

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, UA No. 420, Université de Paris-Sud, 91405 Orsay, France, and the Laboratoire de Chimie des Métaux de Transition, UA No. 419, Université Pierre et Marie Curie, 75232 Paris, France

## Crystal Structures and Magnetic Properties of $\mu$ -Phenolato Copper(II) Binuclear Complexes with Hydroxo, Azido, and Cyanato-*O* Exogenous Bridges

Talal Mallah,<sup>1a</sup> Marie-Laure Boillot,<sup>1a</sup> Olivier Kahn,\*<sup>1a</sup> Jacqueline Gouteron,<sup>1b</sup> Suzanne Jeannin,<sup>1b</sup> and Yves Jeannin\*<sup>1b</sup>

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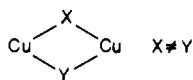
Three complexes of formula  $[\text{Cu}_2(\text{Fdm})\text{(X)}](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$  were synthesized. Fdm<sup>-</sup> is the binucleating ligand deriving from the condensation of 1 mol of 2,6-diformyl-4-methylphenol with 2 mol of 1,1-dimethylethylenediamine. X is OH<sup>-</sup> (1), 1,1-N<sub>3</sub><sup>-</sup> (2), and 1,1-OCN<sup>-</sup> (3). The three crystal structures were refined. Compound 1: space group  $P2_1/c$ ,  $a = 9.124$  (2) Å,  $b = 30.950$  (8) Å,  $c = 9.174$  (5) Å,  $\beta = 99.01$  (3)°,  $Z = 4$ . Compound 2: space group  $P2_1/c$ ,  $a = 8.797$  (3) Å,  $b = 31.84$  (2) Å,  $c = 9.253$  (5) Å,  $\beta = 98.97$  (3)°,  $Z = 4$ . Compound 3: space group  $P2_1/c$ ,  $a = 8.814$  (2) Å,  $b = 31.645$  (6) Å,  $c = 9.233$  (5) Å,  $\beta = 81.19$  (4)°,  $Z = 4$ . In 1-3, the copper(II) ions of the binuclear unit are bridged by the phenolic oxygen atom and by the X exogenous ligand in the plane of the macrocycle and by two perchlorato groups above and below this plane. In 2, N<sub>3</sub><sup>-</sup> bridges in an end-on fashion, and in 3, OCN<sup>-</sup> bridges by its oxygen atom. It is the first time that this kind of coordination for OCN<sup>-</sup> is structurally characterized. The magnetic properties of 1-3 were investigated. In the three compounds, the copper(II) ions are antiferromagnetically coupled with singlet-triplet energy gaps of -367 cm<sup>-1</sup> for 1, -86.5 cm<sup>-1</sup> for 2, and -3.8 cm<sup>-1</sup> for 3. The X-band EPR spectra of 2 and 3 are typical of triplet states with axial zero-field splitting parameters larger than the incident quantum. A first attempt of rationalization of the magnetic properties is proposed.

### Introduction

The understanding of the mechanism of the interaction between paramagnetic centers in polynuclear compounds has made great strides recently.<sup>2</sup> This is particularly true when the interacting centers have only one unpaired electron like copper(II). The magnetic properties of a large number of copper(II) binuclear complexes can be qualitatively interpreted in the frame of the active-electron approximation.<sup>3</sup> In this approximation, the singlet-triplet (S-T) energy gap  $J$  arising from the interaction between two local doublets may be expressed as the sum of an antiferromagnetic contribution  $J_{AF}$  and a ferromagnetic contribution  $J_F$ . If the natural magnetic orbitals  $\phi_A$  and  $\phi_B$  are utilized to describe the unpaired electrons, then  $J_{AF}$  appears to vary as  $S^2$  and  $J_F$  as  $j$  where  $S$  is the overlap integral  $\langle \phi_A(1)/\phi_B(1) \rangle$  and  $j$  the two-electron-exchange integral  $\langle \phi_A(1) \phi_B(2)/r_{12}^{-1}/\phi_A(2) \phi_B(1) \rangle$  between the magnetic orbitals.<sup>2,3</sup>

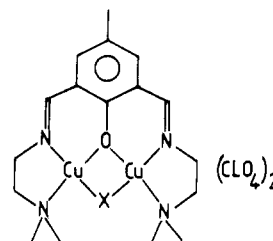
Recently, it has been shown that the active-electron approximation can become invalid when a bridging ligand has highest occupied molecular orbitals (HOMO) close in energy to the magnetic orbitals.<sup>4</sup> This occurs, for instance, with the end-on azido bridge, which has been found to favor a ferromagnetic interaction,<sup>5-7</sup> of which the origin has been attributed to a spin polarization effect.<sup>4</sup>

Another difficulty<sup>8,9</sup> arises when two copper(II) ions are bridged by at least two nonsimilar ligands with a network of the type



The question at hand is then the following: is it possible to decompose the observed interaction into contributions arising from each of the CuXCu and CuYCu linkages? The goal of this paper

is to approach this problem. For that, three compounds noted  $[\text{Cu}_2(\text{Fdm})\text{(X)}](\text{ClO}_4)_2$  of the type



with X = OH<sup>-</sup> (1), 1,1-N<sub>3</sub><sup>-</sup> (2), and 1,1-OCN<sup>-</sup> (3) have been synthesized, their crystal structure solved, and their magnetic properties investigated. The complex 3 is the first one containing an end-on cyanato bridge bound by the oxygen atom.

Several copper(II) complexes designed from 2,6-diformyl-4-methylphenol and containing an exogenous bridge X in addition to the endogenous phenolato bridge have already been reported,<sup>10-20</sup> and in some cases the magnetic properties have also been investigated. This work, however, is the first one where three structurally characterized complexes that only differ by the nature of X are compared.

### Experimental Section

**Syntheses.** Compounds 1-3 were prepared as follows. A  $2 \times 10^{-3}$  mol sample of 1,1-dimethylethylenediamine was added to  $10^{-3}$  mol of 2,6-diformyl-4-methylphenol in 50 mL of methanol. Then, were successively added  $10^{-3}$  mol of LiOH,  $2 \times 10^{-3}$  mol of copper(II) perchlorate, and finally  $10^{-3}$  mol of LiOH for 1, NaN<sub>3</sub> for 2, or NaNCO for 3. The mixture was stirred and filtered. Single crystals of 2 were simply obtained by slow evaporation. For 1, a microcrystalline powder precipitated

- (1) (a) Université de Paris-Sud. (b) Université Pierre et Marie Curie.
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Table I. Crystallographic Data Collection

	compd 1	compd 2	compd 3
formula	[Cu <sub>2</sub> (N <sub>4</sub> OC <sub>17</sub> H <sub>27</sub> )(OH)](ClO <sub>4</sub> ) <sub>2</sub>	[Cu <sub>2</sub> (N <sub>4</sub> OC <sub>17</sub> H <sub>27</sub> (N <sub>3</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	[Cu <sub>2</sub> (N <sub>4</sub> OC <sub>17</sub> H <sub>27</sub> (NCO)](ClO <sub>4</sub> ) <sub>2</sub>
cryst color	dark green	dark green	dark green
cryst size, mm	0.44 × 0.15 × 0.13	0.7 × 0.4 × 0.03	0.52 × 0.16 × 0.03
$\rho_{\text{measd}}$ , kg m <sup>-3</sup>	1.66 × 10 <sup>3</sup>	1.74 × 10 <sup>3</sup>	not measd (1 cryst obtained)
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	20.04	20.0	20.19
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	9.124 (2)	8.797 (3)	8.814 (2)
<i>b</i> , Å	30.950 (8)	31.84 (2)	31.645 (6)
<i>c</i> , Å	9.174 (5)	9.253 (5)	9.233 (5)
$\beta$ , deg	99.01 (3)	98.97 (3)	81.19 (4)
<i>V</i> , Å <sup>3</sup>	2558.7	2560	2544
<i>Z</i>	4	4	4
diffractometer	Nonius CAD4	Philips PW 1100	Nonius CAD4
monochromator	graphite	graphite	graphite
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.71070)	Mo K $\alpha$ (0.71070)	Mo K $\alpha$ (0.71070)
temp, °C	21	21	21
scan type	$\theta$ -2 $\theta$	$\theta$ -2 $\theta$	$\theta$ -2 $\theta$
scan range, deg	1.0 + 0.345 tan $\theta$	0.9 + 0.3 tan $\theta$	1.1 + 0.345 tan $\theta$
2 $\theta$ range, deg	3-43	3-50	3-40
scan speed, deg min <sup>-1</sup>	depending upon reflcn	0.6	depending upon reflcn
bkgd	half of scan time, in two parts; before and after every scan, in fixed position		
no. of std reflcns	3, measd every 100 reflcns	3, measd every 2 h	2, measd every 100 reflcns
reflcns measd	<i>hkl</i> , $\bar{h}kl$ ; 2 octants	<i>hkl</i> , $\bar{h}kl$ ; 2 octants	<i>hkl</i> , $\bar{h}kl$ ; 2 octants
no. of reflcns collcd	3469	2646	2804
no. of independents reflcns merged	2707	2218	2430
no. of reflcns kept for refinement	2090 ( $F > 3\sigma(F)$ )	1984 ( $F > 3\sigma(F)$ )	1485 ( $F > 3\sigma(F)$ )

Table II. Structure Refinements

	compd 1	compd 2	compd 3
computing program		SHELX 76	
diffusion factors		<i>b</i>	
minimized function		$R_w = [\sum_i w_i ( F_o - F_c )^2 / \sum_i w_i F_o^2]^{1/2}$ , with $w_i = 1/\sigma$	
secondary extinction		none obsd	
abs cor		not applied	
weighting scheme	$w = 0.26/\sigma^2(F)$	$w = 2.68/\sigma^2(F)$	$w = 0.71/\sigma^2(F)$
av shift/esd (last cycle)	0.08	0.03	0.09
$N_{\text{ref}}/N_{\text{var}}$ params	8.3	7.5	4.2 <sup>a</sup>
final residuals			
<i>R</i>	0.046	0.056	0.049
<i>R<sub>w</sub></i>	0.041	0.049	0.041

