Contribution from the Chemistry Department,
University of Virginia, Charlottesville, Virginia 22901

Schiff Base Ligands from 3-Aminopropanol. Synthesis, Magnetism, Structure, and Mass Spectroscopy of the Binuclear Copper(II) Complexes $Cu_2Cl_2O_4N_2C_{20}H_{20}$, $Cu_2O_8N_4C_{20}H_{20}$, and $Cu_2O_4N_2C_{28}H_{26}$

EKK SINN

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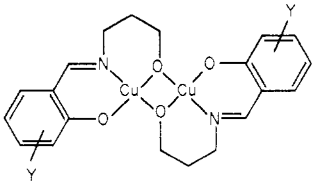
A series of binuclear copper(II) complexes has been synthesized using the Schiff base ligands derived from the condensation of 3-aminopropanol with 2-hydroxy aldehydes or ketones. For ligands derived from (**1a**) 5-chlorosalicylaldehyde, (**1b**) 3-nitrosalicylaldehyde, and (**1c**) 5,6-benzosalicylaldehyde, the binuclear complexes were studied by single-crystal x-ray diffraction, using counter methods, and their structures determined. Crystal data: **1a**, $Cu_2Cl_2O_4N_2C_{20}H_{20}$, space group $P2_1/c$, $Z = 2$, $a = 9.475$ (1) Å, $b = 11.251$ (3) Å, $c = 9.857$ (2) Å, $\beta = 102.84$ (2)°, $V = 1025$ Å^3, $R = 2.4\%$, 1608 reflections; **1b**, $Cu_2O_8N_4C_{20}H_{20}$, space group $P2_1/c$, $Z = 2$, $a = 4.597$ (1) Å, $b = 15.515$ (5) Å, $c = 16.345$ (4) Å, $\beta = 113.28$ (2)°, $V = 1064$ Å^3, $R = 4.2\%$, 1597 reflections; **1c**, $Cu_2O_4N_2C_{28}H_{26}$, space group $P2_1/c$, $Z = 2$, $a = 10.982$ (8) Å, $b = 8.799$ (2) Å, $c = 12.322$ (2) Å, $\beta = 90.68$ (3)°, $V = 1191$ Å^3, $R = 2.9\%$, 1275 reflections. The binuclear structure is held together by propoxy bridges between the copper atoms, and the ligand environment of the metal is quite close to square planar. The compounds all show very strong antiferromagnetic exchange interactions, as expected of the near-planar copper environment. In fact, the structures and magnetic properties fit into and give support to a general correlation between decreasing strength of antiferromagnetic interaction and increasing distortion toward tetrahedral metal environments in binuclear copper(II) complexes, and this correlation is strong enough to be used in the solution of the crystal structures. The bridging, via the highly electronegative propoxy oxygen, is readily reversed by electron impact to form the monomeric cation (three-coordinated copper), which is by far the strongest mass spectral peak. Comparison with other polymeric copper(II) complexes indicates that preferred bridging oxygens are given by the series alkyl–O$^-$ > aryl–O$^-$ > β-diketone enolic O$^-$ > ketonic O > alkyl–OH, which corresponds well to decreasing electronegativity.

Introduction

Structural formulas for binuclear copper(II) complexes of type **1**[1-3] were determined from infrared and magnetic data,



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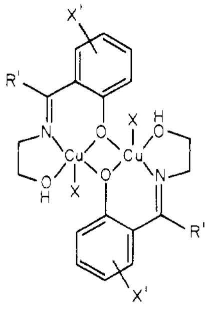

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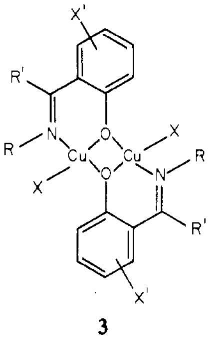

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and the relationship of this type complex with complex **2**[4] by addition and elimination of HX (X = Cl, NO_3) was established.[2,3] In compounds **1** and **2**, the Cu_2O_2 bridge produces pairwise antiferromagnetic exchange interactions, as in **3**, where the relation between structure and magnetic properties has been investigated.[5-7] The four-coordinated copper environment of **1** closely resembles that of complexes **3**, and therefore some of the magnetic and structural correlations for **3** should be applicable in **1**: the strength of the antiferromagnetism increases, and therefore the magnetic moments decrease, as the copper(II)–ligand environment approaches square planar, and this dependence on metal environment outweighs the effect of varying the nature of the ligand X.

For complexes **1** with Y = 5-Cl (**1a**), 3-NO_2 (**1b**), and 5,6-benzo (**1c**), the antiferromagnetic interaction is so strong that the compounds are almost diamagnetic at room temperature, and their magnetic moments show so little temperature dependence that a large singlet–triplet separation ($-2J \geq 800$ cm^{-1}) can be estimated. This requires a copper(II) environment very close to square planar, which in turn requires the entire molecule to be approximately flat because of the extensive conjugation of the ligands.[8] Therefore the entire molecule must be visible in each case as an approximate reciprocal image in a photograph of the diffraction pattern, for a suitable crystal orientation.[9] This method was used for these three complexes, each of which belongs to the same space group, $P2_1/c$. From the unit cell volumes, the molecular formulas, and an assumed atomic volume of 19 ± 2 Å^3 for nonhydrogen atoms, $Z = 2$ in each case, and a center of inversion is required in each of the molecules. The procedure is described below.

Experimental Section

The complexes were prepared as previously described[3] as brown powders which were poorly soluble in all organic solvents. Crystals suitable for x-ray diffraction were obtained by prolonged (3 weeks for **1a**, 6 weeks for **1b** and **1c**) heating (90°C) under reflux in *N*,*N*-dimethylformamide.

Crystal data for **1a**: $Cu_2Cl_2O_4N_2C_{20}H_{20}$, mol wt 548.4, space group $P2_1/c$, $Z = 2$, $a = 9.475$ (1) Å, $b = 11.251$ (3) Å, $c = 9.857$ (2) Å, $\beta = 102.84$ (2)°, $V = 1025$ Å^3, μ(Mo Kα) = 24.6 cm^{-1}, $d_{calcd} = 1.79$ g cm^{-3}, $d_{obsd} = 1.78$ g cm^{-3}, $F(000) = 556$.

Crystal data for **1b**: $Cu_2O_8N_4C_{20}H_{20}$, mol wt 571.5, space group $P2_1/c$, $Z = 2$, $a = 4.597$ (1) Å, $b = 15.515$ (5) Å, $c = 16.345$ (4) Å, $\beta = 113.28$ (2)°, $V = 1064$ Å^3, μ(Mo Kα) = 21.4 cm^{-1}, $d_{calcd} = 1.78$ g cm^{-3}, $d_{obsd} = 1.77$ g cm^{-3}, $F(000) = 580$.

