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Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, UA 420, Institut de Chimie
Moléculaire d'Orsay, and Institut d'Electronique Fondamentale, UA 022, Université de Paris-Sud, 91405 Orsay, France,
and Department of Chemistry, University of Bergen, 5000 Bergen, Norway

Magnetism of $Mn^{II}Cu^{II}$ and $Ni^{II}Cu^{II}$ Ordered Bimetallic Chains. Crystal Structure of $MnCu(pba)(H_2O)_3\cdot 2H_2O$ (pba = 1,3-Propylenebis(oxamato))

Yu Pei,[1a] Michel Verdaguer,[1a,d] Olivier Kahn,*[1a] Jorunn Sletten,*[1b] and Jean-Pierre Renard[1c]

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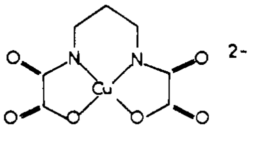
From the dianion $[Cu(pba)]^{2-}$, with pba = 1,3-propylenebis(oxamato), have been synthesized the two compounds $ACu(pba)(H_2O)_3\cdot 2H_2O$, A = Mn (**1**) and Ni (**2**). The crystal structure of **1** has been solved at room temperature. **1** crystallizes in the orthorhombic system, space group *Pnma*, with $a = 12.945$ (1) Å, $b = 21.250$ (4) Å, $c = 5.2105$ (8) Å, and $Z = 4$ (MnCu units). The structure consists of ordered bimetallic chains with octahedral Mn(II) and square-pyramidal Cu(II) ions bridged by oxamato groups. The Mn···Cu intrachain separation is 5.412 Å. The chains are linked together through hydrogen bonding. The shortest interchain metal–metal separations are Mn···Mn = Cu···Cu = 5.211 Å. The magnetic properties have been investigated down to 1.2 K for **1** and down to 3 K for **2**. Both compounds exhibit the magnetic behavior typical of ordered bimetallic chains with large intrachain antiferromagnetic interaction and very weak interchain antiferromagnetic interaction. The values of the intrachain interaction parameters have been deduced from the magnetic data and found as $J = -23.4$ cm^{-1} in **1** and -82.7 cm^{-1} in **2** ($\mathcal{H} = -J\sum_i S_i\cdot S_{i+1}$). The mechanism of the interchain interaction in **1** has been discussed, and a strategy has been suggested to avoid the three-dimensional antiferromagnetic ordering of the ferrimagnetic chains. This strategy could lead to one of the first genuine molecular ferromagnets.

Introduction

For about half a decade, an increasing number of works devoted to the polymetallic magnetic compounds have concerned heteropolymetallic systems. The study of these heteropolymetallic systems utilizes all the concepts valid for the compounds with only one kind of magnetic ions; however, this new field also allowed one to introduce several important and novel concepts. One of them concerns the symmetry requirements to achieve a ferromagnetic interaction between nearest-neighbor metal ions. Such an interaction stabilizing the state of highest spin multiplicity generally arises from the orthogonality, strict (symmetry-imposed) or accidental, of the magnetic orbitals. To our knowledge, the only polymetallic systems where the strict orthogonality has been achieved are heterobinuclear[2,3] or heterotrinuclear[4] complexes. In fact, such an orthogonality is possible with only a few pairs of metal ions and requires relatively high site symmetries. As for the accidental orthogonality, even if it already led to ferromagnetically coupled copper(II)[5] and nickel(II)[6-12] dimers and to linear ferromagnets,[13,14] it depends in quite a critical manner on some structural parameters, of which the value cannot be imposed chemically. At best, one knows that, with some geometries, the accidental orthogonality may eventually occur. In a certain sense, the achievement of a ferromagnetic interaction between two nearest-neighbor metal ions demands going against a natural trend that favors the pairing of the electrons in molecular orbitals of low energy.[15] If the endeavor to find new conditions leading to the parallel alignment of the spins of two nearest-neighbor magnetic centers deserves to be pursued, alternative strategies to obtain ferromagnetic-like behaviors must be sought.

At this stage, it is likely necessary to specify the meaning of the expression "ferromagnetic-like behavior". We shall say that a *polymetallic system exhibits a ferromagnetic-like behavior when the product of its molar magnetic susceptibility times the temperature* $\chi_M T$ *increases upon cooling down.* Such a magnetic behavior obviously occurs for the polymetallic systems in which the interaction between nearest neighbors is ferromagnetic, but it also occurs in the low temperature range for antiferromagnetically coupled polymetallic systems with *irregular spin-state structures.* A polymetallic compound is said to have an irregular spin-state structure when the spin multiplicity of the states does not vary monotonically with the energy. In these systems, in spite of the antiferromagnetic nature of the interaction between nearest neighbors, the spin multiplicity of the ground state may be higher than those of the first excited states. The ordered bimetallic chains, also defined as ferrimagnetic chains, are typical examples of compounds of this type.

Since the report on the first ordered bimetalic chain[16] in 1981, a few other compounds of the same type have been described.[17-21] This paper deals with two compounds of a new family of bimetallic chains, of formula $ACu(pba)(H_2O)_3\cdot 2H_2O$ with A = Mn (**1**) and Ni (**2**). These compounds are obtained by polymerization of the mononuclear dianion $[Cu(pba)]^{2-}$ (pba = 1,3-propylenebis(oxamato)), represented here as[22]



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(1) (a) Institut de Chimie Moléculaire d'Orsay, Université de Paris-Sud. (b) University of Bergen. (c) Institut d'Electronique Fondamentale, Université de Paris-Sud. (d) Permanent address: ENS, Le Parc, 92211 Saint-Cloud, France.

