(8)
Si(4)-O(9)	1.618(4)	C(26)-C(27)	1.398(8)
Si(4)-C(43)	1.850(6)	C(27)-C(28)	1.368(10)
Si(4)-C(37)	1.879(6)	C(28)-C(29)	1.351(9)
Si(5)-O(10)	1.592(4)	C(29)-C(30)	1.420(8)
Si(5)-O(11)	1.645(4)	C(31)-C(32)	1.407(8)
Si(5)-C(49)	1.875(6)	C(31)-C(36)	1.414(7)
Si(5)-C(55)	1.876(6)	C(32)-C(33)	1.374(9)

C(33)-C(34)	1.389(9)
C(34)-C(35)	1.381(9)
C(35)-C(36)	1.376(8)
C(37)-C(42)	1.376(8)
C(37)-C(38)	1.408(9)
C(38)-C(39)	1.391(10)
C(39)-C(40)	1.373(11)
C(40)-C(41)	1.346(10)
C(41)-C(42)	1.386(9)
C(43)-C(44)	1.399(8)
C(43)-C(48)	1.405(8)
C(44)-C(45)	1.374(8)
C(45)-C(46)	1.370(9)
C(46)-C(47)	1.405(9)
C(47)-C(48)	1.399(8)
C(49)-C(50)	1.386(8)
C(49)-C(54)	1.415(8)
C(50)-C(51)	1.398(8)
C(51)-C(52)	1.397(9)
C(52)-C(53)	1.341(10)
C(53)-C(54)	1.378(8)
C(55)-C(56A)	1.353(11)
C(55)-C(60)	1.367(8)
C(55)-C(56B)	1.489(13)
C(56A)-C(57A)	1.418(15)
C(57A)-C(58)	1.287(13)
C(56B)-C(57B)	1.320(16)
C(57B)-C(58)	1.579(15)
C(58)-C(59)	1.374(9)
C(59)-C(60)	1.381(8)
C(61)-C(62)	1.348(8)
C(61)-C(66)	1.415(7)
C(62)-C(63)	1.427(9)
C(63)-C(64)	1.364(8)
C(64)-C(65)	1.371(9)
C(65)-C(66)	1.406(8)
C(67)-C(68)	1.374(8)
C(67)-C(72)	1.409(8)
C(68)-C(69)	1.422(8)
C(69)-C(70)	1.358(9)
C(70)-C(71)	1.383(9)
C(71)-C(72)	1.378(8)
C(73)-C(78)	1.395(7)
C(73)-C(74)	1.404(7)
C(74)-C(75)	1.402(8)
C(75)-C(76)	1.374(9)
C(76)-C(77)	1.396(9)
C(77)-C(78)	1.355(8)
C(79)-C(84)	1.363(8)
C(79)-C(80)	1.434(8)
C(80)-C(81)	1.420(9)
C(81)-C(82)	1.352(10)
C(82)-C(83)	1.363(9)
C(83)-C(84)	1.415(8)
C(85)-C(86)	1.383(8)
C(85)-C(90)	1.401(9)
C(86)-C(87)	1.427(9)
C(87)-C(88)	1.367(11)
C(88)-C(89)	1.353(11)
C(89)-C(90)	1.386(9)
C(91)-C(92B)	1.34(3)
C(91)-C(92A)	1.404(9)
C(91)-C(96B)	1.41(4)
C(91)-C(96A)	1.437(9)
C(92A)-C(93A)	1.408(10)
C(93A)-C(94)	1.380(10)
C(92B)-C(93B)	1.42(5)
C(93B)-C(94)	1.40(5)
C(94)-C(95A)	1.355(10)
C(94)-C(95B)	1.40(4)
C(95A)-C(96A)	1.370(10)
C(95B)-C(96B)	1.39(5)
C(97)-C(98)	1.487(7)
C(98)-C(99)	1.367(7)
C(99)-C(100)	1.409(7)
C(100)-C(101)	1.514(8)
C(102)-C(103)	1.494(9)
C(103)-C(104)	1.373(8)
C(104)-C(105)	1.411(9)
C(105)-C(106)	1.502(8)
C(107)-C(108)	1.477(9)
C(108)-C(109)	1.343(9)
C(109)-C(110)	1.372(9)
C(110)-C(111)	1.521(8)
C(112)-C(113)	1.500(8)
C(113)-C(114)	1.398(8)
C(114)-C(115)	1.370(8)
C(115)-C(116)	1.487(8)
C(117)-C(118)	1.478(13)
C(119)-C(120)	1.81(4)

O(16)-Ni(1)-O(17)	91.86(14)
O(16)-Ni(1)-O(2)	172.99(15)
O(17)-Ni(1)-O(2)	81.14(15)
O(16)-Ni(1)-O(4)	91.36(14)
O(17)-Ni(1)-O(4)	171.99(14)
O(2)-Ni(1)-O(4)	95.62(15)
O(16)-Ni(1)-O(6)	105.30(14)
O(17)-Ni(1)-O(6)	91.39(13)
O(2)-Ni(1)-O(6)	74.79(14)
O(4)-Ni(1)-O(6)	94.83(13)
O(16)-Ni(1)-O(1)	90.15(15)
O(17)-Ni(1)-O(1)	98.10(14)
O(2)-Ni(1)-O(1)	91.11(16)
O(4)-Ni(1)-O(1)	74.56(13)
O(6)-Ni(1)-O(1)	161.64(15)
O(16)-Ni(1)-Al(2)	139.29(11)
O(17)-Ni(1)-Al(2)	78.65(11)
O(2)-Ni(1)-Al(2)	39.08(11)

O(4)-Ni(1)-Al(2)	103.48(11)
O(6)-Ni(1)-Al(2)	36.80(10)
O(1)-Ni(1)-Al(2)	130.18(12)
O(16)-Ni(1)-Al(1)	100.83(10)
O(17)-Ni(1)-Al(1)	136.26(10)
O(2)-Ni(1)-Al(1)	84.58(11)
O(4)-Ni(1)-Al(1)	35.78(10)
O(6)-Ni(1)-Al(1)	124.13(10)
O(1)-Ni(1)-Al(1)	40.99(10)
Al(2)-Ni(1)-Al(1)	113.41(5)
O(3)-Ni(2)-O(9)	76.61(13)
O(3)-Ni(2)-O(2)	105.23(14)
O(9)-Ni(2)-O(2)	174.29(15)
O(3)-Ni(2)-O(17)	91.38(13)
O(9)-Ni(2)-O(17)	106.62(14)
O(2)-Ni(2)-O(17)	78.85(15)
O(3)-Ni(2)-O(7)	176.80(14)
O(9)-Ni(2)-O(7)	104.40(13)
O(2)-Ni(2)-O(7)	74.06(14)
O(17)-Ni(2)-O(7)	85.42(13)
O(3)-Ni(2)-O(22)	93.48(16)
O(9)-Ni(2)-O(22)	87.82(15)
O(2)-Ni(2)-O(22)	86.68(16)
O(17)-Ni(2)-O(22)	165.49(15)
O(7)-Ni(2)-O(22)	89.60(16)
O(3)-Ni(2)-Al(3)	37.82(9)
O(9)-Ni(2)-Al(3)	40.04(10)
O(2)-Ni(2)-Al(3)	142.65(11)
O(17)-Ni(2)-Al(3)	93.78(10)
O(7)-Ni(2)-Al(3)	142.43(10)
O(22)-Ni(2)-Al(3)	98.45(13)
O(3)-Ni(2)-Al(2)	142.87(10)
O(9)-Ni(2)-Al(2)	140.40(10)
O(2)-Ni(2)-Al(2)	38.38(11)
O(17)-Ni(2)-Al(2)	76.56(10)
O(7)-Ni(2)-Al(2)	36.00(9)
O(22)-Ni(2)-Al(2)	91.44(13)
Al(3)-Ni(2)-Al(2)	170.08(5)
O(15)-Al(1)-O(4)	111.74(18)
O(15)-Al(1)-O(18)	125.45(19)
O(4)-Al(1)-O(18)	122.10(19)
O(15)-Al(1)-O(19)	95.91(17)
O(4)-Al(1)-O(19)	93.26(17)
O(18)-Al(1)-O(19)	89.49(17)
O(15)-Al(1)-O(1)	92.59(18)
O(4)-Al(1)-O(1)	85.56(16)
O(18)-Al(1)-O(1)	83.82(17)
O(19)-Al(1)-O(1)	171.24(19)
O(15)-Al(1)-Ni(1)	95.08(12)
O(4)-Al(1)-Ni(1)	42.83(11)
O(18)-Al(1)-Ni(1)	117.85(13)
O(19)-Al(1)-Ni(1)	135.38(13)
O(1)-Al(1)-Ni(1)	45.42(11)
O(7)-Al(2)-O(6)	118.05(18)
O(7)-Al(2)-O(21)	122.58(18)
O(6)-Al(2)-O(21)	119.00(18)
O(7)-Al(2)-O(20)	92.69(16)
O(6)-Al(2)-O(20)	92.41(17)
O(21)-Al(2)-O(20)	90.9(2)
O(7)-Al(2)-O(2)	86.08(17)
O(6)-Al(2)-O(2)	86.39(17)
O(21)-Al(2)-O(2)	91.43(19)
O(20)-Al(2)-O(2)	177.6(2)
O(7)-Al(2)-Ni(1)	97.74(13)
O(6)-Al(2)-Ni(1)	45.02(11)
O(21)-Al(2)-Ni(1)	117.93(14)
O(20)-Al(2)-Ni(1)	135.65(14)
O(2)-Al(2)-Ni(1)	42.71(12)
O(7)-Al(2)-Ni(2)	44.47(11)
O(6)-Al(2)-Ni(2)	101.46(13)
O(21)-Al(2)-Ni(2)	116.35(15)
O(20)-Al(2)-Ni(2)	136.50(13)
O(2)-Al(2)-Ni(2)	42.01(12)
Ni(1)-Al(2)-Ni(2)	61.62(4)
O(10)-Al(3)-O(3)	111.34(17)
O(10)-Al(3)-O(24)	111.22(18)
O(3)-Al(3)-O(24)	137.45(18)
O(10)-Al(3)-O(9)	100.98(17)
O(3)-Al(3)-O(9)	85.94(16)
O(24)-Al(3)-O(9)	86.47(17)
O(10)-Al(3)-O(23)	97.49(18)
O(3)-Al(3)-O(23)	86.89(16)
O(24)-Al(3)-O(23)	87.36(17)
O(9)-Al(3)-O(23)	161.52(18)
O(10)-Al(3)-Ni(2)	103.45(13)
O(3)-Al(3)-Ni(2)	43.42(11)
O(24)-Al(3)-Ni(2)	124.20(14)
O(9)-Al(3)-Ni(2)	43.99(10)
O(23)-Al(3)-Ni(2)	130.18(12)
O(13)-Al(4)-O(12)	112.22(18)
O(13)-Al(4)-O(3)	116.53(18)
O(12)-Al(4)-O(3)	117.82(17)
O(13)-Al(4)-O(1)	104.94(17)
O(12)-Al(4)-O(1)	95.65(19)
O(3)-Al(4)-O(1)	106.28(18)
O(5)-Si(1)-O(4)	108.28(18)
O(5)-Si(1)-C(1)	110.7(2)
O(4)-Si(1)-C(1)	108.7(2)
O(5)-Si(1)-C(7)	106.4(2)
O(4)-Si(1)-C(7)	109.9(2)
C(1)-Si(1)-C(7)	112.8(3)
O(6)-Si(2)-O(5)	106.53(18)
O(6)-Si(2)-C(19)	114.6(2)
O(5)-Si(2)-C(19)	107.5(2)
O(6)-Si(2)-C(13)	109.9(2)
O(5)-Si(2)-C(13)	110.1(2)
C(19)-Si(2)-C(13)	108.1(3)
O(8)-Si(3)-O(7)	107.61(19)
O(8)-Si(3)-C(31)	109.8(2)

O(7)-Si(3)-C(31)	109.4(2)
O(8)-Si(3)-C(25)	103.1(2)
O(7)-Si(3)-C(25)	115.5(2)
C(31)-Si(3)-C(25)	111.0(2)
O(8)-Si(4)-O(9)	107.30(19)
O(8)-Si(4)-C(43)	107.2(2)
O(9)-Si(4)-C(43)	112.1(2)
O(8)-Si(4)-C(37)	104.6(3)
O(9)-Si(4)-C(37)	112.9(2)
C(43)-Si(4)-C(37)	112.2(3)
O(10)-Si(5)-O(11)	113.89(19)
O(10)-Si(5)-C(49)	107.2(2)
O(11)-Si(5)-C(49)	109.6(2)
O(10)-Si(5)-C(55)	111.6(2)
O(11)-Si(5)-C(55)	104.3(2)
C(49)-Si(5)-C(55)	110.2(2)
O(12)-Si(6)-O(11)	114.38(19)
O(12)-Si(6)-C(61)	112.5(2)
O(11)-Si(6)-C(61)	105.9(2)
O(12)-Si(6)-C(67)	106.8(2)
O(11)-Si(6)-C(67)	110.6(2)
C(61)-Si(6)-C(67)	106.4(3)
O(13)-Si(7)-O(14)	110.57(19)
O(13)-Si(7)-C(73)	108.6(2)
O(14)-Si(7)-C(73)	109.0(2)
O(13)-Si(7)-C(79)	112.0(2)
O(14)-Si(7)-C(79)	106.3(2)
C(73)-Si(7)-C(79)	110.4(3)
O(15)-Si(8)-O(14)	112.4(2)
O(15)-Si(8)-C(85)	111.7(2)
O(14)-Si(8)-C(85)	107.2(2)
O(15)-Si(8)-C(91)	109.5(2)
O(14)-Si(8)-C(91)	107.0(2)
C(85)-Si(8)-C(91)	109.0(3)
Al(4)-O(1)-Al(1)	128.6(2)
Al(4)-O(1)-Ni(1)	125.22(18)
Al(1)-O(1)-Ni(1)	93.59(17)
Al(2)-O(2)-Ni(1)	98.22(18)
Al(2)-O(2)-Ni(2)	99.61(18)
Ni(1)-O(2)-Ni(2)	97.36(17)
Al(4)-O(3)-Al(3)	122.2(2)
Al(4)-O(3)-Ni(2)	129.75(19)
Al(3)-O(3)-Ni(2)	98.76(15)
Si(1)-O(4)-Al(1)	136.9(2)
Si(1)-O(4)-Ni(1)	120.23(18)
Al(1)-O(4)-Ni(1)	101.39(16)
Si(1)-O(5)-Si(2)	139.0(2)
Si(2)-O(6)-Al(2)	143.8(2)
Si(2)-O(6)-Ni(1)	115.59(18)
Al(2)-O(6)-Ni(1)	98.18(16)
Si(3)-O(7)-Al(2)	136.4(2)
Si(3)-O(7)-Ni(2)	122.54(19)
Al(2)-O(7)-Ni(2)	99.53(15)
Si(4)-O(8)-Si(3)	148.6(2)
Si(4)-O(9)-Al(3)	139.3(2)
Si(4)-O(9)-Ni(2)	122.0(2)
Al(3)-O(9)-Ni(2)	95.96(14)
Si(5)-O(10)-Al(3)	140.3(2)
Si(6)-O(11)-Si(5)	144.1(3)
Si(6)-O(12)-Al(4)	163.7(2)
Si(7)-O(13)-Al(4)	166.0(3)
Si(7)-O(14)-Si(8)	139.9(2)
Si(8)-O(15)-Al(1)	142.8(2)
C(100)-O(16)-Ni(1)	124.5(3)
C(98)-O(17)-Ni(1)	124.7(3)
C(98)-O(17)-Ni(2)	138.1(3)
Ni(1)-O(17)-Ni(2)	97.20(14)
C(103)-O(18)-Al(1)	130.9(4)
C(105)-O(19)-Al(1)	130.6(4)
C(110)-O(20)-Al(2)	130.4(4)
C(108)-O(21)-Al(2)	128.9(4)
C(113)-O(23)-Al(3)	131.9(4)
C(115)-O(24)-Al(3)	131.4(4)
C(117)-O(25)-C(119)	125.4(13)
C(2)-C(1)-C(6)	116.3(6)
C(2)-C(1)-Si(1)	122.2(4)
C(6)-C(1)-Si(1)	121.5(5)
C(3)-C(2)-C(1)	121.9(6)
C(2)-C(3)-C(4)	120.0(6)
C(5)-C(4)-C(3)	119.1(6)
C(4)-C(5)-C(6)	121.8(7)
C(5)-C(6)-C(1)	120.7(7)
C(12)-C(7)-C(8)	117.9(6)
C(12)-C(7)-Si(1)	120.0(4)
C(8)-C(7)-Si(1)	122.1(5)
C(7)-C(8)-C(9)	120.5(6)
C(10)-C(9)-C(8)	119.5(6)
C(9)-C(10)-C(11)	120.9(7)
C(12)-C(11)-C(10)	119.0(7)
C(11)-C(12)-C(7)	122.2(6)
C(18)-C(13)-C(14)	116.6(5)
C(18)-C(13)-Si(2)	122.6(4)
C(14)-C(13)-Si(2)	120.7(5)
C(15)-C(14)-C(13)	121.8(6)
C(16)-C(15)-C(14)	119.9(6)
C(15)-C(16)-C(17)	120.5(6)
C(16)-C(17)-C(18)	120.0(6)
C(17)-C(18)-C(13)	121.1(5)
C(20)-C(19)-C(24)	115.8(6)
C(20)-C(19)-Si(2)	121.6(5)
C(24)-C(19)-Si(2)	122.5(4)
C(19)-C(20)-C(21)	122.0(6)
C(22)-C(21)-C(20)	119.3(6)
C(23)-C(22)-C(21)	120.6(7)
C(22)-C(23)-C(24)	120.4(7)
C(23)-C(24)-C(19)	122.0(6)
C(30)-C(25)-C(26)	118.9(5)
C(30)-C(25)-Si(3)	123.9(4)
C(26)-C(25)-Si(3)	117.2(5)

		C(62)-C(61)-Si(6)	123.9(4)
		C(66)-C(61)-Si(6)	120.4(4)
C(25)-C(26)-C(27)	121.1(6)	C(61)-C(62)-C(63)	124.7(6)
C(28)-C(27)-C(26)	118.7(6)	C(64)-C(63)-C(62)	117.4(6)
C(29)-C(28)-C(27)	121.5(6)	C(63)-C(64)-C(65)	120.9(6)
C(28)-C(29)-C(30)	119.6(7)	C(64)-C(65)-C(66)	120.0(6)
C(25)-C(30)-C(29)	120.2(6)	C(65)-C(66)-C(61)	121.2(6)
C(32)-C(31)-C(36)	116.3(5)	C(68)-C(67)-C(72)	117.7(5)
C(32)-C(31)-Si(3)	122.5(4)	C(68)-C(67)-Si(6)	123.5(5)
C(36)-C(31)-Si(3)	121.2(4)	C(72)-C(67)-Si(6)	118.5(4)
C(33)-C(32)-C(31)	121.9(6)	C(67)-C(68)-C(69)	121.0(6)
C(32)-C(33)-C(34)	120.3(6)	C(70)-C(69)-C(68)	119.5(6)
C(35)-C(34)-C(33)	119.4(6)	C(69)-C(70)-C(71)	120.7(6)
C(36)-C(35)-C(34)	120.4(6)	C(72)-C(71)-C(70)	119.9(6)
C(35)-C(36)-C(31)	121.6(6)	C(71)-C(72)-C(67)	121.3(6)
C(42)-C(37)-C(38)	116.4(6)	C(78)-C(73)-C(74)	116.5(5)
C(42)-C(37)-Si(4)	126.8(5)	C(78)-C(73)-Si(7)	120.1(4)
C(38)-C(37)-Si(4)	116.6(5)	C(74)-C(73)-Si(7)	123.2(4)
C(39)-C(38)-C(37)	120.6(7)	C(75)-C(74)-C(73)	121.3(5)
C(40)-C(39)-C(38)	120.1(8)	C(76)-C(75)-C(74)	119.5(6)
C(41)-C(40)-C(39)	120.5(8)	C(75)-C(76)-C(77)	119.9(6)
C(40)-C(41)-C(42)	119.5(8)	C(78)-C(77)-C(76)	119.9(6)
C(37)-C(42)-C(41)	122.9(7)	C(77)-C(78)-C(73)	122.9(6)
C(44)-C(43)-C(48)	116.7(5)	C(84)-C(79)-C(80)	118.7(5)
C(44)-C(43)-Si(4)	123.0(5)	C(84)-C(79)-Si(7)	121.7(4)
C(48)-C(43)-Si(4)	120.3(4)	C(80)-C(79)-Si(7)	119.6(5)
C(45)-C(44)-C(43)	122.3(6)	C(81)-C(80)-C(79)	117.9(7)
C(46)-C(45)-C(44)	120.1(6)	C(82)-C(81)-C(80)	121.6(7)
C(45)-C(46)-C(47)	120.5(6)	C(81)-C(82)-C(83)	120.7(6)
C(48)-C(47)-C(46)	118.5(6)	C(82)-C(83)-C(84)	119.6(7)
C(47)-C(48)-C(43)	121.8(6)	C(79)-C(84)-C(83)	121.5(6)
C(50)-C(49)-C(54)	116.6(6)	C(86)-C(85)-C(90)	116.6(6)
C(50)-C(49)-Si(5)	125.4(5)	C(86)-C(85)-Si(8)	122.7(5)
C(54)-C(49)-Si(5)	117.9(5)	C(90)-C(85)-Si(8)	120.3(5)
C(49)-C(50)-C(51)	122.1(6)	C(85)-C(86)-C(87)	121.0(7)
C(52)-C(51)-C(50)	118.6(6)	C(88)-C(87)-C(86)	118.8(7)
C(53)-C(52)-C(51)	120.5(6)	C(89)-C(88)-C(87)	121.9(7)
C(52)-C(53)-C(54)	121.2(7)	C(88)-C(89)-C(90)	119.0(8)
C(53)-C(54)-C(49)	121.1(6)	C(89)-C(90)-C(85)	122.7(7)
C(56A)-C(55)-C(60)	112.3(7)	C(92B)-C(91)-C(92A)	64.2(14)
C(56A)-C(55)-C(56B)	33.9(6)	C(92B)-C(91)-C(96B)	123(2)
C(60)-C(55)-C(56B)	115.1(7)	C(92A)-C(91)-C(96B)	79.3(14)
C(56A)-C(55)-Si(5)	124.1(6)	C(92B)-C(91)-C(96A)	85.3(15)
C(60)-C(55)-Si(5)	121.5(4)	C(92A)-C(91)-C(96A)	116.0(6)
C(56B)-C(55)-Si(5)	119.9(6)	C(96B)-C(91)-C(96A)	72.8(15)
C(55)-C(56A)-C(57A)	121.6(10)	C(92B)-C(91)-Si(8)	120.6(16)
C(58)-C(57A)-C(56A)	121.7(11)	C(92A)-C(91)-Si(8)	121.9(5)
C(57B)-C(56B)-C(55)	121.4(11)	C(96B)-C(91)-Si(8)	115.6(15)
C(56B)-C(57B)-C(58)	116.5(11)	C(96A)-C(91)-Si(8)	122.1(5)
C(57A)-C(58)-C(59)	117.4(8)	C(91)-C(92A)-C(93A)	120.8(7)
C(57A)-C(58)-C(57B)	35.9(6)	C(94)-C(93A)-C(92A)	120.1(7)
C(59)-C(58)-C(57B)	116.7(7)	C(91)-C(92B)-C(93B)	120(3)
C(58)-C(59)-C(60)	117.8(7)	C(94)-C(93B)-C(92B)	121(4)
C(55)-C(60)-C(59)	124.8(6)	C(95A)-C(94)-C(93A)	120.6(7)
C(62)-C(61)-C(66)	115.7(5)	C(95A)-C(94)-C(95B)	62.9(17)

