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Inorganic heterocycles based on alumosilicate-sulfide ligand

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ABSTRACT

The alumosilicate sulfide ligand $[\mathbf{L}\text{Al(SH)}(\mu\text{-O})\text{Si(OH)(O}^t\text{Bu)}_2]$ ($\mathbf{L} = \text{HC[CMeNAr]}_2^-$, Ar = 2,6-$^i\text{Pr}_2\text{C}_6\text{H}_3$) was used for the preparation of cyclic compounds with the aluminum atom covalently bonded to oxygen and sulfur atoms. The reaction of this ligand with trimethylaluminum or trimethylgallium resulted in the formation of $[\{\mathbf{L}\text{Al}(\mu\text{-S})(\mu\text{-O})\text{Si}(\mu\text{-O})(\text{O}^t\text{Bu})_2\}\text{MMe(thf)}]$ (M = Al, Ga) with AlMSiO_2S inorganic cores. While the aluminum derivative is stable, the gallium compound always coexists with the tetrametallic species $[\mathbf{L}\text{Al}(\mu_3\text{-S})(\text{GaMe}_3)(\mu\text{-GaMe}_2)(\mu\text{-O})\text{Si}\{(\mu_3\text{-O})(\text{GaMe}_2)\}(\mu\text{-O}^t\text{Bu})(\text{O}^t\text{Bu})]$. A similar tetrametallic compound can be prepared with aluminum. These compounds represent unprecedented cases of the simplest possible alumosilicate moiety coordinated to three metal atoms. The coordination of three metal atoms to the $(^t\text{BuO})_2\text{Si}(\mu\text{-O})_2$ moiety activates one of the Si–O bonds, as evidenced by the bond lengths of 1.684 and 1.703 Å.

1. Introduction

The chemistry of group 16 derivatives of aluminum has been dominated by alumoxanes and by monometallic aluminum complexes bearing Al–O bonding [1]. To certain extent, this is mainly due to the importance of the first as co-catalysts in polymerization reactions and by the ease of formation of the latter [2]. Aluminum-based chalcogen compounds have been studied to a lesser extent [3], albeit compounds bearing two different group 16 atoms covalently bonded to the same aluminum center are much more scarce. In this regard, our research group has been interested in the synthesis of mixed oxygen-chalcogen group 13 compounds containing reactive functional groups and their use in the formation of multimetallic systems [4]. Thus, metallaligands based on alumoxane-, alumophosphite- and alumosilicate-sulfides have led to the synthesis of heterometallic compounds with unusual inorganic rings: $[(\mu\text{-O})\{^{\text{Mes}}\mathbf{L}\text{M}(\mu\text{-S})_2\}_2\text{M}'(\text{NR}_2)_2]$ ($^{\text{Mes}}\mathbf{L} = \text{HC[CMeNAr]}_2^-$, Ar = 2,4,6-$\text{Me}_3\text{C}_6\text{H}_2$; M = Al, Ga; M′ = group 4 metals, R = Me, Et) [4b,4g], $[\{\mathbf{L}\text{Al}(\mu\text{-S})(\mu\text{-O})\text{P(OEt)}_2\}_2\text{Zn}]$ [4c], $[\mathbf{L}\text{Al(SLi)}(\mu\text{-O})\text{P(OEt)}_2]$ [4c], $[\mathbf{L}\text{Al(SGaMe}_2)(\mu\text{-O})\text{P(OEt)}_2]$ [4d] and $[\{\mathbf{L}\text{Al(SLi)}(\mu\text{-O})\text{Si}\{\text{OLi(thf)}_2\}(\text{O}^t\text{Bu})_2\}_2]$ ($\mathbf{L} = \text{HC[CMeNAr]}_2^-$, Ar = 2,6-$^i\text{Pr}_2\text{C}_6\text{H}_3$) [4e]. Indeed, the alumosilicate compound $[\mathbf{L}\text{Al(SH)}(\mu\text{-O})\text{Si(OH)(O}^t\text{Bu)}_2]$ (**1**) represents an interesting precursor for the formation of Al–O–Si–O–M–S rings. Furthermore, it can also form multimetallic moieties due to the presence of additional coordination sites provided by O^{t}Bu groups from the silicate moiety (Fig. 1).

