on the basis of stereoelectronic considerations to occur preferentially from the endo side of the molecule, *i.e.*, the more directed lobe of the vacant p orbital. Indeed, endo solvation of the partially rehybridized cationic center at C-3 of **4** may result in further deviation from planarity due to the fact that an increase in θ is accompanied by enhanced cyclopropylcarbinyl stabilization.

The results, shown in Chart I together with reported hydrolysis capture ratios, are in excellent accord with the concept of stereoelectronic control in which extensive rehybridization of the carbonium ion center in the transition state for solvent capture has occurred. For example, cation **5**, which is rehybridized in the ground state to a smaller degree than **4**, affords an endo/exo ratio of only 12.4:1 again with preference for the *most hindered side.* Cation **6**, which is only deformed slightly, exhibits a shallow energy minimum and solvolytic generation of **6** affords a product distribution which is easily accounted for on the basis of steric approach control. Cation **7**, which exhibits an unusually high endo/exo ratio, reflects the cyclopropylcarbinyl stabilization in the transition state in addition to steric inhibition to exo attack. Cation **8** has a symmetrical, bisected arrangement, and calculations, as well as experiment, indicate that it is essentially planar at C-2.

A rather dramatic example of the rehybridization phenomenon is given by the tricyclo[2.2.1.0^{2,7}]hepten-3-yl cation **10** which is estimated to be bent 29° and which, if it had a discrete lifetime, would give exclusively the endo product. Our INDO calculations suggest that **10** is lower in energy than an undistorted *anti*-7-norbornenyl cation (**11**, $\phi = 0°$). However, the true cation **11**, in which the cation-containing bridge is bent toward the double bond ($\phi = 51°$, calculated), acquires bishomocyclopropenyl stabilization. Our results now provide a unique explanation for the very high solvolytic rate of *endo*-**10**-OPNB.[16] Further, the increase in the C-2:C-7 product ratio from **11** in the presence of powerful nucleophiles has been suggested to result from a product-like transition state for the formation of an endo tricyclic product,[16] and we describe the transition state as resembling nonplanar cation **10**.

Two final points can be made. The rehybridization phenomenon postulated in this work is completely consistent with the recent observations of Rhodes and DiFate.[17] These workers have demonstrated that cyclopropyl stabilization of an adjacent nonplanar cationic center is quite effective even in the 30° geometry which is closely approached by cations **4** and **5**. Furthermore, it is becoming increasingly obvious that most carbocations that are not symmetrically substituted will exist in a nonplanar form.

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(16) See, for example, S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 5 (1967); J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969); J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).

(17) Y. E. Rhodes and V. G. DiFate, *ibid.*, **94**, 7582 (1972).

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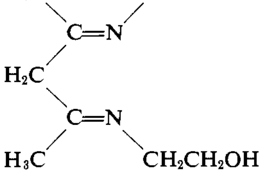
Magnetic Exchange in Binuclear Copper(II) Complexes. Antiferromagnetic Coupling through Hydrogen-Bonded Oxygen–Hydrogen–Oxygen Bridges

Sir:

There have been numerous studies[1–4] of binuclear copper(II) compounds; most of these compounds have copper–copper distances of 3.10 Å or less and their magnetic moments show temperature-dependent behavior that is indicative of exchange coupling. Although the coupling observed for such compounds could be due to direct metal–metal interaction, there is evidence that the coupling results from indirect exchange (superexchange) through the bridging groups.[4] For virtually all of the compounds that show antiferromagnetic coupling, the superexchange could, however, occur by either a σ or a π pathway. We have prepared and studied a binuclear copper(II) complex in which the copper ions are bridged by hydrogen bonded O–H–O bridges with a copper–copper distance of 5.0 Å; although the copper–copper distance rules out direct exchange and the hydrogen bridged arrangement makes a π pathway unlikely, the magnetic properties of the compound indicate antiferromagnetic coupling. This example, thus, provides evidence for indirect exchange *via* a σ pathway.

The compound is the neutral copper(II) complex of the dianion of the tetradentate ligand, I, formed by



I

the condensation of 2,4-pentanedione and 2-aminoethanol. The compound was prepared by the reaction of stoichiometric amounts of copper(II) acetate and potassium hydroxide with an excess of 2,4-pentanedione in 2-aminoethanol as solvent. Although the ligand contains three ionizable protons, only two of the protons (one from the methylene group between the two C=N groups and one from an alcohol OH group) are lost in forming the neutral copper(II) complex; the green needles of empirical formula $CuC_9H_{16}N_2O_2$ could be recrystallized from toluene and the molecular weight, using a vapor pressure osmometer, corresponded to a dimer (498 obsd *vs.* 495 calcd) in chloroform. Precession photographs (Zr-filtered Mo Kα radiation) indicated that the crystals were triclinic and the refinement has confirmed the space group as $P\bar{1}$. The crystal was transferred to a Picker four-circle automated diffractometer and the angle settings for 22 reflections were used to obtain reduced cell parameters of a = 9.554 (2) Å, b = 13.023 (3) Å, c = 11.656 (2) Å, α = 131.36 (1)°, β = 97.96 (2)°, and γ = 94.41 (1)°;

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(1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(2) J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, **6**, 248 (1972).

(3) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 2216 (1972).

