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Synthesis, Structure, and Magnetic Properties of μ-2,2'-Bipyrimidine-N,N',N'',N''' Copper(II) Complexes

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The synthesis, structure, and magnetic properties of polynuclear complexes of Cu(II) bridged by 2,2'-bipyrimidine ($C_8H_6N_4$, bpm) in a bis-bidentate manner, $X_2Cu(bpm)CuX_2$ (X = NO_3, compound **1**; X = Cl, compound **2**; X = Br, compound **3**), are reported. Compounds **2** (X = Cl) and **3** (X = Br) are isostructural, with space group $C2/m$ and Z = 2. For the chloro derivative, $(C_8H_6N_4Cl_4Cu_2)_n$, a = 6.835 (1) Å, b = 13.321 (2) Å, c = 6.806 (1) Å, and β = 90.54 (2)°; for the bromo derivative, $(C_8H_6N_4Br_4Cu_2)_n$, a = 7.100 (1) Å, b = 13.504 (2) Å, c = 7.063 (1) Å, and β = 90.69 (4)°. The structures were refined to R values of 2.6 and 4.5%, respectively. The copper atoms are in the bpm plane. Each copper atom is bound to two cis nitrogen atoms of the bpm and to four halogen atoms. Two halogen atoms are in the plane of the $Cu-C_8H_6N_4-Cu$ entity, with short Cu–X distances. The two others are in axial positions, with long Cu–X distances, giving rise to a distorted-octahedral environment. The metal–metal separations are 5.528 (2) Å for the chloro compound and 5.545 (2) Å for the bromo one. The three complexes exhibit antiferromagnetic coupling with a maximum susceptibility in the 160–195 K range. The values of the singlet–triplet gap are respectively −191, −225, and −236 cm^{-1} for the nitrate, chloride, and bromide derivatives. This antiferromagnetic coupling is explained in the framework of a simple orbital model by the large σ in-plane overlap of the d_{xy} magnetic metal orbitals through the bpm bridge.

Introduction

The interest in inorganic exchange-coupled systems has led to many synthetic endeavors and magnetostructural studies in the past few years.[2] These efforts resulted in a better fundamental understanding of exchange through multiatomic bridges and in the synthesis of models for biological polynuclear active centers and of molecular materials exhibiting new but predictable properties. We have synthesized copper(II) complexes with N donor atoms,[3–5] designed molecular complexes with expected intramolecular exchange through multiatomic bridges,[6–13] and explored the influence of intermolecular interactions upon the magnetic properties.[14–16] We focus here on homo- or heterobinuclear

complexes obtained from 2,2'-bipyrimidine (bpm), which is well-known to bridge transition-metal ions[3,17–22] with unpaired d electrons,[17–19] diamagnetic species,[20–22] and, particularly, Ru(II).[21,22] 2,2'-Bipyrimidine presents a bis-bidentate group C_2XYZW (X = Y = Z = W = N) that allows an almost planar geometry of the Cu–bridge–Cu unit (I).

I
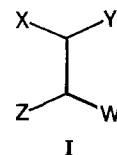
Such C_2XYZW bridges give coupling constants increasing up to 800 cm^{-1}, for Cu–Cu distances larger than 5 Å, in the series oxalato (X = Y = Z = W = O),[6–9] oxamato (X = Y = Z = O; W = N),[10] oxamido (X = W = N; Y = Z = O),[10] dithiooxamido (X = W = S; Y = Z = N),[12] and tetrathiooxalato (X = Y = Z = W = S).[13] For bipyrimidine, magnetic data are available for Cu(II),[17] Mn(II), Co(II), and Ni(II)[18b] binuclear complexes with weak coupling constants and for a bimetallic binuclear Fe(II)–Cu(II) complex with no coupling at all.[17,18a] In view of our preceding findings about the other bis-bidentate bridges, we found it of interest to study the magnetic properties of the parent Cu(II) complex $[(C_8H_6N_4)(NO_3)_4Cu_2]_n$ (**1**), the structure of which has recently been published by two of us.[3] Furthermore, **1** presents an alternating-chain structure where the planar Cu(II)–bipyrimidine–Cu(II) entities are linked by nitrate groups. Synthesis of new copper(II) compounds with counteranions other than nitrate can provide more insight into the interactions within and between the binuclear species. We present the synthesis, structural

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Table I. Single-Crystal X-ray Crystallographic Analysis

