Assembly of a Heterobimetallic Diazasulfate Cluster via an Li_4O_4 Ladder

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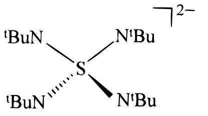
The elegance and symmetry of the structures of cluster compounds of the main group elements continue to pique the imagination of chemists. Recent investigations of ternary systems containing homoleptic polyimido anions of the p-block elements, as their alkali metal derivatives, illustrate the richness of the subject.[1,2] The structures of these clusters involve aggregations of smaller units that maximize interactions between polar $RN^-{-}Li^+$ units, cf. the concept of ring-laddering for lithium amides.[3]

The structural consequences of replacing one or more of the NR groups attached to the p-block element in these ternary clusters by an isoelectronic oxo ligand are not readily predictable. In the only reported examples, dilithium derivatives of the heteroleptic imido/oxo dianions $[OS(N^tBu)(NR)]^{2-}$ ($R = {}^tBu$, $SiMe_3$) were characterized as 36 atom ($Li_{12}S_6O_6N_{12}$) clusters whose novel structures are generated by oligomerization of smaller units via their Li_xO_x face ($x = 2$, $R = {}^tBu$; $x = 3$, $R = SiMe_3$).[4] Extension of this concept to quaternary systems involving the dianions $[O_2S(NR)_x]^{2-}$ ($x = 1, 2$) evokes the possibility of extended structures formed by aggregation through *two* Li_xO_x faces of the fundamental unit.[5] The recent reports of the first tetraazasulfate (**1**)[6] and triazasulfate (**2**)[7] anions, and the interest in sulfamide as a building block for the design of molecular solids,[8] prompt us to describe our studies of the first alkali or alkaline earth metal complexes of a diazasulfate dianion, **3**. The novel heterobimetallic cluster $\{Li_4Mg[O_2S(N^tBu)_2]_3{\cdot}4THF\}_2$ (**5**) is constructed from two $Li_2Mg[O_2S(N^tBu)_2]_2$ and two $Li_2[O_2S(N^tBu)_2]$ molecules aggregated through a central step-shaped Li_4O_4 unit.



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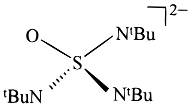

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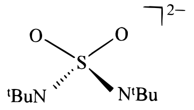

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In an attempt to prepare $Mg[O_2S(N^tBu)_2]$, an isoelectronic analogue of $MgSO_4$, we found that the reaction of *N*,*N′*-bis(*tert*-butyl)sulfamide with $^nBu^{sec}BuMg$ in toluene/tetramethylethylenediamine (TMEDA) results in incomplete magnesiation to give **4** (eq 1).[9]

$$2O_2S(NH^tBu)_2 + MgBu_2 \xrightarrow[\text{toluene}]{\text{TMEDA}} \underset{\mathbf{4}}{Mg(TMEDA)[O_2S(N^tBu)(NH^tBu)]_2} + 2BuH \quad (1)$$

A crystal structure determination of **4**[10] revealed that two $[O_2S(N^tBu)(NH^tBu)]^-$ ligands are chelated in an O,N-bonding mode to Mg^{2+} with an almost linear [172.8(1)°] OMgO unit (Figure 1). The molecule of TMEDA completes the highly distorted octahedron around the Mg^{2+} cation. The $S{-}NH^tBu$ bond lengths are ca. 0.1 Å longer than the $S{-}N^tBu$ bonds of the coordinated nitrogen atoms. To our knowledge the anion in **4** is the first aza analogue of the HSO_4^- anion.

