Inorganica Chimica Acta, 25 (1977) L69–L70
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Spin Coupling in a Trinuclear Copper(II) Complex of 1,3-Diamino-2-propanol

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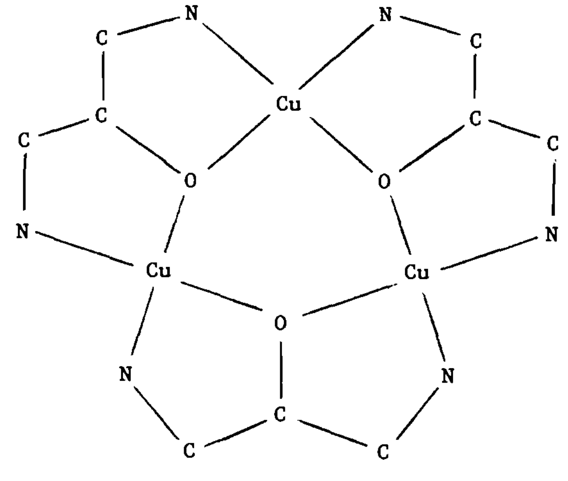
Received September 14, 1977

As part of a continuing investigation of transition metal complexes of aminoalcohols, we have prepared and studied complexes of 1,3-diamino-2-propanol (abbreviated DapoH in formulas). This particular aminoalcohol was of interest because it can coordinate in several different ways; it is known to coordinate through the nitrogens only [1], forming a six-membered chelate ring, and through nitrogens and oxygens [2], forming two five-membered chelate rings. A recent report [3] indicates that this ligand can also serve as a binucleating ligand, forming five-membered chelate rings through oxygen and nitrogen to two metal ions; this type of coordination was observed for a triangular trinuclear copper(II) complex, I. We have observed this type of coordination as well as bidentate coordination in a trinuclear copper(II) complex, $[Cu_3(Dapo)_2(DapoH)_2^{4+}]$. In this paper we report the preparation, structure, and magnetic properties of the iodide salt of this cation, $[Cu_3(Dapo)_2(DapoH)_2]I_4 \cdot CH_3OH$ [4].



I

To prepare the compound, 5 mmol of $Cu(CH_3CO_2)_2 \cdot 2H_2O$ and 15 mmol of 1,3-diamino-2-propanol were mixed in 75 ml of methanol. Addition of an aqueous solution of 15 mmol of KI to the deep blue solution, followed by slow evaporation yielded material suitable for single-crystal X-ray diffraction studies.

Crystals of $[Cu_3(Dapo)_2(DapoH)_2]I_4 \cdot CH_3OH$ are monoclinic, space group $P2_1/c$, a = 12.255(4), b = 12.999(5), c = 19.873(5) Å, β = 97.45(2)°, Z = 4, D_c = 2.30, D_m = 2.29 g cm^{-3}. Intensity data were collected on a Syntex $P2_1$ four-circle difractometer

