A New Phosphine-stabilized Sulfido Trinuclear Cobalt Species. Synthesis and Structure of $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)_2(\mu\text{-}PEt_2)(PHEt_2)_6][ClO_4]_2$

Carlo A. Ghilardi, Stefano Midollini, Annabella Orlandini and Giancarlo Scapacci
Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi, 39-50132 Firenze, Italy

A new triangular cluster of formula $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)_2(\mu\text{-}PEt_2)(PHEt_2)_6][ClO_4]_2$ has been synthesized by reaction of $[Co(H_2O)_6][ClO_4]_2$ with $PHEt_2$ and H_2S; its structure has been determined by X-ray analysis and NMR spectroscopy.

The growing interest in the synthesis, reactivity and characterization of metal–sulfur clusters is well known, owing to their potential role in both enzymatic and catalytic processes.[1] The reaction of transition-metal ions with H_2E (E = S, Se or Te) in the presence of monotertiary phosphines, above all PEt_3, has been found to be an efficacious methodology for the assembly of metal–chalcogen clusters.[2] As an extension we are now investigating this type of reaction in the presence of monosecondary phosphines which are not innocent ligands. Indeed these can allow the formation of phosphide and/or hydride derivatives. We have succeeded in the synthesis of the new cluster of formula $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)_2(\mu\text{-}PEt_2)(PHEt_2)_6][ClO_4]_2$ **1**, where the metal atoms are bridged by S, SH and PEt_2 groups. Compound **1** represents the first sulfido triangular cluster of cobalt atoms stabilized by phosphine ligands.

Black crystals of compound **1** were obtained by reaction of $[Co(H_2O)_6][ClO_4]_2$ and $PHEt_2$ (molar ratio 1:3) with H_2S in acetone–ethanol solution.* The complex is diamagnetic. Its ^1H NMR spectrum in CD_2Cl_2 solution at room temperature shows a doublet at δ 4.14 [6 H, J(PH) 342 Hz],[3] overlapping multiplets in the range δ 2.4–1.0 (40 H), and a multiplet at δ −2.25 (2 H) due to the $PH(CH_2CH_3)_2$, $PH(CH_2CH_3)_2$ and $P(CH_2CH_3)_2$, and SH hydrogen atoms respectively. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the same solution shows, at room temperature, two broad bands at δ 21 (6P) and −12 (1P), attributable respectively to the phosphines and the phosphide groups. The broadness of the signals is likely to be due to the presence of the cobalt quadrupolar nuclei. At low temperature (210 K) the signals remain substantially broad, the absorption at δ 21 becoming a complicated multiplet.

The molecular structure of compound **1** established by X-ray analysis† consists of discrete $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)_2(\mu\text{-}PEt_2)(PHEt_2)_6]^{2+}$ units and ClO_4^- anions. A perspective view of the cluster cation is given in Fig. 1 with selected bond distances and angles. The cation is built up of a triangle of cobalt atoms, symmetrically capped by two triply bridging sulfur ligands; moreover the three cobalt centres are held together by two doubly bridging SH ligands and one doubly bridging phosphide molecule. Although there is no experimental evidence concerning the assignment of S and SH to the μ_3 apical or to the μ in-plane sites, the above formulation was made according to the well known propensity of S to behave as a triply bridging ligand.[6] Each cobalt atom completes its distorted-octahedral geometry, by being co-ordinated to two $PHEt_2$ groups. The distortion from the idealized geometry is evidenced by the values of the axial angles: P(7)–Co(1)–S(4) 154.3(3), P(7)–Co(2)–S(3) 153.6(3) and S(3)–Co(3)–S(4) 165.4(3)°. The $Co_3(\mu\text{-}P)(\mu\text{-}S)_2$ fragment appears almost planar, the largest deviation of the bridging atoms from the least-squares plane of the three cobalt atoms being <0.1 Å. The Co···Co distances are indicative of no significant direct metal–metal bonding and therefore this compound may be regarded as an assembly of three cofacial octahedra. In particular the Co···Co separation facing the bridging phosphido ligand is significantly larger [3.145(5) Å] than the other two [2.978(5) and 3.015(5) Å]. Concerning the $(\mu_3\text{-}S)$–Co distances, those involving the cobalt atoms more largely separated [Co(1) and Co(2)] are significantly larger [average 2.312(6) Å] than those relative to the third cobalt [Co(3)] [average 2.272(1) Å], so that the μ_3-S ligands appear slightly displaced with respect to the three metal atoms.

---

* Diethylphosphine (15 mmol, 1.35 g) was added to $[Co(H_2O)_6][ClO_4]_2$ (5 mmol, 1.8 g) in acetone–ethanol (1:1, 30 cm^3) under a nitrogen atmosphere and H_2S was bubbled through the solution for 10 min, at room temperature. Evaporation of the solvent in a current of nitrogen yielded the crude product, which was filtered off, washed with butanol, then with benzene and dried in a current of nitrogen. Well shaped black crystals were obtained by recrystallization from acetone–butanol (yield 25%) (Found: C, 29.50; H, 6.90; Co, 15.55; S, 10.90. Calc. for $C_{28}H_{78}Cl_2Co_3O_8P_7S_4$: C, 29.60; H, 6.90; Co, 15.55; S, 11.30%).

