A New Coordination Mode for the Tripodal $[Te(NtBu)_3]^{2-}$ Dianion: Preparation and Structures of $\{ClIn[Te(NtBu)_3]\}_2$ and $\{LiIn[Te(NtBu)_3]_2\}\cdot LiCl$

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The complexes $\{ClIn[Te(NtBu)_3]\}_2$ (**1**) and $\{LiIn[Te(NtBu)_3]_2\}\cdot LiCl$ (**2**) are formed from the reaction of $InCl_3$ (or InCl) with $\{Li_2[Te(NtBu)_3]\}_2$ in toluene. The $[Te(NtBu)_3]^{2-}$ dianions in the centrosymmetric dimer **1** act as tridentate [bis(*N*,*N′*-monodentate), μ_2-*N′′*] ligands bridging two indium atoms. Complex **2** involves a spirocyclic indium centre bis(*N*,*N′*-chelated) by two $[Te(NtBu)_3]^{2-}$ ions.

Introduction

The pyramidal tris(imido) chalcogenite anions $[E(NtBu)_3]^{2-}$ (E = S, Se, Te),[1–3] isoelectronic with EO_3^{2-}, are potentially interesting tridentate ligands.[4] The tellurium congener $[Te(NtBu)_3]^{2-}$ acts as an *N*,*N′*-bidentate ligand in $PhB(\mu\text{-}NtBu)_2TeNtBu$[1] and in the anions $[M(\mu\text{-}NtBu)_2TeNtBu]^-$ (M = Sb, Bi).[5] The formation of coordination complexes is often accompanied by redox processes.[1,6,7] For example, the reaction of $[Te(NtBu)_3]^{2-}$ with $PhPCl_2$ produces the spirocycle $Te[(\mu\text{-}NtBu)_2P(Ph)NtBu]_2$, formally a tellurium(IV) complex of the $[PhP(NtBu)_3]^{2-}$ dianion, and elemental tellurium.[1] More dramatically, the stannatellurone $[tBuNSn(\mu\text{-}NtBu)_2TeNtBu](\mu_3\text{-}SnTe)$ is produced from $[Te(NtBu)_3]^{2-}$ and $SnCl_2$.[8] We report here the synthesis and structures of the neutral, dimeric complex $\{ClIn[Te(NtBu)_3]\}_2$ (**1**), in which the $[Te(NtBu)_3]^{2-}$ dianion adopts a novel, tridentate bonding mode, and the lithium chloride adduct $\{LiIn[Te(NtBu)_3]_2\}\cdot LiCl$ (**2**) with a spirocyclic indium centre.

Results and Discussion

Synthesis

The reaction of $\{Li_2[Te(NtBu)_3]\}_2$ with indium trichloride produces two complexes $\{Cl[InTe(NtBu)_3]\}_2$ (**1**) and $\{LiIn[Te(NtBu)_3]_2\}\cdot LiCl$ (**2**) as extremely moisture-sensitive, yellow solids. The relative amounts of **1** and **2** are determined by the stoichiometry. Thus, **1** is obtained in ca. 60% yield from the 1:2 reaction [Equation (1)] while **2** is best prepared by using a 2:3 stoichiometry. The separation of **1** and **2** is difficult because of their similar solubilities, but **2** may be isolated in modest yields by fractional crystallization from benzene.

$$\{Li_2[Te(NtBu)_3]\}_2 + 2\,InCl_3 \rightarrow \{Cl[InTe(NtBu)_3]\}_2 + 4\,LiCl \quad (1)$$

Complex **1** may also be obtained (ca. 65% yield with respect to Te) from the reaction of $\{Li_2Te(NtBu)_3\}_2$ with indium monochloride. However, this process is inefficient with respect to the use of indium, $^2/_3$ of which is reduced to In metal [Equation (2)].

$$\{Li_2[Te(NtBu)_3]\}_2 + 6\,InCl \rightarrow \{Cl[InTe(NtBu)_3]\}_2 + 4\,In + 4\,LiCl \quad (2)$$

Complexes **1** and **2** were characterised by multinuclear (^1H, ^{13}C, ^{125}Te, ^7Li) NMR spectra. However, the ^1H NMR spectra were structurally uninformative. Thus, both **1** and **2** exhibit singlets at $\delta = 1.558$ and 1.407 ppm, respectively, in $[D_8]THF$ at 23 °C indicative of fluxional processes. These resonances broaden upon lowering the temperature, but resolution of these signals was precluded by the low solubility of **1** and **2** at low temperature.

