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Soluble, reactive and stable – unique aluminosilicate ligands and a heterobimetallic derivative $[LAl(SLi)(\mu\text{-}O)Si(OLi\cdot 2thf)(O^tBu)_2]_2$†‡

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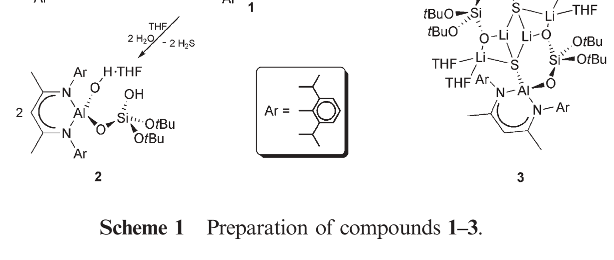
The heterobimetallic aluminosilicate $[LAl(SLi)(\mu\text{-}O)Si(OLi\cdot 2thf)(O^tBu)_2]_2$ was prepared from the $LAl(SH)(\mu\text{-}O)Si(OH)(O^tBu)_2$ ($L = [HC\{C(Me)N(Ar)\}_2]^-$, Ar = 2,6-di-^{i}Pr$_2C_6H_3$) ligand, which can also be hydrolyzed to $LAl(OH\cdot thf)(\mu\text{-}O)Si(OH)(O^tBu)_2$ – leading to the first aluminosilicate–dihydroxide soluble in organic solvents.

Many heterobimetallic aluminosilicate systems can be found in natural minerals such as almandine – $Fe_3Al_2(SiO_4)_3$, pyrope – $Mg_3Al_2(SiO_4)_3$, and spodumen – $LiAlSi_2O_6$ and some are known to have catalytic properties.[1] However, there is only a handful of structurally characterized molecular heterobimetallic aluminosilicate systems reported in the literature.[2] Thus, molecular heterometallic aluminosilicates are highly important as models for catalytic systems and as secondary building units (SBU). In 1995 Roesky and co-workers published the synthesis of $[M(thf)]_4[\{RN(SiMe_3)Si(\mu\text{-}O)_3AlEt\}_4]$ (M = Li, Na).[2a] Kim and co-workers investigated the adsorption of several hydrocarbons, H_2S, elemental halogens and nitric oxides on aluminosilicate monocrystals saturated with different metals (Ca, Mg, Co, Cd, Ag, Pd *etc.*).[2e,f] A lanthanum containing aluminosilicate was prepared by the reaction of $[Ln(AlMe_4)_3]$ with $(^tBuO)_3SiOH$ as a model for a fixation of the Ln–Al polymerization catalyst on a silica surface.[2i] A few other heterobimetallic aluminosilicate have been published containing Cu, Mg or Li.[2] Heterobimetallic oligoalumosiloxanes based on $[(Ph_2SiO)]_8[Al(O)OH]_4$, which contain either Li, Na, Ge, Pb, Sn or Zn have been prepared recently by Veith *et al.*.[2b–d] The tetramethylammonium salt of the aluminum silicate cubane $[NMe_4]_4[H_8Al_4Si_4O_{20}]\cdot 24H_2O$ was reported as the only structurally characterized aluminosilicate containing functional groups on both, aluminum as well as the silicon center, but is not soluble in organic solvents.[3] The synthesis of organic solvent-soluble aluminosilicate ligands is important mainly due to their facile characterization, as well as to their applications as homogeneous catalysts[2i] and molecular models.[4] So far, there is no report on molecular aluminosilicate ligands soluble in organic solvents of formula $HE\text{–}Al\text{–}O\text{–}Si(OR)_2\text{–}EH$ (E = O or S).

Herein we report on a facile synthesis of a unique aluminosilicate–hydroxide–hydrogensulfide ligand $LAl(SH)(\mu\text{-}O)Si(OH)(O^tBu)_2$ ($L = [HC\{C(Me)N(Ar)\}_2]^-$, Ar = 2,6-di-^{i}Pr$_2C_6H_3$) (**1**) from $LAl(SH)_2$[5] and $(^tBuO)_2Si(OH)_2$[6] in 85% yield. Furthermore, the SH group on the Al center can be easily converted into an OH moiety in a reaction with one equivalent of water to give the aluminosilicate–dihydroxide ligand $LAl(OH\cdot thf)(\mu\text{-}O)Si(OH)(O^tBu)_2$ (**2**) in a 75% yield. Moreover, metallaligand **1** and $[(Me_3Si)_2NLi\cdot OEt_2]_2$ were successfully used in the preparation of the unprecedented heterobimetallic aluminosilicate–sulfide $[LAl(SLi)(\mu\text{-}O)Si(OLi\cdot 2thf)(O^tBu)_2]_2$ (**3**) with 90% yield (Scheme 1).

