Magnetic Properties of a Series of Trinuclear Complexes $(CuL)_2Mn\cdot xB$ (L Representing the Deprotonated Form of *N*-(4-Methyl-6-oxo-3-azahept-4-enyl)oxamic Acid and B Representing Respectively H_2O ($x = 5, 4.5, 3, 1$), $(CH_3)_2SO$ ($x = 2$), and C_5H_5N ($x = 4$)). Crystal and Molecular Structure of $(CuL)_2Mn\cdot 2(CH_3)_2SO$

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A series of (Cu, Mn, Cu) complexes have been prepared and characterized. They may be described by the overall formula $(CuL)_2Mn\cdot xB$ where L stands for the deprotonated form of *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid and B for respectively H_2O (with $x = 5, 4.5, 3, 1$), $(CH_3)_2SO$ (with $x = 2$), and C_5H_5N (with $x = 4$). The crystal and molecular structures of $(CuL)_2Mn\cdot 2(CH_3)_2SO$ have been solved. The crystals are monoclinic, space group $P2_1/n$ with cell constants $a = 8.362(2)$ Å, $b = 14.426(3)$ Å, $c = 24.442(6)$ Å, and $Z = 4$. In each (Cu, Mn, Cu) molecular unit the central Mn(II) ion is bridged to two copper(II) ions through two oxamato groups. Short intermolecular Cu···Cu distances lead to the formation of a chain-like packing pattern running parallel to the *c*-axis. Magnetic susceptibility measurements have been performed for the six complexes. Five complexes display the same behavior which corresponds to the occurrence of antiferromagnetic Cu−Mn interactions within isolated trinuclear units. The J values are between $-29.4(2)$ and $-33.8(5)$ cm^{-1}. Surprisingly the field and temperature dependence of the magnetization for $(CuL)_2Mn\cdot 4.5H_2O$ confirms that a magnetic phase transition occurs at low temperature and that, below $T_c = 37$ K, the complex displays weak ferromagnetism.

Introduction

Among the large number of polynuclear complexes which have been prepared and studied in recent years, particular attention has been paid to the complexes involving simultaneously copper(II) and manganese(II) ions. Indeed they have afforded to the field of molecular magnetism very important contributions regarding irregular spin-state structure,[1] one-dimensional ferrimagnetism, and ferromagnetic ordering of high-spin molecules or ferromagnetic chains.[2−12] A great variety of species, including binuclear (Cu,Mn)[7,10,12−15] complexes, trinuclear (Mn, Cu, Mn)[1,13] complexes, and bimetallic chain compounds,[2−12,16] have been considered, but to our knowledge, there is no example of trinuclear (Cu, Mn, Cu) species. It may be noted that two (Cu, Fe, Cu) complexes have been reported.[17,18]

Our previous work[19] related to the complexing ability of the polynucleating ligand L = *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid suggests that it could offer a straightforward route to (Cu, Mn, Cu) complexes. In fact we succeeded in obtaining a series of complexes of the (Cu L)$_2$Mn·xB type with B standing for water ($x = 5, 4.5, 3, 1$), dimethyl sulfoxide (x = 2), and pyridine (x = 4).

Experimental Section

Sodium *N*-(4-Methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-κ^4*N,N′,O,O′*-copper(II)·1.33H$_2$O: NaCuL·1.33H$_2$O. This complex was obtained as previously described .[19]

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Bis[*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-$\kappa^4 N,N',O,O^1$-copper(II)]-$\kappa^4 O^{1'},O^2$-manganese(II).5 H_2O: $(CuL)_2Mn\cdot 5H_2O$ (1). To $NaCuL\cdot 1.33H_2O$ (0.2 g, 6.2×10^{-4} mol) in water (5 mL) was added, with stirring, a slight excess of $Mn(ClO_4)_2.6H_2O$ (0.2 g, 5.5×10^{-4} mol) dissolved in methanol (5 mL). The blue powder which appeared quickly was filtered and washed with cold methanol and then diethyl ether. Yield: 0.17 g (81%). Anal. Calcd for $C_{18}H_{32}Cu_2MnN_4O_{13}$: C, 31.1; H, 4.6; Cu, 18.3; Mn, 7.9; N, 8.1. Found: C, 31.0; H, 4.8; Cu, 18.1; Mn, 7.9; N, 7.9. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 604$ (100), $[(CuL)_2Mn + 1]^+$. UV−vis (Nujol): 590, 409, 370 (sh).