X-ray Crystal Structures of 1 and 2

An X-ray crystallographic study revealed that **1** is a centrosymmetric dimer with a "deck-chair" structure (Figure 1).[9] As illustrated in Scheme 1, the dimer **1** may be viewed to form by association of the putative monomer $ClIn(\mu\text{-}NtBu)_2TeNtBu$, cf. $PhB(\mu\text{-}NtBu)_2TeNtBu$.[1] The $[Te(NtBu)_3]^{2-}$ dianion in **1** behaves as a tridentate ligand. Two of the nitrogen atoms, N(2) and N(3), are coordinated in a monodentate fashion to different indium atoms, while the third [N(3)] bridges those two indium atoms. Selected bond lengths and angles are given in the Figure caption. The mean Te–N bond length of 198.2 pm may be compared with the values of 208.1 and 187.8 pm for the bridging and terminal Te–N bonds, respectively, in $PhB(\mu\text{-}NtBu)_2TeNtBu$.[1] The Te–N bond length involving the

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bridging (four-coordinate) nitrogen atom is slightly longer (by ca. 4 pm) than those involving three-coordinate nitrogen atoms. The geometry about the indium atom is a highly distorted trigonal bipyramid. The mean axial In−N bond length of 215.4(3) pm is significantly shorter than the mean value of 223.7 pm observed for the related five-coordinate monomeric complex $[CyNC(tBu)NCy]_2InCl$.[10] There is a large disparity in the bridging In−N bond lengths of the four-membered In_2N_2 ring. The In−N(1) distance of 220.5(3) pm is in the range reported for five-coordinate indium,[10,11] whereas the In−N(1)* separation of 250.9(3) pm is typical of a long-range intramolecular interaction.[12] This disparity leads to a substantial difference in the geometries of the two InN_2Te rings. The distortion of the tbp geometry is reflected in the bond angles at the indium centre. The axial bond angle N−In−N of 157.14(13)° deviates substantially from linearity. The sum of the bond angles in the equatorial plane is ca. 359°, but there is a notable difference between the values of Cl−In−N(1) and Cl−In−N(1)*, 164.89(8) and 110.19(9)°. The In−Cl distance of 2.4464(13) Å is slightly longer than the values of 2.383(9) and 2.405(1) Å found for related five-coordinate complexes,[10,11] probably as a result of weak Te···Cl interactions [374.67(13) pm, cf. sum of the van der Waals radii is 381[13a] or 400 pm],[13b] which give rise to a tetrameric array of dimeric molecules in the unit cell.

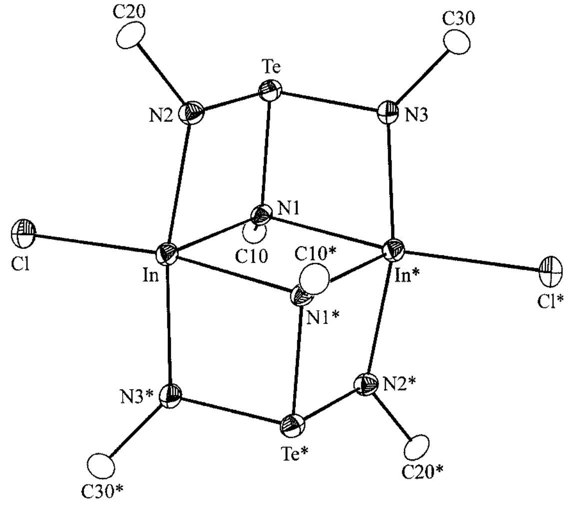
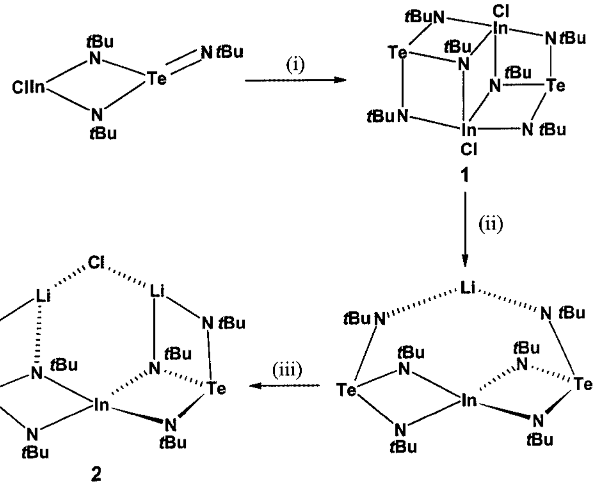


