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Pushing the Frontiers of Hard and Soft Scorpionate Chemistry

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The preparation and structure of the first scorpionate complex of a group 16 element, [Te(κ^2-Tm^{Me})$_2$], is reported. It displays square planar geometry at the Te atom and two distinct ligand conformations. In addition, the first pyrazolylborate complex of a group 15 element, [Bi(Tp)$_2$(pzH)Cl], has been synthesized and characterized.

Since its introduction into the chemical catalog in 1966, the hydrotris(pyrazolyl)-borate anion (Tp) has been used extensively in coordination chemistry.[1] Thus far, it has been observed to form complexes with most metals in the periodic table. However, the limit of its capacity to complex to elements would seem to have been reached at tin[2] in the fifth period and lead[3] in the sixth period. Attempts to form new combinations with the elements beyond group 14 have apparently been abandoned in the belief that no stable species could be obtained. Our recent studies on soft analogues of Tp, in particular the hydrotris(methimazolyl)borate anion (Tm^{Me}), have allowed us and other workers to investigate the scorpionate complexes of groups 13,[4] 14,[5c−e] and 15.[5a,e] Two structural motifs[5a] are observed which parallel those observed for the bismuth complexes with Cp^R ligands,[6] while a bent metallocene halide, [(Cp^R)$_2$BiCl] (Figure 1), is also formed.

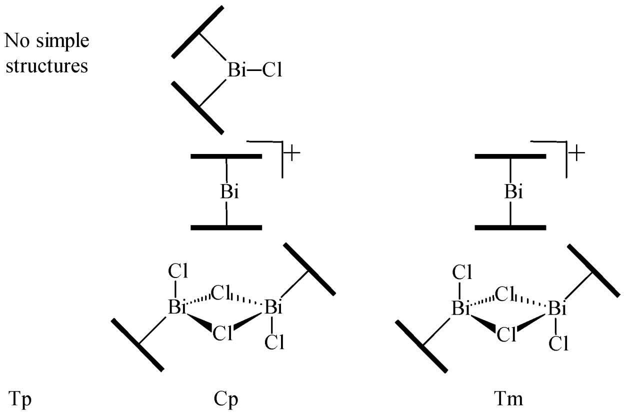

Figure 1. Structural motifs reported for Tp, Cp, and Tm bismuth complexes.[5a,e,6] Cp shares two motifs with Tm; no Tp complexes exist.

In the lower main group, the cationic sandwich complexes of Tm^{Me}, [E(κ^3-Tm^{Me})$_2$]$^{n+}$, would seem to be the dominant motif, recurring with tin(IV)[7] and arsenic(III)[7] and in bismuth(III) complexes[5e] of other related soft scorpionates (eq 1). In view of these observations, two questions enticed us. First, given the formation of both Cp and Tm^{Me} complexes of bismuth, could Tp complexes also be formed? Second, could the chemistry of Tm be further extended to group 16? We answer both questions in the affirmative, and in so doing, a number of intriguing aspects of the chemistry of these ligands have become apparent.

$$EX_n + MTm^{Me}{}_{[excess]} \rightarrow [E(Tm^{Me})_2]^{(n-2)+} + 2MX \quad (1)$$

$$n = 3\text{: } E = As^{3+}, Bi^{3+}, \text{“}Tl^{3+}\text{” post oxidation of } Tl^{+}$$

$$n = 4\text{: } E = Sn^{4+}; M = Na, Tl$$

Reaction of [Te(tu)$_4$Cl$_2$] (tu = thiourea)[8] with excess NaTm results in the formation of a stable yellow complex, [Te(κ^2-Tm^{Me})$_2$], the X-ray crystal structure of which indicates that the central tellurium atom lies in a distorted square planar environment (Figure 2) with the Tm^{Me} ligands coordinated in the κ^2-mode. Square planar geometry has been previously observed for tellurium(II) monodentate thione adducts (e.g.,

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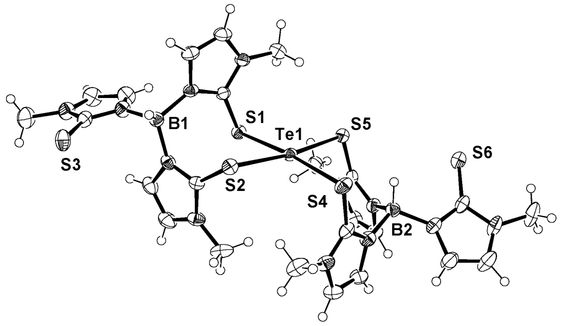

Figure 2. X-ray structure of [Te(κ^2-Tm^{Me})$_2$]. Selected distances (Å) and angles (deg): Te(1)−S(1), 2.5837(9); Te(1)−S(2), 2.7083(10); Te(1)−S(4), 2.8617(10); Te(1)−S(5), 2.6805(10); S(1)−Te(1)−S(2), 86.51(3); S(4)−Te(1)−S(5), 97.79(3); S(1)−Te(1)−S(5), 88.44(3); S(2)−Te(1)−S(4), 87.43(3).

