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Copper(II) Complexes with Bridging Oxime Groups. 1. Structures and Magnetic Properties of Complexes with Imine Oximes of 2,3-Butanedione as Ligands[1]

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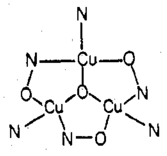
Structures have been determined by single-crystal x-ray diffraction studies for copper(II) complexes of the anions of 2-[2-(α-pyridyl)ethyl]imino-3-butanone oxime (represented by L2py in formulas) and 2-(2-aminoethyl)imino-3-butanone oxime (represented by L2am in formulas). For the first compound, $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$, the structure consists of perchlorate anions and dinuclear cations. The cation occupies a site of twofold symmetry and contains a six-membered ring formed by two copper atoms and two oxime (NO) groups; the ring is distinctly nonplanar with a twisted-boat conformation. The square-pyramidal coordination of each copper atom consists of the three nitrogen atoms of one ligand and the oxime oxygen of the second ligand of the cation in the basal plane and the acetonitrile nitrogen atom in the axial position. Crystal data are as follows: space group *Pbcn*; $Z = 8$ formula units (monomeric); $a = 23.015$ (5), $b = 8.873$ (1), and $c = 16.414$ (6) Å; $\rho_{calcd} = 1.62$ and $\rho_{obsd} = 1.62$ (2) g cm^{-3}; $R = 0.046$ and $R_w = 0.045$ for 2389 reflections with $I \geq 3\sigma(I)$. For the second compound, $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$, the structure contains centrosymmetric tetranuclear cations and perchlorate anions. The asymmetric unit contains two copper atoms bridged by oxime groups to form a six-membered ring similar to that in $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$. The square-pyramidal coordination of the copper atoms is also similar to that in $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$ except for the axial position; for one copper atom of the asymmetric unit the axial position is occupied by a perchlorate oxygen and for the remaining copper atom this position is occupied by the oxime oxygen of a symmetry-related unit to form a four-membered Cu_2O_2 ring about an inversion center. Crystal data are as follows: space group $P\bar{1}$; $Z = 4$ formula units (monomeric); $a = 11.576$ (2), $b = 10.238$ (2), and $c = 12.838$ (3) Å; $\alpha = 123.26$ (2), $\beta = 98.84$ (1), and $\gamma = 126.31$ (1)°; $\rho_{calcd} = 1.80$ and $\rho_{obsd} = 1.82$ (2) g cm^{-3}; $R = 0.038$ and $R_w = 0.040$ for 3387 reflections with $I \geq 3\sigma(I)$. The magnetic properties of both compounds indicate antiferromagnetic coupling which is ascribed to superexchange via a σ pathway through the NO bridges.

Introduction

As part of a general study of polynuclear complexes of first-row transition metal ions, we became interested in the possibility of oxime groups serving as bridging ligands. In complexes, the nitrogen atom of an oxime group is usually coordinated to a metal ion; bridging would be expected to occur through coordination of one or more additional metal ions to the oxygen atom. There are, however, few reported examples[2-7] of structures of first-row transition metal compounds with bridging oxime groups. Most of the known examples[2-6] contain pairs of metal ions bridged by two oxime groups into a six-membered ring and examples with planar,[5,6] chair,[2,3] and boat[4] conformations of the six-membered ring are known. For copper(II) compounds, where the presence of an unpaired electron on each metal ion can give rise to magnetic coupling, there is one example of each of these ring conformations.

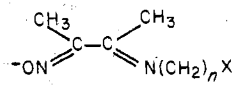
In the compound with the chair conformation,[2,3] each copper(II) ion shows square-pyramidal coordination with the bridging oxygen occupying the axial position. The compound with the chair conformation, tetrakis(*N*,*N'*-dimethylglyoximato)dicopper(II), has been shown to have a triplet ground state with the singlet excited state 29.8 cm^{-1} higher in energy.[8] In the compound with the boat conformation,[4] each copper(II) ion shows trigonal-bipyramidal coordination with the bridging oxygen in an equatorial position. The room-temperature magnetic moments of both compounds are normal values for one unpaired electron per metal ion. The coordination of each copper(II) ion in the compound with a planar ring[6] is square pyramidal but the oxime oxygen occupies a basal position and a perchlorate oxygen occupies the axial position; the compound exhibits strong antiferromagnetic coupling.

The only other report[7] of an oxime-bridged structure for copper(II) is a trinuclear complex of 2-pyridinecarboxaldoxime which contains a planar unit, I, with a μ_3-sulfate group below the plane. The coordination about each copper(II) is square-pyramidal with a sulfate oxygen in the axial position. The magnetic moment of the compound is reasonable for one unpaired electron per trimer and is indicative of strong antiferromagnetic coupling.



I

Several other copper(II) complexes with oxime ligands have been reported[9-11] and several of these have magnetic moments below the spin-only value but not as low as that observed for the planar-ring dimer; in order to correlate the structures and magnetic properties of oxime-bridged complexes of copper(II) we have investigated several complexes with imine–oxime ligands of general formula II (abbreviated LnX in formulas),



II

and in this paper, we report the structures and magnetic properties of the complexes of 2-[2-(α-pyridyl)ethyl]imino-3-butanone oxime and 2-(2-aminoethyl)imino-3-butanone oxime, both of which show antiferromagnetic coupling.

Experimental Section

Preparation of [2-[2-(α-pyridyl)ethyl]imino-3-butanone oximato]copper(II) Perchlorate, $Cu(L2py)ClO_4$. The method of Uhlig and Schneider[9] was used, the crystals were filtered and dried. Anal. Calcd for $Cu(C_{11}H_{14}N_3O)ClO_4$: C, 35.97; H, 3.84; N, 11.44; Cl, 9.65. Found: C, 35.92; H, 4.18; N, 11.18; Cl, 9.80.

Solvated crystals were obtained by recrystallizing the compound from various solvents (methanol, ethanol, water, acetonitrile); due to rapid loss of solvent at room temperature, no analyses were obtained.

Preparation of Perchlorato[2-(2-aminoethyl)imino-3-butanone oximato]copper(II), $Cu(L2am)ClO_4$. A solution of 50 mmol of cupric perchlorate hexahydrate in 50 mL of methanol was added to a mixture of 50 mmol of diacetyl monoxime and 50 mmol of ethylenediamine in 50 mL of methanol. The resulting solution was heated to boiling and filtered while hot. Slow evaporation of the cooled filtrate yielded green-black prisms which were recrystallized from methanol. Anal. Calcd for $Cu(C_6H_{12}N_3O)ClO_4$: C, 23.61; H, 3.96; N, 13.77. Found: C, 24.03; H, 4.04; N, 13.86.

