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Tunable Interaction in μ-Oxamido Copper(II) Binuclear Complexes

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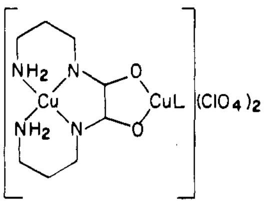
The goal of this paper is to show how it is possible to vary the singlet–triplet energy gap J arising from the interaction between two copper(II) ions through the oxamido bridge in a predictable manner. From the planar monomeric fragment Cu(oxpn), where oxpn is N,N'-bis(3-aminopropyl)oxamido, we have synthesized three complexes, namely $[Cu(oxpn)Cu(bpy)](ClO_4)_2$ (**1**; bpy = 2,2'-bipyridyl), $[Cu(oxpn)Cu(petdien)](ClO_4)_2$ (**2**; petdien = N,N,N',N'',N''-pentaethyldiethylenetriamine), and $[Cu(oxpn)Cu(pmedien)](ClO_4)_2$ (**3**; pmedien = N,N,N',N'',N''-pentamethyldiethylenetriamine). The crystal structures of **1** and **2** have been determined. Crystal data for **1**: monoclinic, space group $P2_1/c$, a = 12.548 (2) Å, b = 19.314 (4) Å, c = 10.549 (1) Å, β = 96.12 (1)° (at 293 K), Z = 4. In **1**, the two copper(II) ions are in square-pyramidal surroundings with almost coplanar basal planes. The Cu···Cu separation is 5.195 (1) Å. Crystal data for **2**: monoclinic, space group $P2_1/c$, a = 12.793 (4) Å, b = 15.500 (6) Å, c = 17.241 (6) Å, β = 108.00 (3)° (at approximately 150 K), Z = 4. In **2**, one of the copper(II) ions is in an almost planar environment; the other one, on the petdien side, is in an environment intermediate between the square pyramid and the trigonal bipyramid. In **3**, the environment of the metal on the pmedien side is expected to be close to a square pyramid with a basal plane perpendicular to the basal plane of the other metal. The singlet–triplet energy gaps J in **1**–**3** were deduced from the temperature dependences of the magnetic susceptibility. J was found to be equal to $-439.7\ cm^{-1}$ in **1**, $-242.0\ cm^{-1}$ in **2**, and $-82.8\ cm^{-1}$ in **3**. The EPR spectra of these compounds are also discussed.

Introduction

For several years, our group has been engaged in the design of coupled polymetallic systems exhibiting expected magnetic properties. A first step was the synthesis of $Cu^{II}–V^{IV}O$ and $Cu^{II}–Cr^{III}$ heterobinuclear complexes in which the interaction is purely ferromagnetic owing to the strict orthogonality of the magnetic orbitals.[2,3] In a following step, we attempted to tune the magnitude of the interaction between two copper(II) ions through a given extended ligand.[4] This was realized in the series of the μ-oxalato copper(II) binuclear complexes $[LCu(C_2O_4)CuL']^{2+}$. The modification of the magnitude of the intramolecular interaction was achieved by playing on the nature of the L and L' terminal ligands, so as to impose the relative orientation of the two magnetic orbitals centered on the metal ions. To some extent, L and L' serve as "adjusting screws" for tuning the magnitude of the interaction. One of the keys of this strategy is the synthesis of dissymmetrical complexes with L $\neq$ L'. With a symmetrical bridge like oxalato, such a synthesis is difficult. In fact, until now it has succeeded only once[4] with $[(dien)Cu(C_2O_4)(H_2O)_2Cu(tmen)](ClO_4)_2$. Many other attempts gave the two symmetrical species $[LCu(C_2O_4)CuL]^{2+}$ and $[L'Cu(C_2O_4)CuL']^{2+}$. On the other hand, a dissymetrical bridge like *cis*-oxamido in which the cis configuration was imposed by the method of preparation was a priori well adapted to develop the strategy of tunable interaction.

This paper is devoted to a series of μ-oxamido copper(II) binuclear complexes. More precisely, we describe the synthesis of three complexes of general formula



where L is 2,2'-bipyridyl (bpy) (**1**), N,N,N',N'',N''-pentaethyldiethylenetriamine (petdien) (**2**), and N,N,N',N'',N''-pentamethyldiethylenetriamine (pmedien) (**3**). The syntheses of Cu(oxpn) and of **1** were first reported by Ojima and Nonoyama.[5] For two of these compounds, namely **1** and **2**, the crystal structure was determined and refined. The magnetic properties were investigated in order to determine accurately the singlet–triplet (S–T) energy gaps. These values will be confronted with the predictions made in the framework of a model where the S–T energy gap is assumed to vary as the square of the overlap integral between the magnetic orbitals. The EPR spectra will also be presented and discussed.

Experimental Section

Syntheses. Cu(oxpn).[5] To a solution of 0.3 mol of 1,3-propylenediamine in 30 mL of ethanol cooled by an ice bath was added dropwise a solution of 0.1 mol of diethyl oxalate in 20 mL of ethanol. The mixture was heated at reflux for 1 h and then cooled down. A 0.08-mol sample of copper(II) hydroxide[6] in suspension in 500 mL of water was added, which led to a violet solution and a brown solid residue. By adding $Cu(OH)_2$ in less than stoichiometric amount, the formation of the blue binuclear complex $Cu(oxpn)Cu(OH)_2$ is avoided. The mixture was filtered. The solid residue was washed with water in order to extract all the expected compound. Red single crystals of Cu(oxpn) were obtained by evaporation of the aqueous solution. Cu(oxpn) is very soluble in water and insoluble in methanol or ethanol. Anal. Calcd for $C_8H_{16}N_4O_2Cu$: C, C, 36.43; H, 6.11; N, 21.24; O, 12.13. Found: C, 36.44; H, 6.08; N, 21.27; O, 12.29.

$[Cu(oxpn)Cu(bpy)](ClO_4)_2$ (1).[5] To 200 mL of an aqueous solution of 264 mg (10^{-3} mol) of Cu(oxpn) were successively added 10 mL of an aqueous solution containing 371 (10^{-3} mol) of copper(II) perchlorate and 10 mL of an aqueous solution containing 158 mg (10^{-3} mol) of bpy. The solution was then filtered. Well-shaped single crystals were obtained by slow evaporation. Anal. Calcd for $C_{18}H_{24}N_6O_{10}Cl_2Cu_2$: C, 31.68; H, 3.54; N, 12.32; O, 23.44; Cl, 10.39. Found: C, 31.38; H, 3.63; N, 12.02; O, 24.07; Cl, 10.95.

$[Cu(oxpn)Cu(petdien)](ClO_4)_2$ (2) was prepared in the same way by using pedtien instead of bpy. Anal. Calcd for $C_{22}H_{49}N_7O_{10}Cl_2Cu_2$: C, 34.33; H, 6.42; N, 12.74; O, 20.79; Cl, 9.21. Found: C, 34.14; H, 6.17; N, 12.58; O, 20.48; Cl, 9.46.

