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Synthesis and Relation between Magnetism and Structure of the Binuclear Copper(II) Oxime Complex $[Cu_2L_2(ClO_4)_2]\cdot[Cu_2L_2(CH_3OH)_2](ClO_4)_2$, Where HL = 1-(*N*,*N*-Dimethyl-2-aminoethyl)-1-phenyl-2-oximopropane

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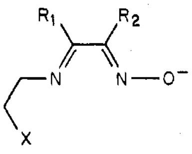
The synthesis, structure, and properties of a new complex with empirical formula $Cu_2L_2(CH_3OH)(ClO_4)_2$ are described, where HL = 1-(*N*,*N*-dimethyl-2-aminoethyl)-1-phenyl-2-oximopropane. From single-crystal X-ray diffraction data, the complex is shown to consist of $[Cu_2L_2(ClO_4)_2]\cdot[Cu_2L_2(CH_3OH)_2]^{2+}(ClO_4^-)_2$. The neutral species $Cu_2L_2(ClO_4)_2$ contains weakly coordinated perchlorato ligands (Cu–O = 2.551 (2) Å) while the ionic dimer $[Cu_2L_2(CH_3OH)_2]^{2+}$ contains somewhat less weakly coordinated methanol (Cu–O = 2.341(3) Å). The Cu–Cu distances are 3.684 (1) and 3.582 (1) Å, respectively, in the neutral and ionic species. Each species has a pair of oxime N–O bridges between the two copper atoms to form a central, nearly planar, six-membered ring. The average angle in the six-membered ring is 120.0 (2)° in the neutral species and 119.5 (2)° in the cationic one, and the deviations of the individual ring angles from 120° can be ascribed to the relatively larger size of copper compared to the other atoms. The coordinated CH_3OH and ClO_4^- groups appear to have little effect. Thus, the six-membered rings may be considered as pseudoaromatic systems containing sp^2 oxygen and nitrogen atoms, with the p_z orbital of each oxygen and nitrogen atom contributing an electron pair and the copper atoms each contributing one unpaired electron to make a total of ten π electrons per ring. The compound is diamagnetic in the range 4–300 K, as is expected for such a system. The magnetic exchange is therefore very large, $|J| \gg 1000\ cm^{-1}$. Crystal data for $[Cu_2L_2(ClO_4)_2]\cdot[Cu_2L_2(CH_3OH)_2]^{2+}(ClO_4^-)_2$: $Cu_4Cl_4O_{22}N_{12}C_{54}H_{80}$, black crystal, space group $P\bar{1}$, $Z = 1$, $a = 10.021$ (4) Å, $b = 10.090$ (5) Å, $c = 21.249$ (8) Å, $\alpha = 91.13$ (2)°, $\beta = 109.36$ (3)°, $\gamma = 117.04$ (3)°, $V = 1768$ Å^3, $R = 5.3\%$ for 3745 reflections.

Introduction

Dimeric copper(II) complexes have long been known to afford the possibility of magnetic-exchange interactions.[1-5] Large interactions may even occur when the link between the metal atoms contains more than one intervening ligand atom. Oxime bridges[6] between copper atoms have been responsible for strong antiferromagnetic,[6-12] weak antiferromagnetic,[13] and ferromagnetic[14,15] interactions. Uhlig and Schneider[7] reacted $Cu(ClO_4)_2$ and ligand **1** ($X = C_5H_4N$, $R_1 = R_2 = CH_3$) to form a dimeric copper(II) complex with a magnetic moment μ(292 K) of 1.04 μ_B which is subnormal and indicative of strong antiferromagnetic interactions. The same is true of complexes reported as $CuL(NO_3)$ and $CuL(ClO_4)$ (L = **1**, X = OH, $R_1 = R_2 = CH_3$) by Ablov et al.[8] although no structure was proposed. Bertrand et al.[10] reported the analogous complex $Cu_2L_2(ClO_4)_2(H_2O)_2$ (L = **1**, X = OH, $R_1 = R_2 = CH_3$), which is diamagnetic (the ultimate limit for antiferromagnetic interactions) and contains a central planar six-membered $(CuON)_2$ ring, for which a σ pathway for exchange was therefore described. The related complex $[Cu_2L_2(ClO_4)_2(CH_3CN)_2]$[11] (L = **1**, $X = C_5H_4N$, $R_1 = R_2 = CH_3$) has a similar structure, but the central six-membered ring is nonplanar and the μ(room temperature) = 1.04 μ_B which indicates a somewhat less strong antiferromagnetic interaction. By use of ligand **1** with $X = NH_2$ and $R_1 = R_2 = CH_3$, the tetranuclear complex $[Cu_4L_4(ClO_4)_2](ClO_4)_2$ (**2**) is obtained.[11] This contains both six-membered $(CuON)_2$ and four-membered $(CuO)_2$ bridges. Mohanty et al. reported temperature-dependent moments μ(273 K) = 0.69 μ_B to μ(367 K) = 0.96 μ_B for dimers of the type $[Cu_2L_2(ClO_4)_2]H_2O$ (L = **1**, $X = N(CH_3)_2$, R_1 and R_2 = CH_3, C_2H_5, or C_6H_5); they assigned the probable structure **3**, with a central $(CuO)_2$ bridge, which is seen to be possible in oximes from the structure of complex **2**. With ligands L, where LH = **4**[14] or **5**,[15] out of plane bridging occurs between the copper atoms. For LH = **4**, the antiferromagnetic interactions are so weak that μ drops little from 293 K (1.77 μ_B) to 93 K (1.71 μ_B), while for LH = **5**, ferromagnetic interactions have been reported though numerical data were not given. Out-of-plane bridging also occurs in $(CuL)_2$ where LH = dimethylglyoxime,[16] and the complex is ferromagnetic, with a triplet–singlet separation of 30 or 40 cm^{-1}.[15]



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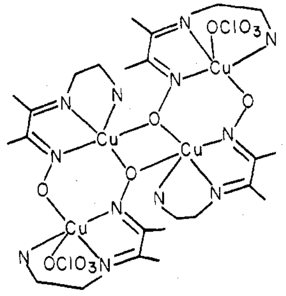

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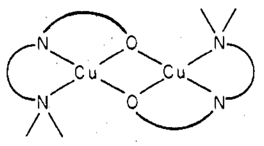

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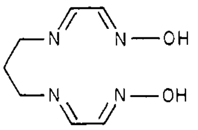

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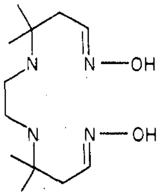

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Significant magnetic interactions are likely to occur in complexes containing pairs of copper(II) atoms bridged by oxime ligands. In the absence of X-ray investigation, it is not possible to predict the structure with certainty when L = **1**

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with X = NH and $R_1 = R_2 = CH_3$. Possibilities include structure **3**, or one based on a six-membered ring formed by oxime N–O bridges linking pairs of copper atoms at opposite corners.[10] We report here the structure and magnetism of a complex of the latter type.

