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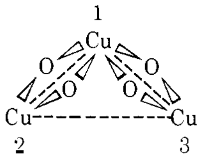
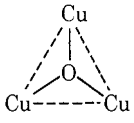
Linear Trinuclear Copper(II) Complex with a Spin-Doublet Ground State

Sir:

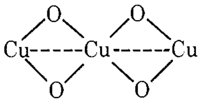
There have been several reports[1-6] of oxygen-bridged trinuclear copper(II) complexes that exhibit varying degrees of antiferromagnetic behavior. The molecular structures[7-9] for a representative number of these complexes have revealed only two kinds of trinuclear copper clusters. Both consist of triangular arrays (I and II) of copper ions but differ in the kind of bridging oxygen atoms (μ_2 or μ_3), the shape of the triangle (isosceles I or equilateral II), and the degree of exchange coupling between copper ions.



I



II

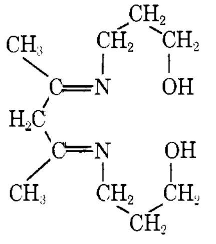


III

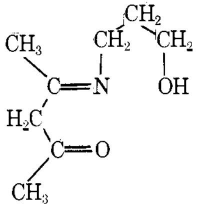
Complexes of type I exhibit subnormal room temperature magnetic moments greater than ~1 BM per copper ion; that is, there is still some population of the spin 3/2 state by the three electrons of the Cu_3 core at room temperature. The magnetic behavior of type I complexes with a few exceptions has been characterized[5,7,10] by assuming a model based upon three interacting spin 1/2 species with exchange coupling between the central copper ion and its neighbors (1–2) and (1–3) but no interactions (2–3) between extreme copper ions of the triad.

Complexes of type II, however, exhibit complete spin pairing, so that only the spin-doublet state ($S = 1/2$) is populated at room temperature. All type II complexes examined to date by X-ray diffraction have shown the copper ions to be positioned at the corners of an equilateral triangle. We wish to report the first example of a trinuclear copper complex having a spin-doublet ground state in which the copper ions are arranged in a strict linear fashion and joined by μ_2-bridging oxygen atoms, III.

The compound is the neutral copper(II) complex of the trianion of the tetradentate ligand, IV, formed by the condensation of 2,4-pentanedione and 3-amino-1-propanol. The compound was prepared by the reaction of copper(II) acetylacetonate with potassium hydroxide in neat 3-amino-1-propanol at 100° over a 3-hr period. Although the initial product is contaminated with the red dimeric complex, $[Cu(PIA)]_2$[11] (where PIA is the dianion of ligand V), separation was accomplished by extensive washings in hot absolute alcohol. Crystallization from a mixture of xylenes gave green needle crystals of empirical formula $Cu_3C_{22}H_{38}N_4O_4$. Precession photographs (Zr-filtered Mo Kα ra-



