Registry No. [Ni(OPDA)$_4$]Cl$_2$·2OPDA, 51266-72-9; Ni(OPDA)$_6$-Cl$_2$, 16999-86-3.

Supplementary Material Available. A listing of the structure factor amplitudes and a table of least-squares planes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1644.

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Crystal and Molecular Structure of Bis{perchlorato[2-(2-hydroxyethyl)imino-3-oximobutanato]aquocopper(II)}. A Copper(II) Dimer with Bridging Oxime Groups

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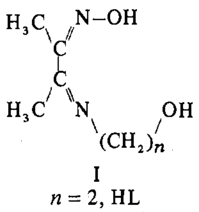
An unusual dimeric structure has been revealed by a single-crystal X-ray diffraction study of CuL(ClO$_4$)(H$_2$O) (where L represents the anion of 2-(2-hydroxyethyl)imino-3-oximobutane). The dimer contains a centrosymmetric, nearly-planar six-membered ring formed by two copper atoms and two oxime (NO) groups. The Cu-N(oxime) and Cu-O(oxime) distances, 1.987 (5) and 1.870 (4) Å, respectively, indicate very strong coordination by both atoms of the oxime group, while the angles at N(oxime), Cu-N-O = 129.4 (3)°, and at O(oxime), Cu-O-N = 121.9 (3)°, are indicative of essentially sp^2 hybridization for the oxime atoms. The square-planar coordination of each copper atom is completed by a nitrogen atom (Cu-N = 1.928 (5) Å) and an oxygen atom (Cu-O = 2.038 (5) Å) of the tridentate ligand; there are also weak axial contacts to the water molecule (Cu-O = 2.492 (6) Å) and the perchlorate group (Cu-O = 2.89 (1) Å). The magnetic moment of zero (the compound shows only temperature-independent paramagnetism) is ascribed to superexchange through the N-O bridges. Crystal data are as follows: space group $P2_1/c$, $Z = 4$ formula units or 2 dimeric units; $a = 7.868$ (2), $b = 14.040$ (7), $c = 11.401$ (5) Å; $\beta = 112.73$ (4)°; $\rho_{\text{calcd}} = 1.85$ and $\rho_{\text{obsd}} = 1.83$ (2) g cm^{-3}. The structure has been refined by full-matrix least-squares refinement to unweighted (R) and weighted (R_w) residuals of 0.057 and 0.056, respectively, for the 1579 reflections above background ($I \geq 3\sigma(I)$).

Introduction

Ablov and coworkers recently reported[1] an interesting complex which was obtained from the reaction of copper(II) perchlorate and the ligand 2-(2-hydroxyethyl)imino-3-oximobutane (hereafter abbreviated HL), I. The complex CuL(ClO$_4$)(H$_2$O) was reported to have a very low magnetic moment (0.41 BM at ambient temperature) characteristic of antiferromagnetic coupling in a polynuclear complex. Because of the possibility of highly unusual oxime bridges, we have investigated the structure of this complex and we have initiated a study of other transition metal complexes with this type of ligand. In this paper we report the details of a single-crystal X-ray diffraction study of [CuL(ClO$_4$)(H$_2$O)]$_2$, a dimeric compound with a planar, six-membered ring. A preliminary communication of these results has appeared.[2] We also report the preparation and properties of the analogous compound of 2-(3-hydroxypropyl)imino-3-oximobutane, CuL′(ClO$_4$)(H$_2$O).



I

$n = 2$, HL
$n = 3$, HL′

Experimental Section

Preparation. The method of Ablov, *et al.*, was used to synthesize CuL(ClO$_4$)(H$_2$O).[1] Dark green prismatic crystals were obtained by recrystallization from methanol. *Anal.* Calcd for Cu(C$_6$H$_{11}$N$_2$O$_2$)(ClO$_4$)(H$_2$O): C, 22.23; H, 4.04; N, 8.64. Found: C, 22.02; H, 3.69; N, 8.54.

By employing the same method and substituting 3-amino-1-propanol for 2-aminoethanol, dark green crystals of CuL′(ClO$_4$)(H$_2$O) were obtained. *Anal.* Calcd for Cu(C$_7$H$_{13}$N$_2$O$_2$)(H$_2$O): C, 24.86; H, 4.47; N, 8.28; Cl, 10.48. Found: C, 25.05; H, 4.20; N, 8.44; Cl, 10.59.