Magnetic Studies. The Faraday method was used to determine the magnetic susceptibility of both compounds at various temperatures, using $HgCo(NCS)_4$ as a calibrant. Diamagnetic corrections were obtained from tabulated values.[12] For $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$, μ_{eff} values of 0.66, 0.33, and 0.10 μ_B/g-atom of copper were obtained at 298, 195, and 93 K, respectively; for $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$, μ_{eff} values of 1.38, 1.09, and 0.34 μ_B/g-atom of copper were obtained at 298, 195, and 93 K, respectively.

Crystallographic Data Collection. $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$. A blue-black crystal with approximate dimensions 0.4 × 0.8 × 0.2 mm was coated with epoxy cement and mounted on a glass fiber using epoxy cement such that the longest crystal dimension (*b* axis) was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) using Mo Kα radiation at a takeoff angle of 6.5°. Fifteen reflections whose 2θ values ranged from 10.00 to 25.00° were machine-centered and an autoindexing procedure was used to select axes. Axial photographs indicated that the crystal belonged to the orthorhombic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities were examined carefully for systematic absences. The absence of $k = 2n + 1$ for $0kl$ reflections, $l = 2n + 1$ for $h0l$ reflections, and $h + k = 2n + 1$ for $hk0$ reflections is consistent with only space group *Pbcn* (No. 60[13]). Unit cell parameters, obtained from the 15 reflections by least-squares refinement, are $a = 23.015$ (5) Å, $b = 8.873$ (1) Å, $c = 16.414$ (6) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, and $V = 3351$ (2) Å^3. The calculated density of 1.62 g cm^{-3} for 8 formula units per unit cell agrees with the experimental density of 1.62 g cm^{-3} measured by the flotation method using a mixture of CCl_4 and 1,2-dibromo-1,1-dichloroethane. ω scans of several reflections with low 2θ angles gave peak widths at half-height of less than 0.24°, indicating a satisfactory mosaic spread for the crystal.

Intensity data were collected using θ–2θ scans with x-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate from 3.5 to 29.3° min^{-1} was used and a scan width of 2.0° was sufficient to collect all of the peak intensity. Stationary-background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with the total background time equal to scan time. No significant fluctuations were observed in the intensities of three standard reflections (−5,5,0; −3,2,1; −8,0,−2) monitored every 100 reflections. Intensities were calculated by subtracting background counts from total scan counts (CT)

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

The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [\mathrm{CT} + (\mathrm{bgd1} + \mathrm{bgd2})]^{1/2}$$

From a total of 3498 reflections collected in a complete octant (*h*, *k*, and *l* positive) of data out to $2\theta = 50.0°$, 2389 were accepted as statistically above background on the basis that *I* was greater than $3\sigma(I)$. Lorentz and polarization corrections were made but no corrections were made for absorption ($\mu = 15.4$ cm^{-1}).

$[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$. A dark green crystal with approximate dimensions 0.2 × 0.3 × 0.7 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension (*a* axis) was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer as described above.

Unit cell parameters obtained are $a = 11.576$ (2) Å, $b = 10.238$ (2) Å, $c = 12.838$ (3) Å, $\alpha = 123.26$ (2)°, $\beta = 98.84$ (1)°, $\gamma = 126.31$ (1)°, and $V = 1109.0$ (4) Å^3. Triclinic space group $P\bar{1}$ was assumed and the successful refinement of the structure has confirmed this choice. The calculated density of 1.80 g cm^{-3} for 4 formula units per unit cell agrees with the experimental density of 1.82 g cm^{-3} measured by the flotation method using a mixture of carbon tetrachloride and 1,2-dibromo-1,1-dichloroethane. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.27°, indicating a satisfactory mosaic spread for the crystal.

Intensity data were collected using θ–2θ scans with x-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate from 7.30 to 29.30° min^{-1} was used and a scan width of 2.00° was sufficient to collect all of the peak intensity. Stationary-background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with the total background time equal to scan time. No significant fluctuations were observed in the intensities of one standard reflection (−2,0,3) monitored every 100 reflections. Intensities and standard deviations were calculated as described above. From a total of 4140 reflections collected in a complete hemisphere ($\pm h$, $\pm k$, $+l$) of data out to $2\theta = 50°$, 3387 were accepted as statistically above background on the basis that *I* was greater than $3\sigma(I)$. Lorentz and polarization corrections were made.

The 14 crystal faces were identified by optical means as the following (perpendicular distance in millimeters from the crystal center to the faces are given in parentheses): $\{010\}$ (0.185), $\{001\}$ (0.255), $\{\bar{1}11\}$ (0.379), $\{\bar{1}01\}$ (0.404), $\{\bar{1}1\bar{1}\}$ (0.535), $\{100\}$ (0.574), $\{\bar{2}10\}$ (0.663). Absorption corrections were calculated by the Gaussian quadrature methods; corrections to F^2 ranged from 1.44 to 1.80.

Solution and Refinement of Structures. All computations were carried out on a CDC Cyber 70/74 computer. Programs used include Zalkin's FORDAP Fourier summation program, Ibers' NUCLS5 modification of the Busing–Martin–Levy ORFLS full-matrix least-squares program, the Busing–Martin–Levy ORFFE function and error program, Johnson's ORTEP and ORTEPII plotting programs, Stewart's ABSORB absorption correction program from the x-ray 72 system, the software package for the Syntex $P2_1$ diffractometer, and various locally written programs.

In structure factor calculations, the scattering factors for all atoms except hydrogen were taken from Cromer and Waber's tabulation;[14] Stewart's hydrogen atom scattering factors were used.[15] The scattering factors of the copper and chlorine atoms were corrected for the real and imaginary anomalous dispersion components using the dispersion factors tabulated by Cromer.[16] The agreement factors are defined in the usual way as

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(|F_o|)^2]^{1/2}$$

$[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$. The positions of the copper atoms were deduced from a three-dimensional Patterson synthesis and refined by least-squares methods; the resulting electron density map was used to locate the positions of eight other sets of nonhydrogen atoms which were then refined to give $R = 0.34$. After the location of 22 nonhydrogen atoms, *R* dropped to 0.17. Anisotropic refinement of these atoms lowered *R* to 0.08. Subsequent location of the disordered perchlorate oxygen atoms and eight hydrogen atoms gave $R = 0.046$ and $R_w = 0.045$.

The maximum shift in the final least-squares cycle was 3.1 standard deviations for the β_{33} temperature factor of O8 of the disordered perchlorate group. The highest remaining electron density was located in the vicinity of the perchlorate group at about 25% of the value of refined positions.

