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# Structural and Magnetic Studies on Macrocyclic Dicopper(II) Complexes. Influence of Electron-Withdrawing Axial Ligands on Spin Exchange[†]

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The antiferromagnetically coupled macrocyclic binuclear copper(II) complexes $[Cu_2(UPM)X_2]\cdot yH_2O$ (X = Cl, Br, I, $N_3$) (UPM derived by template condensation of 4-methyl-2,6-diformylphenol with 1,3-diaminopropane) are structurally similar with a trans-axial arrangement of ligands X. Exchange integrals fall in the range $-2J$ = 720–855 $cm^{-1}$ with Cl < Br < $N_3$ < I. The complex $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II) crystallizes in the monoclinic system, space group $C2/m$, with $a$ = 7.9196 (13) Å, $b$ = 17.1380 (4) Å, $c$ = 11.2232 (14) Å, $\beta$ = 92.111 (13)°, and $Z$ = 2. The complex $[Cu_2(UPM)I_2]\cdot H_2O$ (III) crystallizes in the monoclinic system, space group $P2_1/a$, with $a$ = 8.2826 (8) Å, $b$ = 16.7383 (8) Å, $c$ = 9.6470 (12) Å, $\beta$ = 99.107 (14)°, and $Z$ = 4. Both complexes have an essentially flat, macrocyclic, binuclear structure involving square-pyramidal copper(II) centers. The halogens are bound in a trans-axial arrangement (Cu–Br = 2.737 (2) Å; Cu–I = 3.026 (2) Å, and the copper centers are displaced toward the halogen from the basal $N_2O_2$ donor set (Br, 0.205 (4) Å; I, 0.176 (5) Å).

## Introduction

Macrocyclic dicopper(II) complexes derived from 2,6-diformyl- and 2,6-diacetyl(4-substituted)phenols (Figure 1) are numerous and have been studied from the standpoint of their interesting structural, magnetic, EPR, and electrochemical properties and also as potential models for binuclear copper metalloprotein active sites.[2-18] In general, systems of this sort are strongly antiferromagnetically coupled and exhibit one-electron reduction steps at negative potentials.[4,8,10-12,14,15,18] In a few cases involving ligands with saturated nitrogen donor groups, one- and even two-electron oxidation steps can be observed at positive potentials (1–1.5 V vs SCE).[14,15] The reduction potentials can be changed by the inclusion of electron-withdrawing or electron-donating groups (R and $R^1$ in Figure 1)[10,18] and by varying the size of the macrocyclic ring ($R^2$ in Figure 1).[11,19] Electron-withdrawing groups (e.g. R = $CF_3$ vs $CH_3$) make both one-electron reduction potentials more positive,[18] while electron-releasing groups (e.g. $R^1$ = $CH_3$ and $CH_3CH_2CH_2$ vs H) seem only to influence the second one-electron reduction step, making it more negative (vs SCE).[10]

In this study we have examined a series of compounds $[Cu_2(UPM)X_2]\cdot yH_2O$ (X = Cl, Br, I, $N_3$) (Figure 1, R = $CH_3$, $R^1$ = H, $R^2$ = $(CH_2)_3$) from the standpoint of their structural and magnetic properties. The complex $[Cu_2(UPM)Cl_2]\cdot 6H_2O$ (I) has already been reported[2] and consists of a binuclear phenoxo-bridged macrocyclic structure[5] involving one terminally bound chlorine per copper in a trans-axial arrangement. The structures of the bromo and iodo analogues, $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II) and $[Cu_2(UPM)I_2]\cdot H_2O$ (III), are very similar with the halogens again bound in a trans-axial arrangement. The azide derivative, $[Cu_2(UPM)(N_3)_2]\cdot 3.5H_2O$ (VI), is assumed to have a similar structure, on the basis of spectroscopic evidence. All of the complexes exhibit strong, net antiferromagnetism with $-2J$ falling in the range 720–855 $cm^{-1}$, and the differences in exchange can be attributed to electronic effects associated with the halogen and azide ligands.

## Experimental Section

**Physical Measurements.** Variable-temperature magnetic susceptibility data were obtained in the temperature range 5–300 K by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T $m^{-1}$ were employed. $HgCo(NCS)_4$ was used as calibrant. Infrared spectra were obtained with a Perkin-Elmer 283 spectrometer.

