all of the above in that four-membered Cu_2C_2 rings occur with the C atoms coming from CN groups. The only monomeric example of a CuCN complex is the $Cu(CN)_4^{3-}$ ion in $K_3Cu(CN)_4$.[24] The 1987 reference work edited by Wilkinson[25] contains an excellent review of copper(I) chemistry including a considerable amount of information about copper cyanide complexes.

X-ray Structure Results. In the structure of $(CuCN)_3(HMTA)_2$ reported here, the same sort of ···Cu–CN–Cu–CN··· chains as described in the section above are found, with two-thirds of the Cu atoms three-coordinate and one-third four-coordinate. The three-coordinate coppers have a N from HMTA as the third ligand, and the four-coordinate coppers have two N atoms from two different HMTA molecules as the third and fourth ligands. This results in the one-dimensional HMTA molecules as the third and fourth ligands. This results in the one-dimensional CuCN chains being bound into a two-dimensional sheet by the HMTA molecules. The binding between chains utilizes, in repeating order, a four-coordinate Cu atom followed by two three-coordinate Cu atoms, which give rise to a repeating sequence of ring structures consisting of a Cu_6 ring followed by a Cu_4 ring.

It can be seen from the data in Table II for the three-coordinate copper that the bond distances and bond angles are quite similar to comparable copper(I) complexes. For example, three-coordinate copper atoms in double stalts[14,15,21] typically have Cu–C(cyanide) distances of 1.90–1.92 Å and Cu–N distances of 1.99–2.05 Å, whereas three-coordinate copper atoms in CuCN·L complexes (where L is a nitrogen base)[17] exhibit Cu–C distances of 1.86–1.90 Å, Cu–N distances of 1.89–2.00 Å, and Cu–L distances of 2.07–2.21 Å. Compound **1**, at the three-coordinate copper Cu2, shows Cu–C(N) distances of 1.867 (4) and 1.883 (4) Å and a Cu–L distance of 2.104 (3) Å. Turning to four-coordinate copper, the majority of previously reported complexes[17,19,20] have Cu–C(cyanide) distances of 1.88–1.99 Å, Cu–N distances of 1.99–2.00 Å, and Cu–L distances of 2.11–2.17 Å. In compound **1**, at the four-coordinate copper Cu1, the Cu–C(N) distances ae 1.905 (4) and 1.906 (4) Å and the Cu–L distance is 2.172 (3) Å. The ring structures within **1** show similarities to ring structures contained in other copper cyanide complexes . The $(CuCN)_6$ ring in $K[Cu_2(CN)_3]\cdot H_2O$[21] resembles the Cu_6 ring exhibited by **1**, and the Cu_4 ring in $CuCN\cdot N_2H_4$[20] resembles the Cu_4 ring in **1**.

Acknowledgment. I was fortunate to receive guidance during this project from specialists in coordination chemistry and/or X-ray crystallography since I am working outside of my specialty of organic synthesis. I am indebted to Professor Doyle Britton of the Department of Chemistry at the University of Minnesota for determining the X-ray crystal structure and also for reading and providing helpful comments on this paper. I also owe thanks to Professor Louis H. Pignolet, also of the University of Minnesota, for encouragement and for performing the magnetic susceptibility experiment. I am grateful to the following Macalester students who assisted with the experimental work on this project: Larry M. Rue, Michael W. Fordice, Jerry K. Larson, Bruce Williams, and Larry W. Dahl. I also wish to thank Professor Wayne C. Wolsey of Macalester College for encouragement and helpful discussions.

Supplementary Material Available: Figure 3 of Cu_4 and Cu_6 rings in **1**, a stereoview of the crystal packing, and tables of hydrogen atom coordinates, anisotropic thermal parameters, bond distances and angles, least-squares planes, and intermolecular distances for **1** (11 pages); a listing of observed and calculated structure factors of **1** (15 pages). Ordering information is given on any current masthead page.

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A New Hydrogen-Bonded Dinuclear Complex Involving Copper(II) Ions in a Pseudotetrahedral N_3O Environment: Molecular and Crystal Structure and Magnetic and Spectroscopic Properties

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The preparation, spectroscopic and magnetic properties, and crystal structure of $[CuLpy]_2\cdot 0.5H_2O$ are described (L stands for the dideprotonated form of 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil and py stands for pyridine). Crystals are monoclinic, of space group $P2_1/c$, with cell constants $a = 9.740$ (3) Å, $b = 19.258$ (7) Å, $c = 10.361$ (3) Å, $\beta = 108.57$ (3)°, and $Z = 2$. The structure was solved and refined to $R = 0.059$. The structure comprises discrete dinuclear entities resulting from pairwise association of mononuclear fragments via two extended bridging networks Cu–O–C–O···H–N–Cu, which comprise long hydrogen bonds. The geometry of each CuN_3O chromophore is intermediate between square planar and tetrahedral. The magnetic study points to an antiferromagnetic (singlet) ground state. The magnitude of the magnetic interaction is discussed on the basis of structural data.