Final positional and thermal parameters are listed in Table I; a table of calculated and observed structure amplitudes may be obtained. [See paragraph at end of paper for supplementary material.] Selected interatomic distances and angles are tabulated in Table II;selected least-squares planes are summarized in Table III. The dimeric molecular unit is illustrated in Figure 1.

$[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$. Two independent sets of copper atoms and two independent sets of chlorine atoms were located in the three-dimensional Patterson synthesis; after least-squares refinement, a structure factor calculation gave $R = 0.34$. Location and refinement of all 32 nonhydrogen atoms from electron density maps gave $R = 0.12$. Anisotropic refinement of thermal parameters for all nonhydrogen atoms and refinement of isotropic thermal parameters for all hydrogen atoms gave final values of $R = 0.038$ and $R_w = 0.040$.

The greatest shift in the final refinement was 3.2 standard deviations for one of the positional parameters of a methyl hydrogen atom. Residual electron density was located largely in the vicinity of the perchlorate groups.

Final atomic positions and thermal parameters appear in Table IV, selected interatomic distances and angles are presented in Table V, and selected least-squares planes are summarized in Table VI. An illustration of the tetrameric unit with the atomic numbering scheme appears in Figure 2, and Figure 3 is a stereoview of the unit. A table

Table I. Final Positional and Thermal Parameters[a] for $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.079 50 (2)	0.084 87 (5)	0.234 95 (2)	0.001 28 (1)	0.011 41 (6)	0.002 66 (2)	0.000 15 (2)	0.000 07 (1)	−0.000 32 (3)
Cl	0.366 64 (5)	0.014 07 (13)	0.089 59 (7)	0.002 37 (3)	0.016 82 (18)	0.005 04 (5)	0.001 35 (6)	0.000 26 (3)	−0.001 47 (8)
O1	0.039 7 (1)	0.167 9 (3)	0.328 0 (1)	0.001 4 (1)	0.015 7 (4)	0.003 2 (1)	−0.000 3 (1)	0.000 2 (1)	−0.002 1 (2)
N1	0.014 8 (1)	0.128 2 (3)	0.155 8 (2)	0.001 5 (1)	0.009 2 (4)	0.002 9 (1)	−0.000 2 (1)	0.000 1 (1)	0.000 3 (2)
N2	0.121 8 (1)	0.057 3 (3)	0.130 6 (2)	0.001 6 (1)	0.010 3 (4)	0.003 2 (1)	0.000 1 (1)	0.000 3 (1)	−0.000 8 (2)
N3	0.157 2 (1)	0.112 1 (3)	0.297 4 (2)	0.001 5 (1)	0.010 4 (4)	0.003 5 (1)	−0.000 2 (1)	−0.000 2 (1)	0.000 6 (2)
C1	−0.004 8 (2)	0.217 3 (5)	0.016 3 (2)	0.002 0 (1)	0.018 2 (7)	0.003 2 (2)	0.000 0 (2)	−0.000 2 (1)	0.001 5 (3)
C2	0.032 6 (2)	0.148 3 (4)	0.082 0 (2)	0.001 7 (1)	0.008 9 (4)	0.002 7 (1)	−0.000 7 (1)	0.000 1 (1)	0.000 1 (2)
C3	0.093 9 (2)	0.100 8 (4)	0.068 3 (2)	0.002 0 (1)	0.008 1 (4)	0.003 1 (1)	−0.000 3 (1)	0.000 4 (1)	−0.000 6 (2)
C4	0.117 0 (2)	0.105 5 (7)	−0.017 4 (3)	0.002 2 (1)	0.019 8 (8)	0.003 9 (2)	−0.000 0 (2)	0.000 9 (1)	0.000 3 (3)
C5	0.182 7 (2)	0.005 9 (6)	0.123 7 (3)	0.001 7 (1)	0.015 5 (6)	0.004 4 (2)	0.000 6 (2)	0.000 6 (1)	0.000 1 (3)
C6	0.202 4 (2)	−0.067 0 (5)	0.203 1 (3)	0.001 6 (1)	0.012 8 (6)	0.005 1 (2)	0.001 0 (2)	0.000 3 (1)	0.000 3 (3)
C7	0.205 6 (1)	0.038 7 (4)	0.272 7 (3)	0.001 4 (1)	0.010 7 (5)	0.004 7 (2)	0.000 0 (1)	−0.000 1 (1)	0.001 6 (2)
C8	0.257 9 (2)	0.062 0 (5)	0.313 4 (3)	0.001 5 (1)	0.015 6 (7)	0.007 0 (2)	0.000 4 (2)	−0.000 8 (1)	0.001 2 (3)
C9	0.260 5 (2)	0.154 0 (6)	0.379 9 (3)	0.001 9 (1)	0.020 4 (8)	0.007 1 (3)	0.000 8 (2)	−0.001 4 (1)	0.001 0 (4)
C10	0.210 7 (2)	0.228 9 (5)	0.405 1 (3)	0.002 3 (1)	0.014 6 (6)	0.005 2 (2)	−0.001 7 (2)	−0.000 9 (1)	0.000 8 (3)
C11	0.160 2 (2)	0.205 0 (4)	0.360 8 (2)	0.001 8 (1)	0.011 2 (5)	0.004 0 (2)	−0.001 0 (2)	−0.000 3 (1)	0.000 5 (2)
NCN	0.068 7 (1)	−0.164 2 (4)	0.275 4 (2)	0.002 2 (1)	0.012 4 (5)	0.004 7 (2)	−0.000 4 (1)	−0.000 0 (1)	0.000 5 (2)
C12	0.064 2 (2)	−0.284 4 (5)	0.297 8 (2)	0.001 9 (1)	0.014 0 (6)	0.003 4 (1)	0.000 2 (2)	−0.000 2 (1)	−0.000 1 (3)
C13	0.057 6 (3)	−0.440 1 (5)	0.326 2 (3)	0.004 1 (1)	0.012 0 (7)	0.005 5 (2)	−0.000 1 (3)	−0.000 4 (1)	0.002 1 (3)
O2	0.328 0 (4)	0.125 0 (10)	0.106 2 (6)	0.005 (1)	0.020 (1)	0.010 (1)	0.006 (1)	0.002 (1)	0.000 (1)
O3	0.413 2 (7)	−0.003 2 (29)	0.131 0 (10)	0.005 (1)	0.117 (7)	0.011 (1)	0.013 (1)	−0.005 (1)	−0.019 (2)
O4	0.381 4 (5)	−0.002 8 (12)	0.007 2 (5)	0.004 (1)	0.037 (2)	0.006 (1)	0.000 (1)	0.001 (1)	−0.007 (1)
O5	0.321 2 (6)	−0.103 8 (14)	0.083 9 (11)	0.005 (1)	0.032 (2)	0.020 (1)	−0.002 (1)	0.006 (1)	−0.005 (1)
O6	0.366 0 (5)	−0.076 3 (12)	0.162 9 (6)	0.005 (1)	0.028 (2)	0.008 (1)	0.003 (1)	0.001 (1)	0.004 (1)
O7	0.370 0 (11)	0.168 7 (11)	0.097 2 (9)	0.015 (1)	0.017 (2)	0.014 (1)	−0.001 (1)	0.004 (1)	−0.005 (1)
O8	0.419 7 (7)	−0.023 5 (17)	0.063 7 (17)	0.005 (1)	0.036 (3)	0.030 (2)	0.004 (1)	0.009 (1)	0.008 (2)
O9	0.331 3 (14)	−0.045 2 (39)	0.045 2 (17)	0.012 (1)	0.113 (13)	0.021 (2)	0.005 (3)	0.011 (1)	−0.008 (5)

