Inorg. Chem. **1987**, *26*, 1375–1380

Table IX. $\Delta E_{\text{calcd}} - \Delta G_{\text{hyd}}$ (kcal mol^{-1}) for the Reaction M_1(crown) + $M_2(H_2O)_n$(aq) = M_2(crown) + $M_1(H_2O)_n$(aq)

	M_2			
M_1	Ca	Sr	Ba	Ra
Mg	−18	−25	−35	−7
Ca		−7	−17	+11
Sr			−9	+18
Ba				+28

line-earth-metal ions in the sequence Ba > Sr > Ca > Ra ≫ Mg. Actual thermodynamic data[27] for ΔG_f of crown ether complexes of alkaline-earth-metal ions in aqueous chloride solutions give ΔG_f(Ba) = −5.28 kcal mol^{-1}, ΔG_f(Sr) = −3.71 kcal mol^{-1}, and ΔG_f(Ca) = −0.7 kcal mol^{-1}. It is encouraging that our simple estimate is in agreement with this sequence of stabilities.

Summary

It has been shown that the stabilities of some extraction complexes of alkaline-earth metals can be compared by calculating their energies by molecular mechanics. Configurations of these molecules having minimum energies were found by starting with structures determined by X-ray diffraction analysis and adjusting their parameters. The contributions of the various terms to the total energy can be examined to see which are most important to stability, and in particular, the role of the crown ether molecule as a selective extractant can be assessed. In $Sr(DBP)_2(H_2O)\cdot$18-crown-6 and $Ba(DBP)_2(H_2O)\cdot$18-crown-6 it is seen that the differences in electrostatic components are more important than the differences in ring strain induced in the crowns as they adapt to the cations of different size. Energies of analogous hypothetical molecules containing Ca and Ra were also calculated, and the total energies of the alkaline-earth-metal complexes are in the order Ra < Ba < Sr < Ca. However, when hydration energies of these ions are taken into account, the stabilities of the complexes in aqueous solution are Ba > Sr > Ca > Ra. This is in the same order as measured stabilities of the first three of these ions when complexed with 18-crown-6 in aqueous chloride solutions.

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Supplementary Material Available: Table SI listing torsion angles involving butyl groups, Table SII giving nonbonded interaction parameters, and Table SIII giving force-field parameters (3 pages); a table of observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

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Crystal Structures and Magnetic Properties of Dinuclear Copper(II) Complexes of 2,6-Bis(*N*-(2-pyridylmethyl)formimidoyl)-4-methylphenolate with Azido and Cyanato-*O* Exogenous Ligands

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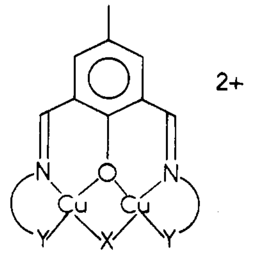
Two complexes of formula $[Cu_2(Famp)(X)](ClO_4)_2$ were synthesized. $Famp^-$ ($=C_{21}H_{19}N_4O^-$) is the binucleating ligand 2,6-bis(*N*-(2-pyridylmethyl)formimidoyl)-4-methylphenolate; X^- is 1,1-N_3^- (**1**) and 1,1-OCN^- (**2**). The crystal structures of **1** and **2** are isomorphous; space group $P2_1$, a = 8.973 (3) and 8.987 (3) Å, b = 14.785 (3) and 14.774 (4) Å, c = 9.650 (1) and 9.664 (1) Å, β = 90.63 (2) and 90.71 (2)°, and Z = 2. The copper(II) ions of the binuclear units are bridged by the phenolic oxygen atom and by the X^- exogenous ligand. Both N_3^- and OCN^- bridge in an end-on fashion and make angles of 18.7 (8) and 18.8 (8)°, respectively, with the plane of the $Famp^-$ ligand. OCN^- bridges by its oxygen atom. The magnetic and EPR properties were investigated: in **1**, the copper(II) ions are antiferromagnetically coupled with a singlet–triplet (S–T) energy gap of −161 cm^{-1}; in contrast, **2** is one of the few copper(II) dinuclear complexes with a triplet ground state. The S–T energy gap is 43 (10) cm^{-1}.

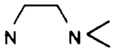
Introduction

We have recently undertaken the study of the magnetic properties of copper(II) dinuclear complexes with two dissimilar bridging ligands.[2,3] More precisely, one of the bridges, a phenolato group, remains constant and the other bridge can be modified. The former bridge may be considered as endogenous and the latter as exogenous. To limit the frame of this study, we have decided to focus on the hydroxo, azido, and cyanato groups as exogenous ligands. Our goal is to investigate several series of compounds of the type



with X^- = OH^-, N_3^-, and OCN^- and various lateral chains N⌒Y.

The first paper along this line has already been published.[3] It was devoted to the compounds $[Cu_2(Fdmen)(X)](ClO_4)_2$, in which the lateral chain was



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[1] (a) Université de Paris-Sud. (b) Université Pierre et Marie Curie. (c) University of New Orleans.

[2] Boillot, M. L.; Kahn, O.; O'Connor, C. J.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 178.

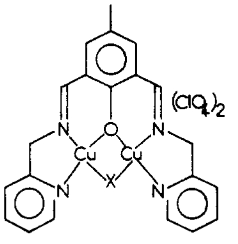
[3] Mallah, T.; Boillot, M. L.; Kahn, O.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 3058.

