Synthesis and Structure of the New Cubane-like Cluster $[Fe_4Te_4(PEt_3)_4]PF_6$, containing only Terminal Phosphine Ligands

Franco Cecconi, Carlo A. Ghilardi, Stefano Midollini and Annabella Orlandini

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, via J. Nardi 39, 50132 Firenze, Italy

The cubane-like $[Fe_4Te_4(PEt_3)_4]PF_6$ and the stellated octahedron $[Fe_6Se_8(PEt_3)_6]PF_6$ clusters have been obtained by reaction of $Fe(ClO_4)_2$ with PEt_3 and H_2X (X = Te, Se), in the presence of PF_6^-; a crystal structure of the tellurium derivative has been determined.

The remarkable interest in the study of cubane-like iron–sulfur clusters has been excited by their occurrence in natural proteins.[1] Notwithstanding the great number of experimental and theoretical studies, the electronic structures and the magnetic properties of these systems are not yet completely clarified.[2,3]

All the non-organometallic Fe_4X_4 (X = S, Se, Te) clusters so far reported contain either exclusively or prevalently anionic terminal ligands, such as RS^-, X^-, RO^-. Now we report the synthesis of $[Fe_4Te_4(PEt_3)_4]PF_6$ **1**, the first example of a cubane-like iron–chalcogen cluster, containing only uncharged terminal ligands. The compound has been prepared by reaction of $Fe(ClO_4)_2 \cdot 6H_2O$ and PEt_3 (molar ratio 1:3) with H_2Te† in ethanol–acetone in the presence of $Bu^n{}_4NPF_6$, by operating under a nitrogen atmosphere (yield 40%). The same assembly reaction, when performed with H_2Se in place of H_2Te, has been found to yield the stellated octahedron-like cluster $[Fe_6Se_8(PEt_3)_6]PF_6$ **2**,‡ analogous to that previously reported for H_2S.[4] The magnetic susceptibilities of the two complexes, which have satisfactory elemental analyses, were measured in the solid state using a Faraday balance at 293 K, and the calculated magnetic moments (μ_{eff} for cluster) were 6.8 and 7.8 μ_B for **1** and **2** respectively.

A complete X-ray§ structural determination revealed that the structure of **1** consists of discrete cluster cations of $[Fe_4Te_4(PEt_3)_4]^+$ and PF_6^- anions. Fig. 1 shows a perspective view of the cluster unit with important bond distances and angles. The cluster cation displays a cubane-like geometry, with the Fe_4Te_4 core constituted by two concentric interpenetrating tetrahedra of iron and tellurium. The two tetrahedra, very different in size, are disposed so that the tellurium atoms

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† H_2Te was produced by reaction of HCl (aq) and Al_2Te_3 in the dark, at 273 K.

‡ A cell constants determination (space group $R\bar{3}$, a = 11.80 Å, α = 92.3°) has shown that **2** is isomorphous with the previously reported $[Fe_6S_8(PEt_3)_6]PF_6$.[4]

§ *Crystal data* for $[Fe_4Te_4(PEt_3)_4]PF_6$: M = 1411.87, orthorhombic, space group *Fddd*, a = 17.244(6), b = 20.357(7), c = 25.959(9) Å, U = 9112.5 Å^3, Z = 8, D_c = 2.06 g cm^{-3}, monochromatic Mo-Kα radiation, λ = 0.7107 Å, μ(Mo-Kα) = 39.8 cm^{-1}. The intensity data were collected within 2θ = 45° on an Enraf-Nonius CAD4 diffractometer, using the ω–2θ scan technique at 293 K. The structure was solved by the heavy atom method and refined by full-matrix least-squares procedures. At convergence R and R_w are both 0.052 for 641 observed absorption-corrected reflections with $I \geqslant 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

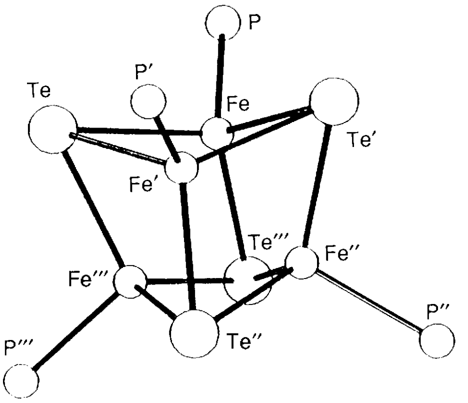

Fig. 1 Perspective view of the cluster unit $[Fe_4Te_4(PEt_3)_4]^+$. PLUTO drawing. Carbon atoms are omitted for clarity. Superscripts refer to the following equivalent positions: (′) $-x, -y + 1, z$ (″) $-x, y, -z + 1$, and (‴) $x, -y + 1, -z + 1$. Imported selected bond distances (Å) and angles (°) (range): Fe···Fe 2.635(5)–2.657(5), Fe–Te 2.585(4)–2.597(4), Fe–P 2.361(9), Te···Te 4.279(3)–4.331(3) P–Fe–Te 105.5(3)–107.5(2), Te–Fe–Te 111.5(1)–113.2(1), Fe–Te–Fe 61.1(1)–61.7(1).

are capping the triangular faces of the iron tetrahedron. Each iron centre completes, with a triethylphosphine group, its tetrahedral geometry, that appears only slightly distorted, as the P–Fe–Te and Te–Fe–Te angles are in the range 105.5(3)–107.5(2) and 111.5(1)–113.2(1)° respectively. Owing to the different size of the tellurium and iron ions the resultant cubane structure is significantly distorted, the average of the Fe···Fe and Te···Te intramolecular contacts being 2.648(7) and 4.30(2) Å respectively. The rather short value of the Fe···Fe contacts, in comparison with similar cubane-like structures, is noteworthy. This value is significantly shorter than those reported[5] for $[Fe_4Te_4(SPh)_4]^{3-}$ and resembles the shortest set of the values found in the $[Fe_4Te_4(TePh)_4]^{3-}$.[6] Although the distortion from the idealized T_d towards compressed or elongated D_{2d} symmetry seems a common feature in this kind of compound,[7] such a distortion is not envisaged in the title phosphine derivative; in fact the range of Fe–Te bond distances is very small [2.585(4)–2.597(4) Å] as is that of the intramolecular contacts Fe···Fe [2.635(5)–2.657(5) Å]. With regard to the Te···Te distances, varying from 4.279(3) to 4.331(3) Å, they are close to each other. In the analogous $[Fe_4Te_4(TePh)_4]^{3-}$ cluster, the average Te···Te contacts, respectively parallel and perpendicular to the idealized $\bar{4}$ axis, are 4.17 and 4.50 Å.

It should be pointed out that the formal oxidation state of the metals in complex **1** ($3Fe^{II}$, $1Fe^{III}$) is the same as that found in the two previously reported clusters having an Fe_4Te_4 core,[5,6] despite the quite different nature of the terminal ligands.

The complete characterization of the two complexes is under current investigation.¶

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¶ *Note added in proof*: After acceptance of this communication, the synthesis by a different route and the structure of the uncharged species $[Fe_4Te_4(PEt_3)_4]$ have been reported, M. L. Sheigerwald, T. Siegrist, S. M. Stuczynski and Y. U. Kwon, *J. Am. Chem. Soc.*, 1992, **114**, 3155.