

the sample at hand, any systematic factors influencing ring conformations.

With the scope of formation and stereochemical pattern of edt complexes largely defined, at least for first-transition-series elements, certain problems and possibilities remain for investigation. These include the means of formation of $[\text{Co}(\text{edt})_2]^-$ in a reaction system initially containing no apparent oxidant, the synthesis of this complex free from $[\text{Co}(\text{edt})_2]^{2-}$, attempted preparation of $[\text{Cr}_2(\text{edt})_4]^{2-}$ in order to determine where the discontinuity between structures II and V occurs, examination of monomer-dimer equilibria in solution, and exploitation of the nucleophilic reactivity of thiolate sulfur atoms as a means of synthesizing new ligand types by template reactions. These matters are currently under investigation in this laboratory.

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Registry No. 1-2Et₄N, 94750-78-4; 2-2Et₄N, 87145-62-8; 2, 87145-61-7; 3-2Et₄N, 94750-80-8; 5, 87526-32-7; 6, 46847-88-5; 7-8-3Me₄N, 94750-84-2; 9-2*n*-Bu₄N, 99686-41-6; 10-Na·2Me₃NCH₂Ph·MeOH, 99686-44-9; 11-2Et₄N, 99686-45-0; 12-2Et₄N, 99686-46-1; TiCl₃, 7705-07-9.

Supplementary Material Available: Listings of crystallographic data for the six compounds in Table I and $(\text{Et}_4\text{N})_2[\text{V}_2(\text{S}_2\text{C}_2\text{H}_4)_4]^{2-}$ anisotropic thermal parameters; hydrogen atom coordinates and temperature factors; calculated and observed structure factors (114 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, Unité Associée au CNRS No. 420, Université de Paris-Sud, 91405 Orsay, France, and Department of Chemistry, University of Bergen, 5000 Bergen, Norway

Interactions in $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$, $\text{Cu}^{\text{II}}\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}$, and $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$ Trinuclear Species. Crystal Structure of Bis(*N,N'*-bis(3-aminopropyl)oxamido)tricopper(II) Perchlorate

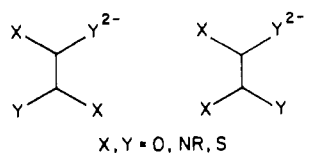
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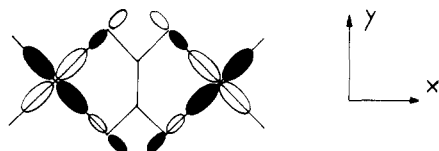
Four trinuclear complexes have been synthesized, namely $[\text{Cu}_3(\text{oxpn})_2](\text{ClO}_4)_2$ (1), $[\text{Cu}_2\text{Zn}(\text{oxpn})_2(\text{H}_2\text{O})_2]\text{X}_2$ with X = ClO₄ (2) and BPh₄ (3), and $[\text{Cu}_2\text{Ni}(\text{oxpn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (4). The binuclear complex $[\text{CuNi}(\text{oxpn})(\text{bpy})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (5) has been joined to this study. oxpn is bis(*N,N'*-bis(3-aminopropyl)oxamido). The crystal structure of 1 has been determined. 1 crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 12.257$ (2) Å, $b = 14.697$ (5) Å, $c = 15.872$ (6) Å, and $\beta = 104.62$ (2)° at 293 K, $Z = 4$. The copper(II) ions are in square-pyramidal surroundings, the basal planes being slightly tilted with respect to one another. Two trinuclear units are related through an inversion center to form a bis trinuclear entity with a separation of 3.251 (2) Å between two central copper atoms. The structures of 2-5 have been deduced from the spectroscopic data. The relative energies of the low-lying states in 1, 4, and 5 have been derived from the magnetic properties studied in the 4.2-300 K temperature range. Weak interactions between two symmetry-related trinuclear units in 1 and between terminal copper(II) ions in 2 and 3 have been detected in addition to the strong interactions between adjacent magnetic centers. The EPR spectra of the compounds have also been investigated. The most interesting is that of 5, which reveals a low-lying triplet state resulting probably from the interaction between two doublet pair states within a bis heterobinuclear entity.

Introduction

It has recently been demonstrated that the bis bidentate ligands like



may have a remarkable efficiency to propagate an antiferromagnetic interaction between two metal centers relatively far from each other.²⁻⁴ Such a situation is realized, for instance, when a $\text{C}_2\text{X}_2\text{Y}_2^{2-}$ bis bidentate ligand bridges two copper(II) ions in elongated tetragonal surroundings with coplanar or almost coplanar basal planes.³⁻⁴ In such surroundings, the magnetic orbitals centered on the copper(II) ions are as



They point from the metal toward the four nearest neighbors and overlap either side of the bridge, which favors a strong antiferromagnetic interaction. The same situation holds when a copper(II) ion is replaced by another magnetic ion with a d_{xy} -type magnetic orbital such as high-spin Fe(III) or Ni(II).^{6,7}

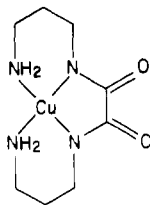
So far, two kinds of strongly antiferromagnetically coupled compounds with $\text{C}_2\text{X}_2\text{Y}_2^{2-}$ bis bidentate bridging ligands have been investigated, namely binuclear complexes^{2,4-6,8-14} and ribbon chains.^{3,7,15,16} In contrast, to our knowledge, no molecular system with more than two magnetic ions bridged by a ligand of this type has been described. More generally, relatively few studies dealing with magnetic trinuclear systems have been reported in comparison

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to the number of studies dealing with either binuclear or one-dimensional systems. Most of these studies are devoted to homotrimeric complexes.¹⁷⁻³¹ A few of them concern heterotrimeric complexes.³²⁻³⁵

In this paper, we describe the syntheses, the structures, and the magnetic and EPR properties of magnetic trinuclear species prepared from the mononuclear complex (*N,N'*-bis(3-aminopropyl)oxamido)copper(II), noted as Cu(oxpn).³⁶



Owing to the oxygen atoms of the oxamido group, two Cu(oxpn) complexes may play the role of bidentate ligands with regard to another metal center, which leads to a trinuclear species. Four complexes of this kind have been investigated, namely [Cu₃(oxpn)₂](ClO₄)₂ (**1**) [Cu₂Zn(oxpn)₂(H₂O)₂]₂X₂ with X = ClO₄ (**2**) and BPh₄ (**3**) and [Cu₂Ni(oxpn)₂(H₂O)₂](ClO₄)₂ (**4**). The crystal structure of **1** has been solved and refined. It shows that two trinuclear units are related through an inversion center with a relatively short separation between the central copper atoms, so that the actual molecular entity is bis trinuclear. In this paper, we also present the study of [CuNi(oxpn)₂(bpy)₂](NO₃)₂·2H₂O³⁷ (**5**), with bpy = 2,2'-bipyridyl, in which the same kind of Cu(I)-Ni(II) interaction as in **4** occurs.

Experimental Section

Syntheses. [Cu₃(oxpn)₂](ClO₄)₂ (**1**). Cu(oxpn) is prepared as described elsewhere.^{12,35} To a solution of 264 mg (10⁻³ mol) of Cu(oxpn) in 20 mL of water was added a solution of 185 mg (5 × 10⁻⁴ mol) of copper(II) perchlorate. The solution was then filtered. Well-shaped small single crystals were obtained by slow evaporation. Anal. Calcd for C₁₆H₃₂N₈O₁₂Cl₂Cu₃: C, 24.33; H, 4.08; N, 14.18; O, 24.3; Cl, 8.98. Found: C, 24.87; H, 4.12; N, 13.90; O, 25.30; Cl, 8.70.