Magnetic Studies. The Faraday method was used to determine the magnetic susceptibility of CuL(ClO$_4$)(H$_2$O) at 77, 195, and 298°K; HgCo(NCS)$_4$ was used as a calibrant and a diamagnetic correction of 128 × 10^{-6} cgsu per formula unit was derived from tabulated values.[3] The resulting susceptibilities per formula unit, 64 × 10^{-6}, 54 × 10^{-6}, and 28 × 10^{-6} cgsu at 77, 195, and 298°K, respectively, are of the magnitude of the temperature-independent paramagnetism of copper(II).

The magnetic susceptibility of CuL′(ClO$_4$)(H$_2$O) was determined in the same way; values of 34 × 10^{-6} and 51 × 10^{-6} cgsu were obtained at 77 and 298°K, respectively.

Crystallographic Data Collection. Precession photographs of the $h0l$, $h1l$, $0kl$, and hkk reciprocal lattice levels and the full diffractometer data set (*vide infra*) revealed Laue symmetry $2/m$ and the systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), uniquely defining the space group as C_{2h}^5-$P2_1/c$ (No. 14).[4] For data collection a well-formed, multifaceted crystal was mounted collinear with the ($0kk$) row of the reciprocal lattice on a glass fiber attached to a goniometer head. The crystal was placed on a Picker automated four-circle diffractometer and 14 medium-intensity reflections at a variety of 2θ values were accurately centered using Zr-filtered Mo

(1) A. V. Ablov, N. I. Belichuk, and M. S. Pereligina, *Russ. J. Inorg. Chem.*, 17, 534 (1972).

(2) J. A. Bertrand, J. H. Smith, and P. G. Eller, *J. Chem. Soc., Chem. Commun.*, 95 (1974).

(3) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Wiley-Interscience, New York, N. Y., 1960, p 403.

(4) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965.

$K\alpha$ radiation (λ 0.7093 Å). The setting angles from these reflections were used to refine cell parameters by a least-squares procedure; the cell parameters obtained are[5] $a = 7.868$ (2) Å, $b = 14.040$ (7) Å, $c = 11.401$ (5) Å, and $\beta = 112.73$ (4)°. With the assumption of 4 formula units per unit cell, the calculated density, 1.85 g cm^{-3}, agrees with the density measured, 1.83 (2) g cm^{-3}, by the flotation method in a carbon tetrachloride-1,3-diiodopropane mixture. The intensities were measured with a scintillation counter mounted 26.5 cm from the crystal and a source-crystal distance of 21.0 cm; the intensities were collected by the θ-2θ scan technique with a takeoff angle of 1.9° and a scan rate of 1° min^{-1}. A symmetrical scan of 2.0° was taken about the calculated position for each reflection out to a maximum 2θ angle of 50° (λ 0.70926 Å). Stationary-background counts of 20 sec were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data. The threshold point was set so that the counting rate would not exceed 10,000 counts/sec. The pulse height analyzer was set for approximately a 90% window centered on the Mo $K\alpha$ peak. Three axial reflections (400, 060, 004) and a null reflection (090) were monitored after every 150 reflections as a check on crystal and instrument stability. An isotropic linear decrease of 8% in the intensities of standards was observed during data collection and appropriate corrections were applied. A total of 2076 unique reflections were collected in a full quadrant of reciprocal space with $2\theta \leqslant 50°$. Corrected intensities (CI) were obtained by subtracting 3 times the actual measured background from the total integrated peak count (CT)

$$\mathrm{CI} = \mathrm{CT} - 3(\mathrm{bgd1} + \mathrm{bgd2})$$

The factor of 3 in the calculation arises from the peak scan time's being 3 times as long as the background counting time. The corrected intensities were assigned standard deviations according to the formula[6]

$$\sigma(I) = [\mathrm{CT} + 0.25(t_\mathrm{c}/t_\mathrm{b})^2(\mathrm{bgd1} + \mathrm{bgd2} + 9.0) + (pI)^2 + 4.5]^{1/2}$$

where t_c is the scan time, t_b is the counting time of each background (either bgd1 or bgd2), and the scalar quantities 4.5 and 9.0 account for truncation of the last counting digit by the Picker scalar. A total of 1579 reflections were accepted as statistically above background on the basis that $\sigma(I)/\mathrm{CI}$ be less than 0.333 with p set at 0.03. Lorentz and polarization corrections were applied in the usual way.