Experimental Section

Synthesis. $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) and 1-phenyl-2-oximo-1-propanone (1 mmol) were dissolved in methanol (50 mL), to which about 3 mL of triethoxymethane had been added. The mixture was then heated, with stirring, and a slight excess of *N*,*N*-dimethylethylenediamine (1.2 mmol) was added to the resulting solution. After cooling, standing for 2–3 days, the solution had deposited shiny green-black crystals of the complex.

Magnetic susceptibility measurements from 4 to 300 K were made on a Josephson junction superconducting susceptometer.[17] Magnetic susceptibility measurements from 300 to 400 K were made by the Gouy method.

Crystal data for $[Cu_2L_2(ClO_4)_2] \cdot [Cu_2L_2(CH_3OH)_2](ClO_4)_2$: $Cu_4Cl_4O_{22}N_{12}C_{54}H_{80}$, fw 1645, black crystal, space group $P\bar{1}$, $Z = 1$, $a = 10.021$ (4) Å, $b = 10.090$ (5) Å, $c = 21.249$ (8) Å, $\alpha = 91.13$ (2)°, $\beta = 109.36$ (3)°, $\gamma = 117.04$ (3)°, $V = 1768$ Å^3, $\rho_{calcd} = 1.55$ g cm^{-3}, $\rho_{obsd} = 1.54$ g cm^{-3}, μ(Mo Kα) = 14.7 cm^{-1}. Crystal dimensions, distances of faces in mm from centroid: $(\bar{1}10)$ 0.37, $(1\bar{1}\bar{1})$ 0.39, $(\bar{1}11)$ 0.39, $(10\bar{3})$ 0.24, $(\bar{1}03)$ 0.24, $(0\bar{1}0)$ 0.37, (001) 0.105, $(00\bar{1})$ 0.105. Maximum and minimum transmission coefficients are 0.79 and 0.51.

The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer by using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 48°$. 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–Kα_2 splitting. The values of A and B were 0.6 and 0.35°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated 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 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 (including the polarization effect of the crystal monochromator) and then for absorption. After the intensities of equivalent reflections were averaged, the data were reduced to 4285 independent intensities of which 3745 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[18] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. The positions of the copper atoms were determined from three-dimensional Patterson functions calculated from all intensity data. These phased the data sufficiently well to permit location of the other nonhydrogen atoms.

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 then 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[19] and those for hydrogen from Stewart et al.[20] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c by using the values of Cromer and Ibers[21] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms which were included in the refinement for three cycles of least squares and then held fixed. The model converged with $R = 5.3$ and $R_w = 7.3\%$. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 7.8\%$; 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 function was featureless. Tables of the observed and calculated structure factors are available.[22] The principal programs used are as previously described.[23]

Results and Discussion

Final positional and thermal parameters for $[Cu_2L_2(ClO_4)_2 \cdot [Cu_2L_2(CH_3OH)_2](ClO_4)_2$ 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. The unit cell contains two oxime-bridged copper(II) species, as well as uncoordinated perchlorate ions. Figure 1 shows a stereoscopic pair view of the ionic species $[Cu_2L_2(CH_3OH)_2]^{2+}$, in which there is a relatively weak bond from the copper to the methanol oxygen (2.341 Å). This species is designated as "A". Figure 2 shows a stereoscopic pair view of the neutral binuclear molecule $Cu_2L_2(ClO_4)_2$, in which a perchlorato oxygen, O(1), is bonded to the copper atom even less strongly (2.551 Å) than the CH_3OH group in the methanol species. The neutral species is designated as "B". The atom numbering is the same as in Figure 1 and is therefore omitted. Except for the slight difference in the Cu–O bond lengths in the methanol and perchlorato species, the structure of the two binuclear species is very similar, and in each case there is a central six-membered ring which is obtained by inversion of a Cu–O–N fragment through the ring center.

Details of the $[Cu_2L_2(CH_3OH)_2]^{2+}$ Structure. The central six-membered $(CuON)_2$ ring in this species is quite close to planarity. The average ring angle is 119.5°. The main deviation from a regular hexagonal ring shape is due to the relatively large size of the Cu atoms and to the difference in the Cu–O and Cu–N bonds. The Cu–O bond is considerably shorter (1.883 Å) than that of Cu–N (2.008 Å) as expected from electronegativity considerations. The coordination of the methanol oxygen atoms makes the overall environment of the copper a distorted square pyramid. Although the copper atom would normally be expected to be displaced considerably above the square base up the axis of the pyramid, the extent of displacement is quite small here (0.055 Å). Thus, the environment of the copper atom, without the apical methanol donor, is quite close to square planar. The average ligand–copper–ligand angle (ignoring the methanol) is 89.7°. The copper–copper separation is 3.684 Å. Each atom is related to an identical atom by an inversion center in the middle of the $(CuON)_2$ ring.