Introduction

Formation of dinuclear complexes between mononuclear transition-metal fragments via hydrogen bonding was first suggested by Yoneda and Kida[1] for the series of complexes $[Co_2(Eta)_3(EtaH)_3]X_3$, where EtaH represents 2-aminoethanol and Eta the related anion. The occurrence of this bonding scheme was definitively established by structural studies performed on various copper(II), nickel(II), and cobalt(III) complexes involving amino and/or imino alcohols as ligands.[2-7] In these complexes

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Table I. Crystallographic Data for $[CuLpy]_2 \cdot 0.5H_2O$

chem formula $Cu_2C_{36}H_{33}N_{12}O_{8.5}$
space group: $P2_1/c$
fw: 448.4
$a = 9.740\ (4)$ Å
$b = 19.259\ (7)$ Å
$c = 10.361\ (3)$ Å
$\beta = 108.58\ (3)°$
$V = 1842\ (1)$ Å^3
$Z = 2$

$T = 20$ ● 1 °C
$\lambda = 0.71073$ Å
$\rho_{obs} = 1.63$ g cm^{-3}
$\rho_{calc} = 1.62$ g cm^{-3}
$\mu = 12.8$ cm^{-1}
transm coeff = 1.000–0.943
$R(F_o) = 0.059$
$R_w = 0.037$

each hydrogen bond functions as a triatomic bridge between two metal ions, according to the scheme M–O–H···O–M. The hydrogen bonds can be included in more extended bridges, which also are effective in pairwise association of mononuclear entities. Examples are found in the series $[Cu_2(tren)_2X_2)]^{2+}$, with X = NCO or NCS.[8-11] Also relevant to the present paper are two polynuclear complexes. The structure of the first complex[12] comprises ladderlike chains in which dimeric units are connected by hydrogen-bonded water molecules. In the second complex,[13] triatomic bridges, Cu–N–H···X–Cu (X = O or Br) support nonnegligible interchain interactions.

In conjunction with structural studies, the magnetic properties of these complexes were investigated. Generally, the triatomic bridges were found to support noticeable antiferromagnetic interactions with $|2J|$ values varying up to about 100 cm^{-1} in the copper–copper complexes of amino or imino alcohols.[2-7,14] Much reduced values were observed for complexes with polyatomic bridges.[8-11]

It may be emphasized that, despite this large variation of the exchange interaction, analyses of the structural data and magnetic properties did not yield any general correlation, even though some particular structural features were found to affect the magnitude of the interaction.

The present paper is devoted to a new example of hydrogen-bonded dinuclear copper(II) complex deriving from the ligand 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil, abbreviated as LH_2 hereafter.

Experimental Section

Synthesis. The ligand LH_2 was prepared by coupling diazotized anthranilic acid with 6-amino-1,3-dimethyluracil according to the method described by Lythgoe et al.[15] The compound was recrystallized from hot pyridine. Yield in pure product: 85%. Anal. Calcd for $C_{13}H_{13}N_5O_4$: C, 51.5; H, 4.3; N, 23.1. Found: C, 51.5; H, 4.3; N, 23.2.

The complex $[CuLpy]_2 \cdot 0.5H_2O$ was prepared according to two different procedures.

Method 1. To a heated and stirred suspension of LH_2 (1 g, 3.3 mmol) in ethanol/water (20/1, 100 mL) was added copper nitrate trihydrate (0.8 g 3.3 mmol) and the mixture refluxed for 1 h. At this point a green precipitate of the $[CuL]_2$ compound appeared, which was filtered off, washed with ethanol, and dried with ethyl ether. Anal. Calcd for $C_{26}H_{22}Cu_2N_{10}O_8$: C, 42.8; H, 3.0; N, 19.2; Cu, 16.6. Found: C, 42.4; H, 3.0; N, 19.1; Cu, 16.6. This complex was dissolved in pyridine/water (20/1, 50 mL), and the resulting black solution was allowed to stand at room temperature. Over the course of several days black needlelike crystals appeared. The crystals were collected by filtration, washed with ethanol, and air-dried. Anal. Calcd for $C_{36}H_{33}Cu_2N_{12}O_{8.5}$: C, 48.2; H, 3.7; N, 18.7; Cu, 14.2. Found: C, 48.2; H, 3.6; N, 19.2; Cu, 14.4. Yield: 79%.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[CuLpy]_2 \cdot 0.5H_2O$