Table I. Crystal Data for $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II) and $[Cu_2(UPM)I_2]\cdot H_2O$ (III)

| | |
|---|---|
| (a) Compound II | |
| chem formula: $Cu_2C_{24}H_{24}Br_2N_4O_2\cdot 4H_2O$ | fw: 759.44 |
| $a$ = 7.9196 (13) Å | space group: $C2/m$ |
| $b$ = 17.1380 (4) Å | $T$ = 295 K |
| $c$ = 11.2232 (14) Å | $\lambda$ = 0.709 30 Å |
| $\beta$ = 92.111 (13)° | $\rho_{calcd}$ = 1.66 g $cm^{-3}$ |
| $V$ = 1522.25 $Å^3$ | $\mu$ = 4.03 $mm^{-1}$ |
| $Z$ = 2 | $R$ = 0.039 |
| | $R_w$ = 0.042 |
| (b) Compound III | |
| chem formula: $Cu_2C_{24}H_{24}I_2N_4O_2\cdot H_2O$ | fw: 399.70 |
| $a$ = 8.2826 (8) Å | space group: $P2_1/a$ |
| $b$ = 16.7383 (8) Å | $T$ = 295 K |
| $c$ = 9.6470 (12) Å | $\lambda$ = 0.709 30 Å |
| $\beta$ = 99.107 (14)° | $\rho_{calcd}$ = 2.01 g $cm^{-3}$ |
| $V$ = 1320.57 $Å^3$ | $\mu$ = 3.97 $mm^{-1}$ |
| $Z$ = 4 | $R$ = 0.053 |
| | $R_w$ = 0.052 |

**Synthesis of Complexes. $[Cu_2(UPM)I_2]\cdot H_2O$ (III).** An aqueous solution (10 mL) of sodium iodide (0.40 g, 2.7 mmol) was added to a stirred, hot, aqueous solution (100 mL) of $[Cu_2(UPM)(ClO_4)_2]\cdot 2H_2O$[2] (0.50 g, 0.66 mmol). The resulting brown, microcrystalline product was filtered off, washed with a water/methanol mixture, and recrystallized from acetonitrile to give dark greenish brown crystals (yield 0.43 g). $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II) and $[Cu_2(UPM)(N_3)_2]\cdot 3.5H_2O$ (VI) were prepared in a similar manner by using sodium bromide and sodium azide, respectively. $[Cu_2(UPM)Cl_2]\cdot 6H_2O$ (I) was prepared according to the

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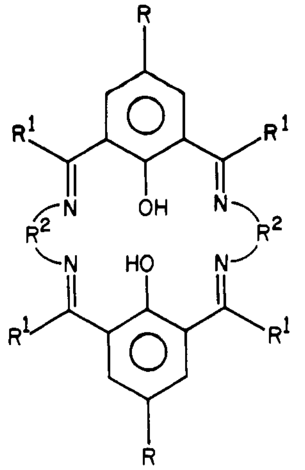

**Figure 1.** Macrocyclic ligands: UPM (R = $CH_3$, $R^1$ = H, $R^2$ = $(CH_2)_3$); UBM (R = $CH_3$, $R^1$ = H, $R^2$ = $(CH_2)_4$).

**Table II.** Final Atomic Positional Parameters and Equivalent Isotropic Debye-Waller Temperature Factors (Esd's) for $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II)

| | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ |
|---|---|---|---|---|
| Br | 0.26328 (18) | 0 | 0.24241 (12) | 5.34 (8) |
| Cu | 0.56442 (17) | 0 | 0.37006 (11) | 2.65 (6) |
| O | $^1/_2$ | 0.0718 (4) | $^1/_2$ | 2.7 (3) |
| N | 0.6606 (8) | 0.0862 (4) | 0.2779 (5) | 3.7 (3) |
| C1 | $^1/_2$ | 0.1482 (5) | $^1/_2$ | 2.5 (4) |
| C2 | 0.4322 (9) | 0.1920 (4) | 0.5948 (6) | 2.6 (3) |
| C3 | 0.4350 (9) | 0.2742 (4) | 0.5924 (6) | 2.9 (3) |
| C4 | $^1/_2$ | 0.3154 (6) | $^1/_2$ | 3.2 (5) |
| C5 | $^1/_2$ | 0.4048 (7) | $^1/_2$ | 4.3 (6) |
| C6 | 0.6449 (10) | 0.1582 (4) | 0.3040 (6) | 3.3 (3) |
| C7 | 0.7509 (17) | 0.0717 (5) | 0.1645 (9) | 8.1 (7) |
| C8 | 0.731 (3) | 0 | 0.1162 (13) | 9.3 (12) |
| OH1 | 0 | 0.2458 (6) | 0 | 6.75 (23) |
| OH2 | 0.7599 (8) | 0.3253 (4) | 0.1292 (6) | 6.43 (16) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