It can be anticipated that compound **1** should not be stable undergoing self-condensation upon elimination of a second molecule of H_2S. Nevertheless, it has been shown recently, that the easy hydrolysis of $LAl(\mu\text{-}S)MCp_2$ (M = Ti, Zr)[7] leads to the unique heterobimetallic hydroxide–oxide–hydrogensulfides $LAl(OH)(\mu\text{-}O)M(SH)Cp_2$.[8] Moreover, the difficulties in the preparation of the Al_2O_2 ring containing species $LAl(\mu\text{-}O)_2AlL$[9] and its easy hydrolysis into the corresponding dihydroxide $[LAl(OH)]_2O$[9,10] demonstrate, that the ring formation is not favored in the case where the aluminum center is being shielded by the bulky β-diketiminato ligand. The driving force for this transformation is the oxophilicity of aluminum and a high ring strain in the parent compounds. Thus, compound **1** is stable and can be stored for several weeks at ambient temperature when protected from humidity, supporting the above conclusions. In comparison, compound **2** starts to decompose within a few days even when stored under an inert atmosphere in a glove-box, when trace impurities are present. Therefore, thorough purification of **2** is necessary, if it should be stored for a longer time. ^{1}H NMR spectroscopy revealed the free ligand to be the only soluble organic product of this decomposition. A similar observation was reported in the case of $LAl(OH)_2$.[11] The composition of compounds **1–3** was estimated by multinuclear NMR spectroscopy, EI-MS spectrometry and confirmed by an X-ray diffraction experiment. The proton of the SH moiety in **1** resonates at δ −0.45 ppm, whereas the signal for the Si–OH moiety was found at δ 1.53 ppm. The valence vibrations of these moieties can be found at $\tilde{\nu}$ 2560 (SH) and 3462 (OH) cm^{-1}, respectively. The Al–OH moiety in **2**



Scheme 1 Preparation of compounds **1–3**.

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† $L = [HC\{C(Me)N(Ar)\}_2]^-$, Ar = 2,6-di-^{i}Pr$_2C_6H_3$).

‡ Electronic supplementary information (ESI) available: Experimental data for **1–3** and further crystallographic details. See DOI: 10.1039/b707895a

resonates at δ 0.95 ppm in ^{1}H NMR, which is significantly shifted downfield compared to $[LAl(OH)]_2O$[9,10] (δ −0.30 ppm), $LAl(OH)_2$[11] (δ 0.20 ppm), $LAl(OH)(\mu\text{-}O)ZrCp_2(SH)$[8] ($\delta$ 0.36 ppm) and LAlMe(OH)[12] (δ 0.50 ppm), but comparable to that of $LAl(OH)(\mu\text{-}O)TiCp_2(SH)$[8] ($\delta$ 1.07 ppm). The substitution of the Al–SH moiety by an Al–OH group decreases the shielding of the proton from the Si–OH moiety in **2**, which resonance was found at δ 2.76 ppm. These signals are essentially silent in the case of **3**, confirming the total substitution of the acidic protons in **1** by lithium atoms.

Single crystals of compounds **1–3** were obtained from saturated hexane–toluene (**1** and **2**) and THF (**3**) solutions at −30 °C.§ Compound **1** crystallizes in a rhombohedral space group $R\bar{3}$ as a centrosymmetric dimer formed by hydrogen bonds (SiO–H···O^{t}Bu 2.14(2) Å) with one molecule of **1** and one third of a molecule of a highly disordered hexane in the asymmetric unit (Fig. 1).