atom	x	y	z	U_{eq},[a] Å^2
Cu	0.0230 (1)	0.01889 (5)	0.31856 (9)	0.0406 (5)
N(1)	–0.3736 (6)	0.0710 (3)	0.0291 (5)	0.040 (4)
C(1)	–0.4227 (9)	0.1271 (4)	0.0992 (7)	0.049 (5)
C(2)	–0.4559 (8)	0.0591 (4)	–0.1066 (7)	0.049 (5)
O(2)	–0.5701 (5)	0.0884 (3)	–0.1582 (5)	0.063 (4)
N(3)	–0.4005 (6)	0.0130 (3)	–0.1791 (5)	0.043 (4)
C(3)	–0.4845 (8)	0.0051 (5)	–0.3252 (7)	0.071 (6)
C(4)	–0.2761 (8)	–0.0258 (5)	–0.1261 (6)	0.050 (5)
O(4)	–0.2372 (6)	–0.0672 (3)	–0.1978 (5)	0.066 (4)
C(5)	–0.1963 (7)	–0.0138 (4)	0.0183 (6)	0.036 (4)
C(6)	–0.2414 (7)	0.0392 (3)	0.0934 (7)	0.030 (5)
N(6)	–0.1628 (6)	0.0553 (3)	0.2167 (5)	0.037 (4)
N(7)	–0.0864 (6)	–0.0575 (3)	0.0664 (5)	0.037 (4)
N(8)	0.0055 (6)	–0.0563 (3)	0.1889 (5)	0.035 (4)
C(9)	0.1115 (8)	–0.1098 (4)	0.2090 (7)	0.037 (5)
C(10)	0.2066 (8)	–0.1255 (4)	0.3370 (6)	0.035 (5)
C(11)	0.3145 (9)	–0.1763 (4)	0.3516 (8)	0.051 (5)
C(12)	0.3267 (9)	–0.2105 (4)	0.2395 (8)	0.056 (6)
C(13)	0.228 (1)	–0.1965 (4)	0.1118 (8)	0.058 (6)
C(14)	0.1243 (9)	–0.1474 (4)	0.0966 (7)	0.044 (5)
C(15)	0.2018 (8)	–0.0927 (4)	0.4698 (7)	0.037 (5)
O(16)	0.1473 (5)	–0.0328 (2)	0.4674 (4)	0.043 (3)
O(17)	0.2555 (6)	–0.1258 (3)	0.5757 (4)	0.051 (3)
N(18)	0.0944 (6)	0.1108 (3)	0.4104 (4)	0.037 (4)
C(19)	0.0742 (9)	0.1691 (4)	0.3367 (7)	0.056 (6)
C(20)	0.1194 (9)	0.2335 (4)	0.3862 (8)	0.057 (5)
C(21)	0.1995 (9)	0.2384 (4)	0.5228 (8)	0.064 (6)
C(22)	0.224 (1)	0.1805 (4)	0.6009 (8)	0.065 (6)
C(23)	0.1731 (8)	0.1183 (4)	0.5425 (7)	0.043 (5)
O(24)[a]	0.566 (3)	0.677 (1)	0.167 (2)	0.10 (1)

[a] U_{eq} has been defined as $U_{eq} = {}^{1}/_{3} \sum_i \sum_j U_{ij}(a_i^* a_j^*)(a_i \cdot a_j)$.

Method 2. The complex was prepared by adding solid copper nitrate trihydrate (0.8 g, 3.3 mmol) to a solution of LH_2 (1 g, 3.3. mmol) in pyridine (50 mL). The mixture was heated at 70 °C for 30 min, and the resulting black solution was set aside. Black crystals developed slowly, and after 2 weeks they were collected by filtration, washed with ethanol, and air-dried. Yield: 65%.

Physical Measurements. Electronic spectra were obtained with a Varian Cary 2300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, and ESR spectra, on a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz (X-band).

Magnetic susceptibility data were collected on powdered samples with the use of a Faraday-type magnetometer using mercury tetrakis(thiocyanato)cobaltate(II) (susceptibility at 20 °C: 16.44×10^{-6} cm^3 mol^{-1}) as a standard. Data were corrected for the diamagnetism of the ligands estimated from Pascal's constants[16] and for TIP.

X-ray Data Collection. Single-crystal data collection was performed at ambient temperature with a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The unit cell parameters for the black needle crystal were obtained from least-squares refinement of 20 well-centered reflections ($15° < 2\theta < 25°$). Because of the small size of the crystal and of its weak diffraction power, the data were collected until $2\theta = 45°$. The data were corrected for Lorentz and polarization factors and for dispersion. The three check reflections collected every 60 reflections showed no significant decrease during the course of data collection.