C(93A)-C(94)-C(95B)	82.0(18)	C(95A)-C(96A)-C(91)	121.9(7)
C(95A)-C(94)-C(93B)	86(2)	C(96B)-C(95B)-C(94)	129(4)
C(93A)-C(94)-C(93B)	64(2)	C(95B)-C(96B)-C(91)	111(3)
C(95B)-C(94)-C(93B)	113(3)	O(17)-C(98)-C(99)	123.4(5)
C(94)-C(95A)-C(96A)	120.6(7)	O(17)-C(98)-C(97)	116.0(5)
		C(99)-C(98)-C(97)	120.6(5)
		C(98)-C(99)-C(100)	126.6(5)
		O(16)-C(100)-C(99)	126.0(5)
		C(108)-C(109)-C(110)	124.7(7)
O(16)-C(100)-C(101)	115.6(5)	O(20)-C(110)-C(109)	121.6(6)
C(99)-C(100)-C(101)	118.4(5)	O(20)-C(110)-C(111)	116.6(6)
O(18)-C(103)-C(104)	124.2(6)	C(109)-C(110)-C(111)	121.8(7)
O(18)-C(103)-C(102)	114.1(6)	O(23)-C(113)-C(114)	122.5(5)
C(104)-C(103)-C(102)	121.6(5)	O(23)-C(113)-C(112)	117.8(5)
C(103)-C(104)-C(105)	121.3(5)	C(114)-C(113)-C(112)	119.7(5)
O(19)-C(105)-C(104)	122.6(6)	C(115)-C(114)-C(113)	122.1(5)
O(19)-C(105)-C(106)	116.4(6)	O(24)-C(115)-C(114)	123.8(5)
C(104)-C(105)-C(106)	121.1(5)	O(24)-C(115)-C(116)	114.1(5)
O(21)-C(108)-C(109)	123.2(6)	C(114)-C(115)-C(116)	122.0(6)
O(21)-C(108)-C(107)	113.1(6)	O(25)-C(117)-C(118)	103.5(10)
C(109)-C(108)-C(107)	123.6(7)	O(25)-C(119)-C(120)	74.7(11)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2457. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	35(1)	22(1)	16(1)	-5(1)	-2(1)	-10(1)
Ni(2)	46(1)	27(1)	17(1)	-9(1)	3(1)	-18(1)
Al(1)	40(1)	24(1)	19(1)	-7(1)	-4(1)	-11(1)
Al(2)	37(1)	26(1)	26(1)	-12(1)	2(1)	-12(1)
Al(3)	36(1)	25(1)	20(1)	-7(1)	-2(1)	-12(1)
Al(4)	33(1)	23(1)	15(1)	-5(1)	-1(1)	-10(1)
Si(1)	41(1)	20(1)	21(1)	-9(1)	1(1)	-11(1)
Si(2)	43(1)	22(1)	20(1)	-6(1)	1(1)	-12(1)
Si(3)	39(1)	28(1)	16(1)	-7(1)	0(1)	-12(1)
Si(4)	41(1)	29(1)	24(1)	-14(1)	3(1)	-14(1)
Si(5)	37(1)	30(1)	21(1)	-6(1)	-4(1)	-12(1)
Si(6)	33(1)	32(1)	21(1)	-7(1)	-1(1)	-9(1)
Si(7)	40(1)	25(1)	16(1)	-5(1)	-1(1)	-10(1)
Si(8)	40(1)	25(1)	29(1)	-4(1)	-11(1)	-11(1)
O(1)	36(3)	26(2)	18(2)	-7(2)	-1(2)	-8(2)
O(2)	41(3)	24(2)	17(2)	-6(2)	-5(2)	-11(2)
O(3)	33(2)	23(2)	16(2)	-10(1)	2(2)	-10(2)
O(4)	43(2)	22(2)	16(2)	-7(2)	-2(2)	-13(2)
O(5)	44(2)	21(2)	22(2)	-5(2)	2(2)	-12(2)
O(6)	37(2)	24(2)	21(2)	-7(2)	4(2)	-12(2)
O(7)	35(2)	28(2)	18(2)	-9(2)	5(2)	-12(2)
O(8)	51(3)	38(2)	23(2)	-16(2)	6(2)	-20(2)
O(9)	40(2)	26(2)	16(2)	-9(2)	1(2)	-13(2)
O(10)	40(2)	27(2)	21(2)	-5(2)	-2(2)	-13(2)
O(11)	36(2)	35(2)	22(2)	-8(2)	-4(2)	-12(2)
O(12)	39(2)	31(2)	22(2)	-7(2)	-3(2)	-12(2)
O(13)	34(2)	31(2)	18(2)	0(2)	-5(2)	-11(2)
O(14)	40(2)	30(2)	20(2)	-2(2)	-8(2)	-10(2)
O(15)	37(2)	21(2)	25(2)	-3(2)	-8(2)	-7(2)
O(16)	34(2)	27(2)	22(2)	-2(2)	-6(2)	-8(2)
O(17)	33(2)	28(2)	18(2)	-6(2)	-2(2)	-11(2)
O(18)	53(3)	35(2)	19(2)	-14(2)	4(2)	-18(2)
O(19)	52(3)	34(2)	22(2)	-7(2)	-8(2)	-19(2)
O(20)	45(3)	40(2)	34(2)	-18(2)	12(2)	-21(2)
O(21)	40(3)	40(2)	33(2)	-15(2)	-2(2)	-10(2)
O(22)	63(3)	45(3)	53(3)	-14(2)	-1(2)	-19(2)
O(23)	45(3)	27(2)	26(2)	-5(2)	0(2)	-16(2)
O(24)	39(2)	25(2)	34(2)	-7(2)	-1(2)	-15(2)
O(25)	274(11)	118(6)	78(5)	10(4)	-40(6)	-101(7)
C(1)	54(4)	33(3)	20(3)	-5(2)	2(3)	-20(3)
C(2)	43(4)	53(4)	34(3)	-14(3)	-3(3)	-19(3)
C(3)	41(4)	66(5)	39(4)	-6(3)	-1(3)	-9(4)
C(4)	58(5)	71(5)	46(4)	-3(4)	-11(4)	-36(4)
C(5)	76(6)	63(5)	69(5)	5(4)	-25(5)	-44(5)
C(6)	67(5)	43(4)	48(4)	-1(3)	-16(4)	-31(4)
C(7)	49(4)	25(3)	28(3)	-9(2)	4(3)	-14(3)
C(8)	64(5)	39(4)	31(3)	-13(3)	1(3)	5(3)
C(9)	98(7)	61(5)	33(4)	-21(4)	5(4)	-6(5)
C(10)	61(5)	47(4)	57(5)	-18(4)	26(4)	-3(4)
C(11)	54(5)	45(4)	69(5)	-26(4)	6(4)	-12(4)
C(12)	42(4)	41(4)	46(4)	-18(3)	2(3)	-8(3)

C(13)	46(4)	30(3)	24(3)	-4(2)	2(3)	-17(3)
C(14)	68(5)	47(4)	29(3)	-19(3)	5(3)	-22(4)
C(15)	71(5)	76(5)	29(3)	-23(4)	-5(4)	-30(4)
C(16)	53(5)	67(5)	29(3)	-9(3)	-11(3)	-16(4)
C(17)	65(5)	40(4)	47(4)	-7(3)	-23(4)	-7(3)
C(18)	51(4)	31(3)	37(3)	-10(3)	-10(3)	-12(3)
C(19)	44(4)	24(3)	26(3)	-12(2)	6(3)	-12(3)
C(20)	54(4)	39(4)	34(3)	-5(3)	9(3)	-19(3)
C(21)	80(6)	45(4)	40(4)	-8(3)	21(4)	-30(4)
C(22)	66(5)	59(5)	62(5)	-23(4)	33(4)	-39(4)
C(23)	55(5)	71(5)	59(5)	-14(4)	1(4)	-39(4)
C(24)	61(5)	40(4)	49(4)	-7(3)	5(4)	-25(4)
C(25)	38(4)	44(4)	20(3)	-9(3)	4(3)	-13(3)
C(26)	68(5)	54(4)	24(3)	-8(3)	-5(3)	-27(4)
C(27)	90(6)	77(6)	30(4)	-14(4)	-9(4)	-35(5)
C(28)	72(6)	72(6)	37(4)	9(4)	-17(4)	-18(4)
C(29)	61(5)	50(4)	44(4)	-4(3)	-11(4)	-6(4)
C(30)	55(4)	42(4)	29(3)	-2(3)	-2(3)	-12(3)
C(31)	40(4)	27(3)	29(3)	-12(2)	2(3)	-11(3)
C(32)	49(4)	57(4)	22(3)	-15(3)	-3(3)	-14(3)
C(33)	49(5)	87(6)	29(3)	-15(4)	2(3)	-19(4)
C(34)	30(4)	91(6)	46(4)	-29(4)	3(3)	-7(4)
C(35)	34(4)	74(5)	44(4)	-22(4)	-4(3)	-4(4)
C(36)	55(5)	46(4)	24(3)	-10(3)	-4(3)	-12(3)
C(37)	43(4)	30(3)	55(4)	-24(3)	-1(3)	-16(3)
C(38)	58(5)	49(5)	77(5)	-13(4)	13(4)	-15(4)
C(39)	49(5)	53(5)	124(8)	-12(5)	22(5)	-1(4)
C(40)	79(7)	41(5)	113(7)	9(5)	-17(6)	-25(5)
C(41)	50(5)	52(5)	77(5)	4(4)	-9(5)	-14(4)
C(42)	43(4)	45(4)	49(4)	-6(3)	-4(3)	-14(3)
C(43)	42(4)	35(3)	32(3)	-15(3)	-1(3)	-10(3)
C(44)	63(5)	39(4)	45(4)	-9(3)	-12(3)	-23(3)
C(45)	60(5)	49(4)	59(4)	-24(4)	-13(4)	-21(4)
C(46)	46(4)	76(5)	67(5)	-43(4)	-13(4)	-18(4)
C(47)	43(4)	60(5)	37(4)	-23(3)	1(3)	-14(3)
C(48)	50(4)	49(4)	41(4)	-24(3)	10(3)	-25(3)
C(49)	34(4)	33(3)	37(3)	-5(3)	-7(3)	-7(3)
C(50)	34(4)	39(4)	59(4)	-5(3)	2(3)	-13(3)
C(51)	45(4)	48(4)	73(5)	9(4)	-3(4)	-26(4)
C(52)	50(5)	28(4)	87(6)	-9(4)	-18(4)	-13(3)
C(53)	68(5)	36(4)	64(5)	-14(4)	-19(4)	-19(4)
C(54)	59(4)	33(3)	38(3)	-7(3)	-19(3)	-15(3)
C(55)	41(4)	35(3)	27(3)	-8(3)	-5(3)	-14(3)
C(58)	109(7)	53(5)	57(5)	17(4)	-36(5)	-46(5)
C(59)	78(6)	48(4)	43(4)	12(3)	7(4)	-7(4)
C(60)	73(5)	41(4)	37(4)	7(3)	10(4)	-8(4)
C(61)	36(4)	36(3)	26(3)	-9(3)	0(3)	-14(3)
C(62)	64(5)	82(5)	24(3)	-11(3)	0(3)	-32(4)
C(63)	60(5)	101(6)	41(4)	1(4)	0(4)	-48(5)
C(64)	61(5)	81(5)	32(4)	-9(4)	11(3)	-35(4)
C(65)	61(5)	69(5)	27(3)	-6(3)	6(3)	-29(4)
C(66)	55(4)	49(4)	31(3)	-9(3)	0(3)	-21(3)
C(67)	35(4)	38(3)	28(3)	-10(3)	5(3)	-13(3)
C(68)	32(4)	42(4)	46(4)	-8(3)	3(3)	-8(3)
C(69)	41(4)	51(4)	63(5)	-9(4)	1(4)	-8(3)

C(70)	60(5)	39(4)	77(5)	-22(4)	15(4)	-15(4)
C(71)	71(6)	51(4)	48(4)	-25(3)	6(4)	-23(4)
C(72)	47(4)	39(4)	28(3)	-12(3)	2(3)	-12(3)
C(73)	46(4)	31(3)	25(3)	-5(2)	-5(3)	-18(3)
C(74)	59(4)	35(3)	27(3)	-3(3)	-4(3)	-19(3)
C(75)	90(6)	38(4)	39(4)	-2(3)	-3(4)	-36(4)
C(76)	141(8)	34(4)	52(5)	-14(3)	-12(5)	-41(5)
C(77)	104(6)	39(4)	27(3)	-14(3)	1(4)	-27(4)
C(78)	78(5)	39(4)	22(3)	-7(3)	-5(3)	-27(4)
C(79)	60(5)	29(3)	23(3)	-8(2)	4(3)	-15(3)
C(80)	105(6)	58(5)	27(3)	-16(3)	9(4)	-45(4)
C(81)	134(9)	78(6)	46(4)	-39(4)	15(5)	-58(6)
C(82)	90(6)	72(5)	35(4)	-23(4)	19(4)	-48(5)
C(83)	72(5)	54(4)	37(4)	-3(3)	9(4)	-28(4)
C(84)	55(5)	42(4)	31(3)	-12(3)	2(3)	-17(3)
C(85)	52(4)	22(3)	45(4)	0(3)	-23(3)	-7(3)
C(86)	94(6)	54(5)	38(4)	-4(3)	-25(4)	-29(4)
C(87)	126(8)	56(5)	70(6)	1(4)	-69(6)	-25(5)
C(88)	80(6)	47(5)	104(7)	-19(5)	-50(5)	-18(4)
C(89)	81(6)	50(5)	95(7)	-9(5)	-47(5)	-18(4)
C(90)	59(5)	49(4)	77(5)	-12(4)	-28(4)	-21(4)
C(91)	37(4)	34(3)	32(3)	-2(3)	-5(3)	-16(3)
C(92A)	53(5)	31(4)	34(4)	-1(3)	2(4)	-13(4)
C(93A)	57(6)	38(5)	46(5)	-16(4)	4(4)	-8(4)
C(94)	53(5)	48(4)	49(4)	-14(3)	6(4)	-11(4)
C(95A)	44(5)	52(5)	39(4)	-13(4)	6(4)	-22(4)
C(96A)	38(5)	30(4)	29(4)	-3(3)	-4(3)	-8(3)
C(97)	45(4)	39(3)	21(3)	-5(2)	-7(3)	-17(3)
C(98)	34(4)	38(3)	25(3)	-7(3)	2(3)	-17(3)
C(99)	33(4)	44(4)	22(3)	-3(3)	-7(3)	-16(3)
C(100)	33(4)	31(3)	30(3)	1(3)	1(3)	-12(3)
C(101)	43(4)	47(4)	35(3)	-2(3)	-7(3)	-9(3)
C(102)	73(5)	56(4)	38(4)	-19(3)	22(4)	-22(4)
C(103)	58(4)	35(3)	26(3)	-12(3)	7(3)	-18(3)
C(104)	72(5)	54(4)	24(3)	-17(3)	4(3)	-27(4)
C(105)	71(5)	31(3)	25(3)	-10(3)	-11(3)	-17(3)
C(106)	91(6)	76(5)	43(4)	-26(4)	-10(4)	-45(5)
C(107)	56(5)	82(6)	61(5)	-13(4)	-7(4)	-18(4)
C(108)	35(4)	43(4)	55(4)	-26(3)	-3(3)	-7(3)
C(109)	50(5)	53(4)	48(4)	-18(3)	6(4)	-18(4)
C(110)	49(5)	44(4)	44(4)	-20(3)	12(3)	-21(3)
C(111)	72(5)	70(5)	46(4)	-17(4)	26(4)	-35(4)
C(112)	67(5)	39(4)	35(3)	-1(3)	8(3)	-19(3)
C(113)	44(4)	40(4)	27(3)	0(3)	-6(3)	-21(3)
C(114)	62(5)	29(3)	34(3)	3(3)	-7(3)	-24(3)
C(115)	48(4)	28(3)	36(3)	-5(3)	-11(3)	-16(3)
C(116)	76(5)	29(3)	47(4)	-9(3)	-7(4)	-21(3)
C(117)	166(12)	86(8)	99(8)	-6(7)	-13(8)	-44(8)
C(118)	137(10)	104(9)	92(8)	-4(6)	31(7)	-2(8)
C(119)	27(6)	890(60)	390(30)	-560(40)	23(10)	-23(15)
C(120)	1740(130)	330(30)	78(12)	-59(16)	170(30)	-600(60)

8.8. Compound 11

Table 1. Crystal data and structure refinement for sh2475.