literature procedure.[2]

C, H, N, and halogen analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada, and all compounds were found to be analytically pure.

**Crystallographic Data Collection and Refinement of the Structures. $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II).** Crystals of II are green in color. The diffraction intensities of an approximately 0.10 × 0.15 × 0.20 mm crystal were collected with graphite-monochromatized Mo K$\alpha$ radiation by using the $\theta/2\theta$ scan technique with profile analysis[20] to $2\theta_{max}$ = 45.0° on an Enraf-Nonius CAD4 diffractometer at 295 K. A total of 2722 reflections were measured, of which 1034 were unique and 752 were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, but no correction was made for absorption. The cell parameters were obtained by the least-squares refinement of the setting angles of 18 reflections with $2\theta$ = 40-45° ($\lambda$(Mo K$\alpha$) = 0.70930 Å).

The structure was solved by direct methods using MULTAN[21] and refined by full-matrix least-squares methods to final residuals of $R$ = 0.039 and $R_w$ = 0.042 for the significant data (0.067 and 0.067 for all data) and unit weights. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic temperature factors are listed in Table II. All calculations were performed with the NRCVAX system of programs,[22] and scattering factors were taken from ref 23. Anisotropic thermal parameters (Table SI) and a listing of structure factors are included as supplementary material.

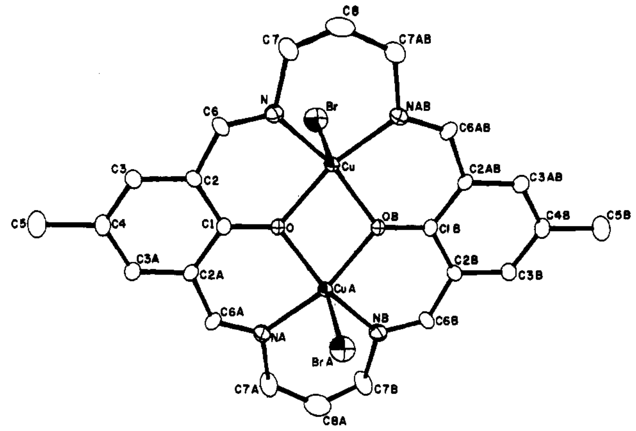

**Figure 2.** Structural representation of $[Cu_2(UPM)Br_2]$ (II) with hydrogen atoms omitted (40% probability thermal ellipsoids).

**Table III.** Final Atomic Positional Parameters and Equivalent Isotropic Debye-Waller Temperature Factors (Eds's) for $[Cu_2(UPM)I_2]\cdot H_2O$ (III)

| | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ |
|---|---|---|---|---|
| I | 0.26496 (9) | 0.09460 (5) | 0.77153 (9) | 4.14 (3) |
| Cu | 0.93259 (14) | 0.04297 (7) | 0.62146 (12) | 2.42 (4) |
| O | 0.9946 (8) | 0.0628 (3) | 0.4352 (6) | 2.50 (24) |
| N1 | 0.8530 (10) | 0.0011 (5) | 0.7889 (8) | 2.8 (3) |
| N2 | 0.8287 (9) | 0.1479 (5) | 0.6207 (8) | 2.8 (3) |
| C1 | 1.0105 (10) | 0.1322 (6) | 0.3744 (9) | 2.5 (3) |
| C2 | 1.0822 (11) | 0.1394 (6) | 0.2489 (9) | 2.6 (3) |
| C3 | 1.0966 (12) | 0.2149 (6) | 0.1887 (11) | 3.0 (4) |
| C4 | 1.0485 (12) | 0.2852 (6) | 0.2474 (10) | 3.0 (4) |
| C5 | 1.0712 (21) | 0.3660 (8) | 0.1852 (16) | 4.5 (6) |
| C6 | 0.9752 (12) | 0.2777 (6) | 0.3657 (10) | 2.9 (4) |
| C7 | 0.9546 (11) | 0.2037 (5) | 0.4305 (9) | 2.5 (3) |
| C8 | 0.8641 (11) | 0.2059 (5) | 0.5429 (10) | 2.5 (3) |
| C9 | 0.7238 (16) | 0.1668 (7) | 0.7248 (14) | 3.9 (5) |
| C10 | 0.7999 (17) | 0.1400 (7) | 0.8683 (11) | 3.9 (5) |
| C11 | 0.7815 (18) | 0.0517 (7) | 0.8922 (13) | 4.1 (5) |
| C12 | 0.8597 (13) | -0.0727 (6) | 0.8247 (11) | 3.2 (4) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