Details of the $[Cu_2L_2(ClO_4)_2]$ Structure. In this neutral species, the distortion of the central $(CuON)_2$ ring, and of the copper environment from planarity, is even less than in $[Cu_2L_2(CH_3OH)_2]^{2+}$. The average ring angle is 120.0°, and the average ligand–copper–ligand angle is 90.0°. The copper environment is again a distorted square pyramidal, with very little displacement (0.038 Å) of Cu above the pyramid base. As the apical Cu–O bond is much longer than in the methanol analogue (2.551 Å instead of 2.341 Å), the apical atom has much less influence on the geometry of the pyramid base and of the central six-membered ring. The intramolecular copper to copper distance is 3.582 Å, a little less than in the ionic methanol adduct. As with the ionic complex, the neutral $[Cu_2L_2(ClO_4)_2]$ has a center of inversion in the six-membered $(CuON)_2$ ring. In both the dimeric species, the nearly planar copper environment achieved is such as to maximize the ring

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cu_4Cl_4O_{22}N_{12}C_{54}H_{80}$[a]

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(A)	0.03876 (8)	−0.02680 (6)	0.42310 (3)	0.0876 (3)	0.0311 (3)	0.0327 (3)	0.0277 (2)	0.0257 (2)	0.0107 (2)
Cu(B)	0.21303 (8)	0.57089 (6)	0.04432 (3)	0.0623 (3)	0.0250 (3)	0.0441 (3)	0.0082 (2)	0.0146 (3)	0.0150 (3)
Cl(1)	0.0596 (2)	0.2609 (2)	−0.08883 (8)	0.1185 (10)	0.0373 (6)	0.0527 (7)	0.0274 (6)	0.0332 (6)	0.0044 (6)
Cl(2)	0.4542 (2)	0.1752 (2)	0.66636 (8)	0.0893 (8)	0.0405 (6)	0.0587 (8)	0.0202 (5)	0.0235 (7)	0.0085 (6)
O(A)	−0.0191 (4)	0.1581 (4)	0.5145 (2)	0.115 (2)	0.037 (1)	0.038 (2)	0.037 (1)	0.041 (1)	0.014 (1)
O(B)	0.1263 (4)	0.6642 (3)	−0.0209 (2)	0.066 (2)	0.027 (1)	0.051 (2)	0.014 (1)	0.021 (1)	0.019 (1)
O(M)	0.3193 (6)	0.1228 (6)	0.4819 (3)	0.096 (3)	0.081 (3)	0.065 (3)	0.018 (2)	0.015 (2)	0.013 (2)
O(1)	0.2018 (5)	0.4025 (4)	−0.0506 (2)	0.075 (2)	0.045 (2)	0.067 (2)	0.010 (2)	0.024 (2)	−0.005 (2)
O(2)	0.0356 (8)	0.1535 (5)	−0.0462 (3)	0.243 (5)	0.044 (2)	0.081 (3)	0.056 (2)	0.076 (3)	0.028 (2)
O(3)	0.0816 (6)	0.2092 (5)	−0.1455 (2)	0.143 (3)	0.090 (3)	0.067 (3)	0.054 (2)	0.038 (2)	−0.012 (2)
O(4)	−0.0784 (6)	0.2865 (6)	−0.1138 (3)	0.121 (3)	0.079 (3)	0.087 (3)	0.041 (2)	0.034 (2)	0.007 (3)
O(6)	0.4981 (13)	0.3007 (7)	0.6429 (4)	0.557 (9)	0.114 (4)	0.187 (5)	0.174 (4)	0.227 (5)	0.083 (4)
O(5)	0.4243 (7)	0.0552 (5)	0.6179 (3)	0.150 (3)	0.071 (2)	0.095 (4)	0.055 (2)	0.026 (3)	−0.005 (3)
O(7)	0.3424 (9)	0.1399 (11)	0.6913 (5)	0.151 (4)	0.169 (7)	0.300 (7)	0.013 (4)	0.145 (3)	−0.032 (6)
O(8)	0.5905 (10)	0.2000 (11)	0.7237 (5)	0.172 (6)	0.230 (7)	0.128 (6)	0.092 (5)	−0.026 (5)	−0.039 (6)
N(A1)	−0.0095 (5)	0.1285 (4)	0.4555 (2)	0.110 (2)	0.050 (2)	0.056 (2)	0.035 (1)	0.031 (2)	0.010 (2)
N(A2)	0.0276 (5)	0.0749 (5)	0.3467 (2)	0.079 (2)	0.043 (2)	0.032 (2)	0.028 (1)	0.021 (2)	0.010 (2)
N(A3)	0.0563 (6)	−0.1722 (5)	0.3609 (2)	0.103 (3)	0.041 (2)	0.040 (2)	0.033 (2)	0.030 (2)	0.009 (2)
N(B1)	0.0301 (5)	0.3893 (4)	0.0529 (2)	0.059 (2)	0.024 (2)	0.037 (2)	0.013 (1)	0.016 (2)	0.008 (2)
N(B2)	0.3330 (6)	0.5020 (5)	0.1146 (2)	0.070 (3)	0.035 (2)	0.058 (3)	0.010 (2)	0.012 (2)	0.021 (2)
N(B3)	0.4413 (6)	0.7498 (5)	0.0621 (3)	0.067 (3)	0.039 (2)	0.061 (3)	0.013 (2)	0.014 (2)	0.021 (2)
C(B1)	−0.0481 (7)	0.1615 (5)	0.1040 (3)	0.088 (3)	0.039 (2)	0.086 (3)	0.018 (2)	0.032 (2)	0.020 (2)
C(A1)	−0.0587 (8)	0.3394 (6)	0.4283 (3)	0.173 (4)	0.057 (2)	0.068 (3)	0.073 (2)	0.066 (3)	0.030 (3)
C(A2)	−0.0237 (6)	0.2167 (5)	0.4136 (3)	0.083 (3)	0.028 (2)	0.038 (2)	0.022 (2)	0.026 (2)	0.018 (2)
C(A3)	−0.0118 (6)	0.1787 (5)	0.3492 (3)	0.069 (3)	0.031 (2)	0.039 (2)	0.018 (2)	0.022 (2)	0.010 (2)
C(A4)	−0.0464 (7)	0.2588 (6)	0.2934 (3)	0.091 (3)	0.035 (2)	0.038 (2)	0.025 (2)	0.031 (2)	0.012 (2)