Identification code	sh2475	
Empirical formula	C87 H81 Al2 Fe2 O17 Si6 · 2 C4 H10 O	
Formula weight	1880.96	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 18.2234(13) Å	α= 90°.
	b = 15.2964(9) Å	β= 100.696(3)°.
	c = 37.322(2) Å	γ = 90°.
Volume	10222.8(12) $Å^3$	
Z	4	
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.433 mm^{-1}	
F(000)	3940	
Crystal size	0.4 x 0.2 x 0.11 mm^3	
Theta range for data collection	1.11 to 28.36°.	
Index ranges	-24<=h<=22, -20<=k<=16, -48<=l<=49	
Reflections collected	85869	
Independent reflections	25406 [R(int) = 0.0919]	
Completeness to theta = 28.36°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25406 / 0 / 1109	
Goodness-of-fit on F^2	1.185	
Final R indices [I>2sigma(I)]	R1 = 0.0760, wR2 = 0.1711	
R indices (all data)	R1 = 0.1752, wR2 = 0.2024	
Largest diff. peak and hole	1.045 and -1.193 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2475. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	9034(1)	7151(1)	1313(1)	29(1)
Fe(2)	7887(1)	6060(1)	849(1)	37(1)
Al(2)	8460(1)	8750(1)	1607(1)	16(1)
Si(1)	6176(1)	5666(1)	708(1)	27(1)
Si(2)	5940(1)	7568(1)	405(1)	25(1)
Si(3)	8721(1)	9015(1)	323(1)	27(1)
Si(4)	9683(1)	9084(1)	1092(1)	28(1)
Si(5)	8426(1)	7028(1)	2106(1)	34(1)
Si(6)	8580(1)	5340(1)	1683(1)	32(1)
Al(1)	7614(1)	8179(1)	788(1)	23(1)
O(1)	9677(2)	6883(2)	962(1)	36(1)
O(2)	9896(2)	6870(2)	1704(1)	38(1)
O(3)	7576(2)	6269(2)	320(1)	32(1)
O(4)	8418(2)	5047(2)	724(1)	39(1)
O(5)	7750(2)	9125(2)	1883(1)	41(1)
O(6)	9147(2)	9468(2)	1880(1)	55(1)
O(7)	8592(2)	5958(2)	1329(1)	28(1)
O(8)	8157(2)	7252(2)	932(1)	25(1)
O(9)	6977(2)	5851(2)	959(1)	29(1)
O(10)	5845(2)	6527(2)	474(1)	28(1)
O(11)	6680(2)	7965(2)	648(1)	27(1)
O(12)	7713(2)	8856(2)	1197(1)	30(1)
O(13)	7973(2)	8763(2)	469(1)	28(1)
O(14)	9454(2)	8951(2)	654(1)	28(1)
O(15)	9158(2)	8478(2)	1309(1)	29(1)
O(16)	8525(2)	7600(2)	1745(1)	29(1)
O(17)	8468(2)	5986(2)	2016(1)	34(1)
C(1)	6261(2)	4742(3)	389(1)	30(1)
C(2)	6661(3)	4001(3)	532(1)	38(1)
C(3)	6764(3)	3305(3)	305(2)	46(1)
C(4)	6465(3)	3333(3)	-58(2)	46(1)
C(5)	6069(3)	4050(3)	-206(1)	42(1)
C(6)	5966(3)	4746(3)	18(1)	34(1)
C(7)	5503(3)	5375(3)	1010(1)	31(1)
C(8)	5001(3)	4677(3)	940(1)	38(1)
C(9)	4492(3)	4494(4)	1163(2)	51(1)
C(10)	4470(3)	5007(4)	1462(2)	60(2)
C(11)	4974(3)	5696(4)	1544(1)	54(2)
C(12)	5473(3)	5869(3)	1323(1)	42(1)
C(13)	5922(3)	7760(3)	-94(1)	28(1)
C(14)	5314(3)	7489(3)	-355(1)	39(1)
C(15)	5296(3)	7650(4)	-721(1)	53(2)
C(16)	5866(4)	8088(3)	-838(1)	50(2)
C(17)	6471(3)	8361(3)	-582(1)	47(1)
C(18)	6495(3)	8203(3)	-215(1)	34(1)
C(19)	5104(3)	8128(3)	524(1)	32(1)
C(20)	4742(3)	7829(3)	798(1)	44(1)
C(21)	4165(3)	8308(4)	907(2)	61(2)
C(22)	3945(3)	9099(4)	737(2)	62(2)
C(23)	4274(3)	9387(4)	468(2)	58(2)
C(24)	4851(3)	8922(3)	357(1)	46(1)

C(25)	8890(3)	8243(3)	-42(1)	34(1)
C(26)	9057(3)	7374(3)	32(1)	38(1)
C(27)	9192(3)	6798(4)	-235(2)	50(1)
C(28)	9164(4)	7090(5)	-583(2)	65(2)
C(29)	8989(4)	7946(5)	-670(2)	67(2)
C(30)	8854(3)	8512(4)	-405(1)	50(1)
C(31)	8613(3)	10156(3)	145(1)	31(1)
C(32)	9201(3)	10746(3)	168(1)	40(1)
C(33)	9078(3)	11599(3)	49(1)	46(1)
C(34)	8383(3)	11880(3)	-92(2)	47(1)
C(35)	7784(3)	11317(3)	-118(2)	51(1)
C(36)	7899(3)	10465(3)	1(1)	45(1)
C(37)	9576(3)	10266(3)	1201(1)	35(1)
C(38)	10172(3)	10751(3)	1387(1)	49(1)
C(39)	10106(4)	11630(4)	1460(2)	69(2)
C(40)	9446(4)	12051(4)	1346(2)	90(2)
C(41)	8846(4)	11597(4)	1147(2)	85(2)
C(42)	8912(3)	10717(3)	1080(2)	56(2)
C(43)	10679(3)	8778(3)	1242(1)	38(1)
C(44)	10979(3)	8662(3)	1611(2)	47(1)
C(45)	11730(4)	8492(4)	1725(2)	68(2)
C(46)	12209(4)	8441(5)	1481(2)	83(2)
C(47)	11926(4)	8555(5)	1116(2)	79(2)
C(48)	11170(3)	8729(4)	995(2)	54(2)
C(49)	7484(3)	7264(3)	2213(1)	39(1)
C(50)	7359(3)	7352(4)	2568(1)	51(1)
C(51)	6646(4)	7511(4)	2633(2)	68(2)
C(52)	6057(4)	7579(4)	2348(2)	70(2)
C(53)	6164(3)	7486(4)	2000(2)	60(2)
C(54)	6862(3)	7332(3)	1930(1)	47(1)
C(55)	9191(3)	7242(3)	2496(1)	41(1)
C(56A)	9340(6)	8012(7)	2649(3)	61(1)
C(57A)	9938(6)	8187(7)	2936(3)	61(1)
C(56B)	9702(9)	8026(9)	2481(4)	61(1)
C(57B)	10274(9)	8181(10)	2780(4)	61(1)
C(58)	10386(4)	7558(4)	3076(2)	65(2)
C(59A)	10307(6)	6690(7)	2930(3)	61(1)
C(60A)	9718(6)	6533(7)	2633(3)	61(1)
C(59B)	9894(9)	6953(9)	3092(4)	61(1)
C(60B)	9307(9)	6776(10)	2792(4)	61(1)
C(61)	7805(3)	4528(3)	1618(1)	35(1)
C(62)	7891(3)	3704(3)	1479(1)	47(1)
C(63)	7332(4)	3085(4)	1445(2)	57(2)
C(64)	6663(3)	3272(4)	1547(1)	51(2)
C(65)	6559(3)	4091(4)	1681(1)	51(1)
C(66)	7118(3)	4711(3)	1715(1)	43(1)
C(67)	9479(3)	4734(3)	1806(1)	42(1)
C(68)	9736(3)	4411(4)	2152(2)	66(2)
C(69)	10383(4)	3941(5)	2240(2)	77(2)
C(70)	10796(4)	3764(4)	1985(2)	83(2)
C(71)	10558(3)	4067(4)	1626(2)	67(2)
C(72)	9903(3)	4539(3)	1546(2)	48(1)
C(73)	10339(3)	6583(3)	1016(2)	45(1)
C(74)	10772(3)	6427(3)	1357(2)	49(1)
C(75)	10539(3)	6574(3)	1682(2)	43(1)

C(76)	11052(3)	6380(4)	2037(2)	67(2)
C(77)	10637(3)	6387(4)	669(2)	69(2)
C(78)	7662(3)	5808(3)	49(1)	33(1)
C(79)	8090(3)	5041(3)	84(1)	41(1)
C(80)	8440(3)	4698(3)	410(1)	39(1)
C(81)	7292(3)	6121(3)	-321(1)	46(1)
C(82)	8896(4)	3885(4)	429(2)	68(2)
C(83)	7806(3)	9672(3)	2147(1)	46(1)
C(84)	8460(4)	10109(4)	2285(1)	56(2)
C(85)	9097(4)	9987(4)	2149(2)	61(2)
C(86)	9809(4)	10448(5)	2311(2)	102(3)
C(87)	7113(3)	9798(4)	2305(2)	62(2)
O(18)	6582(3)	7(3)	1193(2)	96(2)
C(88)	5968(5)	-485(7)	1348(2)	121(3)
C(89)	6675(7)	885(8)	731(5)	210(8)
C(90)	6276(8)	387(8)	819(5)	214(8)
C(91)	5473(7)	53(9)	1490(3)	224(8)
O(19)	2736(8)	5136(9)	1607(4)	145(5)
C(92)	2652(12)	4167(13)	1667(5)	141(7)
C(93)	2851(13)	4109(15)	2094(6)	173(9)
C(94)	2639(12)	5292(13)	1228(5)	140(7)
C(95)	2816(12)	6159(13)	1112(5)	141(7)
O(20)	2107(10)	1534(11)	2059(5)	176(6)
C(96)	1925(12)	1335(13)	2350(6)	133(7)
C(97)	1647(11)	1638(12)	2609(5)	123(6)
C(98)	2420(14)	1239(15)	1798(6)	161(8)
C(99)	2474(14)	1943(15)	1582(6)	169(9)

Table 3. Bond lengths [Å] and angles [°] for sh2475.

Fe(1)-O(8)	1.937(3)	C(3)-C(4)	1.364(7)
Fe(1)-O(1)	1.955(3)	C(4)-C(5)	1.371(7)
Fe(1)-O(2)	1.983(3)	C(5)-C(6)	1.388(6)
Fe(1)-O(7)	2.000(3)	C(7)-C(8)	1.399(6)
Fe(1)-O(15)	2.043(3)	C(7)-C(12)	1.402(6)
Fe(1)-O(16)	2.120(3)	C(8)-C(9)	1.386(6)
Fe(1)-Al(2)	2.9512(13)	C(9)-C(10)	1.368(7)
Fe(1)-Fe(2)	2.9681(10)	C(10)-C(11)	1.394(8)
Fe(2)-O(9)	1.808(3)	C(11)-C(12)	1.363(7)
Fe(2)-O(8)	1.900(3)	C(13)-C(18)	1.389(6)
Fe(2)-O(4)	1.929(3)	C(13)-C(14)	1.395(6)
Fe(2)-O(3)	1.976(3)	C(14)-C(15)	1.384(7)
Fe(2)-O(7)	2.007(3)	C(15)-C(16)	1.373(8)
Al(2)-O(6)	1.827(3)	C(16)-C(17)	1.384(7)
Al(2)-O(16)	1.831(3)	C(17)-C(18)	1.384(6)
Al(2)-O(12)	1.855(3)	C(19)-C(20)	1.393(6)
Al(2)-O(15)	1.884(3)	C(19)-C(24)	1.405(6)
Al(2)-O(5)	1.888(3)	C(20)-C(21)	1.403(7)
Si(1)-O(9)	1.608(3)	C(21)-C(22)	1.391(8)
Si(1)-O(10)	1.632(3)	C(22)-C(23)	1.334(8)
Si(1)-C(7)	1.866(5)	C(23)-C(24)	1.395(7)
Si(1)-C(1)	1.871(4)	C(25)-C(26)	1.380(6)
Si(2)-O(11)	1.598(3)	C(25)-C(30)	1.405(6)
Si(2)-O(10)	1.627(3)	C(26)-C(27)	1.385(6)
Si(2)-C(19)	1.872(5)	C(27)-C(28)	1.366(8)
Si(2)-C(13)	1.881(4)	C(28)-C(29)	1.372(8)
Si(3)-O(13)	1.605(3)	C(29)-C(30)	1.371(7)
Si(3)-O(14)	1.644(3)	C(31)-C(32)	1.391(6)
Si(3)-C(31)	1.865(4)	C(31)-C(36)	1.394(7)
Si(3)-C(25)	1.871(5)	C(32)-C(33)	1.384(6)
Si(4)-O(14)	1.626(3)	C(33)-C(34)	1.348(7)
Si(4)-O(15)	1.648(3)	C(34)-C(35)	1.381(7)
Si(4)-C(43)	1.859(5)	C(35)-C(36)	1.380(6)
Si(4)-C(37)	1.870(5)	C(37)-C(38)	1.390(7)
Si(5)-O(17)	1.633(3)	C(37)-C(42)	1.394(7)
Si(5)-O(16)	1.645(3)	C(38)-C(39)	1.381(7)
Si(5)-C(55)	1.847(5)	C(39)-C(40)	1.361(9)
Si(5)-C(49)	1.869(5)	C(40)-C(41)	1.390(9)
Si(6)-O(7)	1.629(3)	C(41)-C(42)	1.377(7)
Si(6)-O(17)	1.631(3)	C(43)-C(44)	1.395(7)
Si(6)-C(61)	1.862(5)	C(43)-C(48)	1.402(7)
Si(6)-C(67)	1.865(5)	C(44)-C(45)	1.380(8)
Al(1)-O(13)	1.713(3)	C(45)-C(46)	1.375(9)
Al(1)-O(11)	1.717(3)	C(46)-C(47)	1.376(9)
Al(1)-O(8)	1.756(3)	C(47)-C(48)	1.393(8)
Al(1)-O(12)	1.826(3)	C(49)-C(50)	1.394(6)
O(1)-C(73)	1.272(6)	C(49)-C(54)	1.402(7)
O(2)-C(75)	1.273(6)	C(50)-C(51)	1.386(8)
O(3)-C(78)	1.267(5)	C(51)-C(52)	1.369(9)
O(4)-C(80)	1.296(5)	C(52)-C(53)	1.357(8)
O(5)-C(83)	1.282(5)	C(53)-C(54)	1.366(7)
O(6)-C(85)	1.297(6)	C(55)-C(60B)	1.299(15)
C(1)-C(6)	1.392(6)	C(55)-C(56A)	1.317(11)
C(1)-C(2)	1.399(6)	C(55)-C(60A)	1.475(11)
C(2)-C(3)	1.396(6)	C(55)-C(56B)	1.527(16)

C(56A)-C(57A)	1.403(14)
C(57A)-C(58)	1.306(11)
C(56B)-C(57B)	1.40(2)
C(57B)-C(58)	1.445(16)
C(58)-C(59B)	1.299(15)
C(58)-C(59A)	1.433(11)
C(59A)-C(60A)	1.414(13)
C(59B)-C(60B)	1.42(2)
C(61)-C(62)	1.381(7)
C(61)-C(66)	1.397(7)
C(62)-C(63)	1.380(7)
C(63)-C(64)	1.371(8)
C(64)-C(65)	1.376(7)
C(65)-C(66)	1.380(7)
C(67)-C(72)	1.379(7)
C(67)-C(68)	1.381(7)
C(68)-C(69)	1.368(8)
C(69)-C(70)	1.346(9)
C(70)-C(71)	1.409(9)
C(71)-C(72)	1.380(7)
C(73)-C(74)	1.386(7)
C(73)-C(77)	1.527(7)
C(74)-C(75)	1.379(7)
C(75)-C(76)	1.501(7)
C(78)-C(79)	1.401(6)
C(78)-C(81)	1.498(6)
C(79)-C(80)	1.371(7)
C(80)-C(82)	1.491(7)
C(83)-C(84)	1.380(8)
C(83)-C(87)	1.501(7)
C(84)-C(85)	1.363(8)
C(85)-C(86)	1.502(8)
O(18)-C(90)	1.520(15)
O(18)-C(88)	1.546(10)
C(88)-C(91)	1.397(11)
C(89)-C(90)	1.142(14)
O(19)-C(94)	1.411(19)
O(19)-C(92)	1.51(2)
C(92)-C(93)	1.57(2)
C(94)-C(95)	1.45(2)
O(20)-C(96)	1.23(2)
O(20)-C(98)	1.30(2)
C(96)-C(97)	1.26(2)
C(98)-C(99)	1.36(2)
O(8)-Fe(1)-O(1)	92.34(12)
O(8)-Fe(1)-O(2)	171.92(12)
O(1)-Fe(1)-O(2)	87.54(14)
O(8)-Fe(1)-O(7)	79.20(11)
O(1)-Fe(1)-O(7)	97.10(12)
O(2)-Fe(1)-O(7)	92.78(12)
O(8)-Fe(1)-O(15)	89.56(12)
O(1)-Fe(1)-O(15)	97.06(12)
O(2)-Fe(1)-O(15)	98.48(12)
O(7)-Fe(1)-O(15)	162.24(12)
O(8)-Fe(1)-O(16)	96.54(11)
O(1)-Fe(1)-O(16)	168.24(13)
O(2)-Fe(1)-O(16)	84.74(12)
O(7)-Fe(1)-O(16)	92.13(11)
O(15)-Fe(1)-O(16)	75.39(11)
O(8)-Fe(1)-Al(2)	84.56(8)
O(1)-Fe(1)-Al(2)	136.09(9)
O(2)-Fe(1)-Al(2)	101.11(10)
O(7)-Fe(1)-Al(2)	124.93(8)
O(15)-Fe(1)-Al(2)	39.29(8)
O(16)-Fe(1)-Al(2)	38.07(8)
O(8)-Fe(1)-Fe(2)	38.87(8)
O(1)-Fe(1)-Fe(2)	86.35(10)
O(2)-Fe(1)-Fe(2)	133.10(9)
O(7)-Fe(1)-Fe(2)	42.28(8)
O(15)-Fe(1)-Fe(2)	128.41(9)
O(16)-Fe(1)-Fe(2)	105.39(8)
Al(2)-Fe(1)-Fe(2)	115.02(3)
O(9)-Fe(2)-O(8)	110.71(12)
O(9)-Fe(2)-O(4)	115.76(14)
O(8)-Fe(2)-O(4)	133.16(13)
O(9)-Fe(2)-O(3)	98.66(13)
O(8)-Fe(2)-O(3)	91.47(12)
O(4)-Fe(2)-O(3)	87.29(12)
O(9)-Fe(2)-O(7)	104.21(12)
O(8)-Fe(2)-O(7)	79.92(11)
O(4)-Fe(2)-O(7)	83.45(12)
O(3)-Fe(2)-O(7)	157.12(12)
O(9)-Fe(2)-Fe(1)	122.89(9)
O(8)-Fe(2)-Fe(1)	39.78(8)
O(4)-Fe(2)-Fe(1)	105.17(10)
O(3)-Fe(2)-Fe(1)	122.15(9)
O(7)-Fe(2)-Fe(1)	42.13(8)
O(6)-Al(2)-O(16)	114.70(17)
O(6)-Al(2)-O(12)	136.87(16)
O(16)-Al(2)-O(12)	108.34(13)
O(6)-Al(2)-O(15)	89.66(14)
O(16)-Al(2)-O(15)	86.49(13)
O(12)-Al(2)-O(15)	90.31(13)
O(6)-Al(2)-O(5)	88.92(15)
O(16)-Al(2)-O(5)	98.75(14)
O(12)-Al(2)-O(5)	87.22(14)
O(15)-Al(2)-O(5)	174.69(15)
O(6)-Al(2)-Fe(1)	116.84(13)
O(16)-Al(2)-Fe(1)	45.54(9)
O(12)-Al(2)-Fe(1)	91.28(9)
O(15)-Al(2)-Fe(1)	43.35(9)
O(5)-Al(2)-Fe(1)	141.36(11)
O(9)-Si(1)-O(10)	112.08(15)
O(9)-Si(1)-C(7)	108.47(18)
O(10)-Si(1)-C(7)	107.25(18)
O(9)-Si(1)-C(1)	109.23(18)
O(10)-Si(1)-C(1)	109.66(18)
C(7)-Si(1)-C(1)	110.1(2)

