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LETTER

A colorless Cu(II) complex of CuO_6 with a compressed tetragonal octahedron

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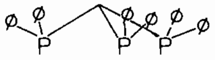
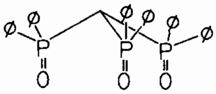
In the course of studies of d^{10} metal cluster chemistry, the tripodal triphosphine, tdmp, was used as bridging ligand to hold the cluster together. An unexpected oxidized product was formed in the reaction of the Cu(II) ion and tripodal phosphine tdpm. Here we report the synthesis and crystal structure of this colorless product, bis(trisdiphenylphosphitomethane) copper(II) perchlorate dihydrate. The complex was prepared by the reaction of excess $Cu(ClO_4)_2\cdot 6H_2O$ (0.2 g, 0.54 mmol) with tdpm (0.1 g, 0.18 mmol) in methanol (about 30 ml) at room temperature for one day. Crystals were obtained by ether evaporation of the methanol at room temperature. Crystal data of $[Cu(II)(HC(\phi_2PO)_3)_2](ClO_4)_2\cdot(H_2O)_2$: $CuP_6Cl_2O_{16}C_{74}H_{66}$, triclinic space group $P\bar{1}$, $a=11.997(3)$, $b=12.264(2)$, $c=13.159(2)$ Å, $\alpha=90.76(1)$, $\beta=107.97(2)$, $\gamma=99.03(2)°$, $V=1815.0(6)$ Å^3, $Z=1$, $D_c=1.401$ g cm^{-3}, $R_F=0.039$, $R_{wF}=0.032$ for 4649 unique reflections ($2\theta<50°$) with $I>2\sigma(I)$ and 457 variables. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα ($\lambda=0.7093$ Å) radiation. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as fixed contributions except the hydrogen atoms of the water molecules.



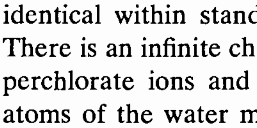
tdpm
trisdiphenylphosphinomethane



tdpom
trisdiphenylphosphitomethane

The structure consists of a cation in which the copper ion is located on a crystallographic inversion center, a perchlorate, and a water molecules which are both located in the general positions. The ORTEP drawing of the cation is shown in Fig. 1. The copper ion is coordinated by six oxygen atoms of two trisdiphenylphosphitomethane ligands in a compressed tetragonally distorted octahedron instead of a trigonally distorted octahedron or an elongated tetragonally distorted octahedron. Among the three unique Cu–O distances, the Cu–O2 distance is the smallest, 1.977(2) Å, and the Cu–O1, Cu–O3 distances, 2.128(2) and 2.152(2) Å, respectively, are identical. The O–Cu–O angles ranging from 87.8(1) to 92.2(1)°, are close to 90°. Another example of a colorless Cu(II) complex is anhydrous Cu(II)SO_4 in which an elongated rhombic octahedron is observed with three sets of Cu–O distances, 1.89, 2.00 and 2.37 Å, respectively [1]. The most closely related structure is the blue complex, $[Cu(methoxyacetate)_2(OH_2)_2]$, in which a compressed tetragonal distortion is observed with Cu–O distances 1.94, 2.14 and 2.15 Å, respectively [2]. In the ligand moiety, all chemically equivalent bond parameters are identical within standard deviations and are normal. There is an infinite chain of hydrogen bonding between perchlorate ions and water molecules. The hydrogen atoms of the water molecule are clearly located from the difference Fourier map and were refined isotropically. The water molecule is hydrogen bonded to two perchlorate ions (*vide infra*) with the following bond parameters: for O(8)–H(8A)- - -O(5) and O(8)–H(8B)- - -O(4); O(8)–H(8A), 0.90(4) Å, H(8A)- - -O(5), 2.13(4) Å, O(8)–H(8A)- - -O(5) 177(3)°, O(8)–H(8B), 0.91(5) Å, H(8B)- - -O(4) 1.93(5) Å, O(8)–H(8B)- - -O(4) 162(5)°, H(8A)–O(8)–H(8B) 102(5)°.

The complex has a magnetic moment of 2.1 BM at 298 K which clearly reveals that the copper ion is in the +2 oxidation state. The reason that the complex is colorless is that its d–d transition falls into the near IR region ($\lambda_{max}=897$ nm). This transition is similar to those of CuF_2 [3] and CuL_2 [4, 5].



This result indicates that the phosphito ligands, tdpom and L, are hard (high nephelauxetic ratio β) and have a ligand-field strength near that of F^- [6].

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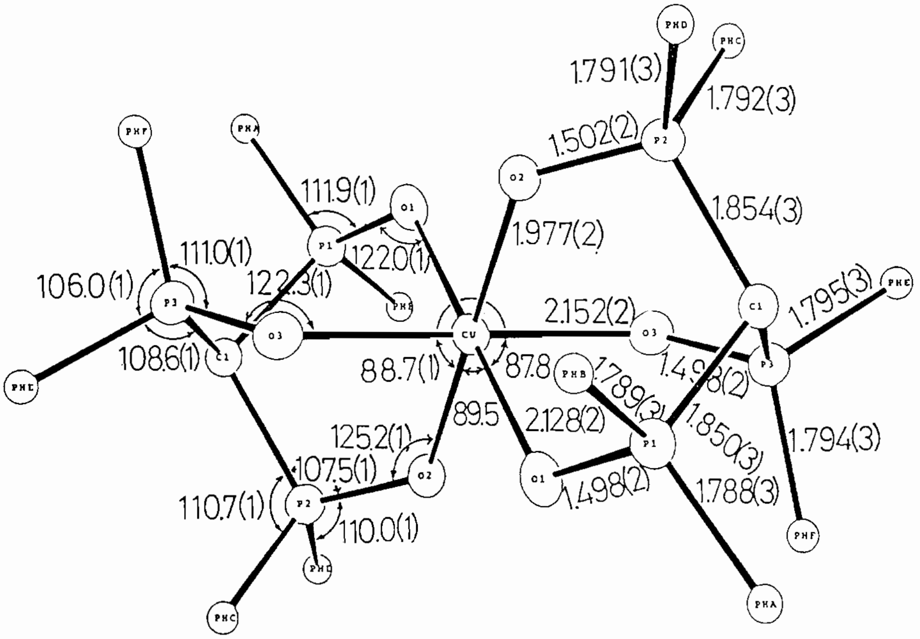

Fig. 1. ORTEP drawing of the cation $[Cu(HC(P\phi_2O)_3)_2]^{2+}$ with 50% probability. The phenyl groups except the attached carbon atoms have been omitted for clarity. The angles around P1, P2, P3, C1 atoms in the range 106–112° are near the tetrahedral angle.

Acknowledgements

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