Metal Polysulfides

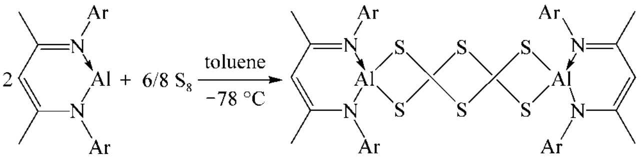
$[LAl(\mu\text{-}S_3)_2AlL]$: A Homobimetallic Derivative of the Sulfur Crown S_8[**]

Ying Peng, Hongjun Fan, Vojtech Jancik, Herbert W. Roesky, and Regine Herbst-Irmer*

Dedicated to Professor Tobin J. Marks on the occasion of his 60th birthday

Metal polysulfides, synthesized by a variety of methods using various reagents as sulfur source, such as S_8, M_2S_n (M = alkali metal), P_4S_{10}, H_2S, and organic polysulfanes, have attracted much attention not only regarding their structure and reactivity but also owing to their potential uses.[1] Metal polysulfide complexes[1b] may be viewed as derivatives of the S_x^{2-} ($x \geq 2$) ion. Transition-metal polysulfides have attracted interest as catalysts and intermediates in enzymatic processes and in catalytic reactions of industrial importance, such as the hydrodesulfurization (HDS) of fossil fuels.[2] Furthermore, the metal polysulfides can be used as precursor for metal–sulfur clusters. In contrast, such complexes containing heavier main-group elements, such as the Group 13, 14, and 15 metals have been much less explored.[1a,d] Among the numerous investigations of the metal polysulfides, complexes with the (μ-S_3) chain are rarely reported. The most common examples are those of transition-metal complexes $[\{(\eta^5\text{-}RC_5H_4)_2Ti(\mu\text{-}S_3)\}_2]$ (R = H, Me)[3] and $[\{(\eta^5\text{-}MeC_5H_4)Ru(PPh_3)(\mu\text{-}S_3)\}_2]$[4] which were obtained by treatment of $[(\eta^5\text{-}RC_5H_4)_2TiS_5]$ (R = H, Me) with PPh_3, and $[\{(\eta^5\text{-}MeC_5H_4)Ru(PPh_3)_2S\}_2][SbF_6]_2$ with $(NBu_4)_2S_6$, respectively. $[LAl^I]$ (**1**) (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$)[5] with its nonbonding lone pair of electrons at aluminum has a singlet carbene-like character and may show unprecedented chemical reaction behavior.[6] Herein, we describe the synthesis and structural characterization of $[LAl(\mu\text{-}S_3)_2AlL]$ (**2**) containing two (μ-S_3) chains.

Compound **2** was synthesized by the reaction of **1** with sulfur in a molar ratio of 2:6[7] (Scheme 1). Cold toluene was added to the mixture of **1** and sulfur at −78 °C. After several minutes a suspension was obtained which was kept at −78 °C for 2 h. Subsequently the suspension was slowly warmed to room temperature under formation of more precipitate. The compound $[LAl(\mu\text{-}S)_2AlL]$[8] was isolated from the precipitate and characterized by its characteristic melting point and EI mass spectrum. Pale yellow crystals of **2** were obtained from the concentrated filtrate at 4 °C, as well as at room temperature. It is noted that even when the above reaction was employed in a molar ratio of 2:3,[7] the isolated product is also **2** however in lower yield (about 10%). Compound **2** was characterized by ^1H and ^{13}C NMR spectroscopy, EI mass spectrometry, and elemental analysis. The most intense peak in the EI mass spectrum of **2** appears at m/z 508 $[M^+-LAlS_4]$. The signals at 540 (38%) and 572 (15%) are assigned to the $[M^+-LAlS_3]$ and $[M^+-LAlS_2]$ fragments, respectively. Compound **2** is sparingly soluble in $[D_6]$benzene, and the solubility does not improve even when heated. **2** does not dissolve in hexane and pentane. When the reaction mixture or the isolated compound is exposed to traces of moisture, the free ligand LH can be detected by ^1H NMR spectroscopy.