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Table I. Information Concerning the Crystallographic Data Collection and Refinement Conditions for [Cu₃(oxpn)₂](ClO₄)₂ (**1**)

mol formula	Cu ₃ Cl ₂ C ₁₆ H ₃₂ N ₈ O ₁₂
fw	790.01
space group	P2 ₁ /c (No. 14)
temp at cryst, K	294
unit cell	
<i>a</i> , Å	12.257 (2)
<i>b</i> , Å	14.697 (5)
<i>c</i> , Å	15.872 (6)
β, deg	104.62 (2)
<i>V</i> , Å ³	2767 (3)
<i>Z</i>	4
<i>D_x</i> , g cm ⁻³	1.897
μ(Mo Kα), cm ⁻¹	25.58
cryst size, mm	0.15 × 0.12 × 0.09
instrument	CAD-4
scan type	ω
scan range Δω, deg	0.70 + 0.35 tan θ
scan speed, deg/min	1.67
radiation	monochromated Mo Kα (λ = 0.71069 Å)
max 2θ, deg	50
no. of measd reflns	4858 (in one octant)
no. of "obsd" reflns (NO)	2944
limit of "obsd" reflns	F _o > 2σ _F
no. of variables refined (NV)	370
agreement factors ^a	
<i>R</i>	0.064
<i>R_w</i>	0.050
<i>s</i>	1.6

^a Agreement factors are defined as follows: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $s = [\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$. Weighting scheme: $w = 1/\sigma_F^2$; $\sigma_F = \sigma_I(ILP)^{-1/2}$; $\sigma_I = [\sigma_c^2 + (0.02N_{net})^2]^{1/2}$. Atomic scattering factors and programs used are those of ref 47 and 48.

[Cu₂Zn(oxpn)₂(H₂O)₂](ClO₄)₂ (**2**). A 264 mg (10⁻³ mol) sample of Cu(oxpn) was stirred in 20 mL of methanol. To this mixture was added a solution of 186 mg (5 × 10⁻⁴ mol) of zinc perchlorate in 10 mL of methanol. The solution was then filtered, and the violet compound was precipitated by adding diethyl oxide. Anal. Calcd for C₁₆H₃₆N₈O₁₄Cl₂Cu₂Zn: C, 23.21; H, 4.38; N, 13.53; O, 27.06; Cl, 8.56. Found: C, 23.01; H, 4.48; N, 13.36; O, 27.00; Cl, 8.76.

[Cu₂Zn(oxpn)₂(H₂O)₂](BPh₄)₂ (**3**). To a solution of 10⁻³ mol of [Cu₂Zn(oxpn)₂(H₂O)₂](ClO₄)₂ in 30 mL of methanol was added a solution of 342 mg (2 × 10⁻³ mol) of sodium tetraphenylborate. Very thin violet needles of the tetraphenylborate derivative were obtained by slow diffusion of water into the solution. Anal. Calcd for C₆₄H₇₆B₂N₈O₄Cu₂Zn: C, 60.65; H, 6.04; N, 8.84. Found: C, 60.71; H, 5.88; N, 8.75.

[Cu₂Ni(oxpn)₂(H₂O)₂](ClO₄)₂ (**4**). This compound was obtained as [Cu₂Zn(oxpn)₂(H₂O)₂](ClO₄)₂ by replacing zinc(II) perchlorate with nickel(II) perchlorate. Anal. Calcd for C₁₆H₃₆N₈O₁₄Cl₂Cu₂Ni: C, 23.40; H, 4.42; N, 13.65; Cl, 8.63; Cu, 15.47; Ni, 7.15. Found: C, 23.30; H, 4.30; N, 13.50; Cl, 8.50; Cu, 15.47; Ni, 7.10.

[Cu(oxpn)Ni(bpy)₂](NO₃)₂·2H₂O (**5**). To a mixture of 264 mg (10⁻³ mol) of Cu(oxpn) stirred in 20 mL of methanol were added a solution of 291 mg (10⁻³ mol) of nickel(II) nitrate in 20 mL of methanol and then a solution of 312 mg (2 × 10⁻³ mol) of 2,2'-bipyridyl. The solution was filtered, and 20 mL of ethanol was added to diminish the solubility of the compound. A violet polycrystalline powder was obtained by slow evaporation. Anal. Calcd for C₂₈H₃₆N₁₀O₁₀CuNi: C, 42.31; H, 4.56; N, 17.62; Cu, 7.99; Ni, 7.38. Found: C, 42.47; H, 4.67; N, 17.49; Cu, 7.9; Ni, 7.4.

Crystallographic Data Collection and Refinement of the Structure. Information concerning the crystallographic data collection and the refinement conditions is given in Table I. Low-temperature data could not be obtained owing to a split of the reflections upon cooling down. To some degree, split reflections were also observed at room temperature. The structure was solved by direct methods. The positions of the three copper atoms were found in the *E* map. The remaining non-hydrogen atoms were located in two subsequent Fourier maps. Isotropic refinement of non-hydrogen atoms led to *R* = 0.121. The oxygen atoms of the perchlorate groups as well as the C2 and C15 atoms showed high thermal parameters. However, the features of a difference map did not justify the introduction of a disordered model. After two cycles of anisotropic refinement, hydrogen atoms at idealized positions were introduced in the

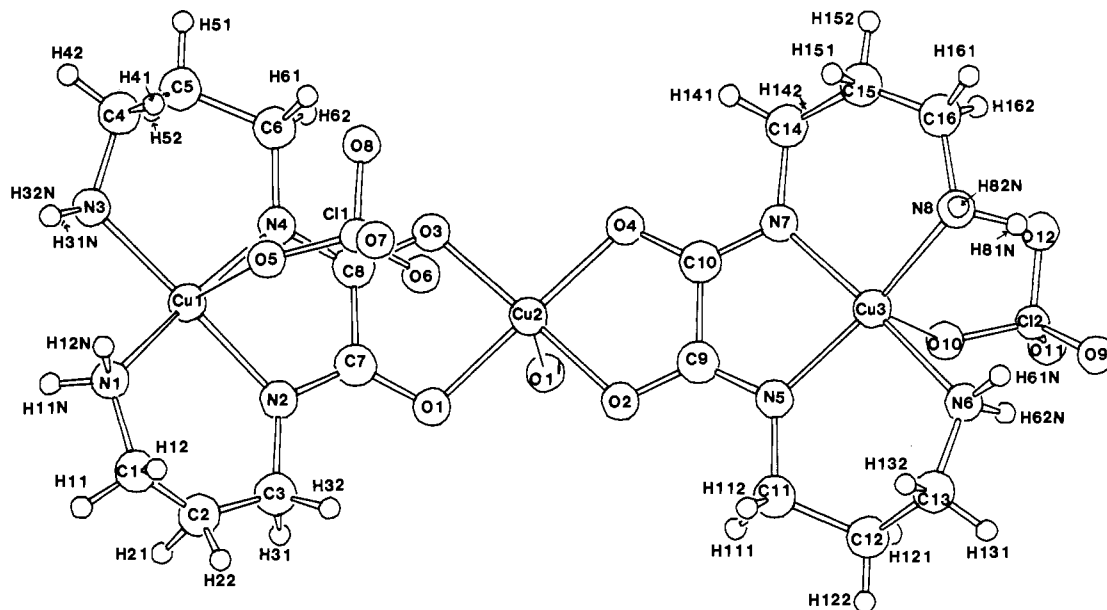


Figure 1. Perspective view of the trinuclear unit $[\text{Cu}_3(\text{oxpn})_2](\text{ClO}_4)_2$ (1).

calculation of the structure factors but were not refined. The further refinement converged at $R = 0.064$, $R_w = 0.050$, and $s = 1.6$. Due to the small size of the used crystal, an absorption correction was not deemed necessary. Final atomic parameters for non-hydrogen atoms are listed in Table II; those for hydrogen atoms, in the supplementary material.

