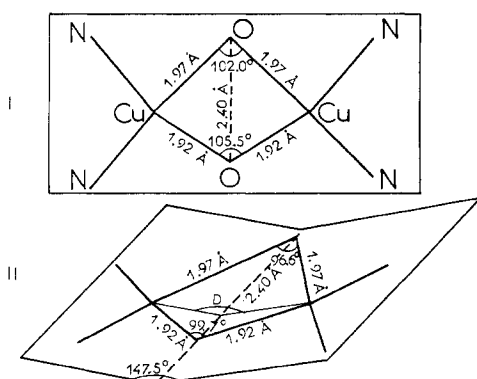


Correspondence

Exchange Interaction in Roof-Shaped Hydroxo-Bridged Copper(II) Dimers

Sir:

In a recent paper,¹ we have described the crystal structure of the new complex tetrakis(cyclohexylamine)di- μ -hydroxo-dicopper(II) perchlorate and studied its magnetic properties. The main interest of this work arose from the structure of this complex which is made of roof-shaped binuclear units $[\text{Cu}(\text{C}_6\text{H}_{11}\text{NH}_2)_2\text{OH}]_2^{2+}$ with a dihedral angle of 147.5° . This structure was described by considering first the hypothetical planar complex I and then by bending it around the axis



joining the oxygen atoms, in the same way as one bends a book, up to obtain the complex II with the actual dihedral angle.

Such an approach of the structure allowed us to investigate the influence of this bending on the magnetic properties of the hydroxo-bridged copper(II) dimers. We have concluded that when a hydroxo-bridged copper(II) dimer with Cu-O-Cu bridging angles larger than 90° is bent in such a way that the dihedral angle D between the two CuO_2 planes becomes smaller, the intramolecular coupling becomes less antiferromagnetic. This results from the variation vs. D of the energies ϵ_A and ϵ_S of the antisymmetric ψ_A and symmetric ψ_S molecular orbitals built from the two magnetic orbitals centered on the one and the other copper(II) ions. When D decreases, ϵ_A decreases whereas ϵ_S remains practically constant, and since ϵ_A is above ϵ_S , the energy gap $\epsilon_A - \epsilon_S$ which governs the magnitude of the antiferromagnetic coupling decreases (see Figure 1). The singlet-triplet separation J for the tetrakis(cyclohexylamine)di- μ -hydroxo-dicopper(II) perchlorate was found equal to -256 cm^{-1} . The intramolecular coupling is therefore clearly less antiferromagnetic than it would be if the Cu_2O_2 network was planar. According to Hatfield and Hodgson's correlation,² the value for the planar complex I would be about -600 cm^{-1} .

We claimed even in the title of ref 1 that the tetrakis(cyclohexylamine)di- μ -hydroxo-dicopper(II) perchlorate was the first example of roof-shaped hydroxo-bridged copper(II) dimer. In fact, while the paper was in press, we discovered that another structure of this kind had been described 12 years ago by Shimizu et al., namely, that of tetrakis(methylamine)di- μ -hydroxo-dicopper(II) sulfate monohydrate $[\text{Cu}(\text{CH}_3\text{N}-$

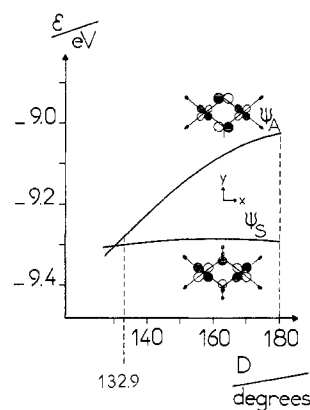
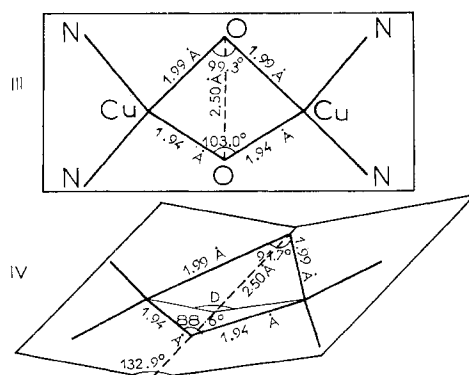


Figure 1. Variation vs. the dihedral angle D of the energies of the symmetric and antisymmetric molecular orbitals for roof-shaped hydroxo-bridged Cu(II) dimers with Cu-O = 1.938 and 1.990 Å and O-O = 2.500 Å.

