$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ as a Metalloligand toward Main-Group Lewis Acids. A "Mexican-Hat-like" Structure for $[Pt_2Tl(\mu_3\text{-}S)_2(PPh_3)_4]X$ ($X = NO_3$, PF_6) with a Two-Coordinate Angular Tl(I)

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Introduction

The ability of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to function as a metalloligand in the synthesis of polynuclear heterometallic aggregates is well-known.[1] The nuclearity of the resultant complexes and the coordination modes of their sulfur center are governed largely by the local geometry of the heterometal, M. The flexible hinge angle of the two Pt(II) planes and the variable S···S nonbonding separation promote the stabilization of varied geometries of M (Figure 1). Among the known examples, only the Ag(I) complex[2] consists of a "naked" heterometal with no subsidiary ligands, and none of the complexes contain an M angularly bridging between both sulfur sites. The present note describes such an unusual structure found in $[Pt_2Tl(\mu_3\text{-}S)_2(PPh_3)_4]X$ ($X = NO_3, PF_6$). This, for the first time, shows the ligating ability of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ toward a Lewis acid of a main group element.

Results and Discussion

Treating $TlNO_3$ with an equimolar quantity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ followed by metathesis with NH_4PF_6 gave the title heterometallics. Conductivity measurements of both salts indicated an 1:1 electrolyte. The infrared spectrum confirmed the uncoordinated NO_3^- in the solid-state structure. The ^{31}P NMR spectrum suggested the chemical equivalence of all the phosphines and rejected a formula such as $[Pt_2(\mu\text{-}STl)(\mu\text{-}S)(PPh_3)_4]X$, which would be isostructural with $[Pt_2(\mu\text{-}SR)(\mu\text{-}S)(PPh_3)_4]X$ ($R = CH_3$, CH_2Cl, $CHCl_2$).[3] Similar tests on the PF_6^- salt suggested it to be isomorphous with the NO_3^- complex.

Since the complex nuclearity and the local geometry of the Tl(I) site are unclear, a single crystal X-ray diffraction study was carried out on the PF_6^- complex. It revealed a very unusual "Mexican-hat-like" structure with the Tl atom occupying the tip of the hat capping symmetrically between the sulfur centers of the $\{Pt_2S_2\}$ metalloligand (Figure 2a). The Tl as a result lies on the crystallographically imposed C_2 axis of the complex.

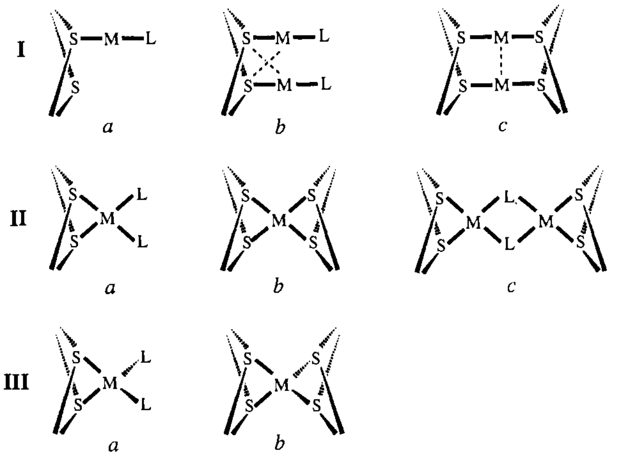

Figure 1. Coordination modes of the sulfur ligands of $\{PtS_2(PPh_3)_4\}$ in some representative polynuclear heterometallic aggregate complexes. Type I: linear heterometal M, e.g. (a) $[(S\text{–}S)Au(PPh_3)]^+$, (b) $[(S\text{–}S)(AuCl)_2]$, and (c) $[(S\text{–}S)_2Ag_2]^{2+}$. Type II: square planar M, e.g. (a) $[(S\text{–}S)Rh(CO)_2]^+$, (b) $[(S\text{–}S)_2Pd]^{2+}$, and (c) $[(S\text{–}S)_2Pd_2(\mu\text{-}Cl)_2]^{2+}$. Type III: tetrahedral M, e.g. (a) $[(S\text{–}S)Ni(dppp)]^{2+}$ and (b) $[(S\text{–}S)_2Hg]^{2+}$ ($S\text{–}S = Pt_2S_2(PPh_3)_4$).