**Table IV.** Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II)

| | | | |
|---|---|---|---|
| Br-Cu | 2.7365 (20) | Cu-N | 1.972 (6) |
| Cu-O | 1.989 (4) | Cu-NB | 1.972 (6) |
| Cu-OA | 1.989 (4) | O-CuA | 1.989 (4) |
| Cu-CuA | 3.124 (2) | | |
| Br-Cu-O | 98.15 (5) | O-Cu-NB | 164.21 (21) |
| Br-Cu-OA | 98.15 (5) | OA-Cu-N | 164.21 (21) |
| Br-Cu-N | 94.11 (20) | OA-Cu-NB | 92.04 (22) |
| Br-Cu-NB | 94.11 (20) | N-Cu-Nb | 97.0 (3) |
| O-Cu-OA | 76.43 (20) | Cu-O-CuA | 103.6 (3) |
| O-Cu-N | 92.04 (22) | | |

**$[Cu_2(UPM)I_2]\cdot H_2O$ (III).** A greenish brown crystal of III, of dimensions 0.20 × 0.20 × 0.20 mm, was examined crystallographically in the same manner as II. A total of 6845 reflections were measured, of which 3842 were unique and 2174 were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic temperature factors are listed in Table III. Anisotropic thermal parameters (Table SII) and a listing of structure factors are included as supplementary material.

## Results and Discussion

**Description of the Structures of $[Cu_2(UPM)Br_2]\cdot 4H_2O$ (II) and $[Cu_2(UPM)I_2]\cdot H_2O$ (III).** The structure of II is shown in Figure 2, and interatomic distances and angles relevant to the copper coordination spheres are given in Table IV. The macrocyclic ligand is almost flat, enclosing two distorted square-pyramidal copper(II) centers, bridged by phenoxide oxygen atoms and bound terminally in a trans arrangement to two bromine atoms. The copper-bromine separation is quite long (2.737 (2) Å), and the copper center is displaced from the strictly planar $N_2O_2$ donor set toward the bromine by 0.205 (4) Å. The copper-copper distance is 3.124 (2) Å, and the phenoxide bridge angle (Cu-O-Cu) is 103.6 (3)°. Structurally, II is very similar to the chloro-

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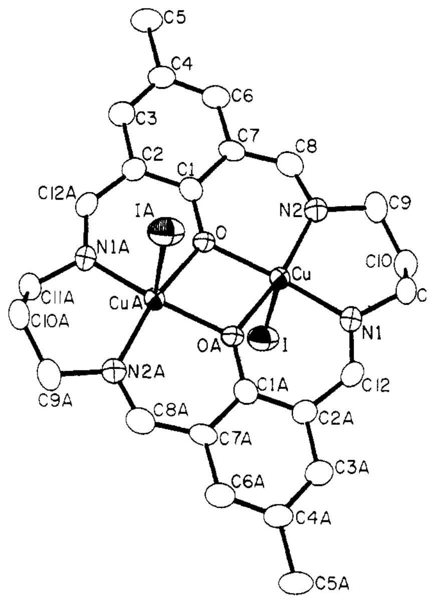

**Figure 3.** Structural representation of $[Cu_2(UPM)I_2]$ (III) with hydrogen atoms omitted (40% probability thermal ellipsoids).