Bis[*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-$\kappa^4 N,N',O,O^1$-copper(II)]-$\kappa^4 O^{1'},O^2$-manganese(II)·3H_2O: $(CuL)_2Mn\cdot 3H_2O$ (2). After a stay of 24 h in a drying oven at 80 °C, complex **1** lost two water molecules. **2** appeared as a violet powder. Anal. Calcd for $C_{18}H_{28}Cu_2MnN_4O_{11}$: C, 32.8; H, 4.3; N, 8.5. Found: C, 32.6; H, 4.4; N, 8.3. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 604$ (100), $[(CuL)_2Mn + 1]^+$. UV−vis (Nujol): 540, 403, 370 (sh).

Bis[*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-$\kappa^4 N,N',O,O^1$-copper(II)]-$\kappa^4 O^{1'},O^2$-manganese(II)·H_2O: $(CuL)_2Mn\cdot H_2O$ (3). First the blue $(CuL)_2Mn\cdot 5H_2O$ complex (0.27 g, 3.9×10^{-4} mol) stirred in acetone dissolved, and a few minutes later, a violet powder appeared. It was filtered and washed with acetone and diethyl ether. Yield: 0.22 g (86%). Anal. Calcd for $C_{18}H_{24}Cu_2MnN_4O_9$: C, 34.7; H, 3.9; N, 9.0. Found: C, 34.6; H, 3.9; N, 8.8. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 604$ (100), $[(CuL)_2Mn + 1]^+$. UV−vis (Nujol): 540, 404, 370 (sh).

Bis[*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-$\kappa^4 N,N',O,O^1$-copper(II)]-$\kappa^4 O^{1'},O^2$-manganese(II)·4.5H_2O: $(CuL)_2Mn\cdot 4.5H_2O$ (4). $(CuL)_2Mn\cdot 1H_2O$ kept in a polyethylene vial for several weeks took water again, giving a gray blue powder, which analyzed as $(CuL)_2Mn\cdot 4.5H_2O$ (see text for thermogravimetric analysis). Quicker methods, such as the method of steam-saturated atmosphere, yielded only complex **1**. Anal. Calcd for $C_{18}H_{31}Cu_2MnN_4O_{12.5}$: C, 31.5; H, 4.5; N, 8.2. Found: C, 31.6; H, 4.4; N, 8.3. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 604$ (100), $[(CuL)_2Mn + 1]^+$. UV−vis (Nujol): 580, 408, 370 (sh).

Bis[*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-$\kappa^4 N,N',O,O^1$-copper(II)]-$\kappa^4 O^{1'},O^2$-manganese(II)·2dmso: $(CuL)_2Mn\cdot$2dmso (5). In dmso, the blue $(CuL)_2Mn\cdot 5H_2O$ complex (0.14 g, 2.0×10^{-4} mol) dissolved, giving a violet solution. Addition of acetone yielded, a few minutes later, a violet precipitate. Yield: 0.13 g (85%). Anal. Calcd for $C_{22}H_{34}Cu_2MnN_4O_{10}S_2$: C, 34.7; H, 4.5; N, 7.4; S, 8.4. Found: C, 34.9; H, 4.6; N, 7.4; S, 8.2. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 604$ (100), $[(CuL)_2Mn + 1]^+$. UV−vis (Nujol): 550, 410, 370 (sh).

Bis[*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato(3−)-$\kappa^4 N,N',O,O^1$-copper(II)]-$\kappa^4 O^{1'},O^2$-manganese(II)·4C_5H_5N: $(CuL)_2Mn\cdot$4py (6). Dissolution of $(CuL)_2Mn\cdot 5H_2O$ (0.09 g, 1.3×10^{-4} mol) in pyridine gave a light blue solution. Addition of diethyl ether yielded, a few minutes later, a blue precipitate. Yield: 0.1 g (84%). Anal. Calcd for $C_{38}H_{42}Cu_2MnN_8O_8$: C, 49.6; H, 4.6; N, 12.2. Found: C, 49.6; H, 4.5; N, 12.0. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 604$ (100), $[(CuL)_2Mn + 1]^+$. UV−vis (Nujol): 600, 414, 370 (sh).