	compd 2	compd 3
formula	$(C_8H_6N_4Cl_4Cu_2)_n$	$(C_8H_6N_4Br_4Cu_2)_n$
unit wt	427.06	604.88
color, habit	green, prismatic	brown, prismatic
cryst size, mm	$0.06 \times 0.04 \times 0.11$	$0.14 \times 0.18 \times 0.15$
space group	$C2/m$	$C2/m$
temp, K	295 (1)	295 (1)
cell dimens		
a, Å	6.835 (1)	7.100 (1)
b, Å	13.321 (2)	13.504 (2)
c, Å	6.806 (1)	7.063 (1)
α, deg	90	90
β, deg	90.54 (2)	90.69 (4)
γ, deg	90	90
V, Å^3	619.6 (2)	677.1 (2)
Z	2	2
D(calcd), g/cm^3	2.288	2.966
radiatn (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
μ(Mo Kα), cm^{-1}	42.1	147.1
orientation reflcns: no.; range (2θ), deg	20; 15–30	20; 15–30
scan method	ω–2θ	ω–2θ
data collcn range (2θ), deg	3–64	3–64
no. of reflcns collcd	1100	1200
no. of reflcns with $I > 3\sigma(I)$	633	901
data collcd	$-10 \leqslant h \leqslant 10$	$-11 \leqslant h \leqslant 11$
	$0 \leqslant k \leqslant 20$	$0 \leqslant k \leqslant 20$
	$0 \leqslant h \leqslant 10$	$0 \leqslant k \leqslant 11$
merg consistent index^a	0.018	0.026
no. of params refined	50	50
R^a	0.025	0.042
$R_w{}^a$	0.026	0.045
largest shift/esd, final cycle	0.05	0.04
largest peak, e/Å^3	0.61	1.25

^{a} See ref 26.

characterization, and magnetic properties for the chloride $[C_8H_6N_4Cl_4Cu_2]_n$ (**2**) and the bromide $[C_8H_6N_4Br_4Cu_2]_n$ (**3**).

Experimental Section

Synthesis. All materials were of reagent grade purity and were used as received. The chloro complex $[C_8H_6N_4Cl_4Cu_2]_n$ (**2**) and the bromo complex $[C_8H_6N_4Br_4Cu_2]_n$ (**3**) were prepared in a manner similar to that for compound **1**,[3] by mixing 25 mL of an ethanolic solution of 2,2'-bipyrimidine (1 mmol) with 25 mL of an aqueous solution of the halogeno copper(II) salt (2 mmol). Single crystals were obtained by slow diffusion of the two solutions placed in the two branches of an H-tube.

Anal. Calcd for $C_8H_6N_4Cl_4Cu_2$: C, 22.50; H, 1.42; N, 13.12. Found: C, 22.42; H, 1.17; N, 12.91. Calcd for $C_8H_6N_4Br_4Cu_2$: C, 15.89; H, 1.00; N, 9.26. Found: C, 15.83; H, 0.90; N, 9.12.

X-ray Data Collection and Structure Refinement. Diffraction data were collected on a Siemens Stoe four-circle diffractometer, by using graphite-monochromated Mo Kα ($\lambda = 0.710\,69$ Å) radiation and an ω–2θ scan technique. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ, and φ values of 20 strong reflections in the range $15° < 2\theta < 30°$.

Crystallographic data and other pertinent information are summarized in Table I.

Lorentz and polarization corrections were applied to the intensity data. Absorption and extinctions corrections were ignored. The structures were solved by using standard Patterson methods and subsequently by using difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structures factors. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms, from the ΔF map, were included with a common thermal parameter.

Of the 1100 measured independent reflections for **2**, 633 were unique with $I \geqslant 3\sigma(I)$, while these numbers were 1200 and 901 for **3**. These data were used in the final refinement of the structural parameters to arrive at final residuals of $R = 0.025$ and $R_w = 0.026$ for **2** and $R = 0.042$ and $R_w = 0.045$ for **3**. Refinement attempts in space groups $C2$ and C_m were unsuccessful.

The weighting scheme used in the last refinement cycles was $w = 1.4917/(\sigma^2|F_o| + 0.000217|F_o|^2)$ for **2** and $w = 1.0000/(\sigma^2|F_o| + 0.003188|F_o|^2)$ for **3**.

Table II. Fractional Coordinates ($\times 10^4$)

atom	x/a	y/b	z/c
	Compound 2		
Cu	0	2925 (1)	5000
Cl	1378 (1)	1781 (1)	7017 (1)
N	977 (2)	4110 (2)	6692 (3)
C(1)	543 (4)	5000	5939 (4)
C(2)	2487 (4)	5000	9316 (5)
C(3)	1975 (3)	4108 (2)	8412 (3)
H(2)	3148 (66)	5000	10495 (99)
H(3)	2267 (47)	3470 (39)	8819 (65)
	Compound 3		
Cu	0	2947 (1)	5000
Br	1357 (1)	1730 (1)	7069 (1)
N	932 (5)	4118 (3)	6643 (4)
C(1)	527 (8)	5000	5902 (7)
C(2)	2394 (10)	5000	9175 (9)
C(3)	1913 (6)	4122 (3)	8299 (5)
H(2	3221 (92)	5000	10257 (72)
H(3)	2065 (99)	3473 (24)	8827 (93)

