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Preparation and Structure of $[Li_2Se(N^tBu)_3]_2$, Containing the Novel $Se(N^tBu)_3{}^{2-}$ Anion

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The first N,N′-diorgano selenium diimide $Se(N^tBu)_2$ was reported as an *in situ* reagent 20 years ago.[1] Subsequently, the thermally unstable compounds $Se(NR)_2$ ($R = {}^tBu$,[2] $SiMe_3$[3]) were isolated and the N,N′-diorgano derivatives ($R = {}^tBu$, ${}^tOct$) were recently characterized in solution by ^1H, ^{15}N, and ^{77}Se NMR spectroscopy.[4] The solid-state structure of these selenium diimides is unknown, but the chelating (N,N′) ligand in the adduct $SnCl_4\cdot Se(N^tBu)_2(thf)_2$ exhibits short Se−N distances (1.710(3) Å).[5] Although selenium diimides with bulky substituents attached to the nitrogen atoms can be handled for a short time at room temperature, only two other reactions of these multiply bonded SeN reagents have been investigated.[6,7]

There is current interest in SeN chemistry[8] and several useful SeN reagents have been discovered, most notably the Se(II) derivative $Se[N(SiMe_3)_2]_2$,[9] Se_2NCl_3,[10a] and the Se−N−Cl cations $N(SeCl_x)_2{}^+$ ($x = 1$,[10a,b] 2[10c,d]). Very recently we found that the reaction of the tellurium diimide dimer ${}^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu$[11] with $LiNH^tBu$ produces the dimeric cluster $[Li_2Te(N^tBu)_3]_2$, containing the $Te(N^tBu)_3{}^{2-}$ dianion, a versatile reagent for the incorporation of other elements into TeN rings and clusters.[12] A subsequent report of the corresponding sulfur(IV) derivative $[Li_2S(N^tBu)_3]_2$[13] by Stalke et al. prompts us to describe the synthesis and structure of $[Li_2Se(N^tBu)_3]_3$ (**1**), which contains the novel tris(*tert*-butylimido)selenite ion, $Se(N^tBu)_3{}^{2-}$, a potentially important reagent for the development of Se−N chemistry.

Compound **1** was obtained according to eq 1 by the reaction of $Se(N^tBu)_2$ with 2 molar equiv of $LiNH^tBu$ in toluene at −78 °C.[14] Recrystallization from *n*-hexanes led to colorless, block-shaped, air- and moisture-sensitive crystals of **1** in *ca*. 50% yield. Pure **1** is a beige-white solid which can be handled in an inert gas atmosphere. It is thermally stable at room temperature but decomposes at 65 °C upon heating.

$$2Se(N^tBu)_2 + 4LiNH^tBu \xrightarrow[-78\ ^\circ C]{toluene} \underset{\mathbf{1}}{[Li_2Se(N^tBu)_3]_2} + 2\,{}^tBuNH_2 \quad (1)$$

The crystal structure of **1** consists of two crystallographically different $Se_2N_6Li_4$ cages, one of which was refined as an ordered $Se_2N_6Li_4$ cage and the other of which was refined as a disordered cage in which two of the Li atoms were disordered over two sites with 0.5 occupancy factors each.[15] An ORTEP drawing of the ordered molecule with the atomic numbering scheme is