Crystal data for **1c**: $Cu_2O_4N_2C_{28}H_{26}$, mol wt 581.6, space group $P2_1/c$, $Z = 2$, $a = 10.982$ (8) Å, $b = 8.799$ (2) Å, $c = 12.322$ (2) Å, $\beta = (3)$°, $V = 1191$ Å^3, μ(Mo Kα) = 19.0 cm^{-1}, $d_{calcd} = 1.63$ g cm^{-3}, $d_{obsd} = 1.60$ g cm^{-3}, $F(000) = 596$.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the

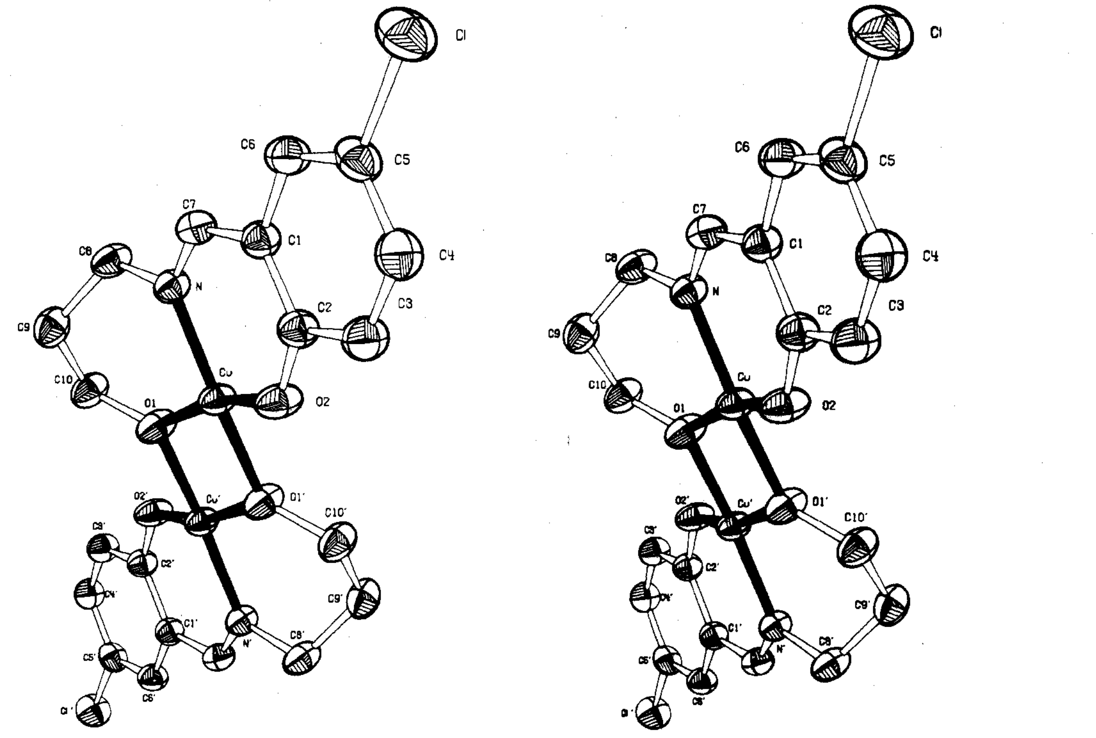

Figure 1. Stereoview of **1a**.

program INDEX to obtain an orientation matrix for data collection and also approximate cell dimensions. The cell parameters matched those obtained from precession photographs. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory.

Infrared spectra were measured on a Unicam SP200 spectrometer.

Magnetic moments were measured by the Gouy technique as previously described.[3,5,7]

Mass spectra were run on a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Collection and Reduction of Data. Diffraction data were collected at 292°K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $0° < 2\theta < 50°$. Scan widths (SW) were calculated from the formula $SW = A + B \tan\theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1 and Kα_2 splitting. The values of A and B were 0.60 and 0.20°, respectively. This calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the estimated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and then for absorption. After averaging the intensities of equivalent reflections, the data were reduced to 1709 independent intensities for **1a**, 2193 for **1b**, and 2290 for **1c**, of which 1608 for **1a** and 1275 for **1c** had $F_o^2 > 3\sigma(F_o^2)$ and 1597 for **1b** had $F_o^2 > 2\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[10] These data were used in the final refinement of the structural parameters.

Refinement of the Structure. Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[11] and those for hydrogen from Stewart.[12] The effects of anomalous dispersion for Cu and Cl were included in F_c using Cromer's values[13] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. To minimize computer time, the initial calculations were carried out on the first 600 reflections collected.

In each case the approximate orientation of the molecular plane, viewed as a reciprocal image on a precession photograph, was assumed to define the Cu_2O_2 plane, the Cu–Cu distance was assumed to be 3 Å (an average distance of 3.05 ± 0.01 Å is typical in the Cu_2O_2 bridge of several type **3** complexes[5]), and the Cu–O bond lengths were taken as 2 Å. For convenience, the center of symmetry of the Cu_2O_2 bridge is located on the origin. The intensity data were phased sufficiently well by the calculated Cu and O positions (R = 33% **1a**, 38% **1b**, 32% **1c**) to permit location of the remaining nonhydrogen atoms by difference Fourier syntheses. After full-matrix least-squares refinement, the models converged with R = 7.3% for **1a**, 13.3% for **1b**, and 8.7% for **1c**. The remaining diffraction data were added to the calculation, anisotropic temperature factors were introduced, and nonmethyl hydrogen atoms were inserted as fixed atoms at the calculated positions, with isotropic temperature factors of 5.0, assuming C–H = 1.00 Å. After convergence the hydrogen atoms were inserted at their new calculated positions. The models converged with R = 2.4, R_w = 3.0%; R = 4.2, R_w = 4.5%; and R = 2.9, R_w = 3.0% for **1a**, **1b**, and **1c**, respectively. One of the methylene carbons, C(9) in **1c**, was found to be positionally disordered; if the disorder is not allowed for, R rises from 2.9 to 3.9%. The error in an observation of unit weight is 1.72, 1.83, and 0.96 for **1a**, **1b**, and **1c**, respectively. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave R = 2.5, 5.0, 3.7 for **1a**, **1b**, **1c**; on this basis, it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference map was featureless. Tables of the observed structure factors are available.[14]

Results and Discussion

Final positional and thermal parameters for the complexes **1a**, **1b**, and **1c** are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figures 1–3 are stereopair views of the dimeric molecules, only one of the two equally occupied positions of the disordered

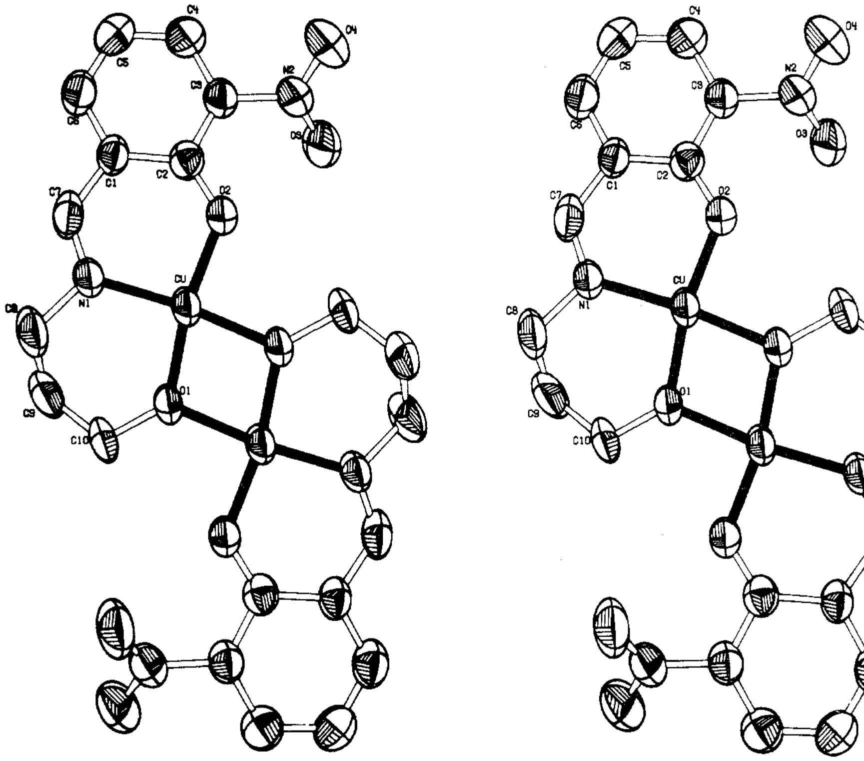

Figure 2. Stereoview of **1b**.

