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Pyramidal Tellurite Ions Te(N^{t}Bu)$_2$(E^{t}Bu)$^-$ (E = O, NH): Syntheses and Structures of [K(THF)Te(N^{t}Bu)$_2$(O^{t}Bu)]$_2$ and {[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]$_2$LiCl}$_2$

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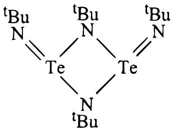
Tellurium compounds often exhibit unique structures and/or reactivities compared to their sulfur (or selenium) analogues.[1] For example, sulfur(IV) diimides RN═S═NR exist as monomers, usually in a *cis,trans* conformation,[2] whereas the corresponding tellurium diimides are dimers, e.g. (^{t}BuN)Te(μ-N^{t}Bu)$_2$Te(N^{t}Bu), **1**,[3] in both the solid state and in solution.



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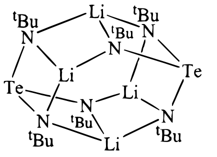

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Sulfur(IV) diimides undergo quantitative adduct formation with R′Li reagents to give dimeric sulfinimidamides {[RNS(R′)NR]Li}$_2$.[4] By contrast, the dimer **1** reacts with PhLi or, preferably, ^{t}BuNHLi to give the Te$_2$N$_6$Li$_4$ cage **2**,[5] which contains the pyramidal tris(*tert*-butylimido)tellurite ion Te(N^{t}Bu)$_3$$^{2-}$. This dianion is a versatile building block for the construction of Te−N heterocycles containing main group elements[5] or transition metals.[6] We now report simple, high-yield syntheses of the novel, isoelectronic monoanions Te(N^{t}Bu)$_2$(O^{t}Bu)$^-$ and Te(N^{t}Bu)$_2$(NH^{t}Bu)$^-$ in the complexes [K(THF)Te(N^{t}Bu)$_2$(O^{t}Bu)]$_2$, **3**·2THF, and {[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]$_2$LiCl}$_2$, **4**, respectively.

Complex **3** is obtained as colorless, moisture-sensitive crystals in *ca.* 85% yield by the reaction of **1** with potassium *tert*-butoxide in toluene at −30 °C.[7]

$$^{t}\mathrm{BuNTe}(\mu\text{-N}^{t}\mathrm{Bu})_2\mathrm{TeN}^{t}\mathrm{Bu} + 2\mathrm{KO}^{t}\mathrm{Bu} \rightarrow [\mathrm{KTe}(\mathrm{N}^{t}\mathrm{Bu})_2(\mathrm{O}^{t}\mathrm{Bu})]_2 \quad (1)$$

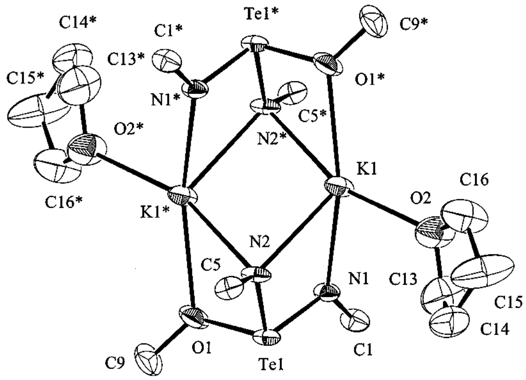
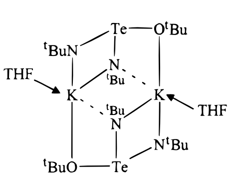
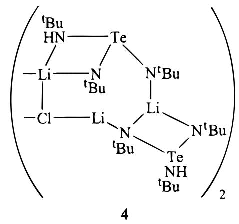


Figure 1. Crystal structure of **3**·2THF. For clarity, only the α-C atoms of ^{t}Bu groups are shown. Selected bond lengths (Å) and bond angles (deg): Te(1)−O(1) 2.049(5), Te(1)−N(1) 1.914(5), Te(1)−N(2) 1.916(5), K(1)−O(1)* 2.785(5), K(1)−O(2) 2.728(6), K(1)−N(1) 2.815(5), K(1)−N(2) 2.764(6); O(1)−Te(1)−N(1) 98.7(2), O(1)−Te(1)−N(2) 97.5(2), N(1)−Te(1)−N(2) 93.1(2). Asterisks indicate atoms related by symmetry: −*x*, −*y*, −*z*.