Table III. Bond Lengths (Å) and Interbond Angles (deg)^a

	2 (X = Cl)	3 (X = Br)
Cu–X	2.252 (1)	2.394 (1)
Cu–X(a)	2.869 (1)	3.018 (1)
Cu–N	2.061 (2)	2.067 (3)
N–C(3)	1.349 (2)	1.354 (4)
N–C(1)	1.324 (2)	1.331 (4)
C(1)–C(1)'	1.472 (3)	1.470 (7)
C(2)–C(3)	1.382 (3)	1.378 (5)
N–Cu–X	92.7 (1)	93.4 (1)
X–Cu–X'	94.5 (1)	93.3 (1)
N–Cu–N'	80.1 (1)	80.1 (1)
N–Cu–X(a)	83.5 (1)	83.7 (1)
N'–Cu–X(a)	84.5 (1)	83.5 (1)
X–Cu–X(a)	91.5 (1)	93.1 (1)
X(a)–Cu–X'	99.1 (1)	98.3 (1)
N–Cu–X'	172.1 (1)	172.9 (1)
X(a)–Cu–X(a')	164.3 (1)	163.4 (1)
Cu–X–Cu(a)	88.5 (1)	86.9 (1)
Cu–N–C(3)	129.9 (2)	130.2 (3)
Cu–N–C(1)	113.5 (2)	113.4 (3)
C(3)–N–C(1)	116.5 (2)	116.3 (3)
N–C(3)–C(2)	120.6 (2)	120.8 (3)
N–C(1)–C(1)'	116.4 (1)	116.5 (1)
N–C(1)–N(b)	127.1 (1)	126.9 (2)
C(3)–C(2)–C(3b)	118.6 (3)	118.7 (2)

^{a} Symmetry code: (') $-x, y, 1 - z$; (a) $^1/_2 - x, ^1/_2 - y, 1 - z$; (b) $x, 1 - y, z$; (a') $-^1/_2 + x, ^1/_2 - y, z$.

The anomalous dispersion corrections were taken from ref 23, atomic scattering factors for all non-hydrogen atom from ref 24, and scattering factors for hydrogen atoms from ref 25. All calculations were performed with the SHELX-76[26] and PARST[27] sets of programs on an IBM 4341 computer from the "Centro di calcolo dell'Università di Messina" and on a VAX/VMS computer from the "Università della Calabria". The refined structures were plotted by using the ORTEP program. Anisotropic temperature factors for **2** and **3** (Table S1) and calculated and observed structure factors (Table S2 for **2** and Table S3 for **3**) are available as supplementary material. Atomic coordinates are gathered in Table II. Main interatomic distances and bond angles are given in Table III. Significant least-squares planes are presented in Tables IV and V.

Magnetism and EPR Spectra. The susceptibility of the complex was measured with a Faraday-type magnetometer, equipped with a helium flow cryostat. The measurements were performed in the 20–300 K temperature range.

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Table IV. Least-Squares Planes for Compound 2^a

Plane 1: Cu–N–C(3)–C(2)–C(3b)–N(b)–
C(1)–C(1)′–N′–C(3)′–C(2)′–C(3b)′–N(b)′–Cu(b)
$0.8683x + 0.0000y - 0.4959z = -1.7154$
[Cu, −0.0001 (6); N, −0.001 (2); C(3), 0.002 (2); C(2), −0.005 (3);
C(3b), 0.002 (2); N(b), −0.001 (2); C(1), −0.001 (3); C(1)′, 0.001
(3); N′, 0.001 (2); C(3)′, −0.002 (2); C(2)′, 0.005 (3); C(3b)′,
−0.002 (2); N(b)′, 0.001 (2); Cu(b), −0.0000 (1); Cl, 0.126 (1);
Cl′, −0.126 (1); H(3), 0.03 (3)]

Plane 2: Cu–Cl–Cl′–Cu(b)–Cl(b)–Cl(b)′
$0.8282x + 0.0000y - 0.5605z = -1.9336$
Because of symmetry, all atoms lie exactly on the plane
[N, −0.101 (2); Cl(a), 2.830]

Plane 3: N–N′–C(1)–C(1)′–Cu
$0.8345x + 0.0000y + 0.5509z = -1.9014$
[N, −0.086 (2); N′, 0.086 (2); C(1), 0.019 (1);
C(1)′, −0.019 (1); Cu, 0.0000 (6)]

Angles (deg) between Planes

1–2	4.4 (1)	1–3	3.7 (1)	2–3	0.7 (1)

^{a} Deviations of relevant atoms from the plane (Å) are given in square
brackets. Symmetry code: see Table III.

Table V. Least-Squares Planes for Compound 3^a

Plane 1: Cu–N–C(3)–C(2)–C(3b)–N(b)–
C(1)–C(1)′–N′–C(3)′–C(2)′–C(3b)′–N(b)′–Cu(b)
$0.8698x + 0.000y - 0.4933z = -1.7791$
[Cu, −0.0001 (6); N, −0.009 (3); C(3), 0.008 (4); C(2), −0.007 (7);
C(3b), 0.008 (4); N(b), −0.009 (3); C(1), −0.004 (6); C(1)′, 0.004
(6); N′, 0.009 (3); C(3)′, −0.008 (4); C(2)′, 0.007 (7); C(3b)′,
−0.008 (4); N(b)′, 0.009 (3); Cu(b), −0.0001 (6); Br, 0.102 (1);
Br′, −0.102 (1); H(3), −0.09 (7)]

Plane 2: Cu–Br–Br′–Cu(b)–Br(b)–Br(b)′
$0.8395x + 0.0000y - 0.5434z = -1.9545$
Because of symmetry, all atoms lie exactly on the plane
[N, −0.087 (3); Br(a), 2.980 (2)]

Plane 3: N–N′–Br–Br′–Cu
$0.8409x + 0.0000y - 0.5411z = -1.9466$
[N, −0.083 (3); N′, 0.083 (3); Br, 0.005 (1);
Br′, −0.005 (1); Cu, 0.0000 (6)]

Angles (deg) between Planes

1–2	3.4 (1)	1–3	3.2 (1)	2–3	0.2 (1)

^{a} Deviations of relevant atoms from the plane (Å) are given in square
brackets. Symmetry code: see Table III.

