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Tetraaza Analogues of Lithium and Sodium Alums: Synthesis and X-ray Structures of the Single Strand Polymer $[Li(THF)_2\{Al[SO_2(N^tBu)_2]_2\}]_\infty$ and the Contact Ion Pairs $[Na(15\text{-crown-5})][Al\{SO_2(N^tBu)_2\}_2]$ and $\{[Na(15\text{-crown-5})][O_2S(\mu\text{-}NBn)_2Al(\mu\text{-}NBnSO_2NBn)]\}_2$

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The reaction of an alkali metal aluminohydride $MAlH_4$ (M = Li, Na) with *N,N′*-bis-(*tert*-butyl)sulfamide or *N,N′*-bis-(benzyl)sulfamide in THF produces the complex ions $\{Al[SO_2(NR)_2]_2\}^-$ (R = ^{t}Bu, Bn). The X-ray structures of $[Li(THF)_2\{Al[SO_2(N^tBu)_2]_2\}]_\infty$ (**1**), $[Na(15\text{-crown-5})][Al\{SO_2(N^tBu)_2\}_2]$, (**2**) and $\{[Na(15\text{-crown-5})][O_2S(\mu\text{-}NBn)_2Al(\mu\text{-}NBnSO_2NBn)]\}_2$ (**3•**3THF) are reported. The two diazasulfate ligands $[SO_2(N^tBu)_2]^{2-}$ are *N,N′* chelated to Al^{3+} in both **1** and **2**. In the lithium derivative **1** the spirocyclic $\{Al[SO_2(N^tBu)_2]_2\}^-$ anions are bridged by the bis-solvated cations $Li(THF)_2+$ to give a polymeric strand. In the sodium salt **2** the complex anion is *O,O′* chelated to Na^+, which is further encapsulated by a 15-crown-5 ligand to give a monomeric ion-pair complex. By contrast, the benzyl derivative **3** forms a dimer in which the terminal $[SO_2(NBn)_2]^{2-}$ ligands are (*N,N′*),(*O,O′*) bis-chelated to Al^{3+} and Na^+, respectively, and the bridging ligands adopt a novel *N,O*-chelate, *N′*-monodentate bonding mode. The central core of **3** consists of two four-membered AlOSN rings bridged by two N^tBu groups. Crystal data: **1**, orthorhombic, $Pna2_1$, $a = 20.159(5)^\circ$, $b = 10.354(3)^\circ$, $c = 15.833(4)^\circ$, $\alpha = \beta = \gamma = 90^\circ$, $V = 3304.7(15)$ Å^3, $Z = 4$; **2**, monoclinic, $P2_1/n$, $a = 16.031(2)$ Å, $b = 9.907(2)$ Å, $c = 23.963(4)$ Å, $\beta = 103.326(2)^\circ$, $Z = 4$; **3**, triclinic, $P\bar{1}$, $a = 12.7237(11)$ Å, $b = 14.0108(13)$ Å, $c = 16.2050(14)$ Å, $\alpha = 110.351(2)^\circ$, $\beta = 111.538(2)^\circ$, $\gamma = 97.350(2)^\circ$, $Z = 1$.

Introduction

Recently we initiated investigations of the consequences of the partial replacement of oxo ligands in the common oxo-anions SO_3^{2-} and SO_4^{2-} by isoelectronic imido (NR) groups.[1−3] Formally this substitution generates heteroleptic imido/oxo anions, e.g. $[O_xS(NR)_{3-x}]^{2-}$ ($x = 1, 2$) or $[O_yS(NR)_{4-y}]^{2-}$ ($y = 1, 2, 3$). As their dilithium derivatives these dianions form clusters involving the aggregation of fundamental building blocks via their sterically unencumbered Li_zO_z ($z = 2, 3$) faces or edges ($z = 1$). For example, the hexameric diazasulfite $\{Li_2[OS(N^tBu)_2]_2\}_6$ is a 36-atom ($Li_{12}S_6N_{12}O_6$) cluster comprised of three $Li_4S_2N_4O_2$ hexagonal prisms.[1] By contrast, the heterobimetallic derivative $\{(THF)_4Li_4Mg[O_2S(N^tBu)_2]_3\}_2$, which contains six diazasulfate dianions, involves a central Li_4O_4 ladder in a 36 atom ($Li_6Mg_2S_6N_{12}O_{10}$) cluster.[2] Further aggregation of these clusters via LiO units is obviated by solvation of two Li^+ ions by three THF molecules each to give *exo*-cluster $Li(THF)_3$ groups.[2] The amorphous nature of dilithium diazasulfates, e.g., $\{Li_2[SO_2(N^iPr)_2]\}_n$ and $\{(THF)Li_2[SO_2(N^tBu)_2]\}_n$, and their tendency to form gels in organic solvents, is indicative of extended structures.[3] Crystalline derivatives can be obtained, however, by use of the template effect of added lithium salts, e.g., $\{(THF{\bullet}Li)_2[O_2S(N^tBu)_2]{\bullet}(THF)LiCl\}_2$.[3]