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Table I. Crystallographic Data Collection and Refinement Conditions for $MnCu(pba)(H_2O)_3{\cdot}2H_2O$ (**1**)

mol formula	$CuMnC_7H_{16}N_2O_{11}$
fw	422.69
space group	*Pnma* (No. 62)
temp at cryst, K	294
unit cell	
a, Å	12.945 (1)
b, Å	21.250 (4)
c, Å	5.2105 (8)
V, Å^3	1433.3 (6)
Z	4
D_x, g cm^{-3}	1.959
μ(Mo Kα), cm^{-1}	23.91
cryst size, mm	0.07 × 0.40 × 0.42
instrument	CAD-4
scan type	ω
scan range ($\Delta\omega$), deg	$0.80 + 0.35 \tan \theta$
scan speed, deg/min	20/8 = 2.5
radiation (λ, Å)	monochr, Mo Kα (0.71073)
max 2θ, deg	50
no. of reflcns measd	2139 (in one octant)
no. of "obsd" reflns, NO	1680
limit of "obsd" reflns	$F_o > 2\sigma_F$
no. of variables refined, NV	141
extinction coeff	1.30×10^{-7}
agreement factors[a]	
R	0.033
R_w	0.033
s	1.7

[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: $w = 1/\sigma_F^2$; $\sigma_F = \sigma_I(I(Lp))^{-1/2}$; $\sigma_I = [\sigma_c^2 + (0.02N_{net})^2]^{1/2}$. Atomic scattering factors and programs used are those of the references.

with Mn^{II} or Ni^{II} ions. The crystal structure of **1** is described as well as the magnetic properties of the two compounds. Both exhibit the behavior characteristic of the ordered bimetallic chains with a large intrachain antiferromagnetic interaction, on which a very weak interchain antiferromagnetic interaction is superimposed. The values of the intrachain interaction parameters are deduced from the magnetic data, and the mechanism of the interchain interaction, which stops the ferromagnetic-like behavior, is discussed. Finally, a strategy is suggested to avoid the three-dimensional antiferromagnetic ordering. This strategy could lead to one of the first genuine molecular ferromagnets.

Experimental Section

Syntheses. $Na_2[Cu(pba)]{\cdot}6H_2O$ was synthesized according to the previously reported procedure.[22]

$MnCu(pba)(H_2O)_3{\cdot}2H_2O$ (**1**) was obtained as well-shaped light blue single crystals by slow diffusion of aqueous solutions of $Na_2[Cu(pba)]{\cdot}6H_2O$ and manganese(II) perchlorate in a U-tube. Anal. Calcd for $C_7H_{16}N_2O_{11}CuMn$ (**1**): C, 19.89; H, 3.82; N, 6.63; Cu, 15.03; Mn, 13.00. Found: C, 19.58; H, 3.82; N, 6.84; Cu, 14.92; Mn, 12.67.

The same procedure, when replacing manganese(II) perchlorate by nickel(II) perchlorate, affords $NiCu(pba)(H_2O)_3{\cdot}2H_2O$ (**2**). Anal. Calcd for $C_7H_{16}N_2O_{11}CuNi$ (**2**): C, 19.72; H, 3.78; N, 6.57; O, 41.27; Cu, 14.90; Ni, 13.76. Found: C, 19.96; H, 3.60; N, 6.93; Cu, 15.12; Ni, 13.35.

Crystallographic Data Collection and Structure Determination. Information concerning conditions for crystallographic data collection and structure refinement is summarized in Table I. The crystal used had the shape of a prismatic needle, elongated along the *c* axis. During data collection three reference reflections were monitored: they showed no significant deterioration. The data were corrected for absorption, the maximum and minimum transmission coefficients being 0.84 and 0.63, respectively. Systematic extinctions showed that the space group might be either *Pnma* or *Pna*2$_1$. The intensity distribution was closer to that expected for a centrosymmetric cell. However, due to the presence of heavy atoms, this indication was not considered conclusive, and both possibilities were tested during the structure determination and refinement. The structure was solved by direct methods in the centrosymmetric space group. The two metal ions and the bridging group were found in the *E* map; the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Isotropic refinement of non-hydrogen atoms led to *R* = 0.09; anisotropic refinement, to 0.045. Examination of the results revealed centrosymmetric surroundings around Mn and a mirror plane through Cu within the limits of error; and correlation coefficients between parameters of pairs of atoms were high. Hence, it was decided to continue the refinement in the centrosymmetric space group. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map and were refined isotropically. In the final least-squares cycles an extinction parameter was included and refined. The refinement converged at *R* = 0.033, R_w = 0.033, and *s* = 1.7. Final atomic parameters are listed in Table V.[23]