Solution and Refinement of the Structure. Computations were carried out on the Univac 1108 computer. Programs employed include Carter's cell parameter and diffractometer setting angle program, Zalkin's FORDAP Fourier summation program, Ibers' NUCLS modification of the Busing-Martin-Levy ORFLS full-matrix least-squares program, the Martin-Busing-Levy ORFFE function and error program, Johnson's ORTEP plotting program, Stewart's ABSORB absorption correction program from the X-ray 72 system, and various locally written programs. In the structure factor calculations, the scattering factors were taken from Cromer and Waber's tabulation[7] for all atoms except hydrogen; Stewart's hydrogen atom scattering factors were used.[8] The scattering factors for copper and chlorine were corrected for the real and imaginary anomalous dispersion components, using the dispersion factors tabulated by Cromer.[9] The agreement factors are defined in the usual way as $R = (\Sigma \| F_\mathrm{o} | - | F_\mathrm{c} \|)/(\Sigma |F_\mathrm{o}|)$ and $R_\mathrm{w} = [\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2/\Sigma w(|F_\mathrm{o}|)^2]^{1/2}$. In all least-squares refinements, the quantity minimized was $\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2$. Atomic coordinates for copper and chlorine, two oxygen atoms, and one nitrogen atom were deduced from a three-dimensional Patterson synthesis and refined to give the initial residuals, $R = 0.288$ and $R_\mathrm{w} = 0.340$. The remaining oxygen, nitrogen, and carbon atoms were located by means of subsequent difference Fourier syntheses and least-squares refinements. Using a weighting scheme based on the variances ($w = 4I/\sigma(I)^2$) and employing isotropic temperature factors for all nonhydrogen atoms, a refinement reduced R to 0.109 and R_w to 0.139. When anisotropic temperature factors were refined for all nonhydrogen atoms, $R = 0.090$ and $R_\mathrm{w} = 0.092$. The 12 principal faces of the crystal were identified as follows (distance from center of crystal to the face in mm given in parentheses): $\{100\}$ (0.16), $\{010\}$ (0.20), $\{001\}$ (0.23), $\{\bar{1}11\}$ (0.15), $\{11\bar{1}\}$ (0.12), $\{011\}$ (0.29). Absorption corrections were calculated by the gaussian quadrature method; corrections on F^2 ranged between 1.50 and 2.01. Refinement with the absorption-corrected data set, after deletion of several reflections having erroneous scans due to instrumental malfunctions, reduced R to 0.068 and R_w to 0.074. All hydrogen atoms were located on a difference Fourier synthesis and their coordinates were refined with temperature factors fixed at the isotropic value of the corresponding carbon or oxygen atom from the cycle before conversion to anisotropic. Two hydrogen atoms, H1C5 and H1C1, failed to refine properly and were fixed in calculated positions (C-H = 0.95 Å, H-C-H = 109.5°). The final refinements reduced R to 0.057 and R_w to 0.056. In the last cycle, the error in an observation of unit weight was 1.1 and the maximum parameter shifts were 0.56σ(y coordinate for H3C4) and 0.39σ(y coordinate for C4). The only features greater than 0.50 e/Å^3 on a final difference Fourier map were a few small bumps of magnitude 0.52-0.84 e/Å^3 in the vicinity of the perchlorate group; a typical height for the perchlorate oxygens which were refined in this structure was about 4.5 e/Å^3.

Final atomic parameters are listed in Table I; final observed and calculated structure factor amplitudes are available.[10] Selected interatomic distances and angles are tabulated in Table II and selected least-squares planes are summarized in Table III. The molecular unit and the molecular packing are illustrated in Figures 1 and 2.

Description of the Structure

The four formula units of $\mathrm{CuL(ClO_4)(H_2O)}$ in the unit cell form dimeric units about inversion centers at the origin and at (0, $^1/_2$, $^1/_2$); the dimeric unit is illustrated in Figure 1. Within the formula unit, the ligand L is coordinated to the copper to form (1) a five-membered chelate ring involving the alcohol oxygen and the imine nitrogen and (2) a five-membered chelate ring involving the imine and oxime nitrogens. The fourth position in the coordination plane of the copper is occupied by the oxime oxygen of the second ligand of the dimer, resulting in bridging oxime groups; these four donor atoms are nearly coplanar, the maximum deviation from the plane being 0.003 Å, and the copper is 0.074 Å from the plane. The bond distances and angles about copper, Table II, are typical for complexes with five-membered chelate rings.[11-13] As is often true with copper(II) complexes, there are additional groups in axial positions; in this case there is a weakly bound water molecule (Cu-O3 = 2.492 (6) Å) and an even more weakly bound perchlorate group (Cu-O4 = 2.89 (2) Å) completing the tetragonal coordination. The copper is slightly displaced from the basal plane toward the water molecule.