Alums are double salts comprised of M^+ (M = alkali metal) and Al^{3+} cations, which are usually highly hydrated, combined with SO_4^{2-} anions. The structure of the prototypical example $KAl(SO_4)_2{\bullet}12H_2O$ consists of SO_4^{2-} ions sandwiched between alternating layers of hexacoordinate K^+ and Al^{3+} ions.[4,5] Since diazasulfate dianions are able to adopt a variety of bonding modes in alkali or alkaline earth metal salts,[2,3] it was of interest to investigate the coordinating ability of this tetradentate ligand in alum analogues. We report here the synthesis and X-ray structures of the first alums containing diazasulfate dianions, viz. the polymer $[Li(THF)_2\{Al[SO_2(N^tBu)_2]_2\}]_\infty$ (**1**) and the contact ion pairs $[Na(15\text{-crown-5})][Al\{SO_2(N^tBu)_2\}_2]$ (**2**) and $\{[Na(15\text{-crown-5})][O_2S(\mu\text{-}NBn)_2Al(\mu\text{-}NBnSO_2NBn)]\}_2$ (**3•**3THF). All three complexes exhibit novel coordination modes for the diazasulfate dianion.

Experimental Section

Reagents and General Procedures. THF was dried (Na/benzophenone) and distilled onto molecular sieves (3 Å) before use. $LiAlH_4$ (Aldrich) was dissolved in Et_2O, the solution was filtered and the solvent was removed before use. $NaAlH_4$ (1 M solution in THF) and 15-crown-5 were commercial samples (Aldrich) used as received. SO_2Cl_2 (Aldrich) was distilled immediately prior to use. $^tBuNH_2$ (Aldrich) and $BnNH_2$ (Aldrich) were predried over KOH and then distilled from CaH_2 onto molecular sieves (3 Å). The compounds $O_2S(NH^tBu)_2$ and $O_2S(NHBn)_2$ were prepared from SO_2Cl_2 and $^tBuNH_2$ or $BnNH_2$ by literature procedures.[6] The handling of air- and moisture-

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Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
formula	$C_{24}H_{52}AlLiN_4O_6S_2$	$C_{26}H_{56}AlN_4NaO_9S_2$	$C_{88}H_{120}Al_2N_8Na_2O_{21}S_4$
fw	590.74	682.84	1854.10
space group	$Pna2_1$ (No. 33)	$P2_1/n$	$P\bar{1}$ (No. 2)
a, Å	20.159(5)	16.031(2)	12.7237(11)
b, Å	10.354(3)	9.9074(14)	14.0108(13)
c, Å	15.833(4)	23.963(4)	16.2050(14)
α, deg	90	90	110.350(2)
β, deg	90	103.326(2)	111.538(2)
γ, deg	90	90	97.350(2)
V, Å^3	3304.7(15)	3703.4(9)	2408.8(4)
Z	4	4	1
T, °C	−80	−80	−80
λ, Å	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.187	1.225	1.278
μ, cm^{-1}	2.27	2.28	1.97
F(000)	1280	1472	984
R_1	0.0540	0.0571	0.0527
wR$_2$	0.1493	0.1714	0.1482

^{a} $R_1 = [\sum||F_o|-|F_c||]/[\sum|F_o|]$ for $[I > 2\sigma(I)]$. ^{b} $wR_2 = \{[\sum w(F_o2\text{-}F_c2)^2]/[\sum w(F_o2)^2]\}^{1/2}$ (all data).

sensitive products and reagents was performed under an atmosphere of argon gas using Schlenk techniques or a glovebox.

Instrumentation. ^{1}H and ^{13}C NMR spectra were collected on a Bruker AM-200 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{7}Li NMR spectra were recorded on a Varian XL-200 instrument operating at 77.75 MHz; chemical shifts are reported relative to 1 M LiCl in D_2O. Solid-state ^{7}Li NMR studies were performed on a Bruker AMX-300 spectrometer (operating at 116.64 MHz) using a BL4 probe; chemical shifts are reported relative to LiCl. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

Preparation of $\{LiAl[SO_2(N^tBu)_2]_2\bullet 2THF\}_\infty$ (1). A gray slurry of $LiAlH_4$ (50 mg, 1.32 mmol) in THF (15 mL) was added dropwise to a clear, colorless solution of $SO_2(NH^tBu)_2$ (0.500 g, 2.40 mmol) in THF (20 mL) at 23 °C. Vigorous gas evolution was observed and the mixture was stirred for 3 h. Filtration through a PTFE filter disk (0.45 μm) gave a clear, colorless solution. Removal of solvent under vacuum gave a fine white powder, which was recrystallized from THF at −25 °C to give **1** (0.497 g, 0.841 mmol, 70%). Anal. Calcd for $C_{24}H_{52}AlLiN_4O_6S_2$: C, 47.2; H, 8.7; N, 10.1. Found: C, 44.64; H, 8.62; N, 9.46. ^{1}H NMR (D_8-THF, 25 °C): δ 3.61 (m, 8 H, OCH_2CH_2), 1.78 (m, 8 H, OCH_2CH_2), 1.36 [s, 36 H, $C(CH_3)_3$]. ^{13}C NMR (D_8-THF, 25 °C): δ 67.6 (OCH_2), 53.0 [$C(CH_3)_3$], 32.4 [$C(CH_3)_3$], 25.5 (OCH_2CH_2). Solid-state ^{13}C NMR: 67.7 (OCH_2), 52.5 [$C(CH_3)_3$], 31.4 [$C(CH_3)_3$], 24.9 (OCH_2CH_2). ^{7}Li NMR (D_8-THF, 25 °C): δ −1.04. Solid-state ^{7}Li NMR: δ 0.04.