$[Cu(oxpn)Cu(pmedien)](ClO_4)_2$ (3). To 264 mg (10^{-3} mol) of Cu(oxpn) stirred in 20 mL of methanol were successively added a solution of 371 mg (10^{-3} mol) of copper(II) perchlorate in 5 mL of methanol and 173 mg (10^{-3} mol) of pmedien in 10 mL of methanol. The solution became almost limpid. It was filtered. Small crystals were obtained by slow diffusion of ethanol into the methanolic solution. Anal. Calcd for $C_{17}H_{39}N_7O_{10}Cl_2Cu_2$: C, 29.19; H, 5.62; N, 14.02; O, 22.87; Cl, 10.14. Found: C, 29.38; H, 5.65; N, 14.08; O, 22.54; Cl, 11.30.

Crystallographic Data Collection and Refinement of the Structure. Information concerning the crystallographic data collections and the refinement conditions is given in Table I.

$[Cu(oxpn)Cu(bpy)](ClO_4)_2$ (1). Low-temperature data could not be obtained owing to a split of the reflections upon cooling down. This may

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Table I. Information Concerning the Crystallographic Data Collection and Refinement Conditions for [Cu(oxpn)Cu(bpy)]$(ClO_4)_2$ (**1**) and [Cu(oxpn)Cu(petdien)]$(ClO_4)_2$ (**2**)

	1	**2**
mol formula	$Cu_2Cl_2C_{18}H_{24}N_6O_{10}$	$Cu_2Cl_2C_{22}H_{49}N_7O_{10}$
M_r	682.41	769.66
space group	$P2_1/c$	$P2_1/c$
temp at cryst, K	293	150
unit cell		
a, Å	12.548 (2)	12.973 (4)
b, Å	19.314 (4)	15.500 (6)
c, Å	10.549 (1)	17.241 (6)
β, deg	96.72 (1)	108.00 (3)
V, Å^3	2539.0 (7)	3297 (2)
Z	4	4
μ(Mo Kα), cm^{-1}	19.54	15.14
instrument	CAD-4	CAD-4
scan type	ω	ω
scan range $\Delta\omega$, deg	0.50 + 0.35(tan θ)	0.60 + 0.35(tan θ)
scan speed, deg/min	4	1.25
radiation	monochromatized Mo Kα	monochromatized Mo Kα
max 2θ, deg	50	45
no. of measd reflcns	4676	4042
no. of "obsd" reflcns (NO)	3953	2743
limit of "obsd" reflcns	$\|F_o\| > 2\sigma_F$	$\|F_o\| > 3\sigma_F$
no. of variables refined (NV)	416	375
agreement factors[a]		
R	0.048	0.094
R_w	0.063	0.096
s	3.25	4.25
extinction coeff	2.87 × 10^{-7}	not refined

[a] Agreement factors are defined as follows: $R = \sum||F_o| - |F_c||/\sum|F_o|$; R_w $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $s = [\sum w(|F_o| - |F_c|^2/(NO - NV)]^{1/2}$. The weighting scheme is defined by $w = 1/\sigma_F^2$; $\sigma_F = \sigma_I(ILp)^{-1/2}$; $\sigma_I = [\sigma_c^2+(0.02N_{net})^2]^{1/2}$; where k = 0.01 for **1** and 0.02 for **2**, respectively. Atomic scattering factors and programs used are those of ref 25 and 26.

be due to an order–disorder transformation. The subsequent refinement showed that a disorder was actually present at room temperature. The copper atoms and the equatorial ligating atoms were located in the *E* map. The positions of the remaining atoms were deduced from subsequent Fourier maps. Isotropic refinement of non-hydrogen atoms led to R = 0.117. High thermal parameters of the atoms of perchlorate group number 2 and of C1 and C2 indicated disorder in these parts of the structure. A difference map showed residual electron densities in these regions. Refinement of atoms with partial occupancy was attempted. The disorder could not be unambiguously resolved, however, and further refinement was based on an ordered model. Since the disorder problem is the factor limiting the accuracy of the structure determination, and also owing to the small size of the crystal (0.16 × 0.17 × 0.36 mm), an absorption correction was not deemed necessary. The hydrogen atoms, excluding those in the disordered region, were located from a difference map and were refined isotropically. Non-hydrogen atoms were refined anisotropically. An extinction parameter was included in the final least-squares cycles. The refinement converged at R = 0.048, R_w = 0.063, and s = 3.25. The comparatively high value for the "goodness of fit" parameter, s, probably reflects the deficiency in the model due to the unresolved disorder. The atomic parameters are given in Table II.

[Cu(oxpn)Cu(petdien)]$(ClO_4)_2$ (2). A preliminary room-temperature investigation revealed appreciable disorder in the structure. It was hoped that a low-temperature study might resolve this problem. However, the subsequent refinement showed that the disorder persists at low temperature (150 K). As refinement with the low-temperature data set gave somewhat lower standard deviations in atomic parameters, these are the results quoted in this paper. The disorder in the perchlorate groups were partly resolved, as a double set of oxygen peaks could be located in the difference Fourier maps. Again, absorption correction was not deemed necessary owing to the quite even shape of the crystal with lengths of the three sides almost equal. Thermal parameters for other atoms, especially for some of the carbon atoms, suggest that disorder is present also in other parts of the molecule. This disorder could not be resolved, however. Disordered perchlorate oxygens were refined isotropically, other atoms anisotropically. Hydrogen atoms were not located. The refinement converged at R = 0.094, R_w = 0.096, and s = 4.25. The atomic parameters are given in Table III.

Table II. Atomic Parameters for Non-Hydrogen Atoms of [Cu(oxpn)Cu(bpy)]$(ClO_4)_2$[a] (**1**)