Table II. Atomic Parameters for $\{[CuMn(C_7H_6N_2O_6)(H_2O)_3]{\cdot}2H_2O\}_n$[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Cu	0.54886 (3)	0.250	0.15663 (8)	2.359 (7)
Mn	0.500	0.000	0.000	3.07 (1)
O1	0.4376 (1)	0.07589 (7)	0.2299 (3)	3.13 (3)
O2	0.5931 (1)	0.07956 (7)	−0.1203 (3)	3.19 (3)
O3	0.6129 (1)	0.18214 (7)	−0.0530 (3)	2.75 (3)
O4	0.6161 (2)	−0.02129 (8)	0.2949 (3)	4.03 (4)
O5	0.6740 (2)	0.250	0.4649 (5)	4.07 (6)
O6	0.2142 (2)	0.0879 (1)	0.0635 (4)	5.12 (5)
N1	0.4633 (1)	0.18259 (8)	0.2863 (4)	2.58 (4)
C1	0.5706 (2)	0.1298 (1)	−0.0108 (4)	2.51 (4)
C2	0.4827 (2)	0.1284 (1)	0.1877 (4)	2.45 (4)
C3	0.3787 (2)	0.1901 (1)	0.4721 (5)	3.22 (5)
C4	0.3901 (3)	0.250	0.6234 (6)	2.87 (6)
H31*	0.315 (2)	0.190 (1)	0.383 (5)	3.7 (6)
H32*	0.372 (2)	0.157 (1)	0.566 (5)	4.3 (6)
H41*	0.337 (3)	0.250	0.759 (8)	4.8 (9)
H42*	0.458 (2)	0.250	0.709 (7)	3.2 (8)
H43*	0.645 (2)	0.006 (1)	0.346 (6)	6.4 (8)
H44*	0.601 (2)	−0.039 (1)	0.419 (5)	4.6 (6)
H51*	0.674 (3)	0.287 (2)	0.542 (7)	11 (1)
H61*	0.199 (2)	0.084 (1)	−0.082 (6)	7.0 (9)
H62*	0.263 (2)	0.079 (1)	0.063 (6)	7.8 (9)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter: $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_i{\cdot}\mathbf{a}_j$.

Magnetic Measurements. In the 3–300 K temperature range, these were carried out with a Faraday-type magnetometer equipped with a continuous-flow cryostat. The independence of the susceptibility from the applied magnetic field was checked at room temperature up to 1 T for both **1** and **2** and at 4.2 K up to 0.1 T for **1** and 0.4 T for **2**. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections were estimated as -140×10^{-6} cm^3 mol^{-1} for both **1** and **2**. In the 1.2–4.2 K temperature range, the magnetic susceptibility of **1** was measured in a mutual-inductance bridge,[24] in a field of 5×10^{-4} T and a frequency of 70 Hz.

Description of the Structure of 1

1 forms ordered bimetallic chains running along the *b*-axis direction. In Figure 1, part of one such chain is depicted projected down the *c* axis. Bond lengths and angles involving non-hydrogen atoms are given in Table III; those involving hydrogen atoms are given in Table VI.[23] The Mn atom is situated at a center of symmetry and has elongated octahedral surroundings; the equatorial positions are occupied by oxygen atoms from the oxamato bridges and the axial positions by water molecules. A crystallographic mirror plane passes through each Cu atom, which has approximately square-pyramidal surroundings. Two nitrogen and two oxygen atoms from the pba ligand are in the basal plane while a water molecule located on the mirror plane occupies the apical position with a Cu–O5 bond length of 2.281 (2) Å. The Cu atom is displaced by 0.25 Å from the basal plane toward the apical water molecule. The sixth position around Cu is screened by the closeness of the C4 atom of a neighboring chain translated one unit cell along the *c* axis (Cu···C4 = 3.488 Å; Cu···H42 = 2.61 Å). The oxamato bridging group O1, O2, C1, C2, N1, O3 is

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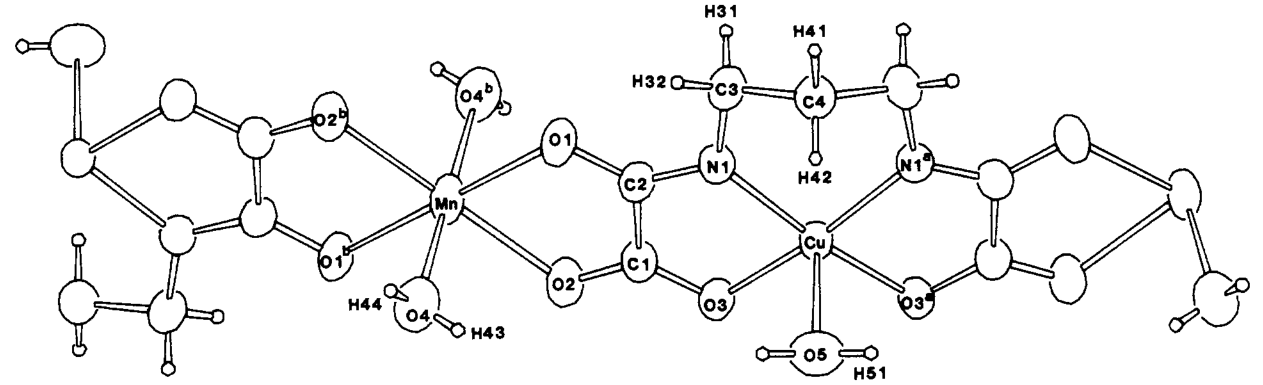


Figure 1. Projection down the crystallographic *c* axis, showing a section of the polynuclear chain. The atomic numbering scheme used is shown.

