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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[14] The compound $TlOTeF_5$ contains Tl–O bonds with at least some covalency, given the values of ν(TeO) for this compound[5] as compared with those for genuinely ionic teflates such as $CsOTeF_5$ (ν(TeO) = 873 cm^{-1})[15] and $[N(n\text{-}Bu)_4{}^+][OTeF_5{}^-]$ (ν(TeO) = 867 cm^{-1}).[16]

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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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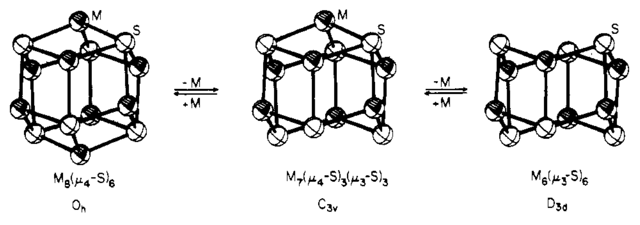

Figure 1. Depiction of the formal structural relationship among M_6S_6, M_7S_6, and M_8S_6 core units of the indicated symmetries by addition of capping atom M. Structures were drawn from the coordinates of $[Co_8S_6(SPh)_8]^{4-}$.[13]

As shown in Figure 1, the cores of clusters **1** and **4** are formally related by, e.g., the trans addition of two Fe atoms to the former. Because the atom coordinates of **4** have not been published, the structural depictions are based on those of $[Co_8S_6(SPh)_8]^{4-}$,[13] whose structure corresponds closely to that of **4**. On topological grounds, the stability of the Fe_6S_6 and Fe_8S_6 cores suggests the existence of a heptanuclear cluster containing the $Fe_7(\mu_4\text{-S})_3(\mu_3\text{-S})_3$ core of idealized C_{3v} symmetry. The latter may be considered a monocapped prismane. We report synthetic entry to such a species by means of cluster assembly from simple reactants under anaerobic conditions.

A suspension of 2.0 g (16 mmol) of $FeCl_2$ in 150 mL of THF was treated with 4.7 mL (32 mmol) of PEt_3, forming a clear brown-orange solution. After the solution was stirred for 2 h, 3.3 mL (16 mmol) of $(Me_3Si)_2S$ was added, resulting in the formation of a deep brown solution. Following a 24-h reaction period, the solvent was removed in vacuo, the dark oily residue was washed with hexanes and ether until the washes were colorless and was dissolved in 20 mL of THF, and the solution was then covered with 80 mL of hexanes. After storage overnight at -20 °C, a black microcrystalline solid was collected and washed with ether and hexanes, affording 1.4 g (61%) of a product corresponding to the composition $Fe_7S_6(PEt_3)_4Cl_3$[18] (**5**; λ_{max} (ϵ_M) 320 (sh, 11 500) nm; ^1H NMR ($CDCl_3$) δ 4.49 (2 H), 2.80 (3 H), 2.19 (6 H), 1.55 (9 H). Single crystals were obtained by ether diffusion into a concentrated THF solution.