O(11)-Si(2)-O(10)	112.72(16)
O(11)-Si(2)-C(19)	109.26(17)
O(10)-Si(2)-C(19)	107.15(18)
O(11)-Si(2)-C(13)	111.15(18)
O(10)-Si(2)-C(13)	109.04(17)
C(19)-Si(2)-C(13)	107.3(2)
O(13)-Si(3)-O(14)	110.73(15)
O(13)-Si(3)-C(31)	107.76(18)
O(14)-Si(3)-C(31)	109.93(18)
O(13)-Si(3)-C(25)	111.06(18)
O(14)-Si(3)-C(25)	106.77(18)
C(31)-Si(3)-C(25)	110.6(2)
O(14)-Si(4)-O(15)	111.04(15)
O(14)-Si(4)-C(43)	109.00(19)
O(15)-Si(4)-C(43)	109.51(19)
O(14)-Si(4)-C(37)	108.80(19)
O(15)-Si(4)-C(37)	110.17(18)
C(43)-Si(4)-C(37)	108.3(2)
O(17)-Si(5)-O(16)	109.51(15)
O(17)-Si(5)-C(55)	106.1(2)
O(16)-Si(5)-C(55)	111.73(19)
O(17)-Si(5)-C(49)	108.18(19)
O(16)-Si(5)-C(49)	108.4(2)
C(55)-Si(5)-C(49)	112.8(2)
O(7)-Si(6)-O(17)	106.84(15)
O(7)-Si(6)-C(61)	113.91(18)
O(17)-Si(6)-C(61)	107.76(19)
O(7)-Si(6)-C(67)	110.14(19)
O(17)-Si(6)-C(67)	110.0(2)
C(61)-Si(6)-C(67)	108.1(2)
O(13)-Al(1)-O(11)	111.95(15)
O(13)-Al(1)-O(8)	111.58(14)
O(11)-Al(1)-O(8)	114.17(14)
O(13)-Al(1)-O(12)	107.17(14)
O(11)-Al(1)-O(12)	107.49(14)
O(8)-Al(1)-O(12)	103.81(14)
C(73)-O(1)-Fe(1)	129.6(3)
C(75)-O(2)-Fe(1)	130.0(3)
C(78)-O(3)-Fe(2)	130.8(3)
C(80)-O(4)-Fe(2)	130.6(3)
C(83)-O(5)-Al(2)	130.8(4)
C(85)-O(6)-Al(2)	131.3(4)
Si(6)-O(7)-Fe(1)	128.31(17)
Si(6)-O(7)-Fe(2)	131.79(17)
Fe(1)-O(7)-Fe(2)	95.59(12)
Al(1)-O(8)-Fe(2)	127.65(16)
Al(1)-O(8)-Fe(1)	129.11(15)
Fe(2)-O(8)-Fe(1)	101.35(12)
Si(1)-O(9)-Fe(2)	132.08(17)
Si(2)-O(10)-Si(1)	146.5(2)
Si(2)-O(11)-Al(1)	158.32(19)
Al(1)-O(12)-Al(2)	125.68(17)
Si(3)-O(13)-Al(1)	144.9(2)
Si(4)-O(14)-Si(3)	140.29(19)
Si(4)-O(15)-Al(2)	132.97(17)
Si(4)-O(15)-Fe(1)	129.62(16)
Al(2)-O(15)-Fe(1)	97.36(12)
Si(5)-O(16)-Al(2)	136.97(17)
Si(5)-O(16)-Fe(1)	125.54(17)
Al(2)-O(16)-Fe(1)	96.39(12)
Si(6)-O(17)-Si(5)	139.94(19)
C(6)-C(1)-C(2)	117.5(4)
C(6)-C(1)-Si(1)	124.6(3)
C(2)-C(1)-Si(1)	118.0(3)
C(3)-C(2)-C(1)	120.4(4)
C(4)-C(3)-C(2)	120.4(5)
C(3)-C(4)-C(5)	120.6(5)
C(4)-C(5)-C(6)	119.4(5)
C(5)-C(6)-C(1)	121.7(4)
C(8)-C(7)-C(12)	116.2(4)
C(8)-C(7)-Si(1)	123.4(3)
C(12)-C(7)-Si(1)	120.4(4)
C(9)-C(8)-C(7)	122.0(5)
C(10)-C(9)-C(8)	119.8(5)
C(9)-C(10)-C(11)	119.8(5)
C(12)-C(11)-C(10)	119.9(5)
C(11)-C(12)-C(7)	122.3(5)
C(18)-C(13)-C(14)	117.8(4)
C(18)-C(13)-Si(2)	121.4(3)
C(14)-C(13)-Si(2)	120.8(4)
C(15)-C(14)-C(13)	120.5(5)
C(16)-C(15)-C(14)	121.3(5)
C(15)-C(16)-C(17)	118.8(5)
C(16)-C(17)-C(18)	120.4(5)
C(17)-C(18)-C(13)	121.3(5)
C(20)-C(19)-C(24)	116.7(4)
C(20)-C(19)-Si(2)	122.8(4)
C(24)-C(19)-Si(2)	120.3(4)
C(19)-C(20)-C(21)	121.7(5)
C(22)-C(21)-C(20)	119.3(5)
C(23)-C(22)-C(21)	120.0(5)
C(22)-C(23)-C(24)	121.7(5)
C(23)-C(24)-C(19)	120.7(5)
C(26)-C(25)-C(30)	116.3(4)
C(26)-C(25)-Si(3)	121.5(3)
C(30)-C(25)-Si(3)	122.2(4)
C(25)-C(26)-C(27)	122.1(5)
C(28)-C(27)-C(26)	119.7(5)
C(27)-C(28)-C(29)	120.2(5)
C(30)-C(29)-C(28)	119.8(5)
C(29)-C(30)-C(25)	121.9(5)
C(32)-C(31)-C(36)	117.2(4)
C(32)-C(31)-Si(3)	123.7(4)
C(36)-C(31)-Si(3)	118.9(3)
C(33)-C(32)-C(31)	121.0(5)
C(34)-C(33)-C(32)	120.7(5)
C(33)-C(34)-C(35)	120.1(5)
C(36)-C(35)-C(34)	119.7(5)
C(35)-C(36)-C(31)	121.3(5)
C(38)-C(37)-C(42)	116.7(5)

C(38)-C(37)-Si(4)	121.4(4)
C(42)-C(37)-Si(4)	121.8(4)
C(39)-C(38)-C(37)	121.9(6)
C(40)-C(39)-C(38)	120.3(6)
C(39)-C(40)-C(41)	119.5(6)
C(42)-C(41)-C(40)	119.9(7)
C(41)-C(42)-C(37)	121.7(6)
C(44)-C(43)-C(48)	117.6(5)
C(44)-C(43)-Si(4)	120.7(4)
C(48)-C(43)-Si(4)	121.5(4)
C(45)-C(44)-C(43)	120.8(5)
C(46)-C(45)-C(44)	121.4(6)
C(45)-C(46)-C(47)	118.7(6)
C(46)-C(47)-C(48)	120.8(6)
C(47)-C(48)-C(43)	120.6(5)
C(50)-C(49)-C(54)	117.3(5)
C(50)-C(49)-Si(5)	122.7(4)
C(54)-C(49)-Si(5)	120.0(4)
C(51)-C(50)-C(49)	120.5(6)
C(52)-C(51)-C(50)	120.2(5)
C(53)-C(52)-C(51)	120.3(6)
C(52)-C(53)-C(54)	120.5(6)
C(53)-C(54)-C(49)	121.2(5)
C(60B)-C(55)-C(56A)	97.6(9)
C(60B)-C(55)-C(60A)	46.3(7)
C(56A)-C(55)-C(60A)	116.0(7)
C(60B)-C(55)-C(56B)	117.3(10)
C(56A)-C(55)-C(56B)	40.0(6)
C(60A)-C(55)-C(56B)	103.2(8)
C(60B)-C(55)-Si(5)	123.5(8)
C(56A)-C(55)-Si(5)	124.5(6)
C(60A)-C(55)-Si(5)	119.4(5)
C(56B)-C(55)-Si(5)	119.1(6)
C(55)-C(56A)-C(57A)	124.8(10)
C(58)-C(57A)-C(56A)	120.3(10)
C(57B)-C(56B)-C(55)	118.2(13)
C(56B)-C(57B)-C(58)	118.6(13)
C(59B)-C(58)-C(57A)	99.0(10)
C(59B)-C(58)-C(59A)	48.3(7)
C(57A)-C(58)-C(59A)	121.2(8)
C(59B)-C(58)-C(57B)	120.3(11)
C(57A)-C(58)-C(57B)	38.7(6)
C(59A)-C(58)-C(57B)	109.3(8)
C(60A)-C(59A)-C(58)	117.6(9)
C(59A)-C(60A)-C(55)	119.9(9)
C(58)-C(59B)-C(60B)	121.6(13)
C(55)-C(60B)-C(59B)	123.0(13)
C(62)-C(61)-C(66)	116.7(5)
C(62)-C(61)-Si(6)	121.5(4)
C(66)-C(61)-Si(6)	121.8(4)
C(63)-C(62)-C(61)	121.9(5)
C(64)-C(63)-C(62)	120.7(5)
C(63)-C(64)-C(65)	118.7(5)
C(64)-C(65)-C(66)	120.7(5)
C(65)-C(66)-C(61)	121.3(5)
C(72)-C(67)-C(68)	116.4(5)
C(72)-C(67)-Si(6)	121.0(4)
C(68)-C(67)-Si(6)	122.5(4)
C(69)-C(68)-C(67)	122.7(6)
C(70)-C(69)-C(68)	120.3(6)
C(69)-C(70)-C(71)	119.6(6)
C(72)-C(71)-C(70)	118.6(6)
C(67)-C(72)-C(71)	122.4(6)
O(1)-C(73)-C(74)	124.8(5)
O(1)-C(73)-C(77)	114.4(5)
C(74)-C(73)-C(77)	120.9(5)
C(75)-C(74)-C(73)	124.3(5)
O(2)-C(75)-C(74)	123.5(5)
O(2)-C(75)-C(76)	116.4(5)
C(74)-C(75)-C(76)	120.1(5)
O(3)-C(78)-C(79)	122.8(4)
O(3)-C(78)-C(81)	117.2(4)
C(79)-C(78)-C(81)	120.1(4)
C(80)-C(79)-C(78)	124.2(4)
O(4)-C(80)-C(79)	124.0(4)
O(4)-C(80)-C(82)	114.2(4)
C(79)-C(80)-C(82)	121.8(4)
O(5)-C(83)-C(84)	122.8(5)
O(5)-C(83)-C(87)	115.6(5)
C(84)-C(83)-C(87)	121.6(5)
C(85)-C(84)-C(83)	122.2(5)
O(6)-C(85)-C(84)	124.0(5)
O(6)-C(85)-C(86)	114.8(6)
C(84)-C(85)-C(86)	121.2(5)
C(90)-O(18)-C(88)	111.3(7)
C(91)-C(88)-O(18)	114.6(10)
C(89)-C(90)-O(18)	112.0(14)
C(94)-O(19)-C(92)	108.5(14)
O(19)-C(92)-C(93)	101.3(16)
O(19)-C(94)-C(95)	117.5(17)
C(96)-O(20)-C(98)	144(2)
O(20)-C(96)-C(97)	143(2)
O(20)-C(98)-C(99)	105(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2475. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	28(1)	32(1)	27(1)	1(1)	2(1)	-3(1)
Fe(2)	38(1)	35(1)	36(1)	-1(1)	4(1)	1(1)
Al(2)	18(1)	17(1)	11(1)	-7(1)	3(1)	-6(1)
Si(1)	29(1)	24(1)	27(1)	0(1)	2(1)	-3(1)
Si(2)	23(1)	23(1)	27(1)	-1(1)	3(1)	-1(1)
Si(3)	25(1)	27(1)	30(1)	3(1)	4(1)	-3(1)
Si(4)	27(1)	26(1)	30(1)	-2(1)	2(1)	-6(1)
Si(5)	34(1)	45(1)	23(1)	0(1)	4(1)	-8(1)
Si(6)	32(1)	34(1)	28(1)	7(1)	3(1)	-2(1)
Al(1)	23(1)	21(1)	23(1)	-2(1)	4(1)	-3(1)
O(1)	31(2)	40(2)	36(2)	6(2)	6(2)	5(2)
O(2)	31(2)	46(2)	33(2)	7(2)	-4(2)	-6(2)
O(3)	40(2)	28(2)	28(2)	0(1)	5(2)	2(2)
O(4)	42(2)	39(2)	33(2)	-2(2)	1(2)	10(2)
O(5)	46(2)	43(2)	34(2)	-16(2)	10(2)	1(2)
O(6)	62(3)	64(2)	44(2)	-28(2)	21(2)	-31(2)
O(7)	29(2)	28(2)	27(2)	3(1)	5(1)	0(1)
O(8)	23(2)	24(2)	26(2)	2(1)	1(1)	-1(1)
O(9)	29(2)	29(2)	28(2)	2(1)	4(1)	-4(1)
O(10)	27(2)	25(2)	31(2)	2(1)	2(1)	-2(1)
O(11)	24(2)	27(2)	30(2)	-3(1)	4(1)	-1(1)
O(12)	29(2)	33(2)	28(2)	-8(1)	3(1)	-3(1)
O(13)	27(2)	27(2)	30(2)	2(1)	7(1)	-1(1)
O(14)	25(2)	29(2)	29(2)	-1(1)	4(1)	-5(1)
O(15)	30(2)	28(2)	27(2)	-3(1)	5(1)	-4(1)
O(16)	32(2)	37(2)	20(2)	-2(1)	5(1)	-5(1)
O(17)	39(2)	36(2)	24(2)	5(1)	2(1)	-7(2)
C(1)	26(3)	24(2)	37(3)	-3(2)	4(2)	-5(2)
C(2)	39(3)	32(3)	40(3)	0(2)	1(2)	-3(2)
C(3)	44(3)	24(3)	67(4)	-3(3)	-1(3)	5(2)
C(4)	37(3)	39(3)	60(4)	-21(3)	2(3)	3(3)
C(5)	36(3)	47(3)	38(3)	-13(2)	-7(2)	6(3)
C(6)	27(3)	31(3)	39(3)	-8(2)	-4(2)	1(2)
C(7)	31(3)	28(3)	32(3)	6(2)	1(2)	1(2)
C(8)	40(3)	41(3)	35(3)	2(2)	8(2)	-5(2)
C(9)	49(4)	49(3)	54(3)	13(3)	9(3)	-19(3)
C(10)	62(4)	70(4)	54(4)	13(3)	31(3)	4(3)
C(11)	75(4)	52(4)	42(3)	1(3)	28(3)	-4(3)
C(12)	47(3)	43(3)	38(3)	-3(2)	13(3)	-9(3)
C(13)	31(3)	23(2)	28(2)	0(2)	2(2)	8(2)
C(14)	40(3)	35(3)	38(3)	-2(2)	-4(2)	0(2)
C(15)	62(4)	55(4)	33(3)	-10(3)	-16(3)	5(3)
C(16)	79(5)	43(3)	27(3)	4(2)	9(3)	4(3)
C(17)	64(4)	40(3)	39(3)	7(2)	15(3)	-4(3)
C(18)	39(3)	34(3)	28(3)	6(2)	1(2)	1(2)
C(19)	26(3)	28(3)	41(3)	-6(2)	2(2)	-3(2)
C(20)	38(3)	40(3)	59(3)	-7(3)	19(3)	-1(3)
C(21)	50(4)	68(4)	71(4)	-18(3)	28(3)	-1(3)
C(22)	37(3)	67(4)	83(5)	-26(4)	13(3)	15(3)
C(23)	46(4)	50(4)	75(4)	-6(3)	6(3)	25(3)

C(24)	35(3)	44(3)	57(3)	3(3)	4(3)	8(3)
C(25)	26(3)	44(3)	30(3)	1(2)	1(2)	-6(2)
C(26)	37(3)	36(3)	42(3)	-3(2)	12(2)	-6(2)
C(27)	43(3)	46(3)	64(4)	-14(3)	19(3)	-1(3)
C(28)	68(5)	81(5)	52(4)	-27(3)	26(3)	1(4)
C(29)	80(5)	91(5)	32(3)	-7(3)	16(3)	5(4)
C(30)	57(4)	56(4)	35(3)	3(3)	6(3)	0(3)
C(31)	33(3)	29(3)	30(2)	2(2)	6(2)	-4(2)
C(32)	31(3)	32(3)	57(3)	11(2)	8(2)	-6(2)
C(33)	36(3)	35(3)	67(4)	7(3)	15(3)	-11(2)
C(34)	49(4)	26(3)	66(4)	15(2)	10(3)	5(3)
C(35)	40(3)	36(3)	74(4)	9(3)	1(3)	7(3)
C(36)	36(3)	33(3)	61(3)	4(3)	-1(3)	-7(2)
C(37)	34(3)	33(3)	41(3)	-7(2)	13(2)	-7(2)
C(38)	48(4)	36(3)	66(4)	-14(3)	17(3)	-8(3)
C(39)	63(5)	51(4)	95(5)	-31(3)	24(4)	-22(3)
C(40)	65(5)	37(4)	168(8)	-32(4)	22(5)	-3(4)
C(41)	64(5)	52(4)	137(7)	-22(4)	10(5)	12(4)
C(42)	51(4)	37(3)	80(4)	-16(3)	13(3)	5(3)
C(43)	37(3)	32(3)	43(3)	-2(2)	1(2)	-9(2)
C(44)	32(3)	52(3)	52(3)	5(3)	-7(3)	-2(3)
C(45)	50(4)	77(5)	64(4)	7(3)	-22(3)	-5(3)
C(46)	32(4)	125(6)	83(5)	16(5)	-11(4)	-6(4)
C(47)	39(4)	117(6)	83(5)	7(4)	16(4)	-3(4)
C(48)	31(3)	74(4)	55(3)	2(3)	5(3)	1(3)
C(49)	44(3)	38(3)	36(3)	-8(2)	14(2)	-15(2)
C(50)	49(4)	66(4)	41(3)	-16(3)	16(3)	-14(3)
C(51)	72(5)	79(5)	63(4)	-32(3)	39(4)	-18(4)
C(52)	45(4)	62(4)	111(6)	-48(4)	33(4)	-17(3)
C(53)	47(4)	67(4)	65(4)	-29(3)	5(3)	-4(3)
C(54)	38(3)	54(3)	48(3)	-18(3)	6(3)	-6(3)
C(55)	43(3)	56(3)	24(2)	3(2)	6(2)	-7(3)
C(61)	38(3)	39(3)	25(2)	10(2)	1(2)	-1(2)
C(62)	56(4)	41(3)	47(3)	-4(2)	15(3)	-7(3)
C(63)	73(5)	43(3)	57(4)	-8(3)	16(3)	-11(3)
C(64)	56(4)	50(4)	40(3)	13(3)	-5(3)	-17(3)
C(65)	36(3)	61(4)	53(3)	17(3)	4(3)	-1(3)
C(66)	43(3)	39(3)	45(3)	9(2)	5(3)	-7(3)
C(67)	35(3)	39(3)	48(3)	17(2)	-1(3)	-10(2)
C(68)	35(4)	92(5)	68(4)	39(4)	2(3)	5(3)
C(69)	53(4)	86(5)	87(5)	45(4)	-2(4)	2(4)
C(70)	43(4)	47(4)	146(7)	27(4)	-17(5)	5(3)
C(71)	51(4)	50(4)	97(5)	-10(4)	6(4)	7(3)
C(72)	42(3)	38(3)	60(4)	-1(3)	1(3)	3(3)
C(73)	44(4)	36(3)	56(3)	4(3)	11(3)	0(3)
C(74)	35(3)	46(3)	65(4)	12(3)	5(3)	8(3)
C(75)	34(3)	35(3)	56(3)	10(3)	-2(3)	-7(2)
C(76)	47(4)	76(4)	66(4)	30(3)	-18(3)	-5(3)
C(77)	59(4)	86(5)	68(4)	8(3)	30(3)	28(4)
C(78)	35(3)	35(3)	32(3)	-3(2)	11(2)	-4(2)
C(79)	45(3)	47(3)	32(3)	-12(2)	11(2)	2(3)
C(80)	34(3)	36(3)	45(3)	-11(2)	4(2)	1(2)
C(81)	51(4)	57(3)	29(3)	-3(2)	1(2)	8(3)
C(82)	81(5)	53(4)	66(4)	-17(3)	-1(4)	27(3)
C(83)	66(4)	34(3)	38(3)	-7(2)	11(3)	6(3)

C(84)	79(5)	52(4)	41(3)	-25(3)	21(3)	-17(3)
C(85)	82(5)	60(4)	42(3)	-23(3)	16(3)	-31(3)
C(86)	101(6)	144(7)	69(5)	-64(5)	33(4)	-78(5)
C(87)	68(4)	74(4)	49(3)	-24(3)	20(3)	13(3)
O(18)	82(4)	75(3)	112(4)	-35(3)	-29(3)	36(3)
C(88)	67(6)	212(11)	80(6)	-47(6)	4(5)	4(7)
C(89)	138(12)	112(10)	390(20)	-23(12)	76(13)	-43(8)
C(90)	144(13)	94(9)	360(20)	33(11)	-76(14)	5(8)
C(91)	159(12)	360(20)	134(9)	-85(11)	-16(8)	136(13)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sh2475.

	x	y	z	U(eq)
H(2)	6864	3971	786	46
H(3)	7045	2809	404	56
H(4)	6531	2851	-209	55
H(5)	5868	4070	-460	50
H(6)	5686	5238	-86	41
H(8)	5009	4317	733	46
H(9)	4158	4015	1109	61
H(10)	4114	4894	1612	72
H(11)	4970	6044	1755	65
H(12)	5811	6343	1382	50
H(14)	4910	7191	-281	47
H(15)	4881	7453	-896	64
H(16)	5845	8202	-1090	60
H(17)	6873	8659	-659	57
H(18)	6912	8401	-42	41
H(20)	4889	7287	914	53
H(21)	3927	8094	1096	73
H(22)	3561	9434	812	75
H(23)	4111	9921	350	69
H(24)	5075	9146	165	55
H(26)	9080	7164	273	45
H(27)	9303	6202	-176	60
H(28)	9265	6699	-766	78
H(29)	8963	8147	-913	80
H(30)	8732	9102	-468	60
H(32)	9695	10559	266	48
H(33)	9488	11991	66	55
H(34)	8306	12467	-174	56
H(35)	7294	11515	-216	61
H(36)	7485	10081	-16	54
H(38)	10639	10469	1467	59
H(39)	10523	11941	1590	82
H(40)	9397	12651	1403	108
H(41)	8391	11892	1056	103
H(42)	8494	10410	949	67
H(44)	10662	8701	1786	57
H(45)	11920	8409	1978	81
H(46)	12725	8329	1564	100
H(47)	12250	8514	945	95

H(48)	10986	8815	742	64
H(50)	7765	7302	2768	61
H(51)	6567	7574	2877	81
H(52)	5570	7693	2394	84
H(53)	5751	7528	1804	72
H(54)	6927	7271	1684	56
H(56A)	9020	8485	2560	73
H(57A)	10017	8765	3028	73
H(56B)	9634	8400	2274	73
H(57B)	10582	8684	2788	73
H(58)	10772	7680	3279	78
H(59A)	10639	6236	3030	73
H(60A)	9661	5972	2522	73
H(59B)	9926	6620	3310	73
H(60B)	8985	6295	2809	73
H(62)	8348	3560	1406	56
H(63)	7411	2523	1350	69
H(64)	6280	2844	1525	61
H(65)	6097	4231	1750	61
H(66)	7033	5274	1808	51
H(68)	9452	4521	2336	79
H(69)	10541	3737	2483	93
H(70)	11245	3438	2047	100
H(71)	10842	3948	1442	81
H(72)	9738	4737	1303	57
H(74)	11261	6204	1366	59
H(76A)	11008	6842	2213	100
H(76B)	11569	6354	1997	100
H(76C)	10916	5817	2131	100
H(77A)	10317	5951	524	103
H(77B)	11147	6158	733	103
H(77C)	10639	6925	526	103
H(79)	8140	4740	-133	49
H(81A)	6751	6155	-332	69
H(81B)	7398	5713	-507	69
H(81C)	7483	6702	-366	69
H(82A)	9370	3973	599	103
H(82B)	8997	3747	186	103
H(82C)	8623	3400	515	103
H(84)	8467	10508	2480	67
H(86A)	9735	10780	2526	154
H(86B)	9949	10849	2131	154
H(86C)	10207	10017	2382	154
H(87A)	6728	10081	2123	94
H(87B)	7227	10168	2522	94
H(87C)	6930	9229	2371	94
H(88A)	5679	-848	1151	145
H(88B)	6212	-886	1542	145
H(89A)	6835	1302	929	314
H(89B)	6419	1198	514	314
H(89C)	7112	581	674	314
H(90A)	6189	-93	638	257
H(90B)	5791	672	823	257
H(91A)	5103	-308	1581	336
H(91B)	5219	444	1298	336

H(91C)	5750	402	1690	336
H(92A)	3003	3821	1551	169
H(92B)	2135	3967	1574	169
H(93A)	3336	3821	2166	260
H(93B)	2467	3770	2184	260
H(93C)	2875	4699	2197	260
H(94A)	2112	5166	1120	168
H(94B)	2951	4866	1124	168
H(95A)	2480	6587	1191	211
H(95B)	2754	6173	845	211
H(95C)	3334	6304	1219	211
H(96A)	2395	1076	2484	159
H(96B)	1595	827	2275	159
H(97A)	1915	2170	2703	184
H(97B)	1689	1203	2804	184
H(97C)	1119	1778	2521	184
H(98A)	2111	776	1659	193
H(98B)	2921	997	1896	193
H(99A)	2484	2479	1727	253
H(99B)	2043	1956	1381	253
H(99C)	2934	1901	1483	253

8.9. Compound 12

Table 1. Crystal data and structure refinement for sh2252.

