An Unusual Heptanuclear Co_4Cu_3 Cluster Complex: A Copper(III) Cluster Derivative?

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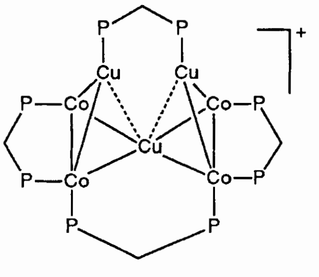
The new cluster cation $[Co_4Cu_3(CO)_8(Me_2PCH_2PMe_2)_4]^+$ contains a central copper atom bridging two Co_2Cu triangles; on the basis of, (*i*) its approximately square-planar stereochemistry, and (*ii*) electron counting considerations, it is suggested that the central copper atom has the d^8 Cu^{III} electron configuration, which is unique in copper clusters.

The structure and bonding in almost all heteronuclear copper–metal clusters can be interpreted in terms of the presence of copper(I), which is typically present as LCu^+ or Cu^+ bridging between metal atoms.[1] The isolobal analogy between LCu^+, LAu^+ and H^+ is often invoked for rationalizing the structures and so, although oxidation state is not usually a useful concept in cluster chemistry, it is commonly used in the heteronuclear clusters of the coinage metals. This article reports a cluster complex which contains a bridging copper atom with approximate square-planar stereochemistry more typical of copper(III).

The new cluster complex $[Co_4Cu_3(CO)_8(\mu\text{-dmpm})_4]BF_4$ **1** (dmpm = $Me_2PCH_2PMe_2$) was prepared in low yield as air-stable black crystals by reaction of $[Co_2(CO)_2(\mu\text{-CO})_2(\mu\text{-}$

dmpm)$_2$][2] with [Cu(MeCN)$_4$]BF$_4$ and was characterized spectroscopically† and by an X-ray structure determination.‡ In the cluster cation (Fig. 1, skeleton with CO ligands omitted shown schematically as **1**) there are two triangles of metal atoms [Co(1)Co(2)Cu(2) and Co(3)Co(4)Cu(3)] bridged by a central copper atom [Cu(1)]. Each Co$_2$Cu triangle has three edge-bridging carbonyl ligands of which one [*e.g.* C(3)O(3)] bridges a CoCo bond and two [*e.g.*C(5)O(5) and C(7)O(7)] are semibridging between cobalt and copper.[3,4] The two Co$_2$Cu triangles are bridged by two dmpm ligands, of which one bridges between equivalent copper atoms [Cu(2)P(1)P(2)Cu(3)] and one bridges between cobalt atoms [Co(1)P(3)P(4)Co(3)], while the remaining dmpm and carbonyl ligands are terminally bound to cobalt. The two Co$_2$Cu triangles lean towards one another such that the non-bonding distance Cu(2)Cu(3) [3.211(4) Å] is much shorter than the corresponding distances Co(1)Co(3) [4.248(4) Å] and Co(2)Co(4) [4.241(4) Å]. In order to span the long Co(1)Co(3) distance the μ-dmpm ligand has bond angles which are significantly distorted from the normal tetrahedral values: Co(1)P(3)C(20), 112.2(1.2)°; P(3)C(20)P(4), 121.8(2.1)°; Co(3)P(4)C(20) = 121.5(1.4)°, indicating considerable angle strain. Indeed the cluster is remarkable in having the versatile μ-dmpm ligands spanning pairs of metal atoms separated by the disparate distances of 2.51, 2.52, 3.21 and 4.25 Å.



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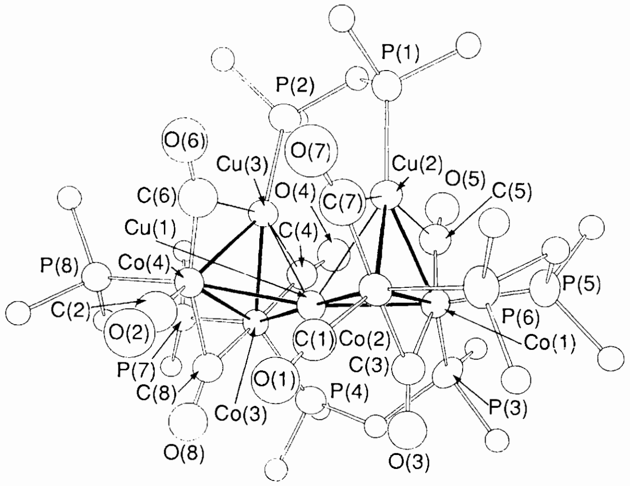

Fig. 1 A view of the structure of the cluster cation [Co$_4$Cu$_3$(CO)$_8$-(μ-dmpm)$_4$]$^+$