Compound **5** crystallizes in cubic space group $Pa\bar{3}$ with a = 20.843 (4) Å and Z = 8.[19] The structure, shown in two perspectives in Figure 2, is built up from the fusion of nine Fe_2S_2 nonplanar rhombs so as to form the Fe_7S_6 monocapped-prismane core in Figure 1. The crystallographically imposed C_{3v} symmetry, with the C_3 axis coincident with the Fe(1)-P(1) bond, relates the three rhombs involving Fe(1) and the six roughly parallel to the C_3 axis, which have Fe-Fe separations of 2.584 (2) and 2.626 (2) Å, respectively. Below capping atom Fe(1) the structure consists of parallel layers of 3 μ_4-S, 3 Fe, 3 Fe, and 3 μ_3-S atoms. Atom Fe(1) is 0.375 Å above plane S(2,2',2''), and atoms Fe(3) and Fe(2) are displaced 0.596 and 0.715 Å, respectively, from their nearest S_3 plane. The $Fe_3(\mu_4\text{-S})_3$ (upper) and $Fe_3(\mu_3\text{-S})_3$ (lower) rings have chairlike conformations, as in the prismane clusters.[2-4,6,7] It is evident that the core, despite its C_{3v} configuration, is not a regular fragment of a cuboctahedron. Thus the S···S distance of 3.743 (4) Å in the upper ring is smaller than that in the bottom (4.030 (4) Å). The reverse holds for Fe···Fe distances, these being nonbonding (4.148 (2) Å) in the upper ring and interactive (2.746 (2) Å) in the lower ring. Associated with this shorter distance is a larger extent of nonplanarity of the lower ring. The Fe atoms in this ring reside in FeS_3P coordination units of irregular structure, emphasized by the markedly open (μ_3-S)-Fe-(μ_3-S) angle of 135.2 (1)°. The FeS_3Cl units of Fe(3,3',3'') lack this distortion and are more nearly tetrahedral with bond angles in the range 104-115°, an entirely common structural aspect of Fe-S clusters. Two other structural features are unusual. The Fe-(μ_4-S) distance of 2.366 (3) Å is the longest of this type reported.[9-12,20] The Fe-Cl distance of 2.189 (3) Å appears unexpectedly short for a cluster with the Fe mean oxidation state of 2.14+ when compared with the results for $[Fe_4S_4Cl_4]^{2-}$[21] (2.216 (2) Å, 2.5+), $[Fe_6S_6Cl_6]^{3-}$[2,6] (2.224 (2) Å, 2.5+), and $[Fe_6S_6Cl_6]^{2-}$[3] (2.189 (8) Å, 2.67+). The cause of this relatively short bond is presently unclear.

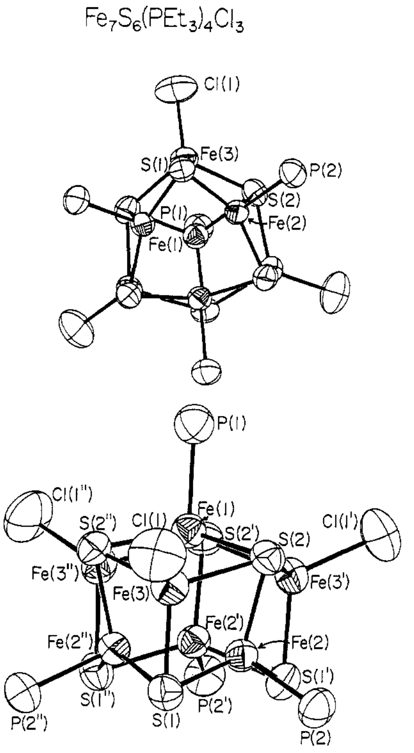

Figure 2. Structure of $Fe_7S_6(PEt_3)_4Cl_3$ (C and H atoms omitted) showing 50% thermal ellipsoids and the atom-numbering scheme: (upper) view down the C_3 axis containing atoms Fe(1) and P(1), showing the asymmetric unit; (lower) side-on view showing primed and unprimed atoms related under C_{3v} symmetry. Interatomic distances (Å) and angles (deg) with esd's: Fe(1)-Fe(2), 2.986 (2); Fe(1)-Fe(3), 2.584 (2); Fe(2)-Fe(2'), 2.746 (3); Fe(2)-Fe(3), 2.626 (2); Fe(3)-Fe(3'), 4.148 (2); Fe(1)-S(2), 2.193 (2); Fe(2)-S(1), 2.179 (3); Fe(2)-S(2), 2.231 (3); Fe(3)-S(1), 2.276 (3); Fe(3)-S(2), 2.366 (3); Fe(1)-P(1), 2.298 (5); Fe(2)-P(2), 2.289 (3); Fe(3)-Cl(1), 2.189 (3); P(1)-Fe(1)-S(2), 99.84 (8); S(2)-Fe(1)-S(2), 117.1 (1); P(2)-Fe(2)-S(1), 93.1 (1); P(2)-Fe(2)-S(2), 99.4 (1); S(1)-Fe(2)-S(1), 135.2 (1); S(1)-Fe(2)-S(2), 111.7 (1); Cl(1)-Fe(3)-S(1), 115.1 (1); Cl(1)-Fe(3)-S(2), 113.9 (1); S(1)-Fe(3)-S(2), 103.7 (1); S(2)-Fe(3)-S(2), 104.7 (1).

