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Superexchange Interactions in Some Binuclear Complexes of Copper(II) with Single Axial Bridging

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The mononuclear copper(II) macrocyclic complex Cu(cyclops)$^+$ forms binuclear 2:1 (Cu:X) adducts with X = CN^-, N_3^-, I^-, Br^-, and pyrazine, which have been isolated and characterized. The electronic and stereochemical properties of these macrocyclic complexes suggest that the coordination about copper(II) is square pyramidal with the axial Cu–X–Cu bridge orthogonal to the macrocyclic N_4 plane. Weakly antiferromagnetic interactions are observed in the solid state for all the dimers with $|J|$ values of 0.5–1.0 cm^{-1}. This extremely weak coupling is attributed to the fact that the spin-containing orbitals, $d_{x^2-y^2}$ on copper(II), are orthogonal to the appropriate orbitals of the bridging ligand X.

Introduction

Although binuclear copper(II) complexes have been of immense interest to inorganic chemists for at least 20 years, there is very little known about monoligand-bridged, binuclear species. For example, while di-μ-chloro and di-μ-hydroxo copper(II) complexes are commonplace, singly bridged μ-chloro or μ-hydroxo copper(II) species are very rare. The major importance of singly bridged binuclear complexes is that they represent the simplest examples of ligand bridging wherein direct metal–metal overlap is unimportant. Thus they should provide excellent models for EPR, magnetic, and optical studies of bridge-mediated, electron-exchange interactions between paramagnetic metal ions.

The present work is concerned with the synthesis of macrocyclic square-pyramidal copper(II) binuclear complexes in which bridging between copper(II) occurs in the axial position. We had previously reported[2] the synthesis of a series of square-pyramidal mononuclear copper(II) complexes with the mononegative, macrocyclic ligand "cyclops" (Figure 1) having the formula Cu(cyclops)X, where X = I^-, Br^-, CN^-, NCO^-, etc. Because of their very strong copper(II)–axial ligand interaction, we anticipated that axial ligand bridging would occur between copper(II) pairs and that discrete binuclear monobridged complexes of formula $[Cu_2(cyclops)_2X]ClO_4$ could be isolated. We report here the synthesis of a series of such complexes where the bridging units are respectively CN^-, N_3^-, I^-, Br^-, and pyrazine. This complements the only other known series[3] of singly bridged binuclear copper(II) complexes—the dimers $[Cu_2(tren)_2X]^{3+}$, where tren is 2,2′,2″-triaminotriethylamine and X = CN^-, OH^-, $C_3H_3N_2^-$ (imidazolate), etc. In these tren complexes copper(II) has a trigonal-bipyramidal geometry with axial ligand bridging.

Experimental Section

Preparation of Complexes. The starting material for all reactions, $Cu(cyclops)ClO_4{\cdot}H_2O$, was prepared as previously reported.[2] All other reagents were commercially available and used without further purification. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Canadian Microanalytical Services Ltd., Vancouver, B.C., Canada.

$[Cu_2(cyclops)_2N_3]ClO_4$. To 16 mL of a hot, stirred methanol solution containing 201 mg (4.29×10^{-4} mol) of $Cu(cyclops)ClO_4{\cdot}H_2O$ was added 28 mg (4.3×10^{-4} mol) of NaN_3. After the azide salt dissolved, the solution was cooled in a freezer for 24 h. The resulting purple crystals were filtered off, washed with ice-cold methanol, and dried over BaO; yield 142 mg. Anal. Calcd for $[Cu_2(C_{11}H_{18}N_4BF_2O_2)_2N_3]ClO_4$: C, 31.4; H, 4.31; N, 18.3. Found: C, 30.9; H, 4.20; N, 18.4.