IV



V

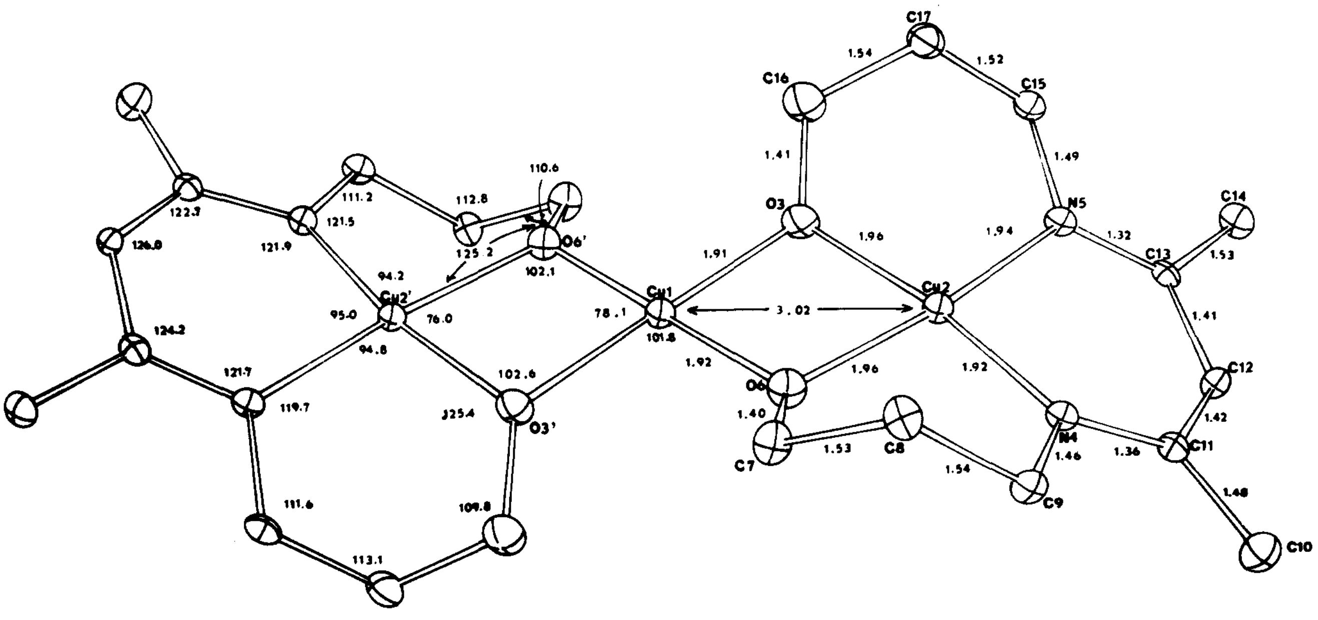


Figure 1. Molecular structure of the trinuclear complex $Cu_3(C_{11}H_{19}N_2O_2)_2$, showing all non-hydrogen atoms. Bond distances and bond angles have deviations in the range 0.01–0.02 Å and 0.2–0.6°, respectively.

diation) indicated that the crystals were triclinic, and the successful refinement of the structure has confirmed the space group as $P\bar{1}$. Reduced cell parameters were obtained from precession photographs which were corrected for shrinkage by superposition of a previously oriented NaCl lattice. Measurements were made directly from the photographs using a film measuring device supplied by Charles Supper Co. A total of 30 reflections were used to obtain reduced cell parameters of $a = 7.564$ (7) Å, $b = 9.547$ (8) Å, $c = 9.575$ (8) Å, $\alpha = 111.83$ (10)°, $\beta = 96.32$ (8)°, and $\gamma = 100.25$ (9)°; the density calculated for one trimer per unit cell, 1.64 g cm^{-3}, agrees well with the experimental value, 1.62 g cm^{-3}, obtained by the flotation method in a mixture of methyl iodide and carbon tetrachloride. Intensity data were collected on a Philips PAILRED diffractometer using equiinclination geometry and a continuous ω-scan technique. Cu Kα radiation (λ 1.5418 Å) and a graphite monochromator crystal ($d(002) = 3.3539$ Å) were used. A total of 2057 reflections were chosen as above background on the basis of the acceptance criterion that $\sigma(I)/I < 0.5$. The reflections were corrected for Lorentz and polarization effects as well as for absorption. The standard heavy atom technique was employed to locate the positions of all nonhydrogen atoms. Full-matrix least-squares refinement of the coordinates and anisotropic temperature factors of all the non-hydrogen atoms have resulted in a conventional R value,

$$R = (\Sigma|F_o - F_c|)/(\Sigma|F_o|)$$

of 0.042 and a weighted R_w value

$$R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2\}^{1/2}$$

of 0.073 using a weighting scheme in which the weights, $w = 1.0/|\Delta \bar{F}|^2$, were obtained from a plot of $|\Delta \bar{F}|$ vs. $|\bar{F}_o|$. Further refinement is in progress, but the main features of the structure are apparent at this stage.

