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A Supramolecular Hexameric Ring from Alumazene and Methylsulfonate[†]

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A dealkylsilylation reaction of alumazene $[2,6\text{-}(i\text{-Pr})_2C_6H_3NAlMe]_3$ (**1**) with trimethylsilyl methylsulfonate in a 1:2 molar ratio in toluene afforded a supramolecular cyclic hexamer $\{Me[2,6\text{-}(i\text{-Pr})_2C_6H_3NAl]_3(O_3SMe)_2\}_6$ (**2**) composed of six intact alumazene rings and possessing two types of bridging sulfonate groups. Changing the reagent molar ratio to 1:3 caused the third sulfonate to partially substitute the last alumazene methyl group in an η^2 fashion and introduced a disorder in the crystal lattice.

Alumazene $[2,6\text{-}(i\text{-Pr})_2C_6H_3NAlMe]_3$ (**1**)[1] is a trimeric iminoalane possessing a remarkable reactivity that is only now starting to be explored. Reactions with transition-metal[2] and main-group-metal[3] fluorides, silanetriols, and triaminosilanes[4] were reported by Roesky et al. Recently, we discovered a novel dealkylsilylation reaction mode in the metatheses of alkylalanes with trimethylsilyl phosphate.[5] The enthalpic driving force in these reactions stems from the oxophilic nature of Al and leads to a remarkable conversion of the Al–C and Si–O bonds to Al–O and Si–C ones. The entropic advantage is gained by the release of a volatile alkyltrimethylsilane. Subsequently, we studied this reaction route in the alumazene and trimethylsilyl phosphate systems and obtained aluminum amide–phosphate with an adamantane-like core.[6] We also observed dealkylsilylation reactivity between alumazene and trimethylsilyl esters of alkyl- and arylphosphonic acids.[7] To extend further the scope of dealkylsilylation, we explored the reactivity of trimethylsilylsulfonates. There is a clear structural analogy between the sulfonate RSO_3^- group and the phosphonate RPO_3^{2-} group in their 3-fold symmetry, in the presence of one pendant organic group, and in their trioxo donor potential. The difference between the two moieties lies in the fact that individual metal–O interactions with the sulfonate group are weaker because of the greater dianionic charge on the phosphonate. On the one hand, various phosphonates have been employed with great success in the generation of a multitude of molecular cages[8] and one-, two-, and three-dimensional extended frameworks.[9] On the other hand, sulfonates were studied along these lines to a much lesser extent, with one reason being that they are considered to be noncoordinating ligands. Examples of successful sulfonate applications in building extended structures include H-

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[†] Dedicated to Professor John G. Verkade on the occasion of his 71st birthday.

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bonded, two-dimensional guanidinium sulfonate networks,[10] the extensive chemistry of sulfonated calixarenes, where the polyanionic sulfonate is assembled with the Keggin cation, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$,[11] and coordination polymers of sulfonates with soft Ag^+ and Ba^{2+} ions.[12]

The bonding ability of sulfonates observed in main-group- and transition-metal coordination compounds[13] is also demonstrated in the present case because Al centers are highly unsaturated and oxophilic. The introduction of a sulfonate group could be carried out by the reaction of metal halides with a Ag salt or metal alkyls or halides with a RSO_2OH acid. Our experience showed that **1** provides in reactions with protic reagents only intractable mixtures of products. Therefore, we used a mild dealkylsilylation reaction of $MeSO_2OSiMe_3$ with alumazene in toluene[14] initially in a 1:3 molar ratio. We expected the substitution of the three methyl groups at Al with the retention of the alumazene ring. The sulfonate ester reacted with the Al−Me moieties and produced $SiMe_4$; this byproduct was identified in the reaction solution by ^1H and ^{13}C NMR spectroscopy. The replacement of the methylsulfonate ester by the triflate as a starting reagent leads to a green reaction solution containing a mixture of products that we were not able to separate.