atom	x	y	z	B_{eq}, Å^2
Cu1	0.37388 (5)	0.12595 (3)	0.25925 (5)	3.49 (1)
Cu2	0.12713 (5)	0.02774 (3)	0.57878 (5)	3.22 (1)
Cl1	0.2373 (1)	0.07703 (7)	0.9023 (1)	4.13 (3)
Cl2	0.6078 (2)	0.2446 (1)	0.4465 (2)	7.98 (5)
O1	0.2445 (3)	−0.0057 (2)	0.4932 (3)	3.56 (7)
O2	0.1334 (2)	0.1103 (2)	0.4766 (3)	3.38 (7)
O3	0.2391 (3)	0.0765 (2)	0.7673 (3)	4.47 (8)
O4	0.2406 (4)	0.0073 (2)	0.9472 (4)	6.5 (1)
O5	0.3265 (4)	0.1139 (2)	0.9599 (4)	6.6 (1)
O6	0.1402 (4)	0.1101 (3)	0.9287 (4)	7.6 (1)
O7	0.5700 (6)	0.3016 (3)	0.4890 (7)	15.3 (2)
O8	0.6088 (6)	0.2488 (6)	0.3163 (6)	19.7 (4)
O9	0.7030 (6)	0.2272 (4)	0.4986 (8)	21.7 (3)
O10	0.5247 (8)	0.1958 (4)	0.4440 (7)	21.2 (3)
N1	0.5027 (4)	0.0928 (3)	0.1839 (4)	5.6 (1)
N2	0.3528 (3)	0.0376 (2)	0.3486 (4)	3.69(9)
N3	0.3875 (4)	0.2157 (2)	0.1684 (4)	4.5 (1)
N4	0.2428 (3)	0.1532 (2)	0.3346 (4)	3.40 (8)
N5	0.1136 (3)	−0.0558 (2)	0.6808 (4)	3.37 (9)
N6	−0.0007 (3)	0.0557 (2)	0.6588 (4)	3.38 (8)
C1	0.5464 (7)	0.0250 (4)	0.2172 (9)	16.0 (2)
C2	0.4889 (6)	−0.0283 (4)	0.2460 (8)	10.1 (2)
C3	0.4113 (4)	−0.0299 (3)	0.3483 (5)	4.8 (1)
C4	0.3165 (5)	0.2753 (3)	0.1881 (5)	4.7 (1)
C5	0.2007 (5)	0.2542 (3)	0.1931 (5)	4.5 (1)
C6	0.1814 (4)	0.2184 (3)	0.3183 (5)	4.0 (1)
C7	0.2753 (4)	0.0405 (2)	0.4187 (4)	3.2 (1)
C8	0.2126 (4)	0.1071 (2)	0.4084 (4)	3.1 (1)
C9	0.0390 (4)	−0.0525 (3)	0.7621 (4)	3.4 (1)
C10	0.0296 (5)	−0.1042 (3)	0.8513 (5)	4.7 (1)
C11	0.0986 (5)	−0.1595 (3)	0.8571 (5)	5.3 (1)
C12	0.1734 (5)	−0.1626 (3)	0.7753 (6)	5.5 (1)
C13	0.1799 (4)	−0.1104 (3)	0.6857 (5)	4.3 (1)
C14	−0.0263 (4)	0.0114 (3)	0.7495 (4)	3.5 (1)
C15	−0.1049 (4)	0.0263 (3)	0.8256 (5)	4.5 (1)
C16	−0.1589 (5)	0.0889 (3)	0.8066 (5)	5.1 (1)
C17	−0.1334 (5)	0.1324 (3)	0.7134 (6)	5.1 (1)
C18	−0.0542 (4)	0.1155 (3)	0.5426 (5)	4.3 (1)

[a] The isotropic equivalent thermal parameter is given as $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i{\cdot}a_j$.

Magnetic measurements were carried out with a Faraday type magnetometer equipped with a continuous-flow cryostat. The polycrystalline powder samples weighed about 10 mg. The independence of the susceptibility against the magnetic field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections were estimated as −328 × 10^{-6}, −425 × 10^{-6}, and −390 × 10^{-6} cm^3 mol^{-1} for **1**, **2**, and **3**, respectively.

EPR. The spectra were recorded at X-band frequency with a Bruker ER 200 D spectrometer equipped with an Oxford Instruments continuous-flow cryostat. The magnetic field was determined with a Hall probe and the klystron frequency with a Hewlett-Packard frequency meter.

Basic Concepts

We have shown that the S–T energy gap J in a binuclear copper(II) complex may be expressed as the sum of a negative antiferromagnetic contribution J_{AF} and a positive ferromagnetic contribution J_F:[7]

$$J = J_{AF} + J_F \tag{1}$$

J_{AF} varies as the square S^2 of the overlap integral between the magnetic orbitals and J_F as the two-electron-exchange integral between these magnetic orbitals. We have also shown that this latter contribution likely is vanishing when the metal centers are bridged by extended polyatomic ligands.[4,7] This assumption was substantiated by the fact that J is actually very close to zero in

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(7) Kahn, O. "Magneto Structural Correlations in Exchange Coupled Systems"; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel: Dordrecht, 1984.

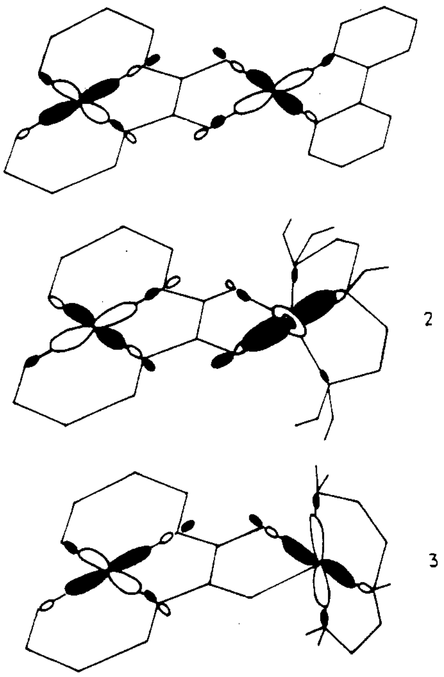
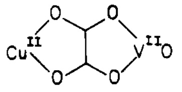


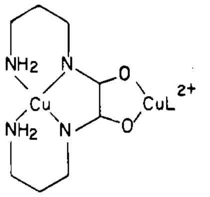
Figure 1. Relative orientations of the magnetic orbitals in **1**, **2**, and **3**.

$[(tmen)Cu(C_2O_4)VO(C_2O_4)]\cdot 3H_2O$,[8] where the bridging network is

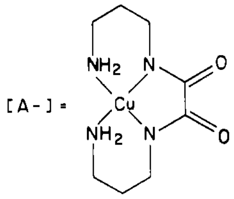


and where the magnetic orbitals centered on the Cu^{II} and $V^{IV}O$ ions are strictly orthogonal.

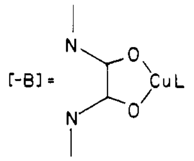
In the complexes



we can define a monomeric fragment[7]



which will remain unchanged along the series, and another monomeric fragment



which may be modified by changing L. The two magnetic orbitals are defined as the highest occupied molecular orbitals for the monomeric fragments [A–] and [–B] in their ground state.[7] In [A–], the copper(II) ion is in planar surroundings and the magnetic orbital is located in the molecular plane and points toward the nearest-neighbor nitrogen atoms, as shown in Figure 1. As for the orientation of the magnetic orbital in [–B], it depends on the nature of L. More precisely, the copper(II) ion in [–B] will tend to adopt a 4, 4 + 1 or 4 + 2 configuration with four nearest neighbors forming a basal plane in which the magnetic orbital will be essentially located.[4] When there is a competition between nonbulky oxygen and nitrogen atoms as nearest neighbors, the copper(II) ion, most often, chooses first the nitrogen atoms and then eventually completes its basal plane with oxygen atoms. Consequently, when L is a diamine,[4,9-12] the magnetic orbital is located in the plane of the oxamido bridge, and when L is a

