Design of a Molecular-Based Ferromagnet through Polymerization Reaction in the Solid State of $Mn^{II}Cu^{II}$ Molecular Units. Crystal Structure of $MnCu(obze)(H_2O)_4 \cdot 2H_2O$ (obze = Oxamido-*N*-benzoato-*N'*-ethanoato)

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Abstract: The compound $MnCu(obze)(H_2O)_4 \cdot 2H_2O$ has been obtained by slow diffusion of equimolar aqueous solutions of $Na_2[Cu(obze)] \cdot 2H_2O$ and Mn(II) perchlorate. The abbreviation obze stands for oxamido-*N*-benzoato-*N'*-ethanoato. $MnCu(obze)(H_2O)_4 \cdot 2H_2O$ crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 17.998$ (1) Å, $b = 6.9949$ (6) Å, $c = 13.784$ (1) Å, $\beta = 97.40$ (1)°, $V = 1720.8$ (4) Å^3, and $Z = 4$ (MnCu units) at 294 K. The structure consists of oxamido-bridged $Mn^{II}Cu^{II}$ discrete units and noncoordinated water molecules. Cu(II) is in square-planar surroundings and Mn(II) in octahedral surroundings with four water molecules in the coordination sphere. $MnCu(obze)(H_2O)_4 \cdot 2H_2O$ magnetically behaves as antiferromagnetically coupled $Mn^{II}Cu^{II}$ isolated pairs with a quintet–septet energy gap $3J = -100.8$ cm^{-1} and may be viewed as an assembly of molecules with a large positive spin density on the manganese side and a small negative spin density on the copper side. These molecules polymerize through very mild experimental conditions to afford a compound of formula $MnCu(obze)(H_2O)_2$. The electronic spectrum of this polymeric compound strongly suggests that the Mn(II) ion retains an octahedral environment and therefore is bound to the oxygen atoms of the carboxylato groups, which provides an exchange pathway between the negative spin density of a $Mn^{II}Cu^{II}$ unit and the positive spin density of the adjacent unit. Temperature dependence of the magnetic susceptibility and temperature and field dependences of the magnetization for $MnCu(obze)(H_2O)_2$ have been investigated. This compound shows a three-dimensional magnetic transition at $T_c = 4.6$ K. Below T_c, the molecular spins $S = 2$ are ferromagnetically aligned. The strategy used to design this molecular-based ferromagnet is reminiscent of an idea put forward by McConnell as early as 1963.

Introduction

The design of molecular-based ferromagnets is a research area which has been particularly active in the last four years.[1,2] To date, three classes of compounds exhibiting a spontaneous magnetization below a critical temperature T_c are well-characteized, namely (i) the donor–acceptor stack compounds like $[Fe(C_5Me_5)_2](TCNE)$[3,4] or $[Mn(C_5Me_5)_2](TCNQ)$,[5] (ii) the Mn(II)–Cu(II) chain compounds,[6-8] and (iii) the Mn(II)–nitronyl nitroxide chain compounds.[9-11] All those compounds are essentially one-dimensional, which is an obvious limitation to obtain high critical temperatures. Indeed, the ferromagnetism is a three-dimensional property so that for one-dimensional systems T_c depends on the magnitude of both intra- and interchain interactions. The former interaction may be large; the latter by definition is very weak. Actually, the critical temperatures are in the range 4–20 K. Other molecular-based compounds presenting a magnetic transition and involving oxalato-bridged $Cr^{III}M^{II}$ pairs with M = Mn, Fe, Co, Ni, or Cu have also been described.[13,14] Although three-dimensional structures have been postulated, the critical temperatures are again around 10 K.

Even if the first genuine achievements are quite recent, the field of the molecular-based ferromagnets is far from being completely new. In fact a rather long period of maturation has been necessary after the first idea and concepts have been put forward. To the best of our knowledge, one of the first mechanisms to design molecular ferromagnets has been suggested by McConnell[15] as early as 1963. This mechanism is the following: A molecular magnetic entity may exhibit regions of noncompensating positive and negative spin densities. If so, the interaction between the positive spin density of a unit and the negative spin density of the adjacent unit may lead to overall ferromagnetic intermolecular interactions. McConnell when proposing this approach had in mind purely organic compounds. The noncompensation of the

spin densities may then arise from spin polarization effects.[16] However, the molecular units we refer to might be inorganic complexes as well. The antiferromagnetically coupled heterobinuclear species are obvious examples of molecular entities with noncompensating spin densities, as emphasized by a recent polarized neutron diffraction study concerning a $Ni^{II}Cu^{II}$ pair.[17] This noncompensation if particularly pronounced for the strongly coupled $Mn^{II}Cu^{II}$ entities with the local spins $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$.

This mechanism implicitly supposes that the intermolecular interactions are large enough. Otherwise, the magnetic behavior would be that of isolated units. Actually, it is now well-established

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that the through-space intermolecular interactions are most often very weak. In order for T_c not to be negligibly small, it seems to be necessary to have some exchange pathway between the positive spin density of a unit and the negative spin density of the adjacent one. Along this line, for a couple of years we have worked with dianionic Cu(II) precursors like
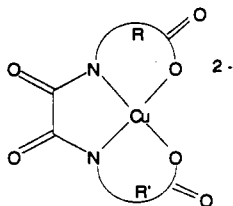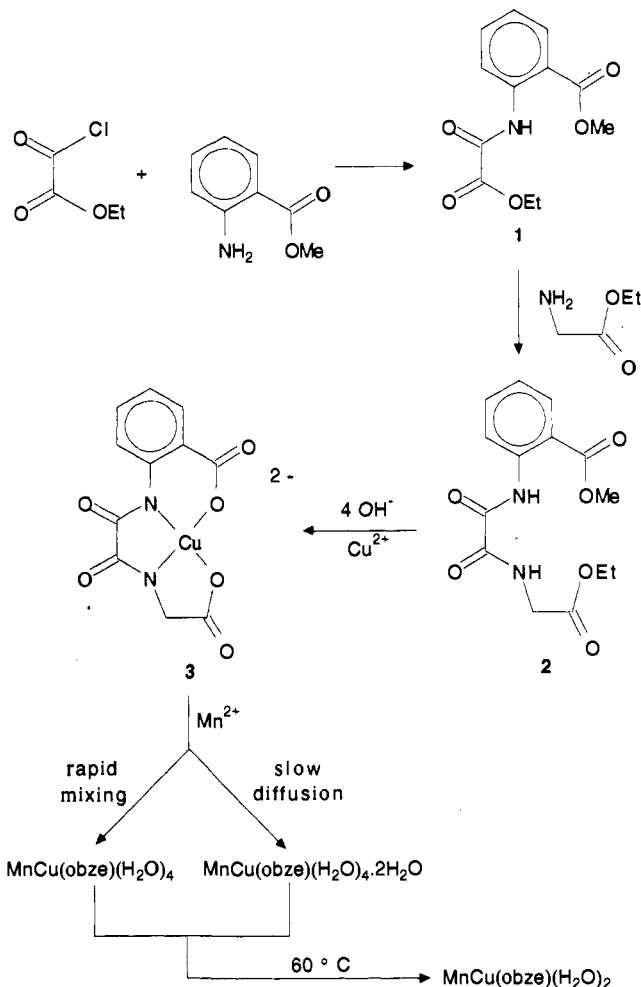