Table III. Bond Distances and Angles Involving Non-Hydrogen Atoms^a

	Distances (Å)		
Cu–O3	1.990 (1)	O2–C1	1.245 (2)
Cu–O5	2.281 (2)	O3–C1	1.260 (2)
Cu–N1	1.933 (1)	N1–C2	1.285 (2)
Mn–O1	2.165 (1)	N1–C3	1.470 (2)
Mn–O2	2.169 (1)	C1–C2	1.538 (3)
Mn–O4	2.197 (2)	C3–C4	1.505 (2)
O1–C2	1.278 (2)		
	Angles (deg)		
O3–Cu–O3^a	92.88 (7)	Mn–O1–C2	112.6 (1)
O3–Cu–O5	95.20 (6)	Mn–O2–C1	113.9 (1)
O3–Cu–N1	83.90 (5)	Cu–O3–C1	111.3 (1)
O3–Cu–N1^a	165.42 (6)	Cu–N1–C2	114.3 (1)
O5–Cu–N1	99.25 (6)	Cu–N1–C3	125.2 (1)
N1–Cu–N1^a	95.66 (8)	C2–N1–C3	120.4 (2)
O1–Mn–O1^b	180.0 (1)	O2–C1–O3	125.1 (2)
O1–Mn–O2	77.68 (5)	O2–C1–C2	117.7 (2)
O1–Mn–O2^b	102.32 (5)	O3–C1–C2	117.1 (2)
O1–Mn–O4	91.24 (6)	O1–C2–N1	128.6 (2)
O1–Mn–O4^b	88.76 (6)	O1–C2–C1	118.0 (2)
O2–Mn–O2^b	180.0 (2)	N1–C2–C1	113.4 (2)
O2–Mn–O4	89.00 (6)	N1–C3–C4	111.3 (2)
O2–Mn–O4^b	91.00 (6)	C3–C4–C3^a	115.6 (3)
O4–Mn–O4^b	180.0 (1)		

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

Table IV. Hydrogen Bonds

D	A	D- - -A, Å	D–H- - -A, deg
O4 ($1 - x$, $-y$, $1 - z$)	O1 (x, y, z)	2.821 (2)	173 (2)
O6 (x, y, z)	O1 (x, y, z)	3.030 (3)	154 (4)
O6 ($x + {}^1/_2$, y, $-{}^1/_2 - z$)	O2 (x, y, z)	2.797 (3)	153 (3)
O5 (x, y, $z - 1$)	O3 (x, y, z)	3.002 (2)	131 (3)
O4 (x, y, z)	O6 ($^1/_2 + x$, y, $^1/_2 - z$)	2.745 (3)	171 (3)

almost planar, the atomic deviations from the best least-squares plane being all less than 0.01 Å. The Mn and Cu atoms deviate by only 0.038 and 0.025 Å, respectively, from this plane. The best plane through Mn, Cu, and the bridging group makes an angle of 158.0° with the plane through the corresponding atoms related by mirror symmetry through Cu.

The chains are linked together through hydrogen bonding involving the oxygen atoms of the bridging groups and the coordinated as well as the uncoordinated water molecules. A list of the various hydrogen bonds is found in Table IV.

The Mn···Cu separation within the chain is 5.412 Å. The shortest separations between metal atoms belonging to neighboring chains are Cu···Cu^c = Mn···Mn^c = 5.211 Å, involving atoms related by a unit-cell translation along the *c* axis. The shortest Cu···Mn^c separation between atoms belonging to neighboring chains related by the unit-cell translation along *c* is 6.923 Å. Chains related by the *a*-glide translation give Cu···Cu^d($x - {}^1/_2$, y, $^1/_2 - z$) = 6.545 Å, Cu···Cu^e($x - {}^1/_2$, y, $-{}^1/_2 - z$) = 7.736 Å, and Mn···Mn^d = Mn···Mn^e = 6.977 Å. The shortest Cu···Mn separation between atoms belonging to chains related by the *a*-glide translation is Cu···Mn($^1/_2 + x$, y, $^1/_2 - z$) = 8.095 Å. The arrangement of neighboring chains related by *a* is illustrated in

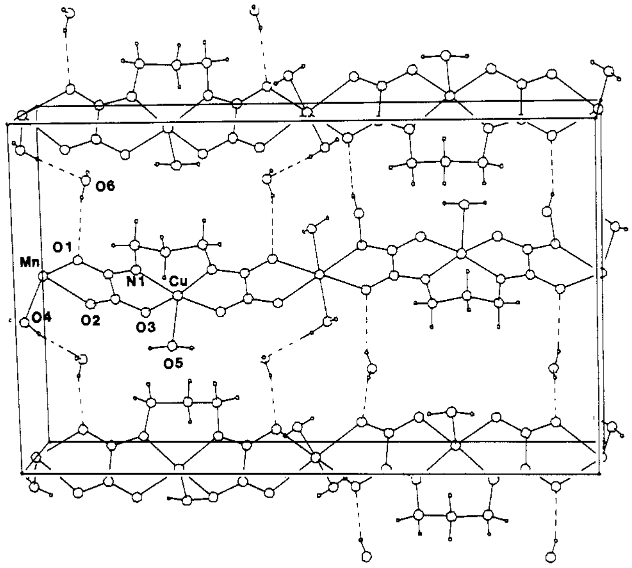


Figure 2. Perspective view of three neighboring chains. The origin of the unit cell is in the upper left-hand corner, the *a* axis running top to bottom of page and the *b* axis left to right. Hydrogen bonds O6(H)···O1 and O4(H)···O6 are indicated as dashed lines. The remaining hydrogen bonds listed in Table IV involve chains translated by one unit cell in the *c* direction relative to the chains shown in this figure.