$[Cu_2(cyclops)_2CN]ClO_4$. This was prepared by the method used for the azide dimer, using 20 mL of methanol, 202 mg (4.32×10^{-4} mol) of $Cu(cyclops)ClO_4{\cdot}H_2O$, and 10 mg ($2.04 \times 10^{-4}$ mol) of dry NaCN; yield 118 mg of glistening green needles. Anal. Calcd for $[Cu_2(C_{11}H_{18}N_4BF_2O_2)CN]ClO_4$: C, 33.4; H, 4.39; N, 15.3. Found: C, 33.4; H, 4.46; N, 15.3.

$[Cu(cyclops)_2(C_4H_4N_2)](ClO_4)_2$. This was prepared by the method used for the azide dimer, using 20 mL of methanol, 204 mg (4.36×10^{-4} mol) of $Cu(cyclops)ClO_4{\cdot}H_2O$ and 17 mg (2.12×10^{-4} mol) of pyrazine; yield 130 mg of small red-purple crystals. Anal. Calcd for $[Cu_2(cyclops)_2(C_4H_4N_2)](ClO_4)_2$: C, 31.9; H, 4.11; N, 14.3. Found: C, 31.9; H, 4.06; N, 14.1.

$[Cu_2(cyclops)_2Br]ClO_4$. To 10 mL of trimethyl orthoformate (TMOF) was added 104 mg (2.22×10^{-4} mol) of $Cu(cyclops)ClO_4{\cdot}H_2O$. The mixture was stirred for 30 min to ensure complete removal of the water, and after subsequent heating, 35.9 mg (1.18×10^{-4} mol) of tetrabutylammonium bromide was added. Immediate precipitation of blue solid ensued. This was filtered off while hot, washed with TMOF, and dried over BaO; yield 73 mg. Anal. Calcd for $[Cu_2(C_{11}H_{18}N_4BF_2O_2)_2Br]ClO_4$: C, 30.0; H, 4.12; N, 12.7. Found: C, 30.1; H, 4.03; N, 12.7.

$[Cu_2(cyclops)_2I]ClO_4$. A blue crystalline product was prepared from TMOF as was done for the bromo dimer by using 8 mL of TMOF, 106 mg (2.26×10^{-4}) of $Cu(cyclops)ClO_4{\cdot}H_2O$ and 42 mg (1.14×10^{-4} mol) of tetrabutylammonium iodide; yield 80 mg. Anal. Calcd for $[Cu_2(C_{11}H_{18}N_4BF_2O_2)_2I]ClO_4$: C, 28.5; H, 3.91; I, 13.7. Found: C, 28.7; H, 4.03; I, 13.5.

$[Cu_3(cyclops)_3I_2]ClO_4$. These black platelets were prepared in methanol by the method used for the azide dimer with 6 mL of methanol, 104 mg (2.22×10^{-4} mol) of $Cu(cyclops)ClO_4{\cdot}H_2O$ and 41 mg (1.11×10^{-4} mol) of tetrabutylammonium iodide; yield 70 mg. Anal. Calcd for $[Cu_3(C_{11}H_{18}N_4BF_2O_2)_3I_2]ClO_4$: C, 28.8; H, 3.87; I, 18.1. Found: C, 28.6; H, 4.23; I, 18.2.

Physical Measurements. Electronic spectra were recorded on a Cary 14 or Perkin-Elmer 320 spectrophotometer. Magnetic susceptibilities were determined by using a PAR vibrating-sample magnetometer as previously described.[4] ESR spectra were obtained on a Varian E-12 X-band spectrometer.

Results and Discussion

The binuclear complexes reported herein have all been prepared by reaction of 2 equiv of $Cu(cyclops)ClO_4{\cdot}H_2O$ with 1 equiv of bridging ligand. In the case of CN^-, N_3^-, and pyrazine, the reactions were carried out in methanol. On the other hand, the binuclear I^- and Br^- complexes could not be prepared in this solvent, apparently because of competition by water and/or methanol as a ligand. For these reactions, trimethyl orthoformate was used as solvent in order to ensure an anhydrous reaction medium.

The coordination symmetry of copper(II) in all five dimers is undoubtedly tetragonal, since the cyclops macrocycle is

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(1) (a) Drexel University. (b) Washington State University. (c) Western Washington University.