containing both oxamido and carboxylato groups capable of binding a Mn(II) ion. Our starting idea was to have oxamido-bridged $Mn^{II}Cu^{II}$ units weakly interacting within the crystal lattice through the carboxylato groups. Actually, this chemistry has shown a rather fascinating versatility. Until now, we have obtained uncoupled carboxylato-bridged $Mn^{II}Cu^{II}$ discrete units,[18] alternating bimetallic chains behaving as antiferromagnetically coupled $Mn^{II}Cu^{II}$ pairs,[18,19] and alternating bimetallic chains presenting the characteristic one-dimensional ferrimagnetic behavior[20] together with a compound showing a ferromagnetic transition at $T_c = 14$ K.[7] From the previous studies, it emerges that (i) the antiferromagnetic interaction through the oxamido bridge is rather large and characterized by an interaction parameter of the order of -28 cm^{-1} ($H = -JS_{MN}S_{Cu}$) and (ii) the interaction through the carboxylato bridge strongly depends on the configuration around this bridge. If the configuration is anti–anti, the interaction is weakly antiferromagnetic; if this configuration is syn–anti, it is negligible.[18,20] In this paper, we report on the results obtained with the novel Cu(II) precursor $[Cu(obze)]^{2-}$
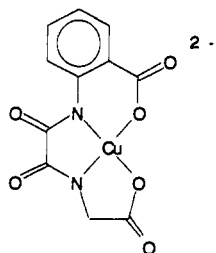
where obze stands for oxamido-N-benzoato-N'-ethanoato. This precursor reacts with Mn(II) to afford oxamido-bridged $Mn^{II}Cu^{II}$ discrete units of formula $MnCu(obze)(H_2O)_4$. These molecular units with a large positive spin density at an extremity and a small negative spin density at the other can very easily polymerize in the solid state to afford a molecular-based material of formula $MnCu(obze)(H_2O)_2$ showing a ferromagnetic transition at $T_c = 4.6$ K.

Experimental Section

Syntheses. The syntheses of $MnCu(obze)(H_2O)_4·2H_2O$ and $MnCu$-(obze)(H_2O)_2 were carried out as shown in Figure 1. Ethyl oxalyl chloride (10^{-2} mol) was added dropwise into 60 mL of a THF solution containing 10^{-2} mol of methyl anthranilate. The mixture was concentrated under vacuum, and **1** precipitated as a white powder. The precipitate was washed with water and dried under vacuum. **1** (5×10^{-3} mol) and 10^{-2} mol of glycine ethyl ester hydrochloride were dissolved in 60 mL of absolute ethanol. An excess of triethylamine was then added, and the solution was heated at reflux for 4 h. The mixture was concentrated under vacuum, and **2** precipitated as a white powder. The precipitate was washed with water and dried under vacuum. Anal. Calcd for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.09; O, 31.14. Found: C, 54.62; H, 5.32; N, 9.02; O, 31.11. The following step consists of synthesizing

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Figure 1. Synthesis scheme for $MnCu(obze)(H_2O)_4·2H_2O$, $MnCu$-(obze)(H_2O)_4, and $MnCu(obze)(H_2O)_2$.

the sodium salt of the Cu(II) precursor **3**. For that 2×10^{-3} mol of **2** and 8×10^{-3} mol of sodium hydroxide were dissolved in 60 mL of a 5/1 water/ethanol mixture. The solution was heated at 60 °C for 15 min. Copper(II) nitrate (2×10^{-3} mol) dissolved in 10 mL of water was then added. The resulting blue solution was concentrated under vacuum, and $Na_2[Cu(obze)]·2H_2O$ was precipitated as a red microcrystalline powder. Anal. Calcd for $C_{11}H_{10}N_2O_8CuNa_2$: C, 32.39; H, 2.47; N, 6.87. Found: C, 32.22; H, 2.28; N, 6.80. Well-shaped single crystals of $MnCu$-(obze)(H_2O)_4)·2H_2O were obtained by slow diffusion within ca. 1 month in an H-shaped tube of two aqueous solutions of 50 mL each, one containing 5×10^{-4} mol of **3** and the other one containing 5×10^{-4} mol of manganese(II) perchlorate. The rapid mixture of the two solutions affords a violet precipitate of $MnCu(obze)(H_2O)_4$. Anal. Calcd for $C_{11}H_{14}N_2O_{10}CuMn$: C, 29.18; H, 3.11; N, 6.19; Cu, 14.04; Mn, 12.14. Found: C, 28.96; H, 3.45; N, 5.79; Cu, 14.00; Mn, 11.95. Warming single crystals of $MnCu(obze)(H_2O)_4·2H_2O$ or polycrystalline powder of $MnCu(obze)(H_2O)_4$ at 60 °C affords $MnCu(obze)(H_2O)_2$. The same result is obtained under vacuum at room temperature. Anal. Calcd for $C_{11}H_{10}N_2O_8CuMn$: C, 31.70; H, 2.42; N, 6.77; Cu, 15.25; Mn, 13.19. Found: C, 31.78; H, 2.27; N, 6.51; Cu, 14.81; Mn, 13.09. We attempted to obtain the X-ray powder patterns of the three compounds containing six, four, and two water molecules, respectively. When grinding $MnCu(obze)(H_2O)_4·2H_2O$, the two noncoordinated water molecules are lost, so that it was not possible to record its powder pattern. On the other hand, the powder patterns of $MnCu(obze)(H_2O)_4$ and $MnCu$-(obze)(H_2O)_2 were compared. Spacing (in Å) for $MnCu(obze)(H_2O)_4$ 10.52 (s), 9.02 (m), 7.07 (w), 5.95 (s), 5.37 (s), 4.87 (w), 4.50 (m), 3.75 (w), 3.33 (very s), 3.02 (w), 2.76 (w), 2.45 (w), 2.22 (w), 2.12 (w) and for $MnCu(obze)(H_2O)_2$ 9.71 (s), 5.94 (s), 5.31 (m), 4.78 (w), 4.19 (w), 3.40 (very s), 3.13 (w), 2.67 (w), 2.29 (w), 2.12 (m) with s = strong, m = medium, w = weak.