Figure 1. ORTEP diagram (30% probability ellipsoids) for **1**; only the α-carbon atoms of *t*Bu groups are shown; selected bond lengths [pm] and bond angles [°]: Te−N(1) 201.0(3), Te−N(2) 197.3(3), Te−N(3) 196.3(4), In−N(1) 220.5(3), In−N(1)* 250.9(3), In−N(2) 217.3(3), In−N(3)* 213.5(3), In−Cl 244.64(13); N(2)−In−N(3)* 157.14(3), N(1)−In−Cl 110.19(9), N(1)−In−N(1)* 84.90(12), Cl−In−N(1)* 164.89(8); symmetry transformations used to generate equivalent atoms: *: $-x + 1$, $-y$, $-z$



Scheme 1. (i) Dimerization, (ii) $\{Li_2[Te(NtBu)_3]\}_2$, (iii) incorporation of LiCl

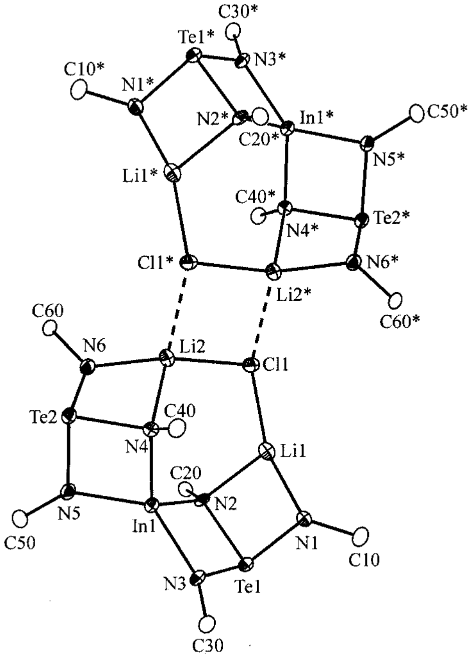


Figure 2. ORTEP diagram (30% probability ellipsoids) for **2** showing the intermolecular Li···Cl interactions; only the α-carbon atoms of *t*Bu groups are shown; symmetry transformations used to generate equivalent atoms: *: $-x + 2$, $-y + 1$, $-z + 1$; selected bond lengths [pm] and bond angles [°]: $|Te-N_{endo}|$ 199.2(3), $|Te-N_{exo}|$ 191.8(1), $|In-N_{axial}|$ 216(1), $|In-N_{eq}|$ 208(1), Li−N 195.0(16)−218.4(16), Li(1)−Cl(1) 220.3(15), Li(2)−Cl(1) 238.1(13); N(2)−In(1)−N(3) 77.3(2), N(2)−In(1)−N(5) 130.9(3), N(3)−In(1)−N(5) 131.4(3), N(5)−In(1)−N(4) 78.2(2), N(3)−In(1)−N(4) 131.2(2), N(2)−In(1)−N(4) 114.4(2)

