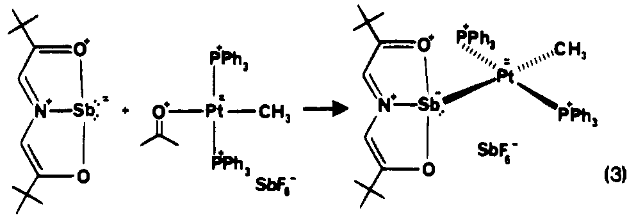
Table I. Bond Lengths and Angles in 3

bond lengths, pm		bond angles, deg	
Sb-O	216.1 (9), 219.2 (10)	O-Sb-O	146.2 (4)
Sb-N	210.3 (12)	N-Sb-O	73.2 (4), 73.3 (4)
C-O	130.0 (2), 128.0 (2)	N-Sb-Pt	118.5 (3)
$C-C_{ring}$	138.0 (2), 137.0 (2)	Sb-Pt-P	89.8 (1), 97.7 (1)
C-N	136.0 (2), 138.0 (2)	P-Pt-C	83.6 (4), 88.8 (4)
Sb-Pt	264.1 (1)	Sb-O-C	115.7 (9), 114.0 (1)
Pt-C	208.0 (2)	C-N-Sb	118.0 (1), 118.0 (1)
Pt-P	230.7 (4), 231.0 (4)	C-C-N	113.0 (1), 112.0 (2)
		C-C-O	118.0 (1), 121.0 (2)

for the ring proton is consistent with the high degree of positive charge in the ligand backbone (as also observed in the spectrum of initial ADSbO). The ^{13}C resonances also exhibit downfield shifts associated with this positive charge still retained in the tridentate ligand on antimony. This is in contrast to what has previously been observed in the metal complexes of ADPO (eq 2).

The reaction of 1 equiv of ADSbO with $(CH_3)_2CO{\cdot}PtCH_3$-(*trans*-$(Ph_3P)_2)^+SbF_6^-$ in ether affords **3** in 30% yield. Complex



10-Sb-3
ADSbO

3

3 is a dark red crystalline solid melting at 221 °C with decomposition.[6] The asymmetry of the molecule is consistent with the nonequivalency of the triphenylphosphines in the $^{31}P\{^1H\}$ NMR resonances at δ 19.4 (apparent dt due to ^{195}Pt satellites, $^2J_{PP}$ = 15.5 Hz, $^1J_{PPt}$ = 2066 Hz) and 37.3 (apparent dt due to ^{195}Pt satellites, $^2J_{PP}$ = 15.5 Hz, $^1J_{PPt}$ = 3041 Hz). The ligand backbone in free ADSbO bears considerable positive charge, as evidenced from multinuclear magnetic resonance spectra.[2] Coordination of the antimony of ADSbO to the platinum cation in **3** further increases the electron demand on the ADSbO backbone and results in a considerable downfield shift in the resonances of the ring protons of the ADSbO moiety in **3** (δ 8.72). These data require the presence of a stereoactive lone pair at the antimony center.

The structure of **3** has been verified by single-crystal X-ray structure determination.[7] The solid-state structure of the complex is illustrated in Figure 1, and pertinent bond distances and angles are given in Table I. There are some slight distortions of the ADSbO moiety upon complexation. The Sb-O bonds increase by about 3 pm, the O-Sb-O angle decreases from 149.6° in free ADSbO to 146.2° in the complex, and finally the Sb-N bond increases about 4 pm in the complex. These changes in bond angles and lengths can be attributed to steric congestion at the platinum center due to the two trans triphenylphosphine ligands although electronic factors may also play a role. It is noteworthy that in spite of the steric congestion the ADSbO system maintains its 10-electron count and planar ligand backbone. ADPO readily forms an adduct with $(CH_3)_2CO{\cdot}PtCH_3$(*trans*-(*p*-$Tol_3P)_2)^+SbF_6^-$ to afford a system in which the phosphorus of the ADPO has rehybridized to an 8-P-4 center resulting in a folded ring system similar to the case of complex **2**.[9]