1 **2**

Scheme 1. Synthesis of **2**.

Single crystals of **2**[9] suitable for X-ray structural analysis were obtained in toluene at 4 °C. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with two co-crystallized molecules of toluene per molecule of **2** (Figure 1). Two (μ-S_3) chains connect two aluminum atoms to form an aluminum polysulfide with an Al_2S_6 eight-membered ring. The two L ligands are almost coplanar. The symmetry of the structure is C_i. In the S_8 structure,[10] the two S_3 units are eclipsed, whereas in **2** they are staggered, thus we cannot simply argue that the two aluminum atoms are replacing the corresponding sulfur atoms in S_8. The S–S bond length (av 2.08 Å) in **2** is

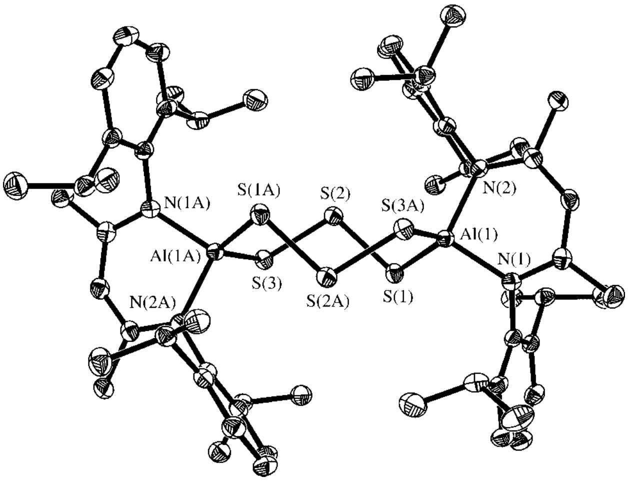


Figure 1. Thermal ellipsoids plot of **2** (thermal ellipsoids set at 50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.882(2), Al(1)-N(2) 1.904(2), Al(1)-S(1) 2.223(1), Al(1)-S(3A) 2.248(1), S(1)-S(2) 2.095(1), S(2)-S(3) 2.073(1); N(1)-Al(1)-N(2) 97.7(1), S(2)-S(1)-Al(1) 98.0(1), S(1)-Al(1)-S(3A) 116.9(1), S(3)-S(2)-S(1) 104.7(1).

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[*] Dipl.-Chem. Y. Peng, V. Jancik, Prof. Dr. H. W. Roesky,
Dr. R. Herbst-Irmer
Institut für Anorganische Chemie der Universität Göttingen
Tammannstrasse 4
37077 Göttingen (Germany)
Fax: (+49) 551-39-3373
E-mail: hroesky@gwdg.de

Dr. H. Fan
Labor für Physikalische und Theoretische Chemie
Universität Siegen, 57068 Siegen (Germany)

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Table 1: The reaction energy of [$L_2Al_2S_n$] ($n=2$–8).[a]

	n						
	2	3	4	5	6	7	8
reaction energy [kJ mol^{-1}]	−648 (S1 S1)	−641 (S1 S2)	−644 (S1 S3)	−602 (S1 S4)	−621 (S1 S5)	−594 (S1 S6)	−609 (S1 S7)
			−571 (S2 S2)	−581 (S2 S3)	−608 (S3 S3)	−570 (S3 S4)	−524 (S4 S4)

[a] The reaction energy is obtained from $E([L_2Al_2S_n])-2E([LAl])-n/8\,E(S_8)$. The notes next to the energies show the conformations. For example, S3 S4 means one bridge has three S atoms, while the other one has four S atoms

slightly longer than that in S_8[10] (av 2.05 Å), [{(η^5-MeC_5H_4)$_2$-Ti(μ-S_3)}$_2$][3] (av 2.06 Å), and [{(η^5-MeC_5H_4)Ru(PPh_3)(μ-S_3)}$_2$][4] (av 2.05 Å). The Al–S bond lengths (av 2.24 Å) are comparable with those in the dimer [LAl(μ-S)$_2$AlL] (av 2.24 Å)[8] and in [LAl(SH)$_2$] (av 2.22 Å).[11] The Al–N bond length (av 1.89 Å) falls within the range of those in aluminum derivatives bearing the L ligand.[12] The S-S-S angle (104.7°) is close to those found in [{(η^5-MeC_5H_4)$_2$Ti(μ-S_3)}$_2$][3] (109.1°) and [{(η^5-MeC_5H_4)Ru(PPh_3)(μ-S_3)}$_2$][4] (105.2°).