Crystallographic Data Collection and Structure Determination. All measurements were carried out at 294 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A needle-shaped crystal of size $0.72 \times 0.14 \times 0.09$ mm,

Table I. Crystallographic Data for MnCu(obze)(H₂O)₄·2H₂O

chemical formula	$C_{11}H_{18}N_2CuMnO_{12}$
fw	488.75
space group	$P2_1/n$
a	17.998 (1) Å
b	6.9949 (6) Å
c	13.784 (1) Å
β	97.40 (1) deg
V	1720.8 (4) Å³
Z	4
T	21 °C
λ	0.71073 Å
δ(obsd)	1.8 g cm⁻³
δ(calcd)	1.886 g cm⁻³
μ	20.091 cm⁻¹
transm coeff	0.22–0.85
$R(F_o)$	0.032
$R_w(F_o)$	0.035

limited by faces {101}, {10-1}, and {010}, was used for data collection. Cell parameters were determined from least-squares refinement of 25 centered reflections (24° < 2θ < 43°). The crytal data are summarized in Table I; a full length table of crystallographic data is given in Table SI (supplementary material). A total of 3052 unique reflections were recorded in the range 2° < 2θ < 50° from the ±h,k,l octants. The intensities of three standard reflections measured every 2 h all declined slightly, about 2%. The random error in any one reflection is calculated as $\sigma_i = [\sigma_c^2 + (0.02F_0^2)^2]^{1/2}$. The data were corrected for Lorentz and polarization effects and for absorption by a Gaussian integration method.

The structure was solved by direct methods and subsequent Fourier syntheses. Refinement was performed with the full-matrix least-squares method. After anisotropic refinement, hydrogen atoms were located in a difference Fourier map and were included in the refinement. For hydrogen atoms on O12 (water of recrystallization) the refinement was not successful, and these atoms were excluded from the final refinement cycles. The refinement based on 2469 reflections with $|F| > 2\sigma_F$ converged at $R = 0.032$, $R_w = 0.035$, $s = 2.09$. The scattering curves with anomalous dispersion terms included were those of Cromer and Waber.[21] All calculations were carried out on a MICRO-VAXII computer with the Enraf-Nonius structure determination programs.[22]

Magnetic Measurements. These were carried out with two instruments, namely (i) a Faraday-type magnetometer equipped with a helium continuous-flow cryostat in the 6–300 K temperature range and (ii) a Métronique Ingéniérie SQUID magnetometer working down to 1.5 K. This magnetometer can be used in low field (a few G) as well as in high field (up to 8 T). Diamagnetic corrections were estimated as –250 × 10⁻⁶ cm³ mol⁻¹ for MnCu(obze)(H₂O)₄·2H₂O and –200 × 10⁻⁶ cm³ mol⁻¹ for MnCu(obze)(H₂O)₂.

EPR Spectra. The X-band powder EPR spectra were recorded at various temperatures between 4.2 and 300 K with a ER 200D Bruker spectrometer equipped with a helium continuous-flow cryostat, and a Hall probe.

Electronic Spectra. These were recorded with a Varian 2300 spectrophotometer. The samples were prepared from powder dispersed in Nujol or in KBr pellets.

Description of the Structure of MnCu(obze)(H₂O)₄·2H₂O

Bond distances and angles for non-hydrogen atoms are listed in Tables II and III, respectively. Atomic positions, anisotropic thermal parameters, distances and angles involving hydrogen atoms, and equations of least-squares planes are given in Tables SII–SV (supplementary material).

The structure consists of Mn^{II}Cu^{II} heterobinuclear molecules, Mn and Cu atoms being bridged by an oxamido group, as shown
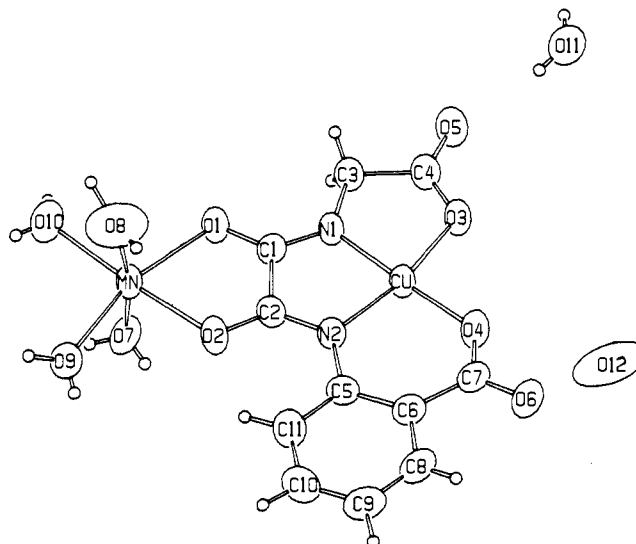
Figure 2. The asymmetric unit in MnCu(obze)(H₂O)₄·2H₂O. Thermal ellipsoids are drawn at the 70% probability level.
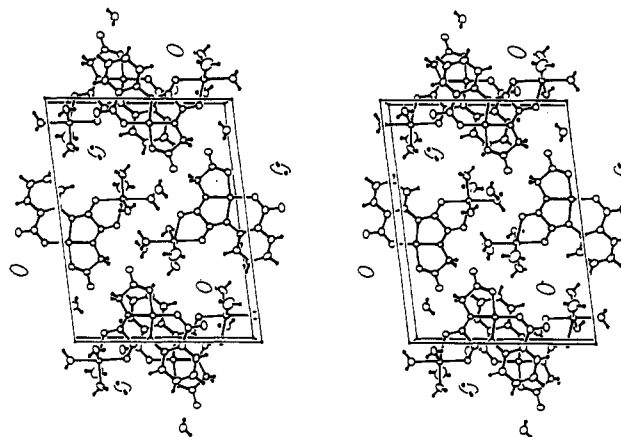
Figure 3. Stereodrawing showing crystal packing as viewed down the b axis. Origin in the unit cell is in the lower left hand corner; the c axis runs horizontally.