The lithiation of **4** with 2 equiv of Li^nBu produces **5** (eq 2).[11]

$$\begin{array}{l} \underset{\mathbf{4}}{4Mg(TMEDA)[O_2S(N^tBu)(NH^tBu)]_2} + 8Li^nBu \\ \qquad\quad \Big\downarrow \text{THF} \\ \underset{\mathbf{5}}{\{Li_4(THF)_4Mg[O_2S(N^tBu)_2]_3\}_2} + 2Mg[O_2S(N^tBu)_2] \end{array} \quad (2)$$

The structure of the quinary system **5** was determined by X-ray crystallography,[12] which revealed a 36 atom $Li_6Mg_2S_6O_{10}N_{12}$

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(9) To synthesize **4**, a solution of dibutylmagnesium (12.0 mL, 12.0 mmol, 1.0 M $^nBu^{sec}BuMg$ solution in heptane) in TMEDA (25 mL) was added slowly to a stirred solution of $O_2S[N(H)^tBu]_2$ (5.00 g, 24.0 mmol) in toluene (100 mL) at 23 °C. The clear, colorless reaction mixture was stirred for 3 h. Removal of solvent in vacuo yielded white amorphous $TMEDA{\cdot}Mg\{O_2S[N^tBu][N(H)^tBu]\}_2$ (6.39 g, 11.5 mmol, 96%); mp 145−147 °C. ^1H NMR (in C_6D_6 at 23 °C): δ 3.60 (s, 2H, NH), 2.23 (br, 16H, TMEDA), 1.54 (s, 18H, ^tBu), 1.44 (s, 18H, ^tBu). IR (KBr, Nujol mull): 3372 (br) cm^{-1} [ν(N−H)].

(10) Crystals of **4** were obtained by recrystallization from TMEDA/*n*-hexane (4:1) at 0 °C (3 days). Crystal data for **4**: $C_{22}H_{54}MgN_6O_4S_2$, $M = 555.14$, monoclinic, space group $P2_1/c$, $a = 14.914(3)$ Å, $b = 9.321(2)$ Å, $c = 23.219(4)$ Å, $\beta = 97.350(4)°$, $V = 3201.3(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.152$ g cm^{-3}, μ(Mo Kα) = 0.220 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, $T = -70$ °C, $F(000) = 1216$.

(11) To synthesize **5**, a 2.5 M solution of ^nBuLi in hexanes (0.72 mL, 1.80 mmol) was added slowly to a stirred solution of **4** (0.50 g, 0.90 mmol) in THF (30 mL) at 23 °C. The colorless reaction mixture was stirred for 3 h. Concentration (ca. 3 mL) and subsequent layering of the solution with *n*-hexane (ca. 2 mL) yielded colorless blocks of $\{(THF)_4Li_4Mg[S(O)_2(N^tBu)_2]_3\}_2$ (0.23 g, 0.12 mmol, 53%); mp 245 °C dec. ^1H NMR (in d_8-THF at 23 °C): δ 3.58 [m, 32H, $O(CH_2)_2(CH_2)_2$], 1.74 [m, 32H, $O(CH_2)_2(CH_2)_2$], 1.26 (s, 18H, ^tBu), 1.25 (s, 18H, ^tBu), 1.22 (s, 18H, ^tBu), 1.21 (s, 18H, ^tBu), 1.20 (s, 18H, ^tBu), 1.19 (s, 18H, ^tBu). ^7Li NMR (in d_8-THF at 23 °C): δ 3.38 (br), 2.63 (br), 2.07 (br) (approximate relative intensities of 1:2:1, respectively).

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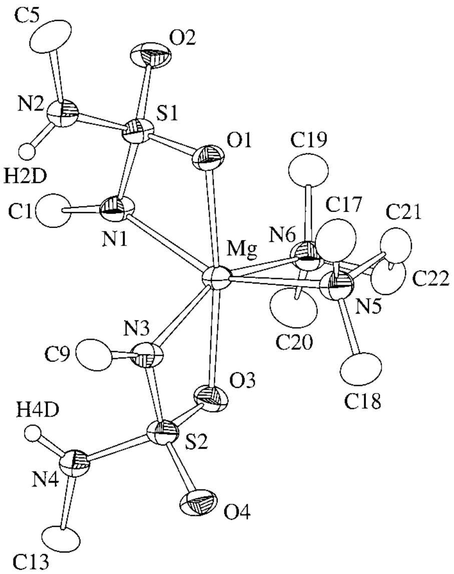