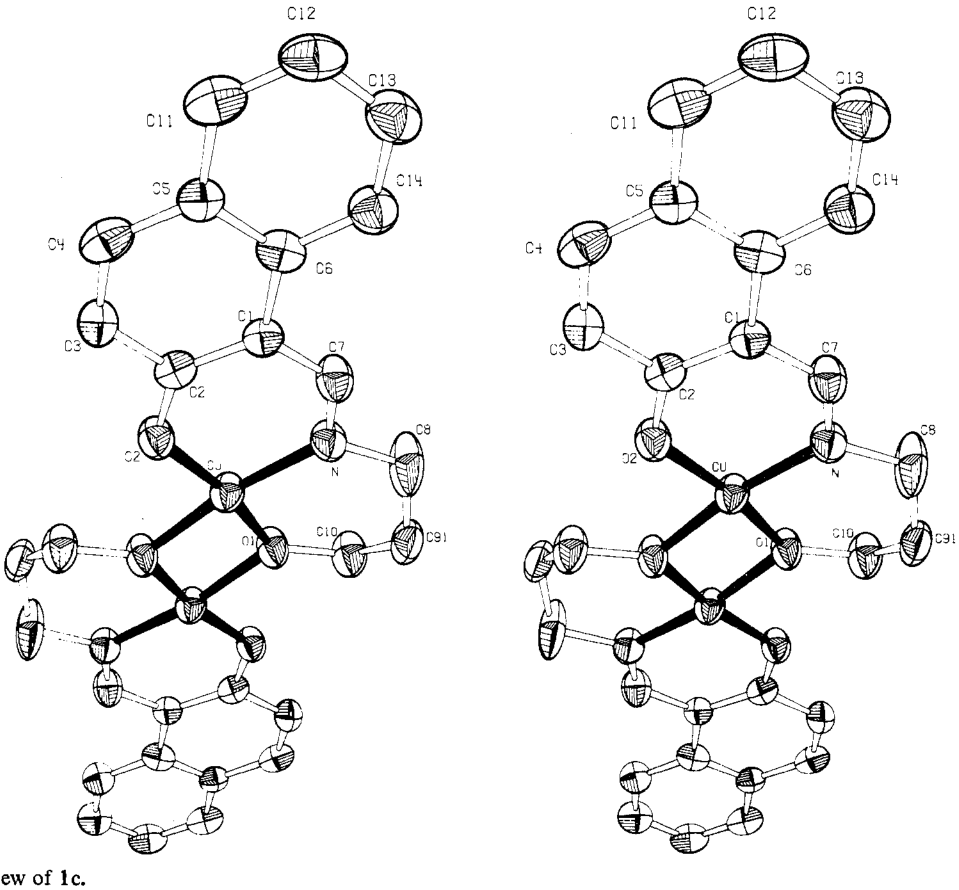

Figure 3. Stereoview of **1c**.

carbon shown in **1c**, while Figures 4–6 show the molecular packing in the unit cells. As is evident from the packing diagrams and the closest intermolecular distances (Table IV), the complexes consist of discrete dimeric molecules, the closest interdimer contacts being a O(1)–C(7) distance of 3.3 Å for **1a**, a O(4)–C(4) distance of 3.3 Å for **1b**, and a Cu–C(11) distance of 3.2 Å for **1c**. The molecules may therefore be considered to be magnetically isolated, given the large intradimer interaction observed in each case.

The infrared spectra of all three complexes **1a**, **1b**, and **1c** contain bands at 1540 cm^{-1} which compares with 1560 cm^{-1} for related dimeric complexes containing phenolic oxygen

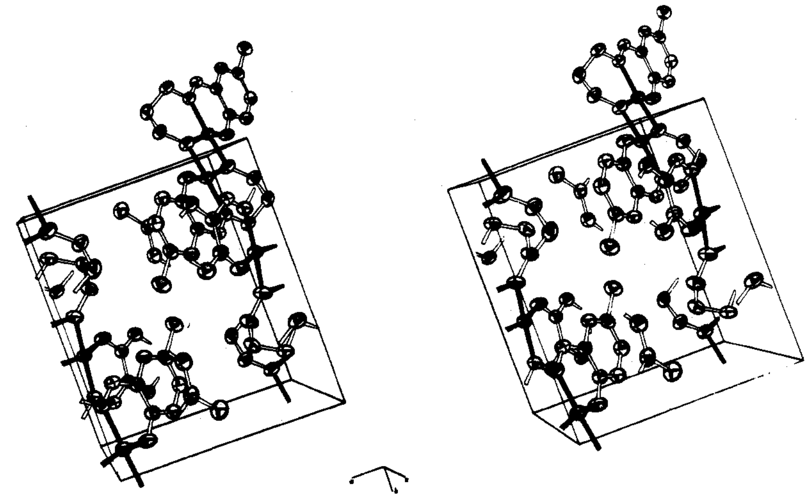

Figure 4. Molecular packing in the unit cell of **1a**.

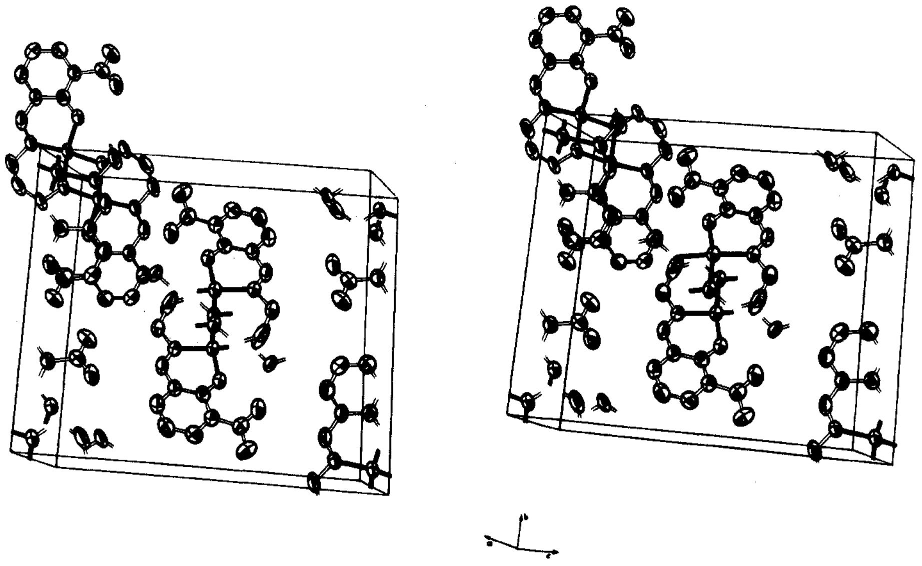

Figure 5. Molecular packing in the unit cell of **1b**.