<sup>a</sup>This poor value is due to the fact that only one small crystal was obtained. <sup>b</sup>International Tables for X-ray Crystallography; Kynoch: Birmingham, England, 1974; Vol. IV.

that was filtered, dried, and redissolved in 100 mL of cold water. Very slow evaporation gave single crystals suitable for X-ray work. For 3, again a microcrystalline powder precipitated that was filtered, dried, and redissolved in 20 mL of a 50/50 mixture of tetrahydrofuran and acetonitrile. Slow evaporation gave the single crystal used for the structure determination. Anal. Calcd for C<sub>17</sub>H<sub>29.6</sub>N<sub>4</sub>O<sub>10.8</sub>Cl<sub>2</sub>Cu<sub>2</sub> (1): C, 30.90; H, 4.51; N, 8.48; O, 26.15; Cl, 10.73; Cu, 19.23. Found: C, 30.6; H, 4.54; N, 8.23; O, 26.05; Cl, 10.05; Cu, 18.98. Calcd for C<sub>17</sub>H<sub>27</sub>N<sub>7</sub>O<sub>9</sub>-Cl<sub>2</sub>Cu<sub>2</sub> (2): C, 30.41; H, 4.05; N, 14.60; O, 21.45; Cl, 10.56; Cu, 18.93. Found: C, 30.46; H, 4.16; N, 14.40; O, 20.83; Cl, 10.12; Cu, 19.3. Calcd for C<sub>18</sub>H<sub>27</sub>N<sub>4</sub>O<sub>10</sub>Cl<sub>2</sub>Cu<sub>2</sub> (3): C, 32.20; H, 4.05; N, 10.43; O, 23.83; Cl, 10.56; Cu, 18.93. Found: C, 31.91; H, 4.15; N, 9.94; O, 23.65; Cl, 10.44; Cu, 18.2.

**Crystallographic Data Collections and Refinement of Structures.** The structures of complexes 1-3 have been solved by x-ray diffraction. Preliminary Laue and precession photographs led to monoclinic unit cells for the three compounds; the space group *P*2<sub>1</sub>/*c* was established from systematic absences. Cell dimensions were obtained by least squares from the setting angles of 20 reflections for 1 and of 25 reflections for 2 and 3. General crystallographic information is given in Tables I and II for the three compounds. Anomalous dispersion was corrected. Concerning absorption, no correction was carried out due to the flat shape of  $\psi$  scan in the three cases.

**Compound 1.** The centrosymmetric direct method of SHELX 76 showed two copper atoms, two bridging oxygen atoms, and the four nitrogen atoms belonging to copper environments. Successive Fourier syntheses and refinements led to  $R = 0.110$  with isotropic thermal parameters and 0.059 with anisotropic thermal parameters for all atoms other than hydrogens. The Fourier difference map showed two supplementary peaks corresponding to two water molecules, O<sub>3</sub> and O<sub>4</sub>, which were refined isotropically. Systematic refinements of their occupation factors for several fixed *U* values led to the following best values of occupation

factors: 0.5 for O<sub>3</sub> ( $U = 0.12$ ) and 0.3 for O<sub>4</sub> ( $U = 0.12$ ). The 27 hydrogens were added in calculated positions and allowed to shift according to the movement of the parent atoms with a refinable overall isotropic thermal parameter. The CH<sub>3</sub> groups were refined as rigid groups with the AFIX option of SHELX program. A last Fourier difference map then showed a hydrogen atom of the O<sub>3</sub> water molecule; it was refined with fixed coordinates and a variable isotropic temperature factor. Atomic parameters and thermal parameters are shown in Tables III and XIII,<sup>21</sup> and main distances and bond angles in Tables IV and V.

**Compound 2.** A three-dimensional Patterson map showed copper and chlorine atoms. Successive Fourier syntheses and refinements dropped *R* to 0.129 with isotropic temperature factors and to 0.078 with anisotropic temperature factors for the 37 atoms other than hydrogens. Hydrogen atoms were added in the same way as for 1. The atomic parameters and the thermal parameters are given in Tables VI and XIV,<sup>21</sup> and main distances and bond angles in Tables VII and VIII.

**Compound 3.** The centrosymmetric direct method of SHELX 76 showed 35 atoms. After refinement of their coordinates, a successive Fourier map showed the last carbon atoms. Refinements led to  $R = 0.098$  with isotropic thermal parameters and 0.064 with anisotropic thermal parameters for the 37 atoms other than hydrogens. The 27 hydrogens were added in the same way as previously. *R* dropped to 0.053. At this stage of the refinement, we focused our attention on the cyanato group; is it coordinated to copper atoms through its nitrogen or through its oxygen? Attempts have been carried out in both possible cases. The following results have been obtained: *R* slightly lower for OCN (0.0490) than for NCO (0.0495); thermal parameters  $B_{\text{eq}}$  and  $U_{\text{iso}}$  more realistic for OCN ( $B_{\text{eq}} = 5.35$  for O and 8.70 for N,  $U_{\text{iso}} = 0.063$  for O and 0.094 for N) than for NCO ( $B_{\text{eq}} = 3.8$  for N and 10.96 for O,  $U_{\text{iso}} = 0.038$  for N and

**Table III.** Atomic Parameters<sup>a</sup> for **1** (OH Bridge)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>iso</sub> , Å <sup>2</sup>
Cu <sub>1</sub>	0.26206 (9)	0.09950 (3)	0.69751 (9)	
Cu <sub>2</sub>	0.45261 (8)	0.13838 (3)	0.50503 (9)	
O <sub>1</sub>	0.2751 (4)	0.1529 (1)	0.5870 (5)	
O <sub>2</sub>	0.4393 (5)	0.0867 (2)	0.6170 (5)	
N <sub>11</sub>	0.2459 (8)	0.0477 (2)	0.8245 (7)	
N <sub>12</sub>	0.0956 (6)	0.1218 (2)	0.7800 (6)	
C <sub>11</sub>	0.094 (2)	0.0503 (4)	0.857 (2)	
C <sub>12</sub>	0.034 (1)	0.0899 (3)	0.872 (1)	
C <sub>13</sub>	0.252 (1)	0.0069 (3)	0.752 (1)	
C <sub>14</sub>	0.347 (3)	0.0515 (6)	0.956 (2)	
C <sub>15</sub>	0.0460 (7)	0.1601 (3)	0.7695 (8)	
C <sub>16</sub>	0.1009 (6)	0.1956 (2)	0.6913 (7)	
C <sub>17</sub>	0.0433 (7)	0.2367 (3)	0.7112 (8)	
N <sub>21</sub>	0.6328 (6)	0.1263 (2)	0.4101 (7)	
N <sub>22</sub>	0.4490 (6)	0.1946 (2)	0.4125 (6)	
C <sub>21</sub>	0.6871 (9)	0.1694 (3)	0.377 (1)	
C <sub>22</sub>	0.5577 (9)	0.1982 (3)	0.310 (1)	
C <sub>23</sub>	0.7478 (9)	0.1019 (4)	0.507 (1)	
C <sub>24</sub>	0.590 (1)	0.1013 (3)	0.273 (1)	
C <sub>25</sub>	0.3786 (8)	0.2279 (2)	0.4440 (8)	
C <sub>26</sub>	0.2669 (7)	0.2283 (2)	0.5414 (7)	
C <sub>27</sub>	0.2071 (7)	0.2685 (2)	0.5677 (7)	
C <sub>1</sub>	0.2164 (6)	0.1909 (2)	0.6066 (7)	
C <sub>2</sub>	0.0954 (7)	0.2732 (2)	0.6522 (8)	
C <sub>3</sub>	0.038 (1)	0.3181 (3)	0.683 (1)	8.0 (4)
O <sub>3</sub>	0.533 (2)	-0.0012 (6)	0.536 (2)	7.4 (6)
O <sub>4</sub>	0.667 (3)	0.0419 (9)	0.832 (3)	
Cl <sub>1</sub>	0.1386 (2)	0.06269 (6)	1.3293 (2)	
O <sub>11</sub>	0.2504 (6)	0.4072 (2)	0.8025 (6)	
O <sub>12</sub>	0.1022 (6)	0.4305 (2)	0.9733 (6)	
O <sub>13</sub>	0.0095 (8)	0.4303 (3)	0.7233 (7)	
O <sub>14</sub>	0.188 (1)	0.4797 (2)	0.817 (1)	
Cl <sub>2</sub>	0.6109 (2)	0.33398 (7)	0.3860 (2)	
O <sub>21</sub>	0.4638 (5)	0.3417 (2)	0.4108 (6)	
O <sub>22</sub>	0.6088 (7)	0.3207 (2)	0.2380 (6)	
O <sub>23</sub>	0.6720 (8)	0.2997 (3)	0.4806 (8)	
O <sub>24</sub>	0.6954 (9)	0.3713 (3)	0.414 (1)	