0020-1669/87/1326-1375$01.50/0

In this work, we seek to answer three questions: (i) To what extent is it possible to decompose the interaction observed in those compounds into contributions arising from each of the CuO(phenolato)Cu and CuXCu linkages? (ii) What is the role of the lateral chains when X is constant? (iii) Finally, what is the magnitude of the ferromagnetic contribution exerted by N_3^- and OCN^- when these groups bridge in a 1,1 fashion? This last question is likely for us the most important. Indeed, for several years, we have been engaged in the design of ferromagnetically coupled polymetallic systems[4-6] and recently we have found that azide, and then cyanate, had quite a remarkable efficiency to favor the ferromagnetic interaction between two copper(II) ions when they bridge in an end-on fashion.[7-10] In contrast, N_3^- strongly favors an antiferromagnetic interaction when it bridges in an end-to-end fashion.[11-14]

The phenolato-bridged copper complexes have also attracted the bioinorganic community as eventual models of copper-containing oxygen-carrying proteins.[14-16] The first structure of a compound of that class, the *Panulirus interruptus* hemocyanin, strongly suggests that actually there is no phenolato bridge, at least in the deoxy form.[17]

This paper is devoted to a second family of compounds, denoted as $[Cu_2(Famp)(X)](ClO_4)_2$, where $Famp^-$ is the binucleating ligand 2,6-bis(*N*-(2-pyridylmethyl)formimidoyl)-4-methylphenolate, of the type



The magnetic properties of the compound with X = OH have already been reported,[18] and the crystal structure has been solved.[19] Here, we report on the synthesis, the crystal structure, and the magnetic and EPR properties of the complexes with $X = N_3^-$ (**1**) and $X = OCN^-$ (**2**).

Experimental Section

Syntheses. The compounds **1** and **2** were prepared as follows: 2×10^{-3} mol of (aminomethyl)pyridine was added to 1.1×10^3 mol of 2,6-diformyl-4-methylphenol in 60 mL of a 50/50 mixture of tetrahydrofuran and acetonitrile. Then were successively added 2×10^{-3} mol of copper(II) acetate and 10^{-3} mol of NaN_3 for **1** and NaNCO for **2**. The mixture was stirred and filtered. A slow evaporation gave apparently well-shaped crystals that actually were all twinned. Anal. Calcd for $C_{21}H_{19}N_7O_9Cl_2Cu_2$ (**1**): C, 35.46; H, 2.69; N, 13.78; O, 20.24. Found: C, 35.15; H, 2.75; N, 13.54; O, 20.25. Calcd for $C_{22}H_{19}N_5O_{10}Cl_2Cu_2$ (**2**): C, 37.14; H, 2.69; N, 9.84; O, 22.49. Found: C, 37.67; H, 2.80; N, 9.80; O, 22.96.

Table I. Crystallographic Data Collection

	1	**2**
chem formula	$Cu_2(C_{21}H_{19}N_4O)N_3(ClO_4)_2$	$Cu_2(C_{21}H_{19}N_4O)$-$(OCN)(ClO_4)_2$
cryst color	dark green	dark green
cryst size, mm	0.21 × 0.12 × 0.05	0.60 × 0.30 × 0.02
ρ_{measd}, g cm^{-3}	1.84	1.77
μ(Mo Kα), cm^{-1}	20.02	20.07
cryst syst	monoclinic	monoclinic
space group	$P2_1$[a]	$P2_1$[a]
a, Å	8.973 (3)	8.987 (3)
b, Å	14.785 (3)	14.774 (4)
c, Å	9.650 (1)	9.664 (1)
β, deg	90.63 (2)	90.71 (2)
V, Å^3	1280.3 (6)	1282.9 (6)
Z	2	2
diffractometer	Nonius CAD4	lab-made diffractometer
monochromator	graphite	graphite, in front of the counter
radiation	Mo Kα (λ = 0.71070 Å)	Mo Kα (λ = 0.71070 Å)
temp, °C	21 ± 1	21 ± 1
scan type	θ–2θ	θ–2θ
scan range, deg	$1.0 + 0.345 \tan \theta$	$1.2 + 0.345 \tan \theta$
2θ range, deg	3.0–50	3.0–50
scan speed, deg min^{-1}	depending upon reflecn	1.9
bkgd	half of scan time, in fixed position, before and after every scan	10 s, in fixed position, before and after every scan
std reflecns	2, measd every other h	2, measd every 100 reflecns
reflecns measd	2 octants; hkl, $\bar{h}kl$	2 octants; hkl, $\bar{h}kl$
reflecns collected	2806	2378
indep reflecns kept for refinement	1729 ($F > 3\sigma(F)$)	1953 ($F > 3\sigma(F)$)

[a] $P2_1$ selected over $P2_1/m$ because a better refinement was obtained.

Table II. Structure Refinements

	1	**2**
computing program	CRYSTALS[a]	SHELX 76[b]
diffusion factors	c (f, f', f'')	
minimized function	$R_w = [\sum_i w_i(\lvert F_o - F_c\rvert)^2/\sum_i w_i F_o^2]^{1/2}$	
secondary extinction	none obsd	
abs cor	not applied (flat ψ scan)	
weighting scheme	unit	$0.94/\sigma^2(F)$
av shift/esd (last cycle)	0.10	0.15
$N_{ref}/N_{var\ param}$	5.4	5.05 (refined by 3 blocks)
scale factors	1.0499	1.0553
final residuals		
R	0.048	0.049
R_w	0.057	0.039

[a] Carruthers, B.; Watkin, D. W. J. "CRYSTALS, an Advanced Crystallographic Computer Program"; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1985. [b] Sheldrick, G. M. "SHELX 76 Program for Crystal Structure Determinations"; University of Cambridge: Cambridge, England, 1976. [c] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

The crystals used in the X-ray work were obtained as follows: 5 mL of a concentrated solution of **1** or **2** in methanol was poured in a long glass tube of 1 cm. diameter. On this solution were poured very slowly 2 mL of pure methanol and then 10 mL of diethyl ether. The tube was plugged. Needle-shaped, dark green crystals appeared within a few days.

Crystallographic Data Collection and Refinement of the Structures. Tables I and II show experimental conditions of data collection and structure refinement.