The S_8 ring can have different cleavage patterns and thus forms various types of structures.[1a] For [$L_2Al_2S_n$] species the product with $n=2$ is known,[8] and herein compound **2** has $n=6$. Theoretical calculations were carried out to estimate the relative stability of the compounds with $n=2$–8. The method used is RI-BP86/TZVP within the TURBOMOLE[13] program. The optimized structure of [$L_2Al_2S_6$] is in good agreement with the X-ray values for **2** (mean deviation <0.04 Å), which shows the reliability of the selected theoretical method. In the calculation the $CHMe_2$ groups in the ligand L were replaced by H atoms. The relative stability of [$L_2Al_2S_n$] was estimated by the reaction energy of $2[LAl]+n/8\,S_8\rightarrow[L_2Al_2S_n]$. The calculated reaction energies are listed in Table 1. All the reactions are exothermic. Compound [$L_2Al_2S_2$][8] is the most stable. However, there are quite a few conformations with only a slightly smaller reaction energy, and thus thermodynamically they are all possible. Most [$L_2Al_2S_n$] species prefer only one bridging S atom, while all the other S atoms are arranged in the second bridge (Table 1). We could isolate **2** but not the (theoretically favored) S1 S5 isomer, this might be due to the very low solubility of the latter species.

Therefore, the theoretical work shows that all [$L_2Al_2S_n$] ($n=2$–8) species have rather stable conformations (and that there can be more than one).[14] These compounds may coexist in the product, and under different reaction conditions another species may be preferentially formed. To obtain a single crystal out of such a mixture is difficult except for $n=2$ where one can use excess of **1** to react with sulfur.

In summary, we report herein the first compound of Group 13 with two (μ-S_3) chains connecting two aluminum atoms under formation of an eight-membered Al_2S_6 ring. Studies of the other possible conformations of [$L_2Al_2S_n$] estimated by calculation are underway.

Experimental Section

All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using Schlenk-line and glovebox techniques.

2: Toluene (30 mL) was added to a mixture of **1** (0.580 g, 1.3 mmol) and S_8 (0.125 g, 3.9 mmol) at −78 °C. The resulting suspension was stirred at this temperature for 2 h and slowly warmed to room temperature. The mixture was stirred for additional 15 h. After removal of the precipitate by filtration, the concentrated solution was kept at room temperature for 3 days to afford pale yellow crystals of **2**. (0.150 g, 22 %). M.p. 185 °C (decomp); EI-MS: *m*/*z* (%) 508 (100) [M^+−$LAlS_4$], 540 (38) [M^+−$LAlS_3$], 572 (15) [M^+−$LAlS_2$]. ^{1}H NMR (500.13 MHz, C_6D_6): $\delta=7.20$–6.90 (m, 12 H, Ar-H), 4.72 (s, 2 H, γ-H), 3.30 (sept, 8 H, $J=6.8$ Hz, C*H*Me_2), 1.50 (s, 12 H, *Me*), 1.37 (d, 24 H, $J=6.8$ Hz, CH*Me*$_2$), 1.00 ppm (d, 24 H, $J=6.8$ Hz, CH*Me*$_2$); ^{13}C NMR (125.77 MHz, C_6D_6): $\delta=171.78$ (CN), 145.74, 143.69, 128.20, 123.83 (Ar), 97.74 (γ-C), 28.92 (*C*HMe_2), 25.45(CH*Me*$_2$), 23.93 (CH*Me*$_2$), 23.55 ppm (*Me*); ^{27}Al NMR: resonance is silent. Elemental analysis (%) calcd for $C_{58}H_{82}Al_2N_4S_6$ (1081.66): C 64.40, H 7.64, N 5.18; found C 64.65, H 7.88, N 4.76 %.

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