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(14) $Se(N^tBu)_2$ was prepared *in situ* according to ref 2 in a modified synthesis from $SeCl_4$ (ÆSAR, 99.5%; 2.21 g, 10 mmol) and ${}^tBuNH_2$ (Aldrich; 6.3 mL, 60 mmol; dried over 3 Å molecular sieves), in dried diethyl ether (80 mL) in an inert gas atmosphere at −40 °C. After filtration and removal of the solvent under dynamic vacuum, cold toluene (10 mL) was added to the obtained $Se(N^tBu)_2$ (1.084 g, 4.90 mmol; yield 49.0% based on $SeCl_4$) kept at 0 °C at all times in order to prevent decomposition. A slurry of $LiNH^tBu$ (0.775 g, 9.80 mmol) in toluene (25 mL) was added dropwise to the stirred orange solution of $Se(N^tBu)_2$ cooled to −78 °C. The mixture was allowed to reach room temperature slowly, and the color of the solution changed from orange to dark green, followed by light green, yellow, and orange, and, finally, red-orange. The volatiles were removed under dynamic vacuum, giving a yellow-brown solid which was washed four times with cold toluene (*ca*. 5 mL; 0 °C), leading to a beige solid $[Li_2Se(N^tBu)_3]_2$ (0.766 g; 2.48 mmol; yield 50.6% based on $Se(N^tBu)_2$); mp 65 °C dec.). Anal. Calcd for $C_{12}H_{27}N_3Li_2Se$: C, 47.09; H, 8.89; N, 13.73. Found: C, 45.78; H, 9.00; N, 13.25. Consistently low C analyses were obtained on several different samples by two analysts, but the bulk material was shown to be pure by ^1H, ^7Li, and ^{77}Se NMR spectra. ^1H NMR (in C_7D_8 at 25 °C, δ): 1.31. ^{77}Se NMR [in C_7D_8 at 25 °C, $\delta(Me_2Se$, neat)]: 1091.6 ($\Delta\upsilon_{1/2} = 24$ Hz). ^7Li NMR [in C_7D_8 at 25 °C, δ(4 M LiCl in D_2O)]: 0.72 ($\Delta\upsilon_{1/2} = 4.9$ Hz). Ms (EI, 70 eV): 614 (M^+, 1.4), 597 ($M - Me^+$, 2.7). IR (KBr plates, Nujol, cm^{-1}): 1351 s, 1304 w, 1260 m, 1224 m, 1205 s, sh, 1185 s, br, 1022 m, 966 m, 933 s, 894 w, 875 w, 800 m, 765 s, 736 s, sh, 733 s, 695 m, 540 w, 491 m, 465 m.

(15) Colorless crystals of $[Li_2Se(N^tBu)_3]_2$ (**1**) were obtained by recrystallization from *n*-hexanes at −20 °C (2 days). Crystals of **1** were transferred to a vial containing Nujol in a drybox, and a single crystal (0.60 × 0.40 × 0.38 mm^3) was then mounted on a glass fiber coated with epoxy. Crystal data for **1**: $(C_{12}H_{27}N_3Li_2Se)_2$, $M = 712.42$, triclinic, space group $P\bar{1}$ (No. 2), $a = 16.373(7)$ Å, $b = 17.536(5)$ Å, $c = 9.873(3)$ Å, $\alpha = 92.72(3)°$, $\beta = 91.50(3)°$, $\gamma = 64.22(2)°$, $V = 2549(1)$ $Å^3$, Z = 3, $D_c = 1.197$ g cm^{-3}, μ(Mo Kα) = 21.96 cm^{-1}, λ(Mo Kα) = 0.710 69 Å. The final R and R_w values were 0.053 and 0.050, respectively, for 2525 observed reflections ($I > 3.00\sigma(I)$) and 485 parameters. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation at −73 ± 1 °C using $\omega-2\theta$ scans ($2\theta_{max} = 50.1°$). Of the 9384 reflections collected, 9041 were unique ($R_{int} = 0.0412$). The structure was determined by direct methods (SIR 92) and expanded using Fourier techniques (DIRDIF 94). The data were corrected for Lorentz and polarization effects. An empirical correction using ψ scans was applied, which resulted in absorption coefficients ranging from 0.781 to 1.0. Refinement was by full-matrix least squares, with all non-hydrogen atoms except Li(3) and Li(4) assigned anisotropic thermal parameters. The atoms Li(3) and Li(4) were disordered over two sites with 0.50 occupancy factors each and were labeled as Li(3a)/Li(3b) and Li(4a)/Li(4b). Hydrogen atoms were included at geometrically idealized positions with C−H 0.95 Å and were not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

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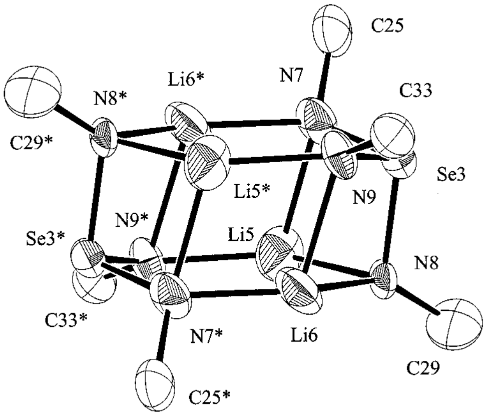
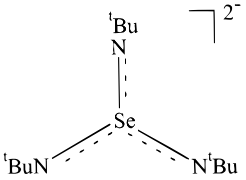