Compound 1. A three-dimensional Patterson map showed copper atoms. Successive Fourier syntheses and refinement led to $R = 0.079$

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Table III. Atomic Parameters for Compound **1**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso), Å^2
Cu(1)	−0.0141 (2)	0.0000	−0.0134 (2)	0.0326
Cu(2)	0.1532 (2)	−0.1047 (2)	−0.2269 (2)	0.0350
O(1)	0.182 (1)	−0.0498 (7)	−0.0438 (9)	0.0353
N(1)	−0.034 (1)	−0.0370 (9)	−0.206 (1)	0.0299
N(2)	−0.101 (2)	−0.010 (2)	−0.303 (2)	0.0671
N(3)	−0.168 (3)	0.012 (3)	−0.398 (3)	0.1598
N(11)	−0.208 (1)	0.0573 (8)	0.031 (1)	0.0326
N(12)	0.032 (1)	0.0230 (7)	0.180 (1)	0.0302
N(21)	0.135 (1)	−0.1709 (8)	−0.404 (1)	0.0390
N(22)	0.354 (1)	−0.1429 (7)	−0.234 (1)	0.0329
C(1)	0.288 (1)	−0.0729 (9)	0.046 (1)	0.0282
C(2)	0.527 (1)	−0.104 (1)	0.240 (1)	0.0321
C(3)	0.654 (2)	−0.119 (1)	0.341 (1)	0.0463
C(11)	−0.220 (1)	0.0778 (9)	0.164 (2)	0.0358
C(12)	−0.087 (2)	0.068 (1)	0.261 (1)	0.0405
C(13)	−0.351 (2)	0.112 (1)	0.214 (2)	0.0444
C(14)	−0.473 (2)	0.126 (1)	0.133 (2)	0.0480
C(15)	−0.461 (2)	0.105 (1)	−0.005 (2)	0.0448
C(16)	−0.326 (2)	0.067 (1)	−0.050 (2)	0.0511
C(17)	0.153 (1)	0.002 (1)	0.240 (1)	0.0360
C(18)	0.279 (1)	−0.045 (1)	0.186 (1)	0.0330
C(19)	0.398 (2)	−0.060 (1)	0.275 (1)	0.0335
C(21)	0.267 (1)	−0.197 (1)	−0.456 (1)	0.0330
C(22)	0.400 (2)	−0.171 (1)	−0.370 (2)	0.0385
C(23)	0.276 (2)	−0.245 (1)	−0.576 (1)	0.0444
C(24)	0.148 (2)	−0.265 (1)	−0.648 (1)	0.0474
C(25)	0.008 (2)	−0.240 (1)	−0.594 (2)	0.0461
C(26)	0.007 (2)	−0.193 (1)	−0.472 (2)	0.0474
C(27)	0.450 (1)	−0.1461 (9)	−0.135 (1)	0.0296
C(28)	0.420 (1)	−0.116 (1)	0.007 (1)	0.0361
C(29)	0.535 (1)	−0.132 (1)	0.101 (1)	0.0379
Cl(1)	−0.0741 (4)	−0.2480 (3)	−1.0227 (4)	0.0446 (8)
O(11)	−0.067 (1)	−0.327 (1)	−0.933 (1)	0.075 (4)
O(12)	−0.091 (1)	−0.1691 (8)	−0.940 (1)	0.056 (3)
O(13)	−0.195 (2)	−0.257 (1)	−1.117 (1)	0.102 (5)
O(14)	0.061 (1)	−0.2423 (9)	−1.100 (1)	0.060 (3)
Cl(2)	−0.3593 (4)	−0.4023 (3)	−0.5948 (4)	0.0509 (9)
O(21)	−0.350 (2)	−0.342 (1)	−0.707 (2)	0.093 (4)
O(22)	−0.497 (2)	−0.448 (1)	−0.607 (2)	0.098 (5)
O(23)	−0.245 (1)	−0.4683 (9)	−0.588 (1)	0.070 (3)
O(24)	−0.357 (2)	−0.3526 (9)	−0.469 (1)	0.082 (4)
H(121)	−0.1124	0.0323	0.3386	0.0500
H(122)	−0.0544	0.1260	0.2910	0.0500
H(13)	−0.3569	0.1260	0.3100	0.0500
H(14)	−0.5629	0.1499	0.1694	0.0500
H(15)	−0.5411	0.1160	−0.0684	0.0500
H(16)	−0.3203	0.0471	−0.1431	0.0500
H(17)	0.1602	0.0187	0.3345	0.0500
H(19)	0.3902	−0.0378	0.3674	0.0500
H(221)	0.4644	−0.2216	−0.3610	0.0500
H(222)	0.4500	−0.1228	−0.4136	0.0500
H(23)	0.3698	−0.2646	−0.6096	0.0500
H(24)	0.1526	−0.2967	−0.7336	0.0500
H(25)	−0.0822	−0.2546	−0.6413	0.0500
H(26)	−0.0859	−0.1763	−0.4335	0.0500
H(27)	0.5457	−0.1695	−0.1540	0.0500
H(29)	0.6212	−0.1628	0.0701	0.0500
H(31)	0.7312	−0.1514	0.2963	0.0500
H(32)	0.6195	−0.1535	0.4179	0.0500
H(33)	0.6902	−0.0626	0.3725	0.0500

[a] Standard deviations in the last significant figures are given in parentheses in this and all succeeding tables.