Magnetic Measurements. These were carried out with a Faraday-type magnetometer equipped with a continuous-flow cryostat. For each sample, independence of the susceptibility from the applied magnetic field was checked. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections were estimated as $-350 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for 1, $-342 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$ for 2, $-407 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for 3, $-344 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for 4, and $434 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for 5. The fittings of the experimental data were carried out by minimizing the R factor defined as $\sum |(\chi_M T)^{\text{obsd}} - (\chi_M T)^{\text{calcd}}|^2 / \sum (\chi_M T)^{\text{obsd}^2}$.

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.

Description of the Structures

Crystal Structure of $[\text{Cu}_3(\text{oxpn})_2](\text{ClO}_4)_2$ (1). A perspective view of the trinuclear unit with the atomic numbering scheme is shown in Figure 1. Bond lengths and angles are given in Table III. Due to high thermal parameters, distances and angles involving the oxygen atoms of the perchlorate groups and the atoms C2 and C15 are of low accuracy.

In the trinuclear unit, each copper atom is in a weakly distorted square-pyramidal environment. The terminal copper atoms are surrounded by four nitrogen atoms in the basal plane and an oxygen atom of the perchlorate group in an apical position with Cu1-O5 and Cu3-O10 apical bond lengths of 2.628 (7) and 2.664 (8) Å, respectively. As for the central copper atom, it is surrounded by four oxygen atoms in the basal plane and a fifth oxygen atom belonging to another trinuclear unit in an apical position with a Cu2-O1' apical bond length of 2.518 (5) Å. The Cu1, Cu2, and Cu3 atoms are displaced from the basal plane toward the apical site by 0.010, 0.083, and 0.086 Å, respectively. The Cu...Cu separations inside the trinuclear unit are $\text{Cu1-Cu2} = 5.120$ (1) Å, $\text{Cu3-Cu2} = 5.198$ (1) Å, and $\text{Cu1-Cu3} = 10.067$ (1) Å.

Two trinuclear units are related through an inversion center to form a bis trinuclear entity as shown in Figure 2 with a relatively short Cu2-Cu2' separation, namely 3.251 (2) Å. Two oxygen atoms from oxamido moieties serve as bridges between the trinuclear units, each oxygen coordinating axially (2.518 (5) Å) to one copper atom and equatorially (1.956 (4) Å) to the other. As a consequence of this peculiar crystal packing, there is a steric repulsion between the terminal ends (the wings) of the two tri-

Table II. Atomic Parameters for Non-Hydrogen Atoms of $[\text{Cu}_3(\text{oxpn})_2](\text{ClO}_4)_2^a$

atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} , Å ²
Cu1	0.14819 (9)	0.48377 (8)	0.25146 (7)	2.95 (2)
Cu2	0.42019 (9)	0.44885 (8)	0.55291 (6)	2.63 (2)
Cu3	0.5921 (1)	0.28335 (8)	0.84575 (7)	2.77 (2)
C11	0.1026 (2)	0.3022 (2)	0.4016 (2)	4.67 (7)
C12	0.8098 (2)	0.4044 (2)	1.0036 (2)	4.45 (7)
O1	0.4310 (4)	0.4301 (4)	0.4333 (3)	2.3 (1)
O2	0.5369 (4)	0.3614 (4)	0.5974 (3)	2.5 (1)
O3	0.2956 (5)	0.5280 (4)	0.5024 (3)	2.6 (1)
O4	0.4035 (5)	0.4553 (4)	0.6713 (3)	3.2 (1)
O5	0.0776 (7)	0.3379 (6)	0.3176 (5)	8.8 (3)
O6	0.2101 (7)	0.3214 (6)	0.4507 (6)	8.5 (3)
O7	0.071 (1)	0.2151 (6)	0.4054 (6)	12.0 (4)
O8	0.0369 (9)	0.354 (1)	0.4434 (7)	14.5 (4)
O9	0.8464 (8)	0.3204 (6)	1.0396 (6)	9.2 (3)
O10	0.756 (1)	0.3995 (6)	0.9174 (6)	13.3 (4)
O11	0.8869 (8)	0.4709 (7)	1.0187 (6)	12.8 (3)
O12	0.732 (1)	0.4321 (9)	1.0440 (9)	18.6 (5)
N1	0.1235 (6)	0.4050 (6)	0.1452 (4)	3.8 (2)
N2	0.3056 (6)	0.4430 (5)	0.2978 (4)	2.7 (2)
N3	0.0017 (7)	0.5465 (6)	0.2034 (5)	4.6 (2)
N4	0.1717 (5)	0.5436 (5)	0.3662 (4)	2.7 (2)
N5	0.6163 (6)	0.2894 (5)	0.7282 (4)	2.7 (2)
N6	0.7143 (7)	0.1904 (5)	0.8860 (5)	3.6 (2)
N7	0.4793 (6)	0.3787 (5)	0.8016 (4)	2.8 (2)
N8	0.5372 (7)	0.2624 (5)	0.9511 (5)	4.2 (2)
C1	0.211 (1)	0.3469 (9)	0.1310 (8)	8.0 (4)
C2	0.314 (1)	0.352 (1)	0.1754 (8)	12.9 (4)
C3	0.3728 (8)	0.3857 (7)	0.2561 (6)	3.8 (2)
C4	-0.0629 (9)	0.5735 (9)	0.2642 (8)	7.0 (4)
C5	-0.0048 (8)	0.6323 (8)	0.3355 (7)	5.5 (3)
C6	0.0904 (8)	0.5918 (6)	0.4029 (6)	3.6 (2)
C7	0.3396 (7)	0.4590 (5)	0.3808 (5)	2.1 (2)
C8	0.2634 (7)	0.5151 (6)	0.4189 (5)	2.4 (2)
C9	0.5474 (7)	0.3452 (6)	0.6784 (5)	2.2 (2)
C10	0.4698 (7)	0.3973 (6)	0.7201 (5)	2.6 (2)
C11	0.6942 (8)	0.2389 (7)	0.6896 (6)	4.0 (2)
C12	0.7913 (8)	0.1994 (7)	0.7565 (6)	4.5 (3)
C13	0.7587 (8)	0.1404 (7)	0.8226 (7)	4.3 (3)
C14	0.4059 (8)	0.4270 (7)	0.8464 (6)	4.4 (3)
C15	0.392 (1)	0.379 (1)	0.9206 (8)	15.0 (4)
C16	0.4556 (9)	0.3216 (9)	0.9747 (6)	6.1 (3)

^aThe isotropic equivalent thermal parameter is given as $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$.

nuclear units. Hence, each CuCuCu unit is slightly butterfly shaped, the angles between the basal planes of the copper atoms being 147.0° (N1N2N3N4/O1O2O3O4), 165.0°