An X-ray analysis revealed that $\{Li\{In[Te(NtBu)_3]_2\}\}\cdot LiCl$ (**2**) is a centrosymmetric dimer (Figure 2). Important structural parameters are given in the Figure caption. Each monomeric unit consists of an indium centre bis(*N*,*N'*-chelated) by two $[Te(NtBu)_3]^{2-}$ dianions in a distorted tetrahedral arrangement. Charge balance is provided by an Li^+ counterion. In addition, one molecule of LiCl is incorporated into the structure so that an $[Li-Cl-Li]^+$ unit bridges the spirocyclic $\{In[Te(NtBu)_3]_2\}^-$ anion, which is *N*,*N'*-chelated to both lithium centres.[14] The asymmetry in this bridge is the result of dimer formation through a weak Li···Cl interaction [Li(2)···Cl(1) = 247.9(3) pm]. A similar dimeric structural arrangement has been reported recently for $[(THF)_2Li_3Cl\{(NtBu)_3\}S]_2$.[15] The spirocyclic structure of **2**, prior to entrapment of LiCl (Scheme 1), is reminiscent of the structures of the group-15 derivatives Li{M[Te(N*t*Bu)$_3$]$_2$} (M = Sb, Bi).[5] However, the bond angles of 84.6(2) and 83.5(3)° subtended at the indium atom are significantly larger than the corresponding bond angles in Li{M[Te(N*t*Bu)$_3$]$_2$} [72.7(3)° (M = Bi) and 75.4(5)° (M = Sb)].[5] The smaller angles presumably reflect the influence of the lone-electron pair located on the group-15 metal atoms. The geometry at the Te atoms is distorted trigonal-pyramidal with a mean Te−N bond length of 196.7(7) pm, cf. $|d(\text{Te}-\text{N})|$ = 197.6(2) pm in {Li$_2$[Te(N*t*Bu)$_3$]}$_2$.[1] As expected, the Li−N and In−N bond lengths involving the four-coordinate nitrogen atoms, N(2) and N(4), are significantly longer than the corresponding bond lengths involving the three-coordinate nitrogen atoms, N(1)/N(6) and N(3)/N(5), respectively. Curiously, however, this disparity is not observed for the Te−N bonds within the TeN$_2$In rings, which are equal within the experimental error.

In summary, complex **1** represents the first example of the bridging tridentate bonding mode [bis(*N*,*N*′-monodentate), μ$_2$-*N*′′] for the [Te(N*t*Bu)$_3$]$^{2-}$ dianion. It is also the first complex of the tris(imidotellurite) dianion that contains an element−halogen bond, which may be utilized for further metathetical reactions.

Experimental Section

General Procedures: Indium(III) chloride and indium(I) chloride (Aldrich, 99.999%) were used as received. {Li$_2$[Te(N*t*Bu)$_3$]}$_2$ was prepared by a literature procedure.[1,14b] Solvents were dried with the appropriate drying agents and distilled onto molecular sieves before use. All reactions and the manipulation of moisture-sensitive products were carried out under argon or under vacuum. ^{1}H NMR spectra were recorded with Bruker ACE 200 and AM 400 spectrometers, and chemical shifts are reported relative to Me$_4$Si in CDCl$_3$. ^{13}C and ^{125}Te NMR spectra were measured with a Bruker AM 400 spectrometer using a 5-mm broadband probe operating at 100.594 and 126.393 MHz, respectively. The samples were externally referenced to K$_2$TeO$_3$ in D$_2$O referred to Me$_2$Te and Me$_4$Si in CDCl$_3$, respectively. Relaxation delays of 3 and 1.5 s were applied for the measurement of the ^{13}C and ^{125}Te NMR spectra, respectively.

Synthesis of {ClIn[Te(N*t*Bu)$_3$]}$_2$ (1): (a) A suspension of InCl$_3$ (0.250 g, 1.128 mmol) in toluene (20 mL) was added to a pale yellow solution of {Li$_2$[Te(N*t*Bu)$_3$]}$_2$ (0.400 g, 0.564 mmol) in toluene (10 mL) at −78 °C. THF (10 mL) was added and the yellow slurry was stirred for 10 min at −78 °C and then allowed to reach 23 °C. After 24 h, the intense yellow solution was filtered and the volatile material was removed from the filtrate under vacuum. The solid residue was extracted with *n*-hexane (10 mL) to give **1** as a pale yellow solid (0.339 g, 0.345 mmol, 61%). ^{1}H NMR ([D$_8$]THF): δ = 1.56 [C(C*H*$_3$)$_3$] ppm. ^{13}C NMR ([D$_8$]THF): δ = 37.4 [C(*C*H$_3$)$_3$], 59.9 [*C*(CH$_3$)$_3$] ppm. ^{125}Te NMR ([D$_8$]THF): δ = 1570.6 ppm. C$_{24}$H$_{54}$Cl$_2$In$_2$N$_6$Te$_2$ (982.47): calcd. C 29.34, H 5.54, N 8.55; found C 28.64, H 5.98, N 8.09; the product was recrystallised from THF to give **1**·(THF)$_{0.5}$: calcd. C 30.66, H 5.74, N 8.25; found C 30.18, H 6.42, N 8.61. **(b)** A solution of {Li$_2$[Te(N*t*Bu)$_3$]}$_2$ (0.110 g, 0.155 mmol) in toluene (10 mL) was added to a suspension of InCl (0.093 g, 0.620 mmol) in THF (10 mL) at 23 °C. The formation of indium metal was observed. After 1.5 h, the volume of the solution was reduced to 4 mL and X-ray quality, yellow crystals of **1** (0.098 g, 0.099 mmol, 64% based on Te) were obtained after 1 d at −20 °C.