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

**Table IV.** Main Interatomic Distances (Å)<sup>a</sup> for **1**

Cu-Cu Distance			
Cu <sub>1</sub> -Cu <sub>2</sub>	2.924 (1) in binuclear unit		
Cu Surroundings			
Cu <sub>1</sub> -O <sub>1</sub>	1.951 (4)	Cu <sub>2</sub> -O <sub>1</sub>	1.942 (4)
Cu <sub>1</sub> -O <sub>2</sub>	1.922 (5)	Cu <sub>2</sub> -O <sub>2</sub>	1.915 (5)
Cu <sub>1</sub> -N <sub>11</sub>	2.000 (6)	Cu <sub>2</sub> -N <sub>21</sub>	2.013 (6)
Cu <sub>1</sub> -N <sub>12</sub>	1.928 (6)	Cu <sub>2</sub> -N <sub>22</sub>	1.933 (6)
Cu <sub>1</sub> ...O <sub>12</sub>	2.505 (6)	Cu <sub>2</sub> ...O <sub>11</sub>	2.787 (6)
Cu <sub>1</sub> ...O <sub>21</sub>	3.07 (1)	Cu <sub>2</sub> ...O <sub>22</sub>	2.693 (6)
Bridging Phenolato Ligand			
O <sub>1</sub> -C <sub>1</sub>		1.319 (8)	
C <sub>1</sub> -C <sub>16</sub>	1.411 (9)	C <sub>2</sub> -C <sub>27</sub>	1.38 (1)
C <sub>17</sub> -C <sub>16</sub>	1.40 (1)	C <sub>26</sub> -C <sub>27</sub>	1.394 (9)
C <sub>2</sub> -C <sub>17</sub>	1.37 (1)	C <sub>1</sub> -C <sub>26</sub>	1.411 (9)
C <sub>2</sub> -C <sub>3</sub>	1.53 (1)	C <sub>26</sub> -C <sub>25</sub>	1.46 (1)
C <sub>16</sub> -C <sub>15</sub>	1.44 (1)	C <sub>25</sub> -N <sub>22</sub>	1.272 (9)
N <sub>12</sub> -C <sub>15</sub>	1.27 (1)	N <sub>22</sub> -C <sub>22</sub>	1.47 (1)
N <sub>12</sub> -C <sub>12</sub>	1.47 (1)	C <sub>22</sub> -C <sub>21</sub>	1.52 (1)
C <sub>12</sub> -C <sub>11</sub>	1.36 (2)	N <sub>21</sub> -C <sub>21</sub>	1.47 (1)
C <sub>11</sub> -N <sub>11</sub>	1.47 (2)	N <sub>21</sub> -C <sub>23</sub>	1.47 (1)
C <sub>13</sub> -N <sub>11</sub>	1.43 (1)	N <sub>21</sub> -C <sub>24</sub>	1.47 (1)
C <sub>14</sub> -N <sub>11</sub>	1.40 (2)		
Perchlorate Ions			
Cl <sub>1</sub> -O <sub>11</sub>	1.432 (6)	Cl <sub>2</sub> -O <sub>21</sub>	1.416 (5)
Cl <sub>1</sub> -O <sub>12</sub>	1.428 (6)	Cl <sub>2</sub> -O <sub>22</sub>	1.415 (6)
Cl <sub>1</sub> -O <sub>13</sub>	1.423 (6)	Cl <sub>2</sub> -O <sub>23</sub>	1.430 (8)
Cl <sub>1</sub> -O <sub>14</sub>	1.396 (8)	Cl <sub>2</sub> -O <sub>24</sub>	1.390 (8)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

0.124 for O). Therefore, it appears that the cyanato group is coordinated through its oxygen atom. The last refinements then were performed with

**Table V.** Main Bond Angles (deg)<sup>a</sup> for **1**

Cu Surroundings			
N <sub>11</sub> -Cu <sub>1</sub> -N <sub>12</sub>	85.6 (3)	N <sub>21</sub> -Cu <sub>2</sub> -N <sub>22</sub>	86.2 (2)
O <sub>1</sub> -Cu <sub>1</sub> -O <sub>2</sub>	81.5 (2)	O <sub>1</sub> -Cu <sub>2</sub> -O <sub>2</sub>	81.9 (2)
N <sub>11</sub> -Cu <sub>1</sub> -O <sub>2</sub>	101.6 (2)	N <sub>21</sub> -Cu <sub>2</sub> -O <sub>2</sub>	101.7 (2)
N <sub>12</sub> -Cu <sub>1</sub> -O <sub>1</sub>	91.0 (2)	N <sub>22</sub> -Cu <sub>2</sub> -O <sub>1</sub>	90.3 (2)
Binuclear Unit			
O <sub>1</sub> -Cu <sub>1</sub> -O <sub>2</sub>	81.5 (2)	Cu <sub>1</sub> -O <sub>1</sub> -Cu <sub>2</sub>	97.4 (2)
O <sub>1</sub> -Cu <sub>2</sub> -O <sub>2</sub>	81.9 (2)	Cu <sub>1</sub> -O <sub>2</sub> -Cu <sub>2</sub>	99.3 (2)
Phenolato Ligand			
C <sub>1</sub> -O <sub>1</sub> -Cu <sub>1</sub>	128.8 (4)	C <sub>1</sub> -O <sub>1</sub> -Cu <sub>2</sub>	129.9 (4)
Cu <sub>1</sub> -N <sub>11</sub> -C <sub>11</sub>	103.5 (7)	Cu <sub>2</sub> -N <sub>21</sub> -C <sub>21</sub>	104.4 (5)
N <sub>11</sub> -C <sub>11</sub> -C <sub>12</sub>	118 (1)	N <sub>21</sub> -C <sub>21</sub> -C <sub>22</sub>	110.4 (6)
C <sub>11</sub> -C <sub>12</sub> -N <sub>12</sub>	111 (1)	C <sub>21</sub> -C <sub>22</sub> -N <sub>22</sub>	105.1 (7)
C <sub>12</sub> -N <sub>12</sub> -Cu <sub>1</sub>	112.5 (5)	C <sub>22</sub> -N <sub>22</sub> -Cu <sub>2</sub>	112.4 (5)
C <sub>12</sub> -N <sub>12</sub> -C <sub>15</sub>	120.7 (7)	C <sub>22</sub> -N <sub>22</sub> -C <sub>25</sub>	120.0 (6)
N <sub>12</sub> -C <sub>15</sub> -C <sub>16</sub>	127.2 (7)	N <sub>22</sub> -C <sub>25</sub> -C <sub>26</sub>	125.0 (7)
C <sub>15</sub> -C <sub>16</sub> -C <sub>1</sub>	123.0 (6)	C <sub>25</sub> -C <sub>26</sub> -C <sub>1</sub>	124.0 (6)
C <sub>1</sub> -C <sub>16</sub> -C <sub>17</sub>	119.1 (6)	C <sub>1</sub> -C <sub>26</sub> -C <sub>27</sub>	119.6 (6)
C <sub>16</sub> -C <sub>17</sub> -C <sub>2</sub>	122.8 (7)	C <sub>26</sub> -C <sub>27</sub> -C <sub>2</sub>	122.2 (6)
C <sub>3</sub> -C <sub>2</sub> -C <sub>17</sub>	121.7 (7)	C <sub>3</sub> -C <sub>2</sub> -C <sub>27</sub>	120.4 (7)
O <sub>1</sub> -C <sub>1</sub> -C <sub>16</sub>	121.3 (6)	O <sub>1</sub> -C <sub>1</sub> -C <sub>26</sub>	120.4 (6)
C <sub>16</sub> -C <sub>1</sub> -C <sub>26</sub>	118.3 (6)	C <sub>27</sub> -C <sub>2</sub> -C <sub>17</sub>	117.9 (7)
Perchlorate Ions			
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>12</sub>	109.7 (4)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>22</sub>	109.5 (3)
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>13</sub>	108.6 (4)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>23</sub>	108.6 (4)
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>14</sub>	110.6 (5)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>24</sub>	110.0 (5)
O <sub>13</sub> -Cl <sub>1</sub> -O <sub>14</sub>	109.4 (5)	O <sub>23</sub> -Cl <sub>2</sub> -O <sub>24</sub>	110.7 (5)
O <sub>12</sub> -Cl <sub>1</sub> -O <sub>13</sub>	108.8 (4)	O <sub>22</sub> -Cl <sub>2</sub> -O <sub>23</sub>	108.2 (4)
O <sub>12</sub> -Cl <sub>1</sub> -O <sub>14</sub>	109.7 (5)	O <sub>22</sub> -Cl <sub>2</sub> -O <sub>24</sub>	109.9 (5)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

**Table VI.** Atomic Parameters<sup>a</sup> for **2** (N<sub>3</sub> Bridge)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu <sub>1</sub>	0.2535 (1)	0.10069 (4)	0.2519 (1)
Cu <sub>2</sub>	0.4478 (1)	0.13728 (4)	0.0485 (1)
O <sub>P</sub>	0.2660 (5)	0.1517 (2)	0.1376 (6)
N <sub>P1</sub>	0.4429 (8)	0.0892 (3)	0.1751 (9)
N <sub>P2</sub>	0.552 (1)	0.0680 (3)	0.239 (1)
N <sub>P3</sub>	0.662 (1)	0.0472 (3)	0.302 (1)
N <sub>11</sub>	0.2317 (9)	0.0499 (2)	0.3744 (9)
N <sub>12</sub>	0.0839 (7)	0.1244 (3)	0.3386 (7)
C <sub>11</sub>	0.065 (1)	0.0502 (3)	0.395 (1)
C <sub>12</sub>	0.022 (1)	0.0938 (3)	0.433 (1)
C <sub>13</sub>	0.335 (1)	0.0543 (4)	0.517 (1)
C <sub>14</sub>	0.261 (1)	0.0087 (3)	0.308 (1)
C <sub>15</sub>	0.0330 (9)	0.1613 (3)	0.3229 (9)
C <sub>16</sub>	0.0897 (9)	0.1942 (3)	0.2414 (9)
C <sub>17</sub>	0.0316 (9)	0.2336 (3)	0.2567 (9)
C <sub>1</sub>	0.2077 (9)	0.1886 (3)	0.1520 (9)
N <sub>21</sub>	0.6260 (8)	0.1240 (3)	-0.0577 (8)
N <sub>22</sub>	0.4412 (8)	0.1902 (3)	-0.0452 (8)
C <sub>21</sub>	0.604 (2)	0.1520 (5)	-0.178 (2)
C <sub>22</sub>	0.554 (1)	0.1946 (3)	-0.152 (1)
C <sub>23</sub>	0.770 (1)	0.1302 (5)	0.037 (1)
C <sub>24</sub>	0.620 (1)	0.0804 (5)	-0.120 (2)
C <sub>25</sub>	0.369 (1)	0.2223 (3)	-0.0196 (9)
C <sub>26</sub>	0.256 (1)	0.2247 (3)	0.0847 (9)
C <sub>27</sub>	0.196 (1)	0.2641 (3)	0.1074 (9)
C <sub>2</sub>	0.083 (1)	0.2705 (3)	0.197 (1)
C <sub>3</sub>	0.025 (1)	0.3138 (3)	0.226 (1)
Cl <sub>1</sub>	0.5971 (3)	0.1735 (1)	0.4255 (3)
O <sub>11</sub>	0.4433 (7)	0.1655 (2)	0.4495 (7)
O <sub>12</sub>	0.5956 (8)	0.1836 (3)	0.2746 (7)
O <sub>13</sub>	0.6869 (8)	0.1377 (2)	0.4610 (8)
O <sub>14</sub>	0.6605 (8)	0.2078 (2)	0.5115 (8)
Cl <sub>2</sub>	0.1450 (3)	0.0650 (1)	-0.1134 (3)
O <sub>11</sub>	0.2512 (7)	0.0972 (2)	-0.1401 (7)
O <sub>22</sub>	0.1015 (7)	0.0708 (2)	0.0291 (7)
O <sub>23</sub>	0.011 (1)	0.0678 (4)	-0.2158 (9)
O <sub>24</sub>	0.215 (1)	0.0260 (3)	-0.116 (1)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