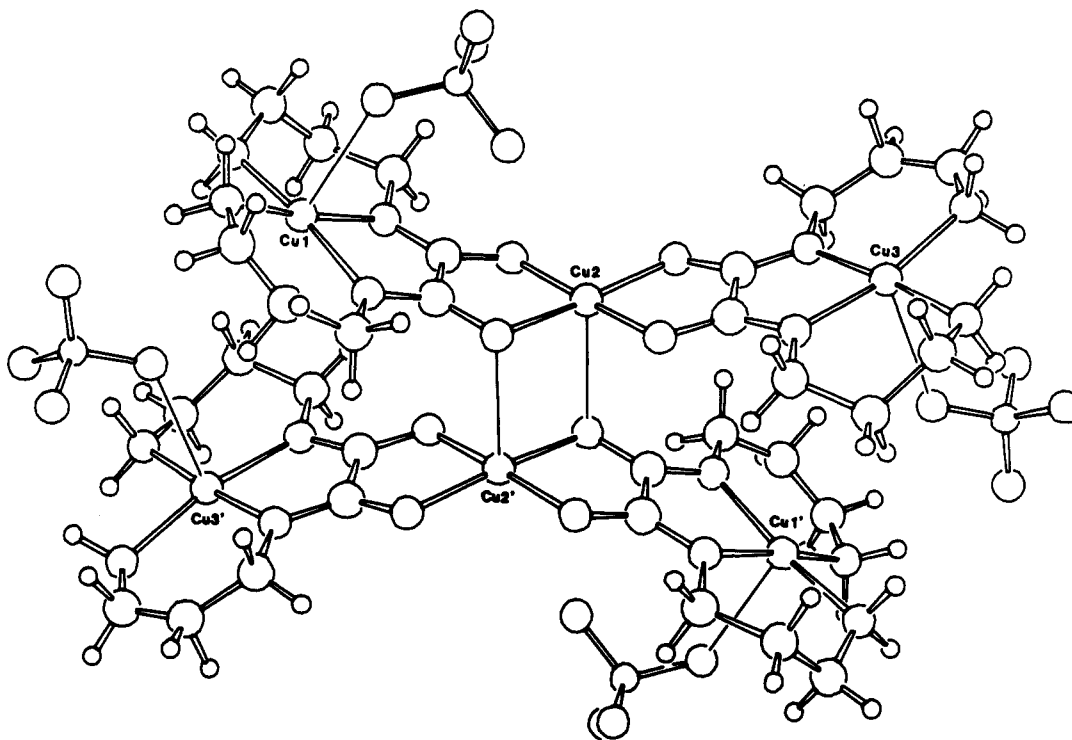
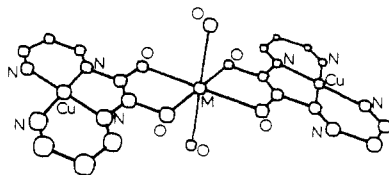


Figure 2. Perspective view of the bis trinuclear entity in 1.

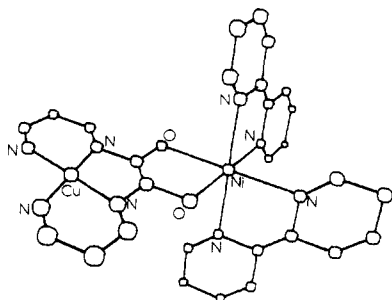
(O1O2O3O4/N5N6N7N8), and 132.3° (N1N2N3N4/N5N6N7N8), respectively. The angle Cu1–Cu2–Cu3 is $154.68(2)^\circ$.

Structure of Compounds 2–5. The structure of the $[\text{Cu}_2\text{M}(\text{oxpn})_2(\text{H}_2\text{O})_2]\text{X}_2$ complexes (2–4) may be deduced unambiguously from the chemical analysis and the spectral and magnetic data. When $\text{M} = \text{Ni}$, the single-ion ground state of the central atom is a spin triplet (see next section), which proves that M completes an octahedral environment by fixing the two water molecules in axial positions. Moreover, the IR spectra show the characteristic $\nu_{\text{C-O}}$ vibrations of the bridging oxamido around 1600 and 1440 cm^{-1} . Consequently, the structure may be schematized as



with possibly a weak interaction between the copper atoms and the perchlorato groups as in 1.

As for $[\text{CuNi}(\text{oxpn})(\text{bpy})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, its IR spectrum displays the same features as those of 1–4, so that its structure may be schematized as



Magnetic Properties and EPR Spectra

$[\text{Cu}_2(\text{oxpn})_2](\text{ClO}_4)_2$ (1). Owing to the favorable relative orientation of the magnetic orbitals and in spite of Cu–Cu separations of about 5.15 \AA , strong antiferromagnetic interaction is

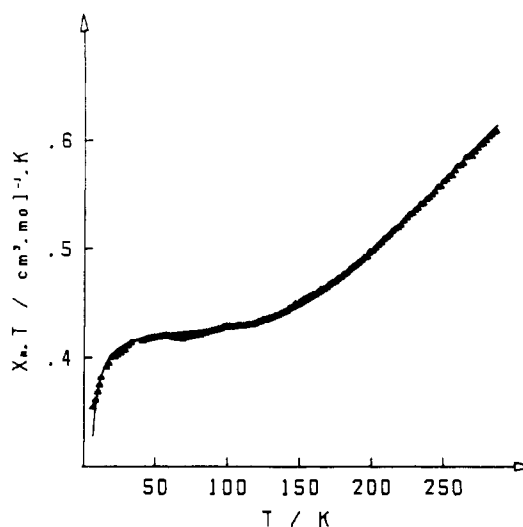


Figure 3. Experimental (\blacktriangle) and calculated (—) temperature dependences of $\chi_M T$ for 1.

expected within each pair of neighboring copper atoms, Cu1–Cu2 and Cu2–Cu3, respectively. As for the interaction between Cu1 and Cu3, separated by $10.067(1)\text{ \AA}$, it is expected to be much weaker if not negligible.

If, in a first approach, we do not take into account the interaction between two trinuclear species related by an inversion center, we can write the spin Hamiltonian appropriate to describe the low-lying states as in eq 1, where the meaning of the symbols

$$\mathcal{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_2) - j\hat{S}_1 \cdot \hat{S}_3 \quad (1)$$

is obvious. In (1), we idealized somewhat the geometry by assuming that the two terminal copper atoms were symmetry-related. The low-lying states are a ground doublet state, an excited doublet state located at $-J + J$, and an excited quartet state at $-3J/2$. In such a case, the magnetic behavior represented in the form of the product $\chi_M T$, the molar susceptibility times the temperature, should follow a Curie law at very low temperature when only the ground doublet state is thermally populated. The experimental data represented in Figure 3 show that, in fact, $\chi_M T$ is not rigorously constant at very low temperature but slightly decreases