Charge-balance considerations dictate that one proton has been lost from the ligand, LH, in forming the complex. Although either the alcohol or oxime proton could be ionized, we feel that the oxime hydrogen has been ionized for the following reasons: (1) the oxime hydrogen should be more acidic than the alcohol proton, (2) the anionic portion of the ligand might be anticipated in the bridging moiety and the oxime does function in the bridge with appropriate geometry, (3) the region in the electron density map near the oxime group is quite flat whereas a good peak was located at a reasonable distance and direction from the alcohol oxygen atom, and (4) the alcohol hydrogen so located was successfully refined.

The most unusual feature of this structure is the bridging arrangement. A six-membered centrosymmetric ring is

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(5) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(6) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973).

(7) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(9) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(10) See paragraph at end of paper regarding supplementary material.

(11) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 4, 203 (1970).

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

(13) D. Y. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 11, 1958 (1972).

Table I. Individual Positional and Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{11}	β_{23}
Cu	−0.1206 (1)	−0.0048 (1)	0.1048 (1)	0.0117 (1)	0.0036 (1)	0.0058 (1)	0.0017 (1)	0.0038 (1)	0.0012 (1)
Cl	0.2471 (2)	0.1455 (1)	0.3483 (1)	0.0148 (3)	0.0050 (1)	0.0080 (1)	−0.0006 (1)	0.0055 (2)	−0.0013 (1)
O1	0.1824 (6)	−0.0803 (3)	0.0315 (4)	0.0158 (8)	0.0045 (2)	0.0078 (4)	0.0028 (3)	0.0063 (5)	0.0024 (2)
O2	−0.3195 (7)	0.0528 (4)	0.1563 (5)	0.0169 (10)	0.0059 (3)	0.0087 (5)	0.0031 (4)	0.0057 (6)	0.0017 (3)
O3	0.3385 (8)	0.1255 (4)	0.0333 (5)	0.0197 (11)	0.0050 (3)	0.0081 (5)	0.0018 (4)	0.0037 (6)	0.0010 (3)
O4	0.1770 (16)	0.1289 (9)	0.2190 (8)	0.0643 (36)	0.0168 (9)	0.0142 (9)	0.0015 (15)	0.0133 (15)	0.0020 (8)
O5	0.1010 (14)	0.1760 (7)	0.3775 (11)	0.0485 (26)	0.0159 (8)	0.0288 (15)	0.0114 (12)	0.0280 (17)	0.0068 (9)
O6	0.3158 (13)	0.0577 (6)	0.4046 (10)	0.0488 (27)	0.0089 (5)	0.0266 (14)	0.0087 (10)	0.0113 (15)	0.0049 (7)
O7	0.3847 (16)	0.2117 (9)	0.3864 (16)	0.0473 (30)	0.0143 (8)	0.0482 (27)	−0.0151 (14)	0.0173 (23)	−0.0083 (13)
C1	0.3194 (9)	−0.2027 (4)	0.2338 (7)	0.0156 (12)	0.0040 (3)	0.0087 (6)	0.0029 (5)	0.0042 (7)	0.0026 (4)
C2	0.1604 (7)	−0.1351 (3)	0.2089 (5)	0.0097 (9)	0.0025 (2)	0.0049 (4)	0.0002 (4)	0.0019 (5)	0.0004 (3)
C3	0.0603 (8)	−0.1296 (4)	0.2955 (5)	0.0125 (11)	0.0037 (3)	0.0061 (5)	−0.0007 (5)	0.0020 (6)	0.0006 (3)
C4	0.1303 (12)	−0.1818 (6)	0.4170 (7)	0.0229 (16)	0.0066 (4)	0.0073 (7)	0.0026 (8)	0.0064 (9)	0.0027 (4)
C5	−0.1909 (12)	−0.0502 (7)	0.3293 (7)	0.0245 (17)	0.0095 (6)	0.0076 (7)	0.0057 (8)	0.0087 (9)	0.0031 (5)
C6	−0.3642 (11)	−0.0076 (7)	0.2411 (8)	0.0234 (16)	0.0085 (5)	0.0118 (8)	0.0050 (9)	0.0111 (10)	0.0030 (6)
N1	0.0984 (6)	−0.0789 (3)	0.1123 (4)	0.0095 (8)	0.0029 (2)	0.0055 (4)	−0.0001 (3)	0.0028 (5)	0.0004 (2)
N2	−0.0771 (7)	−0.0751 (4)	0.2589 (5)	0.0143 (10)	0.0050 (3)	0.0059 (4)	0.0010 (4)	0.0048 (5)	0.0008 (3)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H1C1	0.270	−0.260	0.220	3.5	H2C4	0.256 (12)	−0.149 (5)	0.467 (7)	4.1
H2C2	0.362 (10)	−0.209 (5)	0.164 (7)	3.5	H3C4	0.155 (12)	0.232 (6)	0.403 (8)	4.1
H3C1	0.428 (10)	−0.193 (5)	0.328 (7)	3.5	H1C5	−0.204	−0.101	0.378	4.5
H1O2	−0.388 (11)	0.069 (8)	0.116 (8)	3.2	H2C5	−0.138 (11)	0.014 (5)	0.390 (8)	4.5
H1O3	0.345 (12)	−0.165 (6)	−0.005 (9)	3.6	H1C6	−0.477 (11)	−0.077 (6)	0.176 (8)	4.6
H2O3	−0.301 (12)	−0.133 (6)	−0.077 (8)	3.6	H2C6	−0.447 (12)	0.029 (5)	0.275 (8)	4.6
H1C4	0.048 (11)	−0.169 (5)	0.481 (7)	4.1					