in Figure 2. The Mn atom has somewhat distorted octahedral surroundings with four water molecules and the two oxamido oxygen atoms in the coordination sphere. The Cu atom is coordinated to the two oxamido nitrogen atoms and two carboxylato oxygen atoms in a slightly distorted square-planar arrangement. The axial positions of Cu are screened by the proximity of phenyl rings of centrosymmetrically related molecules Cu⋯C6(1 − x, 1 − y, 2 − z) = 3.311 (2) Å and Cu⋯C10(1 − x, −y, 2 − z) = 3.274 Å, as shown in Figure 3. The dihedral angle between the equatorial planes of the two metal ions is 7.8°. The oxamido group makes angles of 4.9 and 4.0° with the Mn and Cu equatorial planes, respectively.

The Mn⋯Cu distance within the binuclear unit is 5.422 (1) Å. The shorter Cu⋯Cu intermolecular distances occur between molecules related by inversion centers with Cu⋯Cu(1 − x, 1 − y,

Table II. Bond Distances (Å) Involving Non-Hydrogen Atoms in MnCu(obze)(H₂O)₄·2H₂O

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Cu	O3	1.986 (1)	O1	C1	1.267 (2)	C1	C2	1.546 (3)
Cu	O4	1.871 (1)	O2	C2	1.245 (2)	C3	C4	1.522 (3)
Cu	N1	1.889 (2)	O3	C4	1.271 (2)	C5	C6	1.412 (3)
Cu	N2	1.944 (2)	O4	C7	1.272 (2)	C5	C11	1.397 (3)
Mn	O1	2.187 (1)	O5	C4	1.234 (2)	C6	C7	1.500 (3)
Mn	O2	2.136 (1)	O6	C7	1.246 (3)	C6	C8	1.401 (3)
Mn	O7	2.241 (2)	N1	C1	1.277 (2)	C8	C9	1.367 (3)
Mn	O8	2.168 (2)	N1	C3	1.443 (3)	C9	C10	1.362 (3)
Mn	O9	2.148 (2)	N2	C2	1.328 (3)	C10	C11	1.384 (3)
Mn	O10	2.160 (2)	N2	C5	1.414 (2)			

Table III. Bond Angles (deg) Involving Non-Hydrogen Atoms in MnCu(obze)(H$_2$O)$_4$·2H$_2$O

atom	atom 2	atom 3	angle	atom	atom 2	atom 3	angle	atom	atom 2	atom 3	angle
O3	Cu	O4	95.59 (6)	O8	Mn	O9	90.2 (1)	N2	C2	C1	114.4 (2)
O3	Cu	N1	82.31 (6)	O8	Mn	O10	85.0 (1)	N1	C3	C4	107.7 (2)
O3	Cu	N2	167.57 (7)	O9	Mn	O10	94.79 (9)	O3	C4	O5	124.2 (2)
O4	Cu	N1	177.46 (7)	Mn	O1	C1	113.7 (1)	O3	C4	C3	117.1 (2)
O4	Cu	N2	96.81 (6)	Mn	O2	C2	117.0 (1)	O5	C4	C3	118.7 (2)
N1	Cu	N2	85.31 (7)	Cu	O3	C4	115.5 (1)	N2	C5	C6	119.9 (2)
O1	Mn	O2	76.20 (5)	Cu	O4	C7	128.0 (1)	N2	C5	C11	121.7 (2)
O1	Mn	O7	87.91 (7)	Cu	N1	C1	115.8 (1)	C6	C5	C11	118.5 (2)
O1	Mn	O8	97.01 (9)	Cu	N1	C3	117.3 (1)	C5	C6	C7	127.6 (2)
O1	Mn	O9	163.10 (8)	C1	N1	C3	126.8 (2)	C5	C6	C8	117.7 (2)
O1	Mn	O10	101.03 (7)	Cu	N2	C2	111.2 (1)	C7	C6	C8	114.7 (2)
O2	Mn	O7	95.84 (7)	Cu	N2	C5	124.6 (1)	O4	C7	O6	118.7 (2)
O2	Mn	O8	92.8 (1)	C2	N2	C5	124.0 (2)	O4	C7	C6	122.6 (2)
O2	Mn	O9	88.25 (7)	O1	C1	N1	129.6 (2)	O6	C7	C6	118.7 (2)
O2	Mn	O10	176.21 (8)	O1	C1	C2	117.2 (2)	C6	C8	C9	123.1 (2)
O7	Mn	O8	170.9 (1)	N1	C1	C2	113.2 (2)	C8	C9	C10	118.6 (2)
O7	Mn	O9	87.12 (8)	O2	C2	N2	129.8 (2)	C9	C10	C11	121.0 (2)
O7	Mn	O10	86.59 (8)	O2	C2	C1	115.8 (2)	C5	C11	C10	121.1 (2)