Table III. Bond Distances (Å) and Angles (deg) in $[\text{Cu}_3(\text{oxpn})_2](\text{ClO}_4)_2$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Cu1	O5	2.628 (7)	Cl1	O7	1.344 (7)	N5	C11	1.461 (9)
Cu1	N1	2.005 (6)	Cl1	O8	1.395 (9)	N6	C13	1.458 (10)
Cu1	N2	1.976 (6)	Cl2	O9	1.387 (7)	N7	C10	1.298 (8)
Cu1	N3	1.991 (7)	Cl2	O10	1.363 (7)	N7	C14	1.463 (9)
Cu1	N4	1.977 (6)	Cl2	O11	1.338 (7)	N8	C16	1.445 (11)
Cu2	O1	1.956 (4)	Cl2	O12	1.337 (11)	C1	C2	1.284 (14)
Cu2	O1 ^a	2.518 (5)	O1	C7	1.287 (7)	C2	C3	1.392 (12)
Cu2	O2	1.920 (4)	O2	C9	1.282 (7)	C4	C5	1.459 (13)
Cu2	O3	1.926 (4)	O3	C8	1.298 (7)	C5	C6	1.494 (10)
Cu2	O4	1.942 (5)	O4	C10	1.293 (8)	C7	C8	1.485 (9)
Cu3	O10	2.664 (8)	N1	C1	1.431 (12)	C9	C10	1.498 (9)
Cu3	N5	1.963 (6)	N2	C3	1.450 (9)	C11	C12	1.498 (10)
Cu3	N6	2.009 (6)	N2	C7	1.299 (8)	C12	C13	1.491 (11)
Cu3	N7	1.970 (6)	N3	C4	1.448 (12)	C14	C15	1.420 (13)
Cu3	N8	1.978 (7)	N4	C6	1.458 (9)	C15	C16	1.306 (14)
Cl1	O5	1.392 (6)	N4	C8	1.290 (8)			
Cl1	O6	1.380 (7)	N5	C9	1.294 (8)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O5	Cu1	N1	82.5 (2)	N7	Cu3	N8	93.0 (3)	Cu3	N7	C10	112.4 (5)
O5	Cu1	N2	89.6 (3)	O5	Cl1	O6	114.4 (5)	Cu3	N7	C14	129.4 (5)
O5	Cu1	N3	100.0 (3)	O5	Cl1	O7	114.0 (5)	C10	N7	C14	118.2 (6)
O5	Cu1	N4	88.9 (2)	O5	Cl1	O8	103.6 (6)	Cu3	N8	C16	122.1 (5)
N1	Cu1	N2	93.7 (3)	O6	Cl1	O7	114.5 (5)	N1	C1	C2	123.3 (9)
N1	Cu1	N3	90.9 (3)	O6	Cl1	O8	101.7 (6)	C1	C2	C3	137. (1)
N1	Cu1	N4	171.1 (3)	O7	Cl1	O8	107.0 (7)	N2	C3	C2	113.8 (8)
N2	Cu1	N3	169.8 (3)	O9	Cl2	O10	113.0 (5)	N3	C4	C5	116.0 (8)
N2	Cu1	N4	83.7 (2)	O9	Cl2	O11	115.8 (5)	C4	C5	C6	117.3 (8)
N3	Cu1	N4	93.1 (3)	O9	Cl2	O12	105.6 (6)	N4	C6	C5	113.4 (7)
O1	Cu2	O1 ^a	87.7 (2)	O10	Cl2	O11	111.0 (5)	O1	C7	N2	126.9 (7)
O1	Cu2	O2	92.1 (2)	O10	Cl2	O12	106.0 (8)	O1	C7	C8	117.0 (6)
O1	Cu2	O3	85.5 (2)	O11	Cl2	O12	104.4 (8)	N2	C7	C8	116.1 (6)
O1	Cu2	O4	174.3 (2)	Cu2	O1	C7	108.7 (4)	O3	C8	N4	127.3 (7)
O1 ^a	Cu2	O2	89.1 (2)	Cu2	O2	C9	111.7 (4)	O3	C8	C7	115.9 (6)
O1 ^a	Cu2	O3	95.2 (2)	Cu2	O3	C8	110.0 (4)	N4	C8	C7	116.8 (6)
O1 ^a	Cu2	O4	97.6 (2)	Cu2	O4	C10	110.1 (5)	O2	C9	N5	128.0 (7)
O2	Cu2	O3	175.0 (2)	Cu1	N1	C1	121.1 (5)	O2	C9	C10	115.7 (6)
O2	Cu2	O4	85.8 (2)	Cu1	N2	C3	128.3 (5)	N5	C9	C10	116.3 (6)
O3	Cu2	O4	96.1 (2)	Cu1	N2	C7	110.9 (5)	O4	C10	N7	128.4 (7)
O10	Cu3	N5	95.6 (3)	C3	N2	C7	119.6 (6)	O4	C10	C9	116.4 (6)
O10	Cu3	N6	83.0 (3)	Cu1	N3	C4	117.6 (5)	N7	C10	C9	115.2 (6)
O10	Cu3	N7	94.7 (3)	Cu1	N4	C6	128.9 (5)	N5	C11	C12	112.7 (7)
O10	Cu3	N8	96.9 (3)	Cu1	N4	C8	110.7 (5)	C11	C12	C13	114.7 (7)
N5	Cu3	N6	93.1 (3)	C6	N4	C8	118.0 (6)	N6	C13	C12	113.9 (7)
N5	Cu3	N7	83.7 (2)	Cu3	N5	C9	112.2 (5)	N7	C14	C15	112.1 (8)
N5	Cu3	N8	167.3 (3)	Cu3	N5	C11	130.3 (5)	C14	C15	C16	134. (1)
N6	Cu3	N7	175.9 (3)	C9	N5	C11	117.4 (6)	N8	C16	C15	123.5 (9)
N6	Cu3	N8	90.6 (3)	Cu3	N6	C13	120.1 (5)				
Cu2	O1	Cu2 ^a	92.3 (2)	O7	O1	Cu2 ^a	108.4 (4)	Cl1	O5	Cu1	132.4 (4)
Cl2	O10	Cu3	125.7 (6)								

^a 1 - x, 1 - y, 1 - z.

upon cooling down. This behavior indicates that it is not possible to neglect totally the interaction between the trinuclear species. This interaction, however, is certainly weak. Indeed, the magnetic orbitals centered on the Cu2 and Cu2' atoms are unfavorably oriented to overlap since they are located in nearly parallel CuO_4 planes.

To take into account this weak interaction between the trinuclear units, we consider the new Hamiltonian

$$\mathcal{H} = \mathcal{H}^A + \mathcal{H}^B + \mathcal{H}^{AB} \quad (2)$$

where A and B refer to each trinuclear unit. \mathcal{H}^A and \mathcal{H}^B are expressed as in (1), and \mathcal{H}^{AB} is a perturbation term that only couples the two ground doublet states of A and B characterized by the spins \hat{S}_A and \hat{S}_B respectively. In other words, we assume that the interaction between A and B influences the magnetic behavior only in the low-temperature range. \mathcal{H}^{AB} is then expressed as

$$\mathcal{H}^{AB} = -J^{AB} \hat{S}_A \cdot \hat{S}_B \quad (3)$$

To calculate the magnetic susceptibility, we need to add to (2) the Zeeman perturbation $\mathcal{H}_{ZE}^A + \mathcal{H}_{ZE}^B$ with

$$\mathcal{H}_{ZE}^A = \beta [g_1(\hat{S}_1 + \hat{S}_3) + g_2 \hat{S}_2] \cdot \vec{H} \quad (4)$$

In fact, since all the copper(II) ions are in the same kind of environment, we assume that they have identical average g factors. The magnetic susceptibility per trinuclear unit is then given by

$$X = \exp\left[\frac{J^{AB}}{4kT}\right] + 2 \exp\left[\frac{J-j}{kT}\right] + 12 \exp\left[\frac{3J}{2kT}\right] + \exp\left[\frac{2J-2j}{kT}\right] + 12 \exp\left[\frac{5J-2j}{2kT}\right] + 20 \exp\left[\frac{3J}{2kT}\right]$$

$$Y = \exp\left[-\frac{3J^{AB}}{4kT}\right] + 3 \exp\left[\frac{J^{AB}}{4kT}\right] + 8 \exp\left[\frac{J-j}{kT}\right] + 16 \exp\left[\frac{3J}{2kT}\right] + 4 \exp\left[\frac{2J-2j}{kT}\right] + 16 \exp\left[\frac{5J-2j}{2kT}\right] + 16 \exp\left[\frac{3J}{2kT}\right]$$

$$\chi_M T = \frac{N\beta^2 g^2}{k} \frac{X}{Y} \quad (5)$$

The quality of the fitting does not depend on j , which therefore

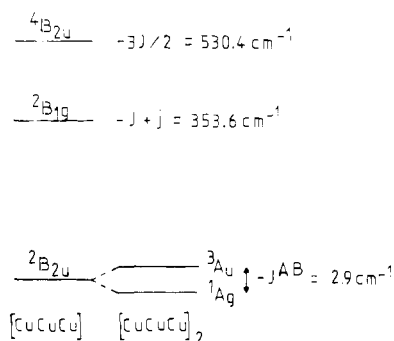


Figure 4. Spectrum of the low-lying states in **1**. The geometry of the trinuclear unit has been idealized to D_{2h} .