3·(THF)$_2$



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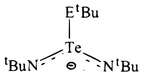

5a (E = O)
5b (E = NH)

The ^{1}H NMR spectrum of an aliquot of the reaction mixture at 23 °C showed only two singlets at δ 1.54 and 1.27 (relative intensities 2:1), indicating the quantitative formation of **3**. An EI mass spectrum (70 eV) of **3** showed a cluster of molecular ion peaks centered at *m/e* = 764, consistent with a dimeric structure in the solid state. Crystallographic-quality crystals of **3** were obtained as a THF adduct.[8] The X-ray structure determination of **3**·2THF showed it to be a centrosymmetric dimer in which the Te(N^{t}Bu)$_2$(O^{t}Bu)$^-$ anions engage in almost symmetrical N,N′-chelation to one K$^+$ ion (Figure 1). The average K−N distance of 2.790 Å is slightly shorter than the value of 2.854 Å found for [{(cyNLi)$_3$Sb}$_2$(^{t}BuOK)$_3$·xC$_6$H$_5$CH$_3$].[9] The O^{t}Bu group forms a bridge to the other K$^+$ ion,

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(6) Chivers, T.; Gao, X. Unpublished results.

(7) A solution of ^{t}BuOK (0.114 g, 1.02 mmol) in toluene (15 mL) was added to a dark orange solution of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (0.275 g, 0.510 mmol) in toluene (20 mL) at −30 °C. The reaction mixture was allowed to reach 23 °C, forming a yellow solution. THF (1 mL) was then added to the solution, and after 30 min of stirring, solvent was removed under vacuum. The solid residue was recrystallized from a small volume (ca. 3 mL) of hexanes to give large colorless crystals of [K(THF)Te(N^{t}Bu)$_2$(O^{t}Bu)]$_2$, which were washed quickly with cold pentane (−30 °C) and dried under vacuum. Yield: 0.395 g, 87%. ^{1}H NMR (C$_6$D$_6$, 23 °C): δ 3.58 (m, 4H), 1.54 (s, 18H), 1.41 (m, 4H), 1.26 (s, 9H). Anal. Calcd for C$_{16}$H$_{35}$N$_2$O$_2$KTe: C, 42.31; H, 7.77; N, 6.17. Found: C, 42.15; H, 7.39; N, 6.02.

(8) Crystal data for **3**: C$_{16}$H$_{35}$N$_2$O$_2$KTe, M_r = 454.16, triclinic, space group $P\bar{1}$ (No. 2), a = 10.851(5) Å, b = 11.664(5) Å, c = 10.414(6) Å, α = 107.81(2)°, β = 116.31(3)°, γ = 92.00(3)°, V = 1102(1) Å^3, Z = 2, ρ_{calcd} = 1.368 g cm^{-3}, F(000) = 464, λ = 0.710 69 Å, T = −103 °C, μ(Mo Kα) = 15.46 cm^{-1}. Data were collected by the $\omega-2\theta$ method on a Rigaku AFC6S diffractometer on a colorless prismatic crystal (0.60 × 0.60 × 0.30 mm) mounted on a glass fiber and coated with epoxy. Of a total of 3911 collected reflections, 3393 were observed [$I > 3.00\sigma_I$]. The structure was solved by Fourier techniques (DIRDIF94, P. T. Beurskens et al., University of Nijmegen, The Netherlands). The data were corrected for absorption, Lorentz, and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Refinement by full-matrix least-squares calculations converged at R = 0.051 and R_w = 0.050. All calculations for **3** and **4** were performed using the teXsan crystallographic package of the Molecular Structure Corp.

(9) Barr, D.; Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Rennie, M.-A.; Russell, C. A.; Wright, D. S. *Angew. Chem.* **1995**, *107*, 1088; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1012.