Materials and Methods. All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). Electronic spectra (Nujol mull) were obtained with a Cary 2300 spectrometer. Magnetic susceptibility data were collected on a powdered sample of the compound with use of a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants[20] (-262×10^{-6} (**1**), -236×10^{-6} (**2**), -210×10^{-6} (**3**), -256×10^{-6} (**4**), -295×10^{-6} (**5**), -393×10^{-6} (**6**) emu mol^{-1}). Positive FAB mass spectra were recorded with a Nermag R10-10 spectrometer using 3-nitrobenzyl alcohol matrix.

Crystallization. Although numerous attempts to crystallize the water-containing complexes were made, no suitable crystals for X-ray diffraction study were obtained. Crystals of $(CuL)_2Mn\cdot$2dmso were obtained by dissolution of the premade complex, or any water-containing complex (0.7 g) in dimethyl sulfoxide (30 mL) and use of a crystal-growth gel technique[21] (silicate gels). The crystals were collected, washed with methanol and diethyl ether, and air-dried.

Table 1. Crystallographic Data for **5**

empirical formula	$C_{22}H_{34}Cu_2MnN_4O_{10}S_2$	formula weight	760.67
a	8.362(2) Å	space group	$P2_1/n$
b	14.426(3) Å	T	20 °C
c	24.442(6) Å	λ	0.710 73 Å
β	92.28(2)°	ρ(calcd)	1.715 g cm^{-3}
		μ	20.53 cm^{-1}
V	2946.1(1) Å^3	R^a	0.0589
Z	4	$R_w{}^b$	0.1106

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(|F_o| - |F_c)^2]/\sum wF_o{}^2]^{1/2}$.

X-ray Structure Determination. The data for the title compound $(CuL)_2Mn\cdot$2dmso (**5**) were collected by a Nicolet R3m diffractometer equipped with a graphite monochromator (Mo Kα radiation, $\lambda = 0.710\,73$ Å). A summary of data collection and refinement is given in Table 1. The data set was corrected for Lorentz and polarization factors, but neither for absorption nor decay. The structure was solved by direct methods and subsequent Fourier syntheses using the SHELXTL PLUS program package.[22] Full-matrix refinement for the anisotropic non-hydrogen atoms was performed on F^2. Hydrogen atoms were included in the refinement at calculated positions using a riding model with U_H(iso) $= 1.2U_{hostatom}$.[23] The sulfur atom of a dimethyl sulfoxide ligand is disordered in an 85/15 ratio for S1 and S11, respectively. Listings for the atomic coordinates and selected bond lengths and angles appear in Tables 2 and 3.

Results and Discussion

When performed in methanol/water the reaction of the precursor $NaCuL\cdot 1.33H_2O$ with $Mn(ClO_4)_2\cdot xH_2O$ leads to the formation of a heterotrinuclear complex which is best represented by the formula $(CuL)_2Mn\cdot 5H_2O$ (**1**) . Heating **1** in the solid phase at 80 °C for 24 h affords complex **2**, $(CuL)_2Mn\cdot 3H_2O$. A third complex, $(CuL)_2Mn\cdot H_2O$ (**3**), is obtained by allowing a suspension of **1** in dry acetone to stand for 24 h at room temperature. An interesting complex, $(CuL)_2Mn\cdot 4.5H_2O$ (**4**), results from a slow rehydratation of **3**. All of these complexes are insoluble in inert solvents. They dissolve readily in the potentially coordinating solvents $(CH_3)_2SO$ (dmso) and C_5H_5N (py), but precipitation of the resulting solutions with diethyl ether yields the solvated species, $(CuL)_2Mn\cdot$2dmso (**5**) and $(CuL)_2Mn\cdot$4py (**6**), respectively. A suspension of **5** or **6** in water readily gives complex **1**. Complex **1** is also recovered if **5** and **6** are kept in a steam-saturated atmosphere for 3 weeks. All attempts to obtain crystals suitable for an X-ray diffraction study have failed except in the case of **5**. Thermogravimetric and spectroscopic techniques have been used to further characterize these species.