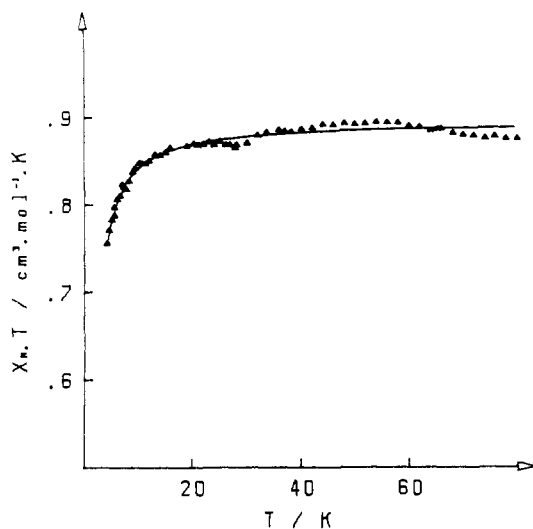


Figure 5. Experimental (\blacktriangle) and calculated (—) temperature dependences of $\chi_M T$ for **2**.

cannot be determined from the magnetic data. An excellent agreement between calculated and experimental $\chi_M T$ values was obtained by imposing $j = 0$ in (5), the other parameters being $J = -353.6 \text{ cm}^{-1}$, $J^{AB} = -2.9 \text{ cm}^{-1}$, and $g = 2.14$. The spectrum of the low-lying states in **1** deduced from the magnetic properties is shown in Figure 4.

The X-band powder EPR spectrum of **1** exhibits a unique quasi-isotropic feature centered at $g = 2.118$ (300 K) and 2.088 (4.2 K). Its temperature dependence confirms that the resonance occurs within the ground doublet state for the trinuclear unit. The spectrum does not show any fine structure or half-field transition corresponding to the low-lying triplet state within the bis trinuclear entity. The most surprising character of the spectrum is the symmetrical aspect. Indeed, the g tensor associated with the ground doublet is related to the local g tensors according to^{27,28}

$$g = (2g_1 - g_2 + 2g_3)/3 \quad (6)$$

and g_1 as shown by the EPR spectrum of $\text{Cu}(\text{oxpn})$ (see Figure 6) is very anisotropic with $g_{\parallel} = 2.170$ and $g_{\perp} = 2.047$. To some extent, the quasi-isotropy of the spectrum of **1** could be due to an averaging effect of the local g tensors.¹²

$[\text{Cu}_2\text{Zn}(\text{oxpn})_2(\text{H}_2\text{O})_2]\text{X}_2$, $\text{X} = \text{ClO}_4^-$ (**2**) and BH_4^- (**3**). We have seen that the interaction j between the terminal copper(II) ions cannot be deduced from the magnetic data for **2**. To estimate this interaction between metal centers very far away from each other, we replaced the central copper(II) ion by the diamagnetic ion Zn(II). Since the zinc atom most likely achieves an octahedral environment by fixing two water molecules, the CuZnCu units cannot give the same kind of bis trinuclear entity as in **1**. The temperature dependence of $\chi_M T$ for **2** is shown in Figure 5. Down to 30 K, $\chi_M T$ is constant and equal to $0.89 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Below 30 K, $\chi_M T$ slightly decreases and reaches $0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 4.2 K. This decrease can be due to intramolecular and/or intermolecular interactions. If we replace ClO_4^- by the much bulkier

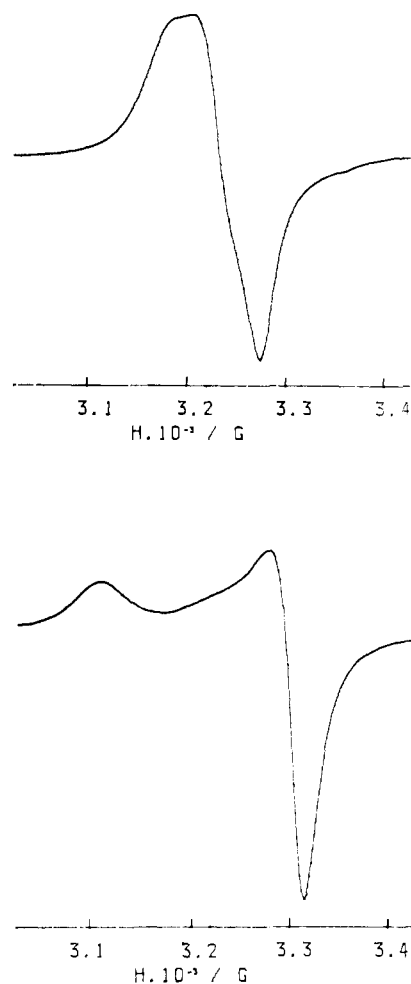


Figure 6. X-Band powder EPR spectra of $\text{Cu}(\text{oxpn})$ (top) and of **2** (bottom).

anion BPh_4^- in order to dilute the trinuclear units in the crystal lattice, we obtain much the same magnetic behavior, which suggests that the weak interaction is largely intramolecular. An upper limit of the singlet-triplet energy gap in **2** and **3** arising from the interaction between the terminal magnetic ions may then be obtained by fitting the magnetic data with the theoretical law for a pair of copper(II) ions:

$$\chi_M T = \frac{2N\beta^2 g^2}{k} \left[3 + \exp\left(-\frac{j}{kT}\right) \right]^{-1} (1 - \rho) + C\rho \quad (7)$$

where the eventual presence of a small proportion ρ of uncoupled impurity is taken into account. The upper limit was found as $j = -1.6 \text{ cm}^{-1}$ with $g = 2.18$. R is then equal to 4.5×10^{-5} .

The EPR spectrum of **2** at 4 K is shown in Figure 6, where it is compared to that of the monomeric fragment $\text{Cu}(\text{oxpn})$. It does not show any half-field signal or fine structure and looks like a spectrum associated with a $S = 1/2$ state. However, in contrast to the situation encountered with zinc adducts of tetradentate Schiff bases,^{27,28} the g values in **2** ($g_1 = 2.062$, $g_2 = 2.088$, $g_3 = 2.118$) are significantly different from those measured with the monomeric fragment $\text{Cu}(\text{oxpn})$.

In spite of the magnetic dilution arising from the presence of BPh_4^- anions between the trinuclear units, the EPR spectrum of **3** does not exhibit any hyperfine structure and is rather similar to that of **2** with $g_{\perp} = 2.051$ and $g_{\parallel} = 2.152$.

$[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**4**). The low-lying states in **4** are a spin singlet, two spin triplets, and a spin quintet. These levels, but the first one, are split in zero field by the combined effect of the local anisotropy of the nickel(II) ion and the anisotropic interactions. The isotropic interaction between the copper(II) and the nickel(II) ions through the oxamido bridge is expected to be strongly antiferromagnetic, so that the ground state will be the

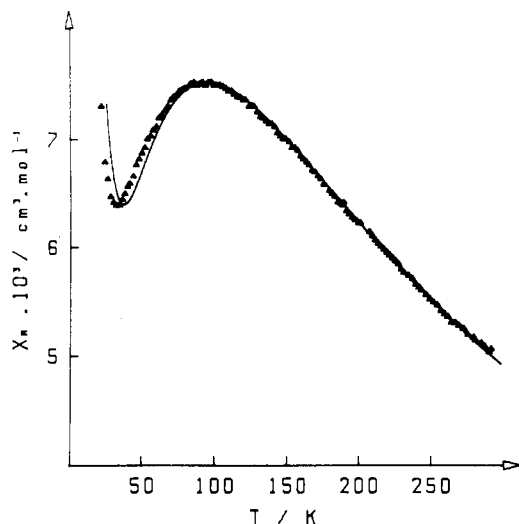


Figure 7. Experimental (▲) and calculated (—) temperature dependences of χ_M for 4.

$$\frac{{}^5B_{2u}}{3J} = 296.1 \text{ cm}^{-1}$$

$$\frac{{}^3B_{1g}}{2J} = 197.4 \text{ cm}^{-1}$$

$$\frac{{}^3B_{2u}}{J} = 98.7 \text{ cm}^{-1}$$

$$\frac{{}^1B_{2u}}{J}$$

Figure 8. Spectrum of the low-lying states in 4. The geometry of the trinuclear unit has been idealized to D_{2h} .