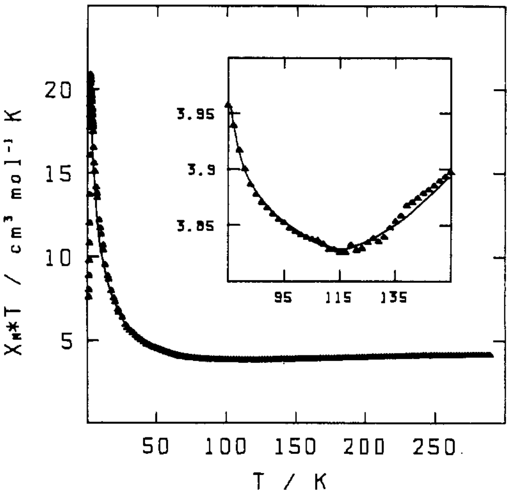


Figure 3. Experimental (△) and theoretical (—) temperature dependences of $\chi_M T$ for $MnCu(pba)(H_2O)_3 \cdot 2\ H_2O$ (**1**).

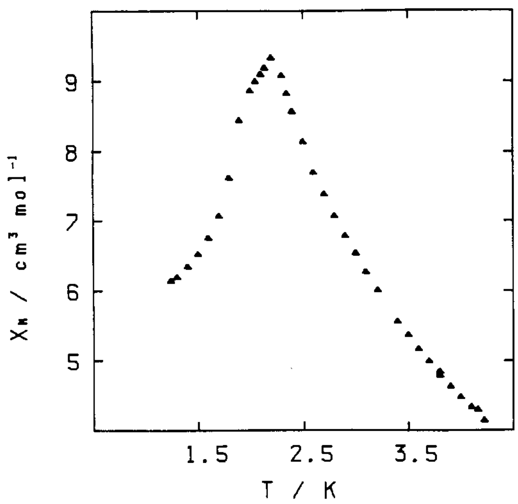
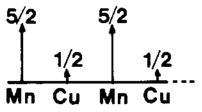


Figure 4. χ_M vs. T plot for MnCu(pba)$(H_2O)_3$·$2H_2O$ (**1**) in the 1.2–4.2 K temperature range.

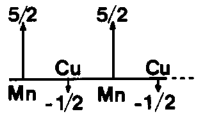
Figure 2. From Debye–Scherrer spectra, **2** was found to be isomorphous with **1**.

Magnetic Properties

Qualitative Approach. The magnetic behavior of **1** is represented in Figure 3, in the form of the χ_MT vs. T plot, χ_M being the molar magnetic susceptibility per MnCu unit and T the temperature. At 290 K, χ_MT is equal to 4.20 cm^3 mol^{-1} K. When the system cools down from room temperature, χ_MT decreases in a very smooth fashion and reaches a rounded minimum about 115 K with χ_MT = 3.81 cm^3 mol^{-1} K. Below 115 K, χ_MT increases more and more rapidly before reaching a sharp maximum at 2.3 K with χ_MT = 20.9 cm^3 mol^{-1} K. Below 2.3 K, χ_MT quickly fails. In Figure 4, we represent the χ_M vs. T plot in the 1.2–4.2 K temperature range. χ_M has a maximum at 2.2 K. This behavior is characteristic of a $Mn^{II}Cu^{II}$ ordered bimetallic chain with a large intrachain antiferromagnetic interaction on which a very weak interchain antiferromagnetic interaction is superimposed.[16,17] Indeed, when extrapolating χ_MT toward the high temperatures, one obtains the paramagnetic limit corresponding to uncoupled Mn^{II} and Cu^{II} ions. Upon cooling down from the high temperatures, the first chain level to be thermally depopulated is that where all the local spins are aligned along the same direction, schematized as

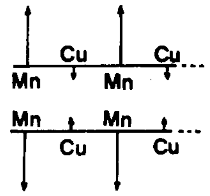


This level has the highest spin multiplicity, so that χ_MT decreases with T. In the opposite limit of T approaching zero, the only populated state is the ground state that, if long-range order were possible in chains, might be schematized as



and the low-temperature magnetic behavior is roughly similar to that of a chain of ferromagnetically coupled $S = 2$ local spins with a divergence of χ_MT. It follows that χ_MT should exhibit a minimum at a finite temperature. This minimum is the signature of antiferromagnetically coupled bimetallic chains.

The maximum of χ_M at 2.2 K and the correlated maximum of χ_MT around 2.3 K are due to interchain interactions that stop the divergence of χ_MT. We have seen in the preceding section that the shortest metal···metal separations between neighboring chains related through both the a-glide and the c translations are Cu···Cu and Mn···Mn. If, as is most likely (vide infra), the interchain $Cu^{II}Cu^{II}$ and $Mn^{II}Mn^{II}$ interactions are antiferromagnetic, the spin structure for two adjacent chains will be as



with a cancellation of the spins at the scale of the lattice and a three-dimensional antiferromagnetic ordering.

The magnetic properties of **2** are qualitatively similar to those of **1**. In particular, the χ_MT vs. T plot shown in Figure 5 exhibits the characteristic minimum, at 83 K with χ_MT = 0.76 cm^3 mol^{-1} K. Again, the divergence of χ_MT in the low-temperature range is stopped by interchain antiferromagnetic interactions. χ_MT actually presents a maximum at 7.3 K with χ_MT = 1.36 cm^3 mol^{-1} K and a rapid fall below the temperature.