Preparation of [Na(15-crown-5)][Al$\{SO_2(N^tBu)_2\}_2$] (2). A clear 1 M solution of $NaAlH_4$ in THF (1.20 mL, 1.20 mmol) was added to a solution containing $SO_2(NH^tBu)_2$ (0.500 g, 2.40 mmol) and 15-crown-5 (0.264 g, 1.20 mmol) in THF (15 mL) at 23 °C. Gas evolution was observed immediately and the solution was stirred for 3 h. Removal of solvent under vacuum gave **2** (0.578 g, 0.85 mmol, 71%) as a spectroscopically pure white powder. X-ray quality prismatic crystals were obtained by layering *n*-hexane over a saturated THF solution of **2** and were ground into a powder to provide the sample for analysis. Anal. Calcd for $C_{26}H_{56}AlN_4NaO_9S_2$: C, 45.73; H, 8.27; N, 8.20. Found: C, 45.12; H, 9.24; N, 8.06, ^{1}H NMR (D_8-THF, 25 °C): δ 3.75 (m, OCH_2CH_2O in 15-crown-5, 20 H), 1.37 [*s*, $C(CH_3)_3$, 36 H]. ^{13}C NMR (D_8-THF, 25 °C): δ 69.8 (15-crown-5), 52.8 [$C(CH_3)_3$], 32.3 [$C(CH_3)_3$].

Preparation of $\{$[Na(15-crown-5)][$O_2S(\mu$-NBn$)_2$Al(μ-NBnSO$_2$-NBn)]$\}_2$ (3). A clear 1 M solution of $NaAlH_4$ in THF (1.36 mL, 1.36 mmol) was added to a solution of $SO_2(NHBn)_2$ (0.750 g, 2.72 mmol) and 15-crown-5 (0.298 g, 1.36 mmol) in THF (15 mL), at 23 °C. Gas evolution was observed immediately and the solution was stirred for 3h. Removal of solvent under vacuum yielded **3** (1.038 g, 0.634 mmol, 93%) as a white solid. The sample of **3** obtained by this procedure contains no THF. Anal. Calcd for $C_{76}H_{96}Al_2N_8Na_2O_{18}S_4$: C, 55.70; H, 5.91; N, 6.84. Found: C, 54.35; H, 5.97; N, 6.67. ^{1}H NMR (D_8-THF, 25 °C): δ 7.45−6.85 (m, C_6H_5, 20 H), 4.09 (s, CH_2Ph, 8 H), 3.51 (broad s, OCH_2CH_2O in 15-crown-5, 20 H).

X-ray Analyses. All data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer. Crystallographic data are summarized in Table 1.

Compound 1. A colorless crystal of **1** (0.44 × 0.37 × 0.24 mm), obtained from a THF solution at −25 °C,[7] was coated with Paratone oil and mounted on a glass fiber. Data were collected using ϕ and ω scans at 0.5° and 15s exposures per frame. The ranges of indices were $0 \le h \le 23$, $0 \le k \le 12$ and $-14 \le l \le 18$. Of a total of 10,379 reflections collected, 4,791 were independent ($R_{int} = 0.0799$) and were used to refine 385 parameters with 3,641 reflections considered observed $[I > 2\sigma(I)]$. An empirical absorption correction was applied.[8] The structure was solved by direct methods[9] and refined by full-matrix least-squares method on F^2.[10] One of the ^{t}Bu groups exhibited disorder. The occupancy factors of C21, C22, C23, C21′, C22′, and C23′ were allowed to refine and then set to a value of 0.5. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined.

Compound 2. A colorless crystal of **2** (0.44 × 0.30 × 0.30 mm) obtained from a THF solution at 23 °C was coated with Paratone oil and mounted on a glass fiber. Data were collected using ϕ and ω scans at 0.5° and 15 s exposures per frame. The ranges of indices were $-17 \le h \le 17$, $0 \le k \le 26$ and $0 \le l \le 11$. Of a total of 9,429 reflections collected, 5,537 were independent ($R_{int} = 0.0616$) and were used to refine 401 parameters with 3,803 reflections considered observed $[I > 2\sigma(I)]$. Structure solution and refinement procedures were the same as those described for **1**.

Compound 3. A colorless crystal of **3**•3THF (0.46 × 0.25 × 0.23 mm) obtained from a THF/hexane (3:1) solution at 23 °C was coated with Paratone oil and mounted on a glass fiber. Data were collected using ϕ and ω scans at 0.3° and 20 s exposures per frame. The ranges of indices were $-13 \le h \le 12$, $-14 \le k \le 13$ and $0 \le l \le 17$, corresponding to a θ-range of 1.49 to 21.97°. Of a total of 14,593 reflections collected, 5,857 were independent ($R_{int} = 0.0416$) and were

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(7) The original structure solution of **1** was determined on a crystal obtained from the product of the reaction of $LiAlH_4$ and $O_2S(NH^tBu)_2$ in THF (eq 1). The data were collected on a Rigaku AFC6S diffractometer (Dr. M. Parvez, private communication). Subsequently, a more accurate structure, which is described here, was provided by a crystal obtained from recrystallization of the product of the reaction of $LiAlH_4$ with [Mg(TMEDA)][$SO_2(N^tBu)(HN^tBu)$]$_2$ (ref 2) in a 1:2 molar ratio in THF.