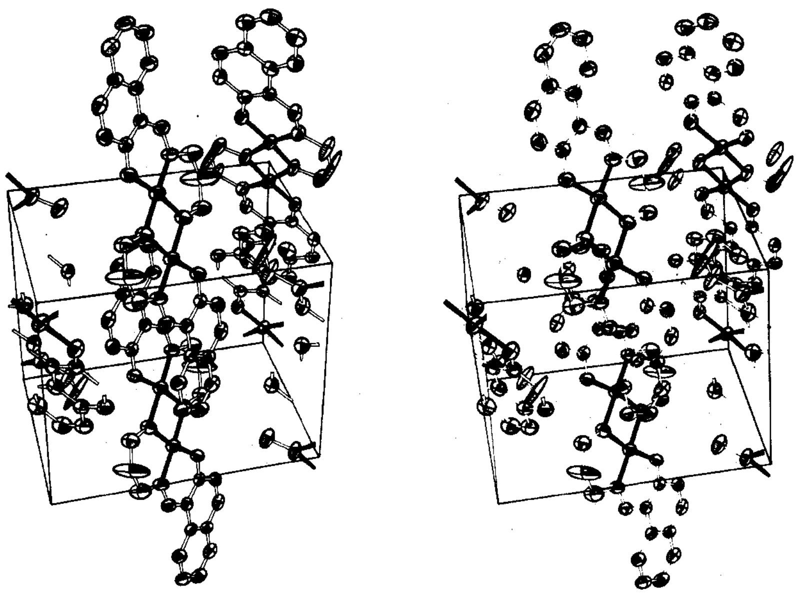

Figure 6. Molecular packing in the unit cell of **1c**.

bridges[3] and is good supporting evidence for the assignment of this band to the phenolic C–O stretch in such Schiff base complexes.

The magnetic moments of the complexes show little temperature dependence: 0.29, 0.32, and 0.25 BM for **1a**, **1b**, and **1c**, respectively, at 273 K, and 0.36, 0.37, and 0.35 BM at 305

Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations

(a) $Cu_2Cl_2O_4N_2C_{20}H_{20}$

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cu	0.06226 (3)	0.08669 (3)	0.11512 (3)	0.00793 (3)	0.00353 (2)	0.00587 (3)	0.00030 (5)	−0.00031 (5)	−0.00089 (5)
Cl	0.51574 (8)	0.40544 (7)	0.68308 (8)	0.01088 (8)	0.00731 (6)	0.00922 (7)	−0.0040 (1)	−0.0016 (1)	−0.0044 (1)
O1	−0.0836 (2)	0.0741 (2)	−0.0536 (2)	0.0103 (2)	0.0042 (1)	0.0077 (2)	0.0026 (3)	−0.0045 (4)	−0.0023 (3)
O2	0.1836 (2)	0.0596 (2)	0.2918 (2)	0.0113 (2)	0.0038 (1)	0.0068 (2)	−0.0003 (3)	−0.0028 (4)	−0.0005 (3)
N	0.0431 (2)	0.2566 (2)	0.1414 (2)	0.0076 (2)	0.0039 (2)	0.0061 (2)	0.0011 (3)	0.0013 (4)	−0.0000 (3)
C1	0.2296 (3)	0.2655 (2)	0.3569 (2)	0.0071 (3)	0.0042 (2)	0.0059 (2)	−0.0003 (3)	0.0023 (4)	−0.0008 (4)
C2	0.2517 (3)	0.1411 (2)	0.3773 (3)	0.0076 (3)	0.0044 (2)	0.0060 (2)	−0.0004 (4)	0.0018 (4)	−0.0004 (4)
C3	0.3526 (3)	0.1037 (2)	0.4987 (3)	0.0092 (3)	0.0051 (2)	0.0075 (3)	0.0004 (5)	−0.0001 (5)	0.0003 (4)
C4	0.4316 (3)	0.1836 (3)	0.5911 (3)	0.0083 (3)	0.0062 (2)	0.0069 (3)	0.0002 (5)	−0.0005 (5)	0.0006 (4)
C5	0.4108 (3)	0.3048 (2)	0.5667 (3)	0.0074 (3)	0.0058 (2)	0.0068 (3)	−0.0027 (4)	0.0018 (5)	−0.0030 (4)
C6	0.3106 (3)	0.3459 (2)	0.4540 (3)	0.0085 (3)	0.0043 (2)	0.0074 (3)	−0.0012 (4)	0.0028 (5)	−0.0013 (4)
C7	0.1232 (3)	0.3149 (2)	0.2425 (3)	0.0085 (3)	0.0037 (2)	0.0072 (3)	0.0001 (4)	0.0038 (5)	−0.0003 (4)
C8	−0.0638 (3)	0.3244 (2)	0.0363 (3)	0.0101 (3)	0.0041 (2)	0.0078 (3)	0.0029 (5)	−0.0004 (5)	0.0004 (4)
C9	−0.2043 (3)	0.2556 (3)	−0.0086 (3)	0.0081 (3)	0.0062 (2)	0.0079 (3)	0.0037 (5)	0.0004 (5)	−0.0003 (4)
C10	−0.1961 (3)	0.1554 (2)	−0.1094 (3)	0.0091 (3)	0.0051 (2)	0.0077 (3)	0.0031 (5)	−0.0025 (5)	−0.0014 (4)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H3	0.3664	0.01655	0.5181	5.0	H82	−0.0841	0.40185	0.0779	5.0
H4	0.5038	0.15495	0.6751	5.0	H91	−0.2301	0.22114	0.0763	5.0
H6	0.2946	0.43338	0.4404	5.0	H92	−0.2819	0.31216	−0.0547	5.0
H7	0.1106	0.40315	0.2416	5.0	H101	−0.1777	0.18991	−0.1977	5.0
H81	−0.0223	0.33956	−0.0471	5.0	H102	−0.2907	0.11196	−0.1302	5.0