Table III. Atomic Parameters for $[Cu(oxpn)Cu(petdien)](ClO_4)_2$[a] (**2**)

atom	x	y	z	B_{eq}, Å^2
Cu1	0.6098 (1)	0.1259 (1)	0.2836 (1)	4.11 (4)
Cu2	0.1981 (1)	0.1534 (1)	0.1183 (1)	4.21 (4)
Cl1	0.1922 (3)	−0.0651 (2)	0.0328 (2)	5.3 (1)
Cl2	0.0504 (4)	0.3497 (3)	0.1422 (4)	13.9 (2)
O1	0.5201 (6)	0.1875 (5)	0.1830 (5)	3.8 (2)
O2	0.4702 (7)	0.1039 (5)	0.2988 (5)	4.3 (2)
O3	0.202 (1)	−0.123 (1)	−0.0284 (9)	5.6 (4)*
O4	0.086 (2)	−0.070 (1)	0.044 (1)	9.6 (6)*
O5	0.220 (2)	0.016 (1)	0.030 (1)	9.1 (6)*
O6	0.275 (2)	−0.094 (1)	0.114 (1)	10.7 (7)*
O7	−0.030 (1)	0.301 (1)	0.081 (1)	4.5 (4)*
O8	0.036 (3)	0.344 (3)	0.231 (3)	21 (2)*
O9	0.147 (2)	0.313 (2)	0.154 (2)	9.6 (7)*
O10	0.023 (2)	0.433 (2)	0.133 (1)	9.5 (7)*
O3A	0.264 (2)	−0.106 (2)	−0.001 (2)	8.2 (8)*
O4A	0.120 (2)	−0.115 (1)	0.058 (1)	3.9 (5)*
O5A	0.124 (2)	0.000 (2)	−0.033 (1)	6.8 (7)*
O6A	0.250 (2)	−0.006 (2)	0.092 (2)	7.6 (7)*
O7A	−0.038 (2)	0.289 (1)	0.119 (1)	6.8 (5)*
O8A	0.027 (2)	0.412 (2)	0.176 (1)	9.1 (7)*
O9A	0.133 (2)	0.297 (1)	0.200 (1)	6.2 (5)*
O10A	0.108 (3)	0.391 (2)	0.072 (2)	14 (1)*
N1	0.3366 (8)	0.1959 (6)	0.1079 (6)	3.8 (3)
N2	0.2891 (8)	0.1163 (7)	0.2297 (6)	4.0 (3)
N3	0.0624 (8)	0.1079 (8)	0.1299 (8)	6.5 (4)
N4	0.107 (1)	0.1899 (8)	0.0089 (8)	6.9 (4)
N5	0.6263 (9)	0.0063 (7)	0.2078 (7)	5.1 (3)
N6	0.7524 (9)	0.1620 (8)	0.2686 (9)	7.6 (4)
N7	0.691 (1)	0.1156 (8)	0.4071 (8)	7.9 (4)
C1	0.4218 (9)	0.1743 (7)	0.1716 (7)	3.1 (3)
C2	0.3906 (9)	0.1277 (8)	0.2380 (7)	3.3 (3)
C3	0.362 (1)	0.2379 (9)	0.0387 (7)	4.9 (4)
C4	0.263 (2)	0.247 (2)	−0.034 (1)	16.2 (8)
C5	0.156 (2)	0.230 (2)	−0.043 (1)	12.4 (8)
C6	0.067 (1)	0.046 (1)	0.195 (1)	7.7 (5)
C7	0.132 (1)	0.078 (1)	0.275 (1)	9.5 (6)
C8	0.263 (1)	0.070 (1)	0.2941 (8)	5.7 (4)
C9	0.712 (1)	0.036 (1)	0.175 (1)	11.9 (6)
C10	0.789 (1)	0.091 (1)	0.220 (1)	10.0 (6)
C11	0.836 (1)	0.169 (1)	0.348 (2)	12.8 (8)
C12	0.812 (2)	0.112 (2)	0.405 (2)	15.9 (9)
C13	0.526 (1)	−0.001 (1)	0.1355 (9)	7.4 (5)
C14	0.535 (2)	−0.075 (1)	0.074 (1)	10.4 (7)
C15	0.662 (2)	−0.073 (1)	0.249 (1)	8.4 (6)
C16	0.559 (2)	−0.109 (1)	0.272 (1)	13.0 (8)
C17	0.731 (1)	0.264 (2)	0.232 (1)	17.6 (8)
C18	0.843 (2)	0.277 (2)	0.237 (2)	20 (1)
C19	0.660 (2)	0.033 (1)	0.443 (1)	13.1 (7)
C20	0.735 (2)	0.030 (2)	0.521 (2)	17 (1)
C21	0.692 (2)	0.197 (1)	0.444 (1)	14.4 (9)
C22	0.598 (2)	0.209 (1)	0.457 (1)	9.8 (6)*

[a] For atoms refined anisotropically the isotropic equivalent thermal parameter is given: $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i\cdot a_j$. Values for atoms isotropically refined are marked with an asterisk. The thermal parameter given for these atoms is defined by $\exp[-B(\sin^2\theta)/\lambda^2]$.

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Table IV. Bond Distances (Å) and Angles (deg) in [Cu(oxpn)Cu(bpy)]$(ClO_4)_2$ (**1**)

