*Inorganica Chimica Acta*, *159* (1989) 1–2

# A New Cobalt–Sulfur Cluster with Triphenylphosphine. Preparation and Structure of $Co_6S_8(PPh_3)_6$

MAOCHUN HONG*, ZHIYING HUANG, XINJIAN LEI, GUOWEI WEI, BEISHENG KANG and HANQIN LIU

*Fuzhou Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China*

(Received November 21, 1988)

Transition-metal clusters with phosphine ligands are a class of compounds of great current interest. These compounds are important because of their novel structural features [1–5] and their potential uses as heterogeneous catalysts [6, 7]. The skeleton of the clusters may not be changed by addition or removal of the valence electrons, yet the metal–metal bond lengths are sensitive to the variation of the total electron count. Recently, several clusters with a $Co_6S_8$ core have been reported [8–10] and the relationship between the bond length and the total electron count has been studied [8]. All of these clusters contain an almost regular $Co_6$ core. We hereby report the synthesis and structural characterization of a new cluster, $Co_6S_8(PPh_3)_6$, with a slightly distorted $Co_6$ octahedron.

## Experimental

### Synthesis

To a stirred solution of $(Ph_3P)_2CoBr_2$ obtained from 2.19 g (10 mmol) of anhydrous $CoBr_2$ and 5.25 g (20 mmol) of $Ph_3P$ in 40 ml of DMF was added a solution of $Na_2S_x$ obtained from 2.40 g (10 mmol) of $Na_2S\cdot 9H_2O$ and 0.32 g (10 mmol) of sulfur in 10 ml of DMF. The blue–green solution immediately turned dark red on mixing. After stirring for 3 days the microcrystals formed were collected, washed with water, acetone and THF:hexane 1:1 (*v*/*v*) successively to give 2.6 g of dark red product. The compound was recrystallized from methylene chloride/hexane. A cyclic voltammogram showed a reversible one-electron oxidation–reduction at +0.63 V *versus* SCE. The compound is paramagnetic with an effective magnetic moment of 4.23 $\mu_B$ per $Co_6S_8(PPh_3)_6$ at 301 K. Dark red crystals of the title compound suitable for X-ray crystallographic analysis were obtained by diffusion of a $CH_2Cl_2$ solution with a top layer of hexane.

### Crystal Data

A single crystal of dimensions 0.3 × 0.4 × 0.5 mm was mounted on a Regaku AFC5R four circle diffractometer equipped with a Mo ray source and graphite monochromator. The crystal is triclinic, space group $P$-1 with $a = 15.052(4)$, $b = 15.219(4)$, $c = 14.201(3)$ Å, $\alpha = 114.80(2)$, $\beta = 92.59(3)$, $\gamma = 117.90(2)°$, $V = 2488.5$ Å$^3$, $Z = 1$, $D_c = 1.457$ g/cm$^3$. A total of 8776 independent reflections were collected in the range $2° < 2\theta < 48°$, of which 5577 reflections with $I > 3\sigma(I)$ were used in the structure determination and refinement after Lp and empirical absorption correction with an AFC5R program. The coordinates of the three cobalt and four sulfur atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference Fourier maps. The structure was refined by a full-matrix least-squares technique with anisotropic temperature factors for the cobalt, sulfur and phosphorus atoms and isotropic temperature factors for all carbon atoms. The final $R$ and $R_w$ were 0.062 and 0.078, respectively.

## Discussion

A perspective view of the cluster is shown in Fig. 1. The cluster possesses crystallographic $C_I$-$\bar{1}$ symmetry and contains a slightly distorted octahedral $Co_6$ core (the octahedron is elongated along the 3-fold axis through the Co(1)–Co(2)–Co(3) face). Each of eight $Co_3$ faces is bridged by one $\mu_3$-S atom lying 1.50 Å above the $Co_3$ face. In addition, each Co atom is terminally coordinated by one triphenylphosphine ligand. Therefore, each cobalt atom is surrounded by four sulfur atoms and one phosphorus atom in a distorted square-pyramidal environment and is linked by four other cobalt atoms in a second nearest sphere. The atomic distances of Co–S, Co–P and Co–Co fall in the range 2.205–2.265, 2.142–2.169 and 2.849–2.894 Å, respectively. The S–S distances are in the range 3.072 to 3.120 Å. Alternatively, the cluster can also be described as a slightly distorted $S_8$ cube, and each Co atom is about 0.50 Å above the corresponding $S_4$ face.

The cluster contains 98 valence electrons, which is 14 electrons more than those counted by the 18-electron rule [11] and one electron more than those in the almost regular $Co_6$ octahedron cluster $[Co_6S_8(PPh_3)_6]^+$ [10]. The average Co–Co atomic distance of 2.870 Å in the title compound is distinctly longer than that in $[Co_6(CO)_{14}]^{4-}$ (2.50 Å, 86 e) [12] and slightly longer than that in the monovalent cation $[Co_6S_8(PPh_3)_6]^+$ [10] (2.81 Å, 97 e), *i.e.* the Co–Co distance is significantly increased by 0.06 Å owing to the addition of one electron. The

---

[*] Author to whom correspondence should be addressed.