Description of the Structure of Complex 5. The structure of $(CuL)_2Mn\cdot$2dmso (**5**) consists of neutral trinuclear units, each unit resulting from the complexation of a Mn(II) ion by two $(CuL)^i$ (i = 1, 2) subunits and two $(CH_3)_2SO$ molecules as shown in Figure 1. Selected bond lengths and angles involving non-hydrogen atoms are listed in Table 3.

Each copper is surrounded by two nitrogen and two oxygen atoms from the ligand L. In both cases, the copper environment

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **5**

	x	*y*	*z*	*U*(eq)
Cu(1)	1392(1)	440(1)	4487(1)	38(1)
Cu(2)	−44(1)	897(1)	506(1)	36(1)
Mn	−419(1)	−898(1)	2465(1)	34(1)
S(1)	723(3)	−3062(2)	2552(1)	46(1)
S(11)	−235(17)	−3179(9)	2147(5)	45(3)
S(2)	−4294(3)	−1429(2)	2793(1)	50(1)
O(1)	930(6)	1439(3)	4947(2)	44(1)
O(2)	83(6)	898(3)	3827(2)	44(1)
O(3)	−1422(6)	1359(4)	−53(2)	44(1)
O(4)	−1779(5)	498(3)	1012(2)	38(1)
O(5)	265(6)	−2267(3)	2174(2)	49(1)
O(6)	−2532(6)	−1588(4)	2776(2)	51(1)
O(21)	1248(6)	−1144(3)	3149(2)	43(1)
O(22)	−735(6)	339(3)	3004(2)	44(1)
O(41)	1313(6)	−241(3)	1939(2)	42(1)
O(42)	−1944(5)	−306(3)	1796(2)	37(1)
N(1)	2680(7)	−260(4)	5015(2)	38(2)
N(2)	1897(7)	−536(4)	4006(2)	39(2)
N(3)	1924(7)	1072(4)	130(2)	37(2)
N(4)	1330(6)	514(4)	1103(2)	39(2)
C(1)	3086(9)	−1189(5)	4830(3)	46(2)
C(2)	3045(9)	−1227(5)	4211(3)	41(2)
C(3)	3281(9)	616(5)	417(3)	45(2)
C(4)	3029(8)	634(5)	1038(3)	45(2)
C(11)	2931(9)	4(5)	5526(3)	41(2)
C(12)	2420(9)	867(6)	5725(3)	42(2)
C(13)	1504(9)	1511(5)	5449(3)	37(2)
C(14)	3783(10)	−641(6)	5930(3)	56(2)
C(15)	1022(10)	2377(5)	5740(3)	54(2)
C(21)	1162(8)	−551(5)	3531(3)	37(2)
C(22)	77(8)	291(5)	3444(3)	36(2)
C(31)	2027(9)	1434(5)	−354(3)	37(2)
C(32)	638(9)	1761(5)	−656(3)	39(2)
C(33)	−912(9)	1695(5)	−516(3)	37(2)
C(34)	3602(9)	1511(6)	−633(3)	51(2)
C(35)	−2222(9)	2029(6)	−897(3)	51(2)
C(41)	662(8)	115(5)	1515(3)	34(2)
C(42)	−1175(8)	96(5)	1433(3)	32(2)
C(51)	1702(11)	−3854(6)	2129(4)	65(3)
C(52)	−958(13)	−3704(7)	2674(5)	99(4)
C(61)	−5108(10)	−1577(8)	2121(3)	77(3)
C(62)	−5068(9)	−2444(6)	3093(3)	60(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

may be described as square planar with slight tetrahedral distortions of less than 0.09 Å. The two mean coordination planes are far from being coplanar with a dihedral angle of 110 .7(1)°. The intramolecular $Cu_1\cdots Cu_2$ distance is equal to 9.779(3) Å. The manganese atom is six-coordinated by four oxamato oxygen atoms and two oxygen atoms from the $(CH_3)_2SO$ molecules, but the coordination polyhedron is far from having the ideal octahedral geometry. It may be noted that one of the dmso molecules is found to be disordered. It is satisfactorily modeled as a 2-fold disorder of the S atom with site occupancies of 85% for S(1) and 15% for S(11). The two dmso molecules adopt a cis geometry with a O(5)−Mn−O(6) angle of 85.8(2)°. The two oxamato groups ($O_2C-C(O)N$) are almost planar, and the dihedral angle between the related planes is equal to 100.2(2)°. Identical separations of 5.464(2) Å are observed between the Cu_i ($i = 1, 2$) ions and the central Mn ion.