Atom	x	y	z	Atom	x	y	z
H5A	0.207 (2)	0.086 (5)	0.106 (3)	H9	0.295 (2)	0.155 (5)	0.413 (2)
H5B	0.191 (2)	−0.067 (5)	0.079 (3)	H10	0.211 (2)	0.287 (5)	0.461 (3)
H6A	0.239 (2)	−0.123 (5)	0.204 (3)	H11	0.126 (2)	0.250 (5)	0.378 (3)
H6B	0.180 (2)	0.145 (5)	0.221 (3)	H4A	0.109 (2)	0.204 (6)	−0.039 (3)
H8	0.288 (2)	0.006 (5)	0.296 (3)	H4B	0.148 (2)	0.089 (5)	−0.023 (3)

[a] For the hydrogen atoms $B_{iso} = 5.0$ Å^2.

Table II. Selected Interatomic Distances and Angles for $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$[a]

	Distances, Å		
Cu-Cu′	3.693 (2)	C12-N4	1.132 (5)
Cu-O1′	1.928 (2)	C1-C2	1.509 (5)
Cu-N1	2.014 (3)	C2-C3	1.489 (5)
Cu-N2	1.986 (3)	C3-C4	1.505 (5)
Cu-N3	2.075 (3)	C5-C6	1.525 (6)
Cu-N4	2.322 (4)	C6-C7	1.480 (6)
N1-O′	1.329 (4)	C7-C8	1.393 (5)
C2-N1	1.292 (4)	C8-C9	1.365 (7)
C3-N2	1.268 (5)	C9-C10	1.387 (7)
C7-N3	1.352 (5)	C10-C11	1.387 (6)
C11-N3	1.330 (5)	C12-C13	1.466 (6)
Cl-O2	1.35 (1)	Cl-O6	1.45 (1)
Cl-O3	1.28 (1)	Cl-O7	1.38 (1)
Cl-O4	1.40 (1)	Cl-O8	1.33 (1)
Cl-O5	1.48 (1)	Cl-O9	1.21 (1)
	Angles, Deg		
O1-Cu-N1	95.0 (1)	C3-N2-Cu	114.2 (2)
N1-Cu-N2	80.2 (1)	C3-N2-C5	120.9 (3)
N2-Cu-N3	91.0 (1)	C5-N2-Cu	124.7 (2)
N3-Cu-O1	88.5 (1)	N2-C5-C6	110.3 (3)
N4-Cu-O1	94.9 (1)	C5-C6-C7	114.6 (4)
N4-Cu-N1	106.7 (1)	C6-C7-C8	120.5 (4)
N4-Cu-N2	100.5 (1)	C6-C7-N3	119.7 (3)
N4-Cu-N3	93.6 (1)	N3-C7-C8	119.0 (4)
N1′-O1′-Cu	120.3 (2)	C1-C8-C9	120.7 (4)
Cu-N1-O1	128.4 (2)	C8-C9-C10	119.3 (4)
Cu-N1-C2	113.3 (2)	C9-C10-C11	117.5 (4)
O1-N1-C2	116.7 (3)	C10-C11-N2	123.3 (4)
N1-C2-C1	123.0 (3)	C11-N3-Cu	120.3 (3)
N1-C2-C3	113.8 (3)	C11-N3-C7	119.3 (3)
C1-C2-C3	123.2 (3)	C7-N3-Cu	120.4 (2)
C2-C3-C4	117.9 (3)	C12-N4-Cu	177.6 (3)
C2-C3-N2	116.4 (3)	C13-C12-N4	179.2 (4)
N2-C3-C4	125.6 (4)		
O2-Cl-O3	122.0 (9)	O6-Cl-O7	118.5 (8)
O2-Cl-O4	115.6 (7)	O6-Cl-O8	97.7 (10)
O2-Cl-O5	93.6 (7)	O6-Cl-O9	104.7 (17)
O3-Cl-O4	107.2 (9)	O7-Cl-O8	121.6 (18)
O3-Cl-O5	122.7 (15)	O7-Cl-O9	103.0 (12)
O4-Cl-O5	92.0 (7)	O8-Cl-O9	108.3 (19)

[a] Primed atoms are related by rotation about the twofold axis at 0, y, $^1/_4$ to atoms listed in Table I.

Table III. Least-Squares Planes within the Molecule $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$

Atom	Dev, Å	Atom	Dev, Å
(a) Plane Involving Four Atoms Strongly Coordinated to Copper			
Equation: $-0.17820x - 0.96690y + 0.18259z + 0.66089 = 0$			
O1	0.041	N3	−0.054
N1	−0.033	Cu	0.311
N2	0.061		
(b) Plane Involving the Six-Atom Iminobutanone Oxime Fragment of L2py			
Equation: $0.32505x + 0.92379y + 0.20237z - 1.74549 = 0$			
N1	−0.065	C3	0.003
N2	0.069	C4	−0.060
C1	0.057	Cu	0.255
C2	−0.015		

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

of calculated and observed structure amplitudes may be obtained. [See paragraph at end of paper for supplementary material.]

Descriptions of Structures

$[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$. The eight formula units of $Cu(L2py)(ClO_4)\cdot CH_3CN$ in the unit cell form dimeric units on twofold axes with centers at (0, y, $^1/_4$), (0, $\bar{y}$, $^3/_4$), ($^1/_2$, $^1/_2 + y$, $^1/_4$), and ($^1/_2$, $^1/_2 - y$, $^3/_4$), where y = 0.08487. Within the formula unit, the ligand is coordinated to the copper atom to form (1) a five-membered chelate ring involving the oxime nitrogen and the imine nitrogen and (2) a six-membered chelate ring involving the imine nitrogen and the pyridine nitrogen. The fourth position in the coordination plane of each copper is occupied by the oxygen of the second ligand of the dimer, resulting in bridging oxime groups. The fifth coordination position of the square pyramid about copper is occupied by the weakly bound acetonitrile nitrogen at 2.322 (4) Å from the copper atom. The copper atom is 0.31 Å above the least-squares plane of the basal coordinating atoms toward the axial ligand.