The Al–SH moiety is involved in a intermolecular hydrogen bond with the oxygen atom from the free O^{t}Bu group as acceptor, AlS–H···O^{t}Bu 2.48(3). Compounds **2** and **3** crystallize in the monoclinic space group $P2_1/n$, as a pseudomerohedral twin with one molecule and a highly disordered THF molecule in the asymmetric unit (**2**), and half of the molecule in the asymmetric unit (**3**), respectively (Fig. 2 and 3). The Si–OH group in **2** is engaged in a hydrogen bond with the Al–OH moiety, whereas the proton from the Al–OH group is obviously interacting with the THF molecule. Even if the THF molecule is disordered over two positions, their orientation and the difficulties in removing the THF under vacuum confirm the presence of a hydrogen bond (OH···O 2.10, 2.13 Å). The Al–O(Si) bond lengths are in all three compounds (1.720 (**1**), 1.711 (**2**) and 1.719 Å (**3**)) comparable to each other and to the endocyclic Al–O bond lengths in $[NMe_4]_4[H_8Al_4Si_4O_{20}]\cdot 24H_2O$ (av. 1.701 Å),[3] $Al[OSi(O^tBu)_3]_3(HO^iPr)\cdot \frac{1}{2}[Al(O^iPr)_3]_4$ (av. 1.704 Å),[13] but they are longer than those of $[\{(^tBuO)_3SiO\}(^iPrO)(\mu\text{-}O^iPr)Al]_2$ (av. 1.688 Å)[13] and shorter than the endocyclic Al–O bond lengths in $[Na(thf)]_4[\{RN(SiMe_3)Si(\mu\text{-}O)_3AlEt\}_4]$ (R = 2,6-di-^{i}Pr$_2$C$_6$H$_3$) (av. 1.764 Å).[2a]

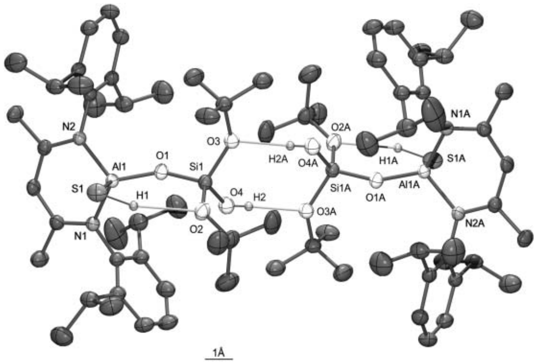

Fig. 1 Thermal ellipsoid plot of **1** at 50% level. Carbon-bound hydrogen atoms and solvating hexane are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.891(2), Al(1)–N(2) 1.885(2), Al(1)–S(1) 2.222(1), Al(1)–O(1) 1.720(2), Si(1)–O(1) 1.591(2), Si(1)–O(2) 1.624(2), Si(1)–O(3) 1.637(2), Si(1)–O(4) 1.611(2), S(1)–H(1) 1.31(3), O(2)–H(3) 0.77(2); N(1)–Al(1)–N(2) 97.5(1), S(1)–Al(1)–O(1) 112.9(1), Al(1)–O(1)–Si(1) 146.5(1), O(1)–Si(1)–O(2) 106.3(1), O(1)–Si(1)–O(3) 112.9(1), O(1)–Si(1)–O(4) 109.3(1), O(2)–Si(1)–O(3) 110.6(1), O(2)–Si(1)–O(4) 112.7(1), O(3)–Si(1)–O(4) 105.2(1).

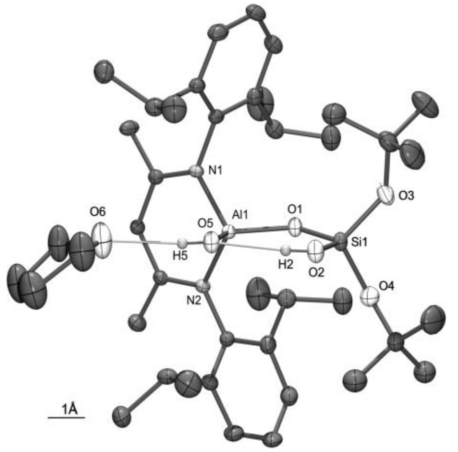

Fig. 2 Thermal ellipsoid plot of **2** at 40% level. Carbon-bound hydrogen atoms and two other positions of the coordinated THF are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.891(3), Al(1)–N(2) 1.894(3), Al(1)–O(5) 1.715(3), Al(1)–O(1) 1.711(2), Si(1)–O(1) 1.602(2), Si(1)–O(2) 1.627(3), Si(1)–O(3) 1.623(3), Si(1)–O(4) 1.625(3), O(5)–H(5) 0.74(1), O(2)–H(2) 0.75(1); O(1)–Al(1)–O(5) 106.3(1), N(1)–Al(1)–N(2) 97.3(1), Al(1)–O(1)–Si(1) 132.8(1), O(1)–Si(1)–O(2) 110.4(1), O(1)–Si(1)–O(3) 112.5(1), O(1)–Si(1)–O(4) 106.7(1), O(2)–Si(1)–O(3) 109.8(1), O(2)–Si(1)–O(4) 112.2(2), O(3)–Si(1)–O(4) 105.2(1).