Structure Determination and Refinement. The structure was solved by using the SHELX system and subsequent ΔF syntheses.[17] A ΔF map calculated after anisotropic refinements of all non-hydrogen atoms of the complex revealed a single maximum of 1.2 e Å^{-3}, which was supposed to belong to the oxygen atom of the disordered water molecule. The anisotropic refinement of all non-hydrogen atoms of the molecule and isotropic refinement of the disordered oxygen atom with a fixed popu-

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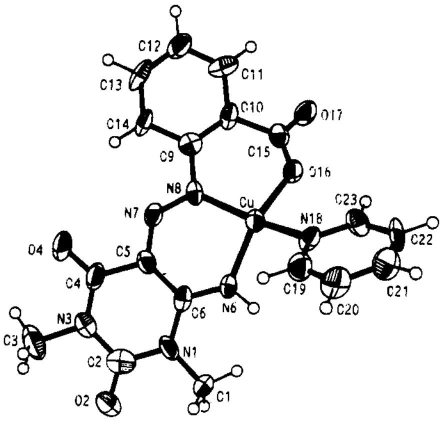

Figure 1. Labeling scheme of the asymetric complex unit of the structure. The thermal ellipsoids have been drawn at the 30% probability level.

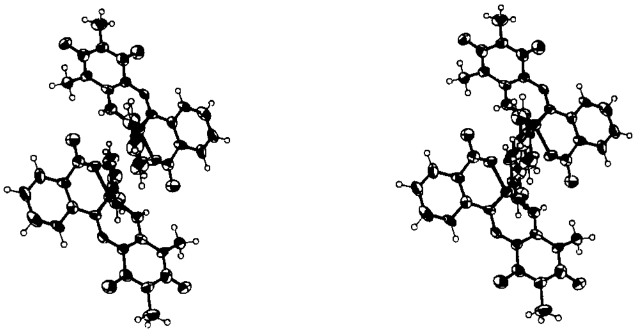

Figure 2. Stereoscopic view of the binuclear complex.

lation parameter of 0.2 converged to $R = 0.071$ and $R_w = 0.052$. The hydrogen atom bonded to N(6), and the strongest hydrogen atom maxima of each methyl group were picked at this stage from the ΔF map. The other hydrogen atoms, except those of the disordered water molecule, were placed at their calculated positions (C–H = 1.0 Å). In the final refinement, all non-hydrogen atoms of the complex molecule were refined anisotropically and the disordered oxygen atom was refined isotropically, but the hydrogen atoms were not refined. The final refined population parameter of 0.25 (1) Å^2 for the disordered oxygen atom agreed well with the population parameter of 0.24 (1) Å^2 observed for a crystal from another crystallization.

The function minimized was $\sum w(\Delta F)^2$ ($w = 1/\sigma_F^2$), resulting in a final R value of 0.059 ($R_w = 0.037$). Scattering factors were those included in the program system, and anomalous dispersion corrections were applied.[18] All calculations were carried out with a VAX 8650 computer, and refinements and all subsequent calculations were completed with XTAL system programs.[19]

Results

As described in the Experimental Section, the present complex is easily obtained either by reacting the ligand LH_2 and $Cu(NO_3)_2{\cdot}3H_2O$ in pyridine at 70 °C or by dissolving the complex $[CuL]_2$ and $Cu(NO_3)_2{\cdot}3H_2O$ in pyridine. According to analytical data, a suitable formulation would be $CuLpy{\cdot}0.25H_2O$ (L represents the dianionic form of LH_2 and py stands for pyridine). However, the EPR spectra of the solid sample were suggestive of some type of molecular interaction so that we have performed a detailed characterization including a structural determination. Due to the insolubility of the complex in all common solvents but pyridine, the latter was used to grow crystals suitable for the X-ray study and also to obtain solution spectra.

Description of the Structure. The molecular structure consists of neutral CuLpy entities held together in pairs by two N–H···O hydrogen bonds and related by a crystallographic center of inversion to form a binuclear complex to which is added half a water molecule. A stereoscopic view of the binuclear complex is shown in Figure 2, while the labeling scheme of the asymetric unit appears in Figure 1. The relevant bond distances and angles are quoted in Table III.

Table III. Interatomic Distances (Å) and Bond Angles (deg) for $[CuLpy]_2{\cdot}0.5H_2O$

Cu–N(6)	1.915 (5)	N(8)–C(9)	1.427 (9)
Cu–N(8)	1.945 (6)	C(9)–C(10)	1.388 (8)
Cu–O(16)	1.909 (4)	C(9)–C(14)	1.41 (1)
Cu–N(18)	2.026 (6)	C(10)–C(11)	1.41 (1)
N(1)–C(1)	1.46 (1)	C(10)–C(15)	1.53 (1)
N(1)–C(2)	1.397 (8)	C(11)–C(12)	1.37 (1)
N(1)–C(6)	1.388 (8)	C(12)–C(13)	1.39 (1)
C(2)–O(2)	1.210 (9)	C(13)–C(14)	1.35 (1)
C(2)–N(3)	1.38 (1)	C(15)–O(16)	1.266 (9)
N(3)–C(3)	1.482 (8)	C(15)–O(17)	1.232 (8)
N(3)–C(4)	1.380 (9)	N(18)–C(19)	1.337 (9)
C(4)–O(4)	1.23 (1)	N(18)–C(23)	1.347 (8)
C(4)–C(5)	1.468 (8)	C(19)–C(20)	1.360 (11)
C(5)–C(6)	1.44 (1)	C(20)–C(21)	1.384 (10)
C(5)–N(7)	1.327 (9)	C(21)–C(22)	1.353 (11)
C(6)–N(6)	1.300 (8)	C(22)–C(23)	1.363 (11)
N(7)–N(8)	1.300 (7)		