[a] The form of the anisotropic thermal ellipsoids is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$.

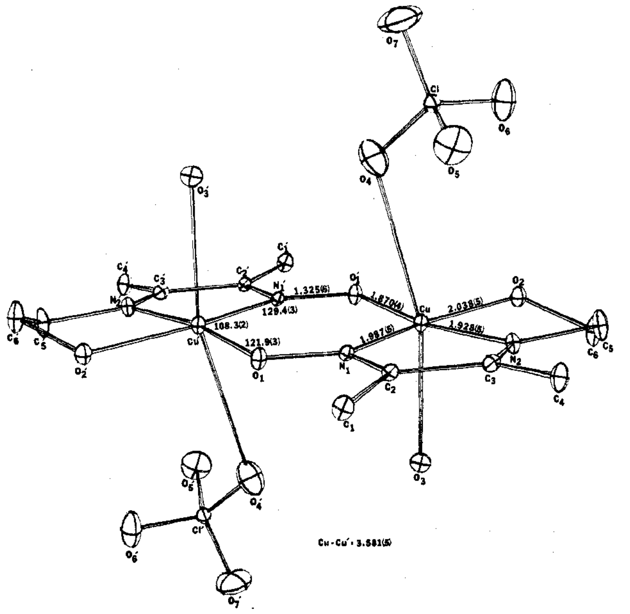

Figure 1. Molecular structure of the dimer $[CuL(ClO_4)(H_2O)]_2$.

formed by two copper atoms and two oxime (NO) groups. Although not required by symmetry, all six atoms of the ring lie very close to the least-squares plane through the six atoms, the maximum deviations being for the nitrogen atoms (0.029 Å). The Cu-O1 (1.870 (4) Å) and Cu-N1 (1.987 (5) Å) distances indicate a strongly coordinated bridging oxime group and the Cu-O1′-N1′ (121.9 (3)°) and Cu-N1-O1 (129.4 (3)°) angles indicate essentially sp^2 hybridization for the oxime atoms.

A water molecule occupies an axial position although its distance from the copper (Cu-O3 = 2.492 (6) Å) indicates weak coordination; the O3-Cu-basal donor angles range from 90.8 (2) to 93.7 (2)°. The perchlorate group appears to be ordered and occupies the sixth octahedral position. The geometries at oxygen (Cu-O4-Cl = 120.8 (7)°) and at copper (O4-Cu-basal donor angles range from 77.4 (3) to 101.1 (3)°) suggest a definite interaction despite the length (2.89 (1) Å) of the Cu-O4 vector. The Cl-O stretching frequency is split into symmetric components at 1065 and 1132 cm^{-1}, a splitting that is normal for monodentate perchlorate coordination.[14]

The six-atom 2-imino-3-oximobutane fragment of L adopts a configuration which is almost planar (maximum deviation from the least-squares plane is 0.15 Å for N1). The C2-C3 distance of 1.484 (8) Å and the C2-N1 and C3-N2 distances of 1.289 (7) and 1.257 (7) Å, respectively, agree well with the corresponding distances in dimethylglyoxime structures[15,16] and indicate the absence of cyclic delocalization.

The ethanolimine portion of L adopts a twist configuration similar to that found in many ethylenediamine chelate rings.[17] Thus, C5 and C6 lie 0.114 and 0.425 Å, respectively, above and below the least-squares plane through the eight donor atoms from the two ligands of the dimer. No unusual inter- or intramolecular contacts, other than those noted above, were observed.

Discussion

The structure determination for $CuL(ClO_4)(H_2O)$ has revealed dimeric units with oxime bridges and a nearly planar $Cu_2O_2N_2$ ring. This type of bridge was postulated by Uhlig and Schneider[18] to explain the magnetic properties of a similar compound, CuL″(ClO$_4$) (where L″ represents the anion of 2-(2-ethylpyridine)imino-3-oximobutane). A structure determination for bis(dimethylglyoximato)copper(II), Cu(Hdmg)$_2$, also revealed a dimeric structure with oxime bridges,[15] but the six-membered $Cu_2O_2N_2$ ring in that structure was distinctly nonplanar with a chair conformation and relatively long (2.30 Å) Cu-O(oxime) distances.