0020-1683/89/$3.50

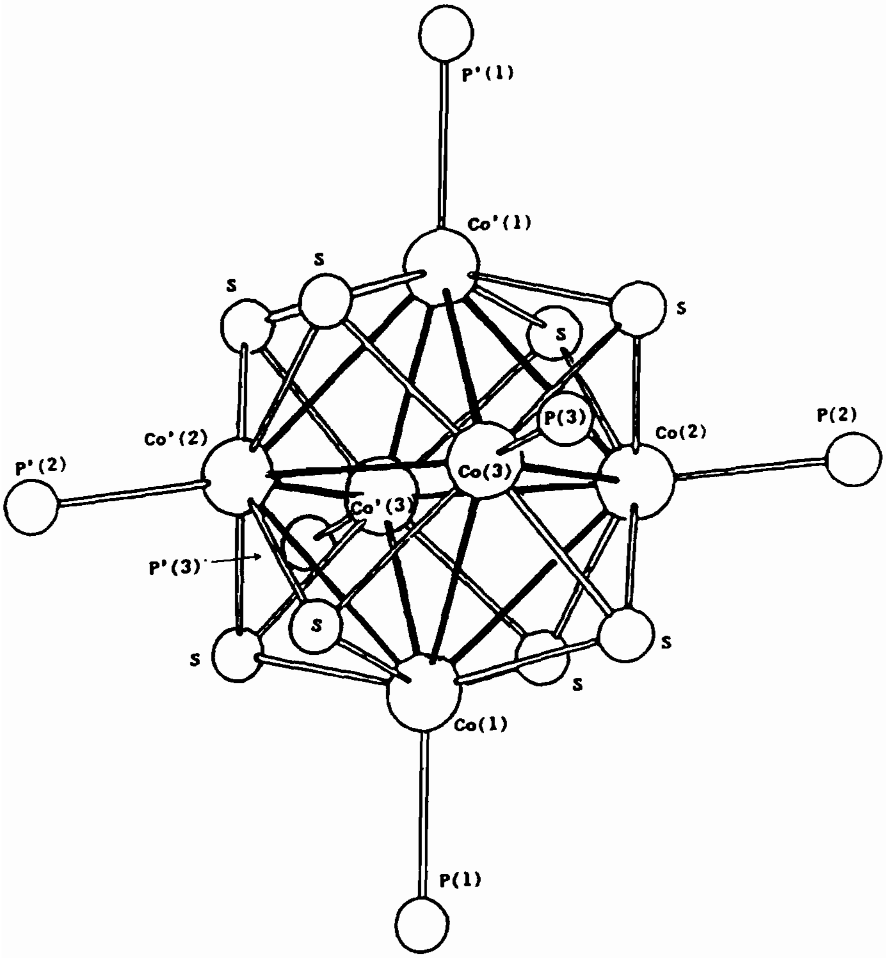

Fig. 1. Crystal structure of the cluster $Co_6S_8(PPh_3)_6$ without phenyl groups. P(1), P(2), P(3) and P'(1), P'(2), P'(3) are the P atoms of the $PPh_3$ ligands. Important bond lengths (Å): Co(1)–Co(2), 2.892(1); Co(1)–Co(3), 2.894(1); Co(2)–Co(3), 2.868(3); Co(1)–Co'(2), 2.858(1); Co(1)–Co'(3), 2.849(3); Co(2)–Co'(3), 2.860(3); Co(1)–S, 2.247(4); Co(2)–S, 2.240(4); Co(3)–S, 2.227(3); Co(1)–P(1), 2.169(3); Co(2)–P(2), 2.158(4); Co(3)–P(3), 2.165(3); and bond angles (°): Co–Co–Co, 58.8–61.2, 88.9–91.1; Co–Co–S, 48.7–51.3, 108.2–111.2; Co–Co–P, 126.5–131.0, 137.8–142.7; S–Co–S, 86.1–88.1, 153.9–155.7; P–Co–S, 93.1–113.0; Co–S–Co, 78.1–80.9; S–S–S, 88.4–91.6.

lengthening of the Co–Co distance in the neutral cluster with respect to the monovalent cation indicates that metal–metal bonding exists and that the extra electron occupies an antibonding orbital. As a matter of fact, the reversible one-electron oxidation–reduction at +0.63 V indicates that removal or addition of one electron to the antibonding orbital of the $[Co_6S_8(PPh_3)_6]^{n+}$ ($n = 0$, 1) is feasible. The average Co–S and Co–P bond lengths in the title cluster are 2.238 and 2. 165 Å, respectively, which agree well with those reported in the monovalent cluster $[Co_6S_8(PPh_3)_6]^+$ and are not affected by the variation of the total electron count.

## References

1 Xinjian Lei, Zhiying Huang, Qiutian Liu, Maochun Hong and Hanqin Liu, submitted for publication.
2 D. Fenske and J. Ohmer, *Angew. Chem., Int. Ed. Engl., 26* (1987) 148.
3 Boon K. Teo, Maochun Hong, Hong Zhang and Debin Huang, *Angew. Chem., Int. Ed. Engl., 26* (1987) 897.
4 Boon K. Teo, Maochun Hong, Hong Zhang, Debin Huang and Xiaobo Shi, *J. Chem. Soc., Chem. Commun.*, (1988) 204.
5 A. Agresti, M. Bacci, F. Cecconi, C. A. Ghilardi and S. Midollini, *Inorg. Chem., 24* (1985) 689.
6 H. Topsoe and B. Clausen, *Catal. Rev., 26* (1984) 395.
7 B. Bogdanovich, P. Gottsch and M. Rubach, *J. Mol. Catal., 11* (1981) 135.
8 F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orladini, *Inorg. Chim. Acta, 76* (1983) L183.
9 F. Cecconi, C. A. Ghilardi and S. Midollini, *Inorg. Chim. Acta, 64* (1981) L47.
10 D. Fenske, J. Hachgenei and J. Ohmer, *Angew. Chem., Int. Ed. Engl., 24* (1985) 706.
11 F. A. Cotton and E. Haas, *Inorg. Chem., 3* (1964) 10.
12 V. G. Albano, P. L. Bellon, P. Chini and F. Scatturin, *J. Organomet. Chem., 16* (1969) 461.