N(6)–Cu–N(8)	91.9 (2)	Cu–N(8)–N(7)	124.7 (4)
N(6)–Cu–O(16)	151.8 (3)	Cu–N(8)–C(9)	122.5 (4)
N(6)–Cu–N(18)	93.5 (2)	N(7)–N(8)–C(9)	111.8 (5)
N(8)–Cu–O(16)	93.6 (2)	N(8)–C(9)–C(10)	121.8 (6)
N(8)–Cu–N(18)	156.4 (3)	N(8)–C(9)–C(14)	120.1 (6)
O(16)–Cu–N(18)	92.4 (2)	C(10)–C(9)–C(14)	118.1 (7)
C(1)–N(1)–C(2)	116.5 (6)	C(9)–C(10)–C(11)	120.1 (7)
C(1)–N(1)–C(6)	119.1 (5)	C(9)–C(10)–C(15)	124.7 (7)
C(2)–N(1)–C(6)	123.9 (6)	C(11)–C(10)–C(15)	115.3 (6)
N(1)–C(2)–O(2)	121.4 (7)	C(10)–C(11)–C(12)	120.3 (6)
N(1)–C(2)–N(3)	117.0 (6)	C(11)–C(12)–C(13)	119.4 (8)
O(2)–C(2)–N(3)	121.6 (6)	C(12)–C(13)–C(14)	120.7 (8)
C(2)–N(3)–C(3)	115.9 (6)	C(9)–C(14)–C(13)	121.4 (6)
C(2)–N(3)–C(4)	125.4 (5)	C(10)–C(15)–O(16)	119.4 (6)
C(3)–N(3)–C(4)	118.7 (3)	C(10)–C(15)–O(17)	117.5 (6)
N(3)–C(4)–O(4)	120.8 (5)	O(16)–C(15)–O(17)	123.1 (7)
N(3)–C(4)–C(5)	115.7 (7)	Cu–O(16)–C(15)	111.8 (4)
O(4)–C(4)–C(5)	123.6 (7)	Cu–N(18)–C(19)	130.2 (4)
C(4)–C(5)–C(6)	120.7 (6)	Cu–N(18)–C(23)	124.7 (5)
C(4)–C(5)–N(7)	112.6 (6)	C(19)–N(18)–C(23)	115.1 (6)
C(6)–C(5)–N(7)	126.7 (5)	N(18)–C(19)–C(20)	125.3 (6)
N(1)–C(6)–C(5)	116.8 (5)	C(19)–C(20)–C(21)	117.2 (7)
N(1)–C(6)–N(6)	122.2 (6)	C(20)–C(21)–C(22)	119.4 (7)
C(5)–C(6)–N(6)	121.0 (6)	C(21)–C(22)–C(23)	119.3 (7)
Cu–N(6)–C(6)	127.7 (5)	N(18)–C(23)–C(22)	123.6 (7)
C(5)–N(7)–N(8)	125.3 (6)		

Table IV. Ideal and Observed Angles (deg) for $[CuLpy]_2{\cdot}0.5H_2O$

	T_d	exptl	D_{4h}
δa_1: N(18)–N(6)–N(8)–O(16)	70.3	34.2	0
δa_2: N(18)–N(8)–O(16)–N(6)	70.3	34.6	0
δa_3: N(18)–N(6)–O(16)–N(8)	70.3	130.8	180
δa_4: O(16)–N(6)–N(18)–N(8)	70.3	34.6	0
δa_5: O(16)–N(18)–N(8)–N(6)	70.3	130.4	180
δa_6: N(8)–N(18)–O(16)–N(6)	70.3	34.1	0
	$\Delta_D = 0$	$\Delta_D = 0.52$	$\Delta_D = 1$

Within each CuLpy entity, the copper ion is four-coordinated. The dideprotonated ligand L affords three coordination sites, namely one oxygen atom of the carboxylate group and two nitrogen atoms belonging to the deprotonated amino group and azo group, respectively. The fourth coordination site is the nitrogen atom of the pyridine. Consideration of the angles around the copper ion shows that the actual conformation of the CuN_3O chromophore is far removed from the limiting geometries, i.e. square planar or tetrahedral. The procedure proposed by Muetterties[20] locates the coordination polyhedron almost exactly at the middle of the $D_{4h} \leftrightarrow T_d$ deformation pathway (Table IV). The lengths of the Cu–N and Cu–O bonds are normal and do not deserve any particular comment.