Figure 1. Crystal structure of Mg(TMEDA)[$O_2S(N^tBu)(NH^tBu)$]$_2$ (**4**). For clarity only α-carbon atoms of ^{t}Bu groups are shown. Bond lengths (Å) and angles (deg): Mg−N(1) 2.220(3), Mg−N(3) 2.205(3), Mg−N(5) 2.299(3), Mg−N(6) 2.290(3), Mg−O(1) 2.084(2), Mg−O(3) 2.081(3), S(1)−O(1) 1.482(2), S(1)−O(2) 1.442(2), S(2)−O(3) 1.477(2), S(2)−O(4) 1.432(2), S(1)−N(1) 1.540(3), S(1)−N(2) 1.637(3), S(2)−N(3) 1.551(3), S(2)−N(4) 1.645(3), O(1)−Mg−N(1) 66.01(9), O(3)−Mg−N(3) 66.37(9), N(1)−Mg−N(3) 99.39(10), N(5)−Mg−N(6) 79.88(11).

cluster with two terminal OLi(THF)$_3$ groups (Figure 2). Each half of the centrosymmetric dimer **5** consists of an $Li_2[O_2S(N^tBu)_2]$ unit and an $Li_2(THF)_4Mg[O_2S(N^tBu)_2]_2$ unit. The two halves are connected by a central Li_4O_4 ladder. The outer rungs of this ladder are formed by Li−O bonds of each $Li_2[O_2S(N^tBu)_2]$ unit while the inner rungs involve O−Li(THF) bonds of the two $Li_2(THF)_4Mg[O_2S(N^tBu)_2]_2$ units. The ^{1}H NMR spectrum of **5** in d_8-THF at 23 °C shows six equally intense resonances for ^{t}Bu groups consistent with retention of the dimeric (C_i) structure in solution.

The dianion in **5** is the first example of a diaza analogue of the SO_4^{2-} anion, **3**. In covalent derivatives, e.g., $O_2S(\mu\text{-}N^tBu)_2PCl$,[13] $L_2Pt[O_2S(NR)_2]$ (L = PR′$_3$, R = H,[14a] L = cod, R = Ph),[14b] and $Fe_2(CO)_6[\mu\text{-}PhNSO_2NPh]$,[15] an *N*,*N*′-bonding mode is observed for the diazasulfate ligand and the O atoms are not involved in coordination. The triazasulfate dianion **2** is also *N*,*N*′ bonded to all three Li$^+$ ions in the lithium iodide adduct $[(THF)_3Li_3(\mu_3\text{-}I)\{OS(N^tBu)_3\}]$.[7] By contrast the dianion **3** exhibits N,O-chelation toward both the Li$^+$ and Mg^{2+} cations in **5**. One of the $[O_2S(N^tBu)_2]^{2-}$ ligands is chelated to two Li$^+$ ions, and a second is chelated to one Li$^+$ and one Mg^{2+} ion. The third dianionic ligand is coordinated to *three* metal ions via chelation to Mg^{2+} and monodentate coordination through an N atom to the three-coordinate Li$^+$ ion and through an oxygen atom to the trisolvated Li$^+$ ion. Undoubtedly solvation of Li(4) by three THF molecules obviates the formation of a more extended structure, which could otherwise occur by aggregation via Li(4)−O(4) units. The Mg^{2+} ion in **5** is five-coordinate (distorted square pyramidal) with trans oxo ligands and trans imido groups and an oxo ligand in the axial position. All nitrogen atoms are three-coordinate. The oxygen atoms O(3), O(4), and O(6) are two coordinate, O(1) and O(2) are three-coordinate, and O(5) is four-coordinate. All lithium ions are four-coordinate with the exception of Li(3), which is three-coordinate. Pertinent details of bond lengths are given in the caption to Figure 2.

