Communications

Metal Polysulfides

[LA1(µ-S₃)₂AlL]: A Homobimetallic Derivative of the Sulfur Crown S₈**

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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), P₄S₁₀, H₂S, 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-} ($x \ge 2$) 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 metalsulfur 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 $(\mu$ -S₃) chain are rarely reported. The most common examples are those of transition-metal complexes $[{(\eta^5-RC_5H_4)_2Ti(\mu S_3$]₂] (R = H, Me)^[3] and [{(η^5 -MeC₅H₄)Ru(PPh₃)(μ -S₃)}₂]^[4] which were obtained by treatment of $[(\eta^5-RC_5H_4)_2TiS_5]$ (R = H, Me) with PPh₃, and $[\{(\eta^5 - MeC_5H_4)Ru(PPh_3)_2S\}_2]$ $[SbF_6]_2$ with $(NBu_4)_2S_6$, respectively. $[LAl^I]$ (1) (L = HC(CMeNAr)₂, Ar = $2,6-iPr_2C_6H_3$)^[5] with its nonbonding lone pair of electrons at aluminum has a singlet carbenelike character and may show unprecedented chemical reaction behavior.^[6] Herein, we describe the synthesis and structural characterization of $[LAl(\mu-S_3)_2AlL]$ (2) containing two $(\mu$ -S₃) 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(μ -S)₂AlL]^[8] was isolated from the precipitate

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Scheme 1. Synthesis of 2.

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 ¹³C 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^+ -LAlS₄]. The signals at 540 (38%) and 572 (15%) are assigned to the $[M^+-LAIS_3]$ and $[M^+-LAIS_2]$ 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.

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 -S₃) chains connect two aluminum atoms to form an aluminum polysulfide with an Al₂S₆ eight-membered ring. The two L ligands are almost coplanar. The symmetry of the structure is C_i . In the S₈ structure,^[10] the two S₃ 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 S₈. 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).

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) —571 (S2 S2)	—602 (S1 S4) —581 (S2 S3)	—621 (S1S5) —608 (S3S3)	—594 (S1 S6) —570 (S3 S4)	—609 (S1 S7) —524 (S4 S4)	

[a] The reaction energy is obtained from $E([L_2Al_2S_n]) - 2 E([LAI]) - n/8 E(S_8)$. 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), $[[(\eta^5-MeC_5H_4)_2-Ti(\mu-S_3)]_2]^{[3]}$ (av 2.06 Å), and $[\{(\eta^5-MeC_5H_4)Ru(PPh_3)(\mu-S_3)\}_2]^{[4]}$ (av 2.05 Å). The Al–S bond lengths (av 2.24 Å) are comparable with those in the dimer [LAl(μ -S)₂AlL] (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 [{($\eta^5-MeC_5H_4$)_2Ti(μ -S_3)}_2]^[3] (109.1°) and [{($\eta^5-MeC_5H_4$)Ru(PPh_3)(μ -S_3)}_2]^[4] (105.2°).

The S₈ 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 [L₂Al₂S₆] 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 CHMe₂ 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 $2[LAI] + n/8S_8 \rightarrow$ $[L_2Al_2S_n]$. 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=2where one can use excess of **1** to react with sulfur.

In summary, we report herein the first compound of Group 13 with two (μ -S₃) chains connecting two aluminum atoms under formation of an eight-membered Al₂S₆ ring. Studies of the other possible conformations of [L₂Al₂S_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*⁺-LAIS₄], 540 (38) [*M*⁺-LAIS₃], 572 (15) [*M*⁺-LAIS₂]. ¹H NMR (500.13 MHz, C₆D₆): δ = 7.20–6.90 (m, 12 H, Ar-H), 4.72 (s, 2H, γ-H), 3.30 (sept, 8H, *J* = 6.8 Hz, CHMe₂), 1.50 (s, 12 H, *Me*), 1.37 (d, 24 H, *J* = 6.8 Hz, CHMe₂), 1.00 ppm (d, 24 H, *J* = 6.8 Hz, CHMe₂); ¹³C NMR (125.77 MHz, C₆D₆): δ = 171.78 (CN), 145.74, 143.69, 128.20, 123.83 (Ar), 97.74 (γ-C), 28.92 (CHMe₂), 25.45(CHMe₂), 23.93 (CHMe₂), 23.55 ppm (*Me*); ²⁷Al NMR: resonance is silent. Elemental analysis (%) calcd for C₅₈H₈₂Al₂N₄S₆ (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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Communications

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