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and the coordination sphere of the K^+ ions is completed by a THF molecule. There is also a weak interaction between K(1) and N(2)* [2.991(6) Å]. The $Te(N^tBu)_2(O^tBu)^-$ anions in **3**·2THF adopt a distorted pyramidal geometry with bond angles in the range 93.1(2)−98.7(2)°, a Te−O bond length of 2.049(5) Å, and a mean Te−N distance of 1.915(5) Å [*cf.* |*d*(Te−N)| = 1.980 Å for the $Te(N^tBu)_3^{2-}$ anion in **2**],[5] consistent with the resonance hybrid **5a** (Te lone pair omitted). The reactions of sulfur diimides RN=S=NR with alkoxides appear to have been investigated only for R = SO_2R', and the pyramidal monomeric anion $S(NSO_2CF_3)_2(OEt)^-$ has been structurally characterized as the Na^+ salt.[10]

Complex **4** is isolated as yellow, moisture-sensitive crystals in >90% yield by the treatment of a solution of **2** in toluene with dry HCl gas at −78 °C.[11] The anion $Te(N^tBu)_2(NH^tBu)^-$, **5b**, isoelectronic with **5a**, is also generated as an intermediate in the formation of cluster **2** from the treatment of dimer **1** with $LiNH^tBu$. However, even with a 1:2 molar ratio of reactants, this reaction leads to the formation of a mixture of **5b** and **2** (^1H NMR). Consequently, the following reaction is superior for the preparation of the monoanion **5b:**

$$2[Li_2Te(N^tBu)_3]_2 + 4HCl(g) \rightarrow \{[LiTe(N^tBu)_2(NH^tBu)]_2{\cdot}LiCl\}_2 + 2LiCl \quad (2)$$

The X-ray structure of **4** revealed a centrosymmetric molecule in which each half of the dimer consists of two $Te(N^tBu)_2(NH^tBu)^-$ anions (and their associated Li^+ cations) and a molecule of LiCl (see Figure 2).[12] The trapping of a LiCl molecule in a (dialkylamino)lithium structure was reported recently for $(^iPr_2NLi)_2LiCl(TMEDA)_2$.[13] Like the isoelectronic $Te(N^tBu)_2(O^tBu)^-$ ion in **3**, the two $Te(N^tBu)_2(NH^tBu)^-$ ions in **4** exhibit one long Te−N bond [2.069(6) and 2.046(6) Å] and two short Te−N bonds [mean values 1.938(5) and 1.949(5) Å], consistent with the resonance hybrid **5b**. The two $Te(N^tBu)_2(NH^tBu)^-$ anions in each half of **4** coordinate in different manners to the lithium cations. This discrepancy is manifested most obviously by the involvement of the ^tBuNH group [N(6)] of one anion in coordination to lithium, and as a consequence, the ranges of NTeN bond angles for the two pyramidal anions are markedly different [91.8(2)−95.0(2)° for Te(1) vs 86.4(2)−105.7(2)° for Te(2)]. Two-, three-, and four-coordinate lithium ions are observed in the structure of **4**, with mean Li−N bond lengths 2.04(1), 2.03(1), and 2.10(1) Å, respectively. The first two values appear to contradict the usual trend of increasing Li−N bond distances with an increase in the coordination number of Li.[14] The mean Li−Cl distance in **4** is 2.38(1) Å; *cf.* |*d*(Li−Cl)| = 2.408(3) Å for $(^iPr_2NLi)_2LiCl(TMEDA)_2$.[13]

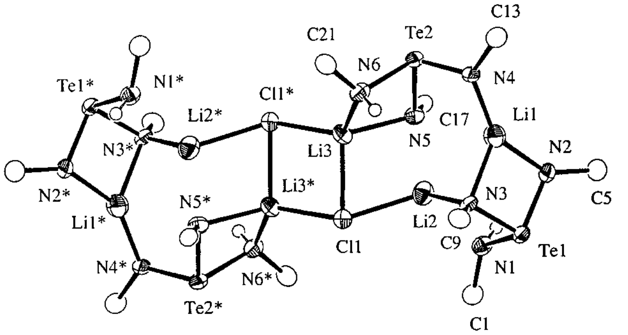

Figure 2. Crystal structure of **4**. For clarity, only the α-C atoms of ^tBu groups are shown. Selected bond lengths (Å) and bond angles (deg): Te(1)−N(1) 2.069(6), Te(1)−N(2) 1.939(5), Te(1)−N(3) 1.937(5), Te(2)−N(4) 1.935(5), Te(2)−N(5) 1.963(5), Te(2)−N(6) 2.046(6), Li(1)−N(2) 1.99(1), Li(1)−N(3) 2.13(1), Li(1)−N(4) 1.97(1), Li(2)−N(3) 2.04(1), Li(3)−N(5) 2.13(1), Li(3)−N(6) 2.08(1), Li(2)−Cl(1) 2.36(1), Li(3)−Cl(1) 2.37(1), Li(3)*−Cl(1) 2.40(1). Li(2)−Cl(1)−Li(3) 72.6(4), Li(3)−Cl(1)−Li(3)* 81.0(4), Li(2)−Cl(1)−Li(3)* 140.5(4). Asterisks indicate atoms related by symmetry: −*x* + 1, −*y*, −*z*.