**Table VII.** Main Interatomic Distances (Å)<sup>a</sup> for 2

Cu-Cu Distance			
Cu <sub>1</sub> -Cu <sub>2</sub>	2.972 (2) in binuclear unit		
Cu Surroundings			
Cu <sub>1</sub> -O <sub>p</sub>	1.951 (5)	Cu <sub>2</sub> -O <sub>p</sub>	1.966 (5)
Cu <sub>1</sub> -N <sub>p1</sub>	1.947 (8)	Cu <sub>2</sub> -N <sub>p1</sub>	1.933 (8)
Cu <sub>1</sub> -N <sub>11</sub>	2.001 (8)	Cu <sub>2</sub> -N <sub>21</sub>	2.022 (8)
Cu <sub>1</sub> -N <sub>12</sub>	1.954 (7)	Cu <sub>2</sub> -N <sub>22</sub>	1.892 (8)
Cu <sub>1</sub> ···O <sub>11</sub>	3.074 (7)	Cu <sub>2</sub> ···O <sub>21</sub>	2.595 (6)
Cu <sub>1</sub> ···O <sub>22</sub>	2.468 (6)	Cu <sub>2</sub> ···O <sub>12</sub>	2.720 (7)
Azido Bridge			
N <sub>p1</sub> -N <sub>p2</sub>	1.24 (1)	N <sub>p2</sub> -N <sub>p3</sub>	1.24 (1)
Bridging Phenolato Ligand			
O <sub>p</sub> -C <sub>1</sub>	1.30 (1)		
C <sub>1</sub> -C <sub>16</sub>	1.44 (1)	C <sub>21</sub> -N <sub>21</sub>	1.42 (2)
C <sub>16</sub> -C <sub>17</sub>	1.37 (1)	N <sub>21</sub> -C <sub>23</sub>	1.44 (1)
C <sub>17</sub> -C <sub>2</sub>	1.41 (1)	N <sub>21</sub> -C <sub>24</sub>	1.50 (2)
C <sub>2</sub> -C <sub>3</sub>	1.51 (1)	C <sub>16</sub> -C <sub>15</sub>	1.42 (1)
C <sub>2</sub> -C <sub>27</sub>	1.40 (1)	C <sub>15</sub> -N <sub>12</sub>	1.26 (1)
C <sub>27</sub> -C <sub>26</sub>	1.39 (1)	N <sub>12</sub> -C <sub>12</sub>	1.47 (1)
C <sub>26</sub> -C <sub>1</sub>	1.41 (1)	C <sub>12</sub> -C <sub>11</sub>	1.50 (1)
C <sub>26</sub> -C <sub>25</sub>	1.49 (1)	C <sub>11</sub> -N <sub>11</sub>	1.51 (1)
C <sub>25</sub> -N <sub>22</sub>	1.25 (1)	C <sub>11</sub> -N <sub>11</sub>	1.51 (1)
N <sub>22</sub> -C <sub>22</sub>	1.51 (1)	N <sub>11</sub> -C <sub>13</sub>	1.49 (1)
C <sub>22</sub> -C <sub>21</sub>	1.46 (2)	N <sub>11</sub> -C <sub>14</sub>	1.49 (1)
Perchlorate Ions			
Cl <sub>1</sub> -O <sub>11</sub>	1.429 (7)	Cl <sub>2</sub> -O <sub>21</sub>	1.436 (7)
Cl <sub>1</sub> -O <sub>12</sub>	1.432 (7)	Cl <sub>2</sub> -O <sub>22</sub>	1.443 (7)
Cl <sub>1</sub> -O <sub>13</sub>	1.397 (8)	Cl <sub>2</sub> -O <sub>23</sub>	1.398 (8)
Cl <sub>1</sub> -O <sub>14</sub>	1.414 (8)	Cl <sub>2</sub> -O <sub>24</sub>	1.38 (1)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

**Table VIII.** Main Bond Angles (deg)<sup>a</sup> for 2

Cu Surroundings			
N <sub>p1</sub> -Cu <sub>1</sub> -O <sub>p</sub>	80.5 (3)	N <sub>p1</sub> -Cu <sub>2</sub> -O <sub>p</sub>	80.4 (3)
O <sub>p</sub> -Cu <sub>1</sub> -N <sub>12</sub>	90.7 (3)	O <sub>p</sub> -Cu <sub>2</sub> -N <sub>22</sub>	90.9 (3)
N <sub>p1</sub> -Cu <sub>1</sub> -N <sub>11</sub>	102.6 (3)	N <sub>p1</sub> -Cu <sub>2</sub> -N <sub>21</sub>	102.8 (3)
N <sub>11</sub> -Cu <sub>1</sub> -N <sub>12</sub>	86.1 (3)	N <sub>21</sub> -Cu <sub>2</sub> -N <sub>22</sub>	86.2 (3)
Binuclear Unit			
O <sub>p</sub> -Cu <sub>1</sub> -N <sub>p1</sub>	80.5 (3)	Cu <sub>1</sub> -O <sub>p</sub> -Cu <sub>2</sub>	98.7 (2)
O <sub>p</sub> -Cu <sub>2</sub> -N <sub>p1</sub>	80.4 (3)	Cu <sub>1</sub> -N <sub>p1</sub> -Cu <sub>2</sub>	100.0 (4)
Azido Bridge			
N <sub>p1</sub> -N <sub>p2</sub> -N <sub>p3</sub>	179 (1)		
Phenolato Bridging Ligand			
C <sub>16</sub> -C <sub>1</sub> -C <sub>26</sub>	116.7 (8)	C <sub>12</sub> -C <sub>11</sub> -N <sub>11</sub>	108.9 (8)
C <sub>1</sub> -C <sub>26</sub> -C <sub>27</sub>	121.7 (8)	C <sub>11</sub> -N <sub>11</sub> -Cu <sub>1</sub>	104.3 (5)
C <sub>26</sub> -C <sub>27</sub> -C <sub>2</sub>	122.7 (9)	C <sub>13</sub> -N <sub>11</sub> -C <sub>14</sub>	109.3 (8)
C <sub>2</sub> -C <sub>17</sub> -C <sub>16</sub>	125.2 (9)	C <sub>26</sub> -C <sub>25</sub> -N <sub>22</sub>	125.2 (9)
C <sub>17</sub> -C <sub>16</sub> -C <sub>1</sub>	119.2 (8)	C <sub>25</sub> -N <sub>22</sub> -Cu <sub>2</sub>	128.5 (7)
C <sub>27</sub> -C <sub>2</sub> -C <sub>3</sub>	122.1 (9)	C <sub>25</sub> -N <sub>22</sub> -C <sub>22</sub>	117.0 (8)
C <sub>17</sub> -C <sub>2</sub> -C <sub>3</sub>	123.5 (9)	N <sub>22</sub> -C <sub>22</sub> -C <sub>21</sub>	105.6 (9)
C <sub>16</sub> -C <sub>15</sub> -N <sub>12</sub>	126.9 (8)	C <sub>22</sub> -C <sub>21</sub> -N <sub>21</sub>	117 (1)
C <sub>15</sub> -N <sub>12</sub> -Cu <sub>1</sub>	126.5 (6)	C <sub>21</sub> -N <sub>21</sub> -Cu <sub>2</sub>	103.4 (7)
C <sub>15</sub> -N <sub>12</sub> -C <sub>12</sub>	122.0 (8)	C <sub>23</sub> -N <sub>21</sub> -C <sub>24</sub>	109.5 (9)
N <sub>12</sub> -C <sub>12</sub> -C <sub>11</sub>	110.0 (9)		
Perchlorate Ions			
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>12</sub>	109.0 (4)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>22</sub>	109.8 (4)
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>13</sub>	109.5 (5)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>23</sub>	109.9 (5)
O <sub>12</sub> -Cl <sub>1</sub> -O <sub>13</sub>	109.4 (5)	O <sub>22</sub> -Cl <sub>2</sub> -O <sub>23</sub>	107.2 (5)
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>14</sub>	110.5 (5)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>24</sub>	109.7 (6)
O <sub>12</sub> -Cl <sub>1</sub> -O <sub>14</sub>	108.6 (5)	O <sub>22</sub> -Cl <sub>2</sub> -O <sub>24</sub>	108.1 (5)
O <sub>13</sub> -Cl <sub>1</sub> -O <sub>14</sub>	109.8 (4)	O <sub>23</sub> -Cl <sub>2</sub> -O <sub>24</sub>	112.1 (7)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

the O-bonded cyanato group. Atomic parameters and thermal parameters are shown in Tables IX and XV,<sup>21</sup> and main interatomic distances and bond angles in Tables X and XI.