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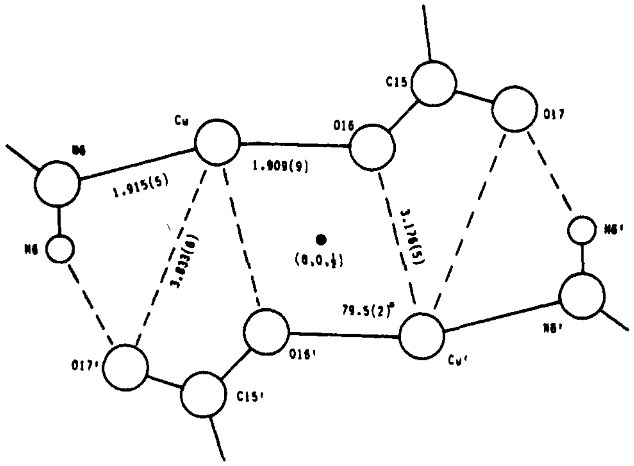

Figure 3. Simplified representation of the bridge.

The tridentate behavior of L results in the formation of two six-membered rings. Within each ring, significant deviations from planarity are observed (Table S4, supplementary material). However, these deviations are more important for the O(16)C(15)C(10)C(9)N(8)Cu ring (with maximum values of 0.214 (9) Å for C(15) and 0.226 (7) Å for N(8)) than for the N(8)N(7)C(5)C(6)N(6)Cu ring (with maximum values of 0.150 (7) and 0.144 (9) Å for N(8) and C(5), respectively). This has to be related to the fact that, according to the interatomic distances (Table III), all the bonds pertaining to the latter ring are intermediate between single and double bonds while, in the former ring, the bond lengths are less removed from their single-bond values. Consequently, the electronic delocalization and the propensity toward planarity are larger in the N(8)···N(6)Cu ring. As expected, the uracil, pyridine, and phenyl rings are almost planar with maximum deviations of 0.048 (9), 0.018 (9), and 0.018 (9) Å, respectively (Table S4, supplementary material).

Regarding the carboxylate group, the two C–O distances differ by 0.034 Å. Similar differences are reported in the literature[21-23] for complexes involving monodendate carboxylates. Interestingly, the plane of this CO_2 group makes an angle of 24.3 (3)° with the plane of the aromatic ring to which it is linked. This results in a lowering of the conjugation which is reflected in the C(10)–C(15) separation of ca. 1.528 (9) Å, which is not very different from the value attributable to a single C–C bond. With a value of ca. 123.1 (7)°, the O(16)–C(15)–O(17) angle is smaller than expected on the basis of literature data.[22,24] This may be due to the presence of a hydrogen bond between O(17) and the N(6′)H group of the other mononuclear entity.

Indeed, the mononuclear fragments are associated into hydrogen-bonded dinuclear units about an inversion center (0, 0, $^1/_2$). A simplified view of the bridging framework is given in Figure 3. The donor–acceptor separation (N–O = 2.919 (8) Å) is large with respect to the values reported in the literature[3-7] for complexes involving triatomic bridges: O···O varies from ca. 2.31 to 2.52 Å. However, larger values are observed for extended bridges such as Cu–N–C–O···H–N–Cu (O···N ~ 2.95 Å). In a recent paper,[25] dynamic hydrogen bonds involved in the formation of a dicopper complex have been shown to display O···O values of 2.867 (7) and 2.956 (7) Å.

It may be underlined that despite the length of the bridges, the Cu···Cu distance of 3.993 (2) Å observed in the present complex is the shortest among the reported values (Cu···Cu separations of ca. 5 Å are observed for triatomic bridges and even larger values for polyatomic bridges).

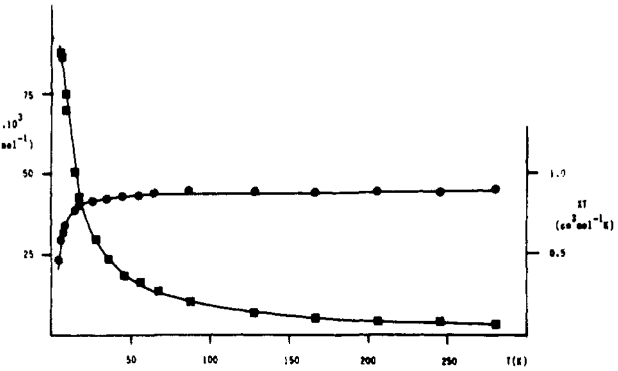

Figure 4. Plot of the $\chi_M T$ product (●) and magnetic susceptibility (■) ($10^3\chi_M$) vs temperature for $[CuLpy]_2 \cdot 0.5H_2O$. The solid lines were generated from the best-fit magnetic parameters.