Identification code	sh2252	
Empirical formula	$C_{56}\ H_{56}\ Al_2\ Li\ O_8\ Si_4$	
Formula weight	1030.27	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 16.5739(8) Å	α= 90°.
	b = 13.1460(5) Å	β= 95.248(4)°.
	c = 24.1491(17) Å	γ = 90°.
Volume	5239.6(5) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.201 mm^{-1}	
F(000)	2164	
Crystal size	0.2 x 0.45 x 0.55 mm^3	
Theta range for data collection	1.69 to 30.29°.	
Index ranges	-23<=h<=23, -18<=k<=18, -34<=l<=34	
Reflections collected	66625	
Independent reflections	7813 [R(int) = 0.0304]	
Completeness to theta = 30.29°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7813 / 0 / 317	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1087	
R indices (all data)	R1 = 0.0477, wR2 = 0.1160	
Largest diff. peak and hole	0.833 and -0.589 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2252. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al	2500	2147(1)	0	15(1)
Si(1)	1340(1)	2926(1)	793(1)	15(1)
Si(2)	2645(1)	1496(1)	1216(1)	16(1)
Li(1)	2500	4198(3)	0	24(1)
O(1)	1805(1)	3032(1)	233(1)	16(1)
O(2)	1930(1)	2348(1)	1279(1)	17(1)
O(3)	2836(1)	1428(1)	575(1)	18(1)
O(4)	3065(1)	4995(1)	564(1)	31(1)
C(1)	405(1)	2158(1)	634(1)	18(1)
C(2)	224(1)	1702(1)	115(1)	24(1)
C(3)	-464(1)	1099(1)	7(1)	32(1)
C(4)	-986(1)	946(1)	414(1)	33(1)
C(5)	-824(1)	1400(1)	931(1)	32(1)
C(6)	-139(1)	2000(1)	1036(1)	27(1)
C(7)	1091(1)	4217(1)	1040(1)	18(1)
C(8)	1111(1)	4483(1)	1602(1)	21(1)
C(9)	872(1)	5452(1)	1760(1)	28(1)
C(10)	618(1)	6166(1)	1359(1)	30(1)
C(11)	609(1)	5923(1)	801(1)	34(1)
C(12)	838(1)	4956(1)	644(1)	28(1)
C(13)	2336(1)	206(1)	1443(1)	18(1)
C(14)	2052(1)	-527(1)	1056(1)	23(1)
C(15)	1872(1)	-1513(1)	1219(1)	30(1)
C(16)	1976(1)	-1778(1)	1774(1)	30(1)
C(17)	2257(1)	-1065(1)	2167(1)	33(1)
C(18)	2435(1)	-83(1)	2004(1)	27(1)
C(19)	3546(1)	1860(1)	1692(1)	20(1)
C(20)	4256(1)	1283(1)	1678(1)	26(1)
C(21)	4933(1)	1464(1)	2049(1)	31(1)
C(22)	4915(1)	2240(1)	2434(1)	33(1)
C(23)	4225(1)	2825(1)	2457(1)	32(1)
C(24)	3541(1)	2629(1)	2090(1)	25(1)
C(25)	3011(2)	6062(1)	684(1)	46(1)
C(26)	3152(1)	6132(2)	1312(1)	45(1)
C(27)	3737(1)	5273(2)	1451(1)	45(1)
C(28)	3431(1)	4450(1)	1046(1)	39(1)

Table 3. Bond lengths [Å] and angles [°] for sh2252.

Al-O(3)#1	1.7295(9)	Si(2)-C(13)	1.8676(13)
Al-O(3)	1.7296(9)	Li(1)-O(4)#1	1.896(2)
Al-O(1)	1.7648(9)	Li(1)-O(4)	1.897(2)
Al-O(1)#1	1.7648(9)	Li(1)-O(1)	2.027(3)
Al-Li(1)	2.696(3)	Li(1)-O(1)#1	2.027(3)
Si(1)-O(1)	1.6222(9)	O(4)-C(25)	1.437(2)
Si(1)-O(2)	1.6445(9)	O(4)-C(28)	1.451(2)
Si(1)-C(7)	1.8578(13)	C(1)-C(2)	1.3976(18)
Si(1)-C(1)	1.8601(13)	C(1)-C(6)	1.3992(19)
Si(2)-O(3)	1.6108(10)	C(2)-C(3)	1.393(2)
Si(2)-O(2)	1.6481(10)	C(3)-C(4)	1.383(2)
Si(2)-C(19)	1.8623(13)	C(4)-C(5)	1.386(2)

C(5)-C(6)	1.387(2)	O(4)-Li(1)-O(1)#1	111.19(5)
C(7)-C(8)	1.3992(17)	O(1)-Li(1)-O(1)#1	81.77(13)
C(7)-C(12)	1.3997(18)	O(4)#1-Li(1)-Al	123.53(9)
C(8)-C(9)	1.3964(19)	O(4)-Li(1)-Al	123.53(9)
C(9)-C(10)	1.387(2)	O(1)-Li(1)-Al	40.89(7)
C(10)-C(11)	1.383(2)	O(1)#1-Li(1)-Al	40.89(7)
C(11)-C(12)	1.389(2)	Si(1)-O(1)-Al	125.62(5)
C(13)-C(14)	1.3944(19)	Si(1)-O(1)-Li(1)	128.42(7)
C(13)-C(18)	1.4005(18)	Al-O(1)-Li(1)	90.38(7)
C(14)-C(15)	1.393(2)	Si(1)-O(2)-Si(2)	129.31(6)
C(15)-C(16)	1.380(2)	Si(2)-O(3)-Al	131.60(6)
C(16)-C(17)	1.385(2)	C(25)-O(4)-C(28)	110.48(13)
C(17)-C(18)	1.390(2)	C(25)-O(4)-Li(1)	130.43(14)
C(19)-C(24)	1.395(2)	C(28)-O(4)-Li(1)	116.48(13)
C(19)-C(20)	1.403(2)	C(2)-C(1)-C(6)	117.32(13)
C(20)-C(21)	1.390(2)	C(2)-C(1)-Si(1)	121.67(10)
C(21)-C(22)	1.382(3)	C(6)-C(1)-Si(1)	121.00(10)
C(22)-C(23)	1.384(3)	C(3)-C(2)-C(1)	121.11(14)
C(23)-C(24)	1.397(2)	C(4)-C(3)-C(2)	120.32(14)
C(25)-C(26)	1.517(3)	C(3)-C(4)-C(5)	119.67(14)
C(26)-C(27)	1.505(3)	C(4)-C(5)-C(6)	119.80(15)
C(27)-C(28)	1.515(2)	C(5)-C(6)-C(1)	121.77(14)
		C(8)-C(7)-C(12)	117.93(12)
O(3)#1-Al-O(3)	113.69(7)	C(8)-C(7)-Si(1)	123.62(10)
O(3)#1-Al-O(1)	116.41(4)	C(12)-C(7)-Si(1)	118.40(10)
O(3)-Al-O(1)	106.05(4)	C(9)-C(8)-C(7)	120.69(13)
O(3)#1-Al-O(1)#1	106.05(4)	C(10)-C(9)-C(8)	120.17(13)
O(3)-Al-O(1)#1	116.41(4)	C(11)-C(10)-C(9)	119.92(13)
O(1)-Al-O(1)#1	97.48(6)	C(10)-C(11)-C(12)	119.91(14)
O(3)#1-Al-Li(1)	123.15(3)	C(11)-C(12)-C(7)	121.36(14)
O(3)-Al-Li(1)	123.15(3)	C(14)-C(13)-C(18)	117.54(12)
O(1)-Al-Li(1)	48.74(3)	C(14)-C(13)-Si(2)	121.03(10)
O(1)#1-Al-Li(1)	48.74(3)	C(18)-C(13)-Si(2)	121.27(10)
O(1)-Si(1)-O(2)	109.78(5)	C(15)-C(14)-C(13)	121.44(13)
O(1)-Si(1)-C(7)	109.00(5)	C(16)-C(15)-C(14)	119.84(14)
O(2)-Si(1)-C(7)	109.13(5)	C(15)-C(16)-C(17)	119.98(14)
O(1)-Si(1)-C(1)	108.98(5)	C(16)-C(17)-C(18)	120.00(14)
O(2)-Si(1)-C(1)	109.03(5)	C(17)-C(18)-C(13)	121.19(14)
C(7)-Si(1)-C(1)	110.91(6)	C(24)-C(19)-C(20)	117.79(13)
O(3)-Si(2)-O(2)	109.46(5)	C(24)-C(19)-Si(2)	123.82(11)
O(3)-Si(2)-C(19)	112.95(6)	C(20)-C(19)-Si(2)	118.22(11)
O(2)-Si(2)-C(19)	108.09(6)	C(21)-C(20)-C(19)	121.37(15)
O(3)-Si(2)-C(13)	108.40(5)	C(22)-C(21)-C(20)	119.64(15)
O(2)-Si(2)-C(13)	111.79(5)	C(21)-C(22)-C(23)	120.35(14)
C(19)-Si(2)-C(13)	106.17(6)	C(22)-C(23)-C(24)	119.83(15)
O(4)#1-Li(1)-O(4)	112.95(18)	C(19)-C(24)-C(23)	121.00(15)
O(4)#1-Li(1)-O(1)	111.18(5)	O(4)-C(25)-C(26)	104.67(16)
O(4)-Li(1)-O(1)	118.28(6)	C(27)-C(26)-C(25)	102.36(16)
O(4)#1-Li(1)-O(1)#1	118.28(6)	C(26)-C(27)-C(28)	102.81(15)
		O(4)-C(28)-C(27)	104.79(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2252. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al	19(1)	13(1)	12(1)	0	2(1)	0
Si(1)	18(1)	13(1)	13(1)	-1(1)	0(1)	1(1)
Si(2)	18(1)	15(1)	13(1)	2(1)	0(1)	1(1)
Li(1)	31(2)	17(1)	24(2)	0	-1(1)	0
O(1)	20(1)	15(1)	14(1)	1(1)	1(1)	2(1)
O(2)	20(1)	19(1)	13(1)	1(1)	0(1)	3(1)
O(3)	22(1)	17(1)	16(1)	3(1)	3(1)	4(1)
O(4)	40(1)	23(1)	28(1)	-7(1)	-3(1)	-2(1)
C(1)	20(1)	16(1)	19(1)	0(1)	-1(1)	1(1)
C(2)	23(1)	26(1)	23(1)	-6(1)	0(1)	-2(1)
C(3)	27(1)	34(1)	33(1)	-13(1)	-2(1)	-6(1)
C(4)	26(1)	31(1)	41(1)	-6(1)	0(1)	-8(1)
C(5)	28(1)	36(1)	33(1)	2(1)	5(1)	-8(1)
C(6)	27(1)	32(1)	21(1)	-1(1)	2(1)	-5(1)
C(7)	21(1)	15(1)	18(1)	-2(1)	3(1)	0(1)
C(8)	25(1)	20(1)	19(1)	-4(1)	3(1)	-2(1)
C(9)	33(1)	25(1)	26(1)	-11(1)	5(1)	-2(1)
C(10)	35(1)	17(1)	40(1)	-7(1)	10(1)	1(1)
C(11)	50(1)	18(1)	34(1)	3(1)	9(1)	10(1)
C(12)	42(1)	20(1)	21(1)	1(1)	5(1)	9(1)
C(13)	17(1)	18(1)	18(1)	4(1)	0(1)	1(1)
C(14)	26(1)	21(1)	23(1)	2(1)	1(1)	-3(1)
C(15)	33(1)	20(1)	38(1)	-1(1)	4(1)	-5(1)
C(16)	26(1)	21(1)	44(1)	12(1)	4(1)	0(1)
C(17)	36(1)	32(1)	29(1)	16(1)	0(1)	-2(1)
C(18)	34(1)	26(1)	19(1)	6(1)	-2(1)	-4(1)
C(19)	21(1)	20(1)	18(1)	5(1)	-1(1)	-3(1)
C(20)	22(1)	26(1)	29(1)	4(1)	0(1)	-2(1)
C(21)	19(1)	42(1)	33(1)	12(1)	-1(1)	-3(1)
C(22)	25(1)	51(1)	21(1)	10(1)	-5(1)	-13(1)
C(23)	36(1)	39(1)	19(1)	-1(1)	-4(1)	-11(1)
C(24)	29(1)	27(1)	19(1)	1(1)	-3(1)	-2(1)
C(25)	67(1)	26(1)	44(1)	-8(1)	-1(1)	-1(1)
C(26)	50(1)	43(1)	43(1)	-14(1)	5(1)	-3(1)
C(27)	52(1)	42(1)	38(1)	-8(1)	-15(1)	1(1)
C(28)	44(1)	32(1)	38(1)	-1(1)	-12(1)	1(1)

8.10. Compound 13

Table 1. Crystal data and structure refinement for sh2436.

Identification code	sh2436	
Empirical formula	C_{72} H_{80} Al_2 Ni O_{17} Si_4	
Formula weight	1442.39	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.338(4) Å	α= 90°.
	b = 11.5875(17) Å	β= 107.036(16)°.
	c = 25.489(4) Å	γ = 90°.
Volume	7155.5(19) $Å^3$	
Z	4	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	0.430 mm^{-1}	
F(000)	3032	
Crystal size	0.37 x 0.26 x 0.08 mm^3	
Theta range for data collection	1.67 to 36.53°.	
Index ranges	-42<=h<=42, -19<=k<=19, -42<=l<=42	
Reflections collected	150271	
Independent reflections	17379 [R(int) = 0.0786]	
Completeness to theta = 36.53°	98.7 %	
Absorption correction	Numerical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17379 / 0 / 444	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1174	
R indices (all data)	R1 = 0.0878, wR2 = 0.1364	
Largest diff. peak and hole	0.739 and -0.772 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2436. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni	10000	7886(1)	2500	14(1)
Si(1)	8765(1)	7870(1)	1613(1)	14(1)
Si(2)	11140(1)	7605(1)	2146(1)	15(1)
Al(1)	9920(1)	7961(1)	1323(1)	15(1)
O(1)	9429(1)	7906(1)	1735(1)	15(1)
O(2)	10481(1)	7830(1)	1977(1)	18(1)
O(3)	10000	6077(2)	2500	56(1)
O(4)	10000	9657(2)	2500	45(1)
O(5)	9921(1)	6331(1)	1238(1)	20(1)
O(6)	9337(1)	8077(1)	650(1)	18(1)
O(7)	9922(1)	9606(1)	1365(1)	20(1)
O(8)	10427(1)	8043(1)	898(1)	21(1)
O(9)	8626(1)	7592(1)	2187(1)	17(1)
C(1)	8763(1)	7701(2)	-251(1)	30(1)
C(2)	9197(1)	7334(1)	263(1)	21(1)
C(3)	9417(1)	6222(1)	302(1)	26(1)
C(4)	9743(1)	5757(1)	795(1)	21(1)
C(5)	9886(1)	4496(1)	835(1)	30(1)
C(6)	9976(1)	11576(2)	1159(1)	41(1)
C(7)	10082(1)	10332(1)	1065(1)	26(1)
C(8)	10351(1)	10028(2)	683(1)	31(1)
C(9)	10534(1)	8909(2)	638(1)	26(1)
C(10)	10898(1)	8676(2)	276(1)	40(1)
C(11)	8458(1)	6636(1)	1145(1)	17(1)
C(12)	8675(1)	5523(1)	1277(1)	21(1)
C(13)	8466(1)	4577(1)	944(1)	25(1)
C(14)	8032(1)	4721(2)	472(1)	30(1)
C(15)	7802(1)	5801(2)	338(1)	38(1)
C(16)	8013(1)	6747(2)	672(1)	30(1)
C(17)	8416(1)	9275(1)	1354(1)	18(1)
C(18)	8513(1)	9918(1)	925(1)	22(1)
C(19)	8242(1)	10963(1)	755(1)	27(1)
C(20)	7873(1)	11392(1)	1014(1)	31(1)
C(21)	7774(1)	10783(2)	1443(1)	33(1)
C(22)	8040(1)	9732(1)	1607(1)	27(1)
C(23)	11344(1)	6181(1)	1915(1)	21(1)
C(24)	11261(1)	5928(2)	1358(1)	33(1)
C(25)	11441(1)	4895(2)	1192(1)	39(1)
C(26)	11700(1)	4078(2)	1581(1)	37(1)
C(27)	11787(1)	4307(2)	2130(1)	43(1)
C(28)	11617(1)	5355(2)	2295(1)	34(1)
C(29)	11498(1)	8801(1)	1894(1)	19(1)
C(30)	11922(1)	8631(2)	1656(1)	35(1)
C(31)	12196(1)	9560(2)	1501(1)	49(1)
C(32)	12047(1)	10668(2)	1573(1)	40(1)
C(33)	11628(1)	10868(2)	1807(1)	36(1)
C(34)	11356(1)	9942(1)	1961(1)	29(1)
O(10)	5000	7427(2)	2500	39(1)
C(35)	4515(1)	8116(2)	2320(1)	44(1)
C(36)	4025(1)	7344(2)	2147(1)	47(1)

Table 3. Bond lengths [Å] and angles [°] for sh2436.