C(A5)	0.0783 (7)	0.3836 (6)	0.2840 (3)	0.073 (3)	0.037 (3)	0.048 (3)	0.010 (2)	0.022 (2)	0.010 (2)
C(A6)	0.0430 (7)	0.4584 (6)	0.2330 (3)	0.101 (3)	0.033 (2)	0.058 (3)	0.026 (2)	0.043 (2)	0.020 (2)
C(A7)	−0.1124 (7)	0.4140 (6)	0.1922 (3)	0.109 (3)	0.052 (3)	0.046 (3)	0.043 (2)	0.032 (2)	0.020 (2)
C(A8)	−0.2361 (8)	0.2924 (7)	0.2015 (3)	0.084 (3)	0.068 (3)	0.053 (3)	0.038 (2)	0.020 (3)	0.026 (3)
C(A9)	−0.2031 (7)	0.2143 (6)	0.2520 (3)	0.077 (3)	0.048 (3)	0.055 (3)	0.025 (2)	0.026 (2)	0.020 (2)
C(A10)	0.0368 (7)	0.0087 (6)	0.2876 (3)	0.104 (3)	0.061 (3)	0.046 (3)	0.048 (2)	0.039 (2)	0.024 (2)
C(A11)	0.1221 (7)	−0.0816 (7)	0.3133 (3)	0.104 (3)	0.062 (3)	0.050 (3)	0.045 (2)	0.035 (2)	0.020 (3)
C(A12)	−0.1057 (9)	−0.3083 (8)	0.3256 (4)	0.102 (4)	0.060 (3)	0.091 (5)	0.024 (3)	0.031 (3)	−0.018 (3)
C(A13)	0.1713 (8)	−0.2285 (7)	0.3982 (4)	0.128 (3)	0.079 (3)	0.077 (4)	0.068 (2)	0.053 (3)	0.037 (3)
C(B2)	0.0728 (6)	0.3093 (5)	0.0937 (3)	0.067 (3)	0.024 (2)	0.041 (3)	0.016 (2)	0.019 (2)	0.004 (2)
C(B3)	0.2494 (6)	0.3772 (5)	0.1299 (3)	0.069 (3)	0.032 (2)	0.041 (3)	0.019 (2)	0.018 (2)	0.007 (2)
C(B4)	0.3202 (6)	0.3072 (5)	0.1809 (3)	0.067 (3)	0.031 (2)	0.052 (3)	0.017 (2)	0.025 (2)	0.017 (2)
C(B5)	0.2926 (7)	0.1592 (6)	0.1646 (3)	0.078 (3)	0.042 (2)	0.072 (3)	0.027 (2)	0.032 (2)	0.022 (3)
C(B6)	0.3591 (7)	0.0957 (6)	0.2141 (4)	0.086 (3)	0.050 (2)	0.105 (4)	0.041 (2)	0.046 (3)	0.040 (3)
C(B7)	0.4533 (8)	0.1787 (7)	0.2789 (3)	0.088 (3)	0.085 (3)	0.082 (4)	0.047 (2)	0.037 (3)	0.052 (3)
C(B8)	0.4834 (8)	0.3227 (7)	0.2959 (3)	0.077 (4)	0.069 (3)	0.052 (3)	0.023 (3)	0.015 (3)	0.025 (3)
C(B9)	0.4177 (7)	0.3869 (6)	0.2473 (3)	0.081 (3)	0.038 (2)	0.048 (3)	0.022 (2)	0.016 (2)	0.012 (2)
C(B10)	0.5096 (8)	0.5904 (7)	0.1405 (4)	0.063 (4)	0.059 (3)	0.089 (4)	0.008 (3)	0.008 (3)	0.031 (3)
C(B111)	0.5510 (17)	0.7472 (16)	0.1343 (6)	0.083 (8)	0.072 (8)	0.037 (6)	0.012 (6)	0.008 (6)	0.016 (6)
C(B112)	0.5529 (15)	0.6786 (14)	0.0903 (7)	0.047 (6)	0.057 (7)	0.098 (9)	0.004 (5)	0.019 (6)	0.039 (6)
C(B12)	0.4786 (9)	0.7649 (10)	0.0019 (4)	0.105 (4)	0.080 (5)	0.120 (5)	−0.013 (4)	0.072 (3)	−0.007 (4)
C(B13)	0.4541 (11)	0.8877 (9)	0.0909 (6)	0.120 (6)	0.051 (4)	0.188 (7)	−0.020 (4)	0.076 (4)	−0.043 (5)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
C(M)	0.426 (2)	0.276 (2)	0.4779 (7)	14.2 (4)	H(111)	0.236 (6)	−0.023 (6)	0.338 (3)	6 (1)
H(5A)	0.177 (6)	0.418 (6)	0.319 (3)	6 (1)	H(112)	0.128 (5)	−0.133 (5)	0.274 (2)	3 (1)
H(6A)	0.112 (7)	0.545 (7)	0.222 (4)	9 (2)	H(B5)	0.227 (5)	0.109 (5)	0.117 (2)	4 (1)
H(7A)	−0.142 (6)	0.458 (6)	0.152 (3)	6 (2)	H(H6)	0.349 (5)	−0.007 (5)	0.207 (2)	4 (1)
H(8A)	−0.331 (6)	0.268 (6)	0.178 (3)	7 (2)	H(B7)	0.499 (6)	0.150 (6)	0.315 (3)	6 (2)
H(9A)	−0.289 (6)	0.133 (6)	0.261 (3)	6 (2)	H(B8)	0.553 (7)	0.385 (7)	0.345 (3)	7 (2)
H(101)	−0.096 (6)	−0.076 (6)	0.256 (3)	6 (2)	H(9B)	0.433 (5)	0.472 (5)	0.258 (3)	4 (1)
H(102)	0.087 (6)	0.086 (6)	0.266 (3)	6 (2)	H(M)	0.366 (8)	0.120 (8)	0.517 (4)	11 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*\cdot c^*]$.

planarity and the exchange overlap.

Magnetic Exchange. The accurate SQUID data[17] (Table IV) showed no apparent paramagnetism up to 300 K except for a small paramagnetic impurity evident only below 20 K and a temperature-independent paramagnetism which became evident when the observed diamagnetic susceptibility was corrected for the diamagnetism of the sample holder and the diamagnetism of the constituent atoms by using Pascal's constants. Extension of the susceptibility measurements up to 400 K by the Gouy method also gave no indication of the presence of thermally populated paramagnetic states. Our data can therefore only give an estimate of the lower limit of the exchange parameter *J* which we place at $J > 1000\ \mathrm{cm}^{-1}$.