**Magnetic Measurements.** They were carried out with a Faraday type magnetometer equipped with a He continuous-flow cryostat. Independ-

**Table IX.** Atomic Parameters<sup>a</sup> for 3 (OCN Bridge)

atom	x/a	y/b	z/c
Cu <sub>1</sub>	0.2611 (2)	0.10058 (4)	0.7530 (2)
Cu <sub>2</sub>	0.4536 (1)	0.13746 (5)	0.9527 (2)
O	0.447 (1)	0.0884 (3)	0.832 (1)
C	0.569 (4)	0.0660 (8)	0.751 (3)
N	0.686 (2)	0.0455 (5)	0.687 (2)
O <sub>p</sub>	0.2727 (8)	0.1518 (2)	0.8673 (8)
N <sub>11</sub>	0.241 (1)	0.0491 (3)	0.630 (1)
N <sub>12</sub>	0.093 (1)	0.1235 (3)	0.665 (1)
C <sub>11</sub>	0.077 (2)	0.0503 (4)	0.608 (2)
C <sub>12</sub>	0.032 (1)	0.0933 (4)	0.568 (2)
C <sub>13</sub>	0.269 (2)	0.0083 (5)	0.698 (2)
C <sub>14</sub>	0.344 (2)	0.0549 (5)	0.489 (2)
C <sub>15</sub>	0.042 (1)	0.1607 (4)	0.679 (1)
C <sub>16</sub>	0.098 (1)	0.1945 (4)	0.760 (1)
C <sub>17</sub>	0.037 (1)	0.2346 (4)	0.743 (1)
N <sub>21</sub>	0.633 (1)	0.1243 (4)	1.057 (1)
N <sub>22</sub>	0.448 (1)	0.1918 (4)	1.048 (1)
C <sub>21</sub>	0.629 (3)	0.156 (1)	1.160 (4)
C <sub>22</sub>	0.559 (2)	0.1947 (5)	1.151 (2)
C <sub>23</sub>	0.624 (3)	0.0833 (9)	1.127 (3)
C <sub>24</sub>	0.776 (2)	0.1265 (9)	0.960 (2)
C <sub>25</sub>	0.374 (1)	0.2244 (4)	1.016 (1)
C <sub>26</sub>	0.263 (1)	0.2253 (4)	0.917 (1)
C <sub>27</sub>	0.201 (1)	0.2648 (4)	0.892 (1)
C <sub>1</sub>	0.213 (1)	0.1890 (4)	0.849 (1)
C <sub>2</sub>	0.091 (1)	0.2712 (4)	0.804 (1)
C <sub>3</sub>	0.032 (2)	0.3142 (4)	0.776 (2)
Cl <sub>1</sub>	0.1542 (4)	0.0634 (1)	1.1160 (4)
O <sub>11</sub>	0.254 (1)	0.0961 (3)	0.147 (1)
O <sub>12</sub>	0.107 (1)	0.0705 (3)	-0.023 (1)
O <sub>13</sub>	0.028 (2)	0.0624 (7)	0.223 (1)
O <sub>14</sub>	0.235 (2)	0.0256 (4)	0.110 (2)
Cl <sub>2</sub>	0.6049 (4)	0.3275 (1)	0.0753 (3)
O <sub>21</sub>	0.4512 (9)	0.1647 (4)	0.549 (1)
O <sub>22</sub>	0.604 (1)	0.1824 (4)	0.726 (1)
O <sub>23</sub>	0.695 (1)	0.1363 (3)	0.537 (1)
O <sub>24</sub>	0.665 (1)	0.2069 (4)	0.488 (1)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

**Table X.** Main Interatomic Distances (Å)<sup>a</sup> for 3

Cu-Cu Distance			
Cu <sub>1</sub> -Cu <sub>2</sub>	2.933 (2) in binuclear unit		
Cu Surroundings			
Cu <sub>1</sub> -O	1.928 (9)	Cu <sub>2</sub> -O	1.92 (1)
Cu <sub>1</sub> -O <sub>p</sub>	1.945 (7)	Cu <sub>2</sub> -O <sub>p</sub>	1.938 (7)
Cu <sub>1</sub> -N <sub>11</sub>	2.009 (9)	Cu <sub>2</sub> -N <sub>21</sub>	2.017 (9)
Cu <sub>1</sub> -N <sub>12</sub>	1.937 (9)	Cu <sub>2</sub> -N <sub>22</sub>	1.93 (1)
Cu <sub>1</sub> ···O <sub>12</sub>	2.483 (9)	Cu <sub>2</sub> ···O <sub>11</sub>	2.655 (9)
Cu <sub>1</sub> ···O <sub>21</sub>	3.08 (1)	Cu <sub>2</sub> ···O <sub>22</sub>	2.71 (1)
Bridging Cyanato Ligand			
O-C	1.40 (4)	C-N	1.28 (4)
Bridging Phenolato Ligand			
O <sub>p</sub> -C <sub>1</sub>	1.31 (1)		
C <sub>1</sub> -C <sub>16</sub>	1.41 (1)	C <sub>1</sub> -C <sub>26</sub>	1.41 (1)
C <sub>16</sub> -C <sub>17</sub>	1.39 (2)	C <sub>26</sub> -C <sub>27</sub>	1.40 (2)
C <sub>2</sub> -C <sub>17</sub>	1.41 (2)	C <sub>2</sub> -C <sub>27</sub>	1.37 (2)
C <sub>2</sub> -C <sub>3</sub>	1.49 (2)	C <sub>26</sub> -C <sub>25</sub>	1.44 (2)
C <sub>16</sub> -C <sub>15</sub>	1.44 (2)	N <sub>22</sub> -C <sub>25</sub>	1.28 (1)
N <sub>12</sub> -C <sub>15</sub>	1.26 (1)	N <sub>22</sub> -C <sub>22</sub>	1.47 (1)
N <sub>12</sub> -C <sub>12</sub>	1.47 (1)	C <sub>22</sub> -C <sub>21</sub>	1.37 (3)
C <sub>12</sub> -C <sub>11</sub>	1.48 (2)	N <sub>21</sub> -C <sub>21</sub>	1.39 (2)
N <sub>11</sub> -C <sub>11</sub>	1.49 (1)	N <sub>21</sub> -C <sub>23</sub>	1.45 (2)
N <sub>11</sub> -C <sub>13</sub>	1.48 (2)	N <sub>21</sub> -C <sub>24</sub>	1.43 (2)
N <sub>11</sub> -C <sub>14</sub>	1.48 (2)		
Perchlorate Ions			
Cl <sub>1</sub> -O <sub>11</sub>	1.42 (1)	Cl <sub>2</sub> -O <sub>21</sub>	1.430 (9)
Cl <sub>1</sub> -O <sub>12</sub>	1.427 (9)	Cl <sub>2</sub> -O <sub>22</sub>	1.42 (1)
Cl <sub>1</sub> -O <sub>13</sub>	1.37 (1)	Cl <sub>2</sub> -O <sub>23</sub>	1.41 (1)
Cl <sub>1</sub> -O <sub>14</sub>	1.39 (1)	Cl <sub>2</sub> -O <sub>24</sub>	1.41 (1)

<sup>a</sup>Standard deviations on the last significant figures are given in parentheses.

Table XI. Main Bond Angles (deg)<sup>a</sup> for 3

Cu Surroundings			
N <sub>11</sub> -Cu <sub>1</sub> -N <sub>12</sub>	85.8 (4)	N <sub>21</sub> -Cu <sub>2</sub> -N <sub>22</sub>	86.2 (4)
N <sub>11</sub> -Cu <sub>1</sub> -O	101.9 (4)	N <sub>21</sub> -Cu <sub>2</sub> -O	102.0 (4)
N <sub>12</sub> -Cu <sub>1</sub> -O <sub>p</sub>	91.3 (4)	N <sub>22</sub> -Cu <sub>2</sub> -O <sub>p</sub>	90.7 (3)
Binuclear Unit			
O <sub>p</sub> -Cu <sub>1</sub> -O	81.0 (4)	Cu <sub>1</sub> -O <sub>p</sub> -Cu <sub>2</sub>	98.1 (3)
O <sub>p</sub> -Cu <sub>2</sub> -O	81.4 (3)	Cu <sub>1</sub> -O-Cu <sub>2</sub>	99.3 (4)
Cyanato Ligand			
Cu <sub>1</sub> -O-C	122 (1)	Cu <sub>2</sub> -O-C	129 (1)
O-C-N	175 (2)		
Phenolato Ligand			
C <sub>1</sub> -O <sub>p</sub> -Cu <sub>1</sub>	128.5 (6)	C <sub>1</sub> -O <sub>p</sub> -Cu <sub>2</sub>	129.4 (6)
Cu <sub>1</sub> -N <sub>11</sub> -C <sub>11</sub>	103.3 (7)	Cu <sub>2</sub> -N <sub>21</sub> -C <sub>21</sub>	103.7 (9)
N <sub>11</sub> -C <sub>11</sub> -C <sub>12</sub>	111 (1)	N <sub>21</sub> -C <sub>21</sub> -C <sub>22</sub>	124 (2)
C <sub>11</sub> -C <sub>12</sub> -N <sub>12</sub>	108 (1)	C <sub>21</sub> -C <sub>22</sub> -N <sub>22</sub>	110 (1)
C <sub>12</sub> -N <sub>12</sub> -Cu <sub>1</sub>	112.7 (8)	C <sub>22</sub> -N <sub>22</sub> -Cu <sub>2</sub>	112.2 (8)
C <sub>12</sub> -N <sub>12</sub> -C <sub>15</sub>	120.9 (9)	C <sub>22</sub> -N <sub>22</sub> -C <sub>25</sub>	121 (1)
N <sub>12</sub> -C <sub>15</sub> -C <sub>16</sub>	127 (1)	N <sub>22</sub> -C <sub>25</sub> -C <sub>26</sub>	126 (1)
C <sub>15</sub> -C <sub>16</sub> -C <sub>1</sub>	123 (1)	C <sub>25</sub> -C <sub>26</sub> -C <sub>1</sub>	124 (1)
C <sub>1</sub> -C <sub>16</sub> -C <sub>17</sub>	120 (1)	C <sub>1</sub> -C <sub>26</sub> -C <sub>27</sub>	120 (1)
C <sub>16</sub> -C <sub>17</sub> -C <sub>2</sub>	123 (1)	C <sub>26</sub> -C <sub>27</sub> -C <sub>2</sub>	124 (1)
C <sub>3</sub> -C <sub>2</sub> -C <sub>17</sub>	122 (1)	C <sub>3</sub> -C <sub>2</sub> -C <sub>27</sub>	122 (1)
O <sub>p</sub> -C <sub>1</sub> -C <sub>16</sub>	122 (1)	O <sub>p</sub> -C <sub>1</sub> -C <sub>26</sub>	121.0 (9)
C <sub>17</sub> -C <sub>2</sub> -C <sub>27</sub>	115 (1)	C <sub>16</sub> -C <sub>1</sub> -C <sub>26</sub>	117 (1)
Perchlorate Ions			
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>12</sub>	110.0 (8)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>22</sub>	109.6 (6)
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>13</sub>	109.5 (8)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>23</sub>	109.5 (7)
O <sub>11</sub> -Cl <sub>1</sub> -O <sub>14</sub>	107.6 (8)	O <sub>21</sub> -Cl <sub>2</sub> -O <sub>24</sub>	108.6 (7)
O <sub>13</sub> -Cl <sub>1</sub> -O <sub>14</sub>	111 (1)	O <sub>23</sub> -Cl <sub>2</sub> -O <sub>24</sub>	109.4 (7)
O <sub>12</sub> -Cl <sub>1</sub> -O <sub>13</sub>	109.7 (8)	O <sub>22</sub> -Cl <sub>2</sub> -O <sub>23</sub>	110.2 (8)
O <sub>12</sub> -Cl <sub>1</sub> -O <sub>14</sub>	108.8 (8)	O <sub>22</sub> -Cl <sub>2</sub> -O <sub>24</sub>	109.5 (8)

<sup>a</sup> Standard deviations on the last significant figures are given in parentheses.

