Homoleptic Bismuth and Antimony Complexes of the Tripodal $[Te(N^tBu)_3]^{2-}$ Anion

Tristram Chivers,*,† Masood Parvez,† Gabriele Schatte,† and Glenn P. A. Yap‡

Departments of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4, and University of Ottawa,
Ottawa, Ontario, Canada K1N 6N5

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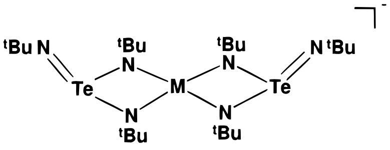
As isoelectronic analogues of the common oxo anions EO_3^{2-} (E = S, Se, Te), the recently discovered pyramidal polyimido anions $E(N^tBu)_3^{2-}$ [1−3] are potentially versatile multidentate ligands. Complexes of these anions with p-block elements may serve as single-source precursors for electronic materials, e.g., SnTe and Bi_2Te_3. The lithium derivatives exist as dimeric, hexagonal prismatic clusters $\{Li_2[E(N^tBu)_3]\}_2$.[1−3] These clusters are readily oxidized to colored neutral radicals $\{Li_3[E(N^tBu)_3]_2\}^{\bullet}$ (E = S, Se); the sulfur derivative is especially persistent.[4,5] Consequently, the development of the coordination chemistry of $[S(N^tBu)_3]^{2-}$ has been thwarted by redox reactions.[6] For example, in attempts to prepare homoleptic M(II) complexes (M = Ge, Sn), Stalke et al. found that "total decomposition of the starting materials" occurred in the reactions of MCl_2 with $[Li_2S(N^tBu)_3]_2$.[6,7] Our preliminary investigations of the ligand behavior of $[Te(N^tBu)_3]^{2-}$ also revealed redox processes in reactions with $PhPCl_2$ or $PhBCl_2$.[3] In the latter case, however, the four-membered-ring $PhB(\mu\text{-}N^tBu)_2Te(N^tBu)$ containing the intact ligand was obtained in moderate yields.[3] We describe here the preparation and structure of the anions $\{M[Te(N^tBu)_3]_2\}^-$ (M = Sb, Bi) as their Li^+ derivatives. These anions are the first homoleptic complexes of pyramidal anions of the type $[E(N^tBu)_3]^{2-}$.



(M = Bi, Sb)

The reaction of $\{Li_2[Te(N^tBu)_3]\}_2$ with MCl_3 in the appropriate solvent at −78 °C, followed by warming to 23 °C, produced **1a** and **1b** as moisture-sensitive dark orange or yellow-orange crystals, respectively.[8] Both complexes **1a** and **1b** were formed in optimum yields (^1H NMR) by using a 1:1 stoichiometry (eq 1). However, the pure products were isolated more easily when molar ratios of 3:4 (M = Bi) or 1:2 (M = Sb) were employed.[8] The solvent of choice was thf for **1a** and toluene for **1b**.[8]

$$\{Li_2[Te(N^tBu)_3]\}_2 + MCl_3 \rightarrow Li\{M[Te(N^tBu)_3]_2\} + 3LiCl \qquad (1)$$

1a: M = Bi
1b: M = Sb

The ^1H NMR spectra of **1a** and **1b** showed three equally intense resonances suggesting three symmetrically equivalent pairs of N^tBu groups. Consistently, three sets of resonances for the α-C atoms and CH_3 substituents of the ^tBu groups were observed in the ^{13}C NMR spectra. Both the ^7Li and ^{125}Te NMR spectra exhibited single resonances. X-ray structural determinations of **1a** and **1b**[9] revealed similar molecular architectures in which two pyramidal $[Te(N^tBu)_3]^{2-}$ ions are chelated to the group 15 element and the pendant N^tBu groups are bridged by a Li^+ ion. An ORTEP

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* To whom correspondence should be addressed. Tel: (403) 220-5741. Fax: (403) 289-9488. E-mail: chivers@ucalgary.ca.

† University of Calgary.

‡ University of Ottawa.