The most remarkable feature of the structure of **1** is the geometry of the bridging copper atom Cu(1). It does not bridge symmetrically between the faces of the Co$_2$Cu triangles but is displaced towards the cobalt atoms such that the Cu(1)Co distances [2.458(4)–2.474(4) Å] are significantly shorter than the Cu(1)Cu distances [2.683(4) and 2.624(3) Å]. The latter distances are in the range found for weak lateral forces between copper(I) atoms,[1,5] but the CuCu bonding is still presumably partly responsible for the tilting of the Co$_2$Cu triangles described above. The four cobalt atoms and Cu(1) are approximately coplanar [dihedral angle between planes Cu(1)Co(1)Co(2) and Cu(1)Co(3)Co(4) 14.8(3)°; ∠Co(2)Cu(1)Co(3) 178.0(1)°; ∠Co(1)Cu(1)Co(4) 168.1(1)°]. Although at least one group 11 cluster complex is known to contain an approximately square-planar metal centre in oxidation state (I),[6] this stereochemistry is much more typical of these metals in oxidation state (III). Furthermore, formal removal of the central copper atom Cu(1) as Cu$^+$ leaves each Co$_2$Cu triangle with an odd electron count, whereas its removal as Cu^{3+} leaves each Co$_2$Cu triangle with an even electron count and each atom of the Co$_2$Cu triangle with its favoured electron count.[1] Together these factors suggest that the cluster contains a formally d^8 copper(III) atom Cu(1).§ This is an unprecedented electron configuration in a copper cluster.[1]

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† *Spectroscopic data*: IR (Nujol mull): ν(CO)/cm^{-1} 1981vs, 1946m, 1917sh (terminal CO), 1879vs, 1860vs, 1838m, 1833m, 1803sh (semibridging CO) and 1713vs (bridging CO); NMR data in [^{2}H$_7$]dimethylformamide: ^{1}H, δ 1.04 (1 Me), 1.18 (1 Me), 1.24 (1 Me), 1.42 (2 Me), 1.64 (1 Me), 1.68 (2 Me) and 2.7 (CH$_2$P$_2$); ^{31}P, δ 3.66 (1 P), 3.28 (2 P) and −31.19 (1 P); m.p. 174–175 °C (decomp.); FAB MS: *m/z* 1195; calc. for Co$_4$Cu$_3$(CO)$_8$(dmpm)$_4$$^+$ 1195, with excellent agreement between observed and calculated isotope patterns. Accurate mass: found, 1194.708; calc. 1194.715.

‡ *Crystal data*: C$_{28}$H$_{56}$BCo$_4$Cu$_3$F$_4$P$_8$O$_8$, M = 1281.72, monoclinic, $P2_1/c$ (No. 14), a = 10.767(2), b = 20.092(2), c = 22.370(3) Å, β = 92.13(1)°, V = 4835.9(2.0) Å^3, Z = 4, D_m (D_c) = 1.78 (1.76) g cm^{-3}, Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation, 6699 unique data ($0 \leqslant 2\theta \leqslant 46°$). Lorentz, polarization and absorption corrections applied, R_1 = 0.0760, R_2 = 0.066 for 3093 observations [$I \geqslant 2.5\sigma(I)$] and 295 variables. The identification of Co and Cu atoms was based on the coordination numbers and stereochemistries of the metal atoms since the atoms were too close in atomic number to be distinguished crystallographically. 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.

§ Because this is a unique electron configuration, the possible presence of hydride ligands has been considered. Note that a formulation as [Co$_4$Cu$_3$H$_2$(CO)$_8$(μ-dmpm)$_4$]$^+$ would require Cu(1) to have oxidation state (I). However, no evidence for hydride was observed in the ^{1}H NMR spectrum (no signals from δ 0 to −50) nor from final difference Fourier maps in the X-ray structure determination. Dissolution of the cluster in a [^{2}H$_7$]dimethylformamide–CCl$_4$ mixture failed to give any trace of CHCl$_3$. This reduction of CCl$_4$ to CHCl$_3$ is a sensitive test for transition metal hydrides. The mass spectrum gave a peak at m/z = 1195 as expected for the cluster cation without hydride ligands.

Formal removal of Cu(1) as Cu^{3+} and the other copper atoms as LCu$^+$ leaves two [Co$_2$L$_6$(μ-CO)]$^{2-}$ units, L = terminal CO or phosphine donor atom, in which each cobalt has an 18-electron count. The use of oxidation states in clusters is fraught with problems; it is used here to indicate that the Cu(1) probably uses dsp^2 hybrids in bonding and has the stereochemistry expected for this bonding state.