The angles between the mean coordination planes of the Cu atoms and the related oxamato planes are 6.84(2)° for the subunit 1 and 8.27(2)° for the subunit 2. This results in deviations of the Cu atoms from the related oxamato planes equal to 0.168(7) (subunit 1) and 0.197(7) Å (subunit 2) while the Mn atom is removed from these planes by 0.060(7) and 0.128(7) Å, respectively.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**

Cu(1)−O(1)	1.878(5)	O(1)−C(13)	1.303(8)
Cu(1)−N(2)	1.893(6)	O(2)−C(22)	1.281(8)
Cu(1)−N(1)	1.931(6)	O(3)−C(33)	1.315(8)
Cu(1)−O(2)	2.024(5)	O(4)−C(42)	1.267(8)
Cu(2)−O(3)	1.875(5)	O(21)−C(21)	1.270(8)
Cu(2)−N(4)	1.903(6)	O(22)−C(22)	1.252(8)
Cu(2)−N(3)	1.934(5)	O(41)−C(41)	1.261(8)
Cu(2)−O(4)	2.027(4)	O(42)−C(42)	1.258(7)
Mn−O(21)	2.164(5)	N(1)−C(11)	1.315(9)
Mn−O(5)	2.184(5)	N(2)−C(21)	1.292(8)
Mn−O(41)	2.189(5)	N(3)−C(31)	1.297(8)
Mn−O(6)	2.190(5)	N(4)−C(41)	1.304(8)
Mn−O(42)	2.205(4)	C(41)−C(42)	1.541(9)
Mn−O(22)	2.240(5)	S(2)−O(6)	1.494(5)
S(1)−O(5)	1.512(5)		
O(1)−Cu(1)−N(2)	177.9(2)	N(4)−Cu(2)−O(4)	82.8(2)
O(1)−Cu(1)−N(1)	97.1(2)	N(3)−Cu(2)−O(4)	166.1(2)
N(2)−Cu(1)−N(1)	83.9(2)	O(21)−Mn−O(5)	86.2(2)
O(1)−Cu(1)−O(2)	96.3(2)	O(21)−Mn−O(41)	95.9(2)
N(2)−Cu(1)−O(2)	82.8(2)	O(5)−Mn−O(41)	90.7(2)
N(1)−Cu(1)−O(2)	166.5(2)	O(21)−Mn−O(6)	99.2(2)
O(3)−Cu(2)−N(4)	175.6(2)	O(5)−Mn−O(6)	85.8(2)
O(3)−Cu(2)−N(3)	96.7(2)	O(41)−Mn−O(6)	164.2(2)
N(4)−Cu(2)−N(3)	84.5(2)	O(21)−Mn−O(42)	166.5(2)
O(3)−Cu(2)−O(4)	96.5(2)	O(5)−Mn−O(42)	105.1(2)
O(41)−Mn−O(42)	76.9(2)	S(1)−O(5)−Mn	123.4(3)
O(6)−Mn−O(42)	89.0(2)	S(2)−O(6)−Mn	138.6(3)
O(21)−Mn−O(22)	76.3(2)	S(2)−O(6)−Mn	138.6(3)
O(5)−Mn−O(22)	161.9(2)	C(21)−O(21)−Mn	113.8(4)
O(41)−Mn−O(22)	95.6(2)	C(22)−O(22)−Mn	112.9(5)
O(6)−Mn−O(22)	92.4(2)	C(41)−O(41)−Mn	112.6(4)
O(42)−Mn−O(22)	92.8(2)	C(42)−O(42)−Mn	113.9(4)

The Cu−N, Cu−O, C−C, C−N, and C−O bond lengths and the related angles do not significantly differ from the values observed in similar complexes[19] and deserve no particular comment. As is generally the case, the diamino chains $N-(CH_2)_2-N$ adopt a gauche conformation with torsion angles of 28.0(8)° and 36.6(8)° in the subunits 1 and 2, respectively.