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(8) **1a.** A solution of sublimed $BiCl_3$ (1.127 mmol) in thf (10 mL) was added to a solution of $\{Li_2[Te(N^tBu)_3]\}_2$ (0.845 mmol) in thf (10 mL) at −78 °C. After 3 h at 23 °C solvent was removed, and the orange-red solid residue was extracted with *n*-hexane (3 × 4 mL) to give **1a** (0.362 mmol, 43% based on the Te reagent) as the hexane-soluble product. ^1H NMR (25 °C, in C_7D_8): δ = 1.29 (s, 9 H, $C(CH_3)_3$), 1.50 (s, 9 H, $C(CH_3)_3$), 1.53 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (25 °C, in d_8-thf): δ 36.5 (s, $C(CH_3)_3$), 38.8 (s, $C(CH_3)_3$), 39.1 (s, $C(CH_3)_3$), 57.6 (s, $C(CH_3)_3$), 58.0 (s, $C(CH_3)_3$), 60.4 (s, $C(CH_3)_3$). ^7Li NMR (25 °C, in C_7D_8, ref 1 M LiCl in D_2O): δ = 0.71 (s). ^{125}Te NMR (25 °C, in d_8-thf, standard K_2TeO_3 in D_2O referred to Me_2Te (δ = 0 ppm)): δ = 1713 (s). **1b.** This complex was obtained in 22% yield (based on the Te reagent) by the reaction of $SbCl_3$ (1.409 mmol) with $\{Li_2[Te(N^tBu)_3]\}_2$ (0.703 mmol) in toluene (25 mL) by using a procedure similar to that described for **1a**. ^1H NMR (25 °C, in C_7D_8): δ = 1.38 (s, 9 H, $C(CH_3)_3$), 1.44 (s, 9 H, $C(CH_3)_3$), 1.62 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (25 °C, in d_8-thf): δ 35.1 (s, $C(CH_3)_3$), 37.8 (s, $C(CH_3)_3$), 38.6 (s, $C(CH_3)_3$), 57.1 (s, $C(CH_3)_3$), 57.7 (s, $C(CH_3)_3$), 59.6 (s, $C(CH_3)_3$). ^7Li NMR (25 °C, in C_7D_8): δ = 0.57 (s). ^{125}Te NMR (25 °C, in C_7D_8): δ = 1684 (s).

(9) Crystals of **1a** were obtained from a thf solution at −20 °C (10 days). Crystal data for **1a**: $C_{24}H_{54}N_6BiLiTe_2$, M = 897.85, monoclinic, space group $P2_1/c$, a = 9.833(4) Å, b = 34.665(9) Å, c = 10.099(4) Å, β = 103.497(5)°, V = 3348(2) Å^3, Z = 4, ρ_{calcd} = 1.781 g cm^{-3}, μ = 6.996 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, T = −70 °C, F(000) = 1720. Data were collected on a Bruker AXS SMART CCD diffractometer on an orange-red block (0.30 × 0.30 × 0.30 mm) mounted on a glass fiber in the range 2.13° ≤ θ ≤ 25.00° (19 727 reflections collected; 5881 unique reflections, R_{int} = 0.0989). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97). The Bi and Li atoms were disordered. The Bi position was refined by using occupancy factors of 0.98 Bi and 0.02 Li. The Li position had a contribution of 0.98 Li and 0.02 Bi atoms. Refinement based on 5879 reflections ($I > 2\sigma(I)$) led to R = 0.0460 and R_w = 0.0902. Crystals of **1b** were obtained from a thf solution at −20 °C (10 days). Crystal data for **1b**: $C_{24}H_{54}N_6SbLiTe_2$, M = 810.62, monoclinic, space group $P2_1/a$, a = 9.988(3) Å, b = 17.753(2) Å, c = 19.456(3) Å, β = 101.16(2)°, V = 3385(1) Å^3, Z = 4, ρ_{calcd} = 1.591 g cm^{-3}, μ(Mo Kα) = 25.35 cm^{-1}, λ(Mo Kα) = 0.710 69 Å, T = −103 °C, F(000) = 1592. Data were collected on a Rigaku AFC6S diffractometer on an orange plate (0.40 × 0.30 × 0.20 mm) coated with Paratone-8277 oil (Exxon) and mounted on a glass fiber using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.1° (6277 reflections collected of which 5911 were unique, R_{int} = 0.074). The structure was solved by direct methods (SIR-92) and expanded using Fourier techniques (DIRDIF-94). The Sb and Li atoms were disordered, and refinement was achieved by using occupancy factors of 0.85 and 0.15 for the respective sites of these atoms. Eight C atoms were also disordered over two sites in each case and were refined isotropically. The final cycle of full-matrix least-squares refinement using F^2 coefficients was based on 2228 observed reflections ($I > 2.00\sigma(I)$) and 319 parameters and led to R = 0.0531 and R_w = 0.1143 (SHELXL-97).