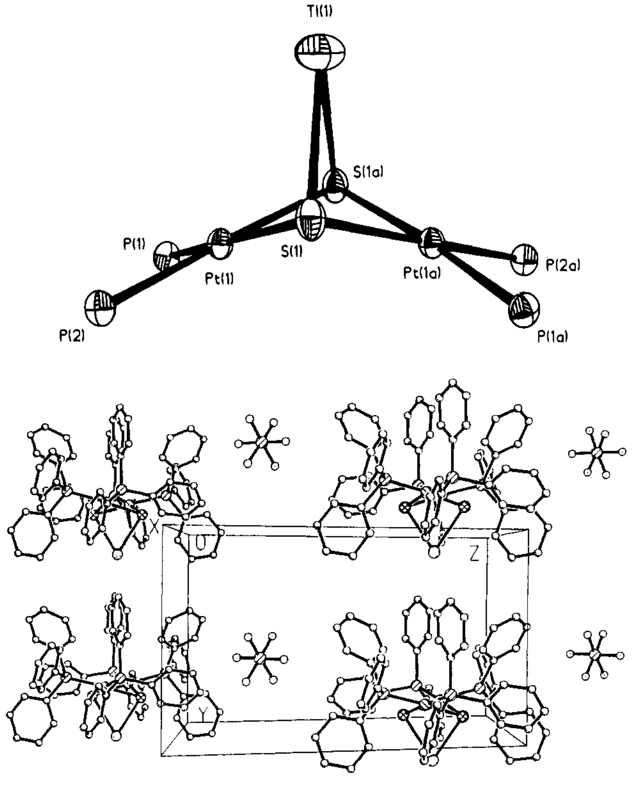

Figure 2. (a) Top: Molecular structure of $[Pt_2Tl(\mu_3\text{-}S)_2(PPh_3)_4]PF_6$ showing only the molecular cation. The phenyl rings are removed for clarity. (b) Bottom: Packing diagram of $[Pt_2Tl(\mu_3\text{-}S)_2(PPh_3)_4]PF_6$ along the *y* axis.

One unusual feature is the angular two-coordinated Tl(I) center. Among the numerous Tl(I) compounds with high coordination numbers,[4] the only crystallographically established structure which contains a two-coordinated Tl(I) is found in the four-membered $\{Tl_2O_2\}$ ring structure in $[TlO(CF_3)_3C_6H_2]_2$.[5,6] The title complex clearly shows that this angular form of Tl(I) can be self-sustained without support from a ring conformation. Intermolecular Tl···S (or Tl···Pt) interactions can be ignored, judging from the large nonbonding distances; the closest contacts come from the intermolecular and intramolecular phenyl hydrogens (3.308 and 3.511 Å, respectively) (Figure 2b). The acute S–Tl–S angle (68.9(1)°) is the smallest S–M–S angle registered for all known mixed-metal aggregates and is remarkably similar to that found in $[Tl([9]aneS_3)]PF_6$ (≃67.5°), in which the Tl(I)

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Table I. Crystallographic Data for $[Pt_2Tl(\mu_3\text{-}S)_2(PPh_3)_4]PF_6$

compn: $C_{72}H_{60}F_6P_5Pt_2S_2Tl$	$Z = 2$
fw = 1852.7	$d_{calc} = 1.838$ g cm^{-3}
space group: *P2/n*	$T = 298$ K
$a = 18.128(4)$ Å	λ(MoKα) = 0.710 73 Å
$b = 10.544(2)$ Å	$\mu = 6.811$ mm^{-1}
$c = 18.348(4)$ Å	no. of obsd rflns: 3634 ($F > 4.0\sigma(F)$)
$\beta = 107.37(3)°$	$R^a = 0.047$
$V = 3347.1(17)$ Å^3	$R_w{}^b = 0.050$

$^aR = \sum||F_o| - |F_c||/\sum|F_o|$. $^bR_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

is eight-coordinated, and the O–Tl–O in $[TlO(CF_3)_3C_6H_2]_2$ (70.8(4)°). The presence of a stereochemically active lone pair could be invoked. Despite some similarities between Tl(I) and Ag(I), the hexanuclear framework of the latter, $[Ag_2Pt_4(\mu_3\text{-}S)_4(PPh_3)_8]^{2+}$, with a strong Ag···Ag interaction, is not found in the present complex.