Short intermolecular metal separations of 3.712(1) Å for $Cu_1..Cu_1(-x+1,-y+1,-z+1)$ and 3.581(1) Å for $Cu_2\cdots Cu_2$ $(-x+1,-y+1,-z)$ lead to the formation of a chain-like packing pattern parallel to the *c*-axis.

Physical Characterization of the Complexes. In the present case the positive FAB gives information about the skeleton of the trinuclear $(CuL)_2Mn$ species but does not give any information concerning solvent molecules. In fact samples prepared from **1**−**6** give superimposable spectra. The observation of a signal at $m/e = 604$ ($[(CuL)_2Mn + 1]^+$) confirms the presence of the $(CuL)_2Mn$ unit in each case.

The thermogravimetric analysis confirms that solvent molecules are involved in the structure of the six complexes. For **5** and **6** the loss of two dmso and four py molecules respectively occurs in the 150−220 °C range. In the $(CuL)_2Mn\cdot xH_2O$ series, the data lead to an evaluation of *x* consistent with the analytical results. More interestingly, we note that the dehydration process occurs in several steps. For the four complexes, one molecule is lost above ca. 220 °C. Below 200 °C, we observe for **1** and **4** two overlapping signals at 105 and 135 °C corresponding to the loss of 4 (2 + 2) and 3.5 (2 + 1.5) water molecules, respectively, and for **2** one single signal at 135 °C corresponding to the loss of 2 water molecules. These data suggest that the water molecules involved in the structure of the complexes belong to different types: lattice water, water coordinated to the Cu and/or Mn ions, and water hydrogen bonded to the ligand L or to another H_2O molecule. These possibilities have been clearly demonstrated by a structural study of the closely related complex $[NaCuL]_3\cdot 4H_2O$.[19]

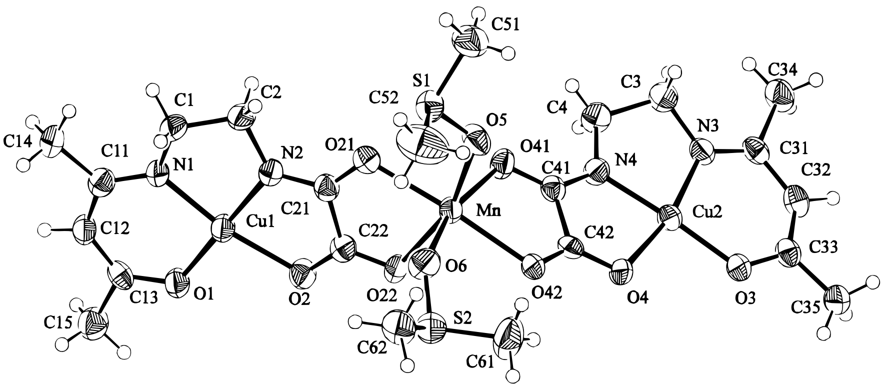

Figure 1. ORTEP[24] drawing showing the numbering scheme and the thermal ellipsoids drawn at the 50 % level of probability. Labeling of the hydrogen atoms as well as the disordered sulfur of minor occupational value have been omitted for clarity.

Recent works[9–11,15] have stressed the importance of UV–visible spectroscopy with regard to the characterization of bimetallic Cu/Mn complexes. The spectra of the title complexes in the solid phase display three absorptions occurring in the 540–600, 404–415, and 360–370 nm ranges, respectively. According to the data reported in the literature,[9–11,15,19] the broad absorption at 600–580 nm for **1**, **4**, and **6** is attributable to a copper ion in square pyramidal chromophore CuN_2O_3 (**1**, **4**) or CuN_3O_2 **(6)** while the absorption at 550–540 nm for **2**, **3**, and **5** is characteristic of a square planar copper(II) ion surrounded by two oxygen and two nitrogen atoms. So, complexes **1** and **4** possess a water molecule on each copper center while pyridine replaces water for **6**. These water or pyridine molecules are loosely tightened to copper for dissolution of **5** and **6** in acetone gives a violet solution with a d–d transition at 550 nm. The sharp absorption peaking in the 404–415 nm range is generally related to a spin-forbidden transition of a six-coordinated manganese ion. As for the third band which is absent from the $(CuL)_2Zn$ and $(CuL)_2Co$ spectra, it is tentatively attributed to a ligand to metal charge-transfer absorption. This LCT band has a feeble intensity as does the band at 408 nm in the case of **4**.