Table IV. Hydrogen Bonds in MnCu(obze)(H$_2$O)$_4$·2H$_2$O

A	B	A–D (Å)	∠A–H–D (deg)
O7 [H71] (x,y,z)	O6 $(1 - x, -y, 2 - z)$	2.664 (3)	171 (3)
O7 [H72] (x,y,z)	O11 $(-^1/_2 + x, ^1/_2 - y, -^1/_2 + z)$	2.712 (3)	176 (3)
O8 [H82] (x,y,z)	O11 $(-^1/_2 + x, ^3/_2 - y, -^1/_2 + z)$	2.798 (3)	165 (4)
O9 [H91] (x,y,z)	O3 $(-^1/_2 + x, ^1/_2 - y, -^1/_2 + z)$	2.700 (3)	169 (3)
O9 [H92] (x,y,z)	O12 $(1 - x, -y, 2 - z)$	2.662 (4)	174 (3)
O10 [H101] (x,y,z)	O5 $(-^1/_2 + x, ^1/_2 - y, -^1/_2 + z)$	2.738 (3)	179 (3)
O10 [H102] (x,y,z)	O7 $(1 - x, -y, 1 - z)$	2.766 (3)	173 (3)
O11 [H111] (x,y,z)	O1 $(^3/_2 - x, ^1/_2 + y, ^3/_2 - z)$	2.755 (3)	160 (3)
O11 [H112] (x,y,z)	O5 (x, y, z)	2.900 (3)	151 (4)
O12 (x,y,z)	O4 (x, y, z)	2.976 (3)^a	
O12 (x,y,z)	O6 (x, y, z)	2.982 (3)^a	
O12 (x,y,z)	O9 $(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$	3.045 (3)^a	

^{a}Hydrogen atoms on O12 could not be unambiguously located. Possible interactions are included in the list. A bifurcated hydrogen bond is possible between O12–H and O4 and O6.

$2 - z) = 4.541$ (1) Å alternating with Cu···Cu$(1 - x, -y, 2 - z)$ $= 6.028$ Å along the b axis. The shortest Cu···Mn intermolecular contact is found between molecules related by the n-glide with Cu···Mn$(^1/_2 + x, ^1/_2 - y, ^1/_2 + z) = 5.817$ (1) Å. Futhermore Mn···Mn$(1 - x, 1 - y, 1 - z)$ pairs of centrosymmetrically related Mn atoms are separated by 5.518 (1) Å, the two coordination spheres being linked through hydrogen bonds between O7 and O10.

The packing of molecules within the crystal lattice is illustrated in Figure 3. Molecules related by inversion centers are stacked along b with a considerable amount of overlap, the short Cu···Cu and Cu···C(phenyl) contacts occurring between these molecules. The molecules are connected through an extensive net of hydrogen bonds, a complete list of which is given in Table IV. The hydrogen-bonding scheme will be further discussed later.

Magnetic and EPR Properties

MnCu(obze)(H$_2$O)$_4$·2H$_2$O. The magnetic behavior of this compound is shown in Figure 4 in the form of the $\chi_M T$ versus T plot. At room temperature, $\chi_M T$ is equal to 4.27 cm^3 K mol^{-1}. This room-temperature value is already below what is expected for isolated Mn(II) and Cu(II) ions, which indicates that the ions are antiferromagnetically coupled. When the temperature is lowered, $\chi_M T$ continuously decreases and reaches a plateau around 20 K with $\chi_M T = 2.77$ cm^3 K mol^{-1}. $\chi_M T$ is then constant down to 2 K. The magnetic data closely follow eq 1:

$$\chi_M T = (2N\beta^2/k)[5g_2^2 + 14g_3^2 \exp(3J/kT)]/[5 + 7 \exp(3J/kT)]$$

(1)

valid for isolated Mn^{II}Cu^{II} pairs with an antiferromagnetic intrapair interaction.[8] N is the Avogadro number, β the Bohr magneton, k the Boltzmann constant, J the interaction parameter occurring in the spin Hamiltonian $-J S_{Mn} \cdot S_{Cu}$, and g_2 and g_3 are the Zeeman factors associated with the $S = 2$ and 3 pair states,
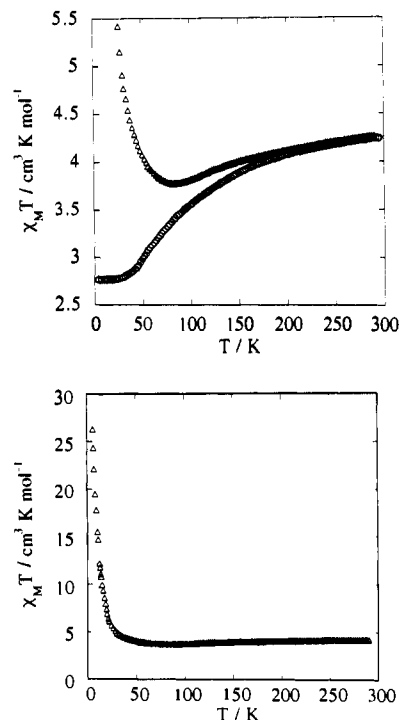

Figure 4. (a) Comparison of the $\chi_M T$ versus T plots for (O) MnCu-(obze)(H$_2$O)$_4$·2H$_2$O and (△) MnCu(obze)(H$_2$O)$_2$ and (b) $\chi_M T$ versus T plot for MnCu(obze)(H$_2$O)$_2$.

