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# One Electron Reduction of a Cobalt-Sulfur Cluster. Synthesis and Molecular Structure of $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]\cdot$nthf

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It is well known that the addition or removal of valence electrons is very important in the understanding of the nature of the bonding in transition metal clusters. Although these compounds can undergo redox reactions without change of the metal framework, the metal–metal bond lengths are very sensitive to variations in the total electron count.

We have recently reported the synthesis and the structural characterization of a metal–sulfur cluster of formula $[Co_6S_8(PEt_3)_6](BPh_4)$, *1*, [1]. This compound is paramagnetic with one unpaired electron per cluster unit. The monocation $[Co_6S_8(PEt_3)_6]^+$ is built up of an octahedron of cobalt atoms with the sulfur atoms triply bridging all the octahedral faces. It seemed therefore of interest to attempt to reduce this compound to obtain the neutral species.

The complex *1* reacts in thf solution at room temperature under a nitrogen atmosphere with an equimolar amount of sodium naphthalenide to form deep-brown crystals of $[Co_6S_8(PEt_3)_6]\cdot$nthf (yield, 85%). *Anal.* Calcd. for $C_{36}H_{90}Co_6P_6S_8\cdot 2.5C_4H_8O$: C, 36.84; H, 7.39; Co, 23.59%. Found: C, 36.77; H, 7.57; Co, 22.53%. This derivative, which is soluble in organic solvents such as benzene and methylene chloride, is diamagnetic.

The molecular structure of the title compound was determined by X-ray diffraction methods. The crystals are trigonal, space group $R\bar{3}$, $a = 11.780(6)$ Å, $\alpha = 92.50(7)°$, $U = 1629.9$ Å$^3$, $Z = 1$, $D_c = 1.527$ g cm$^{-3}$, $\lambda$(Mo-K$\alpha$) = 19.1 cm$^{-1}$. Data collection was carried out on a Philips computer-controlled PW 1100 diffractometer using the $\omega$–$2\theta$ scan technique and graphite monochromated Mo-K$\alpha$ ($\lambda = 0.7107$ Å) radiation. An absorption correction gave transmission factors ranging from 0.76 to 0.65. Full-matrix least-squares refinements converged at the R and $R_W$ factors values of 0.055 and 0.058 for 1289 reflections ($2\theta \leqslant 60°$) with $I \geqslant 3\sigma(I)$. Attempts to take account of the disordered solvent are in progress.

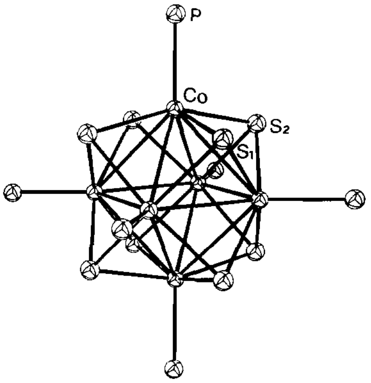

Fig. 1. Inner core of $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$. Only inequivalent atoms are labelled. Important bond lengths: Co–Co′ 2.814(2), Co–Co″ 2.818(2), Co–S1 2.243(3), Co–S2 2.240(3), Co′–S2 2.228(3), Co″-S2 2.222(2), Co–P 2.135(3) Å.

The molecular structure consists of a discrete cluster unit with interspersed molecules of tetrahydrofuran. A perspective view of the cluster is shown in Fig. 1. The neutral species $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$ is strictly isostructural with the monopositive one. The addition of one electron, 97 and 98 electrons respectively, results in a small but significant increase of the metal–metal bond length from 2.794(2) to 2.816(2) Å; but does not affect the sulfur–metal bonds which as we have already pointed out for other metal–sulfur clusters [1, 2] are the actual stabilizing elements of the molecular framework. The weakening of the cobalt–cobalt interactions is accompanied by the strengthening of the Co–P bonds [2.135(3) *vs.* 2.162(2) Å]. The value of the Co–Co distance, which is very long compared with that of 2.50 Å reported for the octahedral face-capped carbonyl cluster $[Co_6(CO)_{14}]^{-4}$ [3], is related to the very high electron number. This compound, together with the very recently reported isostructural $Co_6(\mu_3\text{-}S)_8(CO)_6$ [4], is the most electron-rich metal–sulfur cluster of this octahedral face-capped series. The lengthening of the metal–metal distances with respect to those found in the monopositive derivative seems to indicate that the electron involved in this process occupies an antibonding orbital.

The sensitivity of the metal–metal bond order to the total electron count is clearly shown by the comparison with the isostructural iron cluster $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$ [5] where the decrease in the electron number, 90, lowers the metal–metal bond distances to 2.624(8) Å.

The simultaneous syntheses by different research groups [1, 2, 4–6] clearly indicates a novel chemistry of metal sulfide clusters. Our current interest in this field is directed to two principal goals: (i) synthesis

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of clusters of the $M_{3n}S_{3n+2}$ structural series with different total electron counts; (ii) rationalization of the properties of these compounds. For the latter purpose accurate calculations are in progress employing the self-consistent field SW-X$\alpha$ method.

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