Examination of Figure 3 shows that the oxygen atom O(16) of one mononuclear fragment occupies a position relative to the copper atom Cu′ of the second fragment, which may suggest possible axial interactions and the occurrence of distorted pentacoordinated CuN_3O_2 chromophores. However the Cu′–O(16) and Cu–O(16′) distances of 3.176 (5) Å are seemingly too long for coordination and even semicoordination, as does the intermolecular separation Cu···O(4)^i (i = symmetry operation $-x$, $-y$, $-z$).

Spectroscopic and Magnetic Data. The solid-state infrared spectrum displays features characteristic of the coordination modes of LH_2 and py. The ν(N=N) absorption, which appears at 1410 cm^{-1}, is shifted to lower frequencies by ca. 120 cm^{-1} with respect to its position in the free ligand. Well-defined absorptions are observed at 3475, 3209, and 3060 cm^{-1}. They are attributable to ν(O—H) from the water molecule, ν(N—H) from the deprotonated amino group of L, and ν(C—H) from pyridine, respectively. The ν_{as}(COO) and ν_s(COO) shifts are observed at 1650 and 1400 cm^{-1}. The large splitting is consistent with the bonding mode of the carboxylate group.[21,23,26]

The diffuse-reflectance spectrum comprises four bands in the 300–900-nm range. Two bands of medium intensity centered at 360 and 415 nm are attributable to ligand transitions and/or charge-transfer absorptions. The remaining bands, which peak at 570 and 700 nm, are less intense. They may be attributed to d–d transitions. In solution spectra (pyridine), they appear at 580 and 700 nm.

The ESR spectrum of a powdered sample of $[CuLpy]_2$ is characteristic of a dinuclear system with resonances corresponding to $\Delta M = \pm 1$ ($g_\parallel = 2.20$ and $g_\perp = 2.07$) and $\Delta M = \pm 2$ ($g_{min} = 4.49$) transitions. These signals are devoid of any hyperfine structure. Axial spectra are observed for solutions in pyridine at low temperature. The $\Delta M = \pm 2$ transitions are no longer detected, but hyperfine and superhyperfine structures are clearly perceptible. These spectra are characterized by the following parameters: $g_\parallel = 2.22_2$; $g_\perp = 2.03_4$ and $|A_\parallel(Cu)| = 168 \times 10^{-4}$ cm^{-1}; $|A_\perp(N)| = 15 \times 10^{-4}$ cm^{-1}.

At room temperature the usual isotropic spectrum is obtained with $g_{iso} = 2.110$, $|A_{iso}(Cu)| = 74 \times 10^{-4}$ cm^{-1}, and $|A_{iso}(N)| = 14 \times 10^{-4}$ cm^{-1}.

Magnetic susceptibility data were collected on a powdered sample in the range 5–280 K. The temperature dependence of the product χT (or the magnetic moment $\mu = 2.828\,(\chi T)^{1/2}$) is characteristic of a weakly spin-coupled copper(II) dinuclear complex with a singlet ground state. Indeed, μ varies from 1.91 μ_B at 281.4 K down to 1.35 μ_B at 5.2 K. The experimental susceptibilities corrected for the diamagnetism of the ligands (198 $\times 10^{-6}$ cgs units) are fitted to the Bleaney–Bowers equation[27] to yield $g = 2.18$ and $2J = -6.5$ cm^{-1}.

The criterion of the best fit is the minimum value ($R = 2 \times 10^{-4}$) of the function $R = \sum(X_{obs} - X_{calc})^2/\sum(X_{obs})^2$. The best

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fit is indicated by the solid line in Figure 4, where the experimental values are represented by circles.

Discussion

Analyses of the crystallographic data in terms of the Muetterties procedure show that the geometry of the CuN_3O chromophore lies almost exactly halfway between square planar and tetrahedral. The ESR parameters are expected to reflect such an intermediate geometry.[28-33] Indeed, it is well-known that the main differences seen in the spectra of tetrahedral complexes as compared to those of closely related square-planar ones are larger values of $g_\parallel$ and smaller values of $|A_\parallel(\text{Cu})|$ and $|A_{\text{iso}}(\text{Cu})|$. Comparing $[\text{CuLpy}]_2$ with the previously reported[34] complex $[\text{AECuImH}]^+$ (AE stands for the monoanionic form of 7-amino-4-methyl-5-aza-3-hepten-2-one, and ImH stands for for imidazole), which has a square-planar CuN_3O chromophore, actually shows that $[\text{CuLpy}]_2$ displays a larger value of $g_\parallel$ (2.22_2 instead of 2.17_5) and lower values of $|A_\parallel(\text{Cu})|$ (168×10^{-4} cm^{-1} instead of 190×10^{-4} cm^{-1}) and $|A_{\text{iso}}(\text{Cu})|$ (74×10^{-4} cm^{-1} instead of 86×10^{-4} cm^{-1}).