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Cu1	O10	2.887 (5)	Cl2	O7	1.299 (3)	C1	C2	1.313 (7)
Cu1	N1	1.989 (3)	Cl2	O8	1.377 (4)	C2	C3	1.535 (5)
Cu1	N2	1.983 (2)	Cl2	O9	1.300 (4)	C4	C5	1.516 (4)
Cu1	N3	1.997 (2)	Cl2	O10	1.403 (5)	C5	C6	1.535 (4)
Cu1	N4	1.980 (2)	N1	C1	1.447 (5)	C7	C8	1.505 (4)
Cu2	O1	1.927 (2)	N2	C3	1.496 (3)	C9	C10	1.387 (4)
Cu2	O2	1.932 (2)	N2	C7	1.291 (3)	C9	C14	1.479 (4)
Cu2	O3	2.482 (2)	N3	C4	1.486 (4)	C10	C11	1.371 (5)
Cu2	N5	1.959 (2)	N4	C6	1.474 (4)	C11	C12	1.348 (5)
Cu2	N6	1.974 (2)	N4	C8	1.271 (3)	C12	C13	1.392 (4)
Cl1	O3	1.428 (2)	N5	C9	1.342 (3)	C14	C15	1.373 (4)
Cl1	O4	1.427 (2)	N5	C13	1.340 (4)	C15	C16	1.389 (5)
Cl1	O5	1.403 (2)	N6	C14	1.350 (3)	C16	C17	1.359 (5)
Cl1	O6	1.431 (2)	N6	C18	1.335 (4)	C17	C18	1.351 (4)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O10	Cu1	N1	85.5 (1)	O5	Cl1	O6	110.1 (1)	N2	C3	C2	109.6 (3)
O10	Cu1	N2	101.2 (2)	O7	Cl2	O8	109.9 (2)	N3	C4	C5	112.9 (3)
O10	Cu1	N3	80.3 (2)	O7	Cl2	O9	115.3 (2)	C4	C5	C6	113.5 (3)
O10	Cu1	N4	96.6 (1)	O7	Cl2	O10	105.9 (3)	N4	C6	C5	110.6 (2)
N1	Cu1	N2	94.2 (1)	O8	Cl2	O9	108.8 (2)	O1	C7	N2	128.6 (3)
N1	Cu1	N3	88.2 (1)	O8	Cl2	O10	96.6 (2)	O1	C7	C8	116.6 (3)
N1	Cu1	N4	176.6 (1)	O9	Cl2	O10	118.6 (3)	N2	C7	C8	114.8 (2)
N2	Cu1	N3	177.2 (1)	Cu2	O1	C7	110.9 (3)	O2	C8	N4	127.6 (4)
N2	Cu1	N4	82.84 (9)	Cu2	O2	C8	110.7 (4)	O2	C8	C7	115.5 (3)
N3	Cu1	N4	94.8 (1)	Cu1	N1	C1	119.8 (3)	N4	C8	C7	116.9 (2)
O3	Cu2	O1	96.3 (1)	Cu1	N2	C3	131.0 (2)	N5	C9	C10	121.3 (3)
O3	Cu2	O2	94.4 (1)	Cu1	N2	C7	112.7 (2)	N5	C9	C14	113.8 (2)
O3	Cu2	N5	87.12 (8)	C3	N2	C7	116.3 (2)	C10	C9	C14	124.9 (3)
O3	Cu2	N6	88.03 (8)	Cu1	N3	C4	121.3 (2)	C9	C10	C11	119.2 (3)
O1	Cu2	O2	86.1 (3)	Cu1	N4	C6	128.9 (2)	C10	C11	C12	119.2 (3)
O1	Cu2	N5	95.8 (2)	Cu1	N4	C8	112.4 (2)	C11	C12	C13	120.3 (3)
O1	Cu2	N6	175.1 (2)	C6	N4	C8	118.7 (2)	N5	C13	C12	120.6 (3)
O2	Cu2	N5	177.4 (2)	Cu2	N5	C9	115.0 (2)	N6	C14	C9	114.7 (2)
O2	Cu2	N6	95.8 (2)	Cu2	N5	C13	125.1 (2)	N6	C14	C15	121.9 (3)
N5	Cu2	N6	82.15 (9)	C9	N5	C13	119.3 (2)	C9	C14	C15	123.4 (3)
O3	Cl1	O4	108.7 (1)	Cu2	N6	C14	113.7 (2)	C14	C15	C16	118.0 (3)
O3	Cl1	O5	109.3 (1)	Cu2	N6	C18	127.1 (2)	C15	C16	C17	119.4 (3)
O3	Cl1	O6	108.1 (1)	C14	N6	C18	118.8 (3)	C16	C17	C18	120.0 (3)
O4	Cl1	O5	110.1 (1)	N1	C1	C2	124.2 (6)	N6	C18	C17	121.9 (3)
O4	Cl1	O6	110.4 (1)	C1	C2	C3	126.2 (4)				

nonbulky triamine,[13-17] it is located in a plane perpendicular to the plane of the oxamido bridge. In this latter case, the environment of the copper(II) ion may also acquire some trigonal-bipyramidal character and accordingly the magnetic orbital may acquire some d_{z^2} character with a nonzero spin density on the apical site.[4,16] The situation may be more complicated when L is a bulky triamine, owing to the eventual steric hindrance. Nevertheless, it has been observed that the bulkier the triamine bound to the metal is, the more pronounced the trigonal-bipyramidal character.[13-17]

From the considerations above, we can choose L according to the relative magnitude of the antiferromagnetic interaction we want to achieve. If we wish a very large interaction, L will be taken as a nitrogen-containing bidentate ligand. Indeed, the two magnetic orbitals will then be favorably oriented to overlap of each side of the bridge as schematized in Figure 1. This has been realized by using L = bpy and preparing [Cu(oxpn)Cu(bpy)]$(ClO_4)_2$ (**1**).[5] If, on the contrary, we want to minimize the interaction, L will be taken as a nonbulky nitrogen-containing tridentate ligand, so that the magnetic orbitals will overlap only on one side of the bridge (see Figure 1). The magnitude of the interaction is then expected to be roughly one-fourth of what it is in the previous case since the ratio of the overlap integrals is about 1/2. L = diethylenetriamine would be a particularly good candidate for that;[13,14] unfortunately, we did not succeed in synthesizing [Cu(oxpn)Cu(dien)]$(ClO_4)_2$. On the other hand, we were able to prepare [Cu(oxpn)Cu(pmedien)]$(ClO_4)_2$ (**3**). Finally, if we wish to obtain an interaction of intermediate magnitude, we can choose L as a bulky nitrogen-containing tridentate ligand in order to favor the trigonal-bipyramidal character, which leads to an orbital interaction as shown in Figure 1. This has been achieved with L = petdien in the compound [Cu(oxpn)Cu(petdien)]$(ClO_4)_2$ (**2**).

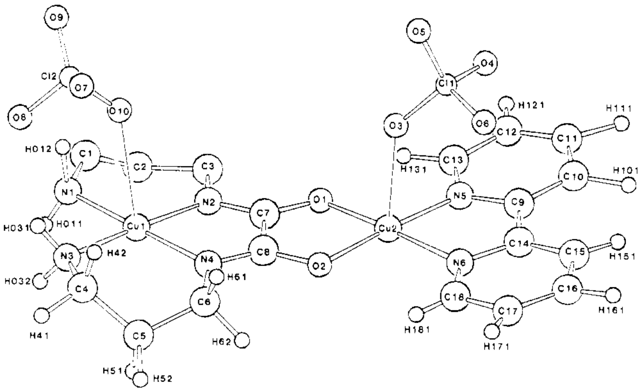

Figure 3. Perspective view of [Cu(oxpn)Cu(bpy)]$^{2+}$ in **1**. Hydrogen atoms were not located in the disorder region C1, C2, and C3.