Figure 1. ORTEP view and numbering scheme of the binuclear $(C_8H_6$-$N_4Br_4Cu_2)_n$ complex (**3**). Thermal ellipsoids are drawn at the 50% probability level. All H atoms are drawn with uniform isotropic thermal parameters.

The X-band EPR spectra were recorded with a Bruker ER200 spectrometer, in the same temperature range.

Results

Description of the Structures. The $[C_8H_6N_4Cl_4Cu_2]_n$ (**2**) and $[C_8H_6N_4Br_4Cu_2]_n$ (**3**) complexes are isostructural. They consist of $X_2Cu(bpm)CuX_2$ binuclear units (X = Cl, Br) bridged by halogen atoms. Two views of the structure showing the numbering scheme and the stacking of the molecular units are shown in Figures 1 and 2.

The coordination around each copper is best described as a distorted octahedron: two nitrogen atoms from the bpm at $\simeq 2.06$ Å and two halogen atoms at 2.252 (1) Å for Cl (and 2.394 (1) Å for Br) build the equatorial plane, whereas the axial positions

are occupied by halogen atoms belonging to another unit at 2.869 (1) Å for Cl (and 3.018 (1) Å for Br). The bpm ligand bridges two copper atoms in a planar arrangement. The intermolecular Cu⋯Cu distances are 5.528 (2) Å in **2** and 5.545 (2) Å in **3**, whereas the distance is 5.371 (1) Å in the nitrate complex **1**.

Selected distances and angles are given in Table III. They are similar for the two complexes, except for the Cu–X values. The main point is that the Cu(bpm)Cu unit is planar. As shown in Table IV and V, the Cu(bpm)Cu unit is exactly planar in compound **1** and almost planar in compound **3**. The deviations from this plane are ±0.126 (1) Å for Cl and Cl′ in **2** and ±0.102 (1) Å for Br and Br′ in **3**. They are +0.018 (2) Å for O(4) and +0.017 (2) Å for O(1) in complex **1**.[3] The larger deviations of the halogen atoms from the plane are accompanied by an increase of the X–Cu–X(a) angles (91.5 (1)° for Cl and 93.1 (1)° for Br) and a corresponding decrease of the Cu–X–Cù(a) angles (88.5 (1)° for Cl and 86.9 (1)° for Br). The four halogen atoms of one binuclear unit are, for symmetry, in the same plane; the angle between this plane and the Cu(bpm)Cu one is 4.4 (1)° for **2** and 3.4 (1)° for **3**.

This distortion from a planar $X_2Cu(bpm)CuX_2$ arrangement corresponds to a B_{3g} vibrational mode and has been observed already; its relative stability compared to that for the planar arrangement and to those for the other possible A_μ, B_{2g}, and B_{1u} distortions has been explained.[13]

The intermolecular Cu⋯Cu(a) shorter separations are respectively 3.418 (1) Å in **1**,[3] 3.600 (1) Å in **2**, and 3.749 (1) Å in **3**, in all the cases smaller than the intramolecular one.

As far as the bridging ligand bpm is concerned, the main difference is the C(1)–C(1)′ distance, which is larger in the halogen complexes (1.472 (3) Å in **2** and 1.470 (7) Å in **3**) than the one found in the nitrato complex (1.432 (8) Å). They are, at any rate, shorter than those found in the free ligand in the gaseous and solid
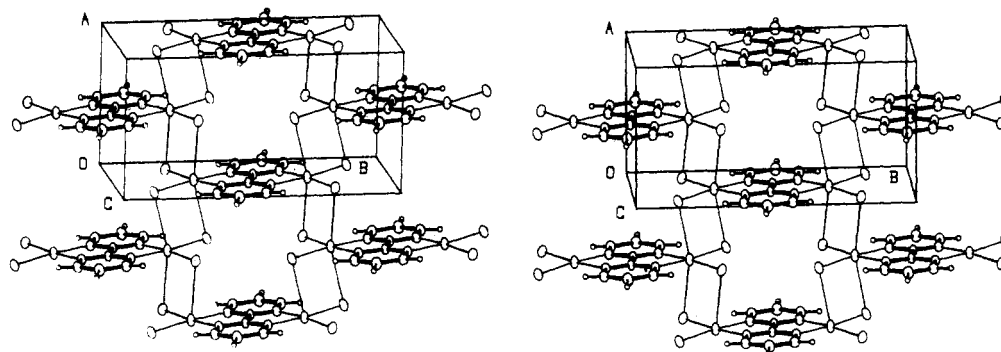