The unit cell contains only one trimeric unit and is illustrated with an atomic numbering scheme in Figure 1. The central copper atom, Cu1 rests on a site of inversion in the space group $P\bar{1}$, which for simplicity was arbitrarily chosen to be the origin of the cell. Copper ions 2 and 2′, which occupy general positions, are centrosymmetrically related to one another and, consequently, lie in a straight line relationship thru the origin defined at Cu1. The copper ions are held together by μ_2-bridging oxygens, O3, O3′, O6, and O6′, from the propoxide portions of the trinegative diimine ligand. The coordination about Cu2 is square planar, and consists of two bridging propoxide oxygens and two imine nitrogen atoms from the same ligand; no donor atom deviates from the coordination plane by more than 0.04 Å (N5, −0.02 (1) Å; N4, 0.02 (1) Å; O3, 0.02 (1) Å; O6, −0.03 (1) Å; and Cu2, 0.02 (1) Å). The four coordination about Cu1 is strictly planar as required by symmetry and consists of four μ_2-bridging propoxide oxygens, two from each of the two tetradentate diimine ligands of the trimer.

Although both Cu1 and Cu2 have square planar coordination, this does not give rise to an entirely planar trimeric unit. Instead, there is a noticeable bend in the Cu_2O_2 four-membered ring as measured by the dihedral angle, 10.2 (4)°, between the Cu1-O3-O6 and Cu2-O3-O6 planes. This nonplanarity in the Cu_2O_2 ring is evident from Figure 1 in that the propanolamine carbons (C16, C17, C15 and C7, C8, C9) are tilted in the same direction away from the coordination plane about Cu2. It is interesting to note that the ligand atoms of the six-membered ring (N5, C13, C12, C11, and N4) are also tilted (in the opposite direction) out of the coordination plane about Cu2, even though the bond lengths, angles, and planarity of the six-membered ring are indicative of a delocalized π-system.

The copper-copper distance of 3.017 (1) Å is only slightly shorter than that reported,[11] 3.026 (6) Å, for the parent dinuclear complex, $[Cu(PIA)]_2$, and is likely due to the bending of the Cu_2O_2 ring. Despite the nonplanarity of the Cu_2O_2 ring, it is evident from the magnetic moment at room temperature, 1.09 BM/(g atom of Cu), that strong antiferromagnetic interactions are operating within the Cu_2O_2 ring. This follows from the fact that there are no intertrimer contacts within 4 Å of either copper atom. Consequently, the principal coupling interaction cannot be intercluster al, but intramolecular. In addition, the bent Cu_2O_2 bridge is indicative of indirect coupling via a σ-pathway, since the effectiveness of a π-pathway would be greatly diminished. The efficiency of a predominately σ-pathway is evidenced in the nearly invariant magnetic moment below room temperature; the magnetic moment per copper drops only 0.04 BM (from 1.09 to 1.05 BM) on lowering the temperature from 296 to 35°K. In effect, two of the three electrons of the copper trimer are paired, and only the spin-doublet state is populated. This behavior is analogous to that found for the copper complexes, $Cu_3(PAO)_3(OH)(SO_4)\cdot 16.3H_2O$ and $Cu_3(PrAO)_3(H_2O)_3O_{0.5}(OH)_{0.5}(ClO_4)_{1.5}\cdot 4H_2O$, whose molecular structures[8,9] have revealed an equilateral triangular array of copper ions (PAO = pyridinaldoxime, and PrAO = 2-propylamino-2-methyl-3-butanone oxime; both PAO and PrAO are minus the oxime proton).

Further work on the synthesis, structure, and magnetic properties of other metal complexes containing diimine ligands is in progress.

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Frontier Orbital Resolution of the Quadricyclyl Cation Puzzle[1]

Sir:

A cyclopropane ring is known to enhance the rate of solvolysis at an adjacent incipient carbocation center by a factor of ~10^9. This enhancement is consistent with the rate of solvolysis for norticyclyl cation (**2**) relative to the unstabilized[2] 7-norbornyl cation (**1**).[3] Furthermore, these stabilizations have been shown to be largely additive upon multiple