$\text{H}_2)_2\text{OH}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$.³ The crystal contains two kinds of crystallographically independent copper atoms. One of each kind has as nearest neighbors two nitrogen atoms of the methylamine ligands and two oxygen atoms of the bridging hydroxo groups. The two mean planes N_2O_2 make a dihedral angle of 129.2° and the two CuO_2 planes a dihedral angle of 132.9° . Owing to this large deviation from planarity, the intramolecular copper-copper distance is only 2.78 Å. The actual coordination of each copper atom is 4 + 1: one of them is weakly bound to a water molecule $[\text{Cu} \cdots \text{O}(\text{H}_2) = 2.37 \text{ Å}]$, the other is weakly bound to the oxygen atom of an hydroxo bridge belonging to a nearest-neighbor molecule $[\text{Cu} \cdots \text{O}(\text{H}) = 2.40 \text{ Å}]$. As expected for copper(II) complexes with coordination 4 + 1, the copper atoms lie slightly out of the basal planes N_2O_2 toward the fifth ligands. The deviations from the basal planes are 0.07 and 0.14 Å, respectively.

The unpaired electron around each Cu(II) is described by a magnetic orbital⁴ built from the d_{xy} metallic orbital pointing toward the nearest-neighbor oxygen and nitrogen atoms. Therefore, the spin densities on the fifth ligands should be negligible. In other words, the very weak $\text{Cu} \cdots \text{O}$ axial interactions play a minor part in the exchange phenomenon. When the same approach as above is used, the structure of $[\text{Cu}(\text{CH}_3\text{NH}_2)_2\text{OH}]_2^{2+}$ may be obtained by bending the planar complex III up to achieve the roof-shaped structure IV.



(1) M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul, and J. Martin-Frere, *Inorg. Chem.*, **18**, 1675 (1979), and references therein.
 (2) V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976), and references therein.

(3) Y. Iitaka, K. Shimizu, and T. Kwan, *Acta Crystallogr.*, **20**, 803 (1966).
 (4) O. Kahn and B. Briat, *Colloq. Int. C.N.R.S.*, No. **255**, 251 (1977).

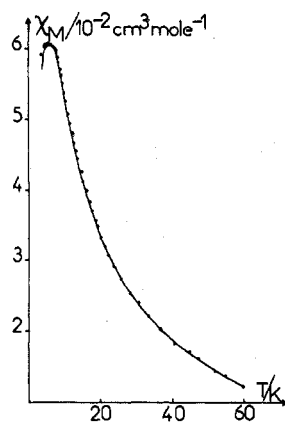


Figure 2. Temperature dependence of the molar magnetic susceptibility of $[\text{Cu}(\text{NH}_2\text{CH}_2)_2\text{OH}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The experimental points are noted as black dots and the best-fitting calculated curve is a continuous line.

This structure IV was somewhat idealized with regards to the actual structure of $[\text{Cu}(\text{CH}_3\text{NH}_2)_2\text{OH}]_2^{2+}$ by assuming the existence of a mirror plane containing the two hydroxo groups. The extended Hückel calculation of the energy gap $\Delta = \epsilon_A - \epsilon_S$ for the hypothetical dimer III carried out with the previously used parametrization¹ leads to almost exactly the same large value as for the hypothetical dimer I, 0.264 and 0.269 eV, respectively. Therefore, the coupling in III is expected to be strongly antiferromagnetic. In Figure 1 are given the variations of ϵ_A and ϵ_S vs. D . A crossover is obtained for $D = 130^\circ$. Thus, for the actual value of the dihedral angle, $D = 132.9^\circ$, one might expect a very small antiferromagnetic coupling or a ferromagnetic coupling. Indeed, in $[\text{Cu}(\text{CH}_3\text{NH}_2)_2\text{OH}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ the J value was found equal to $-7.9 \pm 0.5 \text{ cm}^{-1}$. This result illustrates in a very satisfying manner the influence of the bending on the exchange interaction in copper(II) dimers with $-\text{OH}$ bridges. In this correspondence, as in the previous paper,¹ we focused on the variation of the antiferromagnetic contribution J_{AF} vs. the dihedral angle. For completeness, it would be necessary to examine how the ferromagnetic contribution J_F varies when the Cu_2O_2 network is bent. We intend to approach this problem in our next paper.