Figure 2. Stereoscopic view of complex **3**, exhibiting the planar layers built from the binuclear Cu–bpm–Cu units through the halogen bridges.
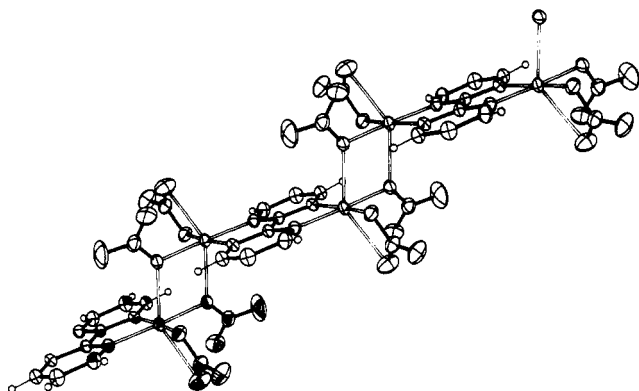
Figure 3. Perspective view of the $(C_8H_6N_4(NO_3)_4Cu_2)_n$ complex (1), showing the alternating-chain arrangement (after ref 3).

**Table VI.** Best Fitted Values for J, g, and ρ

compd	$-J$, cm^{-1}	g	$\rho\%$	$10^{-5}R^a$
1	191	2.13	7.0	4.0
2	225	2.04	5.8	18.0
3	236	2.02	5.7	4.0

$^a R$ is the agreement factor defined as $R = \sum_i((\chi_{obsd})_i - (\chi_{theor})_i)^2 / \sum_i(\chi_{obsd})_i^2$.

states (1.511 (2) and 1.497 (1) Å, respectively)[28] or in another complex, $Cu(ClO_4)_2(bpm)_2\cdot 3H_2O$, a study of which is to be published.[29]

The more substantial difference is the arrangement of the Cu(bpm)Cu units in the network. In the halogen complexes, the units are linked by the halogen atoms along two directions, generating layers of stacking units where all the copper atoms belong to the same plane, parallel to a and b. The angles between this plane and the bpm plane are 60.3 (1)° for **2** and 60.9 (1)° for **3**. The planes containing the bpm molecules within each layer are separated by 2.967 Å in **2** and 3.088 Å in **3**.

There is a partial overlap between bpm units belonging to different layers, as shown in II. The distances between the planes

II
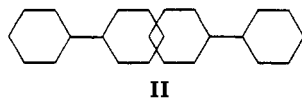
containing the bpm molecules of adjacent layers are 3.431 Å in **2** and 3.558 Å in **3**.

In the nitrate complex, the Cu(bpm)Cu units are linked by the nitrate groups only along one direction, giving rise to chains linked by bpm and by two nitrate groups alternatively (Figure 3). In this case, the second direction is impeded by the chelating bonding mode of one of the nitrate ligands to the copper ions. The two adjacent bpm molecules in the chain are in parallel planes. The distance between these two planes is reduced to 1.946 Å due to the distortion of the Cu(II)–oxygen axial bonds in the direction of the chains.

Magnetic Results. The curves giving the molar susceptibility vs T are displayed in Figure 4. The curves present smooth maxima at about 161, 180, and 195 K for compounds **1–3**, respectively, and increases at low temperature due to uncoupled species. These data can be fitted by a Bleaney–Bowers binuclear law modified to include an amount of $\rho\%$ uncoupled impurities:

$$\chi = 2N\beta^2 g^2(1 - \rho)/(kT(3 + \exp(-J/kt))) + \rho C/T \quad (1)$$

The best fit results are given in Table VI. These results imply a large intramolecular interaction through the bipyrimidine bridge and a weak intermolecular interaction.

EPR Spectra. For $T > 60$ K, the three compounds exhibit the spectrum expected for an axial copper(II) complex. The intensities
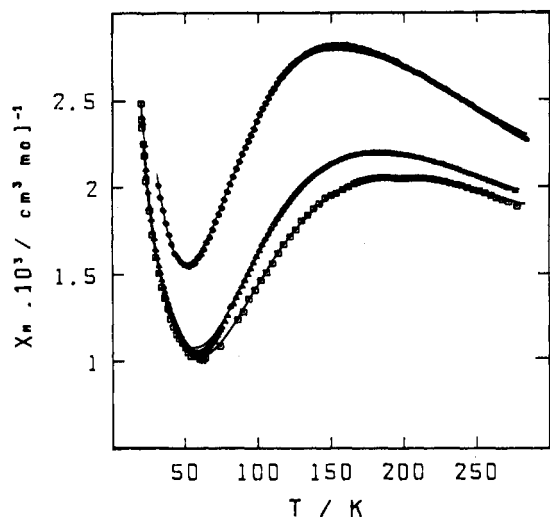
(28) Fernholt, L.; Romming, C.; Samdal, S. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 707.
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Figure 4. Thermal variation of the molar susceptibility: experimental points for **1** (◇), **2** (△), and **3** (□) and theoretical best fits (solid lines).

of the signals decrease with temperature, showing the triplet origin of the spectra. The g values are as follows: for **1**, $g_\| = 2.256$, $g_\perp = 2.033$; for **2**, $g_\| = 2.272$, $g_\perp = 2.068$; for **3**, $g_\| = 2.292$, $g_\perp = 2.082$. No half-field transition is observed, which indicates a weak zero-field splitting.[30,31] For $T < 60$ K, uncoupled copper(II) signals appear. Their intensity increases, and they become predominant at lower T.