(b) $Cu_2O_8N_4C_{20}H_{20}$

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cu	−0.1102 (1)	0.07290 (3)	0.04135 (3)	0.0982 (4)	0.00405 (2)	0.00309 (2)	−0.0035 (2)	0.0187 (1)	0.00020 (4)
O1	−0.0067 (8)	−0.0468 (2)	0.0568 (2)	0.130 (2)	0.0042 (1)	0.0039 (1)	0.002 (1)	0.0302 (7)	0.0013 (2)
O2	−0.2417 (7)	0.1860 (2)	−0.0002 (2)	0.092 (2)	0.0044 (1)	0.0039 (1)	0.000 (1)	0.0215 (7)	0.0006 (2)
O3	−0.5353 (11)	0.2836 (2)	−0.1521 (2)	0.253 (4)	0.0065 (2)	0.0051 (1)	−0.001 (2)	0.0441 (11)	0.0003 (3)
O4	−0.3881 (10)	0.4109 (2)	−0.1089 (2)	0.151 (3)	0.0058 (2)	0.0079 (2)	−0.000 (1)	0.0353 (11)	0.0043 (3)
N1	−0.169 (1)	0.0881 (2)	0.1516 (2)	0.106 (3)	0.0040 (2)	0.0033 (1)	−0.005 (1)	0.0197 (9)	0.0001 (2)
N2	−0.467 (1)	0.3387 (2)	−0.0965 (2)	0.111 (3)	0.0045 (2)	0.0049 (2)	0.004 (1)	0.0224 (11)	0.0018 (3)
C1	−0.413 (1)	0.2311 (3)	0.1146 (2)	0.074 (3)	0.0046 (2)	0.0034 (2)	−0.006 (1)	0.015 (1)	−0.0009 (3)
C2	−0.376 (1)	0.2414 (3)	0.0321 (2)	0.064 (3)	0.0043 (2)	0.0035 (2)	−0.008 (1)	0.011 (1)	−0.0011 (3)
C3	−0.490 (1)	0.3212 (3)	−0.0112 (2)	0.075 (3)	0.0043 (2)	0.0037 (2)	−0.003 (1)	0.014 (1)	0.0001 (3)
C4	−0.627 (1)	0.3843 (3)	0.0223 (3)	0.080 (3)	0.0045 (2)	0.0050 (2)	−0.003 (2)	0.016 (1)	−0.0008 (4)
C5	−0.663 (1)	0.3707 (3)	0.1008 (3)	0.090 (3)	0.0055 (2)	0.0056 (2)	0.001 (2)	0.022 (1)	−0.0024 (4)
C6	−0.556 (1)	0.2949 (3)	0.1457 (3)	0.095 (3)	0.0060 (3)	0.0044 (2)	−0.005 (2)	0.023 (1)	−0.0012 (4)
C7	−0.295 (1)	0.1546 (3)	0.1697 (2)	0.094 (3)	0.0060 (2)	0.0033 (2)	−0.010 (2)	0.019 (1)	−0.0009 (3)
C8	−0.064 (2)	0.0173 (3)	0.2187 (3)	0.191 (6)	0.0056 (2)	0.0031 (2)	−0.010 (2)	0.026 (2)	0.0003 (4)
C9	−0.126 (2)	−0.0657 (4)	0.1839 (3)	0.200 (5)	0.0092 (3)	0.0079 (2)	0.042 (2)	0.059 (1)	0.0110 (4)
C10	0.004 (1)	−0.1037 (3)	0.1259 (2)	0.081 (3)	0.0049 (2)	0.0034 (2)	−0.006 (1)	0.014 (1)	0.0019 (3)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H4	−0.7003	0.4395	−0.0112	5.0	H82	0.1703	0.0223	0.2537	5.0
H5	−0.7614	0.4158	0.1253	5.0	H91	−0.3652	−0.0679	0.1480	5.0
H6	−0.5889	0.2843	0.2016	5.0	H92	−0.0721	−0.1063	0.2349	5.0
H7	−0.3149	0.1545	0.2288	5.0	H101	−0.1247	−0.1573	0.0977	5.0
H81	−0.1746	0.0248	0.2609	5.0	H102	0.2254	−0.1210	0.1621	5.0

(c) $Cu_2O_4N_2C_{28}H_{26}$

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cu	0.12817 (5)	−0.06034 (7)	−0.01355 (5)	0.00541 (4)	0.00966 (6)	0.00508 (3)	0.0016 (1)	0.00254 (6)	0.0026 (1)
O1	−0.0080 (2)	−0.0684 (4)	0.0823 (2)	0.0056 (2)	0.0149 (5)	0.0055 (2)	0.0039 (8)	0.0038 (4)	0.0074 (7)
O2	0.2459 (2)	−0.0179 (3)	−0.1194 (2)	0.0058 (3)	0.0111 (5)	0.0052 (2)	0.0026 (6)	0.0021 (4)	0.0036 (6)
N	0.2277 (3)	−0.2119 (4)	0.0590 (3)	0.0054 (3)	0.0109 (6)	0.0057 (3)	0.0032 (8)	0.0019 (5)	0.0042 (7)
C1	0.4104 (4)	−0.1718 (5)	−0.0501 (3)	0.0053 (4)	0.0083 (6)	0.0043 (3)	−0.0005 (9)	0.0007 (6)	−0.0018 (8)
C2	0.3595 (3)	−0.0629 (5)	−0.1198 (3)	0.0053 (3)	0.0085 (6)	0.0044 (3)	−0.0001 (10)	0.0012 (5)	−0.0022 (9)
C3	0.4350 (4)	0.0078 (5)	−0.2004 (3)	0.0068 (4)	0.0102 (7)	0.0048 (3)	−0.0009 (9)	0.0009 (6)	0.0011 (8)
C4	0.5551 (4)	−0.0281 (5)	−0.2077 (3)	0.0070 (4)	0.0115 (8)	0.0048 (3)	−0.0040 (10)	0.0029 (6)	−0.0029 (9)
C5	0.6104 (4)	−0.1368 (5)	−0.1378 (3)	0.0057 (4)	0.0083 (6)	0.0050 (3)	−0.0000 (9)	0.0009 (6)	−0.0038 (8)
C6	0.5391 (4)	−0.2120 (5)	−0.0586 (3)	0.0056 (4)	0.0089 (7)	0.0051 (3)	0.0012 (9)	0.0005 (6)	−0.0044 (8)
C7	0.3394 (4)	−0.2407 (5)	0.0348 (3)	0.0067 (4)	0.0089 (7)	0.0055 (4)	0.0042 (9)	0.0019 (6)	0.0021 (9)
C8	0.1780 (4)	−0.2988 (6)	0.1520 (4)	0.0107 (5)	0.0189 (9)	0.0102 (4)	0.0103 (13)	0.0113 (8)	0.0173 (11)
C91	0.0499 (8)	−0.3171 (11)	0.1530 (8)	0.0077 (9)	0.0117 (15)	0.0073 (8)	−0.0013 (21)	0.0027 (15)	0.0084 (19)
C92	0.0863 (8)	−0.2343 (12)	0.2131 (7)	0.0098 (9)	0.0171 (18)	0.0066 (7)	0.0090 (23)	0.0081 (13)	0.0144 (19)
C10	−0.0267 (4)	−0.1710 (6)	0.1683 (4)	0.0072 (4)	0.0163 (9)	0.0069 (4)	0.0039 (11)	0.0048 (7)	0.0088 (10)
C11	0.7365 (4)	−0.1729 (6)	−0.1454 (4)	0.0064 (4)	0.0134 (8)	0.0064 (4)	−0.0017 (10)	0.0026 (7)	−0.0059 (10)
C12	0.7898 (4)	−0.2770 (6)	−0.0789 (4)	0.0049 (4)	0.0147 (9)	0.0083 (4)	0.0029 (10)	0.0012 (7)	−0.0056 (10)
C13	0.7198 (4)	−0.3520 (6)	−0.0020 (4)	0.0074 (4)	0.0114 (8)	0.0078 (4)	0.0048 (11)	0.0001 (7)	−0.0001 (10)
C14	0.5977 (4)	−0.3196 (5)	0.0076 (4)	0.0060 (4)	0.0113 (7)	0.0062 (4)	0.0021 (10)	0.0014 (7)	0.0001 (9)

Table I (*Continued*)

(c) $Cu_2O_4N_2C_{28}H_{26}$ (*continued*)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H3	0.3967	0.0852	−0.2519	5.0	H94	0.0597	−0.3179	0.2639	5.0
H4	0.6074	0.0236	−0.2647	5.0	H101	−0.0028	−0.1211	0.2384	5.0
H7	0.3828	−0.3179	0.0806	5.0	H102	−0.1150	−0.1989	0.1702	5.0
H81	0.2037	−0.2459	0.2200	5.0	H103	−0.0698	−0.1163	0.2279	5.0
H82	0.2154	−0.4028	0.1501	5.0	H104	−0.0791	−0.2561	0.1410	5.0
H83	0.2479	−0.3204	0.2024	5.0	H11	0.7868	−0.1209	−0.2011	5.0
H84	0.1462	−0.3969	0.1215	5.0	H12	0.8783	−0.3000	−0.0838	5.0
H91	0.0307	−0.3868	0.2158	5.0	H13	0.7569	−0.4306	0.0463	5.0
H92	0.0238	−0.3658	0.0842	5.0	H14	0.5490	−0.3746	0.0634	5.0
H93	0.1252	−0.1518	0.2557	5.0					