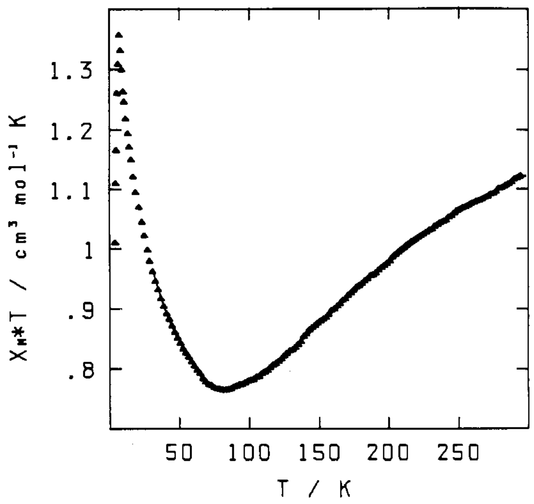


Figure 5. Experimental (△) and theoretical (—) temperature dependences of χ_MT for NiCu(pba)$(H_2O)_3$·$2H_2O$ (**2**).

Quantitative Approach. Several quantitative approaches to the magnetic susceptibility of ordered bimetallic chains have been proposed so far. The first one consists of carrying out the calculation of $(AB)_N$ rings of increasing size with S_A and S_B quantum spins and extrapolating to $N \rightarrow \infty$.[20,25] The spin Hamiltonian taken into account is then

$$\mathcal{H} = -J\sum_{i=1}^{N}\hat{S}_{2i}\cdot(\hat{S}_{2i-1} + \hat{S}_{2i+1}) + \beta\vec{H}\cdot\sum_{i=1}^{N}(g_A\hat{S}_{2i-1} + g_B\hat{S}_{2i}) \qquad (1)$$

with $S_{2i-1} = S_A$, $S_{2i} = S_B$, and $S_{2N+i} = S_i$. In (1), local anisotropies as well as anisotropic interactions have been neglected. In the assumption where the average local g factors g_A and g_B are equal, all the spin states have the same g factor and the spin states do not couple through the Zeeman perturbation. The calculation is then an extension of that of Bonner and Fisher concerning uniform chains of spins $^1/_2$.[26] This approach, however, is severely limited by the storage capacity of the computers, even by taking into account the full D_N symmetry of the problem. Therefore, it is not surprising that it has been essentially applied to the simplest case with $S_A = 1$ and $S_B = {}^1/_2$. Two of us performed the calculation up to $N = 4$ with $g_A = g_B$,[20] and Drillon et al. performed it up to $N = 5$ with eventually $g_A \neq g_B$.[25] The two groups proposed an extrapolation for $N \rightarrow \infty$. In the $g_A = g_B$ case, Drillon et al. found a minimum of χ_MT for $kT/|J| = 0.570$ and in the very low temperature range a divergence of χ_MT in $T^{-0.80}$, which coincides with the law found for a chain of ferromagnetically coupled spins $^1/_2$.[25] The extrapolated results for $N \rightarrow \infty$ can be

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described by the empirical expression

$$\chi_M T = (g^2/4)(1.375 + 1.08928X + 1.15046X^2 + 1.05853X^3 - 0.30149X^4)/(1 + 1.04556X + 3.45447X^2 + 0.92134X^3 - 0.33125X^{4.5}) \quad (2)$$

with $X = |J|/kT$. (2) is only valid for $J < 0$ and $X < 3.38$. The least-squares fitting of the experimental data for **2** in the 40–300 K temperature range by relation 2 leads to $J = -82.7$ cm^{-1} and $g = 2.17$. The agreement factor R defined as

$$[(\chi_M T)^{\text{obsd}} - (\chi_M T)^{\text{calcd}}]^2/[(\chi_M T)^{\text{obsd}}]^2$$

is then equal to 1.7×10^{-5}.

This $(AB)_N$ ring technique has also been utilized for the $S_A = {}^5/_2$, $S_B = {}^1/_2$ case,[27] but only up to $N = 3$, so that the extrapolated results for an infinite chain are likely of poorer accuracy. In fact, for such a case, an alternative approach is indispensable. Such an approach has been proposed by Seiden.[28] It consists of taking S_A as a classical spin and S_B as a quantum spin. Verdaguer et al.[17] have proposed a slightly modified version of this approach, in which the quantum character of S_A is partially taken into account. The calculation does not lead to an analytical expression but can be solved numerically. The following empirical expression has been proposed to fit the numerical results:[17]

$$\chi_M T = (g^2/4)(4.75 - 1.62370X + 2.05042X^2 - 4.52588X^3 - 8.64256X^4)/(1 + 0.77968X - 1.56527X^2 - 1.57333X^3 - 0.11666X^{4.5}) \quad (3)$$

with $X = |J|/kT$. (3) is only valid for $J < 0$ and $X \neq 0.752$. In this approach, the g_A and g_B factors were assumed to be equal. $\chi_M T$ shows a minimum for $kT/|J| = 2.98$, and in the very low temperature range $\chi_M T$ diverges according to a law in $T^{-0.69}$. The fitting of the experimental data for **1** in the 4.2–300 K temperature range with relation 3 leads to $J = -23.4$ cm^{-1} and $g = 1.97$. The R factor defined as above is then equal to 1.3×10^{-4}.