Discussion of the Magnetic Properties

We want to discuss four points, i.e. (i) the exchange pathway through the bpm bridge, (ii) the influence of peripheral ligands upon the coupling constant J and the importance of intermolecular interactions, (iii) the efficiency of bpm to transmit antiferromagnetic interaction compared to that of other ligands, and finally, (iv) the relative ability of copper(II) compared to that of other divalent transition-metal ions such as Mn(II), Co(II), and Ni(II) to obtain strong antiferromagnetic interactions through a bpm bridge.

(i) The exchange interaction through the bipyrimidine bridge is important: the singlet–triplet gap $|J|$ is larger than 190 cm^{-1} for two coppers separated by 5.5 Å. This strong interaction is due to the overlap of the d magnetic orbitals of d_{xy} symmetry centered on each copper(II) ion through the bpm bridge where they are partially delocalized.

On the contrary, the overlap between d_{xy} orbitals belonging to different binuclear units is expected to be small, as discussed in the following paragraph.

We show in Figure 5 the two singly occupied molecular orbitals (MO) obtained from extended Hückel calculations as already described.[10] The two MOs can be considered as the g and u combinations of the magnetic orbitals.

It has been shown within different models (orthogonal or nonorthogonal magnetic orbitals) that in a series of complexes with similar geometries, when the ferromagnetic terms are negligible[2a]

$$|J| \propto \Delta^2$$

A large energy gap Δ between the two MOs favors the pairing of spins and the stabilization of the singlet state. We found for example $\Delta = 0.2$ eV for the chloride derivative **2**. This simple approach explains the antiferromagnetic pairing of Cu(II) spins by a σ in-plane overlap and needs, in this case, no intervention of the delocalized π system of the bpm ligand, which has been invoked to explain the magnetic results in the nickel, cobalt, and manganese complexes[18b] and their spectroscopic properties.[20b–d]

Our result is in apparent contradiction with the one obtained by Petty et al. in the complex $(hfac)_2Cu(bpm)Cu(hfac)_2$ with a

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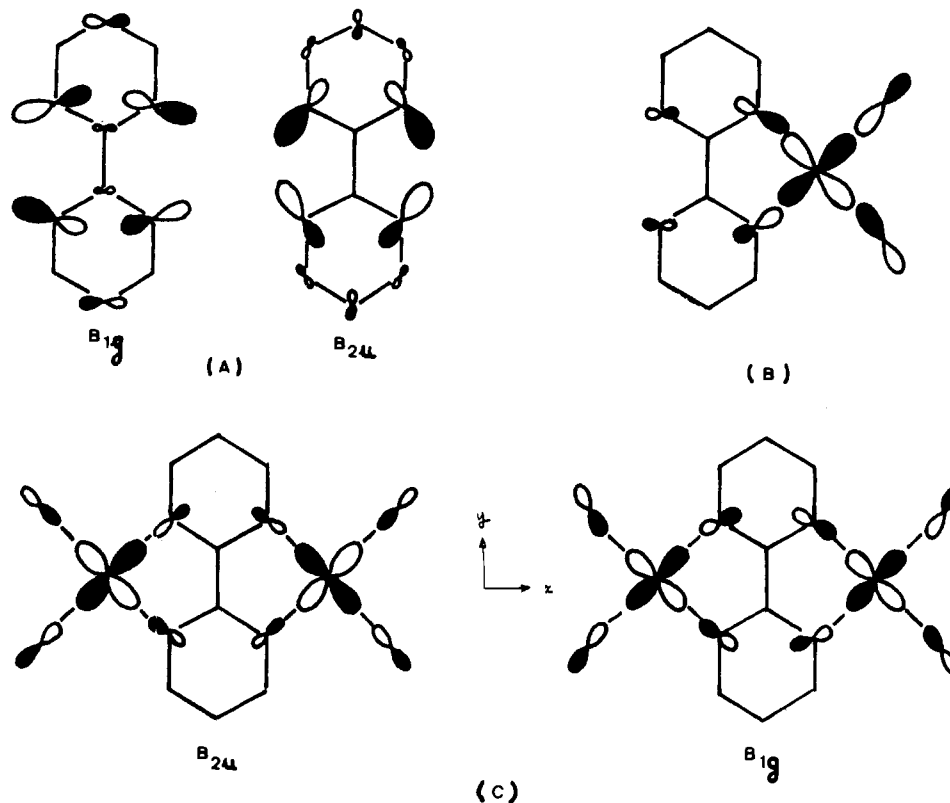
Figure 5. Schematic drawings of the molecular orbitals as obtained from extended Hückel calculations for complex **2**: (A) HOMO of bipyrimidine; (B) magnetic orbital in a hypothetical mononuclear complex; (C) singly occupied MOs in the binuclear complex.