respectively, arising from the interaction between the local S_{Mn} $= 5/2$ and $S_{Cu} = 1/2$ states. The plateau below 20 K corresponds to the temperature range where only the ground $S = 2$ pair state is thermally populated. The least-squares fitting of the experi-
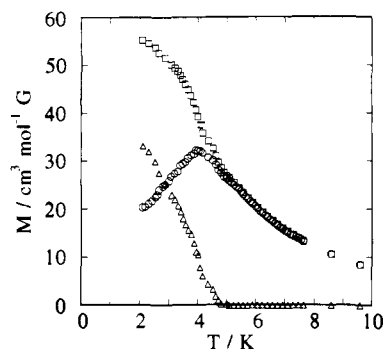
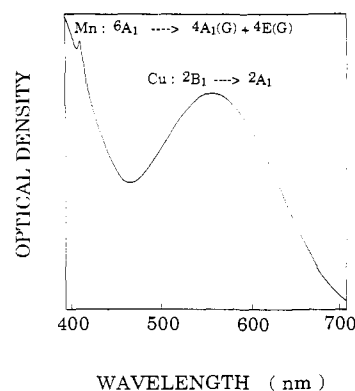**Figure 5.** Magnetization versus T curves for $MnCu(obze)(H_2O)_2$: ($\square$) FCM, ($\bigcirc$) ZFCM, ($\triangle$) remnant magnetization (see text).
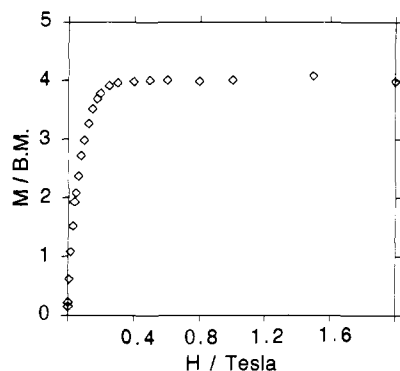
Figure 6. Magnetization versus magnetic field curve for $MnCu$-$(obze)(H_2O)_2$ at 2.5 K.

mental data with eq 1 leads to $J = -33.6$ cm^{-1}, $g_2 = 1.92$, and $g_3 = 1.99$. The agreement factor defined by $\sum[(\chi_M T)^{obs} - (\chi_M T)^{calc}]^2/\sum[(\chi_M T)^{obs}]^2$ is then equal to 4.0×10^{-6}. The energy gap between quintet and septet pair states is equal to $3J = -100.8$ cm^{-1}. g_2 and g_3 in principle may be related to the local Zeeman factors g_{Mn} and g_{Cu} through eq 2.[8,23,24] g_{Mn} and g_{Cu} deduced from this equation are found equal to 1.96 and 2.19, respectively.

$$g_2 = (7g_{Mn} - g_{Cu})/6$$

$$g_3 = (5g_{Mn} + g_{Cu})/6 \qquad (2)$$

$MnCu(obze)(H_2O)_2$. The magnetic properties of the partially dehydrated compound are totally different from those of its precursor. The $\chi_M T$ versus T plot for $MnCu(obze)(H_2O)_2$ is shown in Figure 4b and compared to that of $MnCu$-$(obze)(H_2O)_4\cdot2H_2O$ in Figure 4a. At room temperature, $\chi_M T$ is equal to 4.26 cm^3 K mol^{-1} and smoothly decreases when the temperature is lowered. This decrease is less pronounced than for $MnCu(obze)(H_2O)_4\cdot2H_2O$. Moreover, $\chi_M T$ reaches a minimum around 80 K with $\chi_M T = 3.78$ cm^3 K mol^{-1}, then increases more and more rapidly when the temperature is lowered further, and finally reaches 26 cm^3 K mol^{-1} at 6 K.

This magnetic susceptibility behavior suggests that a ferromagnetic transition takes place, which is confirmed by the magnetization (M) versus temperature (T) curves shown in Figure 5. The field-cooled magnetization (FCM) measured by cooling the sample within a field of 5 G shows a break around 4.6 K and then an inflexion likely due to demagnetization effects. The zero-field cooled magnetization (ZFCM) measured in cooling the sample in zero field and then warming it up within the field of

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Figure 7. Electronic absorption spectrum for $MnCu(obze)(H_2O)_4\cdot2H_2O$.

5 G shows a maximum just below T_c as expected for a powder ferromagnet.[25] Finally, if one cools the sample below T_c within the field and then switches off the field, a remnant magnetization is observed which vanishes at T_c upon warming up. We also measured the variation of M at 2.5 K as a function of the field up to 8 T. The M versus H curve in the 0–2 T field range shown in Figure 6 is typical of what is expected for a powder ferromagnet with a very large zero-field susceptibility $(dM/dH)_{H=0}$ and then a rapid saturation. The saturation magnetization is $M_S = 4.0 \mu_B$, which confirms that all the Mn(II) spins are aligned along a direction and the Cu(II) spins along the opposite direction, or all the $S = 2$ molecular spins per $Mn^{II}Cu^{II}$ units are aligned in a parallel fashion. The temperature and field dependences of M are quite similar to what has been observed for $MnCu$-$(pbaOH)(H_2O)_3$ which shows a ferromagnetic transition at the same temperature $T_c = 4.6$ K.[6]

Let us turn back to the magnetic susceptibility data. The minimum in the $\chi_M T$ versus T plot is quite characteristic of a ferrimagnetic system with alternation of the Mn(II) and Cu(II) ions and antiferromagnetic interaction between nearest neighbor magnetic centers. The actual structure of $MnCu(obze)(H_2O)_2$ is not known. Only if this structure consisted of alternating bimetallic chains with alternation of both the metal ions (Mn(II) and Cu(II)) and the bridges (oxamido and carboxylato), could the magnetic data be interpreted quantitatively. The valid model for such a structure has been established by treating S_{Mn} as a classical spin and S_{Cu} as a quantum spin.[7,19,26] It takes into account four parameters, namely the two interaction parameters $J_1 = J(1 + \alpha)$ and $J_2 = J(1 - \alpha)$ and the local Zeeman factors g_{Mn} and g_{Cu}. For the regular bimetallic chain, α is equal to zero. In the present case, this model with the set of paremeters J, α, g_{Mn}, and g_{Cu} leads to a rather poor agreement between observed and calculated $\chi_M T$ values. The agreement factor is equal to 6 $\times$ 10^{-4}, while it was equal to 4 $\times$ 10^{-6} for $MnCu$-$(obze)(H_2O)_4\cdot2H_2O$. This suggests that the structure of $MnCu(obze)(H_2O)_2$ is not one-dimensional. This important point will be discussed further in the last section.