Ni-O(4)	2.0523(18)	C(30)-C(31)	1.399(3)
Ni-O(2)#1	2.0532(10)	C(31)-C(32)	1.365(3)
Ni-O(2)	2.0533(10)	C(32)-C(33)	1.379(3)
Ni-O(1)	2.0593(10)	C(33)-C(34)	1.394(2)
Ni-O(1)#1	2.0593(10)	O(10)-C(35)	1.425(2)
Ni-O(3)	2.096(2)	O(10)-C(35)#2	1.425(2)
Ni-Al(1)#1	2.9494(6)	C(35)-C(36)	1.488(3)
Ni-Al(1)	2.9495(6)		
Si(1)-O(1)	1.6205(10)	O(4)-Ni-O(2)#1	91.82(3)
Si(1)-O(9)	1.6329(11)	O(4)-Ni-O(2)	91.82(3)
Si(1)-C(17)	1.8781(14)	O(2)#1-Ni-O(2)	176.35(6)
Si(1)-C(11)	1.8786(14)	O(4)-Ni-O(1)	89.35(3)
Si(2)-O(2)	1.6200(11)	O(2)#1-Ni-O(1)	103.27(4)
Si(2)-O(9)#1	1.6271(11)	O(2)-Ni-O(1)	76.77(4)
Si(2)-C(29)	1.8710(15)	O(4)-Ni-O(1)#1	89.35(3)
Si(2)-C(23)	1.8767(15)	O(2)#1-Ni-O(1)#1	76.77(4)
Al(1)-O(1)	1.8501(11)	O(2)-Ni-O(1)#1	103.27(4)
Al(1)-O(2)	1.8532(11)	O(1)-Ni-O(1)#1	178.70(5)
Al(1)-O(5)	1.9016(11)	O(4)-Ni-O(3)	180.000(1)
Al(1)-O(8)	1.9090(11)	O(2)#1-Ni-O(3)	88.18(3)
Al(1)-O(7)	1.9093(11)	O(2)-Ni-O(3)	88.18(3)
Al(1)-O(6)	1.9127(11)	O(1)-Ni-O(3)	90.65(3)
O(5)-C(4)	1.2736(18)	O(1)#1-Ni-O(3)	90.65(3)
O(6)-C(2)	1.2783(17)	O(4)-Ni-Al(1)#1	88.303(9)
O(7)-C(7)	1.2805(18)	O(2)#1-Ni-Al(1)#1	38.48(3)
O(8)-C(9)	1.275(2)	O(2)-Ni-Al(1)#1	141.69(3)
O(9)-Si(2)#1	1.6272(11)	O(1)-Ni-Al(1)#1	141.52(3)
C(1)-C(2)	1.503(2)	O(1)#1-Ni-Al(1)#1	38.42(3)
C(2)-C(3)	1.396(2)	O(3)-Ni-Al(1)#1	91.697(9)
C(3)-C(4)	1.394(2)	O(4)-Ni-Al(1)	88.302(9)
C(4)-C(5)	1.503(2)	O(2)#1-Ni-Al(1)	141.69(3)
C(6)-C(7)	1.498(2)	O(2)-Ni-Al(1)	38.49(3)
C(7)-C(8)	1.388(2)	O(1)-Ni-Al(1)	38.42(3)
C(8)-C(9)	1.393(3)	O(1)#1-Ni-Al(1)	141.52(3)
C(9)-C(10)	1.507(2)	O(3)-Ni-Al(1)	91.698(9)
C(11)-C(16)	1.395(2)	Al(1)#1-Ni-Al(1)	176.606(19)
C(11)-C(12)	1.404(2)	O(1)-Si(1)-O(9)	108.53(5)
C(12)-C(13)	1.393(2)	O(1)-Si(1)-C(17)	113.57(6)
C(13)-C(14)	1.381(2)	O(9)-Si(1)-C(17)	106.46(6)
C(14)-C(15)	1.382(3)	O(1)-Si(1)-C(11)	110.76(6)
C(15)-C(16)	1.395(2)	O(9)-Si(1)-C(11)	105.21(6)
C(17)-C(22)	1.402(2)	C(17)-Si(1)-C(11)	111.82(6)
C(17)-C(18)	1.404(2)	O(2)-Si(2)-O(9)#1	108.16(6)
C(18)-C(19)	1.396(2)	O(2)-Si(2)-C(29)	110.84(6)
C(19)-C(20)	1.386(2)	O(9)#1-Si(2)-C(29)	107.55(6)
C(20)-C(21)	1.385(3)	O(2)-Si(2)-C(23)	114.54(6)
C(21)-C(22)	1.395(2)	O(9)#1-Si(2)-C(23)	105.70(6)
C(23)-C(28)	1.393(2)	C(29)-Si(2)-C(23)	109.69(7)
C(23)-C(24)	1.404(2)	O(1)-Al(1)-O(2)	87.20(5)
C(24)-C(25)	1.390(2)	O(1)-Al(1)-O(5)	93.06(5)
C(25)-C(26)	1.388(3)	O(2)-Al(1)-O(5)	89.67(5)
C(26)-C(27)	1.377(3)	O(1)-Al(1)-O(8)	179.12(5)
C(27)-C(28)	1.395(2)	O(2)-Al(1)-O(8)	92.76(5)
C(29)-C(30)	1.393(2)	O(5)-Al(1)-O(8)	87.82(5)
C(29)-C(34)	1.394(2)	O(1)-Al(1)-O(7)	89.60(5)

O(2)-Al(1)-O(7)	92.44(5)	C(7)-C(8)-C(9)	122.52(15)
O(5)-Al(1)-O(7)	176.69(5)	O(8)-C(9)-C(8)	124.23(14)
O(8)-Al(1)-O(7)	89.53(5)	O(8)-C(9)-C(10)	116.03(16)
O(1)-Al(1)-O(6)	92.32(5)	C(8)-C(9)-C(10)	119.71(16)
O(2)-Al(1)-O(6)	179.16(5)	C(16)-C(11)-C(12)	116.93(13)
O(5)-Al(1)-O(6)	89.67(5)	C(16)-C(11)-Si(1)	123.94(11)
O(8)-Al(1)-O(6)	87.73(5)	C(12)-C(11)-Si(1)	119.11(10)
O(7)-Al(1)-O(6)	88.24(5)	C(13)-C(12)-C(11)	121.65(14)
O(1)-Al(1)-Ni	43.77(3)	C(14)-C(13)-C(12)	119.96(15)
O(2)-Al(1)-Ni	43.59(3)	C(13)-C(14)-C(15)	119.72(15)
O(5)-Al(1)-Ni	94.81(3)	C(14)-C(15)-C(16)	120.14(16)
O(8)-Al(1)-Ni	136.13(4)	C(11)-C(16)-C(15)	121.55(16)
O(7)-Al(1)-Ni	88.47(3)	C(22)-C(17)-C(18)	117.16(13)
O(6)-Al(1)-Ni	135.97(4)	C(22)-C(17)-Si(1)	118.60(11)
Si(1)-O(1)-Al(1)	136.52(6)	C(18)-C(17)-Si(1)	124.23(11)
Si(1)-O(1)-Ni	125.67(6)	C(19)-C(18)-C(17)	121.23(15)
Al(1)-O(1)-Ni	97.81(4)	C(20)-C(19)-C(18)	120.25(16)
Si(2)-O(2)-Al(1)	135.41(6)	C(21)-C(20)-C(19)	119.75(15)
Si(2)-O(2)-Ni	126.41(6)	C(20)-C(21)-C(22)	119.90(16)
Al(1)-O(2)-Ni	97.92(5)	C(21)-C(22)-C(17)	121.71(16)
C(4)-O(5)-Al(1)	127.39(10)	C(28)-C(23)-C(24)	117.28(15)
C(2)-O(6)-Al(1)	127.62(10)	C(28)-C(23)-Si(2)	120.73(12)
C(7)-O(7)-Al(1)	128.12(10)	C(24)-C(23)-Si(2)	121.88(13)
C(9)-O(8)-Al(1)	127.97(11)	C(25)-C(24)-C(23)	121.37(18)
Si(2)#1-O(9)-Si(1)	145.59(7)	C(26)-C(25)-C(24)	119.96(18)
O(6)-C(2)-C(3)	123.58(14)	C(27)-C(26)-C(25)	119.76(16)
O(6)-C(2)-C(1)	116.59(14)	C(26)-C(27)-C(28)	120.12(19)
C(3)-C(2)-C(1)	119.81(14)	C(23)-C(28)-C(27)	121.48(18)
C(4)-C(3)-C(2)	122.59(14)	C(30)-C(29)-C(34)	116.64(15)
O(5)-C(4)-C(3)	124.08(13)	C(30)-C(29)-Si(2)	123.93(12)
O(5)-C(4)-C(5)	115.59(14)	C(34)-C(29)-Si(2)	119.38(11)
C(3)-C(4)-C(5)	120.29(14)	C(29)-C(30)-C(31)	121.54(17)
O(7)-C(7)-C(8)	124.08(15)	C(32)-C(31)-C(30)	120.39(17)
O(7)-C(7)-C(6)	115.66(15)	C(31)-C(32)-C(33)	119.62(17)
C(8)-C(7)-C(6)	120.25(15)	C(32)-C(33)-C(34)	119.98(18)
		C(33)-C(34)-C(29)	121.82(16)
		C(35)-O(10)-C(35)#2	111.8(2)
		O(10)-C(35)-C(36)	108.94(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2 #2 -x+1,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2436. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni	13(1)	16(1)	12(1)	0	4(1)	0
Si(1)	12(1)	14(1)	15(1)	0(1)	3(1)	1(1)
Si(2)	13(1)	16(1)	16(1)	-2(1)	5(1)	1(1)
Al(1)	15(1)	17(1)	13(1)	-1(1)	5(1)	1(1)
O(1)	13(1)	17(1)	14(1)	0(1)	4(1)	1(1)
O(2)	13(1)	26(1)	15(1)	-1(1)	5(1)	3(1)
O(3)	70(2)	18(1)	55(2)	0	-21(1)	0
O(4)	97(2)	16(1)	26(1)	0	24(1)	0
O(5)	23(1)	17(1)	20(1)	0(1)	7(1)	4(1)

O(6)	20(1)	18(1)	15(1)	-2(1)	3(1)	2(1)
O(7)	26(1)	17(1)	18(1)	0(1)	7(1)	-3(1)
O(8)	21(1)	28(1)	17(1)	1(1)	8(1)	1(1)
O(9)	14(1)	21(1)	17(1)	1(1)	5(1)	-1(1)
C(1)	36(1)	30(1)	18(1)	1(1)	-2(1)	-3(1)
C(2)	25(1)	21(1)	15(1)	-1(1)	4(1)	-2(1)
C(3)	37(1)	21(1)	20(1)	-7(1)	8(1)	0(1)
C(4)	26(1)	16(1)	24(1)	-2(1)	12(1)	2(1)
C(5)	37(1)	18(1)	38(1)	-3(1)	14(1)	5(1)
C(6)	72(2)	20(1)	36(1)	2(1)	22(1)	-5(1)
C(7)	34(1)	21(1)	21(1)	3(1)	7(1)	-4(1)
C(8)	41(1)	32(1)	23(1)	7(1)	13(1)	-7(1)
C(9)	25(1)	39(1)	16(1)	3(1)	8(1)	-2(1)
C(10)	37(1)	62(1)	30(1)	14(1)	21(1)	9(1)
C(11)	17(1)	17(1)	17(1)	1(1)	4(1)	-2(1)
C(12)	21(1)	18(1)	23(1)	0(1)	4(1)	-1(1)
C(13)	26(1)	18(1)	32(1)	-4(1)	9(1)	-3(1)
C(14)	38(1)	27(1)	25(1)	-6(1)	6(1)	-13(1)
C(15)	44(1)	29(1)	27(1)	2(1)	-12(1)	-12(1)
C(16)	29(1)	22(1)	28(1)	5(1)	-9(1)	-4(1)
C(17)	16(1)	16(1)	21(1)	0(1)	3(1)	2(1)
C(18)	25(1)	18(1)	23(1)	2(1)	7(1)	5(1)
C(19)	30(1)	20(1)	29(1)	6(1)	7(1)	5(1)
C(20)	28(1)	20(1)	44(1)	7(1)	8(1)	10(1)
C(21)	28(1)	26(1)	49(1)	7(1)	18(1)	12(1)
C(22)	22(1)	25(1)	37(1)	7(1)	13(1)	8(1)
C(23)	17(1)	20(1)	28(1)	-5(1)	9(1)	0(1)
C(24)	26(1)	38(1)	30(1)	-15(1)	-1(1)	12(1)
C(25)	28(1)	42(1)	40(1)	-23(1)	1(1)	10(1)
C(26)	37(1)	23(1)	55(1)	-15(1)	21(1)	-2(1)
C(27)	68(1)	21(1)	52(1)	7(1)	36(1)	13(1)
C(28)	54(1)	21(1)	35(1)	4(1)	26(1)	10(1)
C(29)	17(1)	22(1)	19(1)	1(1)	7(1)	0(1)
C(30)	37(1)	29(1)	49(1)	8(1)	30(1)	7(1)
C(31)	50(1)	43(1)	72(2)	16(1)	47(1)	6(1)
C(32)	38(1)	36(1)	51(1)	13(1)	23(1)	-5(1)
C(33)	39(1)	24(1)	50(1)	3(1)	20(1)	-6(1)
C(34)	30(1)	23(1)	40(1)	-3(1)	19(1)	-4(1)
O(10)	47(1)	29(1)	38(1)	0	8(1)	0
C(35)	44(1)	35(1)	48(1)	4(1)	8(1)	2(1)
C(36)	48(1)	45(1)	48(1)	4(1)	15(1)	-1(1)

8.11. Compound 14

Table 1. Crystal data and structure refinement for sh2513.

Identification code	sh2513	
Empirical formula	$C_{72}\ H_{82}\ Al_2\ Co\ O_{17}\ Si_4$	
Formula weight	1444.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.364(3) Å	α= 90°.
	b = 11.5511(10) Å	β= 108.132(8)°.
	c = 25.647(3) Å	γ = 90°.
Volume	7140.8(12) $Å^3$	
Z	4	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.400 mm^{-1}	
F(000)	3036	
Crystal size	0.35 x 0.5 x 0.65 mm^3	
Theta range for data collection	1.67 to 24.61°.	
Index ranges	-29<=h<=29, -13<=k<=13, -30<=l<=29	
Reflections collected	57380	
Independent reflections	6007 [R(int) = 0.0352]	
Completeness to theta = 24.61°	99.7 %	
Absorption correction	Multi scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6007 / 0 / 588	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0794	
R indices (all data)	R1 = 0.0392, wR2 = 0.0846	
Largest diff. peak and hole	0.386 and -0.233 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2513. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al	4902(1)	7905(1)	1309(1)	17(1)
Co	5000	7871(1)	2500	16(1)
Si(1)	3752(1)	7851(1)	1595(1)	17(1)
Si(2)	6134(1)	7525(1)	2160(1)	17(1)
O(1)	4416(1)	7904(1)	1715(1)	17(1)
O(2)	5471(1)	7738(1)	1966(1)	19(1)
O(3)	3631(1)	7597(1)	2173(1)	20(1)
O(4)	4862(1)	6268(1)	1218(1)	23(1)
O(5)	4308(1)	8077(1)	635(1)	20(1)
O(6)	4949(1)	9555(1)	1362(1)	20(1)
O(7)	5395(1)	7915(1)	880(1)	23(1)
O(9)	5000	6018(2)	2500	51(1)
O(10)	5000	9656(2)	2500	43(1)
O(11)	5000	2363(2)	2500	33(1)
C(1)	3439(1)	6590(2)	1141(1)	20(1)
C(2)	3630(1)	5472(2)	1310(1)	24(1)
C(3)	3425(1)	4512(2)	989(1)	27(1)
C(4)	3020(1)	4642(2)	486(1)	29(1)
C(5)	2815(1)	5726(2)	313(1)	33(1)
C(6)	3020(1)	6689(2)	639(1)	27(1)
C(7)	3390(1)	9244(2)	1320(1)	21(1)
C(8)	3532(1)	9965(2)	947(1)	22(1)
C(9)	3250(1)	10993(2)	767(1)	26(1)
C(10)	2822(1)	11329(2)	957(1)	32(1)
C(11)	2675(1)	10638(2)	1324(1)	45(1)
C(12)	2954(1)	9607(2)	1501(1)	37(1)
C(13)	6334(1)	6063(2)	1969(1)	24(1)
C(14)	6151(1)	5642(2)	1434(1)	42(1)
C(15)	6321(1)	4571(3)	1303(1)	56(1)
C(16)	6681(1)	3903(2)	1697(1)	42(1)
C(17)	6866(1)	4286(2)	2226(1)	38(1)
C(18)	6692(1)	5359(2)	2360(1)	31(1)
C(19)	6498(1)	8683(2)	1897(1)	24(1)
C(20)	6817(1)	8481(2)	1552(1)	35(1)
C(21)	7078(1)	9386(3)	1372(1)	47(1)
C(22)	7029(1)	10497(2)	1537(1)	46(1)
C(23)	6718(1)	10718(2)	1878(1)	49(1)
C(24)	6453(1)	9818(2)	2051(1)	38(1)
C(25)	4767(1)	4426(2)	802(1)	38(1)
C(26)	4645(1)	5701(2)	777(1)	28(1)
C(27)	4303(1)	6187(2)	292(1)	34(1)
C(28)	4124(1)	7336(2)	251(1)	26(1)
C(29)	3690(1)	7752(2)	-256(1)	34(1)
C(30)	5091(1)	11512(2)	1199(1)	37(1)
C(31)	5142(1)	10254(2)	1082(1)	24(1)
C(32)	5397(1)	9911(2)	697(1)	30(1)
C(33)	5523(1)	8763(2)	627(1)	26(1)
C(34)	5836(1)	8462(3)	235(1)	38(1)
C(36)	4511(1)	3045(2)	2331(1)	38(1)
C(37)	4015(1)	2272(2)	2167(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for sh2513.

Al-O(1)	1.8452(13)	C(27)-C(28)	1.395(3)
Al-O(2)	1.8566(14)	C(28)-C(29)	1.498(3)
Al-O(4)	1.9051(14)	C(30)-C(31)	1.497(3)
Al-O(7)	1.9060(14)	C(31)-C(32)	1.395(3)
Al-O(6)	1.9111(14)	C(32)-C(33)	1.388(3)
Al-O(5)	1.9185(14)	C(33)-C(34)	1.505(3)
Al-Co	2.9864(6)	C(36)-C(37)	1.493(4)
Co-O(10)	2.062(2)	O(1)-Al-O(2)	87.43(6)
Co-O(2)#1	2.0838(12)	O(1)-Al-O(4)	92.84(6)
Co-O(2)	2.0840(12)	O(2)-Al-O(4)	90.27(6)
Co-O(1)	2.0959(12)	O(1)-Al-O(7)	179.06(6)
Co-O(1)#1	2.0959(12)	O(2)-Al-O(7)	93.49(6)
Co-O(9)	2.140(2)	O(4)-Al-O(7)	87.35(6)
Co-Al#1	2.9863(6)	O(1)-Al-O(6)	89.94(6)
Si(1)-O(1)	1.6150(13)	O(2)-Al-O(6)	91.45(6)
Si(1)-O(3)	1.6298(13)	O(4)-Al-O(6)	176.79(6)
Si(1)-C(7)	1.879(2)	O(7)-Al-O(6)	89.83(6)
Si(1)-C(1)	1.879(2)	O(1)-Al-O(5)	91.89(6)
Si(2)-O(2)	1.6170(14)	O(2)-Al-O(5)	179.32(6)
Si(2)-O(3)#1	1.6301(14)	O(4)-Al-O(5)	89.72(6)
Si(2)-C(19)	1.867(2)	O(7)-Al-O(5)	87.19(6)
Si(2)-C(13)	1.872(2)	O(6)-Al-O(5)	88.59(6)
O(3)-Si(2)#1	1.6301(14)	O(1)-Al-Co	43.98(4)
O(4)-C(26)	1.275(2)	O(2)-Al-Co	43.66(4)
O(5)-C(28)	1.278(2)	O(4)-Al-Co	95.55(4)
O(6)-C(31)	1.275(2)	O(7)-Al-Co	136.92(5)
O(7)-C(33)	1.271(2)	O(6)-Al-Co	87.57(4)
O(11)-C(36)	1.419(3)	O(5)-Al-Co	135.66(5)
O(11)-C(36)#1	1.419(3)	O(10)-Co-O(2)#1	94.21(4)
C(1)-C(6)	1.397(3)	O(10)-Co-O(2)	94.21(4)
C(1)-C(2)	1.399(3)	O(2)#1-Co-O(2)	171.58(7)
C(2)-C(3)	1.383(3)	O(10)-Co-O(1)	88.94(3)
C(3)-C(4)	1.385(3)	O(2)#1-Co-O(1)	104.69(5)
C(4)-C(5)	1.375(3)	O(2)-Co-O(1)	75.47(5)
C(5)-C(6)	1.391(3)	O(10)-Co-O(1)#1	88.94(3)
C(7)-C(12)	1.390(3)	O(2)#1-Co-O(1)#1	75.48(5)
C(7)-C(8)	1.397(3)	O(2)-Co-O(1)#1	104.68(5)
C(8)-C(9)	1.389(3)	O(1)-Co-O(1)#1	177.88(7)
C(9)-C(10)	1.377(3)	O(10)-Co-O(9)	180.000(1)
C(10)-C(11)	1.371(3)	O(2)#1-Co-O(9)	85.79(4)
C(11)-C(12)	1.389(3)	O(2)-Co-O(9)	85.79(4)
C(13)-C(18)	1.387(3)	O(1)-Co-O(9)	91.06(3)
C(13)-C(14)	1.391(3)	O(1)#1-Co-O(9)	91.06(3)
C(14)-C(15)	1.385(3)	O(10)-Co-Al#1	89.235(12)
C(15)-C(16)	1.369(4)	O(2)#1-Co-Al#1	37.96(4)
C(16)-C(17)	1.365(4)	O(2)-Co-Al#1	142.22(4)
C(17)-C(18)	1.393(3)	O(1)-Co-Al#1	142.27(4)
C(19)-C(24)	1.384(3)	O(1)#1-Co-Al#1	37.69(4)
C(19)-C(20)	1.390(3)	O(9)-Co-Al#1	90.765(12)
C(20)-C(21)	1.393(3)	O(10)-Co-Al	89.234(12)
C(21)-C(22)	1.369(4)	O(2)#1-Co-Al	142.23(4)
C(22)-C(23)	1.373(4)	O(2)-Co-Al	37.96(4)
C(23)-C(24)	1.385(3)	O(1)-Co-Al	37.69(4)
C(25)-C(26)	1.502(3)	O(1)#1-Co-Al	142.26(4)
C(26)-C(27)	1.393(3)	O(9)-Co-Al	90.766(12)