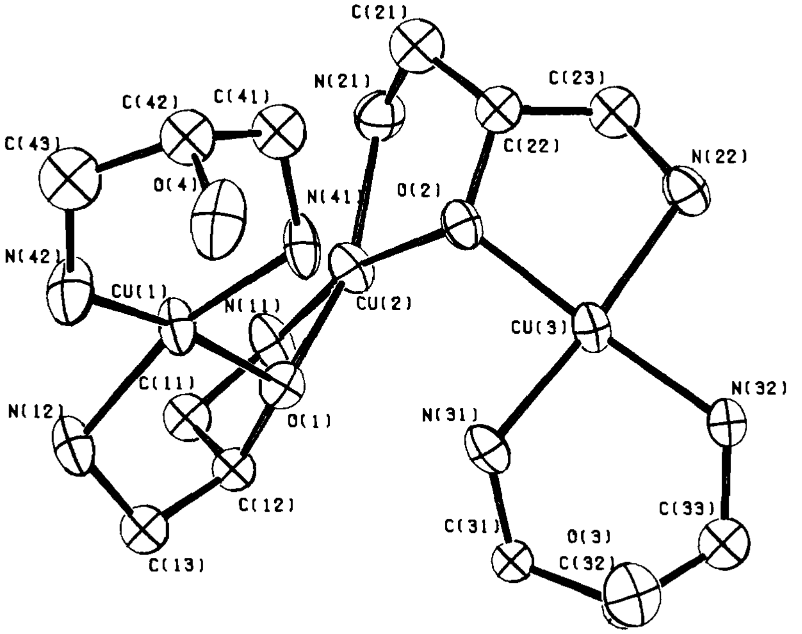


Figure 1. A view of the structure of the trinuclear cation, $[Cu_3(Dapo)_2(DapoH)_2]^{4+}$. Hydrogen atoms are omitted for clarity.

TABLE I. Magnetic Susceptibility of $[Cu_3(Dapo)_2(DapoH)_2]\,I_4$.

T, °K	$\chi_M \times 10^6$	
	Observed	Calculated
298	1011	1026
278	1044	1066
258	1115	1110
238	1172	1157
218	1215	1208
198	1277	1264
178	1319	1324
158	1395	1391
138	1476	1469
118	1556	1565
98	1717	1700

equipped with a graphite monochromator using MoKα radiation. Full-matrix least-squares methods were used to refine: (1) coordinates of 33 non-hydrogen atoms; (2) anisotropic thermal parameters of iodine, copper, oxygen and nitrogen atoms; and (3) isotropic thermal parameters of carbon atoms. Hydrogen atoms were included at calculated positions with isotropic temperature factors of 5.0 but were not refined. Refinement with 3577 unique reflections with $I \geqslant 3\sigma(I)$ converged to a conventional R factor of 0.065 and a weighted factor, R_w, of 0.078.

The trinuclear cation, Figure 1, contains a central, four-coordinate copper(II) chelated to the two deprotonated ligands through the oxygen and one nitrogen of each ligand with a *cis* arrangement. Each of the deprotonated ligands is also coordinated to a terminal copper(II) through the oxygen (bridging) and the remaining nitrogen. The square-planar coordination of each terminal copper(II) is completed by the two nitrogens of a neutral ligand; the alcohol groups of the neutral ligands are not coordinated. Although the cation has no symmetry imposed by the crystallographic site, the two Cu–O distances at the central copper(1.96(1) and 1.99(1) Å), the two Cu–O distances involving terminal copper atoms (2.00(1) and 2.02(1) Å), and the two Cu–O–Cu angles (114.4(6) and 118.2(6)°) are almost equal.

The magnetic moment decreases with temperature and indicates antiferromagnetic coupling. The magnetic susceptibilities for temperature from 98° to 298 °K can be fit to the expression [5] for a trinuclear species assuming identical coupling between nearest neighbor copper(II) ions ($J_{12} = J_{23} = J$) and no coupling between terminal copper(II) ions ($J_{13} = 0$):

$$\chi_M = \frac{N\beta^2 g^2}{12kT}\left[\frac{5\exp 2J/KT + 1}{\exp 2J/KT + 1}\right] + N\alpha$$

The best fit of the experimental data to this equation, Table I, was obtained with g = 2.02, 2J = –196 cm^{-1}, and $N\alpha = 115 \times 10^{-6}$.

It is interesting to compare the magnetic coupling in this compound with that observed for the cyclic compound [3] with three bridging groups, I. The energy separation between the allowed spin states in this compound is 2J and in the cyclic compound is 3J; however, the bridging arrangement is similar in the two compounds and they would be expected to have similar J values. The J values for the present compound, –98 cm^{-1}, is slightly greater than the –79 cm^{-1} of the nitrate salt or the –92 cm^{-1} of the perchlorate salt of the cyclic cation.

References

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3 M. Näsäkkälä, *Ann. Acad. Sci. Fenn., Ser. A II,* No. 181, *6,* (1977).

4 A compound mentioned in reference 3, $[Cu_3(Dapo)_2(DapoH)_2](SCN)_4$, apparently contains the same cation.

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