$-J$ value of 15.8 cm^{-1}. We have already shown that the coupling, with oxalate bridges, is strongly dependent on the overall symmetry of the complex. The weak value of $|J|$ in the Petty complex is consistent with the so-called orbital reversal[9] or orbital switching[32] of the magnetic orbitals of the copper ion: we can foresee from the J value in this complex that there is only a weak overlap through the bpm bridge. For example, the four nearest neighbors of the copper cannot be in the plane of the bpm molecule but are in a plane perpendicular to it, with an inversion center in the middle of the C–C bpm bond, reducing the overlap. Indeed, we have encountered such a situation in a $Cu_2(bpm)_3(H_2O)_2(ClO_4)_4$ compound to be reported.[29]

(ii) The differences between the magnetic properties of the three compounds are small but beyond the limit of experimental errors. We observe a shift of susceptibility maxima toward lower values and higher temperatures when comparing the nitrate to the chloride and to the bromide derivatives. This evolution in the series may be due to three factors: (a) a larger singlet–triplet gap J within the binuclear unit; (b) a larger J' intermolecular interaction; (c) a smaller amount of uncoupled impurities. The percentage of impurities can have a large influence on the location of the susceptibility maxima of strongly coupled compounds when it is varied in large proportions, but the fitted values of Table VI are close to each other. The simulation of susceptibility curves with various amounts of uncoupled species allows us to discard any notion of this influence being preponderant.

As far as the intermolecular interactions are concerned, two different structures are to be discussed: the alternating-chain case of the nitrate compound **1** and the planar layers of stacked binuclear units in the halogen complexes **2** and **3**.

Three observations converge on a weak intermolecular interaction in the three complexes:

In **2** and **3**, the axial distances around the copper are long, the admixture of d_{z^2} orbitals in the ground state is weak, and the overlap between d_{xy} orbitals contained in parallel planes separated by 2.967 Å in **2** and 3.088 Å in **3** is expected to be small. Fur-

thermore, there is no strong overlap between bpm units belonging to different layers, as shown in II. In **1**, the distance between adjacent bpm planes is shorter than in **2** and **3**, but the slippage of the Cu(bpm)Cu units impedes an important interaction.

This is confirmed by Hückel calculations performed on the CuX_2Cu' binuclear units. The gap found in the three cases is much weaker than the one found through the μ-bpm units.

Finally, we fitted our data by the empirical expression proposed by Hatfield for alternating chains[33] or by a modification of the Bleaney–Bowers expression (2), taking into account the intermolecular interactions J' between z neighbors by the means of a zJ' term, in a molecular field approach.

$$\chi_M = 2N\beta^2 g^2 (1 - \rho)/ \\ (k(T - zJ')(3 + \exp(-J/kT))) + \rho C/T \quad (2)$$

In any case, we found intramolecular J values for compounds **1–3** significantly different from each other, close to the values given in Table VI. There was no significant improvement of the fits. We are therefore left with the first hypothesis: the evolution of the magnetic properties is to be interpreted essentially within the binuclear unit.

The structural data show that the Cu(bpm)Cu units are similar in the three compounds: structural differences within the bridge cannot be at the origin of the variation of J; differences in Cu–N and Cu⋯Cu distances, for example, would even favor a trend opposite to the observed one (Table VI). The symmetry of the magnetic orbitals is the same in the three compounds. It is therefore natural to propose that the evolution is mainly due to the tuning of energy of the magnetic orbitals by the peripheral ligands: the less electronegative the peripheral ligands, the higher the magnetic orbital energy and the larger the overlap through the bpm bridge. The importance of the magnetic orbital energy has been first proposed by Hendrickson.[34,35] Here, it leads to

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Table VII. Coupling Constants in Binuclear μ-bpm Complexes with n Unpaired Electrons per Magnetic Center[a]

compd	$-J$, cm^{-1}	$-Jn^2$, cm^{-1}	n
(phtfa)$_2$Mn(bpm)Mn(phtfa)$_2$	0.46[b]	11.5	5
(bmp)Fe(bpm)Fe(bmp)(NCS)$_4$	4.1[c]	65.6	4
(phtfa)$_2$Co(bpm)Co(phtfa)$_2$	3.7[b]	34.7	3
(phtfa)$_2$Ni(bpm)Ni(phtfa)$_2$	5.6[b]	22.4	2
(hfa)$_2$Ni(bpm)Ni(hfa)$_2$	6.5[b]	26.0	2
(hfa)$_2$Cu(bpm)Cu(hfa)$_2$	15.8[d]	15.8	1
(NO$_3$)$_2$Cu(bpm)Cu(NO$_3$)$_2$	191[e]	191	1
(Cl)$_2$Cu(bpm)Cu(Cl)$_2$	225[e]	225	1
(Br)$_2$Cu(bpm)Cu(Br)$_2$	236[e]	236	1

[a] The interaction Hamiltonian is $\hat{H} = -J\cdot\hat{S}_1\hat{S}_2$. [b] From ref 18b. [c] From ref 36; bmp stands for bromazepam. [d] From ref 17. [e] This work.

a surprising result since it is commonly believed that the less electronegative the peripheral ligands, the larger the spin delocalization on them, the weaker the spin delocalization on the bridge, and therefore the smaller the $|J|$ value. Our data show exactly the opposite trend and point out that the coupling constant depends in a subtle manner on the energies of both the terminal and the bridging ligand orbitals relative to the d orbital energies.