The magnitude of the antiferromagnetic exchange interactions is extremely large, especially when the separation of the copper ions (~3.6Å) is considered. The large magnitude of the coupling energies requires a pathway better suited to the efficient transfer of spin information than the simple σ-bonded pathway proposed for similar compounds.[9] The σ-bonded pathway would increase the path distance between copper ions to 5.21 Å. The additional stabilization of antiferromagnetic electron coupling appears most likely due to extensive π overlap throughout the exchange pathway. In fact if one assumes a contribution of one p_z electron pair from each

Table II. Bond Lengths and Selected Interatomic Distances (Å)

Cu(A)–Cu(A)	3.684 (1)	N(B1)–C(B2)	1.298 (2)
Cu(A)–O(A)	1.886 (2)	N(B2)–C(B3)	1.277 (3)
Cu(A)–O(M)	2.341 (3)	N(B2)–C(B10)	1.459 (4)
Cu(A)–N(A1)	2.008 (2)	N(B3)–C(B11)	1.573 (7)
Cu(A)–N(A2)	1.936 (2)	N(B3)–C(B11′)	1.559 (8)
Cu(A)–N(A3)	2.059 (2)	N(B3)–C(B12)	1.440 (5)
Cu(B)–Cu(B)	3.582 (1)	N(B3)–C(B13)	1.442 (5)
Cu(B)–O(1)	2.551 (2)	C(A1)–C(A2)	1.485 (4)
Cu(B)–O(B)	1.887 (2)	C(A2)–C(A3)	1.469 (4)
Cu(B)–N(B1)	1.983 (2)	C(A3)–C(A4)	1.483 (4)
Cu(B)–N(B2)	1.941 (2)	C(A4)–C(A5)	1.391 (4)
Cu(B)–N(B3)	2.068 (2)	C(A4)–C(A9)	1.367 (4)
Cl(1)–O(1)	1.438 (2)	C(A5)–C(A6)	1.375 (4)
Cl(1)–O(2)	1.414 (2)	C(A6)–C(A7)	1.354 (5)
Cl(1)–O(3)	1.423 (2)	C(A7)–C(A8)	1.367 (5)
Cl(1)–O(4)	1.451 (3)	C(A8)–C(A9)	1.385 (4)
Cl(2)–O(5)	1.426 (3)	C(A10)–C(A11)	1.509 (4)
Cl(2)–O(6)	1.307 (4)	C(B1)–C(B2)	1.511 (4)
Cl(2)–O(7)	1.305 (4)	C(B2)–C(B3)	1.472 (4)
Cl(2)–O(8)	1.409 (4)	C(B3)–C(B4)	1.467 (4)
O(A)–N(A1)	1.327 (3)	C(B4)–C(B5)	1.403 (4)
O(B)–N(B1)	1.311 (3)	C(B4)–C(B9)	1.385 (4)
N(A1)–C(A2)	1.293 (3)	C(B5)–C(B6)	1.382 (4)
N(A2)–C(A3)	1.281 (3)	C(B6)–C(B7)	1.365 (5)
N(A2)–C(A10)	1.459 (3)	C(B7)–C(B8)	1.357 (5)
N(A3)–C(A11)	1.492 (4)	C(B8)–C(B9)	1.372 (4)
N(A3)–C(A12)	1.486 (4)	C(B10)–C(B11)	1.463 (9)
N(A3)–C(A13)	1.512 (4)	C(B10)–C(B11′)	1.453 (8)

nitrogen and oxygen in the bridging network plus the unpaired electron residing on each copper ion, the total corresponds to 10 delocalized π electrons in the six-membered ring and meets one criterion for aromaticity. The bond angles of the bridging atoms are approximately 120°, in keeping with sp^2 hybridization stabilized by π bonding, and the six-membered bridging ring is very nearly flat, within experimental error. The bonding geometry is undoubtedly stabilized by the participation of Hückel's number of π electrons, and this stabilization energy accounts in large part for the extremely large coupling energy of the electrons.

It is of interest to compare the bonding and magnetism found in this compound with that found in the structures of other copper oxime complexes and in the free ligands themselves.[6–16,24,25] The following general conclusions may be drawn. Strong antiferromagnetic interactions occur for in-plane bonding via a *planar* $Cu(NO)_2Cu$ ring, as found in this study and in ref 10. Intermediate strength interactions result from in-plane nonplanar $Cu(NO)_2Cu$ rings,[11] while for out-of-plane bonding via the N–O moiety, magnetic-exchange interactions result which may be either weakly ferro-[14,15] or antiferromagnetic.[13]

The postulate that the strong interactions in the planar rings are transmitted via a ring π system presupposes some increase in the bond order of the N–O bond compared to that found in situations where there are weak interactions present. This should be manifested in the structural data by a decrease in the N–O bond distance and also some lengthening of the C=N bond. It can be seen from the data presented in Table V that this hypothesis is followed quite closely, i.e., that the strength of the magnetic interaction is inversely related to the N–O distance. Under this criterion the magnetic interaction in the neutral moiety $Cu_2L_2(ClO_4)_2$, with a N–O bond length of 1.311 (3) Å, should be the strongest yet observed. It is not presently known whether this moiety would retain its structure if crystallized in the absence of the coordinating solvent methanol. The N–O distance in $Cu_2L_2(ClO_4)_2$ should be compared with the values found in the free ligand (1.375 (4) Å[24,25]) and also with those found in complexes with only weak magnetic interactions (1.38 (1) Å,[14] 1.347 (4) Å[11]). It should be pointed out, however, that while the C=N bond length does show some decrease in bond order in going from the free ligand (1.263 (4) Å[24]) to complexes with weak interactions (1.27 (2) Å[14]) to complexes with strong interactions (1.298 (2) Å, this study), there is not the same close correlation between magnetism and bond length as is found in the comparison of N–O length.