The Tl–S length (2.764(3) Å) is the shortest ever reported for Tl(I)–S bonds. It is shorter than those found in $[Tl([9]aneS_3)]PF_6$ (ca. 3.105 Å) and covalent solids such as Tl_4S_3 (Tl(I)–S = 2.90–3.36 Å),[7] $Tl(S_2CNEt_2)$ (3.020–3.888(3) Å),[8] and $[TlSR]_n$ (2.818(7)–3.410(12) Å).[9] The high covalency of the Tl–S bonds dissociates Tl(I) from its usual alkali-metal-like behavior. Upon sulfuration, the Tl dissipates its charge through delocalization within the tbp $\{TlPt_2S_2\}$ assembly. As a result, the PF_6^- ions in the lattice show no affinity for the Tl sites and instead are located in space-filling sites (Figure 2b).

The intramolecular contact Tl···Pt (3.379(1) Å) is slightly higher than those found in $Tl_2Pt(CN)_4$ (3.140(1) Å)[10] and $[Tl(crown\text{-}P_2)Pt(CN)_2]NO_3$ (2.911(2), 2.958(2) Å),[11] which are the only Tl–Pt-bonded complexes known. No formal Tl–Pt bond is envisaged, but weak heterometal interactions similar to those found in $[Pt_2(\mu\text{-}SAuCl)_2(PPh_3)_4]$ (Au–Pt = 3.111–3.218(1) Å)[12,13] cannot be ignored. The planar geometry of the Pt(II) sphere is essentially unperturbed though the Pt–S and Pt–P bonds are marginally weaker than those in other M–Pt–S heterometallics.

The title complex shows no reactivity with $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ or Bu_4NCl. Its inability to capture an extra molecule of the metalloligand was at first sight surprising, despite the exposed Tl(I) sphere and in view of the rapid reactions of $(PPh_3)_4Pt_2(\mu_3\text{-}S)_2MCl_2$ (M = Ni, Pd, Hg) with the nucleophilic metalloligand to yield $M(Pt_2S_2)_2$-type complexes. This however can be interpreted as the lone-pair effect of Tl(I), which significantly suppresses the electrophilicity of the complex. For a similar reason, the Tl site shows no affinity for excess chloride ions which would allow for coordination expansion. The failure of chloride to remove the Tl(I) from the complex demonstrates clearly the strength and covalency of the Tl–S bonds.

Experimental Section

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients of Selected Non-Hydrogen Atoms (Å^2 × 10^3)^a

atom	x	y	z	U_{eq}
Tl(1)	2500	−1022(1)	2500	86(1)
Pt(1)	3276(1)	1776(1)	2209(1)	28(1)
S(1)	1969(2)	1140(3)	1654(2)	38(1)
P(1)	4522(2)	2367(3)	2836(2)	33(1)
P(2)	3290(2)	2335(3)	994(2)	32(1)
P(3)	2500	3988(9)	7500	88(3)
F(1)	2910(13)	5003(20)	7175(13)	205(14)
F(2)	2880(13)	2954(20)	7131(12)	192(12)
F(3)	3155(12)	3986(34)	8174(10)	280(18)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances (Å) and Angles (deg)

Tl(1)–S(1)	2.764(3)	Pt(1)–S(1)	2.380(3)
Pt(1)–S(1a)	2.356(3)	Pt(1)–P(1)	2.295(3)
Pt(1)–P(2)	2.312(3)	Tl(1)···Pt(1)	3.379(1)
S(1)···S(1a)	3.126(5)	Pt(1)···Pt(1a)	3.293(2)
S(1)–Tl(1)–S(1a)	68.9(1)	S(1)–Pt(1)–S(1a)	82.6(1)
P(1)–Pt(1)–P(2)	97.0(1)	S(1)–Pt(1)–P(1)	175.5(1)
S(1)–Pt(1)–P(2)	87.4(1)	Tl(1)–S(1)–Pt(1)	81.8(1)
Tl(1)–S(1)–Pt(1a)	82.2(1)	Pt(1)–S(1)–Pt(1a)	88.1(1)
Pt(1)–Tl(1)–Pt(1a)	58.3(1)		
dihedral angle Pt(1)–S(1)–S(1a)–Pt(1a)		135.7(1)	