The Al–O(H) bond length in **2** at 1.715 Å is comparable to the Al–O(Si) distances in **1–3**, Al–O(H) in $LAl(OH)_2$ (1.711 and 1.706 Å),[11,14] and in the alumoxane $[LAl(\mu\text{-}O)]_2O$,[9,10] but significantly shorter than the terminal Al–O in $[NMe_4]_4[H_8Al_4Si_4O_{20}]\cdot 24H_2O$ (av. 1.783 Å)[3] and the Al–(μ-OH) in $[(Ph_2SiO)]_8[Al(O)OH]_4\cdot(NC_5H_5)_4$ (1.769).[2b]

The Si–O(Al) bond lengths in **1** (1.591 Å) and **2** (1.602 Å) can be compared to those in $Al[OSi(O^tBu)_3]_3(HO^iPr)\cdot \frac{1}{2}[Al(O^iPr)_3]_4$ (av. 1.589 Å)[13] and in $[\{(^tBuO)_3SiO\}(^iPrO)(\mu\text{-}O^iPr)Al]_2$ (av. 1.590 Å),[13]

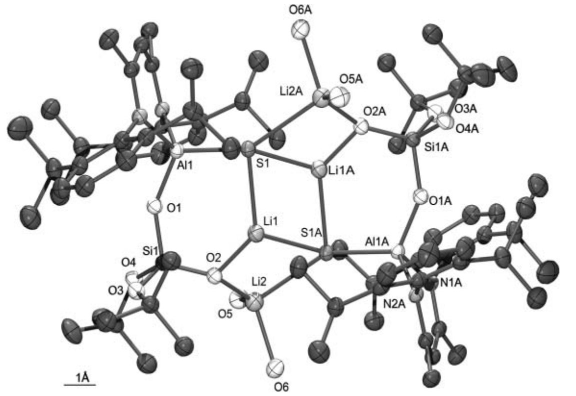

Fig. 3 Thermal ellipsoid plot of **3** at 40% level. Carbon-bound hydrogen atoms, carbon atoms of the coordinated THF and solvating THF are omitted for clarity. The atoms labeled with an additional "A" letter are at equivalent position $2 - x, -y, 1 - z$. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.949(2), Al(1)–N(2) 1.936(2), Al(1)–S(1) 2.189(1), Li(1)–S(1) 2.404(4), Li(1A)–S(1) 2.452(5), Li(2A)–S(1) 2.689(5), Li(1)–O(2) 1.832(5), Li(2)–O(2) 1.870(5), Al(1)–O(1) 1.719(2), Si(1)–O(1) 1.623(2), Si(1)–O(2) 1.593(2), Si(1)–O(3) 1.657(2), Si(1)–O(4) 1.651(2); S(1)–Al(1)–O(1) 116.1(1), Al(1)–O(1)–Si(1) 147.4(1), O(1)–Si(1)–O(2) 112.1(1), O(1)–Si(1)–O(3) 109.4(1), O(1)–Si(1)–O(4) 104.9(1), O(2)–Si(1)–O(3) 113.2(1), O(2)–Si(1)–O(4) 114.0(1), O(3)–Si(1)–O(4) 102.5(1), S(1)–Li(1)–O(2) 129.5(2), Al(1)–S(1)–Li(1) 92.0(1), Si(1)–O(2)–Li(1) 119.0(2).