Experimental Section

$[\text{Cu}(\text{CH}_3\text{NH}_2)_2\text{OH}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was prepared according to reference.³ The magnetic measurements were carried out in the temperature range 4–300 K with a previously described magnetometer¹ on samples prepared by picking up needle-shaped crystals under a binocular lens. The diamagnetism was estimated as $-204 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. Three different samples of about 10 mg coming from different preparations were studied. The chemical analysis of each sample was performed after the magnetic study. As already noticed by Shimizu et al., the results of the chemical analyses were not excellent because of the instability of the compound which tends to lose its methylamine. The best analysis follows. Anal. Calcd for $\text{Cu}_2\text{C}_4\text{H}_{24}\text{N}_4\text{O}_7\text{S}$: Cu, 31.82; C, 12.03; H, 6.06; N, 14.03; S, 8.03. Found: Cu, 31.4; C, 11.58; H, 6.38; N, 13.22; S, 8.41. For absolute assurance that the studied compound had the structure described by Shimizu et al., the X-ray powder spectrum of the sample leading to the chemical analysis given above was recorded on a photographic film and the observed lines were compared to the lines computed from the published unit cell parameters. For the first 15 lines, the agreement was excellent. In addition to the lines corresponding to the expected compound, the spectrum exhibited three extremely weak lines corresponding most likely to the small amount of impurity. We checked that these three unexpected lines were undetectable in the X-ray powder spectra of freshly prepared

samples. The magnetic data were fitted with the expression

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \left[3 + \exp\left(-\frac{J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{N\beta^2 g^2}{2kT} \rho + 2N\alpha$$

in which we took into account the presence of a proportion ρ of monomeric impurity, the molecular weight of which was assumed to be half that of the studied dimer. J , g , and ρ were taken as adjustable parameters and the TIP. $2N\alpha$ was fixed to $-120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. Least-squares fitting led to $J = -7.9 \text{ cm}^{-1}$, $g = 2.15$, and $\rho = 0.124$ for the sample having the best chemical analysis. The agreement factor defined as

$$\frac{\sum (\chi_M^{\text{obsd}} - \chi_M^{\text{calcd}})^2}{\sum (\chi_M^{\text{obsd}})^2}$$

is then equal to 0.74×10^{-4} . Experimental data and theoretical curve in the range 4–60 K are compared in Figure 2. Above 60 K, χ_M closely follows a Curie law. For the two other samples, least-squares fitting led to the same value of J within 0.3 cm^{-1} and of g within 0.004 but, as expected, to larger values of ρ . The rather large proportion ρ of monomeric impurity in all the samples must be related to the instability of the complex and the impossibility of obtaining a perfect chemical analysis. It would be rewarding to assert that J in $[\text{Cu}(\text{C}-\text{H}_3\text{NH}_2)_2\text{OH}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was determined with a very small uncertainty. In fact, we must recognize that the actual uncertainty is probably of the order of 0.5 cm^{-1} . Owing to the care taken in this study, it seems difficult to expect a significantly better accuracy.

Registry No. $[\text{Cu}(\text{CH}_3\text{NH}_2)_2\text{OH}]_2\text{SO}_4$, 59888-85-6.

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Discriminating and Stability Increasing Properties of the Imidazole Moiety in Mixed-Ligand Complexes^{1,2}

Sir:

It has already been recognized several years ago that the presence of an aromatic amine, i.e., a heteroaromatic N base, is crucial for a high stability of a ternary complex;³ this observation was attributed to π back-bonding from the metal ion

- (1) Part 34 of the series "Ternary Complexes in Solution". For Part 33, see: Orenberg, J. B.; Fischer, B. E.; Sigel, H. *J. Inorg. Nucl. Chem.*, in press. For Part 33, see: Orenberg, J. B.; Fischer, B. E.; Sigel, H. *J. Inorg. Nucl. Chem.* 1979, in press. Part 32: Mitchell, P. R.; Prijs, B.; Sigel, H. *Helv. Chim. Acta* 1979, 62, 1723.
- (2) Abbreviations: AMP, adenosine 5'-monophosphate; asp, aspartate; bpy, 2,2'-bipyridyl; en, ethylenediamine; gly, glycinate; ha, histamine; his, histidinate; im, imidazole; mal, malonate; nta, nitrilotriacetate; ox, oxalate; pyr, pyrocatecholate; 5-ssa, 5-sulfosalicylate.
- (3) Sigel, H. *Chimia* 1967, 21, 489.