Figure 1. ORTEP drawing for $[\mathrm{Li_2Se(N^tBu)_3}]_2$. For clarity only α-carbon atoms of ^{t}Bu groups are shown. Selected bond distances (Å) and bond angles (deg): Se(3)−N(7) 1.78(1), Se(3)−N(8) 1.82(1), Se(3)−N(9) 1.81(1), Li(5)−N(7) 2.06(3), Li(5)−N(8) 1.99(3), Li(5)−N(9)* 2.00(3), Li(6)−N(7)* 1.96(3), Li(6)−N(8) 1.97(3), Li(6)−N(9) 2.12(3); N(7)−Se(3)−N(8) 95.9(6), N(7)−Se(3)−N(9) 103.4 (5), N(8)−Se(3)−N(9) 97.1(5). Asterisks designate atoms related by the symmetry operation 2 − *x*, −*y*, −*z*.

shown in Figure 1. The $[\mathrm{Li_2Se(N^tBu)_3}]_2$ dimer contains the first example of a triimidoselenite ion, $\mathrm{Se(NR)_3}^{2-}$, isoelectronic with $\mathrm{SeO_3}^{2-}$ The mean Se−N distance of 1.80 (1) Å (cf. 1.85 and 1.65 Å for single and double SeN bonds, respectively)[5] implies a bond order of 1.25 in reasonable agreement with the value of 1.33 expected for the resonance hybrid **2** (lone pair on Se omitted).



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The geometry at Se is distorted pyramidal with a mean bond angle of 98.8(6)°. The lithium atoms in the $\mathrm{Li_4Se_2N_6}$ cage are all connected to three nitrogen atoms with Li−N distances in the range 1.96(3)−2.12(3) Å. Thus the structure of the dimer **1** can be viewed as a distorted hexagonal prism like that of the Te analogue.[16] Other hexagonal prismatic clusters involving main group elements include $[\mathrm{(THF)MgNPh}]_6$,[17] $(\mathrm{RAlNR'})_6$,[18] $[^t\mathrm{Bu({=}CH_2)OLi}]_6$,[19] $[\mathrm{PhSn(O)(\mu\text{-}O_2CC_6H_{11})}]_6$,[20] and $(\mathrm{NaO^tBu})_6$,[21] all of which possess $\mathrm{A_6X_6}$ cores.

The ^{1}H NMR spectra of **1** in $\mathrm{C_7D_8}$ exhibit a singlet at δ 1.31 throughout the temperature range 185−298 K, implying a highly fluxional structure. The mechanism of the fluxional process has been discussed for $[\mathrm{Li_2Te(N^tBu)_3}]_2$.[16] The proposed fluxional process involves the concerted stretching and contraction of the longest lithium−nitrogen interactions between the two six-membered rings of the hexagonal prism [Li(6)−N(9) in Figure 1]. The ^{7}Li NMR spectrum of **1** in $\mathrm{C_7D_8}$ at 298 K exhibits a singlet as expected (C_{2h} symmetry, with a C_2 axis through the center of the four-membered $\mathrm{Li_2N_2}$ rings). The ^{7}Li chemical shift is 0.72 ppm, indicating that the Li atoms are more shielded in **1** than in the related compounds $[\mathrm{Li_2S(N^tBu)_3}]_2$ [δ(^{7}Li) 2.88][13] and $[\mathrm{Li_2Te(N^tBu)_3}]_2$ [δ(^{7}Li) 5.7].[12]

Previously published IR data for SeN compounds indicate υ(SeN) vibrations are observed in the region 500−950 cm^{-1}.[22] From a comparison of the IR spectrum of **1** with that of $\mathrm{LiNH^tBu}$, we tentatively assign the bands at 765 and 695 cm^{-1} to υ_s(SeN) and υ_{as}(SeN) of the $\mathrm{SeN_3}$ fragment, respectively.

In summary, the novel $\mathrm{Se(N^tBu)_3}^{2-}$ anion is readily accessible as the thermally stable dilithium derivative, which is a potentially versatile reagent for the incorporation of metals into Se−N rings.

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Supporting Information Available: Text and tables giving details of the crystallographic data collection and listings of crystal data, positional and thermal parameters, and bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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