Table IV. Main Interatomic Distances (Å) for Compound **1**

Cu(1)–Cu(2)	2.993 (2) (in dinuclear unit)		
	Cu Surroundings		
Cu(1)–O(1)	1.934 (9)	Cu(2)–O(1)	1.959 (9)
Cu(1)–N(1)	1.94 (1)	Cu(2)–N(1)	1.97 (1)
Cu(1)–N(11)	1.99 (1)	Cu(2)–N(21)	1.98 (1)
Cu(1)–N(12)	1.93 (1)	Cu(2)–N(22)	1.89 (1)
Cu(1)–O(11)	2.71 (1)	Cu(2)–O(14)	2.52 (1)
Cu(1)–O(12)	2.69 (1)	Cu(2)–O(23)	2.82 (1)
	Azido Bridge		
N(1)–N(2)	1.18 (2)	N(2)–N(3)	1.13 (3)
	Bridging Phenolato Ligand		
N(11)–C(11)	1.32 (2)	N(21)–C(21)	1.35 (2)
N(11)–C(16)	1.31 (2)	N(21)–C(26)	1.35 (2)
N(12)–C(12)	1.49 (2)	N(22)–C(22)	1.44 (2)
N(12)–C(17)	1.26 (2)	N(22)–C(27)	1.27 (2)
C(12)–C(11)	1.52 (2)	C(22)–C(21)	1.50 (2)
C(11)–C(13)	1.37 (2)	C(23)–C(21)	1.36 (2)
C(14)–C(13)	1.35 (2)	C(24)–C(23)	1.37 (2)
C(15)–C(14)	1.38 (2)	C(25)–C(24)	1.41 (2)
C(16)–C(15)	1.41 (2)	C(26)–C(25)	1.36 (2)
C(17)–C(18)	1.43 (2)	C(28)–C(27)	1.47 (2)
C(19)–C(18)	1.38 (2)	C(28)–C(29)	1.38 (2)
C(1)–C(18)	1.42 (2)	C(1)–C(28)	1.40 (2)
C(2)–C(19)	1.38 (2)	C(2)–C(29)	1.41 (2)
O(1)–C(1)	1.32 (1)	C(2)–C(3)	1.51 (2)
	Perchlorate Ions		
Cl(1)–O(11)	1.46 (1)	Cl(2)–O(21)	1.41 (2)
Cl(1)–O(12)	1.42 (1)	Cl(2)–O(22)	1.41 (2)
Cl(1)–O(13)	1.41 (1)	Cl(2)–O(23)	1.42 (1)
Cl(1)–O(14)	1.44 (1)	Cl(2)–O(24)	1.42 (1)

Table V. Main Bond Angles (deg) for Compound **1**

	Cu Surroundings		
N(1)–Cu(1)–O(1)	79.8 (4)	N(1)–Cu(2)–O(1)	78.4 (4)
N(1)–Cu(1)–N(11)	104.7 (4)	N(21)–Cu(2)–N(1)	106.2 (5)
N(12)–Cu(1)–O(1)	91.6 (4)	N(22)–Cu(2)–O(1)	92.2 (4)
N(11)–Cu(1)–N(12)	84.0 (4)	N(21)–Cu(2)–N(22)	83.9 (5)
O(11)–Cu(1)–O(1)	94.7 (4)	O(14)–Cu(2)–O(1)	86.4 (4)
O(11)–Cu(1)–N(12)	87.9 (4)	O(14)–Cu(2)–N(22)	95.3 (4)
O(11)–Cu(1)–N(11)	83.0 (4)	O(14)–Cu(2)–N(21)	89.7 (4)
O(11)–Cu(1)–N(1)	96.0 (5)	O(14)–Cu(2)–N(1)	94.3 (4)
O(12)–Cu(1)–O(1)	85.5 (4)	O(23)–Cu(2)–O(1)	103.7 (4)
O(12)–Cu(1)–N(12)	87.8 (4)	O(23)–Cu(2)–N(21)	80.2 (4)
O(12)–Cu(1)–N(11)	96.4 (4)	O(23)–Cu(2)–N(22)	84.7 (4)
O(12)–Cu(1)–N(1)	88.2 (5)	O(23)–Cu(2)–N(1)	87.6 (4)
	Azido Bridge		
N(3)–N(2)–N(1)	176.4 (35)		
	Phenolato Ligand		
C(18)–C(1)–C(28)	116.5 (11)	N(11)–C(11)–C(12)	120.3 (11)
C(27)–C(28)–C(1)	123.2 (11)	C(11)–N(11)–Cu(1)	112.8 (9)
C(28)–C(29)–C(2)	122.1 (13)	C(16)–N(11)–C(11)	118.4 (12)
C(18)–C(19)–C(2)	124.7 (13)	C(28)–C(27)–N(22)	124.0 (12)
C(19)–C(18)–C(1)	119.6 (12)	C(27)–N(22)–Cu(2)	128.2 (9)
C(29)–C(2)–C(3)	122.0 (12)	C(27)–N(22)–C(22)	118.4 (11)
C(19)–C(2)–C(3)	123.0 (12)	C(21)–C(22)–N(22)	110.4 (11)
C(18)–C(17)–N(12)	129.3 (12)	N(21)–C(21)–C(22)	114.7 (11)
C(17)–N(12)–Cu(1)	124.8 (9)	C(21)–N(21)–Cu(2)	113.4 (9)
C(12)–N(12)–C(17)	119.1 (11)	C(21)–N(21)–C(26)	119.4 (12)
C(11)–C(12)–N(12)	106.4 (11)		
	Perchlorate Ions		
O(12)–Cl(1)–O(11)	109.0 (6)	O(22)–Cl(2)–O(21)	107.4 (9)
O(13)–Cl(1)–O(11)	109.7 (10)	O(23)–Cl(2)–O(21)	115.1 (8)
O(13)–Cl(1)–O(12)	110.9 (9)	O(23)–Cl(2)–O(22)	108.1 (9)
O(14)–Cl(1)–O(11)	109.1 (8)	O(24)–Cl(2)–O(21)	108.9 (8)
O(14)–Cl(1)–O(12)	109.8 (7)	O(24)–Cl(2)–O(22)	108.8 (9)
O(14)–Cl(1)–O(13)	108.3 (7)	O(24)–Cl(2)–O(23)	108.3 (8)

for the 41 non-hydrogen atoms with isotropic thermal parameters and to $R = 0.055$ with anisotropic thermal parameters. The 19 hydrogen atoms were then added in calculated positions and allowed to shift according to the movement of the parent atoms with fixed U isotropic thermal parameters equal to 0.05. Positions of perchlorate anion atoms were refined with isotropic thermal parameters instead of anisotropic ones, in order to have a better ratio $N_{\text{ref}}/N_{\text{var param}}$. The atomic parameters are shown in Tables III and X[27] and the main interatomic distances and bond angles in Tables IV and V.

Compound 2. A three-dimensional Patterson map showed copper atoms. Refinement of their coordinates dropped R to 0.33. Successive Fourier syntheses and refinements led to $R = 0.053$ with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were then added in calculated positions as for compound **1**, but with a refineable overall isotropic thermal parameter. The CH_3 groups were refined as rigid groups. The atomic parameters are shown in Tables VI and XI[27] and the main interatomic distances and bond lengths in Tables VII and VIII. For both **1** and **2**, we did not try to look for the absolute configuration.