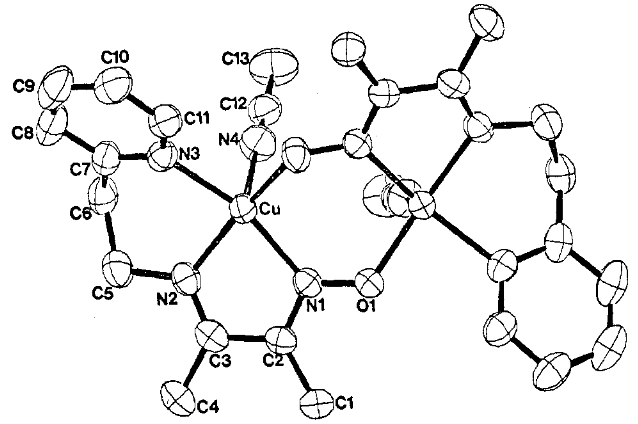


Figure 1. Dimeric molecular unit of $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$ omitting the perchlorate groups.

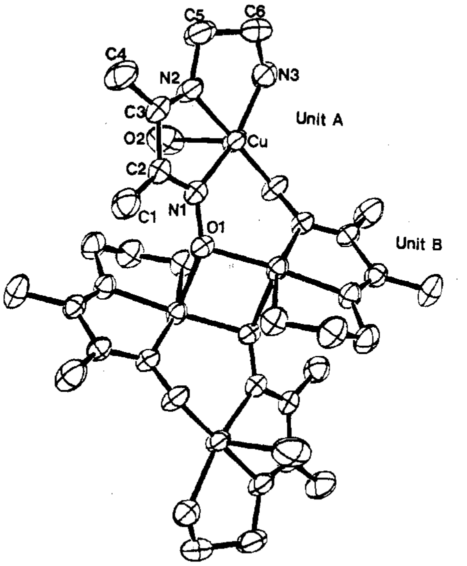


Figure 2. Tetrameric molecular unit of $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$ omitting the perchlorate groups.

The basal planes of the two units of the dimer have a dihedral angle of 32° and give a twisted-boat conformation to the six-membered ring. The Cu–O1 (1.928 (2) Å) and Cu–N1 (2.014 (3) Å) distances are not as short as in the planar ring of $Cu(L2al)(ClO_4)\cdot H_2O$ (L2al represents II with X = OH) but nonetheless indicate strongly coordinated bridging oxime groups. The Cu–O1–N1′ angle, where the primed quantities indicate atoms related by the twofold axis, is 120.3 (2)°; and the Cu–N1–O1′ angle is 128.4 (2)°. These angles indicate essentially sp^2 hybridization for the oxime atoms.

The six-atom 2-imino-3-butanone oxime fragment of (L2py) adopts a configuration which is almost planar, the maximum deviation from the least-squares plane being 0.07 Å for N1. The C2–C3 distance of 1.489 (5) Å and the C2–N1 and C3–N2 distances of 1.292 (4) and 1.268 (5) Å, respectively,

Table IV. Final Atomic Positional and Thermal Parameters for $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$ (for the hydrogen atom $B_{iso} = 5.0$ Å²)

Unit A

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.313 16 (5)	0.029 93 (6)	0.180 46 (3)	0.010 94 (7)	0.012 09 (8)	0.004 17 (3)	0.007 36 (7)	0.000 28 (4)	0.001 58 (4)
Cl	0.206 4 (2)	-0.093 4 (1)	0.423 (1)	0.022 7 (2)	0.017 4 (2)	0.005 5 (1)	0.014 3 (2)	0.004 1 (1)	0.004 6 (1)
O1	0.162 6 (3)	0.162 0 (3)	0.091 5 (2)	0.010 4 (4)	0.014 2 (5)	0.004 3 (2)	0.008 1 (4)	0.001 4 (2)	0.002 5 (2)
N1	0.277 8 (3)	0.196 8 (4)	0.171 5 (2)	0.009 3 (4)	0.012 4 (5)	0.004 2 (2)	0.006 4 (4)	0.002 0 (2)	0.002 8 (3)
N2	0.493 8 (4)	0.245 4 (4)	0.310 5 (2)	0.011 6 (5)	0.015 0 (6)	0.004 3 (2)	0.007 6 (5)	0.000 1 (3)	0.001 9 (3)
N3	0.413 5 (5)	-0.068 3 (5)	0.220 3 (3)	0.016 8 (6)	0.019 7 (7)	0.005 9 (3)	0.013 3 (6)	0.002 2 (3)	0.003 4 (4)
C1	0.378 2 (6)	0.500 2 (6)	0.256 1 (4)	0.014 8 (7)	0.013 8 (8)	0.006 4 (3)	0.008 6 (6)	0.001 4 (4)	0.001 7 (4)
C2	0.380 0 (4)	0.355 4 (5)	0.250 9 (3)	0.010 3 (5)	0.012 5 (7)	0.004 1 (2)	0.006 8 (5)	0.002 2 (3)	0.002 4 (3)
C3	0.507 8 (4)	0.381 5 (5)	0.329 8 (3)	0.010 8 (5)	0.013 2 (7)	0.003 9 (2)	0.006 1 (5)	0.001 8 (3)	0.002 5 (3)
C4	0.643 1 (6)	0.550 7 (6)	0.420 7 (4)	0.013 8 (7)	0.014 7 (8)	0.0075 (4)	0.006 7 (6)	-0.001 2 (4)	0.000 6 (4)
C5	0.603 6 (6)	0.231 9 (7)	0.368 7 (4)	0.014 7 (7)	0.021 1 (10)	0.006 2 (3)	0.011 2 (8)	-0.000 8 (4)	0.002 4 (5)
C6	0.578 8 (6)	0.080 7 (7)	0.282 9 (4)	0.015 6 (7)	0.026 9 (11)	0.007 6 (4)	0.015 5 (8)	0.001 4 (4)	0.005 3 (5)
O2	0.176 8 (5)	-0.064 3 (6)	0.322 3 (3)	0.026 (1)	0.045 (1)	0.012 (1)	0.027 (1)	0.011 (1)	0.019 (1)
O3	0.286 6 (5)	-0.158 5 (5)	0.411 7 (3)	0.026 (1)	0.030 (1)	0.011 (1)	0.021 (1)	0.006 (1)	0.010 (1)
O4	0.061 6 (5)	-0.225 8 (6)	0.429 8 (4)	0.031 (1)	0.033 (1)	0.013 (1)	0.021 (1)	0.013 (1)	0.013 (1)
O5	0.296 0 (8)	0.063 9 (6)	0.523 1 (4)	0.051 (1)	0.025 (1)	0.013 (1)	0.023 (1)	0.004 (1)	-0.001 (1)