In addition to the structural difference, the present compound and bis(dimethylglyoximato)copper(II) show marked-

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(14) J. Lewis and D. Hodgson, *Inorg. Chem.*, **13**, 143 (1974).

(15) A. Vaciago and L. Zamibonelli, *J. Chem. Soc. A*, 218 (1970).

(16) R. J. Olcott and R. M. Holm, *Inorg. Chim. Acta*, **3**, 431 (1969).

(17) J. K. Beattie, *Accounts Chem. Res.*, **4**, 253 (1971).

(18) E. Uhlig and D. Schneider, *Z. Anorg. Allg. Chem.*, **333**, 90 (1964).

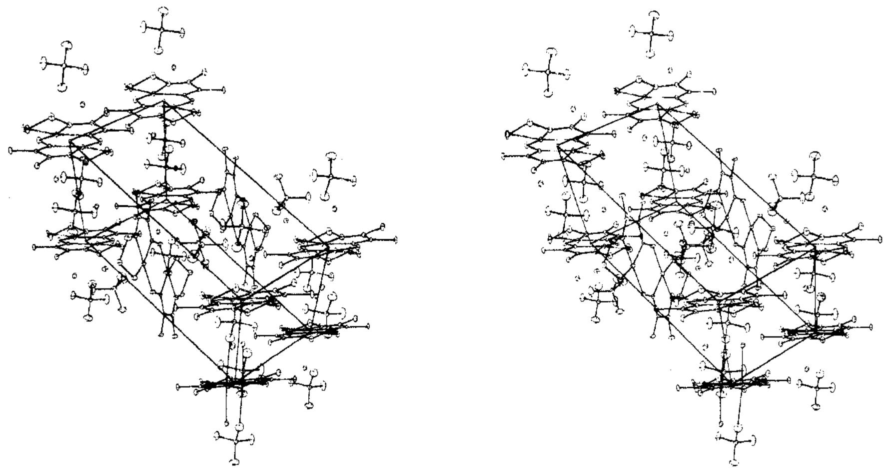


Figure 2. Crystal packing for the dimeric compound $[CuL(ClO_4)(H_2O)]_2$.

Table II. Selected Interatomic Distances (Å) and Angles (deg)[a]

	Distances		
Cu-Cu′	3.581 (3)	Cl-O5	1.381 (8)
Cu-O1′	1.870 (4)	Cl-O6	1.399 (8)
Cu-O2	2.038 (5)	Cl-O7	1.365 (9)
Cu-O3	2.492 (6)	C1-H1C1	0.88 (1)
Cu-O4	2.890 (12)	C1-H2C1	0.98 (8)
Cu-N1	1.987 (5)	C1-H3C1	1.10 (7)
Cu-N2	1.928 (5)	C4-H1C4	1.16 (9)
C1-C2	1.508 (8)	C4-H2C4	1.05 (8)
C2-C3	1.484 (8)	C4-H3C4	0.77 (9)
C3-C4	1.474 (9)	C5-H1C5	0.93 (1)
C5-C6	1.474 (11)	C5-H2C5	1.11 (8)
C2-N1	1.289 (7)	C6-H1C6	1.24 (8)
C3-N2	1.257 (7)	C6-H2C6	1.02 (9)
C5-N2	1.456 (9)	O2-H1O2	0.60 (8)
C6-O2	1.428 (10)	O3-H1O3	0.65 (9)
N1-O1	1.325 (6)	O3-H2O3	0.68 (9)
Cl-O4	1.381 (9)		
	Angles		
N1-Cu-O1′	108.3 (2)	Cl-O4-Cu	120.8 (7)
N1-Cu-N2	81.1 (2)	C2-C1-H1C1	105 (4)
N2-Cu-O2	80.0 (2)	C2-C1-H2Cl	115 (4)
O2-Cu-O1′	90.2 (2)	C2-C1-H3C1	113 (4)
Cu-N1-O1	129.4 (3)	H1C1-C1-H2C1	92 (4)
N1-O1-Cu′	121.9 (3)	H2C1-C1-H3C1	115 (6)
Cu′-Cu-O3	90.9 (2)	H1C1-C1-H3C1	114 (4)
Cu′-Cu-O4	74.4 (2)	C3-C4-H1C4	114 (4)
Cu-N1-C2	117.3 (4)	C3-C4-H2C4	103 (4)
N1-C2-C3	114.4 (5)	C3-C4-H3C4	107 (6)
C3-N2-Cu	116.2 (4)	H1C4-C4-H2C4	103 (6)
Cu-N2-C5	116.6 (4)	H2C4-C4-H3C4	105 (8)
N2-C5-C6	109.0 (6)	H1C4-C4-H3C4	122 (8)
C5-C6-O2	107.4 (6)	N2-C5-H1C5	112 (5)
C6-O2-Cu	112.1 (4)	N2-C5-H2C5	112 (5)
C1-C2-N1	124.1 (5)	C6-C5-H1C5	115 (5)
C2-C3-C4	119.8 (5)	C6-C5-H2C5	97 (4)
C1-C2-C3	121.5 (5)	H1C5-C5-H2C5	111 (4)
N2-C3-C4	125.3 (6)	C5-C6-H1C6	103 (4)
C3-N2-C5	126.5 (5)	C5-C6-H2C6	120 (5)
O1-N1-C2	117.3 (4)	O2-C6-H1C6	106 (4)
O4-Cl-O5	106.4 (7)	O2-C6-H2C6	109 (5)
O4-Cl-O6	105.3 (7)	H1C6-C6-H2C6	111 (6)
O5-Cl-O7	113.3 (9)	C6-O2-H1O2	111 (9)
O5-Cl-O6	111.9 (6)	H1O3-O3-H2O3	112 (11)
O5-Cl-O7	110.2 (8)	H1O3-O3-Cu	115 (8)
O6-Cl-O7	109.6 (8)	H2O3-O3-Cu	101 (7)