Table VI. Atomic Parameters for Compound **2**

atom	*x/a*	*y/b*	*z/c*
Cu(1)	–0.0140 (1)	0.0000	0.0138 (1)
Cu(2)	0.1518 (1)	0.1041 (1)	0.2260 (1)
O	–0.0378 (7)	0.0388 (5)	0.2105 (6)
C	–0.093 (2)	0.006 (1)	0.312 (1)
N	–0.158 (2)	–0.015 (2)	0.413 (2)
O(p)	0.1837 (7)	0.0540 (5)	0.0451 (7)
N(11)	–0.2112 (8)	–0.0529 (6)	–0.0334 (8)
N(12)	0.0321 (8)	–0.0179 (5)	–0.1759 (9)
N(21)	0.1335 (9)	0.1738 (6)	0.4027 (9)
N(22)	0.3556 (9)	0.1458 (6)	0.2332 (8)
C(1)	0.288 (1)	0.0748 (6)	–0.049 (1)
C(2)	0.5244 (9)	0.1070 (9)	–0.241 (1)
C(3)	0.657 (1)	0.120 (1)	–0.340 (1)
C(11)	–0.222 (1)	–0.0743 (7)	–0.164 (1)
C(12)	–0.085 (1)	–0.0656 (7)	–0.255 (1)
C(13)	–0.354 (1)	–0.1106 (7)	–0.217 (1)
C(14)	–0.473 (1)	–0.1222 (8)	–0.128 (1)
C(15)	–0.459 (1)	–0.1017 (7)	0.008 (1)
C(16)	–0.327 (1)	–0.0643 (8)	0.051 (1)
C(17)	0.1512 (9)	0.0013 (8)	–0.2447 (9)
C(18)	0.278 (1)	0.0472 (7)	–0.187 (1)
C(19)	0.395 (1)	0.0637 (7)	–0.278 (1)
C(21)	0.263 (1)	0.2017 (7)	0.454 (1)
C(22)	0.402 (1)	0.1752 (7)	0.372 (1)
C(23)	0.274 (1)	0.249 (1)	0.576 (1)
C(24)	0.145 (1)	0.2705 (9)	0.647 (1)
C(25)	0.007 (1)	0.244 (1)	0.594 (1)
C(26)	0.009 (1)	0.1976 (8)	0.469 (1)
C(27)	0.447 (1)	0.1497 (7)	0.134 (1)
C(28)	0.418 (1)	0.1198 (7)	–0.0055 (9)
C(29)	0.532 (1)	0.1346 (7)	–0.104 (1)
Cl(1)	–0.0753 (2)	0.2500 (2)	1.0234 (3)
O(11)	0.931 (1)	0.3288 (6)	0.935 (1)
O(12)	0.9069 (9)	0.1710 (6)	0.940 (1)
O(13)	1.0617 (8)	0.2437 (7)	1.1018 (8)
O(14)	0.803 (1)	0.259 (1)	1.115 (1)
Cl(2)	0.6378 (3)	0.4048 (2)	0.5945 (3)
O(21)	0.7524 (9)	0.4729 (6)	0.5902 (9)
O(22)	0.642 (1)	0.3565 (7)	0.471 (1)
O(23)	0.501 (1)	0.4507 (8)	0.610 (1)
O(24)	0.656 (1)	0.3453 (7)	0.704 (1)

atom	*x/a*	*y/b*	*z/c*	*U*(iso), Å^2
H(121)	–0.1082	–0.0317	–0.3354	0.0680
H(122)	–0.0507	–0.1240	–0.2814	0.0680
H(13)	–0.3613	–0.1264	–0.3123	0.0375
H(14)	–0.5643	–0.1452	–0.1613	0.0375
H(15)	–0.5389	–0.1126	0.0717	0.0375
H(16)	–0.3190	–0.0463	0.1449	0.0375
H(17)	0.1563	–0.0151	–0.3397	0.0375
H(19)	0.3852	0.0446	–0.3718	0.0375
H(221)	0.4510	0.1268	0.4170	0.0680
H(222)	0.4673	0.2255	0.3643	0.0680
H(23)	0.3685	0.2672	0.6100	0.0375
H(24)	0.1497	0.3029	0.7313	0.0375
H(25)	–0.0836	0.2569	0.6415	0.0375
H(26)	–0.0832	0.1819	0.4291	0.0375
H(27)	0.5423	0.1747	0.1517	0.0375
H(29)	0.6198	0.1650	–0.0759	0.0375
H(31)	0.6277	0.0746	–0.4032	0.1199
H(32)	0.7472	0.1032	–0.2973	0.1199
H(33)	0.6714	0.1757	–0.3886	0.1199