Compound **2** was obtained as single crystals suitable for X-ray diffraction analysis.[15,16] The molecular structure of **2** is shown in Figure 1. The alumazene Al_3N_3 rings were retained intact in the product. Six aluminum amide−sulfonate monomeric units are arranged (Figure 2) as a supramolecular hexagon by intermolecular coordination of the sulfonate O atoms to the Al centers of adjacent alumazene. There are two types of bridging sulfonate groups (Chart 1): one of them spans the alumazene ring, and the second one interconnects the adjacent monomeric molecules. The ideal symmetry point group of **2** is S_6. Of the two possible orientations of O═S−Me moieties of the spanning sulfonate, only the one with the methyl group pointing away from the alumazene ring is present in all units (Figure 2). This arrangement should allow the coordination of the third O atom to the last remaining three-coordinate Al center and the formation of an adamantane cage with η^3 sulfonate (Chart 1) analogous to the phosphate case.[6] However, the last coordination bond is not formed probably because of the decreased Lewis acidity of the Al or a low basicity of O in the bidentate sulfonate group. Both the spanning sulfonate moieties and the terminal O atoms of the interconnecting sulfonates point alternately above and below the plane of the hexagon. The six slightly different Al−N bond distances [1.793−1.810(2) Å] within the alumazene ring are relatively little elongated in comparison to the parent molecule **1** (1.782 Å).[1] Interestingly, the Al−N bond lengths at the three-coordinate $AlCN_2$ and four-coordinate AlN_2O_2 centers are not distinct. We made a similar observation in other alumazene derivatives containing corresponding Al moieties.[6,7]

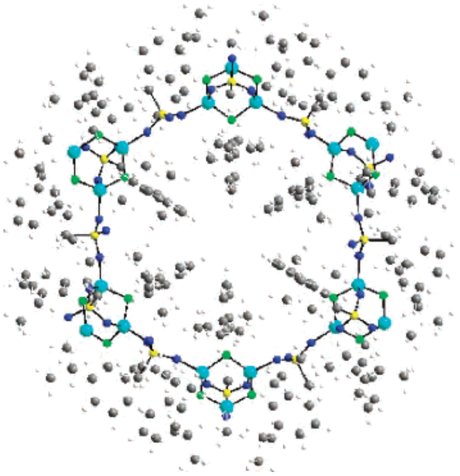


Figure 1. Molecular structure[20] of hexameric **2**. Color code: Al, cyan; N, green; O, blue; S, yellow; C, gray.

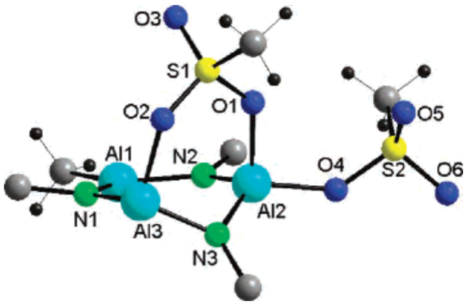
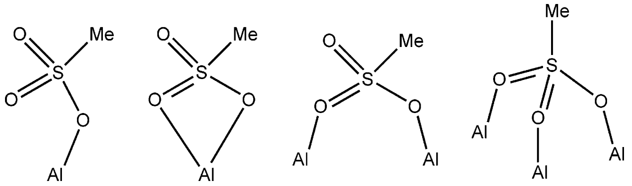


Figure 2. One monomeric unit of **2**. All 2,6-$(i\text{-}Pr)_2C_6H_3$ moieties, except their *ipso*-C, were omitted for the sake of clarity.[20] Selected average distances (Å): Al−N 1.80, Al−O_s 1.87, S1−O_s 1.49, S═O_t 1.41, Al−O_i 1.81, 1.78, S−O_i 1.475, 1.495. Selected average bond angles (deg): N−Al-(C)−N 115.6, N−Al(O)−N 114.0, Al−N−Al 106.8, 2×Al−N−Al 119.6. The labels O_s, O_i, and O_t mean spanning, interconnecting, and terminal O atoms, respectively.