[a] Primed atoms are related by the inversion center at the origin to the atoms listed in Table I.

Table III. Least-Squares Planes within the $[CuL(ClO_4)(H_2O)]_2$ Molecule[a,b]

Atom	Dev, Å	Atom	Dev, Å
(a) Plane of the Four Atoms Strongly Coordinated to Copper			
Equation: $0.44452x + 0.69685y + 0.56285z - 0.02125 = 0$			
O1′	0.001	N1	−0.003
O2	−0.002	N2	0.003
(b) Plane of the Eight Donor Atoms from the L Groups of the Dimer			
Equation: $-0.45001x - 0.69736y - 0.55783z = 0$			
O1	0.018	O1′	0.018
O2	0.006	O2′	0.006
N1	−0.013	N1′	0.013
N2	−0.000	N2′	0.000
Cu	0.066	Cu′	−0.066
C1	−0.056	C1′	0.056
C2	−0.058	C2′	0.058
C3	−0.095	C3′	0.095
C4	−0.305	C4′	0.305
C5	−0.114	C5′	0.114
C6	0.425	C6′	−0.425
(c) Plane of the Six-Membered Ring Containing Two Copper Atoms			
Equation: $-0.43401x - 0.69429y - 0.57411z = 0$			
Cu	0.025	Cu′	−0.025
N1	0.032	N1′	−0.032
O1	−0.030	O1′	0.030
(d) Plane of the Iminooximobutane Fragment			
Equation: $0.44952x + 0.76925y + 0.45408z + 0.33861 = 0$			
C1	−0.066	N1	0.150
C2	0.032	N2	−0.019
C3	−0.019	O1	0.154
C4	0.005	Cu	0.205

[a] Direction cosines of the plane refer to the orthogonal axis system *a, b, c**. [b] All atoms weighted at unity.

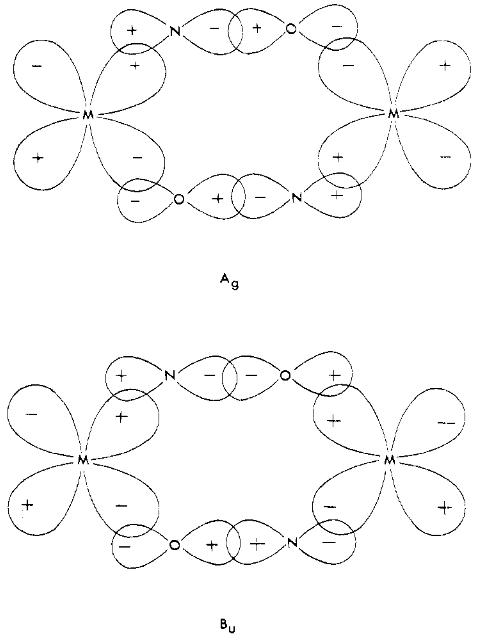
ly different magnetic properties and this difference is interesting in terms of arguments concerning the mechanism of exchange coupling. For $[Cu(Hdmg)_2]_2$, the magnetic moment is essentially constant from 298°K (1.79 BM) to 77°K (1.76 BM), indicative of normal paramagnetic behavior. The magnetic susceptibility of $[CuL(ClO_4)(H_2O)]_2$ is extremely low over this temperature range (64×10^{-6}, 54×10^{-6}, and 28×10^{-6} at 77, 192, and 298°K, respectively) and is of the magnitude of the temperature-independent paramagnetism normally assumed for copper(II); the variation at the different temperatures is probably due to experimental error in measuring the small weight changes involved in the measurements. Similar values were found for $CuL'(ClO_4)(H_2O)$ and these values indicate complete electron pairing even at room temperature for these compounds.