Discussion

Up to now, only one $Mn^{II}Cu^{II}$[16,17] and one $Ni^{II}Cu^{II}$[20] ordered bimetallic chain have been described. The former is $MnCu(dto)_2(H_2O)_3 \cdot 4.5H_2O$ with dto = dithiooxalato. The dto bridge is bound to the Cu atom through its sulfur atoms and to the Mn atom through its oxygen atoms. The magnetic behavior of this compound is qualitatively close to that of **1** with a minimum in the $\chi_M T$ vs. T plot at about 130 K and a maximum at 7.5 K. The intrachain interaction parameter was found as $J = -30.3$ cm^{-1}, which is significantly larger (in absolute value) than that for **1**. This difference confirms that the dithiooxalato bridge is more efficient than the oxamato bridge in transmitting the antiferromagnetic interaction between two metal ions. This is due to the fact that the magnetic orbital around copper(II) is more delocalized toward the sulfur atoms of the dto bridge in $MnCu(dto)_2(H_2O)_3 \cdot 4.5H_2O$ than toward the nitrogen and oxygen atoms of the oxamato bridge in **1**, owing to the weak electronegativity of sulfur as compared to that of nitrogen and oxygen.[29,30]

Another difference between the two $Mn^{II}Cu^{II}$ systems concerns the interchain interactions, which are noticeably more pronounced in the dto derivative than in **1**. Indeed, the maxima of $\chi_M T$ occur at 7.5 and 2.3 K, respectively. This has to be related to the fact that the shortest separation between two metal atoms belonging to two different chains is Cu···Cu = 3.68 Å in $MnCu(dto)_2(H_2O)_3 \cdot 4.5H_2O$ and Cu···Cu = Mn···Mn = 5.211 Å in **1**. In other words, the $Mn^{II}Cu^{II}$ compound described in this paper is a better one-dimensional magnetic system than $MnCu(dto)_2(H_2O)_3 \cdot 4.5H_2O$.

The previously reported $Cu^{II}Ni^{II}$ chain is $NiCu(ox)_2 \cdot 4H_2O$ with ox = oxalato. The available structural information for this compound has been deduced from EXAFS investigations. $NiCu(ox) \cdot 4H_2O$ is apparently a very poor one-dimensional system, and the minimum of the $\chi_M T$ vs. T plot is quenched by the interchain interactions. Since the low-temperature magnetic data are severely affected by the interchain interactions, the intrachain interaction parameter was deduced from the magnetic data above 50 K and found equal to -52.7 cm^{-1}, which is weaker (in absolute value) than that for **2**. This difference again confirms that in the series of the bis bidentate bridges derived from oxalic acid, everything else being unchanged, the oxamato is more efficient than the oxalato bridge in propagating antiferromagnetic interaction.[29,30]

The most interesting aspect of the ordered bimetallic chains is certainly the ferromagnetic-like behavior below the temperature of the minimum of $\chi_M T$. It is important to stress here that the divergence of $\chi_M T$ in the low-temperature range occurs although the intrachain interaction between nearest-neighbor ions is antiferromagnetic. In fact, for a given couple of A and B metal ions, the stronger the antiferromagnetic interaction is, the more shift toward the high temperatures the minimum of $\chi_M T$ and the more extended the temperature range where $\chi_M T$ increases upon cooling down. If we now consider a family of isostructural AB bimetallic chains with S_A and S_B spins, respectively, the larger the difference $S_A - S_B$ is, the more spectacular the divergence of $\chi_M T$. It follows that the $Mn^{II}Cu^{II}$ systems with bridging ligands of which the efficiency to provide strong antiferromagnetic interactions is well established seem ideal to obtain such a ferromagnetic-like behavior. The situation in these systems may be described in terms of polarization along a same direction of the ${}^5/_2$ local spins of the Mn^{II} ions through the antiferromagnetic interaction with the ${}^1/_2$ local spins of the Cu^{II} ions.

The divergence of $\chi_M T$ in both **1** and **2** is limited by the interchain interactions, which give rise to an *antiferromagnetic ordering of the ferrimagnetic chains*. The problem at hand is then whether it is possible to avoid the "catastrophe" occurring at 2.3 K in **1** and 7.3 K in **2**. A solution would be to isolate the chains from each other in a more efficient manner, for instance by replacing the water molecules linked to Mn and Cu atoms by very bulky ligands. This would increase the one-dimensional character of the compounds, and the maxima of $\chi_M T$ would be shifted toward lower temperatures but, in principle, would not be suppressed. A much more drastic solution would be to achieve a three-dimensional *ferromagnetic ordering of the ferrimagnetic chains*, instead of the antiferromagnetic ordering. In the last part of our paper, we comment on this point.

We assumed in the preceding section that the dominant interchain interactions in **1** corresponded to the shortest metal···metal interchain distances, i.e. $Cu^{II}Cu^{II}$ and $Mn^{II}Mn^{II}$. Although more apart from each other, the chains related through the *a*-glide axis could interact more efficiently than those related through the *c* axis owing to the hydrogen-bonding network. Several orbital models to describe the interaction between two magnetic ions have been proposed so far.[31] When these ions are not orbitally degenerate, the interaction parameter J is generally expressed as a sum of a ferromagnetic J_F contribution and an antiferromagnetic J_{AF} contribution. J_F is related to the two-electron-exchange integrals between magnetic orbitals and decreases much faster than J_{AF} when the separation between the magnetic centers increases.[30] All the reported examples of strong ferromagnetic interaction concern pairs of metal ions separated by about 3 Å whereas very strong antiferromagnetic interactions have been found in compounds where the metal–metal separation is as large as 5.7 Å.[29,30] This confirms that the $Cu^{II}Cu^{II}$ and $Mn^{II}Mn^{II}$ interchain interactions in **1** are most likely antiferromagnetic. In other respects, a ferromagnetic interaction is generally related to the orthogonality of the magnetic orbitals.[30] Such an orthogonality is very unlikely when one of the interacting ions has an $S = {}^5/_2$ local state. Indeed, the five d-type orbitals for this ion are then singly occupied. One of them, at least, will overlap a magnetic orbital centered on the