In chloroform solution $Fe_7S_6(PEt_3)_4Cl_3$ retains its solid-state structure, as indicated by the appearance of two sets of ethyl group NMR signals with a 3:1 intensity ratio. The ^1H isotropic shifts of the unique (1.78 (CH_3), 3.15 (CH_2) ppm) and symmetry-related (0.53 (CH_3), 0.85 (CH_2) ppm) ligands arise from cluster paramagnetism. The magnetic moment of 3.95 μ_B ($CDCl_3$, 298 K) is consistent with a quartet ground state or thermal distribution over spin states with $S \geq {}^1/_2$ for this odd-electron (91e) cluster.

The results presented here demonstrate the existence of the $Fe_7(\mu_4\text{-S})_3(\mu_3\text{-S})_3$ core in **5** as a topological link (albeit an imperfect fragment) between the cores of prismatic and cuboctahedral

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(18) Anal. Calcd for $C_{24}H_{60}Cl_3Fe_7P_4S_6$: C, 24.80; H, 5.20; Cl, 9.15; Fe, 33.63; P, 10.66; S, 16.55. Found: C, 24.72; H, 4.94; Cl, 8.94; Fe, 33.20; P, 10.61; S, 16.76.

(19) Diffraction data were collected on a Nicolet P3F four-circle automated diffractometer at ~20 °C with use of graphite-monochromatized Mo K$\bar{\alpha}$ radiation. An empirical absorption correction (μ = 27.4 cm^{-1}) was applied. The merging R value was 4.6%. From 10420 total reflections (+h,+k,+l), the structure was solved by using 1340 unique data ($3 \leq 2\theta \leq 53°$, $I \geq 2.5\sigma(I)$) by a combination of direct methods (MULTAN) and Fourier techniques (CRYSTALS). Isotropic refinement converged at R = 8.3%. All non-hydrogen atoms were anisotropically described. Hydrogen atoms were placed at 0.95 Å from bonded carbon atoms in the final stages of refinement. Anisotropic refinement converged at R (R_w) = 4.8% (5.7%).

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clusters. This set of three structures is complete only with Fe. The clusters $[Co_8S_6(SPh)_8]^{4-,5-}$[13] and $Co_7S_6(PPh_3)_5Cl_2$[14] (with a structure similar to that of **5**) are known but no Co prismane has yet been synthesized. Interconversion of clusters with these cores by capping reactions may be feasible (with some dimensional change in the lower ring of **5**), inasmuch as the cores of $\mathbf{1}^{3-}$ ($[Fe_6S_6]^{3+}$, 69e) and **5** ($[Fe_7S_6]^{3+}$, 77e) differ by Fe(0) and those of **5** and **4** ($[Fe_8S_6]^{5+}$, 83e) by Fe(II). Indeed, **1** has been doubly capped with M = Mo(0) and W(0),[21] affording clusters with $[M_2Fe_6S_6]^{2+,3+}$ cores (82e, 81e). These are nearly isoelectronic with **4** and with cubic $Fe_8S_6Cl_8$, which, together with at least one other cluster product, has been isolated from the reaction system affording **5**. The syntheses, properties, and reactions of these and related clusters will be the subject of a future report. Lastly, our results together with the outstanding work of Fenske et al.[14,17] emphasize the advantage of phosphine ligands and low-polarity solvents in the assembly of high-nuclearity metal–sulfide clusters.