Chart 1. Coordination Modes of Sulfonates



The Al−O (1.87 Å) and S−O (1.49 Å) bond lengths in the spanning sulfonate are equalized while the individual distances in the interconnecting moieties are slightly more disparate and differ by 0.02 Å. Moreover, the interconnecting Al−O distances are shorter (1.807 and 1.780 Å) than the spanning ones, possibly as a result of a less strained geometry. A comparison can be made with the Al−O (1.841

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(14) All manipulations were carried out in a M. Braun Unilab glovebox under dry deoxygenated N_2. To a solution of alumazene **1** (0.500 g, 0.768 mmol) in toluene (10 mL) was slowly added with a syringe neat trimethylsilyl methylsulfonate (0.259 g, 1.54 mmol, 1:2.01). The solution turned yellow and was left at room temperature. A crop of crystals appeared after 2 days. Washing with hexane provided **2** (0.385 g, 0.474 mmol, 62% yield). Mp: 263 °C (dec). Compound **2** is well-soluble in THF, CH_2Cl_2, and $CHCl_3$ and poorly soluble in hexane.

(15) Crystal data: **2**·$13C_7H_8$: $C_{325}H_{464}Al_{18}N_{18}O_{36}S_{12}$, fw = 6069.50, rhombohedral, $R\bar{3}$, $a = 44.3710(8)$ Å, $c = 15.5892(4)$ Å, $V = 26579.9(10)$ Å^3, $Z = 3$, $d_{calcd} = 1.138$ Mg/m^3, R1 $[I > 2\sigma(F)] = 0.0744$, wR2 $[I > 2\sigma(F)] = 0.1621$. $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 95.0P]$ where $P = (F_o^2 + 2F_c^2)/3$.

(16) *SHELXTL*, version 5.10; Bruker AXS Inc.: Madison, WI, 1997.

Å) and S−O (1.504 Å) bond lengths in the monodentate triflate group bound to Al in a *β*-diketiminate complex.[17] The Al−O bond distances in $AlMe_3$ complexes of SO_4^{2-} are slightly longer and range from 1.85 to 1.98 Å.[18] The bond angles in an N−Al(Me)−N moiety (N−Al−N 115.6°) resemble closely the parent alumazene.[1] In the crystalline product obtained from the 1:3 reaction, some of the methyl groups in the Me−Al(1) moiety (Figure 2) were partially substituted by sulfonate bound to Al in an η^2 fashion (Chart 1), and this fact contributed to disorder in the crystal structure and problems in refinement. We took the hint from structural analysis results, and by changing the molar ratio of reagents to 1:2, we were able to direct the reaction to the clean formation of the disubstituted alumazene derivative **2**. Elimination of the disorder led to improved quality of the data.

The structural analysis revealed also a large number of toluene molecules of crystallization within and around the hexameric units. In the solid state, the rings form a molecular array with channels running along the *c* axis. The channel-like structure of **2** facilitates an easy escape of the solvent from the crystal. This made our attempts of elemental analysis fruitless.[19] Mass spectrometric analysis revealed only low molecular weight signals. NMR investigation of the isolated crystals of **2** in C_6D_6, $CDCl_3$, THF-d_8, and toluene-d_8 both at room temperature and at −80 °C revealed several Al−Me (−0.5 to −1.0 ppm), S−Me (2.1−2.5 ppm), *i*-Pr, and aromatic signals that are not consistent with the highly symmetric molecular structure of **2**. This must be a result of the presence of several oligomeric species in solution and their interconversion. Moreover, increasing the ratio to 1:4 leads to a gel, which arises probably from cross-linking of the alumazene units through all three Al centers.

The cyclic hexamer **2** represents a novel type of supramolecular structure in alumazene chemistry, and in its synthesis, the scope of dealkylsilylation was extended to sulfonates. Compound **2** will be used as a building block in following explorations of coordination polymer synthesis.

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Supporting Information Available: Crystallographic data of **2** and ^{1}H NMR spectra of **2** in THF-d_8 and toluene-d_8 at −80 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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