**Table V.** Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(UPM)I_2]\cdot H_2O$ (III)

| | | | |
|---|---|---|---|
| I–CuA | 3.0264 (15) | Cu–N1 | 1.968 (8) |
| Cu–IB | 3.0264 (15) | Cu–N2 | 1.956 (8) |
| Cu–O | 1.974 (6) | O–CuC | 1.975 (6) |
| Cu–OC | 1.975 (6) | Cu–CuA | 3.104 (2) |
| IB–Cu–O | 92.27 (19) | O–Cu–N1 | 167.5 (3) |
| IB–Cu–OC | 95.38 (19) | O–Cu–N2 | 91.4 (3) |
| IB–Cu–N1 | 96.14 (24) | OC–Cu–N1 | 93.7 (3) |
| IB–Cu–N2 | 96.41 (24) | OC–Cu–N2 | 163.3 (3) |
| O–Cu–OC | 76.34 (24) | N1–Cu–N2 | 96.8 (3) |

analogue $[Cu_2(UPM)Cl_2]\cdot 6H_2O$,[5] which has a copper–copper separation of 3.133 Å and a phenoxide bridge angle of 104.5° and square-pyramidal copper centers with similar apical displacements. The solid angle at the phenoxide bridge in II is exactly 360.0°, whereas in $[Cu_2(UPM)Cl_2]\cdot 6H_2O$ an angle of 357.4° indicates slight pyramidal distortion.

The structure of III is shown in Figure 3, and interatomic distances and angles relevant to the copper coordination spheres are given in Table V. Structurally, III is very similar to the bromo analogue (II) with a trans square-pyramidal macrocyclic structure. Copper–nitrogen and copper–oxygen distances are somewhat shorter than those in II, but the phenoxide bridge angle (103.7°) is essentially the same. The copper–copper separation (3.104 Å) is slightly shorter, in keeping with reduced dimensions within the $Cu_2O_2$ framework. The $N_2O_2$ donor set is almost planar, and the copper centers are displaced from their mean plane by 0.176 (5) Å toward the distant iodine atoms (Cu–I = 3.026 (2) Å). The phenoxide bridge has almost trigonal-planar character with a solid angle of 359.1°.

Variable-temperature magnetic susceptibility measurements were performed on powdered samples of compounds I–III in the temperature range 5–300 K. The results are summarized in Table VI. The best fit of the data to the modified Van Vleck equation[24] for exchange-coupled pairs of copper(II) ions (eq 1) was determined in each case with a two-variable nonlinear regression

$$\chi_M = \frac{N\beta^2 g^2}{3kT}[1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1}(1-\rho) + \left(\frac{N\beta^2 g^2}{4kT}\right)\rho + N\alpha \qquad (1)$$

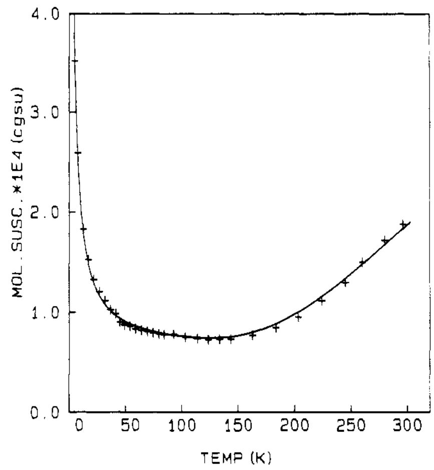

**Figure 4.** Magnetic susceptibility data for $[Cu_2(UPM)Br_2]\cdot H_2O$ (II). The solid line was calculated from eq 1 with $g = 2.06$ (1) and $-2J = 771$ (4) $cm^{-1}$ (corrected for 0.38% paramagnetic impurity).

analysis.[25] In this expression $-2J$ (in the spin Hamiltonian $H = -2J\hat{S}_1\cdot\hat{S}_2$) is the singlet–triplet splitting or exchange integral and other terms have their usual meaning. $\rho$ represents the fraction of a possible magnetically dilute, mononuclear copper(II) impurity. The temperature-independent paramagnetism $N\alpha$, was taken as 60 x $10^{-6}$ cgs units/mol copper, and $\rho$ was treated as a floating parameter. Strong net antiferromagnetic exchange was observed in all cases, with $-2J$ falling in the range 720–855 $cm^{-1}$. A typical experimental variable-temperature magnetic susceptibility data plot, including the best fit theoretical line, for compound II is shown in Figure 4. Similar plots for the other compounds are available as supplementary material.