spin singlet. It follows that the zero-field splittings within the excited spin states will be without detectable influence on the magnetic susceptibility. The relative energy of the low-lying states may be derived from the Hamiltonian (1) where now the indices 1 and 3 refer to the copper(II) ions and index 2 refers to the nickel(II) ion. The spin triplets are located at $-J$ and $-2J + j$, respectively, and the spin quintet is at $-3J$ above the ground spin singlet. The magnetic susceptibility is then calculated from (1), to which the Zeeman perturbation (4) is added. It is found as

$$\chi_M = \frac{2N\beta^2}{kT} \times \frac{g_a^2 \exp\left[\frac{J}{kT}\right] + g_b^2 \exp\left[\frac{2J-j}{kT}\right] + 5g_a^2 \exp\left[\frac{3J}{kT}\right]}{1 + 3 \exp\left[\frac{J}{kT}\right] + 3 \exp\left[\frac{2J-j}{kT}\right] + 5 \exp\left[\frac{3J}{kT}\right]} \quad (8)$$

with³⁸ $g_a = (g_1 + g_2)/2$ and $g_b = g_2$.

The experimental temperature dependence of χ_M is shown in Figure 7. It exhibits a maximum around 90 K, which confirms that the ground state is diamagnetic. Below 30 K, χ_M increases again owing to a small proportion ρ of noncoupled ions. To take this into account, χ_M^{exptl} is expressed as $\chi_M(1 - \rho) + C\rho$. By least-squares fitting, we found $J = -98.7 \text{ cm}^{-1}$, $j = 0$, and $g = 2.12$. R is then equal to 2.4×10^{-5} . The experimental data do not allow us to distinguish the different g factors, and 2.12 is an average value. The spectrum of the low-lying states in 4 as

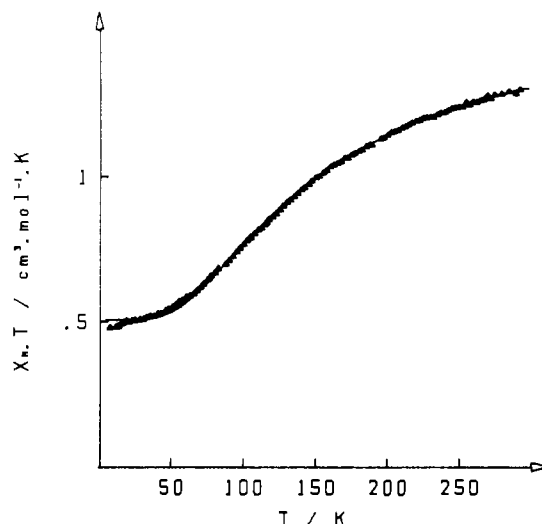


Figure 9. Experimental (▲) and calculated (—) temperature dependences of $\chi_M T$ for 5.

deduced from the magnetic properties is shown in Figure 8.

Owing to the zero-field splitting within the excited magnetic states, 4 is, as expected, EPR silent at any temperature.

[CuNi(oxpn)(bpy)₂](NO₃)₂·2H₂O (5). The magnitude of the interaction between a copper(II) ion and a nickel(II) ion through the oxamido bridge may also be deduced from the magnetic properties of compound 5. In this case, we have two low-lying states, a spin doublet and a spin quartet separated by $3J/2$, and the temperature dependence of $\chi_M T$ is given by

$$\chi_M T = \frac{N\beta^2}{4k} \frac{g_{1/2}^2 + 10g_{3/2}^2 \exp(3J/2kT)}{1 + 2 \exp(3J/2kT)} \quad (9)$$

with³⁸⁻⁴⁰ $g_{1/2} = (4g_2 - g_1)/3$ and $g_{3/2} = (2g_2 + g_1)/3$.

In (9) we again neglected the zero-field splitting within the excited quartet state. The magnetic properties are shown in Figure 9. When the sample is cooled, $\chi_M T$ decreases, then reaches a plateau with $\chi_M T = 0.51 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ corresponding to the temperature range where only the ground doublet state is thermally populated. The fitting of the data leads to $J = -110.6 \text{ cm}^{-1}$, $g_{1/2} = 2.32$, and $g_{3/2} = 2.16$. R is then equal to 8.8×10^{-5} .

The EPR spectrum of 5 shown in Figure 10 is at first view surprising. It does not correspond to that of a simple ground doublet state as it was found for instance in CuNi(fsa)₂en-(H₂O)₂·H₂O.³⁹ Actually, at room temperature, it exhibits an intense feature centered at $g = 2.21$ and a smaller feature at $g = 4.06$. When the sample is cooled, this latter signal progressively disappears and a new very weak signal centered at $g = 4.34$ appears. The presence of the $\Delta M_s = 2$ forbidden transition at half-field below 40 K, in a temperature range where the quartet pair state is totally depopulated, shows that the ground state is not a pure doublet pair state. The nature of the spectrum strongly suggests that in the crystal lattice, the [CuNi(oxpn)(bpy)₂]²⁺ units are symmetry-related two by two and form bis heterobinuclear entities [CuNi]₂. The magnetic properties, at least above 4.2 K, are governed by the interaction between copper(II) and nickel(II) ions within the CuNi pairs whereas the EPR spectrum is that of a low-lying triplet state⁴⁶ associated with the bis heterobinuclear nature of the compound. A similar situation has been observed for Cu(salen)Ni(hfa)₂ and investigated in a thorough manner.⁴⁰ The zero-field splitting within the triplet state was however rather large in this latter compound ($|D| = 0.125 \text{ cm}^{-1}$) whereas it is undetectable in 5.

We have shown that one of the origins of the zero-field splitting within the low-lying triplet state of a [CuNi]₂ bis heterobinuclear

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(39) Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.

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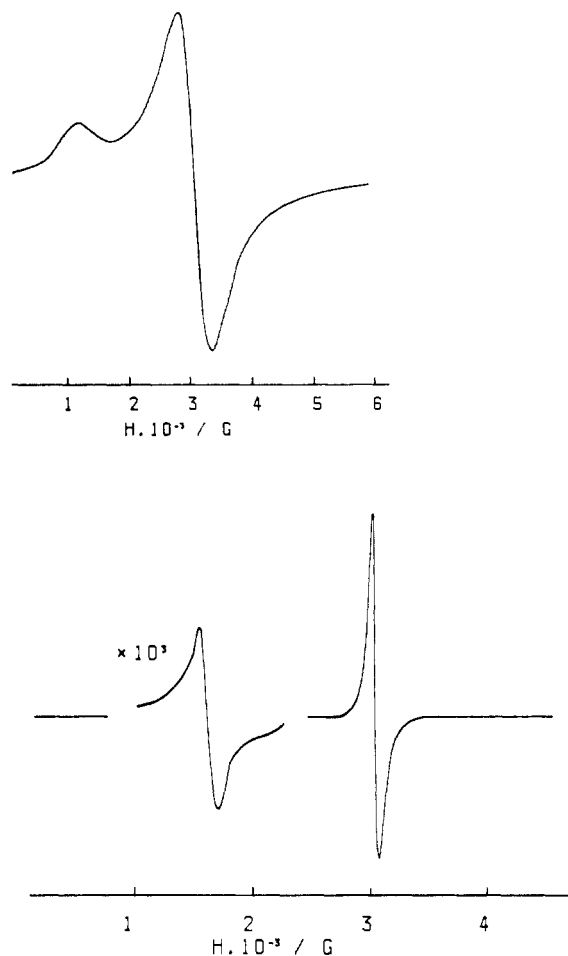


Figure 10. X-Band EPR spectra at 300 K (top) and 10 K (bottom) of **5**.

entity was the admixture of quartet pair state into the doublet pair state through the local anisotropy of the nickel(II) ion characterized by D_{Ni} . This effect varies as D_{Ni}/J . In **5**, $|J|$ is much larger than in $Cu(salen)Ni(hfa)_2$ (98.7 and 23.6 cm^{-1} , respectively), which could explain the differences between the EPR spectra of the two compounds.