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used to refine 696 parameters with 3,949 reflections considered observed [$I > 2\sigma(I)$]. The structure was solved using direct methods[11] and refined by full-matrix least-squares methods on F^2.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The bond distances in the phenyl rings of the benzyl groups were restrained to be the same and, in addition, the atoms of the phenyl rings were restrained to be coplanar. One of the benzyl groups was disordered. Partial occupancy factors were allowed for the involved atoms (C40A−C46A and C40B−C46B). The partial occupancy factors refined to 0.59(2) and 0.41(2), respectively. One of the solvent THF molecules (O11S, C11S, C12S, C13S, C14S) was disordered around the inversion center with a partial occupancy factor of 0.5. The second THF molecule (O1S, C1S, C2S, C3S, C4S) was disordered over two sites with partial occupancy factors of 0.562(15) and 0.438(15), respectively. The third THF molecule is related to the second THF molecule by symmetry.

Results and Discussion

Preparation and Spectroscopic Characterization of [Li(THF)$_2$\{Al[SO$_2$(N^{t}Bu)$_2$]$_2$\}]$_\infty$ (1), [Na(15-crown-5)][Al\{SO$_2$(N^{t}Bu)$_2$\}$_2$] (2) and \{[Na(15-crown-5)][O$_2$S(μ-NBn)$_2$Al(μ-NBnSO$_2$NBn)]\}$_2$ (3). Lithium aluminum hydride $LiAlH_4$ is widely used as a reducing or hydrogenation reagent for both organic and inorganic compounds. For example, $LiAlH_4$ reacts readily with secondary amines to generate tetrakis(dialkylamino)aluminates, e.g., $LiAl(NMe_2)_4$.[12,13] Mono- and disubstituted aluminates $[(R)_2N]_xAlH_{4-x}Li\bullet 2Et_2O$ (R = $SiMe_3$; x = 1, 2) have also been isolated from the reaction of hexamethyldisilylamine with $LiAlH_4$ in diethyl ether and structurally characterized.[14] Recently, the first investigation of the reaction of a primary amine with $LiAlH_4$ was reported.[15]

In this work we have utilized alkali metal aluminum hydrides to deprotonate *N,N′*-bis(alkyl)sulfamides. In THF at 23 °C this reaction readily generates the diazasulfate dianions $[O_2S(NR)_2]^{2-}$ (R = ^{t}Bu, Bn), which form complex ions with aluminum (eq 1).

$$\mathrm{MAlH_4} + 2\mathrm{O_2S(NHR)_2} \xrightarrow{\mathrm{THF}} \mathrm{M\{Al[O_2S(NR)_2]_2\}} + 4\mathrm{H_2} \quad (1)$$

where M = Li, Na and R = ^{t}Bu, Bn.

The ^{1}H NMR spectrum of the lithium derivative [Li(THF)$_2$\{Al[O$_2$S(N^{t}Bu)$_2$]$_2$\}]$_\infty$ (**1**) in D$_8$-THF exhibits a singlet at δ 1.36 (N^{t}Bu) and reveals the presence of ca. two THF molecules for each Li$^+$ cation. The ^{13}C NMR spectrum also indicates a single ^{t}Bu environment. The ^{7}Li NMR spectrum of **1** in D$_8$−THF consists of a singlet at δ −1.04 and a single resonance is also observed in the solid-state ^{7}Li NMR spectrum at δ +0.04.

In the presence of 15-crown-5 the sodium derivative is obtained as the contact ion pair complex [Na(15-crown-5)][Al\{O$_2$S(N^{t}Bu)$_2$\}$_2$] (**2**). The ^{1}H and ^{13}C NMR spectra of **2** in D$_8$−THF show the incorporation of 15-crown-5 in the product and indicate that there are four ^{t}Bu groups for each molecule of the crown ether.

Investigations of phosphorus (III) diazasulfates by Roesky et al. have shown that bulky substituents on nitrogen, e.g., *tert*-butyl groups, favor the formation of four-membered PN_2S rings,[16] whereas the use of less sterically demanding groups, e.g., Me, Et, leads to the formation of eight-membered $P_2N_4S_2$ rings.[17] In a preliminary assessment of the influence of the steric bulk of the NR group on the structure of alumino-diazasulfates the complex \{[Na(15-crown-5)][O$_2$S(μ-NBn)$_2$Al(μ-NBnSO$_2$NBn)]\}$_2$ (**3**), the benzyl analogue of **2**, was prepared according to eq 1. The ^{1}H NMR spectrum for **3** showed the presence of four benzyl groups for each molecule of 15-crown-5.

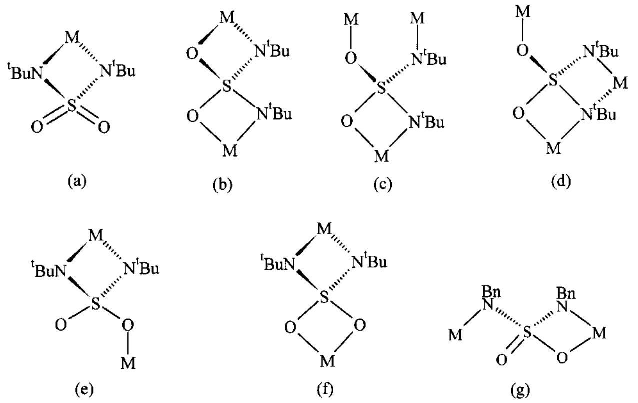

Figure 1. Different coordination modes of $[O_2S(N^tBu)_2]^{2-}$. (a) *N,N′*-chelate; (b) bis-(*N,O*),(*N′,O′*)-chelate; (c) *N,O*-chelate, bis-*N′,O′*-monodentate; (d) bis-(*N,O*),(*N,N′*)-chelate, *O′*-monodentate; (e) *N,N′*-chelate, *O*-monodentate; (f) *N,N′*-chelate, *O,O′*-chelate; (g) *N,O*-chelate, *N′*-monodentate. M may be the same or different metals.