Atom	x	y	z	Atom	x	y	z
H1C1	0.3571 (6)	0.523 (7)	0.317 (4)	H1C5	0.708 (6)	0.342 (7)	0.398 (4)
H2C1	0.462 (6)	0.604 (7)	0.286 (4)	H2C5	0.581 (6)	0.216 (7)	0.434 (4)
H3C1	0.305 (6)	0.458 (7)	0.195 (5)	H1C6	0.633 (6)	0.043 (7)	0.308 (4)
H1C4	0.679 (6)	0.537 (7)	0.486 (4)	H2C6	0.614 (6)	0.100 (7)	0.225 (4)
H2C4	0.627 (6)	0.629 (7)	0.430 (4)	H1N3	0.368 (6)	-0.129 (7)	0.260 (4)
H3C4	0.728 (6)	0.588 (7)	0.412 (4)	H2N3	0.389 (6)	-0.149 (7)	0.163 (4)

Unit B

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.120 05 (5)	0.028 22 (5)	-0.063 84 (3)	0.010 95 (7)	0.011 31 (8)	0.003 95 (3)	0.007 15 (6)	0.002 33 (3)	0.002 96 (4)
Cl	-0.461 68 (12)	0.307 53 (13)	0.031 60 (9)	0.013 2 (2)	0.013 6 (2)	0.008 7 (1)	0.007 5 (1)	0.005 4 (1)	0.004 8 (1)
O1	0.133 8 (3)	-0.184 2 (3)	0.057 2 (2)	0.013 8 (4)	0.012 3 (5)	0.004 0 (2)	0.007 3 (4)	0.000 3 (2)	0.002 5 (2)
N1	0.110 0 (3)	-0.164 9 (4)	-0.042 2 (2)	0.009 4 (4)	0.010 6 (5)	0.004 1 (2)	0.005 7 (4)	0.001 2 (2)	0.002 6 (3)
N2	0.058 3 (4)	-0.116 2 (4)	-0.222 5 (2)	0.012 2 (5)	0.014 3 (6)	0.004 3 (2)	0.008 6 (5)	0.003 0 (3)	0.003 7 (3)
N3	0.128 1 (4)	0.192 5 (4)	-0.130 5 (3)	0.013 5 (5)	0.012 6 (6)	0.006 1 (2)	0.007 7 (5)	0.003 5 (3)	0.004 5 (3)
C1	0.019 9 (7)	-0.461 2 (6)	-0.140 1 (4)	0.023 2 (9)	0.013 2 (8)	0.006 1 (3)	0.011 7 (7)	0.000 1 (4)	0.001 9 (4)
C2	0.056 8 (4)	-0.294 3 (5)	-0.136 4 (3)	0.008 7 (5)	0.011 0 (6)	0.004 6 (2)	0.005 3 (5)	0.001 5 (3)	0.002 5 (3)
C3	0.033 9 (4)	-0.259 5 (5)	-0.240 7 (3)	0.008 6 (5)	0.012 0 (6)	0.004 5 (2)	0.005 7 (5)	0.001 7 (3)	0.002 2 (3)
C4	-0.016 3 (6)	-0.390 9 (6)	-0.355 9 (3)	0.020 6 (8)	0.016 0 (8)	0.004 5 (3)	0.011 1 (7)	0.003 0 (4)	0.002 3 (4)
C5	0.040 5 (6)	-0.048 1 (6)	-0.306 8 (3)	0.018 5 (7)	0.020 3 (9)	0.004 7 (3)	0.013 6 (7)	0.004 5 (4)	0.005 8 (4)
C6	0.145 7 (6)	0.150 5 (6)	-0.242 4 (4)	0.015 9 (7)	0.017 6 (8)	0.006 5 (3)	0.009 9 (7)	0.004 5 (4)	0.006 5 (4)
O2	-0.353 1 (4)	0.366 9 (5)	-0.031 7 (3)	0.020 (1)	0.028 (1)	0.010 (1)	0.015 (1)	0.009 (1)	0.007 (1)
O3	-0.395 5 (9)	0.443 0 (6)	0.127 5 (6)	0.064 (2)	0.019 (1)	0.026 (1)	0.005 (1)	0.034 (1)	0.002 (1)
O4	-0.485 7 (12)	0.169 1 (11)	0.053 5 (7)	0.094 (3)	0.063 (2)	0.033 (1)	0.066 (3)	0.040 (2)	0.036 (1)
O5	-0.591 5 (7)	0.244 2 (16)	-0.032 6 (8)	0.019 (1)	0.126 (5)	0.039 (1)	0.031 (2)	0.015 (1)	0.048 (2)

Atom	x	y	z	Atom	x	y	z
H1C1	0.058 (6)	-0.511 (7)	-0.201 (4)	H1C5	0.072 (5)	-0.078 (7)	-0.366 (4)
H2C1	-0.072 (6)	-0.551 (7)	-0.173 (4)	H2C5	-0.072 (6)	-0.103 (7)	-0.336 (4)
H3C1	0.077 (6)	-0.438 (7)	-0.076 (4)	H1C6	0.115 (6)	0.203 (7)	-0.282 (4)
H1C4	-0.155 (6)	-0.513 (7)	-0.373 (4)	H2C6	0.248 (6)	0.200 (7)	-0.224 (4)
H2C4	-0.022 (6)	-0.368 (7)	-0.409 (4)	H1N3	0.046 (6)	0.185 (7)	-0.138 (4)
H3C4	0.042 (6)	-0.434 (7)	-0.356 (4)	H2N3	0.214 (6)	0.314 (7)	-0.077 (4)

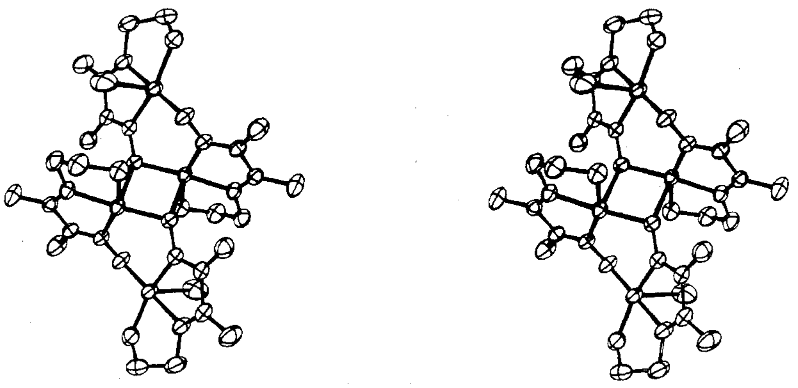


Figure 3. Stereoview of the tetrameric unit $[Cu_4(L2am)_4(ClO_4)_2]$. (Only the coordinated oxygen of the perchlorate group is shown.)