Description of the Structures

[Cu(oxpn)Cu(bpy)]$(ClO_4)_2$ (1). The bond lengths and angles are given in Table IV. The crystal packing is shown in Figure

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Table V. Bond Distances (Å) and Angles (deg) in [Cu(oxpn)Cu(petdien)]$(ClO_4)_2$ (**2**)

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Cu1	O1	2.007 (4)	Cl1	O6A	1.41 (2)	N6	C10	1.537 (12)
Cu1	O2	1.939 (5)	Cl2	O7	1.437 (14)	N6	C11	1.466 (14)
Cu1	N5	2.316 (5)	Cl2	O8	1.593 (14)	N6	C17	1.70 (2)
Cu1	N6	2.024 (7)	Cl2	O9	1.332 (15)	N7	C12	1.57 (2)
Cu1	N7	2.070 (7)	Cl2	O10	1.330 (13)	N7	C19	1.527 (14)
Cu2	O5	2.688 (12)	Cl2	O7A	1.447 (12)	N7	C21	1.409 (11)
Cu2	O9	2.68 (2)	Cl2	O8A	1.214 (15)	C1	C2	1.511 (9)
Cu2	O6A	2.64 (2)	Cl2	O9A	1.47 (2)	C3	C4	1.504 (12)
Cu2	O9A	2.89 (2)	Cl2	O10A	1.73 (2)	C4	C5	1.376 (14)
Cu2	N1	1.974 (5)	O1	C1	1.245 (7)	C6	C7	1.464 (12)
Cu2	N2	2.002 (6)	O2	C2	1.278 (7)	C7	C8	1.625 (11)
Cu2	N3	1.963 (6)	N1	C1	1.339 (8)	C9	C10	1.354 (14)
Cu2	N4	1.976 (7)	N1	C3	1.483 (8)	C11	C12	1.42 (2)
Cl1	O3	1.417 (9)	N2	C2	1.292 (7)	C13	C14	1.580 (11)
Cl1	O4	1.44 (2)	N2	C8	1.450 (8)	C15	C16	1.621 (15)
Cl1	O5	1.312 (13)	N3	C6	1.455 (11)	C17	C18	1.43 (2)
Cl1	O6	1.547 (12)	N4	C5	1.388 (15)	C19	C20	1.41 (2)
Cl1	O3A	1.399 (10)	N5	C9	1.465 (11)	C21	C22	1.31 (2)
Cl1	O4A	1.392 (13)	N5	C13	1.509 (9)			
Cl1	O5A	1.58 (3)	N5	C15	1.423 (10)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Cu1	O2	83.3 (2)	O3	Cl1	O6	107.3 (6)	C9	N5	C15	106.9 (8)
O1	Cu1	N5	91.3 (2)	O4	Cl1	O5	110.2 (8)	C13	N5	C15	114.3 (7)
O1	Cu1	N6	93.8 (3)	O4	Cl1	O6	106.6 (8)	Cu1	N6	C10	108.4 (6)
O1	Cu1	N7	154.3 (2)	O5	Cl1	O6	100.9 (6)	Cu1	N6	C11	109.9 (8)
O2	Cu1	N5	100.8 (2)	O7	Cl2	O8	113.4 (7)	Cu1	N6	C17	105.0 (5)
O2	Cu1	N6	174.1 (3)	O7	Cl2	O9	108.7 (9)	C10	N6	C11	107.5 (9)
O2	Cu1	N7	92.8 (3)	O7	Cl2	O10	108.1 (8)	C10	N6	C17	120.5 (9)
N5	Cu1	N6	84.3 (3)	O8	Cl2	O9	102 (1)	C11	N6	C17	105.4 (8)
N5	Cu1	N7	114.3 (3)	O8	Cl2	O10	93.2 (7)	Cu1	N7	C12	100.1 (7)
N6	Cu1	N7	87.5 (4)	O9	Cl2	O10	129.9 (9)	Cu1	N7	C19	111.4 (5)
O5	Cu2	O9	160.1 (5)	O3A	Cl1	O4A	118.5 (6)	Cu1	N7	C21	108.9 (6)
O5	Cu2	N1	87.2 (3)	O3A	Cl1	O5A	107 (1)	C12	N7	C19	112.1 (9)
O5	Cu2	N2	100.4 (3)	O3A	Cl1	O6A	108.9 (8)	C12	N7	C21	100 (1)
O5	Cu2	N3	91.7 (3)	O4A	Cu1	O5A	107 (1)	C19	N7	C21	122 (1)
O5	Cu2	N4	79.9 (4)	O4A	Cl1	O6A	113.8 (9)	O1	C1	N1	129.3 (6)
O9	Cu2	N1	90.7 (4)	O5A	Cl1	O6A	99 (1)	O1	C1	C2	117.4 (6)
O9	Cu2	N2	99.1 (4)	O7A	Cl2	O8A	110.9 (9)	N1	C1	C2	113.3 (6)
O9	Cu2	N3	90.8 (4)	O7A	Cl2	O9A	99.9 (9)	O2	C2	N2	126.2 (7)
O9	Cu2	N4	80.7 (4)	O7A	Cl2	O10A	121.8 (8)	O2	C2	C1	114.9 (6)
O6A	Cu2	O9A	158.8 (6)	O8A	Cl2	O9A	111 (1)	N2	C2	C1	118.9 (6)
O6A	Cu2	N1	90.4 (4)	O8A	Cl2	O10A	106 (1)	N1	C3	C4	111.3 (7)
O6A	Cu2	N2	77.9 (4)	O9A	Cl2	O10A	107.5 (9)	C3	C4	C5	130.6 (9)
O6A	Cu2	N3	88.1 (4)	Cu1	O1	C1	110.5 (4)	N4	C5	C4	132 (1)
O6A	Cu2	N4	102.3 (4)	Cu1	O2	C2	113.0 (4)	N3	C6	C7	112.2 (8)
O9A	Cu2	N1	101.5 (4)	Cu2	N1	C1	112.7 (5)	C6	C7	C8	115.5 (8)
O9A	Cu2	N2	85.8 (4)	Cu2	N1	C3	131.0 (5)	N2	C8	C7	106.4 (7)
O9A	Cu2	N3	79.7 (4)	C1	N1	C3	115.9 (6)	N5	C9	C10	119 (1)
O9A	Cu2	N4	93.9 (4)	Cu2	N2	C2	110.3 (5)	N6	C10	C9	118 (1)
N1	Cu2	N2	84.2 (2)	Cu2	N2	C6	131.9 (5)	N6	C11	C12	110 (1)
N1	Cu2	N3	178.3 (3)	C2	N2	C8	117.2 (6)	N7	C12	C11	115 (1)
N1	Cu2	N4	96.5 (3)	Cu2	N3	C6	119.3 (5)	N5	C13	C14	112.6 (7)
N2	Cu2	N3	94.6 (3)	Cu2	N4	C5	118.7 (7)	N5	C15	C16	104.5 (8)
N2	Cu2	N4	179.3 (3)	Cu1	N5	C9	100.1 (5)	N6	C17	C18	94 (1)
N3	Cu2	N4	84.7 (3)	Cu1	N5	C13	108.9 (4)	N7	C19	C20	103 (1)
O3	Cl1	O4	111.6 (9)	Cu1	N5	C15	118.9 (5)	N7	C21	C22	109 (1)
O3	Cl1	O5	119.0 (7)	C9	N5	C13	106.0 (9)				

2.[27] The structure consists of $[Cu(oxpn)Cu(bpy)]^{2+}$ cations with weakly coordinated perchlorate anions, as shown in Figure 3. Each copper atom has a slightly distorted square-pyramidal environment with an oxygen atom of ClO_4^- in apical position. The apical bond lengths are Cu1–O10 = 2.887 (5) Å and Cu2–O3 = 2.482 (2) Å. Cu1 and Cu2 are displaced by 0.025 and 0.053 Å, respectively, out of the basal planes toward the apical positions. The bridging group N2N4C7C8O1O2 is planar within experimental uncertainties, the copper atoms being displaced by 0.131 and 0.088 Å, respectively, from this plane. The Cu1···Cu2 separation within the binuclear cation is 5.195 (1) Å. There is a comparatively short contact between two Cu2 atoms of binuclear cations related by a center of symmetry Cu2···Cu2($-x$, $-y$, $1 - z$) = 3.584 (1) Å. Otherwise, there are no Cu···Cu contacts shorter than 6.95 Å. The atoms of the perchlorate group involving Cl2 as well as the atoms C1 and C2 have high thermal parameters, due to the unresolved disorder. Bond distances and angles in these parts of the structure are of low accuracy. The quoted standard deviations are those obtained from the inverse least-squares matrix and are hence grossly underestimated for the disordered atoms.