(2) A. W. Addison, M. Carpenter, L. K-M. Lau, and M. Wicholas, *Inorg. Chem.*, **17**, 1545 (1978).

(3) (a) D. S. Bieksza and D. N. Hendrickson, *Inorg. Chem.*, **16**, 924 (1977); (b) M. S. Haddad and D. N. Hendrickson, *Inorg. Chim. Acta*, **28**, L121 (1978). (c) M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, **17**, 2622 (1978); (d) T. R. Felthouse and D. N. Hendrickson, *ibid.*, **17**, 2636 (1978); (e) M. S. Haddad, D. N. Hendrickson, J. P. Cannady, R. S. Drago, and D. S. Bieksza, *J. Am. Chem. Soc.*, **101**, 898 (1979).

(4) C. P. Landee, S. A. Roberts, and R. D. Willett, *J. Chem. Phys.*, **68**, 4574 (1978).

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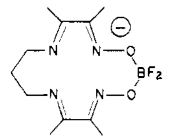

cyclops

Figure 1. Cyclops.

Table I. Optical Absorption Spectra[a]

compd	λ, nm	$\bar{\nu}$, 10^3 cm^{-1}
$[Cu_2(cyclops)_2CN]ClO_4$	659	15.2
$Cu(cyclops)CN \cdot H_2O$	730	13.7
$[Cu_2(cyclops)_2I]ClO_4$	550	18.2
Cu(cyclops)I	635	15.8
$[Cu_2(cyclops)_2Br]ClO_4$	596	16.8
Cu(cyclops)Br	638	15.7
$[Cu_2(cyclops)_2N_3]ClO_4$	539	18.6
$[Cu_2(cyclops)_2(C_4H_4N_2)](ClO_4)_2$	500	20.0
$[Cu(cyclops)(C_4H_4N_2)]^+$ in CH_3NO_2	570	17.5
$Cu(cyclops)N_3$ in CH_3NO_2	617	16.2

[a] All samples were run as Nujol mulls, unless otherwise denoted.

constrained to bind in a square-planar fashion, as confirmed by the structural studies so far reported.[5,6] Bridging must therefore occur via the accessible axial positions in these binuclear species. Moreover, the Nujol mull electronic spectra for the anion-bridged $[Cu_2(cyclops)_2X]^+$ complexes (Table I) are typical of square-pyramidal copper(II) and resemble closely the visible spectra[2] for the several known mononuclear square-pyramidal adducts Cu(cyclops)X. A comparison of the solid-state electronic spectra for the related complexes Cu(cyclops)X and $[Cu_2(cyclops)_2X]ClO_4$ ($X = I^-, Br^-, CN^-$) shows that the composite d–d band in the visible region is found consistently at shorter wavelengths in the binuclear species. This implies that these axial ligands interact less strongly with copper(II) when bridging in the dimers than when terminally bound in the corresponding monomers. For the N_3^- and pyrazine binuclear complexes, the above comparison cannot be accomplished straightforwardly since we have been unable to prepare the mononuclear complexes in the solid state. The mononuclear adducts with N_3^- and pyrazine however can be generated in CH_3NO_2 solutions of $Cu(cyclops)^+$ in the presence of excess, added axial ligand. For example, addition of excess pyrazine to $Cu(cyclops)^+$ in nitromethane yields a blue solution whose limiting spectrum has $\lambda_{max} = 570$ nm, consistent with the appearance of a higher wavelength, composite d–d band for the mononuclear adduct. Likewise $[Cu(cyclops)N_3]$ can be generated in nitromethane by addition of excess NaN_3 plus dicyclohexano-18-crown-6 to a solution of $[Cu(cyclops)OH_2]ClO_4$. The red solution becomes blue-green, exhibiting $\lambda_{max} = 617$ nm, which is substantially higher than that of $[Cu_2(cyclops)_2N_3]ClO_4$ at $\lambda_{max} = 539$ nm. Of the five binuclear species, the pyrazine complex surely has the weakest axial bonding since λ_{max} is lowest (500 nm), implying least axial perturbation of the d-orbital energies and least out-of-plane Cu(II) displacement. On the basis of solid-state electronic spectra, the ordering of bridge strength should be pyrazine $< N_3^- < I^- \approx Br^- < CN^-$.

