chemistry with other first-row transition-metal ions. Indeed, ligand L readily affords complexes with Fe, Co, and Cu, the properties of which will be reported later.

The significance of L extends beyond its implications as a specific ligand; both the ease and generality of its synthesis suggest that use of an analogous procedure with suitable bidentate ligands will provide a general and facile route to three dimensionally articulated ligands. This approach may permit the ready synthesis of specific chelating ligands for complexation not only of transition-metal ions but also of main-group metals such as Pb. Work directed toward extensions of this work to other ligands, including those with other types of donor atoms, will be reported shortly.

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Supplementary Material Available: Listings of positional and thermal parameters, interatomic distances and angles, hydrogen atomic coordinates and temperature factors, and anisotropic temperature factors (4 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Teflate ($OTeF_5^-$) as a Unique Ligand for Metal Complexes: Structure of $[TlOTeF_5(1,3,5\text{-}(CH_3)_3C_6H_3)_2]_2$, a Thallium(I) Complex with Neutral Arene Ligands

Sir:

We have been investigating the chemistry of the pentafluoroorthotellurate anion ($OTeF_5^-$, hereafter referred to as teflate) with respect to its use as a ligand for coordination and organometallic compounds. Complexes such as $Mn(CO)_5(OTeF_5)$,[1] $[AgOTeF_5(C_6H_5CH_3)_2]_2$,[2] $Fe(OTeF_5)_3$,[3] and $Pt(OTeF_5)_2(nor)$ (nor = norbornadiene)[4] reveal that the coordinating properties of teflate are quite different than any other anionic ligand including ClO_4^- and $CF_3SO_3^-$.

We find that the stoichiometrically simple compound $TlOTeF_5$[5] is quite soluble in aromatic hydrocarbons (e.g. 0.39 M in toluene at 25 °C). This behavior, while not unprecedented for Tl(I) salts,[6] is not general. For example, we find that $TlClO_4$ is completely insoluble in toluene. The coordination of neutral arenes to Tl(I) was first suggested by Auel and Amma in 1968.[7] They isolated benzene complexes of $TlAlCl_4$ having compositions $TlAlCl_4\cdot{}^1/_2C_6H_6$ and $TlAlCl_4\cdot 2C_6H_6$, which readily lost benzene in the solid state. Quite recently, Schmidbaur et al. have isolated and structurally characterized a mesitylene (mes) complex of $TlGaBr_4$ having the composition $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$.[8] This solid also loses all traces of the weakly bound arene ligands under a nitrogen atmosphere or in vacuo.

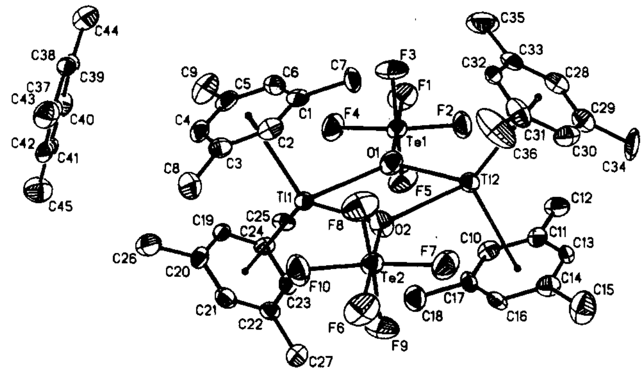

Figure 1. Drawing of the $[TlOTeF_5(mes)_2]_2\cdot mes$ asymmetric unit (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Te1–O1 = 1.780 (8), Te2–O2 = 1.770 (8), Te1–F(av) = 1.848, Te2–F(av) = 1.848; Tl1–O1–Te1 = 125.0 (4), Tl1–O2–Te2 = 121.5 (4), Tl2–O1–Te1 = 123.5 (4), Tl2–O2–Te2 = 127.0 (4), Tl1–O1–Tl2 = 111.4 (3), Tl1–O2–Tl2 = 111.5 (3).