A comparison of key structural parameters and exchange integrals for I–III (Table VI) reveals that despite quite similar binuclear center dimensions, e.g. Cu–O–Cu bridge angles, Cu–O(phenoxide) separations, Cu–Cu separations, out of plane copper displacements, and the solid angles at the phenoxide bridge, exchange integrals vary quite dramatically with Cl (722 $cm^{-1}$) < Br (771 $cm^{-1}$) < I (852 $cm^{-1}$). The Cu–O–Cu bridge angle for I is the largest of the group, and on the basis of the primary importance of this feature to superexchange, the low value of the exchange integral for I is quite significant. The exchange integral for I has been reported in a previous study ($-2J = 588$ $cm^{-1}$)[7] and differs significantly from the value we have observed. The trend of diminished exchange for the chloro complex is, however, still apparent. A comparison of the structural and magnetic features of III with those of the perchlorate complex V, which involves two different molecules in the unit cell, one involving six-coordinate and the other five-coordinate copper(II) centers, reveals similar binuclear center dimensions, except for the more pronounced displacement of the copper centers from the basal plane in III, and comparable exchange. A further comparison of IV and V (Figure 1; UBM, R = Me, $R^1$ = H, $R^2 = (CH_2)_4$), which involves six-coordinate copper(II) centers, shows that minor perturbations to the binuclear center dimensions, including significant, but small, pyramidal distortion at the phenoxide bridge, does not affect exchange significantly.[19] Pyramidal distortions at oxygen bridges in systems of this sort have been shown to influence exchange coupling, but usually much more severe distortion than observed in e.g. V is required to significantly influence the exchange process.[26,27] $\sigma$ overlap between the copper magnetic orbitals and the oxygen bridge is likely to be reduced to some extent as a result of out of plane distortion at the copper center, but for the small distortions apparent in these complexes the effect is likely to be

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**Table VI.** Key Structural Data and Magnetic Data for Macrocyclic Dicopper(II) Complexes

| complex[a] | Cu–O–Cu, deg | $\sum$O, deg | Cu–Cu, Å | Cu–O, Å | out-of-plane displacement, Å | −2J, $cm^{-1}$ | g |
|---|---|---|---|---|---|---|---|
| $[Cu_2(UPM)Cl_2]\cdot 1.5H_2O$ (I) | 104.5 (1) | 357.4 | 3.133 (1) | 1.981 (2) | 0.21 | 722 (20) | 2.12 (5) |
| $[Cu_2(UPM)Br_2]\cdot H_2O$ (II) | 103.6 (3) | 360.0 | 3.124 (2) | 1.989 (4) | 0.205 (4) | 771 (4) | 2.06 (1) |
| $[Cu_2(UPM)I_2]\cdot H_2O$ (III) | 103.7 (3) | 359.1 | 3.104 (2) | 1.974 (6)<br>1.975 (6) | 0.176 (5) | 852 (9) | 2.13 (4) |
| $[Cu_2(UPM)(ClO_4)_2]\cdot 2H_2O$ (IV) | 102.3 (3)<br>103.6 (3) | 358.4<br>359.1 | 3.091 (3)<br>3.096 (3) | 1.981 (6)<br>1.989 (6) | 0.019 (4)<br>0.083 (6) | 850 (2)[b] | |
| $[Cu_2(UBM)(ClO_4)_2]$ (V) | 101.77 (9) | 353.2 | 3.0354 (7) | 1.943 (2)<br>1.970 (2) | 0.004 (1) | 857 (6)[b] | |
| $[Cu_2(UPM)(N_3)_2]\cdot H_2O$ (VI) | | | | | | 780 (7) | 2.15 (4) |

[a] Formulas for I, II, and VI differ from those reported earlier due to loss of solvent on drying prior to magnetic measurements. [b] Reference 19.

small,[28] so that this geometric feature is not likely to dominate the exchange situation.