(iii) For similar planar configurations and comparable Cu···Cu distances, the bpm ligand is less efficient than the bis-bidentate bridges oxalate, oxamate, dithiooxamate, and tetrathiooxalate, where the measured $|J|$ values are greater than or equal to 380 cm^{-1}.[6-15]

The schematic drawings of Figure 5 display the HOMO of bpm, belonging to the right irreducible representations of the point group of the binuclear complex, able to interact with the d$_{xy}$ metallic orbitals. They help one to understand the place of bpm in the series of these bis-bidentate ligands. The X···Y distances in the bridges are 2.229 Å for O···O in oxalato, 2.284 Å for O···N in oxamato, and 2.318 Å for O···N in oxamido, whereas the N···N distances are 2.357 (4) Å in **1**, 2.371 (3) Å in **2**, and 2.383 (5) Å in **3**; the three latter distances are imposed by the presence of the aromatic ring. The overlap through the N···N bridge appears therefore less efficient, everything being equal. Furthermore, Cu-N distances in compounds **1-3** are slightly longer than the ones in the already reported complexes, and consequently the Cu···Cu distances are longer (5.37 Å in **1**, 5.53 Å in **2**, and 5.55 Å in **3**) than those in μ-oxalato (5.14 Å)[9] or in μ-oxamido complexes (5.19 Å).[10]

(iv) Finally, our J values for Cu(II) complexes can be compared in Table VII with the ones of Brewer et al. for Mn(II), Co(II), and Ni(II)[18] and of Real et al. for Fe(II) binuclear compounds.[36]

A structure is available for (hfa)$_2$Co(bpm)Co(hfa)$_2$, where hfa represents hexafluoroacetylacetonate.[18b] The Co-N distance is 2.15 Å, and the Co···Co separation 5.75 Å. The J values, reported in Table VII, are much smaller than in our series (-6.5 cm^{-1} for

Ni(II), -3.5 cm^{-1} for Co(II), and -0.5 cm^{-1} for an analogous (phenyltrifluoroacetylacetonato)manganese(II) derivative). To deal with comparable values, we take into account the number of unpaired electrons on each magnetic center (one for Cu(II), two for Ni(II), three for Co(II), four for Fe(II), and five for Mn(II)) and we compare the $n^2|J|$ values.[37,38] We have

$$|J(\text{Cu})| > 4|J(\text{Ni})| > 9|J(\text{Co})| > 25|J(\text{Mn})| \quad (3)$$
$$191 \text{ cm}^{-1} \quad 31.5 \text{ cm}^{-1} \quad 26 \text{ cm}^{-1} \quad 11.5 \text{ cm}^{-1}$$

This trend demonstrates once more the special efficiency of Cu(II) to produce a strong antiferromagnetic interaction compared to that of other magnetic ions, everything being equal: the Cu(II)–bridging ligand distances are the shortest and the energies of the Cu(II) d orbitals are the lowest of the bivalent-ion complexes in the first transition series. This allows a larger spin density delocalization on the bridge and a larger $|J|$ value for the d$_{xy}$ exchange pathway. Furthermore, the ferromagnetic contributions in a Cu(II) binuclear unit are reduced to the minimum and can be neglected, which is not the case in a multielectron center where

$$J = 1/n^2\sum_{\mu,\nu}J_{\mu\nu} = 2/n^2\sum_{\mu,\nu}j_{\mu\nu} + 2\Delta_{\mu\mu}\cdot S_{\mu\mu} \quad (4)$$

The ferromagnetic terms $j_{\mu\nu}$, even weak, are numerous for magnetic orbitals of different symmetry μ and ν.[37,38] They partially counterbalance the antiferromagnetic terms $\Delta_{\mu\mu}\cdot S_{\mu\mu}$, where $S_{\mu\mu}$ and $\Delta_{\mu\mu}$ are the overlap and energy gap terms already defined for the $\mu\mu$ exchange pathway.

Conclusion

We reported the structure of two new isostructural Cu(II) compounds and the magnetic properties of three Cu(II) 2,2'-bipyrimidine-bridged complexes, which display a large antiferromagnetic interaction, tuned by the peripheral anionic ligands. The large coupling arises from the important overlap of the d$_{xy}$ magnetic orbitals, coplanar with the bpm bridge. The planarity of the system is essential to obtain such an important antiferromagnetic coupling. We shall report soon on other μ-bipyrimidine Cu(II) complexes where this situation is not realized and where the interaction is much less important.[29]

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