Our previous study reveals, that both functional groups in **1** can be deprotonated and substituted by a metal center. Such is the case of the reaction of **1** with 2 equiv of $\text{Li[N(SiMe}_3)_2]$ which afforded the dimeric dilithium salt $[\{\mathbf{L}\text{Al(SLi)}(\mu\text{-O})\text{Si}\{\text{OLi(thf)}_2\}(\text{O}^t\text{Bu})_2\}_2]$ (**2**) with a penta-cyclic inorganic core [4e]. In our search for unusual inorganic heterocycles, we became interested in the possibility of deprotonating both groups by the same metal atom and forming covalent S–Al–O–Si–O–M rings. This should be possible as the oxygen homologue $[\mathbf{L}\text{Al(OH)}(\mu\text{-O})\text{Si(OH)(O}^t\text{Bu)}_2]$ can be transformed with group 4 metal amides into the corresponding cyclic or spirocyclic compounds [5]. Moreover, the Al–SH group is more reactive than the Al–OH moiety and the Al–S bond length in **1** is with 2.22 Å significantly longer than the Al–O distance in $[\mathbf{L}\text{Al(OH)}(\mu\text{-O})\text{Si(OH)(O}^t\text{Bu)}_2]$ (1.75 Å) [4e]. This places the sulfur atom almost out of the protective zone of the ^{i}Pr groups and

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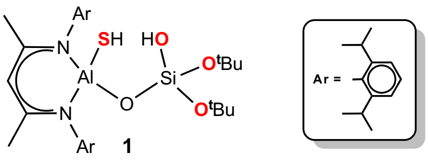

1

Fig. 1. Bidentate alumosilicate ligand **1** with the possible coordination sites highlighted.

increases the possibility to form the desired six-membered ring. Furthermore, MMe_3 (M = Al, Ga) have been reported to deprotonate Si–OH groups [6], and in the case of trimethylgallium, it has also proven to deprotonate the Al–SH group [4d]. Therefore, trimethylaluminum should also be sufficiently reactive to deprotonate the latter. Herein, we report on the synthesis and structural characterization of aluminum and gallium multimetallic systems supported by the metallaligand [**L**Al(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$] (**1**).

2. Results and discussion

2.1. Synthetic aspects and spectral characterization

Compound **1** was reacted with one equivalent of $AlMe_3$ in THF giving [{**L**Al(μ-S)(μ-O)Si(μ-O)(O^{t}Bu)$_2$}AlMe(thf)] (**3**) as the sole product in a 65% yield, as confirmed by ^{1}H NMR spectroscopy. When toluene is used instead of THF, the unsolvated dimeric form [({**L**Al(μ-S)(μ-O)Si(μ$_3$-O)(O^{t}Bu)$_2$}{μ$_3$-AlMe})$_2$] (**3a**) was isolated. The HR-MS spectrum for this compound contains a peak at *m*/*z* 763.3438 belonging to the $[M - THF + K]^+$ ion[3].

In the presence of an excess of $AlMe_3$, a different product was isolated, as evidenced by its crystallization in the form of large prismatic crystals. This product was later identified as [**L**Al(μ$_3$-S)(AlMe$_3$)(μ-AlMe$_2$)(μ-O)Si{(μ$_3$-O)(AlMe$_2$)}(μ-O^{t}Bu)(O^{t}Bu)] (**4**). Compound **4** decomposes rather quickly when separated from the solution or exposed to vacuum. This was revealed by the ^{1}H NMR spectrum of a sample of dried crystals which showed the presence of an inseparable mixture of products. Nonetheless, taking some of the crystals of **4** out of the mother liquor in a glove box and allowing them to dry for 5 min under nitrogen atmosphere produced a sample of **4** with almost no decomposition suitable for MS, EA and ^{1}H NMR analyses. However, these analyses had to be performed within minutes from the separation of the crystals. In the HR-MS spectrum of **4** peaks at *m*/*z* 819.4273 and 835.4045 were identified as belonging to the $[M - AlMe_3 + Na]^+$ and $[M - AlMe_3 + K]^+$ ions, respectively. The ^{1}H NMR spectrum of these crystals exhibits four different types of aluminum bound methyl groups with relative intensities of 9:3:3:6, suggesting the molecular structure [**L**Al(μ$_3$-S)(AlMe$_3$)(μ-AlMe$_2$)(μ-O)Si{(μ$_3$-O)(AlMe$_2$)}(μ-O^{t}Bu)(O^{t}Bu)]. Unfortunately, **4** decomposes rather swiftly once re-dissolved, thus hampering the acquisition of the ^{13}C NMR spectrum. However, the molecular structure of **4** was confirmed by X-ray diffraction studies.