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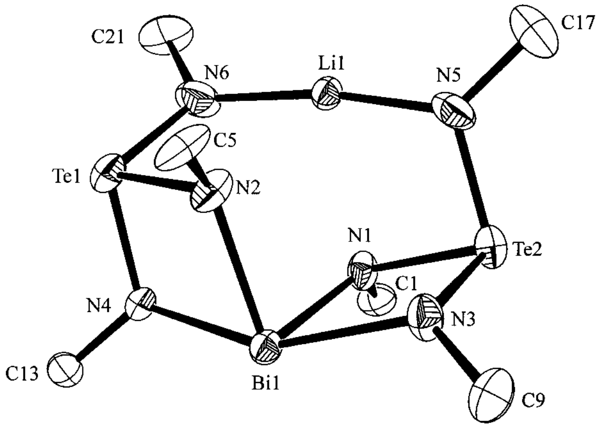

Figure 1. Crystal structure of Li{Bi[Te(N^tBu)$_3$]$_2$} (**1a**). For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Li{M[Te(N^tBu)$_3$]$_2$} (**1a**, M = Bi; **1b**, M = Sb)

	1a	**1b**
Li(1)−N(5)	1.871(12)	1.908(15)
Li(1)−N(6)	2.008(12)	2.064(14)
Te(1)−N(2)	2.029(8)	2.024(13)
Te(1)−N(4)	1.976(7)	1.978(13)
Te(1)−N(6)	1.916(8)	1.906(16)
Te(2)−N(1)	2.044(7)	2.050(12)
Te(2)−N(3)	1.974(8)	1.963(15)
Te(2)−N(5)	1.905(8)	1.913(14)
M(1)−N(1)	2.238(8)	2.206(15)
M(1)−N(2)	2.246(7)	2.197(15)
M(1)−N(3)	2.337(8)	2.166(12)
M(1)−N(4)	2.347(8)	2.199(12)
Li(1)···N(1)	2.534(14)	2.548(16)
Li(1)···N(2)	2.533(15)	2.575(16)
N(2)−Te(1)−N(4)	85.7(3)	84.3(5)
N(2)−Te(1)−N(6)	89.2(3)	90.4(6)
N(4)−Te(1)−N(6)	104.9(3)	104.5(6)
N(1)−Te(2)−N(3)	85.0(3)	83.9(6)
N(1)−Te(2)−N(5)	88.0(3)	88.1(6)
N(3)−Te(2)−N(5)	105.7(3)	104.8(7)

drawing of the bismuth complex **1a** is displayed in Figure 1. Since the structural data for **1a** are of higher quality than those for **1b**, the discussion of structural details will focus on the bismuth complex. However, the trends in geometrical parameters for **1a** and **1b** are very similar (see Table 1).