The structures of these 10-Sb-4 systems are in contrast to that of the ADPO systems, in which the phosphorus switches from a 10-electron center to an 8-electron center upon complexation to the metal. The antimony maintains a high electron count, using one lone pair of electrons for coordination to the metal while the other lone pair remains at the pnictogen and is stereoactive. By contrast, the lighter pnictogen (P) must rehybridize to place a lone pair of electrons in a more directional sp^3 orbital. The (approximate) sp^2 orbitals that contain the lone pairs at heavier pnictogen centers (antimony) achieve sufficient overlap with the orbitals of the metals that there is no need to rehybridize. We are currently studying systems that will utilize both lone pairs of electrons at the heavier pnictogen to bridge transition metals.

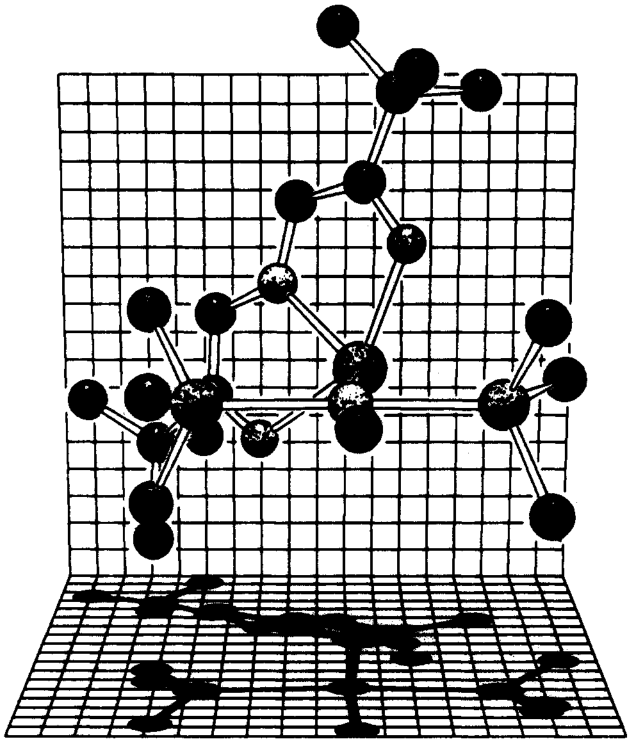


Figure 1. KANVAS[8] drawing of **3**. The hydrogens and all but the *ipso*-carbons of the phenyl rings have been omitted for clarity.

Acknowledgment is made to Dr. David Thorn for helpful discussions and a supply of the bis(triphenylphosphine)methylplatinum and bis(tri-*p*-tolylphosphine)methylplatinum cations.

Registry No. 1, 104130-26-9; 3, 104130-28-1; (COD)PtI_2, 12266-72-7; $PtCH_3$(*trans*-$(Ph_3P)_2)^+SbF_6^-$, 104130-30-5.

Supplementary Material Available: A view of 3, complete description of the X-ray crystallographic structure determination of 3, and tables of experimental details, positional and thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the Nickel(II) Complex of 1,1,1-Tris(((2-(methylthio)ethyl)thio)methyl)ethane, an All-Sulfur Ligand That Promotes Hexakis(thioether) Coordination

Sir:

Prompted by the potential analogy of thioethers to phosphines and by the occurrence of thioether coordination in blue copper proteins,[1] we[2-6] and others[7,8] have recently been investigating the

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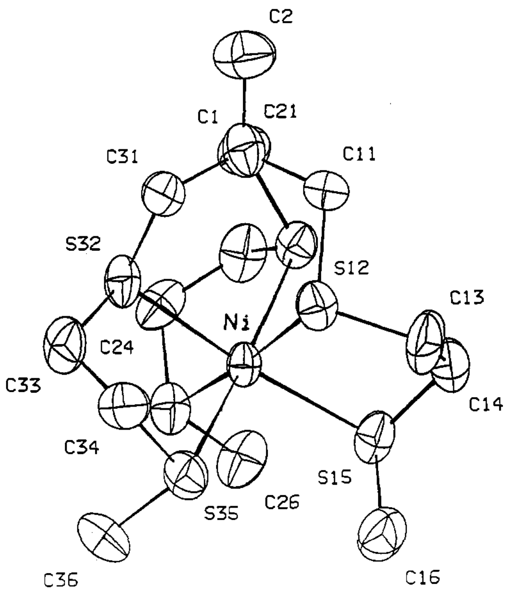
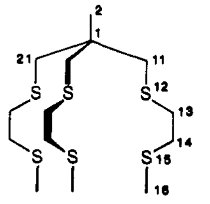