Interestingly, the ESR parameters characterizing $[\text{CuLpy}]_2$ fall nicely into the correlations [$A_\parallel(\text{Cu})$ vs $g_\parallel$; $A_{\text{iso}}(\text{Cu})$ vs g_{iso}; $g_\parallel$ vs ω;[35] $g_\parallel/A_\parallel$ vs ω[35]] that have been reported[28,29,31] for complexes with CuN_4 and CuN_2O_2 cores. Furthermore, applying these correlations to the data derived from solution spectra suggests that the geometry of the coordination polyhedron is not very different in solution and in the solid state with ω values of ca. 40 and 36.0°, respectively. Consistent with this suggestion is the fact that almost identical d–d spectra are obtained for solution and solid samples.

The assignment of d–d transition bands is difficult in the case of pseudotetrahedral copper(II) complexes.[28-31] Keeping in consideration that the correlations of the ESR parameters vs ω which have been established for CuN_4 complexes seemingly hold well for $[\text{CuL py}]_2$, we are inclined to think that its electronic properties would be mainly dependent on the structural distortion and not very sensitive to the difference of ligand field strengths of the O and N donors in the N_3O set. In the hypothesis, the graph[36] representing the dependence of the energy of the d levels on the values of ω may be used to propose the following attributions:

$$E[xz, yz \rightarrow x^2 - y^2],\ E[xy \rightarrow x^2 - y^2] \quad 14\,300\ \text{cm}^{-1}$$

$$E[z^2 \rightarrow x^2 - y^2] \quad 17\,550\ \text{cm}^{-1}$$

The reference axes are chosen so as to lead to a $b_1(d_{x^2-y^2})$ ground state for tetrahedral and square-planar geometries, in accordance with ESR data.

As noted previously, the geometry of the CuN_3O core seems to be little affected by the physical state. However, there is a major difference between solution and solid samples. In the former case, the ESR spectrum does not provide any indication of magnetic interaction whereas, for solid samples, convincing evidences of interaction are gained from the ESR spectrum and the temperature dependence of the magnetic susceptibility. Analysis of these data leads to a singlet–triplet separation of $|2J| = 6.5$ cm^{-1}, the singlet being the ground state. Obviously, the $|2J|$ value is small with respect to the values obtained for the majority of dinuclear copper(II) complexes of amino- or imino-alcohols (up to ca. 95 cm^{-1}).[2-5] Assuming that the exchange is supported by the bridging network, a better comparison would involve complexes with extended bridges rather than triatomic bridges. In the series $[\text{Cu}_2(\text{tren})_2\text{X}_2]^{2+}$, extended bridges have been shown[11] to mediate smaller interactions ($|2J| \leq 0.32$ cm^{-1} for X = NCO; $|2J| \leq 0.14$ cm^{-1} for X = NCS) than do the O–C–O···H–N bridges in $[\text{CuLpy}]_2$. This is rather unexpected especially as the structure of the latter complex displays several features which have been previously recognized as unfavorable to the propagation of strong interactions. First, the separation between the donor and the acceptor of the hydrogen bond is very large. Then, the geometry of the CuN_3O chromophore is severely distorted from square planar.[37,38] This distortion and the rotation of the carboxylate group with respect to the plane of the phenyl ring result in nonplanarity of the bridge. Finally, it may be noted that the carboxylate groups participate in the bridging network in a syn–anti conformation, which is much less effective in mediating exchange interaction than the syn–syn conformation.[12,13,21,39]

As previously reported, there is to date no general relationship between magnetic and structural data for the hydrogen-bonded dinuclear complexes. However, some particular structural features have been shown to affect the magnitude of the interaction in closely related complexes. Applying these empirical trends to $[\text{CuLpy}]_2$ suggests that the interaction would be lower than observed. The reasons for this discrepancy are not obvious. One may speculate that in addition to the O–C–O···H–N bridges, other exchange pathways may be operative. In the description of the structure we have noted that the Cu···Cu separation is smaller in $[\text{CuLpy}]_2$ than in other hydrogen-bonded dicopper complexes. However, the observed value is too large for supporting a significant direct exchange process. Similarly, it is unlikely that the pathways through O(16) and O(16′), which comprise long Cu–O(16′) and Cu–O(16) separations, can mediate noticeable interaction. Furthermore, the spin densities along these directions are low due to the fact that these axes are approximately orthogonal to the planes of the magnetic orbitals of the $d_{x^2-y^2}$ type. There remains the possibility that, even though these secondary pathways are expected to support very feable contribution, their cumulative effect could lead to a relatively large value of the exchange interaction.

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Supplementary Material Available: Tables S1–S4, listing crystallographic data, fractional atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal displacement parameters, bond lengths and angles, and least-squares planes (11 pages); structure factor tables (9 pages). Ordering information is given on any current masthead page.

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