Al#1-Co-Al	178.47(2)	C(9)-C(8)-C(7)	121.44(19)
O(1)-Si(1)-O(3)	108.34(7)	C(10)-C(9)-C(8)	120.3(2)
O(1)-Si(1)-C(7)	113.39(8)	C(11)-C(10)-C(9)	119.5(2)
O(3)-Si(1)-C(7)	106.65(8)	C(10)-C(11)-C(12)	120.2(2)
O(1)-Si(1)-C(1)	111.21(8)	C(11)-C(12)-C(7)	121.8(2)
O(3)-Si(1)-C(1)	105.15(8)	C(18)-C(13)-C(14)	116.81(19)
C(7)-Si(1)-C(1)	111.60(9)	C(18)-C(13)-Si(2)	120.59(16)
O(2)-Si(2)-O(3)#1	108.72(7)	C(14)-C(13)-Si(2)	122.57(16)
O(2)-Si(2)-C(19)	111.29(8)	C(15)-C(14)-C(13)	121.1(2)
O(3)#1-Si(2)-C(19)	106.41(8)	C(16)-C(15)-C(14)	120.8(2)
O(2)-Si(2)-C(13)	113.43(8)	C(17)-C(16)-C(15)	119.7(2)
O(3)#1-Si(2)-C(13)	106.31(8)	C(16)-C(17)-C(18)	119.7(2)
C(19)-Si(2)-C(13)	110.31(9)	C(13)-C(18)-C(17)	121.9(2)
Si(1)-O(1)-Al	137.10(8)	C(24)-C(19)-C(20)	117.2(2)
Si(1)-O(1)-Co	124.44(7)	C(24)-C(19)-Si(2)	118.73(16)
Al-O(1)-Co	98.33(6)	C(20)-C(19)-Si(2)	124.07(17)
Si(2)-O(2)-Al	137.32(8)	C(19)-C(20)-C(21)	121.1(2)
Si(2)-O(2)-Co	124.28(7)	C(22)-C(21)-C(20)	120.1(2)
Al-O(2)-Co	98.38(6)	C(21)-C(22)-C(23)	119.9(2)
Si(1)-O(3)-Si(2)#1	148.42(9)	C(22)-C(23)-C(24)	119.8(3)
C(26)-O(4)-Al	127.61(13)	C(19)-C(24)-C(23)	121.9(2)
C(28)-O(5)-Al	128.36(13)	O(4)-C(26)-C(27)	124.23(19)
C(31)-O(6)-Al	128.20(13)	O(4)-C(26)-C(25)	116.02(19)
C(33)-O(7)-Al	128.03(13)	C(27)-C(26)-C(25)	119.74(19)
C(36)-O(11)-C(36)#1	112.5(2)	C(26)-C(27)-C(28)	123.3(2)
C(6)-C(1)-C(2)	116.81(18)	O(5)-C(28)-C(27)	123.16(19)
C(6)-C(1)-Si(1)	124.19(15)	O(5)-C(28)-C(29)	116.52(19)
C(2)-C(1)-Si(1)	119.00(14)	C(27)-C(28)-C(29)	120.31(19)
C(3)-C(2)-C(1)	121.80(19)	O(6)-C(31)-C(32)	124.16(19)
C(2)-C(3)-C(4)	120.0(2)	O(6)-C(31)-C(30)	115.46(18)
C(5)-C(4)-C(3)	119.6(2)	C(32)-C(31)-C(30)	120.36(19)
C(4)-C(5)-C(6)	120.2(2)	C(33)-C(32)-C(31)	122.61(19)
C(5)-C(6)-C(1)	121.5(2)	O(7)-C(33)-C(32)	124.39(18)
C(12)-C(7)-C(8)	116.75(19)	O(7)-C(33)-C(34)	115.7(2)
C(12)-C(7)-Si(1)	118.63(16)	C(32)-C(33)-C(34)	119.9(2)
C(8)-C(7)-Si(1)	124.62(15)	O(11)-C(36)-C(37)	109.5(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2513. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al	20(1)	19(1)	14(1)	1(1)	6(1)	4(1)
Co	16(1)	19(1)	13(1)	0	5(1)	0
Si(1)	16(1)	18(1)	15(1)	1(1)	3(1)	1(1)
Si(2)	17(1)	20(1)	16(1)	0(1)	6(1)	3(1)
O(1)	17(1)	19(1)	15(1)	0(1)	5(1)	1(1)
O(2)	19(1)	24(1)	15(1)	0(1)	7(1)	4(1)
O(3)	16(1)	26(1)	19(1)	1(1)	5(1)	-1(1)
O(4)	28(1)	19(1)	22(1)	1(1)	8(1)	4(1)
O(5)	25(1)	19(1)	17(1)	-1(1)	6(1)	2(1)
O(6)	24(1)	19(1)	19(1)	1(1)	8(1)	0(1)

O(7)	25(1)	27(1)	19(1)	3(1)	10(1)	4(1)
O(9)	58(2)	21(1)	58(2)	0	-5(1)	0
O(10)	79(2)	19(1)	37(2)	0	26(1)	0
O(11)	39(1)	26(1)	32(1)	0	8(1)	0
C(1)	20(1)	23(1)	17(1)	0(1)	6(1)	-2(1)
C(2)	23(1)	25(1)	19(1)	3(1)	1(1)	-1(1)
C(3)	30(1)	20(1)	30(1)	3(1)	5(1)	-1(1)
C(4)	32(1)	25(1)	26(1)	-6(1)	5(1)	-9(1)
C(5)	33(1)	33(1)	22(1)	1(1)	-5(1)	-4(1)
C(6)	29(1)	24(1)	24(1)	3(1)	1(1)	2(1)
C(7)	18(1)	21(1)	19(1)	-2(1)	2(1)	2(1)
C(8)	21(1)	20(1)	24(1)	-2(1)	6(1)	2(1)
C(9)	29(1)	22(1)	25(1)	2(1)	4(1)	1(1)
C(10)	31(1)	24(1)	38(1)	3(1)	5(1)	11(1)
C(11)	39(1)	45(2)	62(2)	14(1)	29(1)	22(1)
C(12)	35(1)	37(1)	46(1)	15(1)	23(1)	14(1)
C(13)	22(1)	25(1)	26(1)	-1(1)	10(1)	4(1)
C(14)	47(2)	44(2)	29(1)	-7(1)	3(1)	24(1)
C(15)	63(2)	55(2)	38(2)	-21(1)	1(1)	28(1)
C(16)	49(2)	28(1)	52(2)	-6(1)	21(1)	13(1)
C(17)	48(2)	32(1)	42(1)	11(1)	24(1)	17(1)
C(18)	36(1)	32(1)	28(1)	3(1)	16(1)	10(1)
C(19)	21(1)	29(1)	22(1)	5(1)	7(1)	4(1)
C(20)	35(1)	38(1)	39(1)	9(1)	23(1)	7(1)
C(21)	39(1)	60(2)	52(2)	19(1)	31(1)	10(1)
C(22)	38(1)	45(2)	57(2)	22(1)	20(1)	-5(1)
C(23)	59(2)	31(1)	65(2)	3(1)	33(2)	-8(1)
C(24)	45(2)	29(1)	51(2)	1(1)	29(1)	-3(1)
C(25)	52(2)	22(1)	41(1)	-4(1)	16(1)	6(1)
C(26)	40(1)	21(1)	26(1)	-3(1)	16(1)	3(1)
C(27)	57(2)	26(1)	20(1)	-8(1)	11(1)	1(1)
C(28)	35(1)	26(1)	16(1)	-2(1)	9(1)	-1(1)
C(29)	46(2)	30(1)	19(1)	-1(1)	2(1)	-3(1)
C(30)	60(2)	21(1)	32(1)	4(1)	19(1)	-2(1)
C(31)	30(1)	23(1)	18(1)	4(1)	4(1)	0(1)
C(32)	40(1)	30(1)	23(1)	5(1)	15(1)	-4(1)
C(33)	26(1)	37(1)	15(1)	3(1)	7(1)	1(1)
C(34)	43(2)	49(2)	29(1)	7(1)	22(1)	8(1)
C(36)	41(1)	30(1)	41(1)	6(1)	9(1)	3(1)
C(37)	41(2)	40(1)	40(2)	2(1)	7(1)	0(1)

8.12. Compound 15

Table 1. Crystal data and structure refinement for sh2473.

Identification code	sh2473	
Empirical formula	$C_{72}\ H_{81}\ Al_2\ Mg\ O_{17}\ Si_4$	
Formula weight	1409.00	
Temperature	169(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.4731(12) Å	α= 90°.
	b = 11.5789(6) Å	β= 108.069(2)°.
	c = 25.8068(13) Å	γ = 90°.
Volume	7236.3(6) $Å^3$	
Z	4	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	2972	
Crystal size	0.33 x 0.25 x 0.1 mm^3	
Theta range for data collection	1.66 to 28.28°.	
Index ranges	-32<=h<=33, -15<=k<=11, -33<=l<=34	
Reflections collected	26444	
Independent reflections	8681 [R(int) = 0.0427]	
Completeness to theta = 28.28°	96.4 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8681 / 0 / 445	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1323	
R indices (all data)	R1 = 0.0893, wR2 = 0.1476	
Largest diff. peak and hole	0.734 and -0.905 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sh2473. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al	9907(1)	7119(1)	1330(1)	16(1)
Mg	10000	7028(1)	2500	22(1)
Si(1)	11130(1)	7484(1)	2166(1)	16(1)
Si(2)	8760(1)	7144(1)	1604(1)	16(1)
O(1)	9425(1)	7098(1)	1741(1)	17(1)
O(2)	10468(1)	7280(1)	1991(1)	18(1)
O(3)	8624(1)	7398(2)	2172(1)	21(1)
O(4)	9868(1)	8744(1)	1233(1)	22(1)
O(5)	9317(1)	6939(1)	664(1)	21(1)
O(6)	10402(1)	7109(2)	909(1)	22(1)
O(7)	9956(1)	5469(1)	1376(1)	21(1)
O(8)	10000	2615(2)	2500	38(1)
O(9)	10000	5273(3)	2500	49(1)
O(10)	10000	8992(5)	2500	130(2)
C(1)	11334(1)	8936(2)	1975(1)	21(1)
C(2)	11165(1)	9343(3)	1444(1)	40(1)
C(3)	11344(1)	10394(3)	1308(2)	52(1)
C(4)	11699(1)	11068(3)	1703(1)	43(1)
C(5)	11875(1)	10697(3)	2230(1)	45(1)
C(6)	11692(1)	9634(3)	2364(1)	35(1)
C(7)	11482(1)	6326(2)	1893(1)	22(1)
C(8)	11424(1)	5180(3)	2030(1)	41(1)
C(9)	11687(2)	4288(3)	1854(2)	54(1)
C(10)	12012(1)	4510(3)	1529(2)	50(1)
C(11)	12076(1)	5623(3)	1384(1)	50(1)
C(12)	11816(1)	6535(3)	1567(1)	36(1)
C(13)	8449(1)	8393(2)	1149(1)	20(1)
C(14)	8026(1)	8287(2)	658(1)	30(1)
C(15)	7812(1)	9240(3)	334(1)	37(1)
C(16)	8015(1)	10323(3)	497(1)	33(1)
C(17)	8427(1)	10468(2)	986(1)	30(1)
C(18)	8641(1)	9509(2)	1306(1)	25(1)
C(19)	8406(1)	5750(2)	1329(1)	21(1)
C(20)	7978(1)	5368(3)	1516(1)	40(1)
C(21)	7700(1)	4346(3)	1336(2)	52(1)
C(22)	7841(1)	3672(3)	959(1)	38(1)
C(23)	8262(1)	4025(2)	768(1)	32(1)
C(24)	8543(1)	5047(2)	951(1)	26(1)
C(25)	9662(1)	9300(2)	788(1)	27(1)
C(26)	9330(1)	8809(2)	309(1)	33(1)
C(27)	9147(1)	7670(2)	274(1)	25(1)
C(28)	8722(1)	7234(3)	-234(1)	36(1)
C(29)	9784(1)	10568(2)	809(1)	40(1)
C(30)	10520(1)	6270(3)	641(1)	27(1)
C(31)	10384(1)	5129(2)	702(1)	33(1)
C(32)	10137(1)	4777(2)	1085(1)	26(1)
C(33)	10080(2)	3512(2)	1191(1)	43(1)
C(34)	10833(1)	6573(3)	252(1)	43(1)
C(35)	9513(1)	1928(3)	2333(2)	51(1)
C(36)	9019(1)	2698(3)	2170(2)	56(1)

Table 3. Bond lengths [Å] and angles [°] for sh2473.

Al-O(1)	1.8563(17)	C(25)-C(29)	1.498(4)
Al-O(2)	1.8625(17)	C(26)-C(27)	1.392(4)
Al-O(4)	1.8962(18)	C(27)-C(28)	1.504(4)
Al-O(6)	1.9039(17)	C(30)-C(31)	1.387(4)
Al-O(5)	1.9130(17)	C(30)-C(34)	1.507(4)
Al-O(7)	1.9157(18)	C(31)-C(32)	1.388(4)
Al-Mg	2.9562(7)	C(32)-C(33)	1.506(4)
Mg-O(9)	2.032(4)	C(35)-C(36)	1.492(5)
Mg-O(2)#1	2.0504(15)	O(1)-Al-O(2)	86.23(7)
Mg-O(2)	2.0505(15)	O(1)-Al-O(4)	94.07(8)
Mg-O(1)#1	2.0520(16)	O(2)-Al-O(4)	90.94(8)
Mg-O(1)	2.0522(15)	O(1)-Al-O(6)	178.89(8)
Mg-O(10)	2.274(6)	O(2)-Al-O(6)	93.91(8)
Mg-Al#1	2.9562(7)	O(4)-Al-O(6)	87.03(8)
Si(1)-O(2)	1.6214(16)	O(1)-Al-O(5)	92.12(7)
Si(1)-O(3)#1	1.6304(17)	O(2)-Al-O(5)	178.28(8)
Si(1)-C(7)	1.869(3)	O(4)-Al-O(5)	89.67(8)
Si(1)-C(1)	1.871(3)	O(6)-Al-O(5)	87.73(8)
Si(2)-O(1)	1.6201(16)	O(1)-Al-O(7)	89.60(7)
Si(2)-O(3)	1.6334(17)	O(2)-Al-O(7)	91.50(8)
Si(2)-C(13)	1.876(3)	O(4)-Al-O(7)	175.72(8)
Si(2)-C(19)	1.877(2)	O(6)-Al-O(7)	89.29(8)
O(3)-Si(1)#1	1.6304(17)	O(5)-Al-O(7)	87.99(8)
O(4)-C(25)	1.279(3)	O(1)-Al-Mg	43.41(5)
O(5)-C(27)	1.283(3)	O(2)-Al-Mg	43.38(5)
O(6)-C(30)	1.279(3)	O(4)-Al-Mg	98.90(6)
O(7)-C(32)	1.278(3)	O(6)-Al-Mg	136.57(6)
O(8)-C(35)	1.423(4)	O(5)-Al-Mg	134.92(6)
O(8)-C(35)#1	1.423(4)	O(7)-Al-Mg	85.28(6)
C(1)-C(2)	1.385(4)	O(9)-Mg-O(2)#1	98.19(6)
C(1)-C(6)	1.389(4)	O(9)-Mg-O(2)	98.19(6)
C(2)-C(3)	1.384(4)	O(2)#1-Mg-O(2)	163.63(11)
C(3)-C(4)	1.375(5)	O(9)-Mg-O(1)#1	92.28(6)
C(4)-C(5)	1.363(5)	O(2)#1-Mg-O(1)#1	76.56(6)
C(5)-C(6)	1.397(4)	O(2)-Mg-O(1)#1	102.77(6)
C(7)-C(12)	1.391(3)	O(9)-Mg-O(1)	92.28(6)
C(7)-C(8)	1.394(4)	O(2)#1-Mg-O(1)	102.77(6)
C(8)-C(9)	1.383(4)	O(2)-Mg-O(1)	76.56(6)
C(9)-C(10)	1.373(5)	O(1)#1-Mg-O(1)	175.44(11)
C(10)-C(11)	1.365(5)	O(9)-Mg-O(10)	180.000(2)
C(11)-C(12)	1.404(4)	O(2)#1-Mg-O(10)	81.81(6)
C(13)-C(14)	1.392(4)	O(2)-Mg-O(10)	81.81(6)
C(13)-C(18)	1.397(3)	O(1)#1-Mg-O(10)	87.72(6)
C(14)-C(15)	1.389(4)	O(1)-Mg-O(10)	87.72(6)
C(15)-C(16)	1.373(4)	O(9)-Mg-Al	92.06(3)
C(16)-C(17)	1.379(4)	O(2)#1-Mg-Al	140.47(5)
C(17)-C(18)	1.390(4)	O(2)-Mg-Al	38.60(4)
C(19)-C(20)	1.395(4)	O(1)#1-Mg-Al	141.31(4)
C(19)-C(24)	1.396(4)	O(1)-Mg-Al	38.43(4)
C(20)-C(21)	1.383(4)	O(10)-Mg-Al	87.94(3)
C(21)-C(22)	1.378(4)	O(9)-Mg-Al#1	92.06(3)
C(22)-C(23)	1.376(4)	O(2)#1-Mg-Al#1	38.60(4)
C(23)-C(24)	1.387(4)	O(2)-Mg-Al#1	140.47(5)
C(25)-C(26)	1.385(4)	O(1)#1-Mg-Al#1	38.43(4)

O(1)-Mg-Al#1	141.30(4)	C(8)-C(7)-Si(1)	119.01(19)
O(10)-Mg-Al#1	87.94(3)	C(9)-C(8)-C(7)	121.7(3)
Al-Mg-Al#1	175.89(6)	C(10)-C(9)-C(8)	120.4(3)
O(2)-Si(1)-O(3)#1	108.19(8)	C(11)-C(10)-C(9)	119.4(3)
O(2)-Si(1)-C(7)	111.71(10)	C(10)-C(11)-C(12)	120.5(3)
O(3)#1-Si(1)-C(7)	106.17(10)	C(7)-C(12)-C(11)	120.9(3)
O(2)-Si(1)-C(1)	114.01(10)	C(14)-C(13)-C(18)	116.6(2)
O(3)#1-Si(1)-C(1)	106.42(10)	C(14)-C(13)-Si(2)	124.1(2)
C(7)-Si(1)-C(1)	109.89(11)	C(18)-C(13)-Si(2)	119.30(18)
O(1)-Si(2)-O(3)	107.89(9)	C(15)-C(14)-C(13)	121.8(3)
O(1)-Si(2)-C(13)	111.82(10)	C(16)-C(15)-C(14)	120.0(3)
O(3)-Si(2)-C(13)	104.91(10)	C(15)-C(16)-C(17)	120.0(3)
O(1)-Si(2)-C(19)	113.65(10)	C(16)-C(17)-C(18)	119.6(3)
O(3)-Si(2)-C(19)	106.46(10)	C(17)-C(18)-C(13)	121.9(2)
C(13)-Si(2)-C(19)	111.51(11)	C(20)-C(19)-C(24)	116.7(2)
Si(2)-O(1)-Al	135.04(10)	C(20)-C(19)-Si(2)	118.5(2)
Si(2)-O(1)-Mg	126.78(9)	C(24)-C(19)-Si(2)	124.80(18)
Al-O(1)-Mg	98.16(7)	C(21)-C(20)-C(19)	121.8(3)
Si(1)-O(2)-Al	134.87(10)	C(22)-C(21)-C(20)	120.3(3)
Si(1)-O(2)-Mg	127.05(9)	C(23)-C(22)-C(21)	119.2(3)
Al-O(2)-Mg	98.02(7)	C(22)-C(23)-C(24)	120.5(3)
Si(1)#1-O(3)-Si(2)	146.29(11)	C(23)-C(24)-C(19)	121.5(2)
C(25)-O(4)-Al	127.52(17)	O(4)-C(25)-C(26)	124.1(2)
C(27)-O(5)-Al	127.83(16)	O(4)-C(25)-C(29)	116.0(2)
C(30)-O(6)-Al	128.30(17)	C(26)-C(25)-C(29)	119.8(2)
C(32)-O(7)-Al	128.09(17)	C(25)-C(26)-C(27)	123.1(2)
C(35)-O(8)-C(35)#1	112.0(4)	O(5)-C(27)-C(26)	123.3(2)
C(2)-C(1)-C(6)	116.8(2)	O(5)-C(27)-C(28)	116.0(2)
C(2)-C(1)-Si(1)	122.7(2)	C(26)-C(27)-C(28)	120.7(2)
C(6)-C(1)-Si(1)	120.4(2)	O(6)-C(30)-C(31)	123.7(2)
C(3)-C(2)-C(1)	121.6(3)	O(6)-C(30)-C(34)	116.3(3)
C(4)-C(3)-C(2)	120.4(3)	C(31)-C(30)-C(34)	120.0(2)
C(5)-C(4)-C(3)	119.7(3)	C(30)-C(31)-C(32)	122.9(2)
C(4)-C(5)-C(6)	119.6(3)	O(7)-C(32)-C(31)	124.1(2)
C(1)-C(6)-C(5)	121.9(3)	O(7)-C(32)-C(33)	115.5(2)
C(12)-C(7)-C(8)	117.0(2)	C(31)-C(32)-C(33)	120.3(2)
C(12)-C(7)-Si(1)	124.0(2)	O(8)-C(35)-C(36)	109.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2473. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al	18(1)	17(1)	15(1)	0(1)	6(1)	-2(1)
Mg	15(1)	37(1)	14(1)	0	4(1)	0
Si(1)	15(1)	18(1)	17(1)	1(1)	6(1)	-2(1)
Si(2)	15(1)	18(1)	16(1)	-1(1)	3(1)	-1(1)
O(1)	16(1)	18(1)	17(1)	-1(1)	5(1)	-2(1)
O(2)	17(1)	19(1)	17(1)	0(1)	6(1)	-3(1)
O(3)	17(1)	28(1)	18(1)	-1(1)	5(1)	1(1)
O(4)	26(1)	18(1)	21(1)	0(1)	6(1)	-3(1)
O(5)	24(1)	20(1)	18(1)	2(1)	5(1)	-2(1)