X-ray Structure of [Li(THF)$_2$\{Al[SO$_2$(N^{t}Bu)$_2$]$_2$\}]$_\infty$ (1). By analogy with the multidentate ligand SO_4^{2-},[18] a large variety of bonding modes can be anticipated for the heteroleptic $[O_2S(N^tBu)_2]^{2-}$ dianion. Those that have been established to date are shown in Figure 1 (a-d). The *N,N′* bonding mode (a) is commonly observed for covalent derivatives,[16,19,20] whereas coordination to Li$^+$ or Mg^{2+} involves *N,O* chelation and a variety of tetradentate arrangements (b−d) have been observed in the heterobimetallic system \{Li$_4$(THF)$_4$Mg[O$_2$S(N^{t}Bu)$_2$]$_3$\}$_2$[2] and the 64-atom cluster \{THF•Li$_2$[O$_2$S(N^{t}Bu)$_2$]\}$_8$•2LiOH•2LiCl.[3] An X-ray structure determination showed that **1** consists of the spirocyclic anion \{Al[SO$_2$(N^{t}Bu)$_2$]$_2$\}$^-$ linked through one of the oxygen atoms by the bis-solvated cation Li(thf)$_2^+$ to give a polymeric strand (Figure 2). Selected bond lengths and bond angles are given in Table 2. The $[SO_2(N^tBu)_2]^{2-}$ ligands are chelated to Al^{3+} in an *N,N′* bonding mode. The *N,N′*-chelate, *O*-monodentate architecture [Figure 1e] represents the first tridentate bonding mode for $[O_2S(N^tBu)_2]^{2-}$.

The four-membered AlN_2S rings in **1** are nearly planar with a mean torsion angle of 4.1(2)°. The environment about aluminum is highly distorted from tetrahedral geometry with mean endocyclic and exocyclic ∠ NAlN bond angles of 77.7 and 127.3°, respectively. The mean Al−N distance of 1.838 Å is typical for Al−N bonds involving four-coordinate aluminum.[21] The environment around sulfur is also somewhat distorted with mean ∠ NSN and ∠ OSN bond angles of 91.2 and 113.4°, respectively, and a mean value of 111.1° for ∠ OSO. The mean endocyclic bond angle at nitrogen | ∠ SNAl | = 95.4°.

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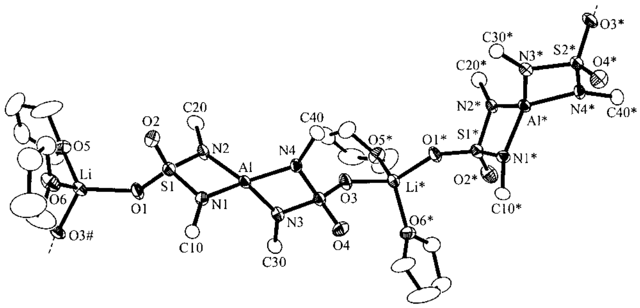

Figure 2. Molecular structure of $[\mathrm{Li(THF)_2\{Al[SO_2(N^tBu)_2]_2\}}]_\infty$ (**1**) showing two of the repeating units in the polymer chain. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown. Displacement ellipsoids are plotted at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[\mathrm{Li(THF)_2\{Al[SO_2(N^tBu)_2]_2\}}]_\infty$ (**1**)

S(1)-O(2)	1.427(4)	Al−N(2)	1.828(4)
S(1)−O(1)	1.463(4)	Al−N(1)	1.839(4)
S(1)−N(1)	1.600(4)	Al−N(3)	1.838(4)
S(1)−N(2)	1.627(4)	Al−N(4)	1.844(4)
S(2)−O(4)	1.451(4)	O(1)−Li	1.914(10)
S(2)−O(3)	1.457(4)	O(3)−Li*[a]	1.889(9)
S(2)−N(4)	1.612(4)	O(5)−Li	1.955(10)
S(2)−N(3)	1.616(5)	O(6)−Li	1.982(8)
O(2)−S(1)-O(1)	111.9(2)	S(1)−O(1)-Li	135.3(3)
O(2)−S(1)-N(1)	114.4(3)	S(2)−O(3)-Li*[a]	149.1(4)
O(1)−S(1)-N(1)	112.2(2)	C(10)−N(1)-S(1)	125.0(3)
O(2)−S(1)-N(2)	113.8(2)	C(10)−N(1)-Al	138.8(3)
O(1)−S(1)-N(2)	112.1(2)	S(1)−N(1)-Al	95.9(2)
N(1)−S(1)-N(2)	91.0(2)	C(20)−N(2)-S(1)	124.7(3)
O(4)−S(2)-O(3)	110.3(2)	C(20)−N(2)-Al	139.9(3)
O(4)−S(2)-N(4)	114.7(2)	S(1)−N(2)-Al	95.4(2)
O(3)−S(2)-N(4)	112.4(2)	C(30)−N(3)-S(2)	124.8(4)
O(4)−S(2)-N(3)	113.9(2)	C(30)−N(3)-Al	139.4(4)
O(3)−S(2)−N(3)	113.2(2)	S(2)−N(3)−Al	95.40(19)
N(4)−S(2)-N(3)	91.3(2)	C(40)−N(4)-S(2)	124.0(3)
N(2)−Al-N(1)	77.77(19)	C(40)−N(4)-Al	140.5(3)
N(2)−Al-N(3)	128.7(2)	S(2)−N(4)-Al	95.3(2)
N(1)−Al-N(3)	125.65(19)	O(1)−Li-O(5)	113.8(4)
N(2)−Al-N(4)	129.14(19)	O(1)−Li-O(6)	112.1(5)
N(1)−Al-N(4)	125.7(2)	O(5)−Li-O(6)	108.2(4)
N(3)−Al-N(4)	77.65(18)	O(3)#-Li−O(5)[a]	98.8(4)
		O(3)#-Li−O(6)[a]	109.6(4)