The complexes $[Cu_2(cyclops)_2X]^+$ represent the first known series of binuclear monobridged square-pyramidal copper(II) complexes. Only one other monobridged binuclear copper(II) series is known, namely, $[Cu_2(tren)_2X]^{3+}$, where copper(II) is trigonal bipyramidal and is bridged via an axial position.[3] While a few other examples are known[7,8] such as $[Cu_2(Me_6[14]4,11\text{-diene-}N_4)_2CN](ClO_4)_3$, these are isolated cases and a series of such complexes with different bridging ligands has never been reported. One reason for the scarcity of singly bridged binuclear copper(II) species is that generally more than one site per copper(II) is available for bridging, thus resulting in the formation of polymeric chains.

What seems unique about the cyclops dimers is that they indeed exist in preference to the one-dimensional polymeric chain $[Cu(cyclops)X]_n$ with octahedrally elongated copper(II) coordination. An example of this polymer is the linear chain $[Cu(hfac)_2pyr]_n$,[9] hfac = hexafluoroacetylacetonate, which results from the reaction of $Cu(hfac)_2$ with pyrazine. The reason such one-dimensional chains are not formed with $Cu(cyclops)^+$ undoubtedly is due to the remarkable nature of the macrocycle, cyclops. The flexibility of cyclops permits "doming"[5] of the ligand in a fashion similar to that in metalloporphyrins.[10] When $Cu(cyclops)^+$ becomes five-coordinate via axial binding as in Cu(cyclops)X, the macrocycle folds in such a way that the nitrogen lone pairs are directed above the N_4 plane toward the copper(II) which sits 0.3–0.6 Å above the N_4 plane in the direction of the axial ligand, X^-.[5] The large out-of-plane displacement of copper(II) lessens electrostatic repulsions between the nitrogens and copper(II), sacrifices little in Cu–N-bond strength, and simultaneously allows for strong Cu–X-bonding interaction. Polymer formation, on the other hand, would reverse the above and for $[Cu(cyclops)X]_n$ would require that the macrocycle return to a planar, nondomed, configuration with copper(II) in the center of the N_4 cavity. This process should be unfavorable energetically because the Cu–X bond would be weakened substantially. For the 14 Cu(cyclops)X systems reported previously, we have never observed polymer formation.[2] The largest polynuclear cluster yet isolated is $[Cu_3(cyclops)_3I_2]ClO_4$, vide infra, which contains three $Cu(cyclops)^+$ units. For complexes such as $[Cu(cyclops)(pyr)]^+$, where the axial ligand is electrically neutral, polymer formation also should not occur because the polymeric chains $[Cu(cyclops)(pyr)]_n^{n+}$ would be destabilized further by their accumulated electronic charge of n^+.

The magnetic properties of these binuclear complexes were investigated in order to determine if exchange coupling could occur at all via the bridging ligands. If these complexes are of the anticipated tetragonal symmetry, the unpaired electron on copper(II) should be in $d_{x^2-y^2}$ orbitals as it is in the mononuclear adducts.[2] Since this orbital is orthogonal to the appropriate σ- and π-donor/acceptor orbitals of the bridging ligands, all five dimers should exhibit zero magnetic exchange coupling and perfect Curie–Weiss law behavior.