When crystalline solids are isolated from aromatic hydrocarbon solutions of $TlOTeF_5$ and the crystals are dried under a nitrogen atmosphere in the glovebox, $TlOTeF_5$ is recovered unchanged. This very weak affinity of Tl(I) for arene ligands stands in contrast to that of Ag(I): the crystalline solid $[AgOTeF_5(tol)_2]_2$ (tol = toluene) does not liberate toluene even after prolonged vacuum-drying.[2] The weak but finite affinity of Tl(I) for benzene can be seen by titrating solid $TlOTeF_5$ with benzene vapor at 21 °C in a Hg-filled tensimeter.[9] At a mole ratio of benzene/$TlOTeF_5$ of 1/1, 20 Torr of benzene vapor is observed, showing a saturation pressure of 78.8 Torr at the ratio of 2/1 and higher. In sharp contrast to this behavior, solid $TlClO_4$ does not interact with benzene: even at a benzene/$TlClO_4$ ratio of 0.37/1, the total pressure of the mixture was identical with the vapor pressure of pure benzene.

Cooling a mesitylene solution of $TlOTeF_5$ afforded crystals of $[TlOTeF_5(mes)_2]_2\cdot mes$ suitable for study by X-ray diffraction.[10] A view of the asymmetric unit, one dimeric Tl(I) complex and one lattice mesitylene molecule, is shown in Figure 1. The coordination sphere around each thallium atom is pseudotetrahedral, being made up of two oxygen atoms from two bridging teflate groups and two η^6-mesitylene (mes) molecules. Although the complex has no crystallographically imposed symmetry, it is nearly a centrosymmetric dimer having idealized C_{2h} symmetry with the idealized C_2 axis passing through O1 and O2. The four Tl–O bond distances range from 2.69 (1) to 2.72 (1) Å. The O–Tl–O angles are 68.5 (3) and 68.6 (3)° for Tl1 and Tl2, respectively, while the angles formed by the arene centroid–Tl vectors are 118 and 121° for Tl1 and Tl2, respectively.

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(10) At 143 K, the unit cell was triclinic (a = 11.048 (3) Å, b = 14.643 (3) Å, c = 16.345 (4) Å, α = 102.43 (2)°, β = 99.10 (2)°, γ = 92.70 (2)°, V = 2540.6 (7) Å^3, ρ_{calcd} = 1.94 g cm^{-3}, space group $P\bar{1}$, Z = 2). Intensity data (ω (Wyckoff) scans, Mo Kα radiation, graphite monochromator, λ = 0.7107 Å) were collected with a Nicolet R3m/E diffractometer, in the range $4° < 2\theta < 50°$. Of the 8945 reflections measured, 6484 were observed ($|F| > 2.5\sigma(|F|)$) after an empirical absorption correction (μ = 76.1 cm^{-1}, T_{max} = 0.562, T_{min} = 0.409) and Lorentz and polarization corrections. The structure was solved by analysis of the Patterson map. Least-squares refinement (Sheldrick, G. M. SHELXTL Nicolet XRD, 1985) of 595 parameters (positional and anisotropic thermal parameters for all non-hydrogen atoms) yielded R = 0.054, R_w = 0.044, GOF = 1.16, and a normal probability plot with a slope of 1.01. The maximum (1.26 e Å^{-3}) in the final difference electron density map was located less than 0.8 Å from O2; the minimum was −1.46 e Å^{-3}.

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As discussed above, the weak interaction between neutral arenes and Tl(I) has long been documented. Nevertheless, prior to this work the only structurally characterized Tl(I)–neutral arene complex was $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$.[8] This tetrameric compound consists of two $Tl(mes)^+$ and two $Tl(mes)_2^+$ cations bridged in a complicated way by four $GaBr_4^-$ anions. In both types of cations, the mesitylene molecules are η^6 coordinated to Tl(I). The two symmetry-related $Tl(mes)_2^+$ units in $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$ and the two independent $Tl(mes)_2^+$ units in our compound are structurally very similar. If one averages the Tl–C bond distances for each η^6-mesitylene ligand, the values for the $Tl(mes)_2^+$ units in $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$ are 3.32 and 3.34 Å[6] while in $[TlOTeF_5(mes)_2]_2$ they are 3.29, 3.33, 3.38, and 3.39 Å for the mesitylene molecules containing C1, C10, C19, and C28, respectively. The dihedral angles formed by the planes of the mesitylene ligands in each $Tl(mes)_2^+$ unit are 60.5° for $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$,[6] 51.5° for Tl1, and 49.0° for Tl2. The small differences between the two compounds are probably the consequence of the number of anion atoms coordinated to each Tl(I) atom: only two oxygen atoms in $[TlOTeF_5(mes)_2]_2$ vs. four bromine atoms for the $Tl(mes)_2^+$ units in $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$.[6,8]