Figure 1. CHEMGRAF drawing of the $[Ni(L)]^{2+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity). Complete atomic numbering for the ligand atoms is shown here and in the drawing of L.

properties of homoleptic hexakis(thioether) complexes of transition-metal ions.[9] Earlier work[2-6] has shown that this new environment can be imposed on transition-metal ions by coordination to crown thioethers and that it induces unusual electronic structure—and therefore perhaps unusual reactivity—on them. Any future applications of homoleptic thioether complexes of crown-type ligands will, however, be hindered by the somewhat involved synthesis of the ligands. We now wish to report our initial work on the preparation and coordination chemistry of 1,1,1-tris(((2-(methylthio)ethyl)thio)methyl)ethane (L) (including the



L

atomic numbering scheme used in the structural work—vide infra), a new ligand that makes the homoleptic hexakis(thioether) environment readily available. Moreover, the synthesis used here may afford a general route into analogous three dimensionally articulated ligands.

Despite the reputed difficulty of S_N2 displacements at neopentyl carbon atoms, the ligand 1,1,1-tris(((2-(methylthio)ethyl)thio)-methyl)ethane (L) is easily synthesized by treatment of an ethanolic solution of sodium 2-(methylthio)ethanethiolate at reflux with a solution of 1,1,1-tris(hydroxymethyl)ethane tritosylate. After being stirred overnight, the colorless solution was evaporated, and the residue was extracted with ether before removal of the solvent to yield the crude product as a colorless oil (yield: 72%). Owing to its high boiling point, the ligand is best purified as its nickel(II) complex. Addition of the ligand to a solution of $[Ni(OH_2)_6](BF_4)_2$ in acetic anhydride immediately yields a violet solution that upon the slow addition of ether deposits violet microcrystals of $[Ni(L)](BF_4)_2$. Anal. Calcd for $C_{14}H_{30}S_6B_2F_8Ni$: C, 26.99; H, 4.86; Ni, 9.42. Found (Oxford microanalytical service): C, 27.52; H, 4.88; Ni, 9.56. Treatment of the complex with water followed by extraction with CH_2Cl_2 yields the free ligand as a viscous liquid. NMR ($CDCl_3$, Me_4Si): δ 1.05 (s) [3 H], 2.10 (s) [9 H], 2.65 (s) [6 H], 2.68 (s) [12 H]. TLC (silica gel, CH_2Cl_2): 0.44. Recrystallization of the nickel(II) complex from CH_3NO_2 yielded prisms suitable for crystallographic studies.[10]

X-ray diffraction reveals that reaction of L with nickel(II) yields a homoleptic hexakis(thioether) Ni(II) complex, the first structurally characterized examples of which were reported only very recently.[2,6,7] The six-coordinate cation has idealized octahedral symmetry (Figure 1), with nickel–sulfur bond distances ranging from 2.397 (2) to 2.436 (2) Å, and an average S–Ni–S bond angle between chelating sulfur atoms of 86.2° (range 85.9 (1)–86.3 (1)°). The trigonal faces at the capped and open ends are 2.65 Å apart, with a trigonal-twist angle between them of 58.3°. Interestingly, all three of the 2,5-dithiahexane "arms" of $[Ni(L)]^{2+}$ adopt the "*ob*" conformation (i.e., the C–C vectors are oblique with respect to the threefold axis of the complex),[11] in contrast to the corresponding Co(II) complex, in which one arm assumes the "*lel*" conformation.[12] The Ni–S distances to the three S atoms at the closed end of the molecule (S12, S22, S32) are 0.03 Å shorter on average (2.40 vs. 2.43 Å) than those to the three (S15, S25, S35) at the open end (Ni–S distances 2.397 (2)–2.415 (2) Å and 2.422 (2)–2.436 (2) Å, respectively). The average Ni–S bond length (2.42 Å) agrees with those found earlier for $Ni(thiodiglycol)_2(Br)_2$ (2.43 Å),[13] and $[Ni(24S6)]^{2+}$ (2.43 Å),[6,14] in contrast to the significantly smaller average value of 2.38 Å found for $[Ni(18S6)]^{2+}$ [2] and $[Ni(9S3)_2]^{2+}$.[7]