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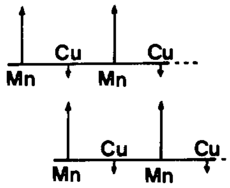
nearest-neighbor ion, giving again an antiferromagnetic interaction.[3] This is true not only for the $Mn^{II}Mn^{II}$ interaction in **1** but also for any hypothetical $Mn^{II}Cu^{II}$ interaction. At first sight, one might believe that it is not possible to achieve a ferromagnetic ordering since all the interchain interactions are certainly antiferromagnetic. In fact, there is an evident solution to this problem: replacing the $Cu^{II}Cu^{II}$ and $Mn^{II}Mn^{II}$ interchain interactions by $Mn^{II}Cu^{II}$ interactions. This is realized, for instance, if every other chain is displaced by half of a repeat unit along the *b* axis. The low-temperature spin structure for two adjacent chains may then be schematized as



with a parallel alignment of all the $^5/_2$ spins. Even if the displacement of every other chain is less than half of a repeat unit, the $Mn^{II}Cu^{II}$ interchain interaction may be dominant and a three-dimensional ferromagnetic ordering may occur. We will report soon on the first compound of this kind.[32]

Registry No. **1**, 101935-07-3; **2**, 105661-45-8; $Na_2[Cu(pba)]$, 61344-73-8.

Supplementary Material Available: Tables V and VI, giving anisotropic thermal parameters and bond distances and angles involving hydrogen atoms (2 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of Kentucky, Lexington, Kentucky 40506, and The Ohio State University, Columbus, Ohio 43210

Chemical Behavior and Structure of Triply Bridged Pyrazaboles of the Type $RB(\mu\text{-}pz)_2(\mu\text{-}OBRO)BR$[1]

L.-Y. Hsu,† J. F. Mariategui,‡ K. Niedenzu,*‡ and S. G. Shore†

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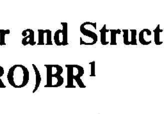
Triply bridged pyrazaboles of the type $RB(\mu\text{-}pz)_2(\mu\text{-}OBRO)BR$ (**1**, R = C_2H_5, C_6H_5; Hpz = pyrazole) are thermally quite stable and can be sublimed without decomposition even under atmospheric pressure. At room temperature they are resistant to water but are not soluble. Dissolution of **1** in protonic solvents occurs with complete breakdown of the molecule. Halogenation of **1** (R = C_2H_5) with $SOCl_2$ yields the pyrazabole $RClB(\mu\text{-}pz)_2BRCl$. The latter compound is a valuable material for the preparation of various other pyrazaboles. Thus, reaction with alkali-metal alkoxide or with alcohol in the presence of triethylamine gives access to $R(R'O)B(\mu\text{-}pz)_2BR(OR')$ (R' = CH_3, C_2H_5), the first examples of *B*-alkoxypyrazaboles; with $(CX_3CO)_2O$ (X = H, F), the species with R' = CX_3CO are obtained. The crystal and molecular structures of **1** with R = C_2H_5 were determined. The molecule crystallizes in the monoclinic system in space group $P2_1/c$ with $a = 7.587$ (2) Å, $b = 12.415$ (2) Å, $c = 16.387$ (3) Å, $\beta = 90.50$ (2)°, and $Z = 4$.

Introduction

Recently, it has been shown that triply bridged pyrazaboles of the type $RB(\mu\text{-}pz)_2(\mu\text{-}OBRO)BR$ (**1**) are formed with surprising ease on interaction of triorganylboroxins, $(\text{-BRO-})_3$, with pyrazole, Hpz.[2,3] Subsequently, such species have been observed as products



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in various other reactions, suggesting that the framework of **1** is chemically quite stable. The present study reports a more detailed investigation of the chemical properties of species of type **1** and of products derived thereof. In addition, the crystal and molecular structures of **1** with R = C_2H_5 have been determined by X-ray diffraction.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded of solutions in $CDCl_3$ on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference shift (internal Me_4Si for ^1H and ^{13}C NMR, external $Et_2O{\cdot}BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in Hz. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer.

Crystals of **1** with R = C_2H_5 were obtained from methylene chloride/hexane. A prismatic specimen was mounted on the tip of a thin glass fiber for X-ray examination and data collection. All data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by least-squares refinement of the angular setting from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 15–30°. Four standard reflections were monitored and showed no significant decay. The data were corrected for Lorentz and polarization effects. All crystallographic computations were carried out by using the SDP package. The structure was solved by a combination of direct methods (MULTAN 11/82) and difference Fourier techniques. Refinement was by full-matrix least squares. Analytical atomic scattering factors were used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all atoms. All of the non-hydrogen atoms were located on the *E* map. In the final refinements the thermal parameters of these atoms with the exception of H24 and H25 were located on Fourier difference maps and their positional and isotropic

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† The Ohio State University.

‡ University of Kentucky.

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