Synthesis of {LiIn[Te(N*t*Bu)$_3$]$_2$}·LiCl (2): A suspension of InCl$_3$ (0.169 g, 0.764 mmol) in toluene (10 mL) was added to a pale yellow solution of {Li$_2$[Te(N*t*Bu)$_3$]}$_2$ (0.400 g, 0.563 mmol) in toluene (10 mL) at −78 °C. The suspension was stirred for 15 min at −78 °C and then allowed to reach 23 °C. After 3 h, the yellow solution was filtered and the solvent was removed from the filtrate under vacuum. The solid residue was extracted with *n*-hexane (5 mL) to give **2** as a yellow solid (0.238 g, 0.109 mmol, 19%). ^{1}H NMR (C$_6$D$_6$): δ = 1.29 [C(C*H*$_3$)$_3$, 9 H], 1.38 [C(C*H*$_3$)$_3$, 9 H] ppm. ^{1}H NMR ([D$_8$]THF): δ = 1.41 ppm. ^{13}C NMR ([D$_8$]THF): δ = 38.1 [C(*C*H$_3$)$_3$], 53.7 [*C*(CH$_3$)$_3$] ppm. ^{7}Li NMR ([D$_8$]THF): δ = 2.06 ppm. ^{125}Te NMR ([D$_8$]THF): δ = 1589 ppm. The presence of hexane and small amounts of **1** was evident from the NMR spectra. **2**·(C$_7$H$_{14}$)$_{0.5}$: calcd. C 36.46, H 6.91, N 9.45; found C 35.73, H 7.68, N 9.30.

X-ray Analyses: All measurements were made with a Bruker AXS SMART 1000 CCD. A yellow prismatic crystal of **1** (0.21 × 0.20 × 0.15 mm) was coated with Paratone oil and mounted on a glass fibre. C$_{24}$H$_{54}$Cl$_2$In$_2$N$_6$Te$_2$, *M* = 982.47, monoclinic, space group *P*2$_1$/*n*, *a* = 10.1689(18), *b* = 15.684(3), *c* = 11.874(2) Å, β = 110.650(2)°, *V* = 1768.0(5) Å, *D*$_c$ = 1.845 Mg m^{-3}, *Z* = 2, μ(Mo-*K*$_\alpha$) = 3.095 mm^{-1}, *T* = 193(2) K. Of a total of 5507 collected reflections 3301 were unique and 2771 had $I > 2\,\sigma(\text{I})$. The data were corrected for absorption by semi-empirical methods. The structure was solved by direct methods[16] and refined by full-matrix least-squares methods on F^2.[17] A yellow plate-like crystal of **2** (0.21 × 0.16 × 0.10 mm), obtained by fractional crystallization from C$_6$D$_6$, was coated with Paratone oil and mounted on a glass fibre. C$_{24}$H$_{54}$ClInLi$_2$N$_6$Te$_2$, *M* = 846.08, triclinic, space group $P\bar{1}$, *a* = 10.6736(15), *b* = 13.483(2), *c* = 14.357(2) Å, α = 98.885(3), β = 113.036(2), γ = 106.574(2)°, *V* = 1737.5(4) Å^3, *D*$_c$ = 1.617 Mg m^{-3}, *Z* = 2, μ(Mo-*K*$_\alpha$) = 2.424 mm^{-1}, *T* = 193(2) K. Of a total of 14227 collected reflections 6963 were unique and 4782 had $I \geq 2\,\sigma(I)$. A faced-indexed absorption correction was applied. The structure was solved by the heavy-atom method[18] and refined by full-matrix least-squares methods on F^2.[17] CCDC-183320 (**1**) and -183321 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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