All manipulations were routinely carried out under dry argon atmosphere using freshly-distilled dried solvents. Infrared spectra were obtained for KBr disks using a Shimadzu IR-470 spectrometer. All NMR spectra were recorded at 25 °C on a Bruker ACF 300 spectrometer. $^{31}P\{^1H\}$ spectra were run at 121.49 MHz and externally referenced to 85% H_3PO_4. Conductivities were measured by using a Horiba ES-12 conductivity meter. Elemental analyses were performed by the microanalytical laboratory in our department. The complex $Pt_2S_2(PPh_3)_4$ was synthesized according to the literature method from *cis*-$PtCl_2(PPh_3)_2$ and $Na_2S{\cdot}9H_2O$.[14]

Preparation of $[Pt_2TlS_2(PPh_3)_4]X$ (X = NO_3, PF_6). $TlNO_3$ (0.036 g, 0.136 mmol) was added to a suspension of $Pt_2S_2(PPh_3)_4$ (0.205 g, 0.136 mmol) in MeOH (50 mL) and the mixture stirred for $^1/_2$ h to give a bright yellow solution. The mixture was evaporated to dryness and the residue recrystallized from CH_2Cl_2/hexane. Yield: 0.192 g (80%). Anal. Calcd: C, 48.86; H, 3.39; N, 0.91; P, 7.01; S, 3.62; Pt, 22.05. Found: C, 47.82; H, 3.26; N, 0.72; P, 6.77; S, 3.23; Pt, 20.38. ^{31}P NMR ($CDCl_3$): $\delta = 21.54$ (J(P–Pt) = 2970, ^3J(P–Pt) = 23 Hz). ^{31}P NMR (CD_2Cl_2): $\delta = 20.64$ (J(P–Pt) = 2999, ^3J(P–Pt) = 22 Hz). IR (cm^{-1}): 1375 (NO_3^-). Molar conductivity Λ_m (10^{-3} M, CH_2Cl_2): 53.1 Ω^{-1} cm^2 mol^{-1}. The PF_6^- salt was prepared by metathesis with NH_4PF_6 in MeOH. Anal. Calcd: C, 46.68; H, 3.24; F, 6.16; P, 8.37; S, 3.46; Pt, 21.07; Tl, 11.02. Found: C, 46.54; H, 2.97; F, 6.29; P, 7.59; S, 4.42; Pt, 18.44; Tl, 12.26. ^{31}P NMR (CD_2Cl_2): $\delta = 20.47$ (J(P–Pt) = 2983. IR (cm^{-1}): 834 (PF_6^-). Λ_m (10^{-3} M, CH_2Cl_2): 52.0 Ω^{-1} cm^2 mol^{-1}.

X-ray Crystal Structure Determination. Yellow crystals suitable for a single-crystal X-ray structure determination were grown by the slow diffusion of hexane into a CH_2Cl_2 solution of the complex. The crystal used for analysis was of dimensions 0.35 × 0.35 × 0.5 mm. The unit cell constants were determined by least-squares fits to the setting parameters of 20 independent reflections. Crystallographic details are listed in Table I. A total number of 5822 independent reflections, $7° < 2\theta < 45°$, was measured by ω-scanning on a Siemens R3M/V2000 diffractometer. The intensity data were reduced and corrected for Lorentz and polarization effects using the applied programs. The crystal structure was solved by direct methods using the XS program of SHELXTL-Plus[15] and refined by full-matrix least-squares analysis with the XLS program of SHELXTL-Plus. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters.

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Supplementary Material Available: Tables giving details of the X-ray structural analysis, crystallographic data, refined atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

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