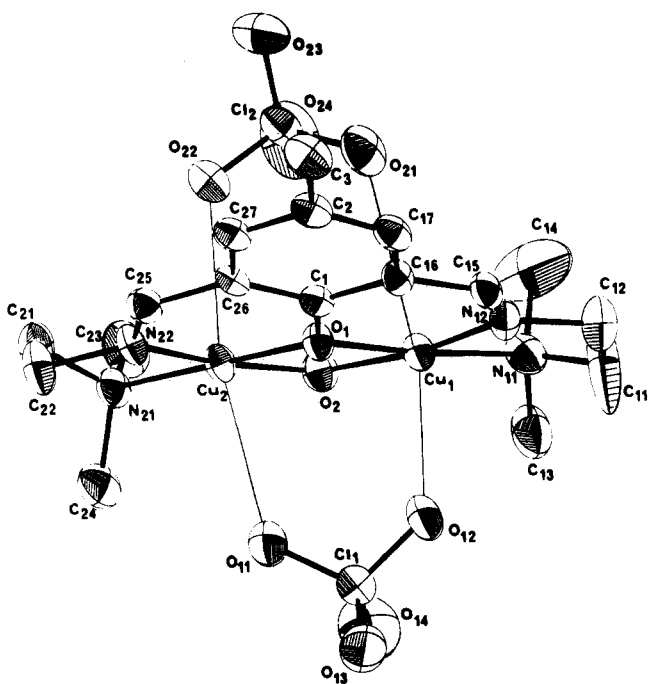


Figure 1. Perspective view of  $[\text{Cu}_2(\text{Fdmen})(\text{OH})](\text{ClO}_4)_2$  (1).

ence of the magnetic susceptibility vs. the magnetic field was checked at room temperature. Diamagnetic corrections were estimated at  $-304 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for 1 and  $-290 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for 2 and 3. The EPR spectra were recorded with a Bruker ER 200 D spectrometer equipped with a He continuous-flow cryostat, a Hall probe, and a frequency meter.

#### Description of the Structures

Each unit cell contains four binuclear  $[\text{Cu}_2(\text{Fdmen})(\text{X})]^{2+}$  cations and eight perchlorate anions, with 3.2 water molecules in addition for compound 1. Both copper atoms of the binuclear

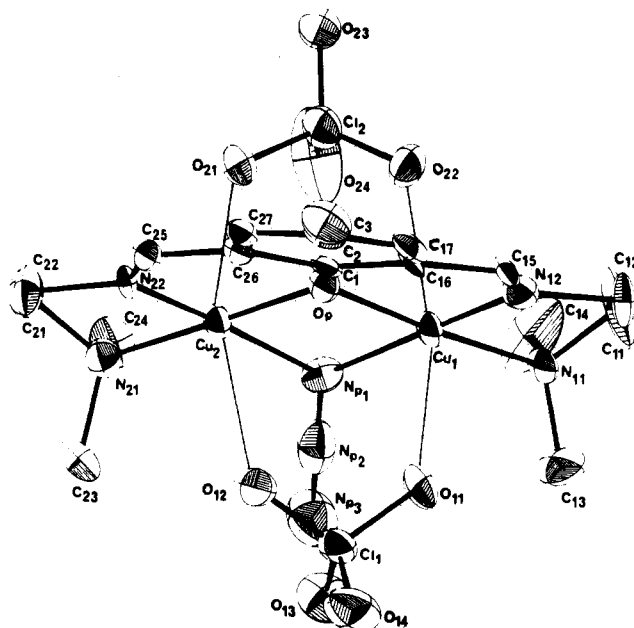


Figure 2. Perspective view of  $[\text{Cu}_2(\text{Fdmen})(\text{N}_3)](\text{ClO}_4)_2$  (2).

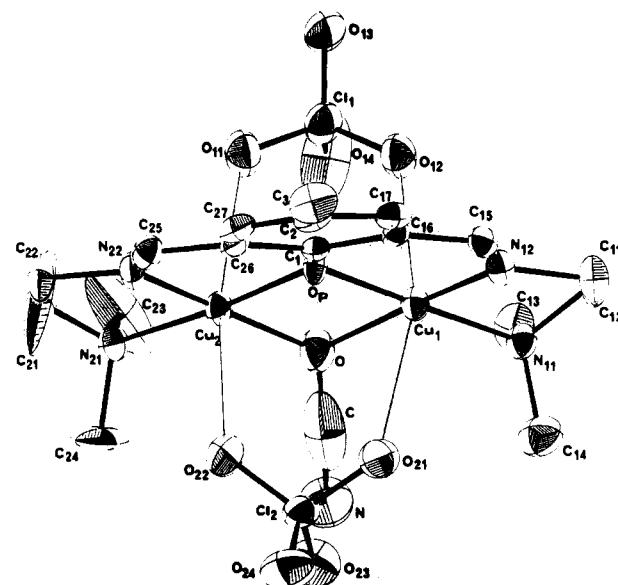
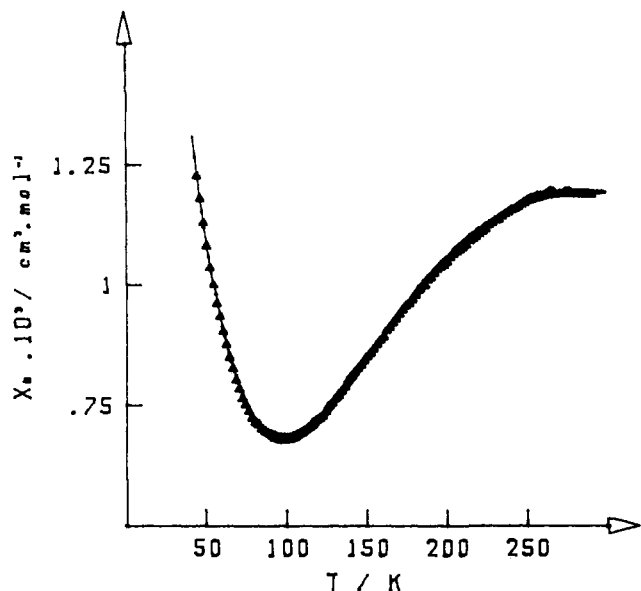


Figure 3. Perspective view of  $[\text{Cu}_2(\text{Fdmen})(\text{OCN})](\text{ClO}_4)_2$  (3).

unit are connected by a double bridge: oxygen of the phenolato ligand and coordinated atom of the second bridging group, i.e. nitrogen for the azido group, oxygen for the hydroxo and cyanato groups. The (Cu<sub>1</sub>, Cu<sub>2</sub>, two bridging atoms) networks are roughly planar, with dihedral angles of 179 (1), 174 (1), and 176 (1)<sup>o</sup> for compounds 1–3, respectively. In the three compounds, the copper(II) ions are in 4 + 2 surroundings. Each basal plane includes the two bridging atoms and two nitrogen atoms of the ligand. The apical positions are occupied by oxygen atoms of the two perchlorate anions, which build two additional bridges between Cu<sub>1</sub> and Cu<sub>2</sub>. The perspective views of the structures with the labeling of the atoms are given in Figures 1–3. We discuss now some details for each structure.

**Compound 1.** The mean deviations of Cu<sub>1</sub>N<sub>11</sub>N<sub>12</sub>O<sub>1</sub>O<sub>2</sub> and Cu<sub>2</sub>N<sub>21</sub>N<sub>22</sub>O<sub>1</sub>O<sub>2</sub> with regard to the mean planes are only 0.029 and 0.025 Å, respectively. Moreover, these planes are almost coplanar with a dihedral angle of 1.5<sup>o</sup>. The Cu–O apical bond lengths are in the range 2.5–3.1 Å. The CuOcu bridging angles are 97.4 (2)<sup>o</sup> on the phenolato side and 99.3 (2)<sup>o</sup> on the hydroxo side. The Cu<sub>1</sub>...Cu<sub>2</sub> separation is 2.924 (1) Å.