EPR Properties

The X-band EPR spectra of both $MnCu(obze)(H_2O)_4\cdot2H_2O$ and $MnCu(obze)(H_2O)_2$ show a single and symmetrical resonance centered at $g = 2.03$. The line widths, however, are significantly different and equal to 358 G for the former compound and 275 G for the latter. They are almost independent of the temperature. The spectrum of $MnCu(obze)(H_2O)_4\cdot2H_2O$ does not correspond to magnetically isolated $Mn^{II}Cu^{II}$ pairs. If so, it would present four lines at low temperature due to the zero-field splitting within the $S = 2$ ground state.[27,28] EPR reveals long-range interactions not detectable through magnetic susceptibility measurements.[29,30]

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Concerning the line widths, it is well-established that they result from the combined effect of dipolar interactions which broaden the lines and exchange interactions which narrow the lines. In the present case, this latter effect dominates when passing from the hydrated to the partially dehydrated form. The same evolution has been found between MnCu(obbz)·5H$_2$O and MnCu-(obbz)·H$_2$O.[7]

Electronic Spectra

The electronic absorption spectrum of MnCu(obze)(H$_2$O)$_4$·2H$_2$O shown in Figure 7 is typical of oxamido- or oxamato-bridged Mn^{II}Cu^{II} compounds.[31] It displays a broad band at 546 nm (18315 cm^{-1}) and a very sharp one at 406 nm (24631 cm^{-1}). The former band corresponds to the $^2B_1 \rightarrow {}^2A_1$ transition in D_4 symmetry for Cu(II) in square-planar environment and the latter to the $^6A_1 \rightarrow {}^4A_1$(G) + ^{4}E(G) spin forbidden transition for Mn(II) in octahedral environment. This transition activated by an exchange mechanism does not depend on the ligand field to first order, as there is no electron jump between the t$_2$ and e orbitals. Its frequency is equal to that of the $^6S \rightarrow {}^4G$ free-ion transition. The other two spin forbidden transitions of higher energy observed for MnCu(pbaOH)(H$_2$O)$_3$ are here hidden by $\pi \rightarrow \pi^*$ transitions of the aromatic ring.

The spectrum of MnCu(obze)(H$_2$O)$_2$ is very similar to that of the hydrated pair with the Cu(II) broad band at 540 nm (18519 cm^{-1}) and the Mn(II) spin forbidden band at 405 nm (24691 cm^{-1}). At the first view, this result is rather surprising since two water molecules are removed from the Mn(II) coordination sphere. Its implications will be analyzed in the following section.
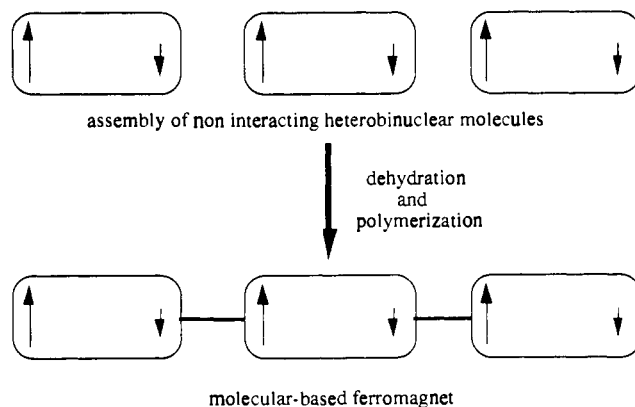
Discussion

The crystals obtained by slow diffusion contain MnCu-(obze)(H$_2$O)$_4$ discrete units with four water molecules in the Mn(II) coordination sphere and two additional noncoordinated water molecules. If the reaction between Mn(II) and [Cu(obze)]$^{2-}$ ions is carried out by mixing together rapidly the aqueous solutions containing the reactants, the obtained product is MnCu-(obze)(H$_2$O)$_4$, the magnetic and spectroscopic properties of which are rigorously similar to those of MnCu(obze)(H$_2$O)$_4$·2H$_2$O. A gentle heating at 60 °C during a short while or the primary vacuum at room temperature affords a new compound of formula MnCu(obze)(H$_2$O)$_2$, the magnetic properties of which are strongly modified. Thermogravimetric analysis experiment confirms that MnCu(obze)(H$_2$O)$_2$·2H$_2$O loses first two water molecules just above the room temperature and then two additional water molecules above ca. 50 °C. The questions we are faced with then are the following: what chemical process occurs during the dehydration, and what is the structure of this new compound containing only two water molecules?

For some time, we have hoped to be able to solve the structure of MnCu(obze)(H$_2$O)$_2$. Indeed, when a well-shaped single crystal of MnCu(obze)(H$_2$O)$_4$·2H$_2$O is partially dehydrated, its macroscopic aspect does not change. However, X-ray diffraction shows a strongly disordered mosaic structure. It follows that the only available structural information comes from X-ray powder patterns. MnCu(obze)(H$_2$O)$_2$ is well crystallized. Its powder pattern is clearly different from and, in the meantime, quite reminiscent of that of MnCu(obze)(H$_2$O)$_4$. The loss of two water molecules results in a shrinkage effect and an intensity change of some of the lines. The two water molecules which are removed with respect to MnCu(obze)(H$_2$O)$_4$ were obviously bound to the Mn atom. Two possibilities may then be considered as for the Mn(II) coordination sphere in MnCu(obze)(H$_2$O)$_2$: either Mn(II) is 4-fold coordinated with two oxamido oxygen atoms and two water molecules or it is again in octahedral surroundings. The fact that the electronic absorption spectrum is almost unchanged with respect to MnCu(obze)(H$_2$O)$_4$·2H$_2$O strongly substantiates the