The ^1H and ^7Li NMR data for **4** indicate a fluxional structure in C_7D_8 solution. Even at 200 K, the ^1H NMR spectrum does not distinguish between the two types of $Te(N^tBu)_2(NH^tBu)^-$ anions that are apparent in the solid-state structure. Three equally intense singlets at δ 1.68, 1.47, and 1.35, corresponding to three inequivalent N^tBu groups, are observed in addition to a broad singlet at δ 2.09 (N*H*). The resonances at δ 1.68 and 1.47 collapse to give a single resonance at δ 1.54 upon warming. At 185 K, the ^7Li NMR spectrum exhibits two sharp singlets at δ 2.75 and 1.18 (reference 1 M $LiClO_4$ in D_2O) with relative intensities of 1:2. When the sample is warmed to 300 K, these two signals collapse to give one resonance at δ 2.29. All changes in the NMR spectra are reversible. Further details and a possible mechanism for this fluxional process will be presented in the full paper.

The facile, high-yield syntheses of **3** and **4** provide an excellent source of $Te(N^tBu)_2(E^tBu)^-$ (E = O, NH), which provide a monoanionic alternative to $Te(N^tBu)_3^{2-}$ for the incorporation of other main group elements into Te−N rings and cages.[5] The multifarious ligand behavior of the trithiotellurite ion (TeS_3^{2-}) was demonstrated recently.[15] These novel imidotellurite analogues are also potentially versatile ligands.

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Supporting Information Available: Tables listing experimental details of X-ray structural determinations, crystal data, positional parameters, bond distances, bond angles, torsion angles, and thermal parameters (23 pages). Ordering information is given on any current masthead page.

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(11) Dry HCl gas (10.7 mL at 23 °C, 1 atm, 0.440 mmol) was added slowly from a gastight syringe to a stirred solution of $[Li_2Te(N^tBu)_3]_2$[5] (0.156 g, 0.220 mmol) in toluene (30 mL) at −78 °C. The pale yellow solution was allowed to reach 23 °C, and a small amount of LiCl was removed by filtration. Solvent was removed under vacuum, and the residue was washed with hexanes (2 × 10 mL) to give $\{[LiTe(N^tBu)_2(NH^tBu)]_2LiCl\}_2$ (0.148 g, 91%) as yellow crystals. Analytical samples and crystals of **4** suitable for an X-ray structural determination were obtained by recrystallization from toluene. Anal. Calcd for $C_{25}H_{56}ClLi_3N_6Te_2$: C, 38.94; H, 7.63; N, 11.35. Found: C, 38.67; H, 7.55; N, 11.44.

(12) Crystal data for **4**: $C_{24}H_{56}ClLi_3N_6Te_2$, $M_r = 740.22$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.973(3)$ Å, $b = 15.751(4)$ Å, $c = 10.891(2)$ Å, $\alpha = 98.14(2)°$, $\beta = 102.71(2)°$, $\gamma = 77.82(2)°$, $V = 1785.9(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.376$ g cm^{-3}, $F(000) = 744$, $\lambda = 0.710\,69$ Å, $T = -123$ °C, μ(Mo Kα) = 17.28 cm^{-1}. A yellow plate of **4** (0.60 × 0.32 × 0.08 mm) was mounted in a glass capillary. Of a total of 6317 collected reflections, 3996 were observed [$I > 3.00\sigma_I$]. The structure was solved by the heavy atom method (DIRDIF94). The data were corrected for absorption, Lorentz, and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to C atoms were included at geometrically idealized positions with C−H = 0.95 Å, while those on N atoms were located from a difference map and were not refined. Refinement by full-matrix least-squares calculations converged at $R = 0.037$ and $R_w = 0.037$.

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