A point concerning the EPR spectrum of **5** remains to be discussed, namely the nature of the signal at $g = 4.06$ visible at room temperature. This signal could be associated with a resonance within the excited manifold arising from the interaction between the quartet excited state of a $CuNi$ pair and the doublet ground state of the other.

The spectrum of the low-lying states in **5** as deduced from magnetic and EPR properties is shown in Figure 11.

Discussion and Conclusion

We shall discuss successively the results concerning compounds **1–5**.

In **1**, the interaction between $Cu1$ and $Cu2$ was found significantly weaker than in the binuclear complex $[Cu(oxpn)Cu(bpy)](ClO_4)_2$ ¹² where the magnetic orbitals have the same relative orientations; the J values are -353.6 and -439.7 cm^{-1} , respectively. This difference is clearly due to the fact that in **1** the $Cu(C_2-N_2O_2)Cu$ bridging networks are not rigorously planar, which diminishes the overlap between the magnetic orbitals. As for the weak interaction between the terminal metal centers, it cannot be determined accurately from the magnetic data. The only effect of j is to modify slightly the relative energy of the excited doublet with regard to those of the ground doublet and the highest quartet, which remain invariant. In contrast, a weak interaction between trinuclear units as it occurs in **1** is easily detected in the low-temperature range by the deviation of the magnetic susceptibility with regard to the Curie law. The separation J^{AB} between low-lying singlet and triplet states within the bis trinuclear entity may

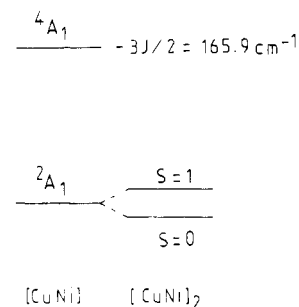


Figure 11. Spectrum of the low-lying states in **5**. The geometry of the binuclear unit has been idealized to C_{2v} .

be related to the interaction parameters J^{ij} between pairs of copper(II) ions Cu_i and Cu_j . For that, we must build the spin functions associated with the singlet and triplet states and determine the energies of these states using the spin Hamiltonian

$$\mathcal{H}^{AB} = -\sum_i \sum_j J^{ij} \hat{S}_{A_i} \cdot \hat{S}_{B_j} \quad (10)$$

The calculation leads to

$$J^{AB} = \frac{1}{9} [J^{22} + 4(J^{11} + J^{13} + J^{31} + J^{33}) - 2(J^{21} + J^{23} + J^{32} + J^{12})] \quad (11)$$

At first, when looking at the structure of Figure 2, we may think that all the J^{ij} parameters are negligible but J^{22} . If this were so, J^{22} would be equal to $9J^{AB}$, i.e. -26.1 cm^{-1} , which appears as too large a value for the interaction between the central copper atoms. Indeed, the delocalization of the magnetic orbital centered on $Cu2$ toward the $O1'$ apical site is certainly extremely weak. We can notice, however, that S–T energy gaps in the range ± 20 cm^{-1} were reported for copper(II) dimeric species with parallel basal planes.^{41,42}

A weak interaction between the terminal copper(II) ions has been detected from the magnetic and EPR properties of **2** and **3**. The j value of -1.6 cm^{-1} is certainly an upper limit since the magnetic data include the effect of the intramolecular as well as intermolecular interactions. The only indication that the intramolecular pathway is dominant comes from the fact that the tetraphenylborate derivative (**3**) exhibits the same magnetic behavior as the perchlorate one (**2**). More generally, it is difficult to distinguish between intra- and intermolecular effects when the magnitude of the interaction is weak.⁴³ The only way to solve this problem unambiguously would be to cool down the sample enough to observe the onset of the magnetic order and to deduce the magnitude of the intermolecular interaction from the value of the critical temperature. It should be noticed that $j = -1.6$ cm^{-1} for two copper(II) ions separated by more than 10 Å is beyond the limit value of -0.2 cm^{-1} deduced from the empirical relation proposed by Coffman and Buettner.⁴⁴ The most striking result along this line was reported by Felthouse and Hendrickson,⁴⁵ who found a S–T energy gap of -9 cm^{-1} with a copper–copper separation of more than 12 Å.

The interaction parameters between the copper(II) and nickel(II) ions deduced from the magnetic properties of **4** and **5** are, as expected, close to each other. Compound **5** reveals quite an interesting aspect of the complementarity between magnetic and EPR techniques. The magnetic properties lead to the magnitude

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of the interaction between copper(II) and nickel(II) within the Cu-Ni unit and show a doublet ground pair state whereas the EPR properties are those associated with the bis heterobinuclear entity (CuNi)₂. It is particularly unfortunate that we have not been able to grow single crystals of **5** suitable for an X-ray investigation in order to confirm the presence of such (CuNi)₂ species.

In this paper, we have shown that the magnetic properties of homo- and heterotrinnuclear species can be interpreted in a relatively accurate way. This is particularly true when the interacting metal centers have no first-order angular momentum and when the interaction between adjacent sites is important, as in **1** and **4**. In the near future, we intend to develop this aspect and to approach the study of the magnetic and EPR properties of molecular species with more than three magnetic centers.

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*.]

Registry No. **1**, 99727-38-5; **2**, 99727-40-9; **3**, 99781-74-5; **4**, 99727-42-1; **5**, 63000-43-1; Cu(oxpn), 20102-49-2.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters for non-hydrogen atoms, and atomic coordinates for hydrogen atoms not refined in the least-squares refinement (12 pages). Ordering information is given on any current masthead page.

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Catechol-Quinone Redox Series Involving Bis(bipyridine)ruthenium(II) and Tetrakis(pyridine)ruthenium(II)

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A series of species belonging to the redox chain RuN₄(cat), [RuN₄(sq)]⁺, and [RuN₄(q)]²⁺ have been prepared and characterized by electronic, IR, and ESR spectroscopy and electrochemistry. The N₄ unit is bis(bipyridine) or tetrakis(pyridine), and the dioxolene ligands are catechol, 3,5-di-*tert*-butylcatechol, and tetrachlorocatechol and their one- and two-electron-oxidation products. Evidence is presented that oxidation of the dioxolene ligand to quinone occurs before oxidation of Ru(II) to Ru(III). Rich electronic spectra and electrochemistry are reported and assigned. The positions of the charge-transfer bands (metal to ligand, and ligand to ligand) are discussed in terms of the electrochemical potentials.

Introduction

There has been growing interest in catechol and its oxidation products (semiquinone and quinone) as ligands.²⁻³² Interest

centers mainly on the generation of redox chains, structural characterization, magnetic effects, the identification of effective oxidation levels, relationships with some natural biological catechol systems, and the quite complex electrochemistry that can arise through internal electron transfers and disproportionation. With the aim of developing polyelectron redox catalysts, we have studied complexes of the type RuN₄(0-0), where (0-0) is a variously substituted bidentate dioxolene ligand in the redox chain catechol-semiquinone-quinone and N₄ is two bipyridine (bpy) or four pyridine (py) units.

The dioxolenes are noninnocent ligands, which may coordinate in three different formal oxidation states. This can lead to ambiguity in assessing the oxidation state of the central ion. For example, in analogous dithiolene complexes considerable delocalization is thought to occur in the metal-ligand bond.³³ In dioxolene complexes, oxidation state assignments are generally

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