The crystallographic analysis shows that there is 0.8 water molecule per binuclear unit. Three-tenths of a molecule occupies



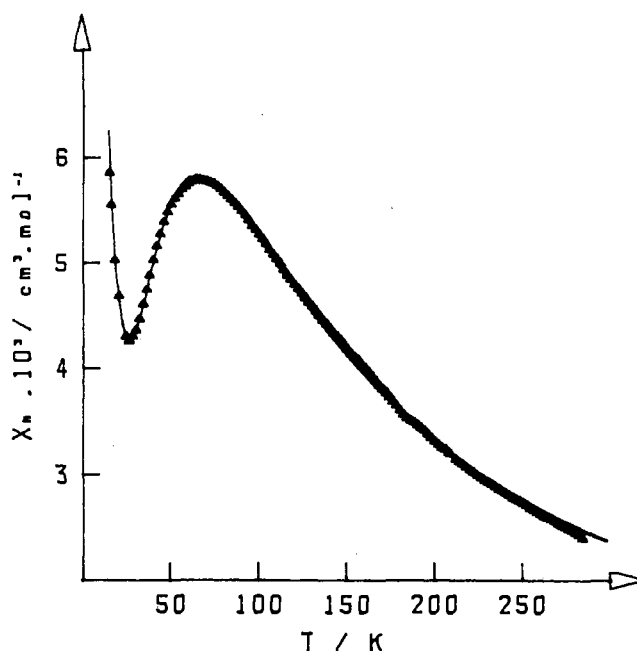
**Figure 4.** Experimental and calculated temperature dependences of the molar powder magnetic susceptibility for  $[\text{Cu}_2(\text{Fdmen})(\text{OH})](\text{ClO}_4)_2 \cdot 0.8\text{H}_2\text{O}$  (1·0.8H<sub>2</sub>O).

site O<sub>4</sub> and 0.5 molecule occupies the two sites of O<sub>3</sub> related by symmetry center  $1/2, 0, 1/2$ . A hydrogen bond occurs either with the O<sub>14</sub> atom of a perchlorate group or with the O<sub>14</sub> atom of the symmetry-related perchlorate group, the O<sub>3</sub>–O<sub>14</sub> distance being 2.75 Å.

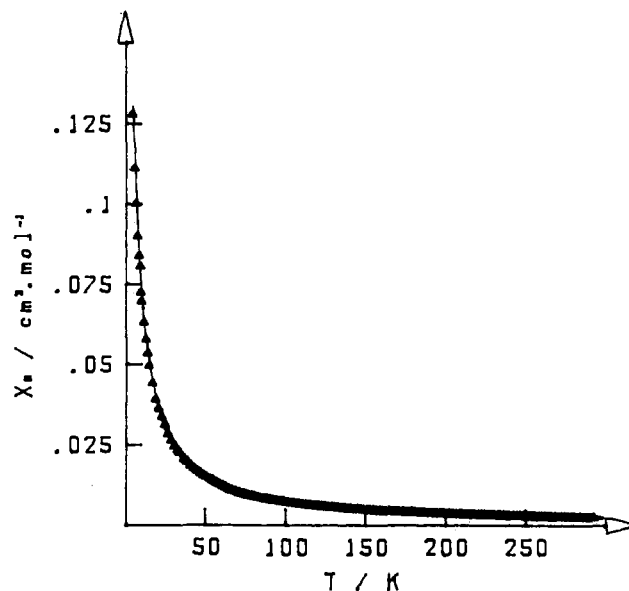
**Compound 2.** The two mean planes are again almost coplanar with a dihedral angle of 1.9°. The Cu–O apical bonds are all larger than 2.46 Å. The CuOCu bridging angle is 98.7 (3)°, and the CuNCu bridging angle is 100.0 (4)°. The Cu<sub>1</sub>...Cu<sub>2</sub> separation is 2.972 (2) Å.

The three nitrogen atoms of the azido group are as expected collinear, and the two Np<sub>1</sub>–Np<sub>2</sub> and Np<sub>2</sub>–Np<sub>3</sub> bond lengths are found equal to 1.24 (1) Å. The azido group is not in the plane of the CuONCu bridging network but makes an angle of 43.8° with this plane. A similar situation had been found in  $[\text{Cu}_2(\text{Fdmen})(\text{N}_3)(\text{CH}_3\text{COO})]\text{PF}_6$ .<sup>18</sup>

**Compound 3.** The two basal planes around Cu<sub>1</sub> and Cu<sub>2</sub> are coplanar within standard deviations. All the Cu–O apical distances are larger than 2.48 Å. By far, the most important feature of this compound is the coordination of the cyanato group by the oxygen atom. In several cases, such a coordination had been postulated from spectroscopic data<sup>22,23</sup> but, to our knowledge, had never been characterized by X-ray diffraction data. On the contrary, all the X-ray investigations gave evidence of terminal cyanato groups bound by the nitrogen atom.<sup>18,24,25</sup> The arguments were lower R values and more reasonable temperature factors for the N-bound case with regard to the O-bound case. When NCO<sup>–</sup> bridges in an end-to-end fashion, the problem oxygen vs. nitrogen also exists. Duggan and Hendrickson<sup>26</sup> solved it by comparing the temperature factors obtained in both situations and by calculating the Fourier peak electronic density. In the present case, we think that the use of the Fourier peak heights is not perfectly straightforward. Indeed, the shape of the thermal ellipsoids suggests some electronic delocalization, making the correct evaluation of the peak height quite debatable. Nevertheless, a careful observation of Fourier peaks shows a higher electronic density for the bonded atom (4.6 e Å<sup>–3</sup>) than for the terminal atom (3.2 e Å<sup>–3</sup>). We also looked at the  $R$ ,  $B_{\text{eq}}$ , and  $U_{\text{iso}}$  values. For



**Figure 5.** Experimental and calculated temperature dependences of the molar powder magnetic susceptibility for  $[\text{Cu}_2(\text{Fdmen})(\text{N}_3)](\text{ClO}_4)_2$  (2).



**Figure 6.** Experimental and calculated temperature dependences of the molar powder magnetic susceptibility for  $[\text{Cu}_2(\text{Fdmen})(\text{OCN})](\text{ClO}_4)_2$  (3).

**3**, those three tests lead to the same conclusion, namely O coordination. In the case of  $[\text{Cu}_2(\text{Fdmen})(\text{NCO})(\text{CH}_3\text{COO})]\text{PF}_6$ , the same tests led to the opposite conclusion, namely N coordination. Recently, we solved the crystal structure of a novel  $\mu$ -phenolato,  $\mu$ -cyanato copper(II) complex in which NCO<sup>–</sup> is again O-bound.<sup>27</sup> The CuOCu bridging angles are 98.1 (3)° on the phenolato side and 99.3 (4)° on the cyanato side. The Cu<sub>1</sub>...Cu<sub>2</sub> separation is 2.933 (2) Å.

The three atoms of OCN<sup>–</sup> in **3** are almost collinear with a NCO angle of 175°. The O–C length is longer than the C–N one, 1.40 (4) and 1.28 (4) Å, respectively. The cyanato group makes an angle of 28.4° with the CuO<sub>2</sub>Cu bridging network. Moreover, the longest axis of the thermal vibration ellipsoid of the middle carbon atom runs along the C–O and C–N bonds; this elongation is much more pronounced than in the azido group of **2**.

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**Table XII.** Parameters Obtained by Least-Squares Fitting of Magnetic Data

	$J/\text{cm}^{-1}$	$g$	$\rho$	$10^5 R^a$
1	-367	2.05	0.042	5
2	-86.5	2.06	0.048	4
3	-3.8	2.04	0.026	9

<sup>a</sup>  $R$  is defined as  $\sum(\chi_M^{\text{obsd}} - \chi_M^{\text{calcd}})^2 / \sum(\chi_M^{\text{obsd}})^2$ .

### Magnetic Properties

The temperature dependences of the molar powder magnetic susceptibility,  $\chi_M$ , for compounds 1–3 are shown in Figures 4–6. For 1 and 2,  $\chi_M$  exhibits a rounded maximum characteristic of an intramolecular antiferromagnetic interaction. This maximum occurs around 276 K for 1 and 66 K for 2. For both compounds,  $\chi_M$  shows a Curie tail in the low-temperature range due to the presence of a small proportion  $\rho$  of uncoupled copper(II). In contrast, the magnetic susceptibility of 3 continuously increases upon cooling down. However, the product  $\chi_M T$ ,  $T$  being the temperature, is constant and equal to  $0.78 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  down to 40 K and then decreases below 40 K and reaches  $0.54 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 4.2 K, which shows that a very weak antiferromagnetic interaction occurs. For the three compounds,  $\chi_M$  may then be expressed as

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \left[ 3 + \exp\left(\frac{-J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{N\beta^2 g^2}{2kT} \rho \quad (1)$$

where the symbols have their usual meaning. Least-squares fittings of the experimental data lead to the  $J$ ,  $g$  and  $\rho$  values of Table XII. The S–T energy gap is equal to  $-367 \text{ cm}^{-1}$  in 1,  $-86.5 \text{ cm}^{-1}$  in 2, and  $-3.8 \text{ cm}^{-1}$  in 3.

The powder EPR spectra of the three compounds have been recorded. Only that of 2 is rather well resolved. At 77 K, it exhibits four features at 1244, 4400, 5667, and 7124 G that vanish upon cooling down to 4.2 K. This spectrum is typical of a triplet state with an axial zero-field splitting parameter  $D$  larger than the value of the incident quantum. If the  $g$  and  $D$  tensors were coincident, their principal values could be deduced from the resonant fields by using Wasserman's equations.<sup>6</sup> These equations lead to  $g_x = 2.03$ ,  $g_y = 2.04$ ,  $g_z = 2.16$ ,  $|D| = 0.336 \text{ cm}^{-1}$ , and  $|E| = 0.047 \text{ cm}^{-1}$ . However, the agreement between observed and calculated resonant fields is far from being excellent, which indicates that  $g$  and  $D$  are actually not coincident. The EPR spectrum of 3 at 4.2 K, although poorly resolved, is again that of a triplet with features covering all the magnetic field range up to 8000 G. This confirms that the magnetic behavior of this compound is due to a weak intramolecular antiferromagnetic interaction.