The chelating [Te(N^tBu)$_3$]$^{2-}$ anions subtend an angle of 72.7(3)° at bismuth. The four-membered BiN$_2$Te rings are essentially planar with asymmetrically bridging N^tBu groups [|*d*(Te−N)| = 1.975(1) and 2.036(7) Å, |*d*(Bi−N)| = 2.342(5) and 2.242(4) Å, cf. |*d*(Bi−N)| = 2.192(7) Å in Li$_2$[Bi$_2$(N^tBu)$_4$]·thf].[10] The shortest Te−N distances [|*d*(Te−N)| = 1.909(6) Å] involve the N^tBu groups linked to the Li$^+$ ion, cf. |*d*(Te−N)| = 1.976(2) Å in {Li$_2$[Te(N^tBu)$_3$]}$_2$.[11] The geometry at Bi can be viewed as a very distorted trigonal bipyramid with ∠NBiN values of 154.4(3)° and 86.0(3)°. The Li$^+$ ion forms an almost linear [∠NLiN = 173.2(8)°] but, inexplicably, unsymmetrical [*d*(Li−N) = 1.871(12) and 2.008(12) Å] bridge between the two pendant N^tBu groups. However, the ^{1}H and ^{13}C NMR data (Table 1) are consistent with C_2 symmetry for **1a**,**b** in solution, i.e., a C_2 axis passing through M and Li. The Li$^+$ ion is also engaged in two weak interactions with N(1) and N(2) [2.534(14) and 2.533(15) Å, respectively]. Wright et al. have presented a convincing case for the dominant role of the p-block metal (Sn, Sb, or Bi) in determining the structures of heterometallic (p-block and alkali metals) clusters.[12] It is possible that this tendency induces the weak Li···N interactions in **1a** and **1b**.

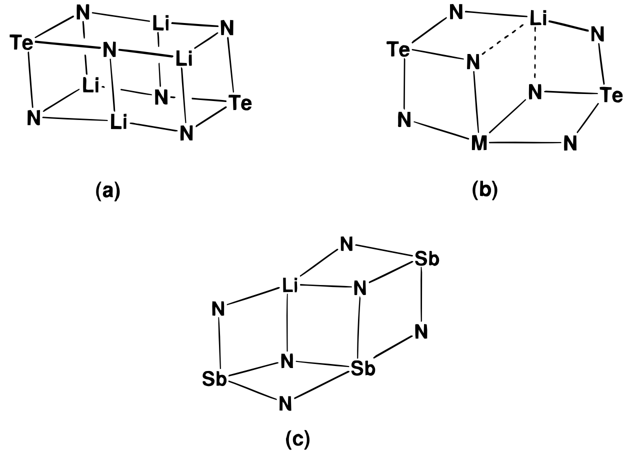

Figure 2. Comparison of the cluster frameworks in (a) {Li$_2$[Te(N^tBu)$_3$]}$_2$,[11] (b) Li{M[Te(N^tBu)$_3$]$_2$} (M = Sb, Bi), and (c) Li[Sb$_3$(cyN)$_4$(NMe$_2$)$_2$].[14] Terminal imido and amido substituents attached to Te and Sb are omitted for clarity.

The structures of **1a** and **1b** can be related to that of {Li$_2$[Te(N^tBu)$_3$]}$_2$[11] by the replacement of three Li$^+$ ions by the M^{3+} ion (Figure 2). Alternatively, the structures can be viewed as two seco heterocubes[13] joined at a common LiNMN face. Thus the core structure is a mirror image of the related antimony complex [LiSb$_3$(Ncy)$_4$(NMe$_2$)$_2$][14] (Figure 2). However, the almost linear geometry at the two-coordinate Li$^+$ ion in **1a** and **1b** (∠N(5)−Li(1)−N(6) = 173.2(8)° and 169.2(7)°, respectively) represents a significant difference from the four-coordinate geometry of the Li$^+$ center in the Sb$_3$ complex.[14]

In summary, the synthesis and structural characterization of {M[Te(N^tBu)$_3$]$_2$}$^-$, the first homoleptic complexes of the pyramidal [E(N^tBu)$_3$]$^{2-}$ dianion (E = S, Se, Te), indicate that the trisimido tellurite is a more promising ligand than its lighter chalcogen congeners for the development of the coordination chemistry of these novel, tripodal ligands.

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

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