Table V. Selected Interatomic Distances (Å) and Angles (deg) in $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$

Distances			Angles		
Atoms	Unit A	Unit B	Atoms	Unit A	Unit B
Cu-O1′[a]	1.905 (3)	1.935 (3)	N1-Cu-N2	79.9 (1)	80.1 (1)
Cu-N1	2.001 (3)	1.997 (3)	N2-Cu-N3	83.3 (2)	84.0 (1)
Cu-N2	1.950 (3)	1.940 (3)	N3-Cu-O1′	96.1 (2)	95.6 (1)
Cu-N3	2.015 (3)	2.017 (3)	N1-Cu-O1′	100.9 (1)	100.6 (1)
O1-N1	1.345 (4)	1.347 (4)	Cu-N1-O1	127.1 (2)	127.2 (2)
C2-N1	1.292 (5)	1.291 (5)	Cu-O1′-N1′	112.9 (2)	113.4 (2)
C3-N2	1.261 (5)	1.271 (5)	O1-N1-C2	117.8 (3)	117.4 (3)
C5-N2	1.470 (5)	1.467 (5)	N1-C2-C1	112.9 (3)	112.9 (3)
C6-N3	1.463 (6)	1.484 (5)	N1-C2-C3	123.3 (3)	123.5 (3)
C1-C2	1.481 (6)	1.482 (6)	C1-C2-C3	123.6 (3)	123.6 (3)
C2-C3	1.494 (5)	1.487 (5)	C2-C3-C4	120.3 (4)	119.5 (3)
C3-C4	1.495 (6)	1.494 (5)	C2-C3-N2	115.2 (3)	115.2 (3)
C5-C6	1.512 (7)	1.513 (6)	C4-C3-N2	124.4 (4)	125.3 (3)
Cl-O2	1.422 (3)	1.430 (3)	C3-N2-C5	127.8 (3)	128.3 (3)
Cl-O3	1.328 (5)	1.434 (4)	N2-C5-C6	106.9 (3)	106.2 (3)
Cl-O4	1.341 (6)	1.435 (4)	C5-C6-N3	109.9 (4)	109.7 (3)
Cl-O5	1.350 (6)	1.407 (5)	C2-N1-Cu	115.1 (2)	114.8 (2)
C1-HC1A	0.88 (5)	1.12 (5)	C3-N2-Cu	116.8 (3)	116.5 (2)
C1-HC1B	0.84 (5)	0.82 (5)	C5-N2-Cu	115.2 (3)	115.2 (3)
C1-HC1C	0.85 (5)	0.85 (5)	C6-N3-Cu	107.8 (3)	106.7 (3)
C4-HC4A	1.02 (5)	1.00 (5)	N1′-O1′CuI[b]		88.8 (1)
C4-HC4B	0.82 (5)	1.01 (5)	O1′-Cu-O1′I		86.9 (1)
C4-HC4C	0.88 (5)	0.78 (5)	N1-Cu-O1′I		87.0 (1)
C5-HC5A	0.96 (5)	0.96 (5)	N2-Cu-O1′I		88.2 (1)
C5-HC5B	0.93 (5)	1.01 (5)	N3-Cu-O1′I		96.5 (1)
C6-HC6A	0.96 (5)	1.00 (5)	O1′-Cu-O2	118.8 (1)	
C6-HC6B	0.91 (5)	0.93 (5)	N1-Cu-O2	95.6 (1)	
N3-HN3A	0.86 (5)	0.90 (5)	N2-Cu-O2	88.5 (2)	
N3-HN3B	0.82 (5)	0.97 (5)	N3-Cu-O2	88.6 (1)	
			O2-Cl-O3	108.1 (2)	109.6 (3)
CuA-CuB	3.550 (2)		O2-Cl-O4	108.7 (2)	116.2 (4)
CuB-CuBI	3.268 (2)		O2-Cl-O5	111.3 (3)	108.7 (4)
CuA-O2A	2.574 (4)		O3-Cl-O4	108.8 (3)	108.0 (7)
CuB-O1′I	2.530 (4)		O3-Cl-O5	109.8 (3)	111.4 (5)
			O4-Cl-O5	110.1 (3)	102.5 (6)

[a] Prime indicates atoms in the adjacent unit of the asymmetric dimer. [b] I indicates atoms related by the center of inversion in the tetramer.

Table VI. Least-Squares Planes within the Molecule $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$[a, b]

Atom	Dev, Å	Atom	Dev, Å
(a) Plane Involving Four Atoms Strongly Coordianted to CuA			
Equation: $-0.64055x - 0.49684y + 0.58553z + 0.71778 = 0$			
O1B	0.312	C5A	−0.291
N1A	0.252	C6A	−0.893
N2A	−0.033	CuA	0.110
N3A	−0.231		
(b) Plane Involving Four Atoms Strongly Coordinated to CuB			
Equation: $0.86337x + 0.50331y + 0.03576z - 1.30712 = 0$			
O1A	−0.071	C5B	−0.136
N1B	0.068	C6B	0.551
N2B	−0.082	CuB	0.011
N3B	0.068		
(c) Plane Involving Six-Atom Iminobutanone Oxime Fragment of (L2am)A			
Equation: $-0.55848x - 0.49978y + 0.66206z + 0.17078 = 0$			
C1A	0.003	N1A	0.002
C2A	0.045	N2A	0.006
C3A	0.015	CuA	−0.011
C4A	−0.046		
(d) Plane Involving Six-Atom Iminobutanone Oxime Fragment of (L2am)B			
Equation: $0.89649x + 0.44296y + 0.00911z - 1.42991 = 0$			
C1B	−0.039	N1B	0.011
C2B	0.037	N2B	−0.041
C3B	0.008	CuB	−0.069
C4B	0.020		

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

agree well with the corresponding distances in dimethyglyoxime structures[3] and indicate the absence of cyclic delocalization. These segments are folded down away from the axial nitrile groups in the molecule.

The perchlorate ions are disordered and were refined with two sets of oxygen positions, each with multipliers of 0.5. No unusual inter- or intramolecular contacts other than those noted above were observed.