[Cu(oxpn)Cu(petdien)](ClO_4) (2). The bond lengths and angles are given in Table V, and the crystal packing is shown in Figure 4.[27] The structure consists of $[Cu(oxpn)Cu(petdien)]^{2+}$ cations shown in Figure 5 and weakly coordinated perchlorate anions. On the oxpn side, the copper(II) ion is in a 4 + 2 environment; within experimental error, Cu2 is in the N1N2N3N4 basal plane with two perchlorate groups in apical positions. Due to the disorder of the perchlorate groups, the axial Cu–O distances are not accurately determined. From the refinement of the disordered model, two sets of distances are obtained, in the range 2.64–2.89 Å. On the petdien side, Cu1 is in an environment intermediate between a square pyramide and a trigonal bipyramid. In a square-pyramidal description, the basal plane is made up of O1, O2, N6, and N7 while N5 occupies the apical position with a Cu1–N5 bond

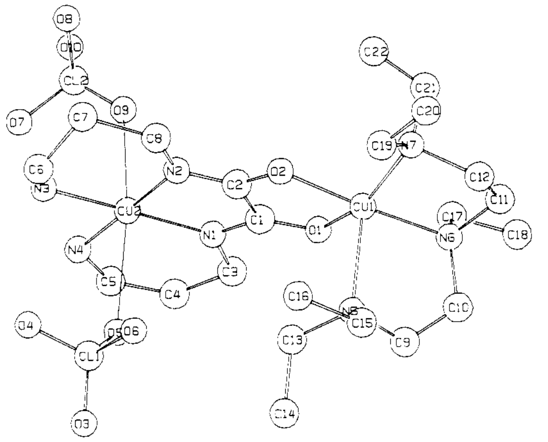


Figure 5. Projection of the binuclear unit of **2**. For the disordered perchlorate groups only one set of oxygen atoms are drawn.

Table VI. Parameters Deduced from the Magnetic Data[a]

	J, cm^{-1}	g	ρ	10^4R
1	−439.7	2.26	0.031	2.9
2	−242.0	2.02	0.068	2.5
3	−82.8	2.12	0.031	9

[a] R is defined as $\sum(\chi_M^{\text{calcd}})^2/\sum(\chi_M^{\text{obsd}})^2$.

length of 2.316 (5) Å. The basal atoms deviate from the least-squares plane by ca. 0.18 Å, and Cu1 is pulled out of this plane toward N5 by 0.27 Å. The bond angles in the equatorial plane vary from 83.2 (2) to 93.8 (3)° about the theoretical 90° value while the angles at Cu1 involving the apical position N5 vary between 84.3 (3) and 114.3 (3)°. A trigonal-bipyramidal description places O1, N5, and N7 in the trigonal plane and O2 and N6 in axial positions. Cu1 deviates only by 0.02 Å from this trigonal plane, and the trigonal axis does not show too much distortion from linearity, O2–Cu1–N6 being 174.1 (3)°. However, the angles in the trigonal plane depart significantly from the theoretical 120° value, with values of 91.3 (2) 114.3 (3), and 154.3 (2)°. Moreover, the Cu1–N5 bond length in the trigonal plane is much longer than the other two. With regard to [(petdien)Cu(C_2O_4)Cu(petdien)](BPh_4)$_2$ investigated by Hendrickson et al., one can say that the trigonal-bipyramidal character is less pronounced in our compound. Indeed, in [(petdien)Cu(C_2O_4)Cu(petdien)](BPh_4)$_2$, the angles in the trigonal plane are 97.5 (2), 131.4 (2), and 131.1 (2)°.

Magnetic Properties and EPR Spectra

The S–T energy gap J for each of the compounds **1**–**3** was deduced from the temperature dependence of the molar magnetic susceptibility χ_M, expressed according to

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

where the symbols have their usual meaning. ρ is the proportion of noncoupled impurity of which the molecular weight is assumed to be equal to that of the binuclear complex. In (2), we neglected an additional term arising from the coupling of the $M_s = 0$ components of the singlet and the triplet states in a dissymmetrical complex, which has been shown not to play any role when J is larger than a few wavenumbers.[2]

The magnetic properties of **1**–**3** are compared in Figure 6. They are characteristic of antiferromagnetically coupled copper(II) pairs with a rounded maximum in the susceptibility expected above room temperature for **1** and occurring around 212 K for **2** and around 75 K for **3**. Least-squares fittings of the experimental data using relation 2 led to the parameters given in Table VI. In **1**, the interaction is very large with $J_1 = -439.7$ cm^{-1}. In **2**, J_2 is -242.0 cm^{-1}, and in **3**, J_3 is -82.8 cm^{-1}. These values have to be compared to the predictions made in the section devoted to the basic concepts. As expected, J_1 in **1** is very large in absolute value in spite of the separation of 5.195 (1) Å between the metal centers. J_3 is fairly close to $J_1/4 = -110$ cm^{-1}. As for J_2, its value is actually intermediate between J_1 and J_3.

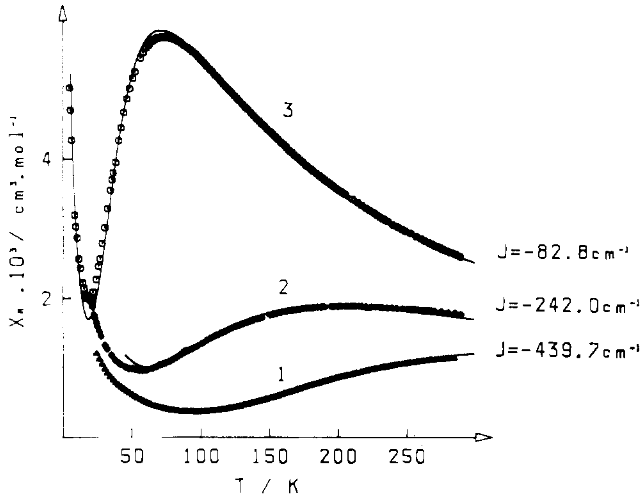


Figure 6. Magnetic susceptibilities of 1–3: (▲) experimental data; (—) calculated curves.