Table VII. Main Interatomic Distances (Å) for Compound **2**

Cu(1)–Cu(2)	2.977 (2) (in dinuclear unit)		
	Cu Surroundings		
Cu(1)–O(p)	1.973 (7)	Cu(2)–O(p)	1.917 (7)
Cu(1)–O	1.994 (6)	Cu(2)–O	1.966 (7)
Cu(1)–N(11)	1.995 (6)	Cu(2)–N(21)	1.999 (9)
Cu(1)–N(12)	1.893 (8)	Cu(2)–N(22)	1.935 (8)
Cu(1)···O(12)	2.721 (9)	Cu(2)···O(13)	2.524 (9)
Cu(1)···O(11)	2.685 (8)	Cu(2)···O(21)	2.774 (8)
	Cyanato Bridge		
O–C	1.20 (2)	C–N	1.18 (2)
	Bridging Phenolato Ligand		
O(p)–C(1)	1.33 (1)	C(2)–C(3)	1.53 (1)
C(1)–C(18)	1.40 (1)	C(1)–C(28)	1.42 (1)
C(18)–C(19)	1.38 (1)	C(28)–C(29)	1.40 (1)
C(19)–C(2)	1.38 (1)	C(29)–C(2)	1.39 (2)
C(18)–C(17)	1.45 (1)	C(28)–C(27)	1.44 (1)
C(17)–N(12)	1.28 (1)	C(27)–N(22)	1.26 (1)
N(12)–C(12)	1.48 (1)	N(22)–C(22)	1.47 (1)
C(12)–C(11)	1.51 (1)	C(22)–C(21)	1.52 (1)
C(11)–N(11)	1.31 (1)	C(21)–N(21)	1.34 (1)
N(11)–C(16)	1.33 (1)	N(21)–C(26)	1.33 (1)
C(16)–C(15)	1.38 (1)	C(26)–C(25)	1.38 (2)
C(14)–C(15)	1.35 (2)	C(24)–C(25)	1.40 (2)
C(14)–C(13)	1.38 (2)	C(24)–C(23)	1.37 (2)
C(13)–C(11)	1.41 (1)	C(23)–C(21)	1.38 (2)
	Perchlorate Ions		
Cl(1)–O(11)	1.44 (1)	Cl(2)–O(21)	1.441 (8)
Cl(1)–O(12)	1.427 (9)	Cl(2)–O(22)	1.39 (1)
Cl(1)–O(13)	1.457 (8)	Cl(2)–O(23)	1.41 (1)
Cl(1)–O(14)	1.40 (1)	Cl(2)–O(24)	1.38 (1)

Table VIII. Main Bond Angles (deg) for Compound **2**

	Cu Surroundings		
O–Cu(1)–O(p)	79.9 (3)	O–Cu(2)–O(p)	82.0 (3)
O(p)–Cu(1)–N(12)	91.0 (3)	O(p)–Cu(2)–N(22)	91.4 (3)
O–Cu(1)–N(11)	104.2 (3)	O–Cu(2)–N(21)	104.8 (3)
N(11)–Cu(1)–N(12)	84.7 (3)	N(21)–Cu(2)–N(22)	82.7 (3)
	Cyanato Bridge		
O–C–N	171 (2)		
	Phenolato Bridging Ligand		
C(18)–C(1)–C(28)	118.5 (8)	C(18)–C(17)–N(12)	124.3 (9)
C(28)–C(27)–N(22)	125.2 (9)	C(1)–C(28)–C(27)	125.3 (8)
C(17)–N(12)–Cu(1)	129.9 (7)	C(27)–N(22)–Cu(2)	126.6 (7)
C(28)–C(29)–C(2)	123.6 (9)	C(17)–N(12)–C(12)	115.4 (8)
C(27)–N(22)–C(22)	119.5 (9)	C(2)–C(19)–C(18)	123.3 (9)
N(12)–C(12)–C(11)	108.5 (8)	N(22)–C(22)–C(21)	108.3 (8)
C(19)–C(18)–C(1)	120.3 (9)	C(12)–C(11)–N(11)	118.3 (8)
C(22)–C(21)–N(21)	116.0 (9)	C(29)–C(2)–C(3)	120.7 (9)
C(11)–N(11)–Cu(1)	113.0 (6)	C(21)–N(21)–Cu(2)	114.4 (7)
C(19)–C(2)–C(3)	123.2 (9)	C(11)–N(11)–C(16)	119.9 (8)
C(21)–N(21)–C(26)	118.0 (9)		
	Perchlorate Ions		
O(11)–Cl(1)–O(12)	109.4 (5)	O(21)–Cl(2)–O(22)	108.8 (6)
O(11)–Cl(1)–O(13)	109.5 (6)	O(21)–Cl(2)–O(23)	106.9 (6)
O(12)–Cl(1)–O(13)	110.0 (5)	O(22)–Cl(2)–O(23)	110.5 (7)
O(11)–Cl(1)–O(14)	108.8 (7)	O(21)–Cl(2)–O(24)	112.0 (6)
O(12)–Cl(1)–O(14)	109.7 (7)	O(22)–Cl(2)–O(24)	109.1 (6)
O(13)–Cl(1)–O(14)	109.4 (5)	O(23)–Cl(2)–O(24)	109.7 (7)

Magnetic Measurements. These were carried out with a Faraday type magnetometer equipped with a continuous-flow cryostat in the 300–19 K temperature range for **1** and 300–2 K range for **2**. The independence of the magnetic susceptibility vs. the magnetic field was checked at room temperature. The diamagnetic correction was estimated at -267×10^{-6} cm^3 mol^{-1} for both **1** and **2**. 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

The compounds **1** and **2** are isomorphous. For both systems, the unit cell contains two dinuclear $[Cu_2(Famp)(X)]^{2+}$ cations and four perchlorate anions. The dinuclear unit for **2** is shown in Figure 1, with the labeling of the atoms. The two copper atoms of the dinuclear unit are connected by a double bridge: the oxygen atom of the phenolato ligand and the coordinated X_p atom of the second bridging group. The Cu(1)Cu(2)OX_p networks are nearly planar, with dihedral angles across OX_p equal to 167.2 and 171.6° for **1** and **2**, respectively. The copper(II) ions are in 4 + 2 environments. Each basal plane is made up of two nitrogen atoms and the oxygen atom of the Famp ligand and the bridging atom of the exogenous ligand. Both apical positions are occupied by oxygen atoms of perchlorate anions. Around Cu(1), the mean deviation of the atoms Cu(1), N(11), N(12), O, and X(p) from the basal plane is 0.035 Å for **1** and 0.05 Å for **2**, and the apical distances are almost equal. Around Cu(2), the mean deviation of the atoms Cu(2), N(21), N(22), O, and X(p) from the basal

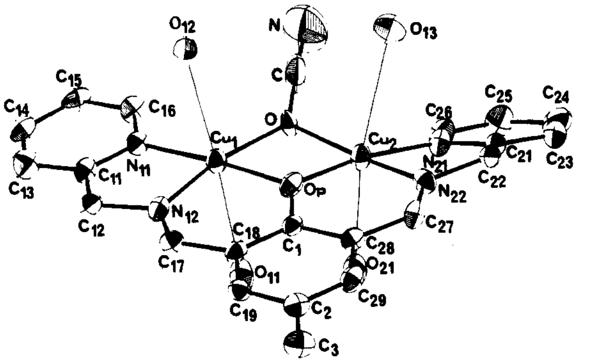

Figure 1. Perspective view of the dinuclear cation $[Cu_2(Famp)(OCN)]^{2+}$ in **2**.