latter hypothesis. If so, the Mn(II) ion completes its coordination sphere with oxygen atoms coming from the carboxylato groups belonging to neighboring molecules. Quite interestingly, a careful examination of the packing of MnCu(obze)(H$_2$O)$_4$·2H$_2$O indicates that two of the four water molecules bound to a Mn(II) ion are hydrogen bonded to noncoordinated carboxylato oxygen atoms belonging to adjacent molecules; O7(x, y, z) is hydrogen bonded to O6(1 − x, −y, 2 − z) and O10(x, y, z) to O5(−$^1/_2$ + x, $^1/_2$ − y, −$^1/_2$ + z), with distances at 2.664 and 2.738 Å, respectively. The corresponding Mn···O6 and Mn···O5 separations are rather short and equal to 4.036 and 4.141 Å, respectively. The reaction of partial dehydration might then be described as a polymerization proceeding through the departure from the Mn(II) coordination sphere of the two water molecules involving the O7 and O10 atoms and the formation of Mn(x, y, z)–O6(1 − x, −y, 2 − z) and Mn(x, y, z)–O5(−$^1/_2$ + x, $^1/_2$ − y, −$^1/_2$ + z) bonds. The structure is then three-dimensional, in contrast with the one-dimensional structure found for MnCu(obp)(H$_2$O)$_3$·H$_2$O,[19] MnCu(obzp)(H$_2$O)$_3$·H$_2$O,[20] and MnCu(Br$_4$obbz)(H$_2$O)$_3$·2.5H$_2$O.[18] This polymerization scheme, although the most likely, is not the only possibility. For instance, removal of O10 or O7 may give Mn(H$_2$O)$_2$Mn units across a center of symmetry (1 − x, −y, 1 − z); the second water molecule to be removed could then perhaps be O9, leaving an Mn···O3 contact. Or maybe even O8 could be removed. Although O8 apparently is not hydrogen bonded to any of the carboxylate groups, it is situated only 3.018 Å from O6(1 − x, 1 − y, 2 − z). Any one of these schemes will also give a three-dimensional polymerization. The magnetic ordering at T_c = 4.6 K is obviously consistent with the polymeric nature of the compound.

To our knowledge, this kind of polymerization taking place in the solid state through very mild experimental conditions is not well documented. It is worth mentioning that this process is irreversible. MnCu(obze)(H$_2$O)$_2$ is thermodynamically more stable than the hydrated form, and the energy barrier to overcome from the latter species to the former one is low. This polymerization is somewhat reminiscent of the condensation reaction of the alkoxides involved in the sol-gel process.[32] It opens quite interesting perspectives as far as the molecular-based magnetic materials are concerned. In the present case, it provides some exchange pathway between the negative spin density of an oxamido-bridged Mn^{II}Cu^{II} unit and the positive spin density of the adjacent unit. As a conclusion, the strategy used to design this novel molecular-based ferromagnet is schematized below. For the sake of simplicity, we have represented a one-dimensional array of local spins, while the actual structure would be two- or three-dimensional.

assembly of non interacting heterobinuclear molecules

dehydration
and
polymerization

molecular-based ferromagnet

The last point we would like to address briefly concerns the best definition for this new type of magnetic materials. Solid-state physicists certainly would speak of ferrimagnets since Mn(II) and Cu(II) local spins are oriented along opposite directions. Such a definition is correct but ignores the specificity of molecular chemistry. Actually, we have strongly coupled Mn^{II}Cu^{II} molecular units with S = 2 molecular spins. Before polymerization, those

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molecular spins are randomly oriented within the crystal lattice; after polymerization, they tend to align along the same direction with a ferromagnetic ordering of the molecular spins below T_c. Therefore, we prefer to speak of a molecular-based ferromagnet. Of course, this definition problem is a little bit byzantine and does not deserve much space. The choice is a matter of sensitivity. Our definition emphasizes the molecular approach.

Vanadium-Promoted Reductive Coupling of CO and Facile Hydrogenation To Form *cis*-Disiloxyethylenes

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Abstract: Reaction of trimethylsilyl reagents with $Na[V(CO)_2(dmpe)_2]$ leads to reductive coupling of the two CO ligands to form a coordinated bis(trimethylsiloxy)acetylene ligand. When Me_3SiOTf was used, a novel six-coordinate, paramagnetic ($\mu_{eff} = 2.81$ μ_B at 20 K) $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2]OTf$ complex was obtained, while addition of Me_3SiBr afforded diamagnetic $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Br]$, analogues of which are known in Nb and Ta chemistry. Both complexes were characterized in the solid state by single-crystal X-ray diffraction, and the latter was identified in solution by NMR spectroscopy. Significantly, these vanadium complexes react with hydrogen at room temperature and mild pressures in the absence of external catalysts to afford exclusively the cis isomer of bis(trimethylsiloxy)ethylene in good yield. In an experiment designed to investigate the mechanism of the reductive coupling reaction, vanadium carbyne species were prepared by addition of 1 equiv of a trialkyl- or triarylsilyl chloride to $Na[V(CO)_2(dmpe)_2]$. One such complex, $[V(COSiPh_3)(CO)(dmpe)_2]$, was crystallized and structurally characterized as the first unambiguous example of a vanadium carbyne complex. Carbynes of this kind are known to be intermediates in the reductive coupling of CO ligands in $[M(CO)_2(dmpe)_2X]$ compounds (M = Nb, Ta; X = halide, triflate). These results significantly extend the generality of CO reductive coupling chemistry to a first-row transition metal.

Introduction

There is considerable interest in the conversion of carbon monoxide and hydrogen to useful C2 oxygenates.[1–3] Modification of Fischer–Tropsch systems by changing operating conditions and catalysts can shift product distributions to favor oxygenate formation,[4] but more promising are rhodium catalysts which produce mixtures of ethylene glycol and methanol at operating temperatures of 150–300 °C and pressures of 50–3000 atm.[5,6]

Several homogeneous systems have been discovered that couple two CO molecules with the creation of a new carbon–carbon bond. Alkyl and hydride complexes of the group 4 transition metals react with CO to yield ene–diolate ligands bound to one or more metals (Chart 1, product type A).[7–9] Subsequent work revealed that complexes of the group 5,[10,11] actinide,[12,13] and lanthanide[14–16]

Chart I
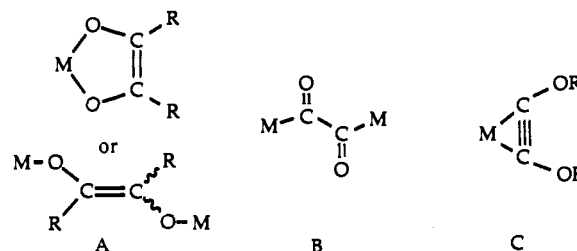
metals behave similarly. Coupling of CO ligands to afford ene-diolate products is significantly influenced by the high metal-oxygen bond energies found for these oxophilic metals. Removal of the newly formed C2 oxygenates from these metal complexes has not yet been reported, presumably because of the inherently strong metal–oxygen bonds.[17]

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