O(6)	24(1)	23(1)	21(1)	-1(1)	10(1)	-2(1)
O(7)	28(1)	16(1)	18(1)	-1(1)	8(1)	1(1)
O(8)	42(2)	32(2)	37(2)	0	7(1)	0
O(9)	68(2)	31(2)	56(2)	0	28(2)	0
O(10)	120(5)	91(4)	157(7)	0	12(4)	0
C(1)	18(1)	22(1)	24(1)	1(1)	8(1)	-2(1)
C(2)	38(2)	39(2)	35(2)	10(1)	1(1)	-20(1)
C(3)	56(2)	46(2)	46(2)	23(2)	4(2)	-21(2)
C(4)	51(2)	22(2)	62(2)	5(2)	26(2)	-11(1)
C(5)	60(2)	34(2)	46(2)	-18(2)	26(2)	-25(2)
C(6)	42(2)	35(2)	30(2)	-4(1)	16(1)	-14(1)
C(7)	18(1)	27(1)	22(1)	-3(1)	7(1)	0(1)
C(8)	48(2)	28(2)	56(2)	-3(1)	30(2)	4(1)
C(9)	63(2)	30(2)	77(3)	-8(2)	35(2)	5(2)
C(10)	48(2)	46(2)	59(2)	-20(2)	23(2)	10(2)
C(11)	43(2)	62(2)	57(2)	-14(2)	36(2)	1(2)
C(12)	36(2)	40(2)	42(2)	-4(1)	24(1)	-5(1)
C(13)	20(1)	20(1)	20(1)	-2(1)	6(1)	2(1)
C(14)	29(1)	27(2)	25(2)	-4(1)	-3(1)	0(1)
C(15)	38(2)	34(2)	25(2)	0(1)	-9(1)	5(1)
C(16)	39(2)	28(2)	30(2)	8(1)	5(1)	12(1)
C(17)	33(1)	21(1)	34(2)	0(1)	7(1)	3(1)
C(18)	24(1)	26(2)	20(1)	-3(1)	0(1)	1(1)
C(19)	16(1)	22(1)	21(1)	0(1)	1(1)	-3(1)
C(20)	35(2)	38(2)	54(2)	-15(2)	25(1)	-15(1)
C(21)	40(2)	45(2)	80(3)	-15(2)	34(2)	-23(2)
C(22)	33(2)	25(2)	51(2)	-6(1)	6(1)	-13(1)
C(23)	37(2)	24(2)	32(2)	-7(1)	6(1)	-4(1)
C(24)	27(1)	23(1)	28(1)	-2(1)	9(1)	-6(1)
C(25)	35(1)	20(1)	27(1)	5(1)	12(1)	-1(1)
C(26)	49(2)	28(2)	19(1)	9(1)	6(1)	-3(1)
C(27)	31(1)	28(2)	15(1)	3(1)	5(1)	1(1)
C(28)	45(2)	37(2)	18(1)	2(1)	1(1)	1(1)
C(29)	54(2)	20(2)	44(2)	7(1)	11(2)	-4(1)
C(30)	25(1)	41(2)	17(1)	-4(1)	8(1)	1(1)
C(31)	48(2)	30(2)	25(2)	-7(1)	18(1)	5(1)
C(32)	33(1)	22(1)	21(1)	-2(1)	5(1)	2(1)
C(33)	75(2)	22(2)	37(2)	-5(1)	23(2)	1(2)
C(34)	47(2)	59(2)	31(2)	-7(2)	25(1)	-8(2)
C(35)	54(2)	38(2)	58(2)	-8(2)	12(2)	-7(2)
C(36)	48(2)	58(2)	56(2)	-6(2)	9(2)	-3(2)

8.13. Compound 16

Table 1. Crystal data and structure refinement for sh2205.

Identification code	sh2205	
Empirical formula	C_{60} H_{70} Br_2 Mg_3 O_9 Si_4	
Formula weight	1280.27	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.7405(9) Å	α= 90°.
	b = 11.4100(4) Å	β= 108.749(2)°.
	c = 24.9847(9) Å	γ = 90°.
Volume	6408.7(4) $Å^3$	
Z	4	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	1.421 mm^{-1}	
F(000)	2656	
Crystal size	0.15 x 0.4 x 0.55 mm^3	
Theta range for data collection	1.81 to 28.93°.	
Index ranges	-32<=h<=32, -15<=k<=15, -33<=l<=33	
Reflections collected	37334	
Independent reflections	8434 [R(int) = 0.0802]	
Completeness to theta = 28.93°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8434 / 0 / 360	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1111	
R indices (all data)	R1 = 0.0810, wR2 = 0.1246	
Largest diff. peak and hole	0.866 and -1.151 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh2205. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2788(1)	959(1)	2011(1)	23(1)
Si(1)	4191(1)	1640(1)	1143(1)	12(1)
Si(2)	5522(1)	1287(1)	1431(1)	12(1)
Mg(1)	5000	1060(1)	2500	10(1)
Mg(2)	3754(1)	1891(1)	2244(1)	13(1)
O(1)	4840(1)	1590(2)	1049(1)	14(1)
O(2)	4275(1)	1498(2)	1808(1)	12(1)
O(3)	5602(1)	1414(2)	2097(1)	13(1)
O(4)	3628(1)	3626(2)	2290(1)	20(1)
O(5)	5000	-736(2)	2500	16(1)
C(1)	3743(1)	445(2)	698(1)	15(1)
C(2)	3429(1)	-401(3)	894(1)	18(1)
C(3)	3152(1)	-1336(3)	557(1)	22(1)
C(4)	3180(1)	-1447(3)	14(1)	22(1)
C(5)	3475(1)	-605(3)	-196(1)	23(1)
C(6)	3753(1)	325(3)	143(1)	18(1)
C(7)	3857(1)	3090(2)	871(1)	16(1)
C(8)	3264(1)	3204(3)	534(1)	22(1)
C(9)	3020(2)	4286(3)	331(1)	28(1)
C(10)	3370(2)	5279(3)	463(1)	27(1)
C(11)	3964(2)	5197(3)	793(1)	25(1)
C(12)	4201(1)	4111(3)	993(1)	22(1)
C(13)	5686(1)	-249(2)	1271(1)	16(1)
C(14)	5288(1)	-888(3)	835(1)	24(1)
C(15)	5405(2)	-2045(3)	724(1)	34(1)
C(16)	5926(2)	-2568(3)	1037(2)	34(1)
C(17)	6331(2)	-1957(3)	1463(2)	35(1)
C(18)	6208(1)	-811(3)	1580(1)	27(1)
C(19)	5995(1)	2381(2)	1219(1)	14(1)
C(20)	6613(1)	2453(3)	1496(1)	17(1)
C(21)	6954(1)	3312(3)	1353(1)	23(1)
C(22)	6692(1)	4109(3)	932(1)	26(1)
C(23)	6090(1)	4046(3)	646(1)	24(1)
C(24)	5745(1)	3193(3)	791(1)	19(1)
C(25)	4134(1)	4402(3)	2437(1)	29(1)
C(26)	4191(2)	5137(3)	2956(1)	40(1)
C(27)	3055(1)	4186(3)	2203(1)	25(1)
C(28)	2903(2)	5064(4)	1731(2)	41(1)
C(29A)	4460(2)	-1424(4)	2370(2)	21(1)
C(29B)	4728(4)	-1397(7)	1992(3)	26(2)
C(30)	4332(2)	-2243(4)	1936(2)	65(1)

Table 3. Bond lengths [Å] and angles [°] for sh2205.

Br(1)-Mg(2)	2.4228(9)	Si(2)-O(1)	1.6301(19)
Si(1)-O(2)	1.6166(18)	Si(2)-C(19)	1.867(3)
Si(1)-O(1)	1.6345(18)	Si(2)-C(13)	1.867(3)
Si(1)-C(1)	1.862(3)	Mg(1)-O(3)#1	2.0353(16)
Si(1)-C(7)	1.865(3)	Mg(1)-O(3)	2.0354(16)
Si(1)-Mg(2)	3.2484(10)	Mg(1)-O(5)	2.049(3)
Si(2)-O(3)	1.6183(18)	Mg(1)-O(2)	2.0707(18)

Mg(1)-O(2)#1	2.0707(18)	C(19)-Si(2)-C(13)	112.40(11)
Mg(1)-Mg(2)#1	2.9734(9)	O(3)#1-Mg(1)-O(3)	157.15(12)
Mg(1)-Mg(2)	2.9734(9)	O(3)#1-Mg(1)-O(5)	101.42(6)
Mg(2)-O(3)#1	1.932(2)	O(3)-Mg(1)-O(5)	101.42(6)
Mg(2)-O(2)	1.9445(18)	O(3)#1-Mg(1)-O(2)	80.70(7)
Mg(2)-O(4)	2.011(2)	O(3)-Mg(1)-O(2)	93.79(7)
O(3)-Mg(2)#1	1.9321(19)	O(5)-Mg(1)-O(2)	103.95(6)
O(4)-C(25)	1.441(4)	O(3)#1-Mg(1)-O(2)#1	93.79(7)
O(4)-C(27)	1.455(3)	O(3)-Mg(1)-O(2)#1	80.70(7)
O(5)-C(29B)	1.439(8)	O(5)-Mg(1)-O(2)#1	103.95(6)
O(5)-C(29B)#1	1.439(8)	O(2)-Mg(1)-O(2)#1	152.09(12)
O(5)-C(29A)	1.448(5)	O(3)#1-Mg(1)-Mg(2)#1	129.64(6)
O(5)-C(29A)#1	1.448(5)	O(3)-Mg(1)-Mg(2)#1	40.16(5)
C(1)-C(2)	1.400(4)	O(5)-Mg(1)-Mg(2)#1	108.58(3)
C(1)-C(6)	1.401(3)	O(2)-Mg(1)-Mg(2)#1	127.26(6)
C(2)-C(3)	1.387(4)	O(2)#1-Mg(1)-Mg(2)#1	40.61(5)
C(3)-C(4)	1.386(4)	O(3)#1-Mg(1)-Mg(2)	40.16(5)
C(4)-C(5)	1.388(4)	O(3)-Mg(1)-Mg(2)	129.65(6)
C(5)-C(6)	1.386(4)	O(5)-Mg(1)-Mg(2)	108.58(3)
C(7)-C(8)	1.394(4)	O(2)-Mg(1)-Mg(2)	40.61(5)
C(7)-C(12)	1.399(4)	O(2)#1-Mg(1)-Mg(2)	127.26(6)
C(8)-C(9)	1.390(4)	Mg(2)#1-Mg(1)-Mg(2)	142.83(6)
C(9)-C(10)	1.380(5)	O(3)#1-Mg(2)-O(2)	86.60(8)
C(10)-C(11)	1.388(5)	O(3)#1-Mg(2)-O(4)	108.67(9)
C(11)-C(12)	1.387(4)	O(2)-Mg(2)-O(4)	113.05(9)
C(13)-C(18)	1.388(4)	O(3)#1-Mg(2)-Br(1)	120.68(7)
C(13)-C(14)	1.395(4)	O(2)-Mg(2)-Br(1)	119.18(7)
C(14)-C(15)	1.395(4)	O(4)-Mg(2)-Br(1)	107.44(7)
C(15)-C(16)	1.372(5)	O(3)#1-Mg(2)-Mg(1)	42.79(5)
C(16)-C(17)	1.373(5)	O(2)-Mg(2)-Mg(1)	43.88(5)
C(17)-C(18)	1.391(4)	O(4)-Mg(2)-Mg(1)	117.19(7)
C(19)-C(24)	1.395(4)	Br(1)-Mg(2)-Mg(1)	135.32(4)
C(19)-C(20)	1.408(4)	O(3)#1-Mg(2)-Si(1)	108.45(6)
C(20)-C(21)	1.390(4)	O(2)-Mg(2)-Si(1)	21.92(5)
C(21)-C(22)	1.378(4)	O(4)-Mg(2)-Si(1)	103.21(6)
C(22)-C(23)	1.378(4)	Br(1)-Mg(2)-Si(1)	107.03(3)
C(23)-C(24)	1.393(4)	Mg(1)-Mg(2)-Si(1)	65.68(2)
C(25)-C(26)	1.514(5)	Si(2)-O(1)-Si(1)	136.75(11)
C(27)-C(28)	1.501(4)	Si(1)-O(2)-Mg(2)	131.40(11)
C(29A)-C(30)	1.388(6)	Si(1)-O(2)-Mg(1)	132.64(10)
O(2)-Si(1)-O(1)	109.48(9)	Mg(2)-O(2)-Mg(1)	95.51(7)
O(2)-Si(1)-C(1)	113.47(11)	Si(2)-O(3)-Mg(2)#1	134.46(10)
O(1)-Si(1)-C(1)	105.84(10)	Si(2)-O(3)-Mg(1)	128.48(10)
O(2)-Si(1)-C(7)	111.23(10)	Mg(2)#1-O(3)-Mg(1)	97.05(8)
O(1)-Si(1)-C(7)	106.74(11)	C(25)-O(4)-C(27)	115.5(2)
C(1)-Si(1)-C(7)	109.73(12)	C(25)-O(4)-Mg(2)	119.50(18)
O(2)-Si(1)-Mg(2)	26.68(6)	C(27)-O(4)-Mg(2)	124.92(18)
O(1)-Si(1)-Mg(2)	134.23(7)	C(29B)-O(5)-C(29B)#1	116.8(7)
C(1)-Si(1)-Mg(2)	107.06(8)	C(29B)-O(5)-C(29A)	53.4(4)
C(7)-Si(1)-Mg(2)	91.01(8)	C(29B)#1-O(5)-C(29A)	91.6(4)
O(3)-Si(2)-O(1)	110.41(9)	C(29B)-O(5)-C(29A)#1	91.6(4)
O(3)-Si(2)-C(19)	110.46(11)	C(29B)#1-O(5)-C(29A)#1	53.4(4)
O(1)-Si(2)-C(19)	105.42(11)	C(29A)-O(5)-C(29A)#1	114.3(4)
O(3)-Si(2)-C(13)	109.98(11)	C(29B)-O(5)-Mg(1)	121.6(3)
O(1)-Si(2)-C(13)	108.05(11)	C(29B)#1-O(5)-Mg(1)	121.6(3)

C(29A)-O(5)-Mg(1)	122.9(2)
C(29A)#1-O(5)-Mg(1)	122.9(2)
C(2)-C(1)-C(6)	117.3(2)
C(2)-C(1)-Si(1)	124.2(2)
C(6)-C(1)-Si(1)	118.3(2)
C(3)-C(2)-C(1)	121.3(2)
C(4)-C(3)-C(2)	120.2(3)
C(3)-C(4)-C(5)	119.7(3)
C(6)-C(5)-C(4)	119.9(3)
C(5)-C(6)-C(1)	121.6(3)
C(8)-C(7)-C(12)	117.3(3)
C(8)-C(7)-Si(1)	122.0(2)
C(12)-C(7)-Si(1)	120.6(2)
C(9)-C(8)-C(7)	121.7(3)
C(10)-C(9)-C(8)	119.6(3)
C(9)-C(10)-C(11)	120.3(3)
C(12)-C(11)-C(10)	119.4(3)
C(11)-C(12)-C(7)	121.6(3)
C(18)-C(13)-C(14)	116.9(3)
C(18)-C(13)-Si(2)	121.6(2)
C(14)-C(13)-Si(2)	121.5(2)
C(15)-C(14)-C(13)	121.4(3)
C(16)-C(15)-C(14)	119.9(3)
C(15)-C(16)-C(17)	120.0(3)
C(16)-C(17)-C(18)	119.9(3)
C(13)-C(18)-C(17)	121.8(3)
C(24)-C(19)-C(20)	117.2(2)
C(24)-C(19)-Si(2)	121.1(2)
C(20)-C(19)-Si(2)	121.7(2)
C(21)-C(20)-C(19)	121.0(3)
C(22)-C(21)-C(20)	120.3(3)
C(21)-C(22)-C(23)	120.0(3)
C(22)-C(23)-C(24)	119.9(3)
C(23)-C(24)-C(19)	121.6(3)
O(4)-C(25)-C(26)	113.4(3)
O(4)-C(27)-C(28)	112.8(2)
C(30)-C(29A)-O(5)	119.9(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh2205. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	17(1)	29(1)	26(1)	-4(1)	8(1)	-5(1)
Si(1)	12(1)	14(1)	10(1)	0(1)	4(1)	0(1)
Si(2)	12(1)	17(1)	11(1)	-1(1)	6(1)	-1(1)
Mg(1)	10(1)	11(1)	10(1)	0	4(1)	0
Mg(2)	12(1)	14(1)	13(1)	1(1)	6(1)	2(1)
O(1)	14(1)	20(1)	10(1)	0(1)	6(1)	-1(1)
O(2)	11(1)	15(1)	11(1)	0(1)	4(1)	1(1)
O(3)	12(1)	16(1)	11(1)	-2(1)	6(1)	-1(1)
O(4)	18(1)	16(1)	27(1)	-1(1)	12(1)	3(1)
O(5)	17(1)	8(1)	22(1)	0	8(1)	0
C(1)	14(1)	16(1)	14(1)	-2(1)	4(1)	3(1)
C(2)	18(1)	20(2)	15(1)	0(1)	6(1)	0(1)
C(3)	21(1)	18(2)	24(2)	0(1)	4(1)	-4(1)
C(4)	22(1)	17(2)	23(1)	-8(1)	2(1)	0(1)
C(5)	25(2)	27(2)	16(1)	-7(1)	7(1)	2(1)
C(6)	18(1)	25(2)	15(1)	-1(1)	9(1)	-3(1)
C(7)	19(1)	18(2)	11(1)	0(1)	7(1)	0(1)
C(8)	26(2)	18(2)	22(1)	1(1)	5(1)	3(1)
C(9)	30(2)	25(2)	25(2)	4(1)	2(1)	10(1)
C(10)	43(2)	19(2)	22(2)	8(1)	13(1)	12(1)
C(11)	39(2)	15(2)	24(2)	1(1)	17(1)	-2(1)
C(12)	25(2)	23(2)	18(1)	-2(1)	8(1)	-3(1)
C(13)	19(1)	16(1)	18(1)	-1(1)	12(1)	-3(1)
C(14)	30(2)	21(2)	22(1)	-6(1)	9(1)	0(1)
C(15)	48(2)	26(2)	29(2)	-15(1)	16(2)	-7(2)
C(16)	49(2)	16(2)	42(2)	-5(1)	24(2)	3(2)
C(17)	33(2)	21(2)	50(2)	-1(2)	11(2)	9(2)
C(18)	25(2)	18(2)	35(2)	-5(1)	7(1)	-1(1)
C(19)	19(1)	14(1)	12(1)	-5(1)	9(1)	-1(1)
C(20)	18(1)	20(2)	16(1)	-1(1)	8(1)	0(1)
C(21)	21(1)	28(2)	22(1)	-7(1)	12(1)	-10(1)
C(22)	35(2)	26(2)	24(2)	-5(1)	19(1)	-12(1)
C(23)	35(2)	22(2)	18(1)	2(1)	13(1)	-4(1)
C(24)	24(1)	21(2)	15(1)	-2(1)	10(1)	-1(1)
C(25)	28(2)	21(2)	39(2)	-3(1)	14(1)	-5(1)
C(26)	62(3)	24(2)	29(2)	1(2)	6(2)	-6(2)
C(27)	24(2)	24(2)	33(2)	5(1)	15(1)	10(1)
C(28)	41(2)	51(2)	34(2)	15(2)	16(2)	21(2)
C(29A)	18(2)	13(2)	34(3)	2(2)	9(2)	1(2)
C(30)	68(3)	26(2)	64(3)	11(2)	-28(2)	-11(2)