Furthermore, we investigated the use of $GaMe_3$ in the preparation of the homologue of **3**, as gallium is weaker Lewis acid and is therefore more chalcophilic than aluminum. Complete deprotonation of **1** and the formation of [{**L**Al(μ-S)(μ-O)Si(μ-O)(O^{t}Bu)$_2$}GaMe(thf)] (**5**) and of [**L**Al(μ$_3$-S)(GaMe$_3$)(μ-GaMe$_2$)(μ-O)Si{(μ$_3$-O)(GaMe$_2$)}(μ-O^{t}Bu)(O^{t}Bu)] (**6**) was observed, even if less than three equivalents of $GaMe_3$ were used. This behavior did not allow the isolation and characterization of **5**, as it always coexisted in a mixture with **6**, as well as with other unidentified products. Nonetheless, due to the different shape of the crystals for **5** and **6**, both molecular structures could be determined by hand picking the appropriate crystals. The HR-MS spectra for these crystals shows peaks at *m*/*z* 805.2902 belonging to the $[M+K]^+$ (**5**) or at *m*/*z* 867.2999 representing the $[M - GaMe_3 - Me]^+$ fragment of **6**. The ^{1}H NMR spectrum of gently dried crystals of **6** shows the presence of minor amounts of at least four other compounds. However, the existence of a very broad singlet at δ 0.11 ppm with integration of 21 H atoms confirms the coordination of **1** to two $GaMe_2$ moieties and further coordination of a $GaMe_3$ molecule to the sulfur atom even in solution. Nonetheless, we were not able to isolate compound **5** in a pure form, which contrasts with the rather high stability of the aluminum homologue **3**. Due to the problems in isolation and purification of compounds **4**–**6**, no further characterization of these molecules was pursued. The synthesis of compounds **3**–**6** is summarized in Scheme 1.

2.2. Molecular description of compounds 3–6

Crystals of all compounds suitable for X-ray diffraction studies were obtained either from saturated toluene (**3a**, **4**, **6**) or THF/toluene (**3**, **5**) solutions at −24 °C (Table 1). Compounds **3**–**6** crystallized in the monoclinic $P2_1/n$ space group with one molecule and one THF molecule (**3**, **5**), half a molecule and one toluene molecule (**3a**) or one molecule and one toluene molecule (**4**, **6**) in the asymmetric unit. The molecular structures of compounds **3**–**6** are shown in Fig. 2 and selected bond lengths and angles are listed in Table 2.

The molecular structures of compounds **3** and **5** are isomorphous and the structure of **3** is in agreement with the structure proposed from ^{1}H NMR spectroscopy data. In both cases a doubly deprotonated ligand **1** coordinates to a MMe fragment forming a non-planar six-membered $AlMSiO_2S$ ring and the tetrahedral coordination sphere of the metal is completed by a THF molecule. Compound **3a** crystallizes as a dimeric compound with a central Al_2O_2 ring. The coordination of the Al(2) atom in **3** and Ga(1) atom in **5** to four different atoms creates geometrical enantiomers crystallizing as racemic mixtures in the same crystal. The structural analysis of the isomorphous compounds **4** and **6** confirmed the coordination of two MMe_2 fragments and one MMe_3 molecule to the double deprotonated ligand **1**. One of the MMe_2 unit coordinates to the deprotonated sulfur and oxygen atoms, whereas the second unit coordinates to the Si–O oxygen atom and one oxygen atom from the O–^{t}Bu moiety. Finally, the MMe_3 moiety coordinates to the sulfur atom. This coordination pattern also generates two enantiomers that crystallize as a racemic mixture in the same crystal. In these compounds, the six-membered $AlMSiO_2S$ ring is fused by a shared edge with a four-membered ring MO_2Si. Also in these cases, the six-membered rings are not planar and this deviation is caused by steric reasons in **3**, **3a** and **5**. However, in **4** and **6** it is the result of the coordination of the second MMe_2 fragment to the silicate moiety. The deprotonation of the SH group and the coordination of the metal atoms to the sulfur atom in these compounds has a small effect on the Al–S bond length (2.222(1) **1**, 2.206(1) **3**, 2.227(1) **4**, 2.212(1) **5** and 2.219(1) Å **6**) with the exception of that in **3a** which is with 2.150(1) Å one of the shortest observed to date. This bond distance is identical to that observed between Al(1) and the bridging sulfur atom S(1) in [(μ-S){$^{\mathbf{Mes}}$**L**Al(SH)}$_2$] ($^{\mathbf{Mes}}$**L** = $HC[CMeNAr]_2^-$, Ar = 2,4,6-$Me_3C_6H_2$) (2.150(3) Å, but the Al(2)–S(1) distance in this molecule is 2.163(3) Å [4a]. Nonetheless, these bonds are longer than those in the lithium or imidazolium salts of aluminium sulfides [(**L**Al(SH){SLi(thf)$_2$})$_2$] (2.123(1) Å) [7], $[\{C_xH\}^+\{$**L**Al(SH)(S)$\}^-]$ (C_xH^+ = 1,3-di-^{t}Bu- or 1,3-bis-mesitylimidazolium (1+), 2.116(1) and 2.115(1) Å, respectively) [8]. Furthermore, they are also longer than that in the

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[3] The alkaline metal stems from storing the dry THF, used to dissolve the compounds for the analysis, over elemental potassium or from the borosilicate glass of the storage bottle.