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Synthesis and Structural Characterization of a Paramagnetic Octahedral Cobalt–Sulfur Cluster, $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]BPh_4$

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In the course of a systematic investigation of the reactions of hydrogen sulfide with 3d metal ions in the presence of mono(tertiary phosphines), we have recently synthesized and structurally characterized novel high nuclearity metal–sulfur clusters such as $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$ [1] and $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$ [2].

We report now the synthesis and the structure determination of the compound $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]BPh_4$.

Hydrogen sulfide was bubbled through an acetone–ethanol deoxygenated solution of $Co(BF_4)_2\cdot 6H_2O$ and PEt_3 (molar ratio *ca.* 1:3) at room temperature, for 10 min. After a day, $NaBPh_4$ was added and the solution was filtered. On standing in air the filtrate deposited dark-brown crystals of $[Co_6S_8(PEt_3)_6]BPh_4$. *Anal.* Calcd. for $C_{60}H_{110}BCo_6P_6S_8$: C, 43.99; H, 6.77; Co, 21.58; S, 15.66. Found: C, 43.79; H, 7.06; Co, 21.35; S, 15.51. The compound, obtained in a yield of *ca.* 30%, is air stable and soluble in common polar organic solvents such as acetone, 1,2-dichloroethane and nitroethane, where it behaves as 1:1 electrolyte. The compound is paramagnetic with a bulk magnetic moment of 2.15 BM per $[Co_6S_8(PEt_3)_6]BPh_4$ at 297 K.

A complete X-ray structure determination of the title compound has been carried out. The crystals are triclinic, space group $P\bar{1}$, $a = 19.481(9)$, $b = 15.562(7)$, $c = 12.390(6)$ Å, $\alpha = 92.70(8)$, $\beta = 94.50(7)$, $\gamma = 94.10(9)°$, $U = 3729.78$ Å^3, $Z = 2$, $D_c = 1.458$ g cm^{-3}, μ(Mo-Kα) = 16.44 cm^{-1}. Data collection was carried out on a Philips PW 1100 diffractometer using the ω–2θ scan technique and graphite monochromatized Mo Kα radiation. An absorption correction giving transmission factors ranging from 0.92 to 0.70 was applied. The structure was solved by the heavy atom technique and refined by full-matrix least-squares. The phenyl rings of the tetraphenylborate anion were treated as rigid groups. The final R and R_w values are 0.050 and 0.051 for 4251 reflections ($2\theta \leqslant 40°$) with $I \geqslant 3\sigma(I)$.

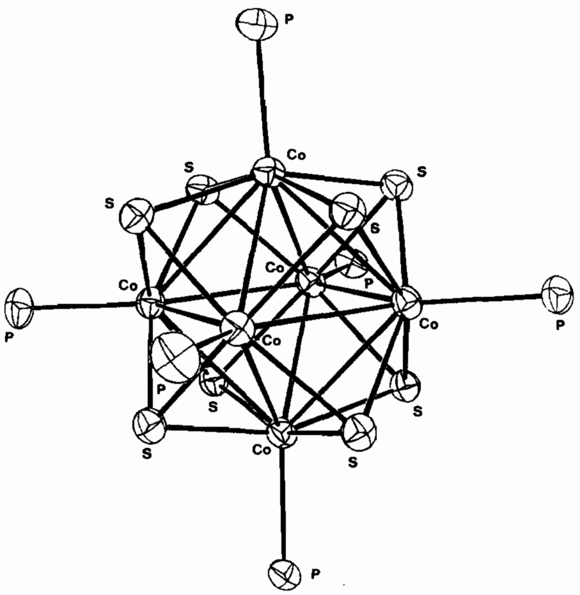

Fig. 1. Inner core of $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$.

The molecular structure of the compound consists of discrete $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$ cations and BPh_4^- anions. The inner core of the cation is shown in Fig. 1. In the cation, which is isostructural with the iron derivative [2], each cobalt atom is located at the vertices of an octahedron with the sulfur ligands triply bridging all the octahedral faces. Moreover, a triethylphosphine group is coordinated to each metal atom. Each metal atom is definitely surrounded by four sulfur and one phosphorus atoms in a square pyramidal environment, with four other cobalt atoms. The cation has no crystallographic symmetry, however the inner core may be considered to possess idealized O_h symmetry. The octahedral framework is slightly distorted with the Co–Co distances ranging from 2.771(4) to 2.808(3) Å, the average Co–Co distance of 2.794(2) Å* being significantly longer than both the sum of the cobalt single bond radii (2.32 Å) [3] and the value found in the octahedral face-capped carbonyl cluster $[Co_6(CO)_{14}]^{-4}$ (Co–Co *av.* = 2.50 Å) [4]. The most striking structural difference between the two clusters $[Co_6S_8(PEt_3)_6]^+$ and $[Fe_6S_8(PEt_3)_6]^{2+}$ is the average metal–metal distance which goes from 2.794(2) to 2.624(8) Å [2].

The lengthening of the metal–metal distances in the cobalt with respect to the iron derivative is

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*The estimated errors on the means were calculated using the formula $[\Sigma_n(d_n - d)^2/n(n-1)]^{1/2}$.

panied by the shortening of the metal–sulfur (2.233(2) *vs.* 2.257(3) Å) and metal–phosphorus (2.162(2) *vs.* 2.296(4) Å) distances. These differences seem to be indicative of an increase in the electron number in the metal skeleton (30 and 37 for iron and cobalt respectively) which results in a reduction of the direct metal to metal interactions, the metal–ligand linkages becoming relatively more important in cementing the cluster.

The paramagnetism of the title compound is in agreement with the presence of an odd valence electron number in the cation. However, as previously pointed out for the iron derivative [2], a specific theoretical analysis is necessary to elucidate the relationship between the magnetic properties and the electronic structure in these singular polynuclear compounds.

References

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