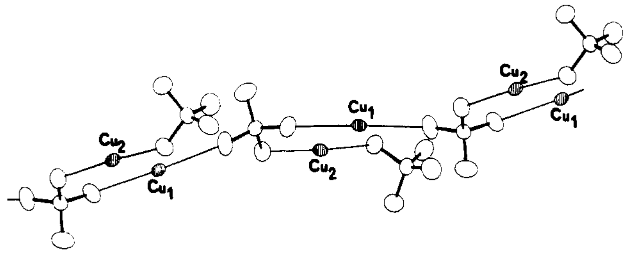

Figure 2. Interactions between the dinuclear cations through the perchlorate groups in **1** and **2**.

plane is longer, equal to 0.10 Å for both **1** and **2**, and the apical distances are different: 2.52 (1) and 2.82 (1) Å for **1** and 2.52 (1) and 2.77 (1) Å for **2**. In all cases, the copper atom is located in the basal plane.

In **1**, the bridging angles are Cu–O–Cu = 100.5 (3)° and Cu–N–Cu = 99.7 (3)°. The Cu(1)···Cu(2) separation is 2.993 (2) Å. The azido group is almost linear and makes an angle of 18.7° with the plane of the Famp ligand.

In **2**, OCN^- is found to bridge the copper atoms through its oxygen atom. We compared the R and B_{eq} values coorresponding to both the O-coordination and N-coordination. Those two tests are in favor of the O-coordination, as it is summarized:

	O-coordination	N-coordination
R	0.0390	0.0395
B_{eq}, Å^2	4.05 (O)	3.08 (N)
	7.03 (C)	7.08 (C)
	9.5 (N)	12.08 (O)

The bridging angles are Cu–O(phenolato)–Cu = 97.5 (3)° and Cu–O(OCN)–Cu = 99.8 (3)°. The Cu(1)···Cu(2) separation is 2.977 (2) Å. The direction of the cyanato group makes an angle of 18.8° with the plane of the Famp ligand.

The two perchlorate groups are bound quite differently to dinuclear units. The first one is bound to three different copper atoms; one oxygen atom is bound to Cu(1), a second oxygen atom to Cu(2) of the same dinuclear unit, and a third one to Cu(1) of another dinuclear unit. Consequently, this ClO_4 group provides a supplementary bridge between the metal centers within a dinuclear unit and connects these dinuclear units, making an infinite chain along the b axis, as shown in Figure 2. As for the second perchlorate group, one oxygen atom only is involved in a weak bond with Cu(2).

Magnetic Properties

Compound 1. The temperature dependence of the molar magnetic susceptibility χ_M for **1** is shown in Figure 3. χ_M exhibits a rounded maximum about 140 K characteristic of an intramolecular antiferromagnetic interaction. In the low-temperature range, χ_M shows a Curie tail due to the presence of a small proportion ρ of uncoupled copper(II). The theoretical expression for χ_M is

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

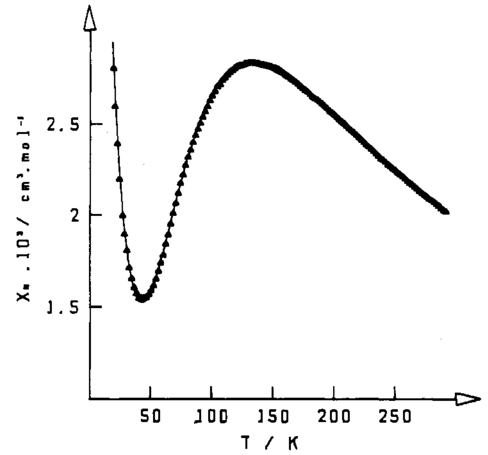

Figure 3. Experimental and calculated temperature dependences of the molar magnetic susceptibility for $[Cu_2(Famp)(N_3)](ClO_4)_2$ (**1**).

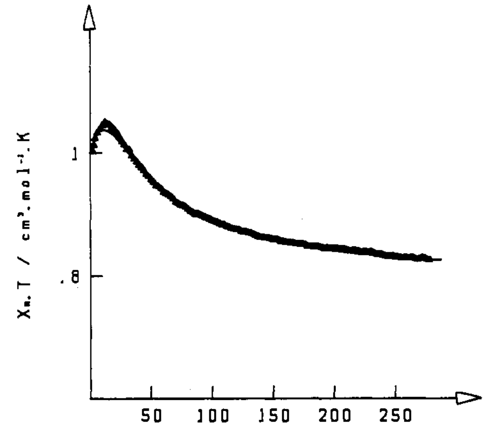

Figure 4. Experimental and Calculated temperature dependences of χ_MT for $[Cu_2(Famp)(OCN)](ClO_4)_2$ (**2**).

where the symbols have their usual meaning, J being here the singlet–triplet energy gap. The magnetic susceptibility of the uncoupled copper(II) impurity is assumed to follow a Curie law. The minimization of R, defined as $\sum(\chi_M^{obsd} - \chi_M^{calcd})^2/\sum(\chi_M^{obsd})^2$, leads to $J = -161$ cm^{-1} and $g = 2.01$ with $R = 2 \times 10^{-5}$.

Compound 2. Not only does the temperature dependence of χ_M for **2** not exhibit any maximum down to 2 K but also, in the 300–10 K range, χ_M increases upon cooling down more quickly than expected for a Curie law. In such a case, it is appropriate to plot the temperature dependence of χ_MT shown in Figure 4. At 290 K, χ_MT is equal to 0.830 cm^3 mol^{-1} K, increases upon cooling down, then reaches a rounded maximum about 10 K with $\chi_MT = 1.040$ cm^3 mol^{-1} K, and finally seems to decrease slightly below 10 K. Such a behavior reveals an intramolecular ferromagnetic interaction with a spin triplet ground state. The decrease of χ_MT below 10 K is almost within the experimental uncertainties. If it does actually exist, it could be due to both the zero-field splitting within the triplet state and very small intermolecular interactions. To account for these interactions, we may correct eq 1 using the molecular field exchange model[28] as shown in eq 2, where χ'_M is the corrected magnetic susceptibility actually

$$\chi'_M = \frac{\chi_M}{1 - (zJ'/N\beta^2g^2)\chi_M} \quad (2)$$

measured, χ_M is the magnetic susceptibility in the absence of the exchange field (eq 1), and zJ' is the product of the molecular field exchange constant and the number of interacting nearest neighbors.