[a] Symmetry transformations used to generate equivalent atoms: $*-x + 1/2, y + 1/2, z + 1/2$; $\#-x + 1/2, y - 1/2, z - 1/2$.

The mean S−N bond distance of 1.614 Å is indistinguishable from the corresponding value of 1.615 Å reported for the parent sulfamide $\mathrm{O_2S(NH^tBu)_2}$.[22] The mean terminal S=O bond length of 1.439 Å is marginally shorter than the value of 1.460 Å for the S−O distances involving the two-coordinate oxygen atoms in the polymer chain. The mean Li−O distances are 1.901 Å for Li−O(S) and 1.969 Å for Li−O(THF), typical values for four-coordinate $\mathrm{Li^+}$ ions.[23]

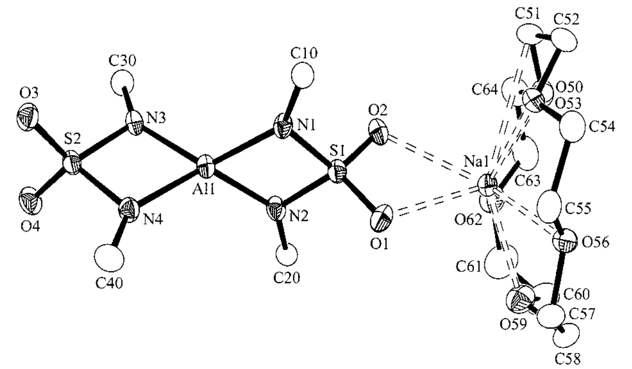

Figure 3. Molecular structure of $\mathrm{[Na(15\text{-}crown\text{-}5)][Al\{SO_2(N^tBu)_2\}_2]}$ (**2**). For clarity, only the α-carbon atoms of ^{t}Bu groups are shown. Displacement ellipsoids are plotted at the 30% probability level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $\mathrm{[Na(15\text{-}crown\text{-}5)][Al\{SO_2(N^tBu)_2\}_2]}$ (**2**)

S(1)−O(2)	1.452(3)	Al(1)−N(2)	1.842(3)
S(1)−O(1)	1.466(3)	Al(1)−N(1)	1.854(3)
S(1)−N(1)	1.617(3)	Na(1)...O(2)	2.479(3)
S(1)−N(2)	1.617(3)	Na(1)...O(1)	2.500(3)
S(2)−O(3)	1.450(3)	Na(1)...O(50)	2.447(3)
S(2)−O(4)	1.452(3)	Na(1)...O(53)	2.407(3)
S(2)−N(4)	1.624(3)	Na(1)...O(56)	2.455(3)
S(2)−N(3)	1.625(3)	Na(1)...O(59)	2.467(3)
Al(1)−N(3)	1.839(3)	Na(1)...O(62)	2.447(3)
Al(1)−N(4)	1.840(3)		
O(2)−S(1)-O(1)	109.47(16)	C(40)−N(4)-S(2)	123.3(3)
O(2)−S(1)-N(1)	114.52(16)	C(40)−N(4)-Al(1)	138.8(3)
O(1)−S(1)-N(1)	113.24(16)	S(2)−N(4)-Al(1)	95.49(15)
O(2)−S(1)-N(2)	113.85(16)	O(4)−S(2)-N(4)	114.16(17)
O(1)−S(1)-N(2)	113.86(17)	O(3)−S(2)-N(3)	113.57(17)
N(1)−S(1)-N(2)	91.05(14)	O(4)−S(2)-N(3)	112.34(16)
O(3)−S(2)-O(4)	112.12(16)	N(4)−S(2)-N(3)	90.94(15)
O(3)−S(2)-N(4)	112.14(16)		
N(3)−Al(1)-N(4)	78.04(14)	C(20)−N(2)-S(1)	123.6(2)
N(3)−Al(1)-N(2)	128.85(14)	C(20)−N(2)-Al(1)	140.2(2)
N(4)−Al(1)-N(2)	126.09(14)	S(1)−N(2)-Al(1)	96.11(15)
N(3)−Al(1)-N(1)	127.32(14)	C(30)−N(3)-S(2)	122.7(2)
N(4)−Al(1)-N(1)	127.12(14)	C(30)−N(3)-Al(1)	140.3(2)
N(2)−Al(1)-N(1)	77.33(13)	S(2)−N(3)-Al(1)	95.47(15)
C(10)−N(1)-S(1)	124.5(2)		
C(10)−N(1)-Al(1)	139.2(2)		
S(1)−N(1)-Al(1)	95.54(14)		