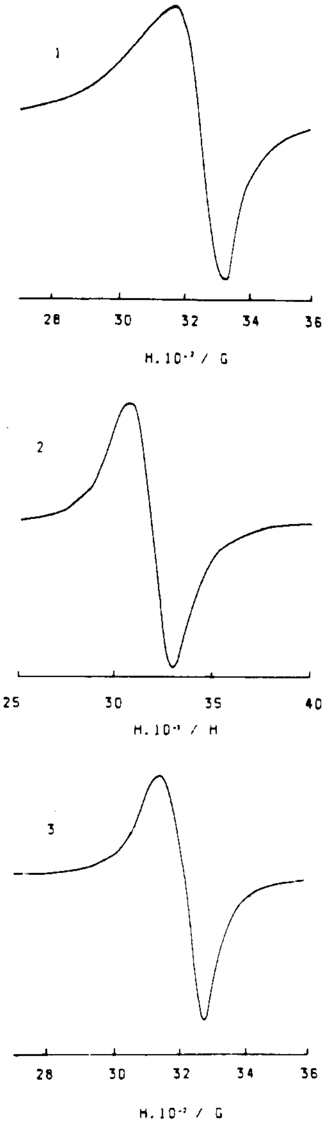


Figure 7. X-Band powder EPR spectra for 1–3.

The X-band powder EPR spectra at 300 K for the three compounds **1**–**3** are given in Figure 7. Each of them only exhibits a quasi-isotropic feature around $g = 2.1$. These spectra show neither fine structure nor a half-field transition, which is characteristic of a pair triplet state. Nevertheless, the temperature dependences of the intensity of the signal prove that the resonances occur in excited states.

The fine structure of a triplet state for a copper(II) pair has two origins, namely the dipolar interaction and the combined effect of the local spin–orbit coupling and of the exchange interaction, which leads to the anisotropic and antisymmetric exchanges.[18,19] In μ-oxamido complexes with metal centers separated by about 5.2 Å, the zero field splitting within the triplet state due to the dipolar interaction may be calculated by using the approximation of the point magnetic dipoles. It is found as $|D| \simeq 0.02$ cm^{-1}, which is actually undetectable owing to the observed line widths. As for the contribution to the zero field splitting due to the anisotropic exchange, it has been estimated as[7,8,20]

$$D \simeq {}^1/_{32}(\Delta g_z)^2 J_{xy,x^2-y^2} \qquad (3)$$

for a symmetrical planar complex with *xy*-type local ground states. Δg_z is the deviation of the Zeeman component g_z with regard to the g_e gyromagnetic factor of the free electron, and J_{xy,x^2-y^2} is the magnitude of the S–T splitting within the excited states arising from the interaction between the *xy* ground state of an ion and the $x^2 - y^2$ excited state of the other. This relation (3) should remain roughly valid for $[Cu(oxpn)Cu(bpy)](ClO_4)_2$ (**1**) where the two ground states are actually of the *xy* type. J_{xy,x^2-y^2} involves orthogonal orbitals and consequently is purely ferromagnetic. We have already mentioned that the ferromagnetic contributions through extended bridges are vanishing.[8,21] Therefore, one understands why, in spite of the large isotropic exchange, the anisotropic exchange in **1** is very small and undetectable. The relation (3) is no longer valid for the compounds **2** and **3**. The estimation of the anisotropic exchange in dissymmetrical complexes where the local ground states have not the same symmetry is very tedious, and we will not attempt to approach this problem in this paper.

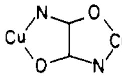
The antisymmetric exchange may also induce a zero field splitting within the triplet state varying as d^2/J where d is a coupling term between singlet and triplet low-lying states[18,19] and J is the energy gap between these states. In our three compounds, J could be too large in order for the singlet–triplet coupling to be operative.

Finally, the EPR signals for **1–3** look much more isotropic than in the monomeric fragments like Cu(oxpn). This could be due to the deorientation of the local tensors $\mathbf{g}_A$ and $\mathbf{g}_B$, which partly averages the **g** tensor of the pair triplet state. Indeed **g** is equal to $^1/_2(\mathbf{g}_A + \mathbf{g}_B)$.

Conclusions

The possibility to tune the interaction through a given bridging network by playing on the nature of the terminal ligands is a new attainment in the field of molecular magnetism, and this strategy opens vast perspectives. It is however important to realize that a severe limitation subsists concerning the synthesis of the compounds. For instance, we could expect to minimize the S–T gap in $[Cu(oxpn)Cu(dien)]^{2+}$, but in spite of many attempts, including the change of counteranion, we did not succeed in preparing this complex. This difficulty could be due to the fact that some dissymmetrical complexes would be too constrained.

This paper represents the second example of tunable exchange; the first one dealt with μ-oxalato complexes.[4] The interaction in **1** ($J = -439.7$ cm^{-1}) is larger than in $[(tmen)(H_2O)Cu(C_2O_4)Cu(H_2O)(tmen)](ClO_4)_2$ ($J = -385.4$ cm^{-1}) where the magnetic orbitals are also favorably oriented. This arises from the fact that the magnetic orbital is more delocalized toward the bridging nitrogen atoms in Cu(oxpn) than toward the bridging oxygen atoms in $(tmen)Cu(C_2O_4)\cdot 4H_2O$ owing to the weak electronegativity of nitrogen as compared to oxygen.[22,23] This effect is even more pronounced when the oxamido bridge has the trans configuration.[23,24]



For instance,[22] in $[(tmen)(H_2O)Cu(C_2O_2N_2H_2)Cu(H_2O)(tmen)](ClO_4)_2$, J was found as large as -581 cm^{-1}. In this latter case, the two magnetic orbitals have, of course, the same energy, which favors their overlap.

Before closing, we would like to say a few words about the model used to propose this strategy of tunable exchange. This model may be criticized, especially because it is apparently not appropriate for quantitative theoretical calculations, owing to the difficulty arising from the nonorthogonality of the magnetic orbitals. Nevertheless, it bore witness of its heuristic character to design bimetallic systems exhibiting expected magnetic properties. Its main advantage is its simplicity. It uses a language familar to the inorganic chemist, for whom the overlap between orbitals is actually the cornerstone of the chemical bond. Finally, it is adapted to both symmetrical and dissymmetrical binuclear complexes. In contrast, the case of the dissymmetrical complexes like those described in this paper has never been considered, to our knowledge, in the models using orthogonalized magnetic orbitals.

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. [Cf.: *J. Chem. Educ.* **1978**, 55, A355. *Chem. Eng. News* **1983**, *61* (Dec 5), 4; **1963**, *41* (July 8), 47.]

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Registry No. 1, 98735-45-6; **2**, 98720-59-3; **3**, 98720-60-6; Cu(oxpn), 20102-49-2; 1,3-propylenediamine, 109-76-2; diethyl oxalate, 95-92-1.

Supplementary Material Available: Listings of structure factor amplitudes and general temperature factor expressions and crystal packing diagrams of compounds **1** (Figure 2) and **2** (Figure 4) (23 pages). Ordering information is given on any current masthead page.

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