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

Table II. Bond Lengths (A)

	1a, $Cu_2Cl_2O_4N_2C_{20}H_{20}$		
Cu–O(1)	1.917 (1)	C(1)–C(2)	1.422 (3)
Cu–O(1′)	1.933 (1)	C(1)–C(6)	1.414 (3)
Cu–O(2)	1.886 (1)	C(1)–C(7)	1.446 (3)
Cu–N	1.943 (2)	C(2)–C(3)	1.419 (3)
Cl–C(5)	1.755 (2)	C(3)–C(4)	1.377 (3)
O(1)–C(10)	1.419 (2)	C(4)–C(5)	1.391 (3)
O(2)–C(2)	1.314 (2)	C(5)–C(6)	1.372 (3)
N–C(7)	1.290 (3)	C(8)–C(9)	1.518 (3)
N–C(8)	1.488 (2)	C(9)–C(10)	1.516 (3)
	1b, $Cu_2O_8N_4C_{20}H_{20}$		
Cu–O(1)	1.909 (2)	N(2)–C(3)	1.464 (4)
Cu–O(1′)	1.926 (2)	C(1)–C(2)	1.433 (4)
Cu–O(2)	1.892 (2)	C(1)–C(6)	1.392 (5)
Cu–N(1)	1.939 (3)	C(1)–C(7)	1.458 (5)
O(2)–C(2)	1.288 (4)	C(2)–C(3)	1.419 (4)
O(3)–N(2)	1.196 (4)	C(3)–C(4)	1.386 (5)
O(4)–N(2)	1.220 (4)	C(4)–C(5)	1.373 (5)
O(1)–C(10)	1.419 (4)	C(5)–C(6)	1.371 (5)
N(1)–C(7)	1.277 (4)	C(8)- C(9)	1.391 (6)
N(1)–C(8)	1.491 (4)	C(9)–C(10)	1.430 (6)
	1c, $Cu_2O_4N_2C_{28}H_{26}$		
Cu–O(1)	1.914 (4)	C(2)–C(3)	1.432 (9)
Cu–O(2)	1.883 (4)	C(3)–C(4)	1.369 (8)
Cu–N(1)	1.932 (6)	C(4)–C(5)	1.427 (9)
O(2)–C(2)	1.313 (7)	C(5)–C(6)	1.409 (9)
C(1)–C(2)	1.395 (9)	C(5)–C(11)	1.435 (9)
O(1)–C(10)	1.434 (8)	C(6)–C(14)	1.411 (9)
N(1)–C(7)	1.301 (8)	C(8)–C(9)	1.285 (13)
N(1)–C(8)	1.498 (9)	C(9)–C(10)	1.338 (12)
C(1)–C(6)	1.462 (8)	C(11)–C(12)	1.347 (10)
C(1)–C(7)	1.439 (9)	C(12)–C(13)	1.378 (10)
		C(13)–C(14)	1.374 (9)

Table III. Bond Angles (deg)

	1a, $Cu_2Cl_2O_4N_2C_{20}H_{20}$		
O(1)–Cu–O(1′)	76.4 (1)	C(1)–C(2)–C(3)	117.5 (2)
O(1)–Cu–O(2)	164.4 (1)	C(2)–C(3)–C(4)	121.9 (2)
O(1)–Cu–N	96.7 (1)	C(3)–C(4)–C(5)	119.4 (2)
O(1)–Cu–O(2)	93.1 (1)	Cl–C(5)–C(4)	118.8 (2)
O(1)–Cu–N	169.1 (1)	Cl–C(5)–C(6)	120.1 (2)
O(2)–Cu–N	95.3 (1)	C(4)–C(5)–C(6)	121.1 (2)
Cu–O(1)–Cu′	103.6 (1)	C(1)–C(6)–C(5)	120.4 (2)
C(7)–N–C(8)	118.0 (2)	N–C(7)–C(1)	126.6 (2)
C(2)–C(1)–C(6)	119.6 (2)	N–C(8)–C(9)	111.1 (2)
C(2)–C(1)–C(7)	122.9 (2)	C(8)–C(9)–C(10)	113.7 (2)
C(6)–C(1)–C(7)	117.5 (2)	O(1)–C(10)–C(9)	111.6 (2)
O(2)–C(2)–C(1)	124.1 (2)		
O(2)–C(2)–C(3)	118.4 (2)		
	1b, $Cu_2O_8N_4C_{20}H_{20}$		
O(1)–Cu–O(1′)	76.6 (1)	C(2)–C(1)–C(7)	121.3 (3)
O(1)–Cu–O(2)	167.7 (1)	C(6)–C(1)–C(7)	117.7 (3)
O(1)–Cu–N(1)	96.5 (1)	O(2)–C(2)–C(3)	121.4 (3)
O(1)–Cu–O(2)	92.9 (1)	C(1)–C(2)–C(3)	114.1 (4)
O(1′)–Cu–N(1)	170.7 (1)	N(2)–C(3)–C(2)	119.0 (3)
O(2)–Cu–N(1)	94.5 (1)	N(2)–C(3)–C(4)	117.3 (3)
Cu–O(2)–C(2)	127.6 (2)	C(2)–C(3)–C(4)	123.7 (3)
O(3)–N(2)–O(4)	122.4 (3)	C(3)–C(4)–C(5)	120.1 (4)
O(2)–C(2)–C(1)	124.4 (3)	C(4)–C(5)–C(6)	118.8 (4)
C(7)–N(1)–C(8)	118.0 (3)	C(1)–C(6)–C(5)	122.3 (3)
O(3)–N(2)–C(3)	119.7 (3)	N(1)–C(7)–C(1)	127.3 (3)
O(4)–N(2)–C(3)	117.9 (3)	N(1)–C(8)–C(9)	115.2 (3)
C(2)–C(1)–C(6)	120.9 (3)	C(8)–C(9)–C(10)	125.7 (5)
Cu–O(1)–Cu	103.4 (1)	O(1)–C(10)–C(9)	112.2 (3)
	1c, $Cu_2O_4N_2C_{28}H_{26}$		
O(1)–Cu–O(2)	168.7 (2)	C(4)–C(5)–C(6)	119.1 (6)
O(1)–Cu–N(1)	97.0 (2)	C(4)–C(5)–C(11)	121.3 (7)
O(2)–Cu–N(1)	94.1 (2)	C(6)–C(5)–C(11)	119.6 (7)
Cu–O(2)–C(2)	127.4 (4)	C(1)–C(6)–C(5)	119.5 (7)
O(2)–C(2)–C(1)	125.1 (6)	C(1)–C(6)–C(14)	124.0 (6)
C(7)–N(1)–C(8)	117.8 (6)	C(5)–C(6)–C(14)	116.5 (6)
C(2)–C(1)–C(6)	119.6 (6)	N(1)–C(7)–C(1)	128.1 (6)
C(2)–C(1)–C(7)	121.0 (6)	N(1)–C(8)–C(9)	122.9 (8)
C(6)–C(1)–C(7)	119.3 (6)	C(8)–C(9)–C(10)	136.6 (11)
O(2)–C(2)–C(1)	125.1 (6)	O(1)–C(10)–C(9)	116.6 (7)
O(2)–C(2)–C(3)	115.3 (6)	C(5)–C(11)–C(12)	121.7 (7)
C(1)–C(2)–C(3)	119.6 (6)	C(11)–C(12)–C(13)	118.9 (7)
C(2)–C(3)–C(4)	120.9 (7)	C(12)–C(13)–C(14)	121.5 (8)
C(3)–C(4)–C(5)	121.3 (7)	C(6)–C(14)–C(13)	121.9 (7)