ESR powder spectra of the μ-N_3^- and μ-pyrazine salts indicated that the solids were not magnetically dilute but exhibited weak superexchange interactions. For the μ-pyrazine complex in solution (nitromethane), the colors observed and ESR results obtained at room temperature and at 77 K revealed complications due to cleavage and disproportionation of this 2:1 Cu:pyr adduct, so that an ESR spectrum characteristic of the $[Cu_2(cyclops)_2(pyr)]^{2+}$ moiety could not be obtained. Similarly the ESR spectra for the halide-bridged

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(5) (a) O. P. Anderson and J. C. Marshall, *Inorg. Chem.*, **17**, 1258 (1978); (b) O. P. Anderson and A. B. Packard, *ibid.*, **18**, 1940, 3064 (1979); (c) O. P. Anderson, private communication.

(6) (a) R. R. Gagné, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, **99**, 7170 (1977); (b) R. R. Gagné, J. L. Allison, and G. C. Lisensky, *Inorg. Chem.*, **17**, 3563 (1978).

(7) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3443 (1974).

(8) M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 481 (1979).

(9) H. W. Richardson, J. R. Wasson, and W. E. Hatfield, *Inorg. Chem.*, **16**, 484 (1977).

(10) J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., American Elsevier, New York, 1975, pp 317–76.

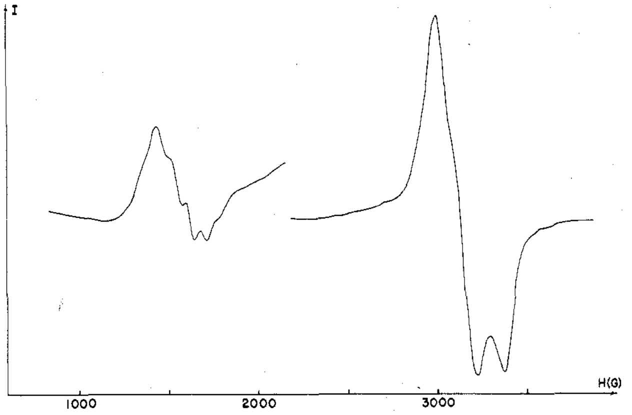

Figure 2. A 9.080-GHz ESR spectrum of $[Cu_2(cyclops)_2N_3]ClO_4$ in CH_3NO_2 at 77 K. The $g = 4$ region was recorded at a gain 10 times greater than that for the $g = 2$ region.

Table II. Magnetic Data for $Cu(cyclops)^+$ Dimers

bridge	J, cm^{-1}	$\bar{g}^a$	bridge	J, cm^{-1}	$\bar{g}^a$
N_3^-	−0.56	2.07	Br^-	−0.58	2.04
CN^-	−0.90	2.09	$C_4H_4N_2$	−0.57	2.02
I^-	−0.90	2.08			

[a] These values agree adequately with values from the ESR spectrum, where obtained for the solid.

species were not particularly informative. However, in the case of the μ-N_3^- species, the spectrum in Figure 2 was obtained from nitromethane solution (the color of which is invariant with temperature). The appearance of the $g = 2$ region is reminiscent of that reported for the binuclear complex Cu_2(sal-*m*-pda)$_2$ ($J \simeq -0.5$ cm^{-1}).[11] More germanely, the seven-line $\Delta M = 2$ transition at $g = 4.5$ is clearly indicative of an interacting pair of Cu(II) atoms, providing evidence for intramolecular coupling as an exchange pathway in these systems.

For all five $Cu(cyclops)^+$ binuclear complexes, magnetic susceptibilities were measured over the temperature range 4.5–80 K. The data were fit to the Bleany–Bowers equation by a least-squares procedure, using $N\alpha = 120 \times 10^{-6}$ cgsu/mol for the TIP correction.

$$\chi_m = \frac{2N\bar{g}^2\beta^2}{3kT}\,[1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1} + N\alpha$$

The best fit values for $\bar{g}$ and J, the superexchange coupling constant, are listed in Table II. All five complexes show extremely weak antiferromagnetic superexchange coupling ranging from $J = -0.56$ cm^{-1} to $J = -0.90$ cm^{-1} for CN^- and I^-. A plot of χT vs. T is shown in Figure 3 for $[Cu_2(cyclops)_2CN]ClO_4$. At temperatures above the Neel point, the above plot is a more sensitive indicator of exchange coupling than the traditional χ vs. T display. The fact that coupling is observed, albeit extremely small, could result from slight off-axis binding of the axial bridging ligand to copper(II) along with a Cu(II)–bridge–Cu(II) angle substantially larger than 90°. Were the bridging angle about 90°, then very weak ferromagnetic exchange coupling would be expected.