Table III. Bond Angles (deg)

O(A)–Cu(A)–O(M)	92.97 (9)	O(2)–Cl(1)–O(4)	110.7 (2)	O(B)–N(B1)–C(B2)	118.3 (3)	C(A6)–C(A7)–C(A8)	119.6 (3)
O(A)–Cu(A)–N(A1)	105.04 (8)	O(3)–Cl(1)–O(4)	108.9 (2)	Cu(B)–N(B2)–C(B3)	116.5 (2)	C(A7)–C(A8)–C(A9)	120.4 (3)
O(A)–Cu(A)–N(A2)	169.49 (9)	O(5)–Cl(2)–O(6)	109.6 (2)	Cu(B)–N(B2)–C(B10)	117.0 (2)	C(A4)–C(A9)–C(A8)	120.3 (3)
O(A)–Cu(A)–N(A3)	90.42 (8)	O(5)–Cl(2)–O(7)	114.4 (3)	C(B3)–N(B2)–C(B10)	126.3 (3)	N(A2)–C(A10)–C(A11)	106.5 (2)
O(M)–Cu(A)–N(A1)	93.7 (1)	O(5)–Cl(2)–O(8)	106.2 (3)	Cu(B)–N(B3)–C(B11)	104.5 (3)	N(A3)–C(A11)–C(A10)	109.8 (3)
O(M)–Cu(A)–N(A2)	95.68 (9)	O(6)–Cl(2)–O(7)	116.9 (4)	Cu(B)–N(B3)–C(B11′)	102.7 (3)	N(B1)–C(B2)–C(B1)	122.9 (3)
O(M)–Cu(A)–N(A3)	94.6 (1)	O(6)–Cl(2)–O(8)	105.9 (4)	Cu(B)–N(B3)–C(B12)	112.7 (2)	N(B1)–C(B2)–C(B3)	113.8 (2)
N(A1)–Cu(A)–N(A2)	80.37 (9)	O(7)–Cl(2)–O(8)	102.7 (4)	Cu(B)–N(B3)–C(B13)	109.1 (2)	C(B1)–C(B2)–C(B3)	123.3 (2)
N(A1)–Cu(A)–N(A3)	162.04 (9)	Cu(A)–O(A)–N(A1)	124.1 (1)	C(B11)–N(B3)–C(B12)	126.8 (4)	N(B2)–C(B3)–C(B2)	114.6 (2)
N(A2)–Cu(A)–N(A3)	82.97 (9)	Cu(B)–O(B)–N(B1)	122.7 (1)	C(B11)–N(B3)–C(B13)	89.5 (4)	N(B2)–C(B3)–C(B4)	123.8 (3)
O(B)–Cu(B)–O(1)	89.66 (8)	Cu(A)–N(A1)–O(A)	129.5 (2)	C(B11′)–N(B3)–C(B12)	90.8 (4)	C(B2)–C(B3)–C(B4)	121.6 (2)
O(B)–Cu(B)–N(B1)	108.18 (8)	Cu(A)–N(A1)–C(A2)	113.9 (2)	C(B11′)–N(B3)–C(B13)	129.1 (4)	C(B3)–C(B4)–C(B5)	121.8 (3)
O(B)–Cu(B)–N(B2)	171.48 (9)	O(A)–N(A1)–C(A2)	116.5 (2)	C(B12)–N(B3)–C(B13)	111.4 (3)	C(B3)–C(B4)–C(B9)	120.4 (2)
O(B)–Cu(B)–N(B3)	88.17 (9)	Cu(A)–N(A2)–C(A3)	116.1 (2)	N(A1)–C(A2)–C(A1)	122.1 (2)	C(B5)–C(B4)–C(B9)	117.8 (3)
O(1)–Cu(B)–N(B1)	88.24 (7)	Cu(A)–N(A2)–C(A10)	116.7 (2)	N(A1)–C(A2)–C(A3)	114.1 (2)	C(B4)–C(B5)–C(B6)	120.3 (3)
O(1)–Cu(B)–N(B2)	92.21 (9)	C(A3)–N(A2)–C(A10)	126.2 (2)	C(A1)–C(A2)–C(A3)	123.7 (2)	C(B5)–C(B6)–C(B7)	119.5 (3)
O(1)–Cu(B)–N(B3)	96.55 (9)	Cu(A)–N(A3)–C(A11)	105.5 (2)	N(A2)–C(A3)–C(A2)	115.1 (2)	C(B6)–C(B7)–C(B8)	121.4 (3)
N(B1)–Cu(B)–N(B2)	80.20 (9)	Cu(A)–N(A3)–C(A12)	109.5 (2)	N(A2)–C(A3)–C(A4)	125.6 (2)	C(B7)–C(B8)–C(B9)	119.7 (3)
N(B1)–Cu(B)–N(B3)	163.04 (9)	Cu(A)–N(A3)–C(A13)	114.0 (2)	C(A2)–C(A3)–C(A4)	119.3 (2)	C(B4)–C(B9)–C(B8)	121.2 (3)
N(B2)–Cu(B)–N(B3)	83.36 (9)	C(A11)–N(A3)–C(A12)	113.2 (3)	C(A3)–C(A4)–C(A5)	121.0 (3)	N(B2)–C(B10)–C(B11)	106.8 (4)
O(1)–Cl(1)–O(2)	109.2 (2)	C(A11)–N(A3)–C(A13)	107.6 (3)	C(A3)–C(A4)–C(A9)	120.1 (3)	N(B2)–C(B10)–C(B11′)	107.5 (4)
O(1)–Cl(1)–O(3)	108.9 (2)	C(A12)–N(A3)–C(A13)	107.1 (3)	C(A5)–C(A4)–C(A9)	118.8 (3)	N(B3)–C(B11)–C(B10)	109.9 (5)
O(1)–Cl(1)–O(4)	108.7 (2)	Cu(B)–N(B1)–O(B)	127.7 (3)	C(A4)–C(A5)–C(A6)	120.0 (3)	N(B3)–C(B11′)–C(B10)	111.2 (6)
O(2)–Cl(1)–O(3)	110.5 (2)	Cu(B)–N(B1)–C(B2)	114.6 (2)	C(A5)–C(A6)–C(A7)	120.9 (3)		

Table IV. Magnetic Susceptibility Data, with Correction for Paramagnetic Impurity (T in K; χ in 10^{-6} cgsu)[a]

T	4.3	8.15	16.8	24.7	32.7	48.0	65.0	75.0	94.0	108	143	177	212	249	293
χ	276	133	−4	−31	−66	−98	−45	−80	−156	−125	−160	−138	−134	−143	−111
χ_{imp}	420	224	108	74	56	38	28	24	19	17	13	11	9	7	6
χ_{cor}[b]	−144	−91	−112	−105	−122	−136	−73	−104	−175	−142	−173	−149	−143	−150	−117

[a] $\chi_{dia} = -193 \times 10^{-6}$ cgsu. Therefore TIP ≈ 60×10^{-6} cgsu. [b] Average $(-129 \pm 30) \times 10^{-6}$ cgsu.