K. All three complexes therefore exhibit very strong antiferromagnetic interactions, which render them almost diamagnetic. The magnetic moments for such a dimeric system are given in terms of the singlet–triplet separation, $-2J$, by $\mu_{\text{eff}} = g[(1 + 1/3e^{-2J/0kT})^{-1} + 0.0005T/g^2]^{1/2}$, in the standard notation,[5-7,15] where the term $0.0005T/g^2$ arises from the second-order Zeeman effect and the values of β and k are included in the constant. Because of the very low observed paramagnetism (no maximum in the magnetic susceptibility vs. temperature curve at accessible temperatures), the values of $-2J$ cannot be estimated accurately, though the lower limit of 800 cm^{-1} is clearly implied. These properties are closely similar to magnetic properties of the parent complex (Y = H)[3] and two other derivatives.[16] The distortion of the copper environment CuO(1)O(1′)O(2)N from planarity is conveniently though crudely measured by the dihedral angle τ between the plane CuO(1)Cu′O(1′) and that of the remaining ligands. Values of 0 and 90°, respectively, for τ are then necessary but not sufficient conditions for planar and tetrahedral ligand environments about the copper atoms. Table V gives best fit least-squares planes through appropriate sets of atoms which show that the complexes **1a**, **1b**, and **1c** are quite close to being flat molecules, though a related molecule (type **1**, Y = 5-NO2) is much closer to being completely planar. Table VI gives τ and $|J|$ values for the present complexes as well as others of types **1** and **2**. These results demonstrate that the correlation between the copper geometry and strength of antiferromagnetic interaction, originally proposed for a few complexes of type **2**, is quite well supported and that the correlation is definitely not confined to complexes

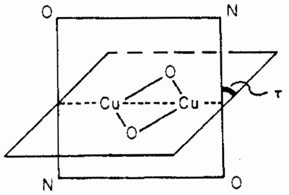

Table IV. Closest Intermolecular Distances

Mol 1	Mol 2	Dist, A	Mol 1	Mol 2	Dist, A
		1a, $Cu_2Cl_2O_4N_2C_{20}H_{20}$			
Cu	C(1)	3.682 (2)	Cl	C(6)	3.653 (2)
Cu	C(5)	3.650 (2)	O(1)	C(6)	3.622 (3)
Cu	C(6)	3.682 (2)	O(1)	C(7)	3.346 (3)
Cl	O(2)	3.565 (2)	O(2)	C(8)	3.466 (3)
Cl	C(2)	3.511 (2)			
		1b, $Cu_2O_8N_4C_{20}H_{20}$			
O(1)	C(9)	3.762 (7)	O(3)	C(6)	3.487 (4)
O(1)	C(10)	3.795 (4)	O(3)	C(10)	3.622 (5)
O(2)	C(1)	3.589 (4)	O(4)	C(4)	3.331 (5)
O(2)	C(6)	3.540 (5)	O(4)	C(5)	3.395 (5)
O(2)	C(10)	3.526 (4)	O(4)	C(8)	3.453 (6)
		1c, $Cu_2O_4N_2C_{28}H_{26}$			
Cu	C(5)	3.808 (6)	O(1)	C(12)	3.475 (9)
Cu	C(11)	3.179 (7)	O(2)	C(8)	3.337 (9)
Cu	C(12)	3.300 (8)	O(4)	C(7)	3.38 (1)
Cu	C(13)	3.989 (8)			

of type **2**. The data support the hypothesis that the strength of antiferromagnetic interaction is determined by the efficiency of the Cu–O–Cu superexchange overlap: on this basis, the $-2J$ values for complexes of type **1** should be large, as observed. The interplanar angles (Table V) vary between complexes **1a**, **1b**, and **1c**, but the approach to planarity over the entire molecule is much closer in each case than for any corresponding plane in type **3** complexes. This must be at least partly due to intramolecular steric interactions that occur in some type **3** complexes[6] which do not occur in type **1**.

There is no systematic relation observable, in Table VI, between the magnetic interactions and the Cu–O–Cu' angle,[18,19] in type **1** and **3** complexes. This does not mean that this angle is unimportant but merely that it does not vary enough to play an important part; i.e., this variable has fortuitously been held approximately fixed over the range of complexes in Table VI, enabling the effect of the metal environment to be examined closely. Equally interesting is the absence of significant inductive effects[20–28] upon varying substituents directly on the metal atoms (O, Br, Cl) as well as at other sites. Clearly the environments of the metal atoms and the bridging oxygens have the greatest effect on J and substituents are relatively unimportant except for any structural modifications they produce in the Cu_2O_2 bridge.

The correlation between τ and J also holds approximately for a five-coordinated dimer related to complexes **3**, if the four strongest bonds only are considered, and the weaker fifth bond (to a bidentate nitrato group) is ignored.[29] However, two hydroxy-bridged copper dimers provide evidence that the correlation between magnetism and tetrahedral distortion cannot be considered in isolation, without taking into account other features of the Cu_2O_2 bridge, such as the Cu–O–Cu angle. $[CuLOH]_2X\cdot nH_2O$ complexes (L = bpy, phen; X = $(ClO_4)_2$, I_2, Br_2, Cl_2, $(NCS)_2$, SO_4, $(PF_6)_2$)[30] have long been postulated as intramolecular ferromagnets;[31] even the possibility of intradimer ferromagnetic interactions in copper complexes was first formally proposed in the literature.[15b] The proposed ferromagnetism was finally confirmed experimentally[32–34] for $[Cu(bpy)OH]_2SO_4\cdot H_2O$ which was

Table V. Coefficients of Least-Squares Planes, $AX + BY + CZ = D$, for **1a**, $Cu_2Cl_2O_4N_2C_{20}H_{20}$, **1b**, $Cu_2O_8N_4C_{20}H_{20}$, and **1c**, $Cu_2O_4N_2C_{28}H_{26}$[a]