(4) D. M. L. Goodgame, N. J. Hill, D. F. Marshorn, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Commun.*, 629 (1969).

the density calculated for two dimers per unit cell, 1.55 g cm^{-3}, agrees well with the experimental value, 1.56 g cm^{-3}, obtained by the flotation method in a mixture of *n*-heptane and carbon tetrachloride. Intensity data were collected by the θ–2θ scan technique; a total of 2289 unique reflections were collected and 1272 of those were selected as above background on the basis that $\sigma(I)/I < 0.30$. The reflections were corrected for Lorentz and polarization effects and calculated absorption corrections were applied. The structure was determined by the heavy-atom method and refined, using anisotropic temperature factors for all nonhydrogen atoms (hydrogen atoms have not been included in these calculations), to a conventional R value, $R = (\Sigma|F_o - F_c|)/(\Sigma|F_o|)$, of 0.0796 and a weighted R_w value, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$, of 0.0657 using a weighting scheme based on counting statistics ($w = 4I/\sigma(I)^2$) and minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Further refinement is in progress but the main features of the structure are apparent at this stage.

The unit cell contains two discrete centrosymmetric, dimeric units that, although crystallographically independent, are virtually identical. The structure is illustrated in Figure 1 and the values for bond distances and bond angles are the average values for the two units (the greatest difference in corresponding bond distances or bond angles was only four times the estimated standard deviation). Within each unit, the coordination of the copper is essentially planar (the copper is only 0.02 Å out of the least-squares plane of the four donor atoms and none of the donor atoms is more than 0.01 Å out of that plane), and there are only small deviations from planarity for the copper atom and the entire tetradentate ligand associated with it (the greatest deviation from the plane of the donor atoms is 0.46 Å for C9). The square-planar copper(II) complexes are connected into dimers by hydrogen bonding of the alcohol group of one complex and the alkoxide group of the other to form an eight-membered ring. The average oxygen–oxygen distance of 2.29 (1) Å is shorter than any hydrogen bonded oxygen–oxygen distance previously reported and is almost as short as the fluorine–fluorine distance[5] in the HF_2^- ion (2.26 Å); the observation that the compound retains the dimeric units when dissolved in chloroform is a further indication that strong hydrogen bonds exist within these units.

Although the average copper–copper distance for the two units is 4.979 (6) Å, the room temperature magnetic moment of 1.69 BM per gram atom of copper is below the spin-only value for one unpaired electron, 1.73 BM; the moment drops to 1.56 BM at 193°K and to 1.14 BM at 77°K. These values are indicative of antiferromagnetic coupling with a coupling constant, J, of approximately 100 cm^{-1}. Although much larger coupling constants have been observed for binuclear copper(II) complexes, the value is surprisingly large in view of the copper–copper distance and the nature of the bridging; the only coupling mechanism which seems at all reasonable for this compound is indirect coupling *via* a σ pathway. It is not clear, however, which factor—the greater copper–copper distance, the absence of a π pathway, or the different types of bridging—causes the coupling to be less than that observed for many oxygen-bridged copper complexes with a copper–copper distance of approximately 3.0 Å.

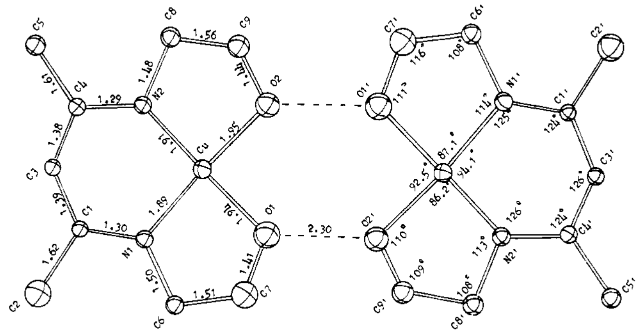

Figure 1. Molecular structure of the dinuclear complex, $[CuC_9H_{16}N_2O_2]_2$, showing all nonhydrogen atoms. Bond distances and bond angles are average values for the two independent molecules in the unit cell; standard deviations of all bond lengths are in the range 0.01–0.03 Å and standard deviations of all bond angles are in the range 0.6–23.°.

We have also prepared and studied the corresponding nickel(II) complex and found it to be isostructural with the copper(II) complex; in fact, the only significant differences in the two structures were the C–CH_3 distances (1.53 Å and 1.52 Å for the nickel compound). The C–CH_3 values for the nickel structure are in good agreement with previous structures; we have no explanation for the longer distances observed for the copper compound at this point in the refinement. The only previous example of cooperative hydrogen bonding in transition metal complexes was a cobalt(III)–nickel(II) complex[6] with 2-aminoethanol ligands which involved hydrogen bonding between octahedral faces of the two complexes. Further work on the synthesis, structure, and magnetic properties of hydrogen bonded polynuclear complexes is in progress.

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(6) J. A. Bertrand, W. J. Howard, and A. R. Kalyanaraman, *Chem. Commun.*, 437 (1971).

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Line-Shape Effects in the Electron Spin Resonance Spectra of Fluoroalkyl Radicals[1]

Sir:

The study of temperature-dependent line shapes in solution esr spectra of acyclic alkyl radicals has yielded valuable information concerning the barriers hindering internal rotations and the equilibrium conformations in

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(1) Presented in part at the First Winter Fluorine Conference, St. Petersburg, Fla., Jan 1972, and at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.