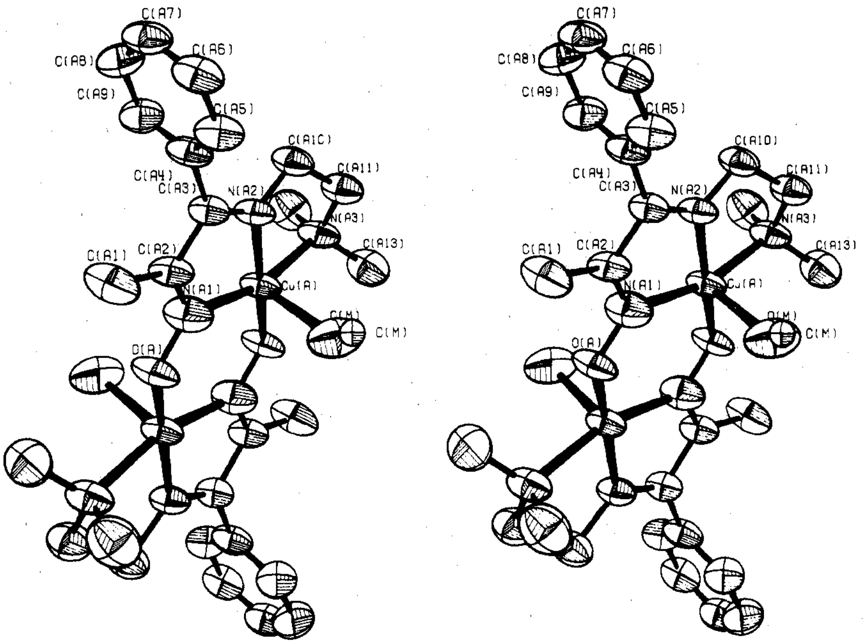


Figure 1. Stereoscopic view of the ionic species $[Cu_2L_2(CH_3OH)_2]^{2+}$.

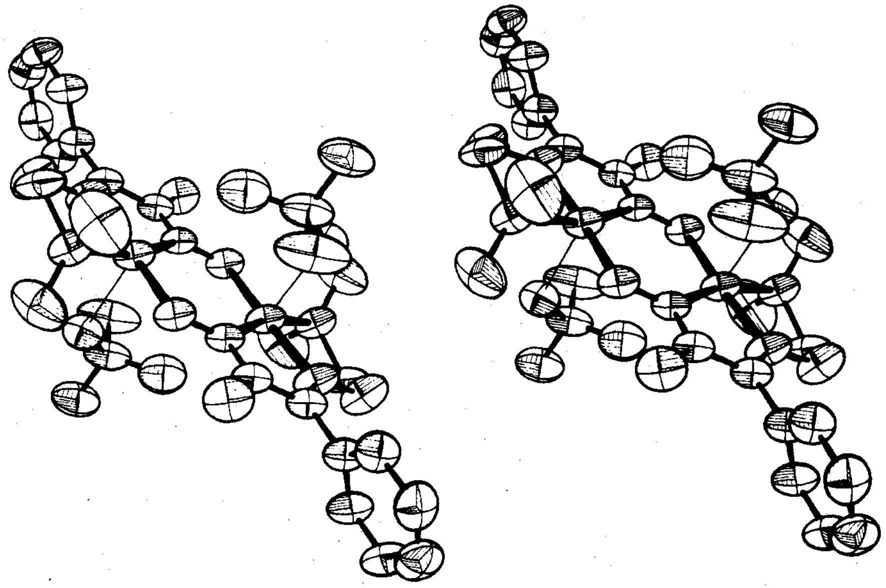
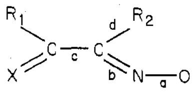


Figure 2. Stereoscopic view of the neutral species $Cu_2L_2(ClO_4)_2$.

Table V



$R_1, R_2 = H, CH_3, C_6H_5$; X = RN, ROH, O

complex	type of interacn[a]	bond length[b]				bond angles[b]				ref
		a	b	c	d	ab	bc	cd	bd	
$[Cu_2L_2(ClO_4)_2]$	s.a.f.	1.311 (3)	1.298 (2)	1.472 (4)	1.511 (4)	118.3 (3)	113.8 (3)	123.3 (2)	122.9 (3)	this study
$[Cu_2L_2(CH_3OH)_2]$	s.a.f.	1.327 (3)	1.293 (3)	1.469 (4)	1.485 (4)	116.5 (2)	114.1 (2)	123.7 (2)	122.1 (2)	this study
$[CuL(ClO_4)(H_2O)]_2$	s.a.f.	1.325 (6)	1.289 (7)	1.484 (8)	1.508 (8)	117.3 (4)	114.4 (5)	121.5 (5)	124.0 (5)	10
$[CuL_2py(CH_3CN)]_2{}^{2+}$	i.a.f.	1.329 (4)	1.292 (4)	1.489 (5)	1.509 (5)	116.7 (3)	113.8 (3)	123.3 (3)	123.0 (3)	11
$[CuL(ClO_4)]$	w.a.f.	1.344 (6)	1.282 (7)	1.513 (8)	1.487 (8)	120.6 (4)	111.8 (5)	123.2 (5)	125.0 (5)	13
		1.345 (6)	1.282 (7)	1.510 (8)	1.487 (8)	120.8 (4)	112.2 (5)	123.1 (5)	124.7 (5)	13
$[Cu_4(L_2am)_4(ClO_4)_2]^{2+}$	w.a.f.	1.345 (4)	1.292 (5)	1.494 (5)	1.481 (6)	117.8 (3)	123.3 (3)	123.6 (3)	112.9 (3)	11
		1.347 (4)	1.291 (5)	1.487 (5)	1.482 (6)	117.4 (3)	123.5 (3)	123.6 (3)	112.9 (3)	11
$[Cu(LH)]_2Br_2$	w.f.	1.38 (1)	1.27 (2)	1.52 (2)	1.48 (2)	117 (1)	121 (1)	118 (1)	121 (1)	14
$[Cu(dmg)_2]_2$	w.f.	1.33 (4)	1.27 (4)	1.53 (4)	1.45 (4)	116 (1)	111 (1)	125 (1)	124 (1)	16
L'H		1.375 (4)	1.263 (4)	1.478 (5)		112.0 (2)	117.3 (2)			24