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Supplementary Material Available: Tables of positional and thermal parameters for $Fe_7S_6(PEt_3)_4Cl_3$ (2 pages); a table of calculated and observed structure factors for $Fe_7S_6(PEt_3)_4Cl_3$ (14 pages). Ordering information is given on any current masthead page.

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Articles

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Singlet–Triplet Transitions of Aromatic Compounds Coordinating to a Paramagnetic Chromium(III) Ion

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Received September 27, 1985

Chromium(III) compounds of 2,2′-bipyridine, 4,7-diphenyl-1,10-phenanthroline, acetylacetone, benzoylmethane, and phthalocyanine exhibit a fine structured absorption band with a moderate intensity below the strong band of the ligand excitation (^{1}LE). A mirror-image relation was observed between the absorption band of the chromium(III) compound and the phosphorescence band of the ligand coordinating to Be^{2+}, Zn^{2+}, or Rh^{3+}. The structured bands are assigned to a spin-allowed transition in which a quartet state composed of ^{3}LE and $^{4,2}(d^3)$ is excited. The intensities of the structured absorption bands are in agreement with those calculated on the basis of the intensity borrowing from the ^{1}LE transition via the charge-transfer excited state lying above. The assignment is consistent with the fact that a magnetic circular dichroism band of the chromium(III) compound was found in the same energy region as the structured absorption band.

Introduction

Electronic absorption bands of tervalent chromium compounds have been assigned to ligand field d–d transitions (LF), charge-transfer transitions (CT), and intraligand excitation transitions (LE).[1-4] Though most of the bands are structureless and ascribed to spin-allowed transitions of LF, CT, and LE, some structured bands with low intensity (molar absorption coefficient $\epsilon < 1$ M^{-1} cm^{-1}; 1 M = 1 mol·dm^{-3}) are characteristic of the spin-forbidden LF transition in the red region and those with high intensity ($\epsilon > 10^4$ M^{-1} cm^{-1}) are characteristic of LE in large ligands having conjugated π electrons in the visible and ultraviolet regions.[4] However, some well-structured bands with moderate intensity of 300–2000 M^{-1} cm^{-1}, which are seen on coordination of aromatic compounds to a chromium(III) ion, are left unassigned. For instance, 2,2′-bipyridine (bpy) coordinating to a paramagnetic chromium(III) ion presents a band at 22 000–26 000 cm^{-1} having three peaks with moderate intensity (300–2000 M^{-1} cm^{-1}) below an intense LE band at 32 050 cm^{-1}. König and Herzog,[5] who observed the strange band group of $[Cr(bpy)_3]^{3+}$ for the first time, found no explanation for the intensity and the band structure. More recently, Serpone et al.[6] observed a structured band in the electronic absorption spectra of several chromium(III) compounds of bpy or 1,10-phenanthroline. The intensities (270–1700 M^{-1} cm^{-1}) and energies (20 700–22 500 cm^{-1}) of the lowest bands varying with substituents in bpy and 1,10-phenanthroline could not be fully explained in terms of LF transition. Hanazaki et al.[7] assigned a similarly structured band group at 22 000–28 000 cm^{-1} of $Cr(acac)_3$ to a spin-allowed LE transition, which is intensified on coordination of acac to chromium(III) ion. According to them, the excited state is mainly constructed from the triplet excited state of aceylacetonate ion (^{3}LE) and the quartet and the doublet states of the metal center via direct coupling between unpaired electrons in the ligand and the metal center. However, since the transition energy to ^{3}LE was unknown at that time, some workers preferred to assign the first spike at 23 260 cm^{-1} to the LF transition.[8]

The aim of the present publication is to reexamine the moderate-intensity (300–2000 M^{-1} cm^{-1}), fine-structured bands of acetylacetonate ion, dibenzoylmethanate ion, 2,2′-bipyridine, 4,7-diphenyl-1,10-phenanthroline, and phthalocyaninate ion coordinating to a chromium(III) ion, which are observed at 24 000,

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