J, g, and zJ' were determined by minimizing

$$R = \sum[(\chi_MT)^{obsd} - (\chi_MT)^{calcd}]^2/\sum[(\chi_MT)^{obsd}]^2$$

The parameters were found as $J = 43$ cm^{-1}, $g = 2.04$, and $zJ' =$

Table IX. S–T Energy Gap (cm^{-1}) for the Compounds [Cu_2(Fdmen)(X)](ClO_4)$_2$ and [Cu_2(Famp)(X)](ClO_4)$_2$

X	Fdmen series	Famp series
OH	−367	−364
N_3^-	−86.5	−161
OCN^-	−3.8	+43

−0.08 cm^{-1} with $R = 3.7 \times 10^{-4}$. As has already been pointed out,[20,21] the uncertainty on J in such a case of ferromagnetic interaction is much larger than in the preceding case of antiferromagnetic interaction. This uncertainty may be estimated here as ±10 cm^{-1}. The ferromagnetic nature of the interaction, however, is beyond doubt.

For both **1** and **2**, the X-band EPR spectra are very badly resolved with broad features covering all the magnetic field range up to 8000 G, in addition to a sharp signal at $g \approx 2.1$ assigned to the uncoupled copper(II). For **1**, this spectrum vanishes upon cooling down to 4.2 K, which confirms that it is associated with a triplet excited state. For **2**, in contrast, the lower the temperature is, the more intense the spectrum. The poor resolution of these spectra precludes any quantitative interpretation.

Discussion

The first point deserving to be stressed is the O-coordination of the cyanato bridge in **2**. If such a coordination had already been postulated from spectroscopic data,[22,24] it has been characterized only once before,[3] in [Cu_2(Fdmen)(OCN)](ClO_4)$_2$. Surprisingly, the N-coordination has been found in a compound of the same type,[2] namely

$$[Cu_2(\mathrm{Fdmen})(NCO)(CH_3CO_2)](PF_6)$$

It is obviously impossible from this limited set of structural data to specify the factors favoring one type of coordination over the other one.

We propose now to discuss the magnetic properties in a comparative fashion, by taking into account the two series of compounds already investigated, [Cu_2(Fdmen)(X)](ClO_4)$_2$ and [Cu_2(Famp)(X)](ClO_4)$_2$. The results are summarized in Table IX. The comparison can be carried out either within a series for X varying or between the series for two compounds with the same exogenous bridge X. Let us consider first the three compounds of the Famp series. The singlet–triplet (S–T) energy gap varies as

$$J_{\mathrm{OCN}}\ (43\ \mathrm{cm^{-1}}) > J_{\mathrm{N_3}}\ (-161\ \mathrm{cm^{-1}}) > J_{\mathrm{OH}}\ (-364\ \mathrm{cm^{-1}})$$

which is parallel to what has been found in the Fdmen series. There is, however, quite an important difference between the two series. For the Fdmen derivatives, the three compounds had a singlet ground state, even if this singlet was stabilized by only 3.8 cm^{-1} with regard to the triplet for X = OCN. In contrast, [Cu_2(Famp)(OCN)](ClO_4)$_2$ is one of the few copper(II) dinuclear complexes with a triplet ground state. One can recall here that 2 or 3 years ago, the compounds of this kind were so rare that some authors expressed their skepticism on the existence of such compounds.[25]

As expected, the hydroxo compound exhibits a rather strong antiferromagnetic interaction. The two Cu–O–Cu bridging angles are large, 99.19° on the phenolato side and 100.44° on the hydroxo side, which favors the pairing of the electrons.[26] The azido compound has also a singlet ground state, but with a smaller S–T energy gap, in spite of an increase of the Cu–O(phenolato)–Cu angle, 100.5° instead of 99.19°. This is consistent with the fact that N_3^- exerts a ferromagnetic contribution, which in the present case does not entirely compensate the strong antiferromagnetic contribution due to the phenolato bridge. As for the cyanato compound, it is worthwhile to notice that it has the smallest bridging angle around the phenolato oxygen atom (3° smaller than in the azido compound), which likely explains why the ferromagnetic effect due to OCN^- in **2** takes over.

The comparison between the Famp and Fdmen derivatives does not reveal yet any clear trend. We can, however, note the following points: (i) The nature of the lateral chains is not innocent. So, as far as the hydroxo complexes are concerned, the S–T energy gaps in the Famp and the Fdmen derivatives are almost equal (−364 and −367 cm^{-1}, respectively) whereas the bridging angles are significantly smaller in the latter compound. In the near future, we shall show how the role of these $N\frown Y$ groups can be important. (ii) Concerning the azido and cyanato compounds now, one may remark that the angle between the direction of these exogenous ligands and the plane of the bridging network is much more pronounced in the Fdmen (43.8° for X = N_3^- and 28.4° for X = OCN^-) than in the Famp derivatives (18.7° for X = N_3^- and 18.8° for X = OCN^-). When the set of the experimental data is more extended, we hope to be able to propose a more heuristic rationalization of the magnetic properties of these compounds with dissimilar bridges. From this paper and the preceding one dealing with this problem, there already emerges a confirmation of the ferromagnetic contribution exerted by the 1,1-azido and cyanato-*O* bridges. Apparently, OCN^- is even more efficient than N_3^- in this respect. [Cu_2(Famp)(OCN)](ClO_4)$_2$ is a new compound of the limited class of copper(II) dinuclear complexes with a triplet ground state.

Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms (Tables X and XI) (2 pages); listings of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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