$[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$. The four formula units of $Cu(L2am)ClO_4$ in the unit cell can be thought of as two asymmetric dimers joined together to form a centrosymmetric tetramer, Figure 2, about the origin. The two independent copper atoms (unit A and unit B in Figure 2) have similar square-pyramidal coordination arrangements. A ligand L2am is coordinated to each copper to form (1) a five-membered chelate ring involving the oxime nitrogen and the imine nitrogen and (2) a five-membered chelate ring involving the imine nitrogen and the amine nitrogen. The fourth position in the base of the square pyramid is occupied by the oxygen of the second ligand of the asymmetric unit, resulting in bridging oxime groups; the six-membered ring formed by the bridging oxime groups is in a twisted-boat conformation. The fifth coordination site of each copper atom is occupied by an oxygen atom but the nature of these oxygens is different. In unit A the axial atom is an oxygen atom of a perchlorate group and in unit B the axial atom is an oxime oxygen from the symmetry-related dimer, forming a planar (symmetry required) four-membered Cu_2O_2 ring.

The copper atom of unit B is only 0.01 Å out of the least-squares plane of the four basal coordinating atoms and the axial–copper–basal angles show only small distortions from 90° (86.9–96.5°). The copper atom of unit A is 0.11 Å out of the basal plane toward the axial oxygen and the axial–copper–basal angles vary from 88.5 to 118.8°. The axial copper–oxygen distances of 2.530 (4) Å for the bridging oxygen and 2.574 (4) Å for the perchlorate oxygen indicate weak interactions in the same range as the copper–oxygen (water) axial interaction in $Cu(L2al)(ClO_4)\cdot H_2O$. The bridging oxygen–copper–basal angles range from 86.9 (1) to 96.5 (1)° and the perchlorate oxygen–copper–basal angles range from 88.5 (2) to 111.8 (1)°.

Unlike $[Cu(L2py)(CH_3CN)]_2^{2+}$, there is no symmetry imposed on the six-membered $Cu_2N_2O_2$ ring; however, a comparison of the two ring systems, and the basal coordination planes of the copper atoms in each dimer, reveals a close structural similarity. The two basal planes are twisted to form a twisted-boat conformation as in $[Cu(L2py)CH_3CN]_2^{2+}$, but only the angles at the nitrogen atom are comparable for the two complexes. CuA–O1B (1.905 (3) Å), CuB–O1A (1.935 (3) Å), CuA–N1A (2.001 (3) Å), and CuB–N1B (1.997 (3) Å) are not as short as in the planar ring of $Cu(L2al)(ClO_4)(H_2O)$ but, like $Cu(L2py)(ClO_4)\cdot CH_3CN$, they indicate a strongly coordinated bridging group. The CuA–O1B–N1B (112.9 (2)°) and CuB–O1A–N1A (113.4 (2)°) angles are less than the 120° observed in the previous structure and indicate a variation from sp^2 hybridization for the oxime oxygen atom resulting from coordination to the second copper atom. The CuA–N1A–O1A (127.1 (2)°), and CuB–N1B–O1B (127.2 (2)°) angles indicate sp^2 hybridization of nitrogen as expected.

The six-atom 2-imino-3-butanone oxime fragment of (L2am) on each copper atom adopts a nearly planar configuration (the maximum deviation from the best plane in unit A of the asymmetric dimer is 0.04 Å for C2, and in unit B, 0.04 Å for N2). The C2–C3 distances of 1.494 (5) and 1.487 (5) Å, the C2–N1 distances of 1.292 (5) and 1.291 (5) Å, and the C3–N2 distances of 1.261 (5) and 1.271 (5) Å, for unit A and unit B, respectively, agree well with the corresponding distances in dimethylglyoxime structures[3] and indicate the absence of cyclic delocalization.

The perchlorate anion which is not coordinated appears to be associated with N3A by hydrogen bonding to O2B. The O2B–N3A distance is 3.041 (6) Å and H1N3B–O2B is 2.228 (5) Å. Further evidence is the comparison of the lengths of the principal axes of the thermal ellipsoids. The averages of the first and second principal axes of O3B, O4B, and O5B are 18% and 17% higher than the same axes of O2B; however, the average length of the third principal axis of O3B, O4B, and O5B was 2.24 times the length of the third principal axis of O2B. ORTEP plots show that the O3B, O4B, and O5B atoms appear to be vibrating around the ClB–O2B axis.

Results and Discussion

Although the two structures differ in the degree of association, dimer vs. tetramer, they are similar in the coordination about copper (square pyramidal) and the conformation of the six-membered $Cu_2N_2O_2$ ring. The main difference in the dimeric portion of each structure is the direction of bending of the basal planes from a planar conformation; in $Cu(L2py)(CH_3CN)(ClO_4)$ the bending causes the axial groups to move together while in $Cu(L2am)ClO_4$ the bending causes the axial groups to move apart, Figure 3. In both cases, the six-membered ring includes only basal donor atoms in contrast to the axial–basal arrangement in dimeric $Cu(dmgH)_2$.

In the case of $Cu(L2py)(CH_3CN)ClO_4$, the antiferromagnetic coupling must result from superexchange via a σ pathway since the copper–copper distance (3.693 (2) Å) is sufficient to rule out direct interaction and the nonplanar six-membered ring rules out superexchange via a π pathway. The exchange pathway would involve $d_{x^2-y^2}$ orbitals on the two copper atoms and the σ_N and σ_O orbitals of the oxime groups as suggested for the planar system $Cu(L2al)(ClO_4)H_2O$; the symmetric and antisymmetric linear combinations would have different energies and the coupling would be antiferromagnetic. On the other hand, the axial–basal arrangement in $[Cu(dmgH)_2]_2$ would involve a pathway[2] $d_{x^2-y^2}|\sigma_N|\sigma_O|d_{z^2}$, the symmetric and antisymmetric linear combinations would have identical energies, and ferromagnetic coupling would be expected. For the tetrameric $Cu(L2am)(ClO_4)$, the dimeric asymmetric unit, like $Cu(L2py)(CH_3CN)(ClO_4)$, would be expected to show antiferromagnetic coupling while the axial–basal arrangement in the four-membered Cu_2O_2 ring, like that of $[Cu(dmgH)_2]_2$, would be expected to show ferromagnetic coupling. The observed magnetic moment of $Cu(L2am)(ClO_4)$ would be expected to be greater than that of $Cu(L2py)(CH_3CN)(ClO_4)$ at any temperature.

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Registry No. $[Cu(L2py)(CH_3CN)]_2(ClO_4)_2$, 62197-87-9; $[Cu_4(L2am)_4(ClO_4)_2](ClO_4)_2$, 62228-11-9; diacetyl monoxime, 57-71-6; ethylenediamine, 109-76-2.

Supplementary Material Available: Listings of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

References and Notes

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