but are significantly shorter than in **3** (1.623 Å) and the Si–O(H) bond lengths in **1** (1.624 Å) and **2** (1.627 Å). The substitution of the Si–O(H) and Al–S(H) protons in **1** by the lithium cations results in a short Si–O(Li) (1.593 Å) and Al–S(Li) (2.189 Å) bond lengths in **3** (compare to the Al–S bond length 2.222 Å in **1**). However, the Al–S bond length in **3** is comparable to those in $[LAl(SLi)_2(thf)_2]_2\cdot 2THF$ (2.173–2.186 Å).[7] Other effects of the substitution is the greater distortion of the O–Si–O angles in the SiO_4 tetrahedron in **3** (102.5–114.0°) compared to **1** (105.2–112.9°) and **2** (105.2–112.5°). The two lithium atoms in **3** have different coordination environments due to the steric bulk of the ligand **1**. The Li(1) is coordinated only to two sulfur atoms and one oxygen atom arranged in a nearly planar environment (sum of the angles is 349°), whereas Li(2) is coordinated to one oxygen atom, one sulfur atom and two THF molecules and has a distorted tetrahedral geometry. The inorganic core in **3** is best described as a centrosymmetric 12-membered ring $(Si–O–Al–S–Li–O–)_2$ capped by the two remaining Li atoms (Li(1) and Li(1A)) to form two nearly planar six-membered rings (Si–O–Al–S–Li–O) (sum of the angles is 716°, the theoretical value for a six-membered ring is 720°) separated from each other by three four-membered rings (two Li–O–Li–S and one S_2Li_2). The S–Li bond lengths in **3** (2.689, 2.453 and 2.404 Å) are in the range observed for similar species (2.327–2.964 Å). The Al–O–Si angles in **1** (146.5°) and **3** (147.4°) are similar to those in $[NMe_4]_4[H_8Al_4Si_4O_{20}]\cdot 24H_2O$ (av. 143.0°)[3] and $[\{(^tBuO)_3SiO\}(^iPrO)(\mu\text{-}O^iPr)Al]_2$ (147.2 and 149.8°),[13] but more obtuse than that in **2** (132.8°) and more acute than the corresponding Al–O–Si angle in $Al[OSi(O^tBu)_3]_3(HO^iPr)\cdot \tfrac{1}{2}[Al(O^iPr)_3]_4$ (158.8°).[13]

In summary, we have isolated and characterized unique molecular aluminosilicates $LAl(EH)(\mu\text{-}O)Si(OH)(O^tBu)_2$ (E = S, O), containing functional groups on both the aluminum as well as the silicon center. These compounds show great potential for the preparation of heterometallic aluminosilicates as was demonstrated by the synthesis of the dilithium salt $[LAl(SLi)(\mu\text{-}O)Si(OLi\cdot 2thf)(O^tBu)_2]_2$. Currently, the studies on the reactivity of **1–3** are subject of the ongoing research.

Notes and references

§ *Crystal data*: $\mathbf{1}\cdot\tfrac{1}{3}$hexane: $C_{39}H_{65.66}AlN_2O_4SSi$, M = 713.73, colorless prism, 0.27 × 0.23 × 0.21 mm^3, rhombohedral–hexagonal setting, $R\bar{3}$, Z = 18, $a = b$ = 31.536(5), c = 22.246(4) Å, V = 19160(6) Å^3, D_c = 1.113 Mg m^{-3}, μ(Mo-Kα) = 0.162 mm^{-1}, 34889 measured reflections, 7499 independent (R_{int} = 0.0859), 636 parameters, R_1 = 0.0575 for 5435 reflections with $I > 2\sigma(I)$ and wR_2 = 0.1388 for all data. CCDC 628448. **2**: $C_{41}H_{69}AlN_2O_6Si$, M = 741.05, colorless block, 0.29 × 0.28 × 0.13 mm^3, monoclinic, $P2_1/n$, Z = 4, a = 9.504(1), b = 22.740(2), c = 20.130(2) Å, β = 90.87(2)°, V = 4350(1) Å^3, D_c = 1.132 Mg m^{-3}, μ(Mo-Kα) = 0.118 mm^{-1}, 55277 measured reflections, 7629 independent (R_{int} = 0.0945), 529 parameters, R_1 = 0.0651 for 5747 reflections with $I > 2\sigma(I)$, wR_2 = 0.1846 for all data. CCDC 628449. **3**: $C_{94}H_{158}Al_2Li_4N_4O_{13}S_2Si_2$, M = 1754.26, monoclinic, space group $P2_1/n$, Z = 2, a = 13.248(2), b = 23.568(4), c = 16.509(2) Å, β = 100.91(3)°, V = 5061(1) Å^3, D_c = 1.151 Mg m^{-3}, μ(Mo-Kα) = 0.151 mm^{-1}, 39473 measured reflections, 9260 independent (R_{int} = 0.0852), 679 parameters, R_1 = 0.0539 for 6312 reflections with $I > 2\sigma(I)$, wR_2 = 0.1304 for all data. CCDC 628450. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707895a

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