† Crystal data for $C_{28}H_{78}Cl_2Co_3O_8P_7S_4$: $M = 1135.7$, monoclinic, space group $P2_1/c$, $a = 19.949(8)$, $b = 13.593(6)$, $c = 19.602(8)$ Å, $\beta = 101.2(1)°$, $U = 5199.4$ Å^3, $Z = 4$, $D_c = 1.450$ g cm^{-3}, $F(000) = 2376$, μ(Mo-Kα) = 14.5 cm^{-1}, black crystal (0.12 × 0.30 × 0.45 mm) coated in paraffin. A total of 7806 data were recorded on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique and graphite-monochromatized Mo-Kα radiation (λ = 0.7107 Å), within 2θ < 46°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares refinement using SHELX 76 [4] with $w = 1/\sigma^2(F_o)$; R and R' were 0.077 and 0.076 respectively for 2072 observed $[I > 3\sigma(I)]$, absorption corrected, reflections. The rather high R values are probably due to the poor quality of the crystals because of which low-angle and low-intensity reflections were collected; moreover both the ClO_4^- anions are affected by disorder.

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

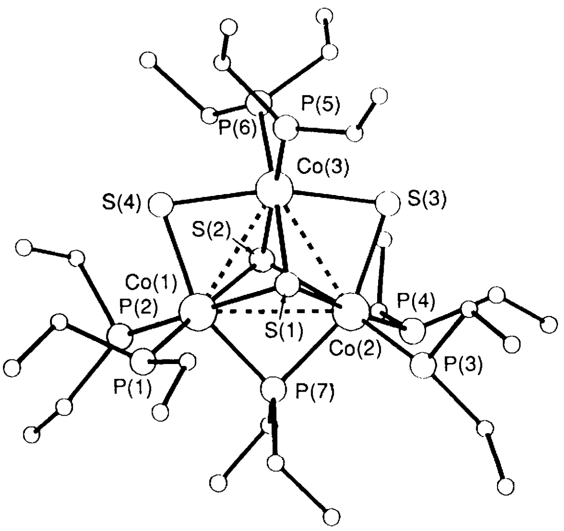

Fig. 1 Perspective view of the cluster unit $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)_2\text{-}(\mu\text{-}PEt_2)(PHEt_2)_6]^{2+}$ (PLUTO[5] drawing). Selected bond distances (Å) and angles (°): Co(1)···Co(2) 3.145(5), Co(1)···Co(3) 2.978(5), Co(2)···Co(3) 3.015(5), Co–(μ_3-S) 2.271(8)–2.329(8), Co–(μ-S) 2.343(8)–2.383(8), Co–(μ-P) 2.235(9)–2.259(9), Co–P_{term} 2.225(12)–2.256(9); P(1)–Co(1)–S(2) 174.6(3), P(2)–Co(1)–S(1) 172.3(3), P(7)–Co(1)–S(4) 154.3(3), P(3)–Co(2)–S(2) 168.8(3), P(4)–Co(2)–S(1) 176.1(3), P(7)–Co(2)–S(3) 153.6(3), P(5)–Co(3)–S(2) 175.0(3), P(6)–Co(3)–S(1) 172.6(4), S(3)–Co(3)–S(4) 165.4(3), Co–(μ_3-S)–Co 81.2(3)–85.9(3), Co–(μ-S)–Co 78.1(2)–79.3(3), Co–(μ-P)–Co 88.8(3)

Since this compound is the first triangular cluster of cobalt atoms stabilized by phosphine ligands* an interesting comparison can be made with the recently reported triangular cluster of rhodium atoms of formula $[Rh_3(\mu_3\text{-}S)_2(\mu\text{-}S)(\mu\text{-}Cl)_2\text{-}(PEt_3)_6]^+$ which is isostructural and isoelectronic.[2e] In particular the separations Rh···Rh, with one value larger [3.247(3) Å] and two shorter [3.172(3) and 3.188(3) Å], closely resemble the Co···Co distances, taking into account the different covalent radii.

References

1 J. M. Berg and R. H. Holm, in *Iron–Sulfur Proteins*, ed. T. G. Spiro, Wiley, New York, 1982, vol. 4; B. Bogdanovic, P. Gottsch and M. Rubach, *J. Mol. Catal.*, 1985, **11**, 135.

2 (*a*) F. Cecconi, C. A. Ghilardi and S. Midollini, *J. Chem. Soc., Chem. Commun.*, 1981, 640; (*b*) F. Cecconi, C. A. Ghilardi and S. Midollini, *Inorg. Chem.*, 1983, **22**, 3802; (*c*) F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini and P. Zanello, *Polyhedron*, 1986, **5**, 2021; (*d*) F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1987, 831; (*e*) F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca and J. A. Ramirez, *Inorg. Chim. Acta*, 1989, **155**, 5; (*f*) A. Muller, N. H. Schladerbeck and H. Bogge, *J. Chem. Soc., Chem. Commun.*, 1987, 35; (*g*) F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orlandini, *J. Chem. Soc., Chem. Commun.*, 1992, 910.

3 F. Cecconi, C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and G. Scapacci, *Inorg. Chim. Acta*, 1991, **189**, 105.

4 G. M. Sheldrick, SHELX 76, System of Computing Programs, University of Cambridge, 1976.

5 PLUTO, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, 1989.

6 A. Muller and E. Diemann, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, p. 515.

7 K. S. Hagen, G. Christou and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 309.

Received 23*rd June* 1992; *Communication* 2/03311I

---

* A sulfido monocapped triangular cluster of cobalt atoms, stabilized by bridging and terminal dithiolate ligands, has been reported, with the metal centres tetrahedrally co-ordinated and the doubly bridging dithiolate ligands below the plane of the three cobalt atoms.[7]