Five-Co-ordinate Copper(II) in a Cubane-type Structure

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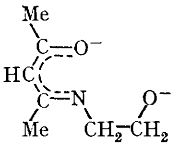
MANY polynuclear copper(II) complexes with bridging oxygen atoms are known and almost all such complexes exhibit sub-normal magnetic moments;[1] the only exceptions for which detailed structures are known[2,3] are the μ_4-oxo-compounds of the general formula $Cu_4OX_6L_4$ (where X represents a halogen and L a unidentate ligand). Recently, the complex of copper(II) with the tridentate Schiff base (I) derived from acetylacetone and 2-aminoethanol was reported[4] to have a normal magnetic moment of 1·84 B.M.; the molecular weight of the compound indicated that it was tetrameric.



The compound $CuC_7H_{11}NO_2$ crystallized as tetragonal crystals with $a = 14{\cdot}46(3)$ and $c = 7{\cdot}63(2)$ Å; $D_m = 1{\cdot}70$, $D_c = 1{\cdot}71$ g.cm.$^{-3}$, $Z = 2$. Systematic absences for reflections $h00$, $h = 2n + 1$, and hhl, $l = 2n + 1$, indicate space group $P\bar{4}2_1c$. The two tetramers are, thus, required to occupy sites of $\bar{4}$ symmetry and the asymmetric unit consists of one formula unit.

A total of 394 unique, non-zero reflections were collected from the hxl, $x = 0$—3, and hhl zones with a precession camera and Mo-K_α radiation. Co-ordinates for copper were obtained from a three-dimensional Patterson synthesis and successive structure-factor calculations and Fourier syntheses revealed the positions of all other non-hydrogen atoms; full-matrix least-squares refinement of all atomic co-ordinates, individual isotropic thermal parameters, and individual layer scale factors (a total of 49 parameters) converged to a conventional R value of 0·089.

The resulting structure (Figure) consists of a distorted tetrahedron of copper ions with oxygen atoms above each face of the tetrahedron; the four copper ions and the four oxygens form a slightly distorted cube similar to that reported[5] for compounds of the formula [M(acac)(MeO)(MeOH)]$_4$ (M= Co, Ni, Mg; acac represents the anion of a β-diketone). The co-ordination about each copper is bipyramidal; the two oxygens of the tridentate ligand occupy axial positions with an O–Cu–O angle of 178·0(9); the nitrogen and alkoxide oxygens from adjacent ligands occupy the equatorial positions with O–Cu–N angles of 153·1(8) and 120·3(8) and an O–Cu–O angle of 81·3(7). The distances from the copper to the donor atoms of the tridentate ligand are 1·90(2), 1·91(2), and 1·98(2) for the nitrogen, the oxygen of the acetylacetonate, and the oxygen of the 2-aminoethanol, respectively; the distances from the copper to the oxygen atoms of adjacent ligands are 2·00(2) and 2·32(2).

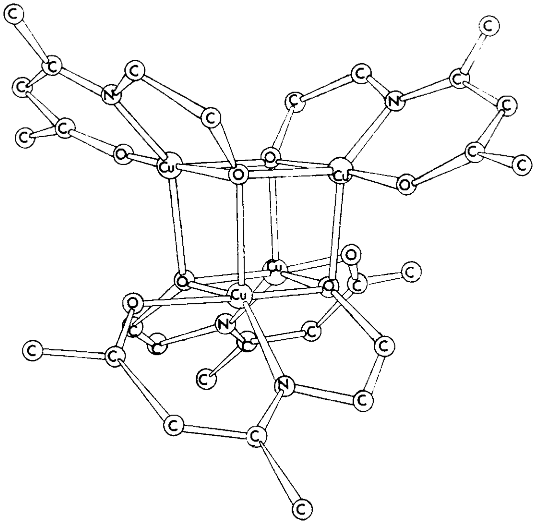


FIGURE. *Molecular structure of* [Cu($C_7H_{11}NO_2$)]$_4$.

Each bridging oxygen atom is bonded to three copper(II) ions and one carbon atom; all outer orbitals of these oxygens are, thus, involved in σ-bonding and there are no low-energy orbitals available for super-exchange through a π-interaction. The fact that these compounds and the μ_4-oxo-compounds mentioned above [in which the μ_4-oxygen is bonded to four copper(II) ions] exhibit normal magnetic moments while all other copper(II) complexes with bridging oxygen atoms exhibit sub-normal moments supports the suggestion[1] that super-exchange occurs through a π-interaction.

A corresponding nickel(II) compound was isolated[4] as the monomethanolate; this green, paramagnetic compound was observed to lose methanol readily to form a red, diamagnetic compound. The previously unreported cobalt(II) compound was prepared by the same method, but crystallized as the unsolvated compound. X-Ray powder-diffraction patterns of the copper and cobalt compounds are identical but the powder pattern of the desolvated nickel compound is markedly different.

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