The fact that the copper-copper distance (3.02 Å) in the normal-moment compound, $[Cu(Hdmg)_2]_2$, is considerably shorter than that in the strongly coupled compound, $[CuL(ClO_4)(H_2O)]_2$ (3.581 (3) Å), offers further support for the generally accepted view[19] that direct metal-metal exchange is insignificant in comparison to superexchange through the bridging atoms in such compounds. Recent studies[20-22] of several compounds with polyatomic bridges show significant coupling over even longer distances (5-6 Å) and offer further evidence of indirect coupling.

There has been considerable discussion of possible mechanisms of superexchange and both σ and π pathways have been suggested. For one of the polyatomic-bridged compounds mentioned above, exchange through O-H-O bridges almost certainly occurs by a σ pathway since hydrogen has no orbitals that are appropriate for π bonding. In addition, recent correlations[23] between the angle at oxygen for dimeric copper-hydroxide complexes with both planar and bent four-membered rings provides evidence for a σ pathway. In $[Cu(Hdmg)_2]_2$, the conformation of the six-membered ring would eliminate the possibility of a π system and would require the nitrogen σ orbital to overlap with the half-filled copper d_{xy} orbital (or $d_{x^2-y^2}$ orbital, depending on orientation of axes) and the oxygen σ orbital to overlap with the filled copper d_{z^2} orbital; ferromagnetic coupling would be expected. In $[CuL(ClO_4)(H_2O)]_2$, the planar six-membered ring would provide a π pathway but the overlap of oxygen and nitrogen σ orbitals with the half-filled copper d_{xy} orbital would also provide a σ pathway.

The type of explanation suggested previously[12] for exchange coupling by a π mechanism in four-membered ring compounds can be applied equally well to six-membered ring compounds. The explanation relates the magnitude of the antiferromagnetic coupling constant to the deviation of the ring angle at copper from 90°; in the four-membered ring compounds, this angle was considerably less than 90° and in the planar six-membered ring compound this angle (108.3 (2)°) is considerably greater than 90°. The explanation requires a π-type molecular orbital, involving d_{xz} or d_{yz} orbitals, to be raised above the σ-type molecular orbital which involves the d_{xy} orbital and there is no evidence for this type or reordering. Furthermore, that approach does not explain the fact that there is stronger coupling in the six-membered ring compound.

A similar molecular orbital treatment can be used to explain the coupling through a σ mechanism. Since the symmetry of the ring is approximately C_{2h}, the pair of half-filled copper d_{xy} orbitals interacts with different combinations of ligand orbitals (A_g antibonding and B_u bonding ligand orbitals), Figure 3. The resulting molecular orbitals will have different energies and the electrons can be paired in the lower orbital to give a singlet ground state. A similar treatment is possible for the case of a four-membered ring compound but in that case similar ligand orbitals are involved and the energy separation depends on the angle at oxygen.



A_g

B_u

Figure 3. B_u and A_g symmetry molecular orbitals.

It is interesting that the room-temperature magnetic moment of $CuL''(ClO_4)$, 1.04 BM, is intermediate to those of $[Cu(Hdmg)_2]_2$ and $[CuL(ClO_4)(H_2O)]_2$. Although a dimeric structure with bridging oxime groups as was postulated is probably correct, there must be some interesting structural difference to account for the difference in magnetic properties; crystals of $CuL''(ClO_4)$ are presently being investigated.

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Registry No. $[CuL(ClO_4)(H_2O)]_2$, 51293-02-8; $[CuL'(ClO_4)(H_2O)]_2$, 51293-03-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1649.

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(19) A. P. Ginsberg, *Inorg. Chim. Acta, Rev.*, **5**, 45 (1971).

(20) J. A. Bertrand and F. T. Helm, *J. Amer. Chem. Soc.*, **95**, 8184 (1973).

(21) D. M. Duggan and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 411 (1973).

(22) A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, 11, 2884 (1972).

(23) K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 9, 423 (1973).