X-ray Structures of $\mathrm{[Na(15\text{-}crown\text{-}5)][Al\{SO_2(N^tBu)_2\}_2]}$ (2) and $\mathrm{\{[Na(15\text{-}crown\text{-}5)][O_2S(\mu\text{-}NBn)_2Al(\mu\text{-}NBnSO_2NBn)]\}_2}$ (3•3THF). The structure of **2** is depicted in Figure 3 and selected bond lengths and bond angles are given in Table 3. In contrast to the polymeric structure of **1**, the spirocyclic $\mathrm{\{Al[SO_2(N^tBu)_2]_2\}^-}$ anion in **2** is *O,O′* chelated to $\mathrm{Na^+}$. This is the first example of the bis-(*N,N′*),(*O,O′*)-chelating mode for a diazasulfate dianion [Figure 1f]. Polymerization is pre-empted by encapsulation of the $\mathrm{Na^+}$ ion by the 15-crown-5 ligand. The Na−O distances fall within the narrow range of 2.406(3) to 2.498(3) Å with a mean value of 2.458 Å. Related structures involving seven-coordinate $\mathrm{Na^+}$ ions include $\mathrm{[Na(15\text{-}crown\text{-}5)][NO_3]}$[23] and $\mathrm{[Na(15\text{-}crown\text{-}5)][ClO_4]}$.[24] The second $\mathrm{[SO_2(N^tBu)_2]^{2-}}$ ligand in **2** adopts the familiar *N,N′*-chelating mode [Figure 1a]. The dimensions of the complex ion $\mathrm{\{Al[SO_2(N^tBu)_2]_2\}^-}$ in **2** are essentially the same as those in **1**: $|\,d(\mathrm{Al-N})\,| = 1.844$ Å, $|\,\angle \mathrm{NAlN}\,|$ (endocyclic) = 77.7°, $|\,\angle \mathrm{NAlN}\,|$ (exocyclic) = 127.3°, $|\,d(\mathrm{S-N})\,| = 1.621$ Å, $|\,\angle \mathrm{NSN}\,| = 91.0°$, $|\,\angle \mathrm{NSO}\,| = 113.5°$, $|\,\angle \mathrm{SNAl}\,| = 95.7°$. The four-membered $\mathrm{AlN_2S}$ rings are planar with torsion angles < 1°. The mean S−O distance for the noncoordinated oxygen atoms O(3) and O(4) of 1.451 Å is comparable to the corresponding value of 1.459 Å for the oxygen atoms chelated to the $\mathrm{Na^+}$ cation. This chelation is reflected in a small difference of 2.6° in the ∠ OSO bond angles.

In contrast to the monomeric structure of **2**, the *N,N′*-bisbenzyl derivative **3** is dimeric (see Figure 4). The terminal $\mathrm{[O_2S(NBn)_2]^{2-}}$ ligands adopt the bis-(*N,N′*),(*O,O′*) chelation observed for **2** [Figure 1f] while the central $\mathrm{[O_2S(NBn)_2]^{2-}}$ ligands in **3** assume a novel *N,O*-chelate, *N′*-monodentate bonding mode [see Figure 1g]. As a consequence, the central core of **3** involves two four-

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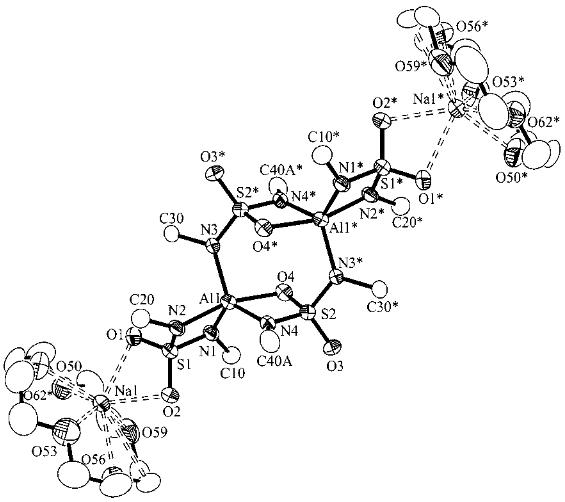

Figure 4. Molecular structure of $\{[Na(15\text{-crown-}5)][O_2S(\mu\text{-}NBn)_2Al(\mu\text{-}NBnSO_2NBn)]\}_2$ (**3**•3THF). For clarity, only the α-carbon atoms of Bn groups are shown. Displacement ellipsoids are plotted at the 30% probability level.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{[Na(15\text{-crown-}5)][O_2S(\mu\text{-}NBn)_2Al(\mu\text{-}NBnSO_2NBn)]\}_2$ (**3**•3THF)[a]