Bond angles at the carbon atoms at both the bridgehead and the methylene groups adjacent to it show that the ligand suffers relatively little strain upon coordination to Ni(II). Bridgehead bond angles from the unique methyl group to the three methylene groups (i.e., ∠C2–C1–(C11,C21,C31)) are all essentially 107° (within 0.2°); similarly, bridgehead bond angles between methylene groups (e.g., ∠C11–C1–C21) are all within a degree of 111.5°. The bond angles at the methylene groups (e.g., ∠C1–C11–S12) show greater deviation from tetrahedral values: they range from 113.9 (5) to 115.9 (6)°. Taken collectively, these small deformations of L upon coordination augur well for its coordination

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(10) Crystal data: (1,1,1-tris(((2-(methylthio)ethyl)thio)methyl)ethane)-nickel(II) tetrafluoroborate, $C_{14}H_{30}S_6B_2F_8Ni$, M_r 623.06, monoclinic, space group $P2_1/n$, $a = 10.062$ (2) Å, $b = 14.348$ (2) Å, $c = 17.337$ (2) Å, $\beta = 91.72$ (1)°, $Z = 4$, $d_{calcd} = 1.65$ g/cm³. A crystal (0.33 × 0.35 × 0.33 mm) was sealed in an X-ray capillary under nitrogen for crystallographic studies. An Enraf Nonius CAD4 diffractometer with Mo Kα radiation (0.71069 Å) was used in the ω–2θ mode for collection of 4362 unique data (excluding systematic absences) with $2\theta \leq 52°$. Four standard reflections that were measured every hour showed no decay. Calculations were performed with the CRYSTALS crystallographic programs on a VAX 11/750 computer, with atomic scattering factors from the usual source. The Ni atom was found by Patterson synthesis, and the remaining atoms were found by Fourier difference syntheses and full-matrix least-squares refinement based on 1998 data with $I > 3\sigma(I)$. At convergence $R = 3.62\%$ ($R_w = 3.85\%$) for 279 parameters, where $R = \sum(||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and $w = 1/\sigma^2F$. Tables of positional and thermal parameters are available as supplementary material.

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(14) Abbreviations used in this paper are as follows: 9S3, 1,4,7-trithiacyclononane (trithia-9-crown-3); 18S6, 1,4,7,10,13,16-hexathiacycloeicosane (hexathia-18-crown-6).

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.

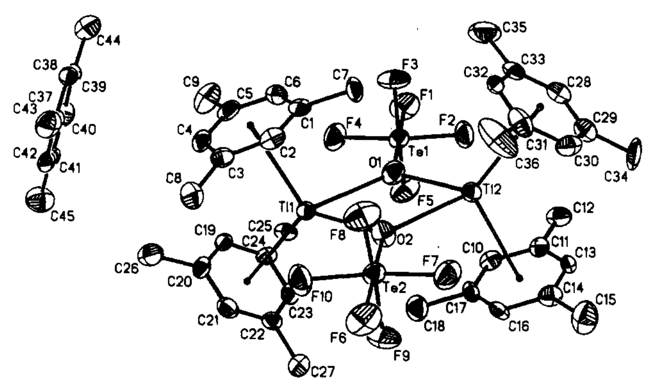

Figure 1. Drawing of the $[TlOTeF_5(mes)_2]_2\cdot$mes asymmetric unit (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Te1–O1 = 1.780 (8), Te2–O2 = 1.770 (8), Te1–F(av) = 1.848, Te2–F(av) = 1.848; Tl1–O1–Te1 = 125.0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