Although the best description of the arene ligand coordination in $[TlOTeF_5(mes)_2]_2$ is η^6, the Tl–C bond distances for any one mesitylene ligand vary over a range of values. The smallest range involves the ring containing C28 (Tl–C = 3.35 (1)–3.43 (1) Å) while the largest involves the ring containing C10 (Tl–C = 3.13 (1)–3.52 (1) Å). We suggest that this variation is the consequence of nonbonded interactions instead of some intrinsic electronic effect.[11] As in $[Tl_4(mes)_6^{4+}][GaBr_4^-]_4$,[8] no stereochemical activity of the $6s^2$ electron pair is recognizable in the coordination spheres of Tl1 or Tl2.

Along with $[TlOTeF_5(mes)_2]_2$, two other compounds have been shown unambiguously to contain bridging teflates.[2,12] Infrared and Raman spectral data have been used to suggest that other compounds contain $OTeF_5$ groups bonded to more than one metal.[2] The nearly centrosymmetric dimer $[TlOTeF_5(mes)_2]_2$ displays ν(TeO) bands at 820 (IR) and 826 cm^{-1} (Raman). The noncoincidence of IR and Raman ν(TeO) bands for $TlOTeF_5$ implies that this compound also contains bridging teflates in the solid state.[5] While this structural feature is unknown for the vast amount of nonmetal $OTeF_5$ chemistry,[13] it is now apparent that teflate can readily bridge two metals.

In summary, the compound $[TlOTeF_5(mes)_2]_2$ provides an example with which to gauge the variability or constancy of two recently discovered structural features, Tl(I)–arene coordination and bridging $OTeF_5$ groups. The high solubility of $TlOTeF_5$ in aromatic hydrocarbons may be related to structural and/or electronic properties of $OTeF_5^-$ as a ligand.[14-16] We plan to study the structural and chemical properties of a wide range of binary metal teflates.

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Supplementary Material Available: A table of atomic positional parameters and equivalent isotropic thermal parameters for all non-hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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$Fe_7S_6(PEt_3)_4Cl_3$: A Topological Link between the Prismatic and Cuboctahedral Structures of Iron–Sulfur Clusters

Sir:

In addition to the familiar clusters containing the $Fe_2(\mu\text{-}S)_2$ and $Fe_4(\mu_3\text{-}S)_4$ cores,[1] it is now established that there exists a series of iron–sulfur clusters of higher nuclearity, containing six and eight Fe atoms. The rich structural chemistry of such clusters is emerging but has already been made evident by the demonstration of three distinct types of hexanuclear species: $[Fe_6S_6X_6]^{2-,3-}$[2-7] (**1**), $[Fe_6S_8(PEt_3)_6]^{2+}$[8] (**2**), and $[Fe_6S_9(SR)_2]^{4-}$[9-11] (**3**). Types **1** (X = Cl^-, Br^-, I^-, RO^-, RS^-) and **2** contain the prismatic $[Fe_6(\mu_3\text{-}S)_6]^{2+,3+}$ (D_{3d}) and cuboctahedral $[Fe_6(\mu_3\text{-}S)_8]^{2+}$ (O_h) cores, respectively. The $[Fe_6S_9]^{2-}$ core of the clusters **3** is less regular, contains μ-S, μ_3-S, and μ_4-S bridging atoms, and has idealized C_{2v} symmetry. The single example of an octanuclear Fe–S cluster is $[Fe_8S_6I_8]^{3-}$[12] (**4**), which features the cuboctahedral $[Fe_8(\mu_4\text{-}S)_6]^{5+}$ core, very similar to the cores present in $[Co_8S_6(SPh)_8]^{4-,5-}$[13] and $Ni_8S_6(Ph_3P)_6Cl_2$.[14] The last two clusters have the *anti*-M_6S_8 arrangement in that the positions of metal and sulfur atoms are reversed compared to their positions in **2** and other M_6S_8 clusters.[14-17]

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