### Discussion

The first problem to approach in this section is that of the eventual additivity of the contributions to the observed interaction arising from the CuXCu and CuYCu linkages in the network. For that, we may express the  $S$  and  $j$  integrals defined in the introduction as

$$S = \int_{\text{space}} \rho(i) d\tau(i) \quad (2)$$

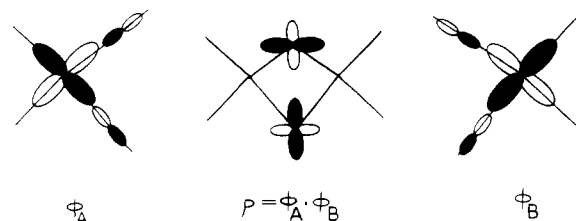
$$j = \int \int_{\text{space}} \frac{\rho(i) \rho(j)}{r_{ij}} d\tau(i) d\tau(j) \quad (3)$$

with

$$\rho(i) = \phi_A(i) \phi_B(i) \quad (4)$$

$\rho(i)$  is the overlap density between the magnetic orbitals.<sup>28</sup> It has been shown that in bibringed copper(II) complexes where the direct metal–metal interaction is negligible, this overlap density is nonvanishing only around the X and Y bridges,<sup>28,34</sup> so that we may write

$$\rho(i) \approx \rho_X(i) + \rho_Y(i) \quad (5)$$



**Figure 7.** Magnetic orbitals  $\phi_A$  and  $\phi_B$  and overlap density  $\rho$  in a disymmetrical bibringed copper(II) complex with  $S_X > 0$  and  $S_Y < 0$  (see text).

where  $\rho_X(i)$  and  $\rho_Y(i)$  are the contributions to the total overlap density around the X and Y bridges, respectively. From (2), (3), and (5), it comes out

$$S \approx S_X + S_Y \quad (6)$$

$$j \approx j_X + j_Y + 2 \int \int_{\text{space}} \frac{\rho_X(i) \rho_Y(j)}{r_{ij}} d\tau(i) d\tau(j) \quad (7)$$

with

$$S_X = \int_{\text{space}} \rho_X(i) d\tau(i) \quad (8)$$

$$j_X = \int \int_{\text{space}} \frac{\rho_X(i) \rho_X(j)}{r_{ij}} d\tau(i) d\tau(j) \quad (9)$$

and identical relations for  $S_Y$  and  $j_Y$ . Relations 6 and 7 allow us to answer the question concerning the additivity. For that, we must distinguish the  $J_{AF}$  and  $J_F$  terms: (i)  $J_{AF}$  varies as  $S^2$ . It follows that two situations may occur: if  $S_X$  and  $S_Y$  are of the same sign,  $J_{AF}$  will be larger (in absolute value) than the sum of the contributions along each linkage; if  $S_X$  and  $S_Y$  are of opposite sign,  $J_{AF}$  will be weaker (in absolute value) than this sum. This latter situation is schematized in Figure 7, where around the X bridge the positive lobes of the overlap density prevail over the negative lobes and around the Y bridge the opposite situation holds. Consequently,  $S_X$  is positive and  $S_Y$  negative. Such a situation with an antisynergic effect of the two linkages could eventually occur if one of the bridging angles was larger and the other one smaller than the value corresponding to the accidental orthogonality of the magnetic orbitals ( $S_X = S_Y = 0$ ).<sup>28</sup> A similar problem has already been discussed by Reed and co-workers<sup>8</sup> and by Kida and co-workers,<sup>9</sup> who introduced the concept of countercomplementarity. (ii)  $J_F$  varies as  $j$ , and in (7)  $j_X$  and  $j_Y$ , which are quasi-one-center integrals, are much larger than the last integral, so that the ferromagnetic contributions arising from each of the linkages are roughly additive. It is important to notice here that these results are valid only in the active-electron approximation. When the nature of at least one of the bridges is such that it is necessary to go beyond this approximation, it does not seem possible to conclude anything as far as the additivity is concerned. Maybe the best attitude is then to examine a large number of experimental data. This paper is a first step along this line.

The three compounds 1–3 exhibit an antiferromagnetic interaction, of which the magnitude strongly depends on the nature of the exogenous bridge X. For  $X = \text{OH}^-$ , the singlet state is strongly stabilized; for  $X = 1,1\text{-N}_3^-$ , it is more weakly stabilized and for  $X = 1,1\text{-OCN}^-$ , it is very weakly stabilized. Before trying to rationalize these results, we must recall the following points concerning the magnetic properties of planar bibringed copper(II) complexes:

(i) In planar bis( $\mu$ -hydroxo) copper(II) dimers, the S–T energy gap varies in a continuous way vs. the value of the bridging angle with a S–T accidental degeneracy for a bridging angle close to  $97.5^\circ$ , a singlet ground state for larger angles, and a triplet ground state for smaller angles.<sup>29</sup> The same trend was obtained for the

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mono( $\mu$ -hydroxo) copper(II) complexes. In this latter case, however, CuOCu is always found larger than  $110^\circ$  and the interaction is always antiferromagnetic.<sup>30</sup>

(ii) In bis( $\mu$ -phenolato) copper(II) dimers, the interaction is always strongly antiferromagnetic with S-T energy gaps in the range  $400\text{--}700\text{ cm}^{-1}$ .<sup>31-32</sup> Although, to our knowledge, no clear dependence of the magnitude of the interaction vs. the value of the bridging angle has been reported so far, a trend similar to that observed with hydroxo-bridged compounds may be expected.

(iii) In the two copper(II) complexes reported so far,<sup>6,7,33</sup> with two end-on azido bridges, the triplet state has been found to be the ground state, its stabilization with regard to the singlet state being of the order of  $100\text{ cm}^{-1}$ . In addition, a  $\mu$ -hydroxo,  $\mu$ -1,1-azido complex has also been described, in which the triplet state is stabilized by more than  $200\text{ cm}^{-1}$  with regard to the singlet state.<sup>5</sup> These results clearly indicate that the end-on azido bridge has quite a remarkable ability to favor a ferromagnetic interaction. This property has been attributed to a spin polarization effect.

From the considerations above, one qualitatively understands the nature and the magnitude of the interaction in **1**. The two CuOCu linkages favor the pairing of the electrons. Indeed, on the hydroxo side, the CuOCu angle is  $99.3^\circ$ . Since the values of the two bridging angles are of the same order of magnitude, there is no antisynnergic effect. Likely, the stabilization of the singlet state would be more pronounced if the bridging angle on the phenolato side was larger.

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More interesting is the situation in **2**. The antiferromagnetic contribution due to the phenolato bridge may be expected to be larger than in **1** due to the fact that the CuOCu angle is significantly larger ( $98.7^\circ$  instead of  $97.4^\circ$ ). On the other hand, the end-on azido bridge exerts a ferromagnetic contribution, so that altogether the singlet state is much less stabilized than in **1** with  $J = -86.5\text{ cm}^{-1}$ .

In **3**, finally, the two CuOCu linkages apparently exert almost opposite contributions. On the phenolato side, the antiferromagnetic contribution may be expected to be intermediate between those occurring in **1** and **2** since CuOCu is  $98.1^\circ$  instead of  $97.4^\circ$  in **1** and  $98.7^\circ$  in **2**. The cyanato-O bridge appears to be at least as efficient as the azido one to favor a ferromagnetic interaction.

In the absence of additional experimental data, it does not seem reasonable to go farther in the interpretation of the magnetic properties. We may anticipate however that the angle between the plane of the bridging network and the group  $\text{N}_3^-$  or  $\text{OCN}^-$  plays an important role in the magnitude of the interaction. New results dealing with the same kinds of bridging networks will be presented in the near future.

**Safety Notes.** Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution.

**Registry No.** **1**, 103001-54-3; **2**, 101661-17-0; **3**, 102920-55-8; 1,1-dimethylethylenediamine, 811-93-8; 2,6-diformyl-4-methylphenol, 7310-95-4.

**Supplementary Material Available:** Listings of atomic parameters for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms (Tables XIII-XV) (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

## Characterization of [*rac*-5,7,7,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) 3-Sulfidopropionate Dimethanolate, [Cu(tet b)SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>] $\cdot$ 2CH<sub>3</sub>OH, a Stable Copper(II)-Aliphatic Thiolate Complex

Elizabeth John, Parimal K. Bharadwaj, Joseph A. Potenza,\* and Harvey J. Schugar\*

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The synthesis, X-ray structure, and preliminary electronic spectra of the title complex, the first stable Cu(II)-aliphatic thiolate compound, are presented. Crystals of  $\text{CuSO}_4\text{N}_4\text{C}_{19}\text{H}_{40}\text{O}_2\text{S}\cdot 2\text{CH}_3\text{OH}$  are monoclinic, space group  $P2_1/n$ , with  $a = 14.003(2)\text{ \AA}$ ,  $b = 13.683(2)\text{ \AA}$ ,  $c = 14.548(4)\text{ \AA}$ ,  $\beta = 91.85(2)^\circ$ ,  $Z = 4$ , and  $R_F(R_{wF}) = 0.051(0.058)$  for 2276 reflections. The structure contains neutral Cu(II) monomers with distorted-trigonal-bipyramidal  $\text{N}_4\text{S}$  ligand donor sets. Equatorial ligation is provided by the sulfidopropionate S atom (Cu-S =  $2.314(2)\text{ \AA}$ ) and two amine N atoms from the tet b ligand (Cu-N =  $2.153(4)$ ,  $2.169(4)\text{ \AA}$ ), while two shorter axial Cu-N(tet b) bonds ( $2.031(4)$ ,  $2.001(4)\text{ \AA}$ ) complete the coordination. The macrocyclic tet b ligand is folded in its lowest energy conformation, and the carboxylate group is stabilized by hydrogen bonding to the tet b and solvate molecules. Electronic absorptions at  $\sim 27800$  and  $\sim 23800\text{ cm}^{-1}$  are assigned as  $\text{S} \rightarrow \text{Cu(II)}$  LMCT while additional spectral features in the  $12000\text{--}17000\text{ cm}^{-1}$  range are assigned as ligand field transitions. Spectroscopic comparisons are presented between the title complex and a structurally similar Cu(tet b) complex of the aromatic thiolate *o*-sulfidobenzoate.

### Introduction

The scope of stable Cu(II) aliphatic thiolate complexes has been limited to the type 1 sites in "blue" copper metalloproteins,<sup>1</sup> Cu(II)-doped liver alcohol dehydrogenase,<sup>2</sup> and the  $\text{Cu}_A$  site in

cytochrome *c* oxidase.<sup>3</sup> There has been considerable interest in identifying the contributions of the Cu(II) aliphatic thiolate subunit of both biological and synthetic chromophores to their electronic spectral and vibrational features. While it has been clear for some time that the prominent absorption at  $\sim 16000\text{ cm}^{-1}$  exhibited by type 1 Cu(II) systems must be due to  $\sigma(\text{thiolate}) \rightarrow \text{Cu(II)}$  LMCT,<sup>1</sup> the identification and origins of the expected

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