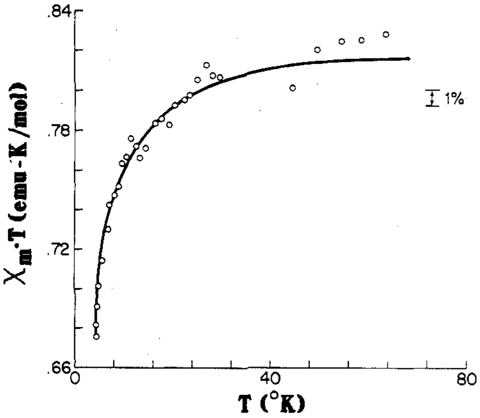

Figure 3. Plot of the function χ_mT vs. temperature for $[Cu_2(cyclops)_2CN]ClO_4$. The circles represent the experimental values; the solid line represents the best least-squares fit.

Most analogous to the $Cu(cyclops)^+$ dimers for a comparison of magnetic properties are the linear chains $[Cu(hfac)_2L]_n$ mentioned previously. In these complexes the copper(II) exhibits "4 + 2" elongated octahedral coordination with bridging at both axial positions. Significantly, Hatfield observed simple paramagnetic behavior to 1.8 K for the ligands L = pyrazine, 1,5-naphthyridine, and 1,4-diazabicyclo[2.2.2]octane.[9] Unfortunately, there are no "4 + 2" linear chains of Cu^{2+} with CN^-, N_3^-, I^-, or Br^- as bridging ligands; so comparison here is impossible.

In summary the experimental evidence to date indicates that superexchange coupling is extremely small ($|J| < 1$ cm^{-1}) in square-planar-based copper(II) systems where bridging occurs axially and is orthogonal to the spin-containing $d_{x^2-y^2}$ orbitals of copper(II).

The remaining complex, not yet discussed, is the trinuclear $[Cu_3(cyclops)_3I_2]ClO_4$ which from its solid-state electronic spectrum gives evidence that the average copper(II)–ligand environment is intermediate in strength between that of Cu(cyclops)I and $[Cu_2(cyclops)_2I]ClO_4$. Magnetic susceptibility measurements show linear Curie–Weiss behavior to 4.5 K and a room-temperature moment of 1.79 μ_B/copper(II). We propose that this complex is a "tridecker" with a central Cu(II) having axially elongated "4 + 2" coordination and with two terminal five-coordinate copper(II) atoms having normal axial iodide coordination. If this is the case, the central copper(II)–cyclops unit should be planar in contradistinction to the nonplanar, domed structure proposed for the mononuclear and binuclear species.

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Registry No. $[Cu_2(cyclops)_2N_3]ClO_4$, 73395-89-8; $[Cu_2(cyclops)_2CN]ClO_4$, 73395-91-2; $[Cu_2(cyclops)_2(C_4H_4N_2)](ClO_4)_2$, 73395-96-7; $[Cu_2(cyclops)_2Br]ClO_4$, 73395-98-9; $[Cu_2(cyclops)_2I]ClO_4$, 73395-78-5; $[Cu_3(cyclops)_3I_2]ClO_4$, 73395-94-5; $Cu(cyclops)ClO_4$, 64783-10-4; $[Cu(cyclops)(C_4H_4N_2)]^+$, 73395-92-3; $Cu(cyclops)N_3$, 73395-79-6.

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(11) E. F. Hasty, L. J. Wilson, and D. N. Hendrickson, *Inorg. Chem.*, **17**, 1834 (1978).