[a] s.a.f. = strong antiferromagnetic; i.a.f. = intermediate antiferromagnetic; w.a.f. = weak antiferromagnetic; w.f. = weak ferromagnetic.

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Registry No. $[Cu_2L_2(ClO_4)_2]\cdot[Cu_2L_2(CH_3OH)_2](ClO_4)_2$, 70072-45-6; 1-phenyl-2-oximo-1-propanone, 119-51-7; *N*,*N*-dimethylethylenediamine, 110-18-9.

Supplementary Material Available: Listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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A New Synthesis of Bis(3,3′-dimethyl-2,2′-dipyridylamine)copper(II) and the Crystal Structure of the Complex

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The copper(II) complex (**1**) of the deprotonated form of 3,3′-dimethyl-2,2′-dipyridylamine has been prepared by reacting the ligand with freshly prepared copper(II) hydroxide. The crystal and molecular structure have been determined. Crystal data: space group $P2_12_12_1$, $Z = 4$, $a = 8.639$ (1) Å, $b = 14.358$ (4) Å, $c = 17.510$ (3) Å, $V = 2172$ Å^3, $R = 3.9\%$ for 1875 reflections. The copper environment is pseudotetrahedral, with a dihedral angle of 57.4° between the two CuN_2 ligand planes. This accurate structure provides a new and somewhat better calibrant for the correlation between the spectra and structures of pseudotetrahedral copper(II) complexes than the known $[Cu(HDPA)_2](ClO_4)_2$ complex (**2**) ($R = 9.4\%$), where HDPA = 2,2′-dipyridylamine. The differences between complexes **1** and **2** include a slightly closer approach to tetrahedral configuration of copper(II) in complex **1** and far greater deviation of the ligands from planarity in **2**, as well as a major displacement of the metal atom from one of the ligand planes. Although the difference between the dihedral angles in the two complexes is small (57.4 and 55.6°), the trend is in the right direction when compared to spectral assignments.

Introduction

There has been considerable interest in the relationship of the magnetic, spectroscopic, and structural properties of 2,2′-dipyridylamine (HDPA)[1-15] and its complexes with bivalent transition metals, particularly copper(II),[1-8] nickel(II),[2,9] palladium(II),[10] cobalt(II),[11] and iron(II).[12] A variety of stereochemical arrangements has been inferred for the cobalt, iron, and nickel complexes. Gouge and Geldard[1] have examined $[Cu(HDPA)_2]^{2+}$, $Cu(DPA)_2$, and a series of copper(II) complexes with stereochemically similar ligands, which produced a pseudotetrahedral metal environment. The known structure[7] of $Cu(HDPA)_2(ClO_4)_2$ could then be used to calibrate the spectra of the various copper complexes in terms of distortion from regular tetrahedral geometry. The accuracy of this known structure is limited ($R = 9.4\%$), presumably due to some disorder in the perchlorate groups. Thus, a much more accurate related structure, such as that of the deprotonated 3,3′-dimethyl-2,2′-dipyridylamine complex of copper(II) $[Cu(MPA)_2]$ which we report here, would be very useful for the correlation with spectral and magnetic properties. A further interest in such a structure is that despite the extensive studies on ligands of this type, no crystal structure determination of any first-series transition-metal complexes with a deprotonated ligand has been reported. The only known structure with a deprotonated ligand is that of the DPA complex of palladium(II),[10] in which the ligand is extremely distorted to enable the metal atom to acquire its normal square-planar configuration.

Experimental Section

Preparation of the Complex. To a solution of 0.76 g (3.82 mmol) of 2,2′-iminobis(3-picoline)[16] in 75 mL of distilled benzene was added 0.200 g (2.05 mmol) of $Cu(OH)_2$, freshly prepared by precipitation from a $CuCl_2$ solution by the addition of aqueous KOH. The mixture was heated at reflux for 24 h, during which time the color turned a deep green. The mixture was cooled and filtered and the filtrate concentrated to a volume of about 15 mL on a rotary evaporator. Absolute ether was added to the remaining solution, and when the solution stood in a refrigerator overnight, the complex separated as purple crystals; 531 mg (61%), mp 237–239 °C. When the filtrate was concentrated, followed by refrigeration, an additional 118 mg (13%) of product was obtained; mp 237–239 °C.

Crystal data for $[Cu(MPA)_2]$: $CuN_6C_{24}H_{24}$, mol wt 460, space group $P2_12_12_1$, $Z = 4$, $a = 8.639$ (1) Å, $b = 14.358$ (4) Å, $c = 17.510$ (3) Å, $V = 2172$ Å^3, $\rho_{calcd} = 1.407$ g cm^{-3}, $\rho_{obsd} = 1.41$ g cm^{-3}, μ(Mo Kα) = 10.7 cm^{-1}. Crystal dimensions, distances in mm of faces from centroid: (100) 0.38, ($\bar{1}00$) 0.38, (011) 0.27, ($0\bar{1}\bar{1}$) 0.27, ($01\bar{1}$) 0.152, ($0\bar{1}1$) 0.152. Maximum and minimum transmission coefficients are 0.87 and 0.82.

The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was

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