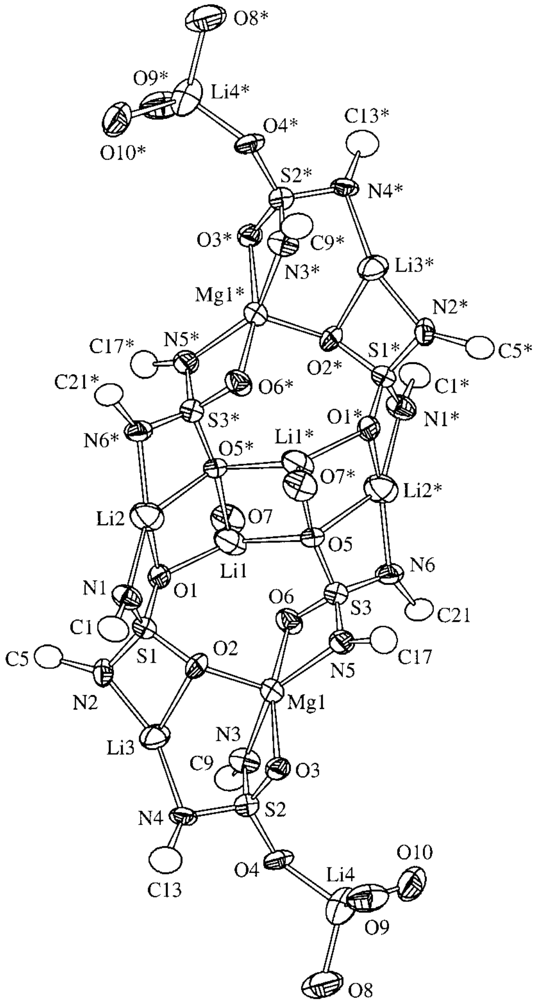

Figure 2. Crystal structure of $\{Li_4(THF)_4Mg[O_2S(N^tBu)_2]_3\}_2$ (**5**). For clarity only the oxygen atoms of THF molecules and α-carbon atoms of ^{t}Bu groups are shown. Bond lengths (Å): Mg(1)−O(2) 1.972(9), Mg(1)−O(3) 2.064(8), Mg(1)−O(6) 2.085(8), Mg(1)−N(3) 2.092(5), Mg(1)−N(5) 2.052(10), S−O (range) 1.478(8)−1.498(8), S−O (mean) 1.488(8), S−N (range) 1.537(10)−1.585(9), S−N (mean) 1.558(10), Li−N (range) 1.89(2)−2.07(2), Li(3)···N(3) 2.42(2), Li−O (range) 1.88(2)−2.13(2), Li−O(THF) (range) 1.91(2)−1.96(2), Li(1)···O(6) 2.35(2). Starred atoms are related by the symmetry transformation $-x + 1$, $-y + 1$, $-z + 1$.

In summary, the combination of magnesiation followed by lithiation provides crystalline material that allows the first structural characterization of an ionic diazasulfate complex. This heterobimetallic strategy may be useful in the initial structural characterization of hitherto unknown heteroleptic imido/oxo anions of p-block elements isoelectronic with **2** and **3**, e.g., $[O_xP(NR)_{4-x}]^{3-}$ and $[O_xSi(NR)_{4-x}]^{4-}$.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for **5**: $(C_{40}H_{86}N_6O_{10}S_3MgLi_4)\cdot 0.5C_4H_8O$, M = 995.46, triclinic, space group $P\bar{1}$ (No. 2), a = 13.944(8) Å, b = 17.369(7) Å, c = 13.641(8) Å, α = 107.75(5)°, β = 112.96(5)°, γ = 90.06(4)°, V = 2870(4) Å^3, Z = 2, ρ_{calcd} = 1.152 g cm^{-3}, μ(Mo Kα) = 0.193 mm^{-1}, λ(Mo Kα) = 0.710 69 Å, T = −103 °C, F(000) = 1080.

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