The marked difference in exchange between compounds I–III and the $-2J$ trend Cl < Br < I, which parallels the trend in electronegativity of the halogens, clearly indicates that the axially bound halogens have a primary influence on exchange, even though they are bound orthogonally to the copper magnetic orbital. The similarity in the magnitude of the exchange integrals of compounds III–V can be rationalized in terms of a general similarity in binuclear center dimensions but also on the basis that iodine has a small electron-withdrawing effect and would not polarize electron density in the copper magnetic orbital manifold to a significant extent. The much smaller values of exchange integral observed for I and II indicate that the more electronegative bromine and chlorine ligands are effectively polarizing the electron density in the copper magnetic orbitals, with the result that I and II exhibit more paramagnetism than III. The effect can be imagined as a modulation of the molecular microcircuitry associated with superexchange between the two copper centers. The observation of such an orthogonal perturbation is unusual, but it has been observed before in cases where isostructural pairs of chloro and bromo complexes have involved terminal halogens bound directly to copper magnetic orbitals.[28-30]

Variable-temperature magnetic data for the azido complex (VI) (5–300 K; data treatment as for I–III) are given in Table VI (a susceptibility data plot is available as supplementary material). This complex is strongly coupled with $-2J = 780$ (7) $cm^{-1}$, which is between the values of compounds I and IV. Structurally, VI is assumed to be similar to compounds I–III, with a trans arrangement of terminally bound azide groups. The infrared spectrum shows a very strong, single azide absorption at 2015 $cm^{-1}$, which can be associated with a highly symmetric *trans*-bis(azido) derivative.[31] The fact that spin exchange for the azido compound is comparable with that of the bromo derivative (II) suggests that, assuming a similarity in the binuclear center dimensions, the azide ligands are also exhibiting a polarizing effect on the electron density in the copper magnetic orbital envelope.

The copper magnetic orbitals interact directly with the phenoxide bridging oxygen atoms in this type of complex, and so their delocalization should be affected by the electronegativity of the bridging atom and possibly by perturbations within the phenoxide group itself. In a study of the complexes $[Cu_2(L)](ClO_4)_2$ (Figure 1; L = UPM and $UPMCF_3$, R = $CH_3$ and $CF_3$, respectively), which have comparable binuclear, macrocyclic structures,[18] the magnetic properties are essentially the same ($-2J = 710$ and 712 $cm^{-1}$, respectively), indicating that the electron-withdrawing $CF_3$ group does not influence magnetic exchange significantly, despite the fact that metal-centered electrochemical reductions are shifted to more positive potentials in the $CF_3$ derivative. However, in other binuclear copper(II) complexes involving the bridging ligands oxalate, oxamide, and dithioxamide, which have related structures, the effect of reduced electronegativity of the bridging atoms is clearly reflected in a trend of increasing antiferromagnetic exchange resulting from increased delocalization of the copper magnetic orbitals.[28]

One way of testing this effect in a macrocyclic system of the type under discussion would be to replace the phenoxide oxygen atom directly with sulfur. This has, to our knowledge, not yet been done. However, in a related, nonmacrocyclic system a comparison of pentadentate, binucleating phenoxide and thiophenoxide bridging ligands derived from 4-methyl-2,6-diformylphenol and 4-methyl-2,6-diformylthiophenol shows that the phenoxide-bridged dicopper(II) derivatives are strongly antiferromagnetically coupled but the thiophenoxide analogues unexpectedly exhibit almost Curie-like behavior.[32] The significant reduction in antiferromagnetic exchange in the sulfur derivatives is attributed to the marked pyramidal distortion ($sp^3$ character) of the sulfur bridge, which is not the case for the analogous oxygen-bridged derivatives, which have mainly $sp^2$ character.

In the present study a very different perturbation on the copper magnetic orbitals has been demonstrated, and it indicates that fine tuning of the magnetic exchange in binuclear copper(II) complexes can be effected in subtle ways that do not involve a direct interaction with those magnetic orbitals.

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**Supplementary Material Available:** Anisotropic thermal parameters and bond length and angle data for II (Tables SI and SIII, respectively) and III (Tables SII and SIV, respectively), atomic positional parameters for hydrogen atoms in II and III (Tables SV and SVI, respectively), and variable-temperature magnetic susceptibility plots for I, III, and VI (Figures S1–S3, respectively) (12 pages); observed and calculated structure factors for II and III (69 pages). Ordering information is given on any current masthead page.

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