Plane	Atoms	*A*	*B*	*C*	*D*	Distances from plane, A
I	Cu, Cu', O(1), O(1')	0.7924	0.3169	−0.5213	0	Cu, 0; Cu', 0; O(1), 0; O(1'), 0
		−0.7691	−0.3351	−0.5442	0	Cu, 0; Cu'; 0; O(1), 0; O(1'), 0
		−0.3563	−0.7872	−0.5033	0	Cu, 0; Cu', 0; O(1), 0; O(1'), 0
II	Cu, Cu', O(2), O(2'), N(1), N(1')	0.9067	0.1519	−0.3935	0	Cu, 0.0189; Cu', −0.0189; O(2), −0.0050; O(2'), 0.0050; N(1), −0.0052; N(1'), 0.0052
		−0.7866	−0.4490	−0.4239	0	Cu, 0.0010; Cu', −0.0010; O(2), −0.0003; O(2'), 0.0003; N(1), −0.0003; N(1'), 0.0003
		−0.3610	−0.7181	−0.5950	0	Cu, −0.0279; Cu', 0.0279; O(2), 0.0073; O(2'), −0.0073; N(1), 0077; N(2'), −0.0077
III	O(2), O(2'), N(1), N(1')	0.9071	0.1530	−0.3922	0	O(2), 0; O(2'), 0; N(1), 0; N(1'), 0
		−0.7867	−0.4489	−0.4238	0	O(2), 0; O(2'), 0; N(1), 0; N(1'), 0
		−0.3635	−0.7172	−0.5946	0	O(2), 0; O(2'), 0; N(1), 0; N(1'), 0
IV	Cu, O(2), N(1)	−0.9108	0.1631	−0.3793	0.0470	Cu, 0; O(2), 0; N(1), 0
		−0.7873	−0.4480	−0.4236	0.0025	Cu, 0; O(2), 0; N(1), 0
		−0.3862	−0.7087	−0.5904	−0.0690	Cu, 0; O(2), 0; N(1), 0
V	C(1)–C(6)	0.8516	0.0116	−0.5241	−0.5715	C(1), −0.0045; C(2), 0.0166; C(3), −0.0141; C(4), −0.0012; C(5), 0.0141; C(6), −0.0109
		−0.6960	−0.5551	−0.4555	−0.2800	C(1), −0.0073; C(2), 0.0004; C(3), 0.0058; C(4), −0.0052; C(5), −0.0018; C(6), 0.0081
		−0.2220	−0.7211	−0.6563	−0.4930	C(1), 0.0016; C(2), −0.0059; C(3), 0.0055; C(4), −0.0006; C(5), −0.0038; C(6), 0.0033
VI	Cu, O(2), C(1), C(2), C(7), N(1)	0.8723	0.0856	−0.4814	−0.2500	Cu, 0.0955; O(2), −0.0837; C(1), 0.0702; C(2), −0.0004; C(7), −0.0123; N(1), −0.0693
		−0.7230	−0.5382	−0.4332	−0.1826	Cu 0.0606; O(2), −0.0620; C(1), 0.0451; C(2), 0.0085; C(7), −0.0201; N(1), −0.0319
		−0.3101	−0.7259	−0.6139	−0.1065	Cu, −0.0555, O(2), 0.0680; C(1), −0.0270; C(2), −0.0278; C(7), 0.0139; N(1), 0.0284
VII[b]	N(2), O(3), O(4)	−0.8546	−0.4112	−0.3170	−3.2164	N(2), 0; O(3), 0; O(4), 0
	C(5), C(6), C(10'), C(11'), C(12'), C(13')	−0.2853	−0.7191	−0.6336	0.0787	C(5), −0.0555; C(6), 0.0228; C(10'), 0.0632; C(11'), 0.0095; C(12'), 0.0300, C(13'), −0.0699

Interplanar Angles, Deg

	I-II	I-III	I-IV	I-V	II-III	II-IV	III-IV	V-VI	V-VII
1a	13.7	13.7	13.8	17.9	0.1	1.1	1.0	5.0	
1b	9.6	9.5	9.5	14.3	0.0	0.1	0.1	2.2	59.3
1c	6.6	6.6	6.9	12.3	0.2	1.6	1.4	5.6	3.9

[a] First horizontal row of values for each plane refers to **1a**, second horizontal row to **1b**, and third horizontal row to **1c**. [b] No plane VII for **1a**.

Table VI. Some Magnetic and Structural Features

	Complex	$-J$, cm^{-1}	τ, deg	Cu–O–Cu, deg	Ref	For type 1 complexes			
						R	R′	X	X′
1a	$Cu_2Cl_2O_4N_2C_{20}H_{20}$	≥400	13.7	103.7	[a]	5-Cl	H		
1b	$Cu_2O_8N_4C_{20}H_{20}$		9.6	103.5	[a]	3-NO_2	H		
1c	$Cu_2O_4N_2C_{28}H_{26}$		10.4	104.0	[a]	5,6-benzo	H		
1d	$Cu_2O_8N_4C_{20}H_{20}$	≥500	4.0	106.0	16	5-NO_2	H		
3a	$Cu_2Cl_2O_2N_2C_{18}H_{20}$	240	33.1	103.3	5	C_2H_5	H	Cl	H
3b	$Cu_2Cl_2Br_2O_2N_2C_{34}H_{34}$	220	35.5	101.2	6	C_4H_9	C_6H_5	Br	5-Cl
3c	$Cu_2Br_2O_2N_2C_{18}H_{20}$	205	35.7	104.6	5	C_2H_5	H	Br	H
3d	$Cu_2Cl_2O_2N_2C_{16}H_{16}$	146	39.3	102.2	5	CH_3	H	Cl	H

[a] Present work.

found to contain five-coordinated copper, with relatively small distortion from planarity if the weak apical fifth bond is ignored.[32,33] The magnetism and structure are rather similar to those of $[Cu(bpy)OH(NO_3)]_2$.[19,35]

The effect of the Cu–O–Cu angle on J has been documented for a wide range of complexes,[18,19,36,37] but it can also not be taken in isolation; for this correlation is violated by the comparison of complexes **1** and **2**:[3,4] J is always larger for **1** than for **2**, yet Cu–O–Cu is smaller. Clearly the copper geometry is also important in determining the superexchange overlap along the Cu–O–Cu bonds.

Substituent effects, especially in ligand phenyl rings, at one time seemed important, in terms of inductive effects, in determining J values, but with the accumulation of more data it now appears that the only consistent effect of substituent groups is in the extent to which they alter structures, e.g., via alteration of molecular packing.[18,27,28]

Similar correlations between structure and magnetism should become possible for other types of dimers[38–42] as more structural data become available.

The mass spectra of the various type **1** complexes are closely similar. The bridging, via the electronegative propoxy oxygen, is readily reversed by electron impact to form the monomeric cation (M/2, three-coordinated copper), which is the strongest mass spectral peak for **1a**, **1b**, and **1c** and the complexes **1** with Y = H, 5-Br, 5-CH_3. This however, is not structurally diagnostic for the type of bridging oxygens, since phenolic oxygen bridges, as in type **2** and **3** complexes, would give the same spectra. Other significant peaks observed in these type **1** complexes, are M (the molecular ion), M – H_2O, M – CuH_2, and M – C_3H_4O, each of the peaks being identified by intercomparison between complexes and isotope distribution patterns. Thus removal of a copper or bridging oxygen does not necessarily break up the dimeric structure. The fragmentation pattern for m/e below M/2 is as expected.

The similarity of the mass spectra and other properties of type **1** complexes suggests the same basic structure for all such complexes. Comparison of the structures of type **1**, **2**, and **3** complexes[3–8] indicates that phenolic oxygens readily form bridges between metal atoms and are preferred for bridging over alkyl–OH oxygens which are less readily deprotonated (when there is a choice, as in **2**). However, on deprotonation, alcoholic oxygens are more electronegative than deprotonated aryl oxygens and are therefore preferred for bridging, as in **1**. Added to further literature data[7,17] this permits the arrangement of various types of ligand oxygens into a series according to preference as metal-bridging oxygens: alkyl–O$^-$ > aryl–O$^-$ > β-diketone enolic O$^-$ > ketonic O > alkyl–OH.

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Registry No. **1a**, 21584-53-2; **1b**, 57255-99-9; **1c**, 20753-19-9.

Supplementary Material Available: Listings of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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