S(1)−O(1)	1.464(3)	Al(1)−N(3)	1.891(3)
S(1)−O(2)	1.461(3)	Al(1)−N(4)	1.872(3)
S(1)−N(1)	1.602(3)	Al(1)−O(4)	2.008(2)
S(1)−N(2)	1.599(3)	Na(1)•••O(1)	2.464(3)
S(2)−O(3)	1.438(3)	Na(1)•••O(2)	2.427(3)
S(2)−O(4)	1.495(3)	Na(1)•••O(50)	2.466(4)
S(2)−N(3)*	1.597(3)	Na(1)•••O(53)	2.370(4)
S(2)−N(4)	1.581(3)	Na(1)•••O(56)	2.442(4)
Al(1)−N(1)	1.869(3)	Na(1)•••O(59)	2.446(4)
Al(1)−N(2)	1.937(3)	Na(1)•••O(62)	2.413(4)
O(2)−S(1)-O(1)	109.82(15)	N(1)−Al(1)-N(4)	120.63(14)
O(2)−S(1)-N(2)	115.42(16)	N(1)−Al(1)-N(3)	117.94(14)
O(1)−S(1)-N(2)	111.61(16)	N(4)−Al(1)-N(3)	120.79(14)
O(2)−S(1)-N(1)	111.64(15)	N(1)−Al(1)-N(2)	74.66(13)
O(1)−S(1)-N(1)	115.24(16)	N(4)−Al(1)-N(2)	103.05(13)
N(2)−S(1)-N(1)	92.31(15)	N(3)−Al(1)-N(2)	99.54(13)
O(3)−S(2)-O(4)	115.86(16)	N(1)−Al(1)-O(4)	94.32(12)
O(3)−S(2)-N(4)	115.02(16)	N(2)−Al(1)-O(4)	163.39(13)
		N(3)−Al(1)-O(4)	96.61(12)
		N(4)−Al(1)-O(4)	71.53(12)
O(4)−S(2)-N(4)	95.09(15)	C(40A)-N(4)−S(2)	122.7(15)
O(3)−S(2)-N(3)	109.76(16)	C(40A)-N(4)−Al(1)	138.6(15)
O(4)−S(2)-N(3)*	107.33(15)	S(2)−N(4)-Al(1)	98.00(16)
N(4)−S(2)-N(3)*	112.97(16)	C(20)−N(2)-S(1)	120.3(3)
S(2)−O(4)-Al(1)*	95.38(12)	C(20)−N(2)-Al(1)	137.8(3)
C(10)−N(1)-S(1)	119.3(2)	S(1)−N(2)-Al(1)	95.22(14)
C(10)−N(1)-Al(1)	134.8(2)	C(30)−N(3)-S(2)*	116.6(2)
S(1)−N(1)-Al(1)	97.80(15)	C(30)−N(3)-Al(1)	119.9(2)
		S(2)−N(3)-Al(1)	123.13(17)

[a] Starred atoms are related by the symmetry transformation: $-x+1$, $-y$, $-z+1$.

membered $\overline{\text{AlNSO}}$ rings bridged by two N^tBu groups. The metrical parameters for the terminal $[O_2S(NBn)_2]^{2-}$ ligands, [∠ NSN = 92.31(15)°, ∠ NAlN = 74.66(13)°, and |d(S−O)| = 1.462(3) Å], are similar to those found for the diazasulfate ligand in **2**. The mean S−N bond distances for the terminal and bridging diazasulfate ligands in **3** do not differ significantly, 1.600 vs 1.589 Å. The four-membered AlN_2S ring is planar with torsion angle < 1°.

The formation of the central eight-membered ring in **3** (presumably via AlNSN ring-opening) parallels the behavior of the related covalent phosphorus (III) systems $[SO_2(NR)_2PR']_2$ (R = Me, Et; R′ = Me, Ph).[17] In the case of **3**, however, the SO_2 groups are aligned to allow a strong Al−O interaction. The Al−O distance is 2.008(3) Å, cf. values in the range 1.74−2.29 Å for five-coordinate Al complexes.[25] The geometry at aluminum in **3** is distorted trigonal bipyramidal. The bond angles ∠ NAlN in the trigonal plane are in the narrow range 117.9−120.8°, but the N(2)−Al(1)-O(4) arrangement is distinctly nonlinear [163.39(13)°]. As a result of the Al−O interaction there is a small, but significant, difference of ca. 0.06 Å in the S═O distances of the bridging ligand. A similar difference between coordinated and noncoordinated SO bond lengths has been observed for the $[O_2S(N^tBu)(NH^tBu)]^-$ monoanion in $Mg[SO_2(N^tBu)(NH^tBu)]_2$.[2] The four-membered $\overline{\text{AlNSO}}$ rings in **3** are essentially planar with torsion angles of < 1°. The bond angle ∠ OSO is 115.86(16)° for the bridging (*O*-monodentate) ligand, cf. 109.82(15)° in the *O*,*O*′-chelating terminal ligand. The bond angles within the four-membered $\overline{\text{AlNSO}}$ ring are ∠ NAlO = 71.53(12)°, ∠ AlOS = 95.38(7)°, ∠ OSN = 95.09(15)° and ∠ SNAl = 98.00(16)°. The Na−O distances in **3** fall within the range 2.370(4)-2.466(4) Å with a mean value of 2.433 Å.

Conclusions

The first investigations of alum analogues of the diazasulfate dianion have revealed three new bonding modes for this versatile ligand. In addition, it is shown that the structures of these double salts are influenced significantly by the nature of the group attached to nitrogen. The complex hydrides $MAlH_4$ (M = Li, Na) are potentially versatile reagents for the synthesis of other complex salts involving imido/oxo anions with main group element centers, e.g. triazaaluminophosphates $M_3\{Al_3[OP(NR)_3]_4\}$.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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