$[Te(L)_4]^{2+}$; L = thiourea[9] ∠S−Te−S; 90.6°, 89.3°, 180°; Te−S, 2.686 Å, 2.690 Å; L = ethylenethiourea[10] 90.2°, 89.3°, 172.1°; Te−S 2.702 Å, 2.654 Å) which are unrestrained by a bridgehead atom.

The most striking structural feature of the complex is the asymmetric disposition of the ligand about the tellurium center. Unusually in Tm^R chemistry two different ligand conformations are observed in the same compound. In one ligand the sulfur atoms adopt a *syn*, *syn*, *syn* conformation with respect to the boron hydride, reminiscent of the arrangement in the uncomplexed Tm^{Me} anion,[11] while in the other ligand they adopt a *syn*, *syn*, *anti* arrangement. Both ligands are coordinated in a bidentate (κ^2) fashion, which is known for Tm^R where R is a bulky group,[12] but this is the first observation of this arrangement for the parent Tm^{Me}. It is also notable that when such bidentate coordination occurs, there is usually a short M···H−B contact, generally described as an agostic interaction,[5c] but in this case no such interaction occurs. The lack of ligand coordination in the axial sites is clearly a result of significant lone pair electron density on tellurium, which serves to repel the electron rich thione sulfurs and the hydridic hydrogens. The ligand conformation also has a marked influence on the tellurium coordination sphere. The all *syn* arrangement of the ligand appears to be far more sterically strained as evidenced by a bite angle of 97.79° and one average (2.68 Å) and one very long (2.86 Å) Te−S distance. The "twisted" ligand conformation on the other hand has a small bite angle (86.51°) and one short (2.58 Å) and one average (2.60 Å) Te−S distance, suggesting a much more energetically favored conformation. It is unclear why both conformations are observed in the solid state, since in the solution NMR spectrum of this compound single, broad resonances due to the ring protons are observed, suggesting significant fluxionality.

In our analysis of the comparative chemistry of Tm^R, Tp, and Cp,[11] we find both a structural homology and structural progression. In view of the structural motifs observed for bismuth Tm^{Me} and Cp complexes (Figure 1) and the recently reported bismuth phthalocyanine structures,[13] we reasoned that a Tp complex of bismuth should also be attainable.

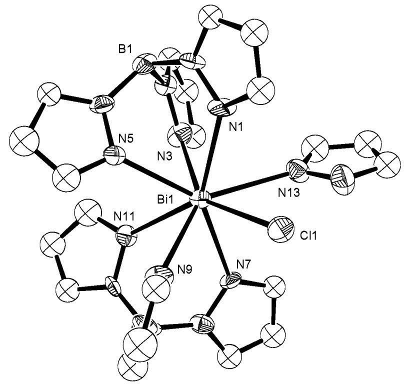

Figure 3. X-ray crystal structure of [Bi(κ^3-Tp)$_2$(pzH)Cl] (pzH = pyrazole). Selected bond distances (Å) and angles (deg): Bi(1)−Cl(1), 2.837(4); Bi(1)−N$_{Tp}$, 2.54 (av); Bi(1)−N(13), 2.80(1); N−Bi(1)−N bite angles in the range 68.7−77.6°.

Treating $BiCl_3$ with a sufficient amount of NaTp in cold (0 °C) acetone leads to the copious formation of elemental bismuth. However, filtration and reduction of the solution volume at low temperature led to the formation of a small number of white crystals and a white powder. X-ray diffraction reveals an eight coordinate geometry for the elusive [Bi(Tp)$_2$(pzH)Cl]. The Tp ligands lie at an angle of ∼46° to one another exposing sites to which the halide and pyrazole coordinate. The free pyrazole is undoubtedly formed as a byproduct of the reduction of Bi^{III} to metallic Bi by the Tp ligand. The various donors are arranged around the central atom at angles which generate minimal distortion consistent with a stereochemically inactive lone pair[3] and indicative of predominantly electrostatic bonding. This contrasts with the six coordinate thiazolylborato complexes of bismuth[5a,e] which display greater covalent character. The species reported here is structurally most similar to the Cp homologue[6b] and, strikingly, the trivalent yttrium complex of Reger et al.[14] Thus, it is instructive that this bismuth−Tp complex adopts the one motif that is absent from soft Tm chemistry (Figure 1) elegantly demonstrating that the combination of metal and ligand character controls the structural outcome.

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Supporting Information Available: Text giving experimental details. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Details of the X-ray crystal structure determinations (226549 and 226550) may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk. Web: http://ccdc.cam.ac.uk.)

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