Considered together, the thermogravimetric and spectroscopic data suggest that the H_2O molecules directly bonded to the copper ions are lost below 200 °C together with the lattice and hydrogen bonded molecules. The molecule leaving above 220 °C would be bonded to the manganese ion. Indeed complex **3** only contains one water molecule which is lost above 220 °C and, according to the position of the related d–d transition, is not bonded to a copper ion. In this instance, to reach the six-coordination suggested by the electronic spectrum, the manganese ion has to find a supplementary donor which can be only supplied by another $(CuL)_2Mn$ entity since the donor centers available within one molecular unit are restricted to five oxygen atoms, four from the two $(CuL)^i$ subunits and one from the water molecule. The net result would be the formation of a chain-like structure. This conclusion could be extended to all of the members of the $(CuL)_2Mn{\cdot}xH_2O$ series if we admit that the one water molecule leaving above 220 °C is bonded to the manganese ion. However, the possibility of a five-coordinated manganese ion cannot be completely discarded on the basis of the spectral data since absorptions centered at ca. 410 nm have been reported for various MnO_5 chromophore.[25]

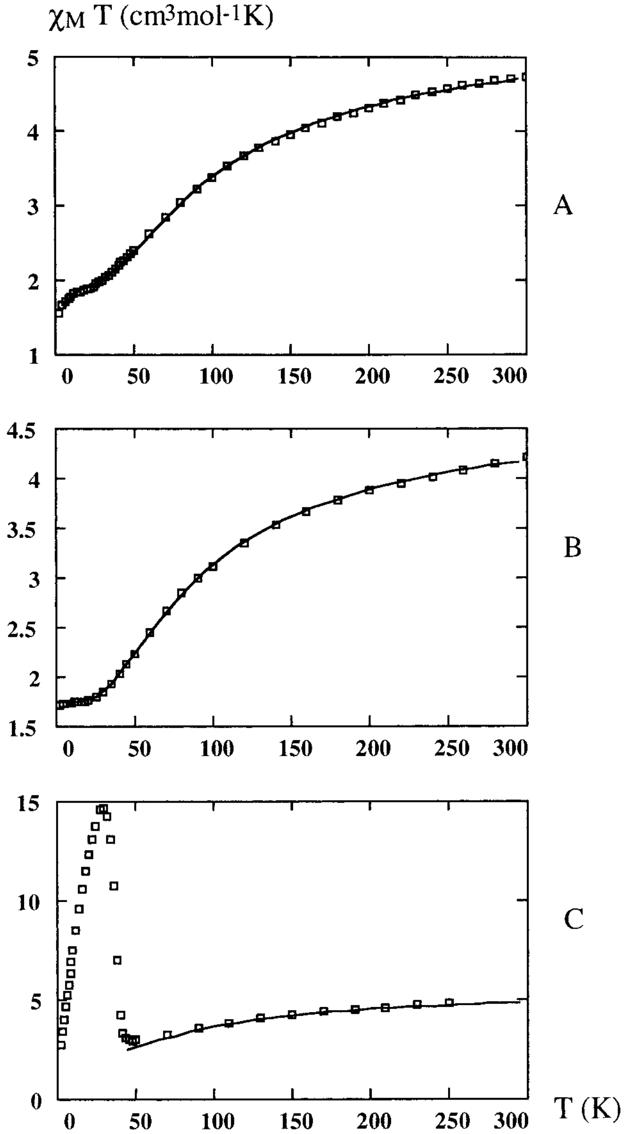

Figure 2. Thermal variation of χ_MT for **1** (A), **6** (B), and **4** (C). The full lines correspond to the best data fits (see text).

Magnetic Studies. Complexes **1**–**3**, **5**, and **6** display very similar magnetic properties. The thermal variations of χ_MT for **1**, **4,** and **6** are represented in Figure 2. For the five complexes, the room temperature value of χ_MT is slightly below the value (5.12 cm^3 K mol^{-1}) that would be anticipated for two isolated Cu(II) ions and one isolated Mn(II) ion. On lowering of the temperature χ_MT continuously decreases and around 20 K reaches a plateau ($\chi_MT = 3.0$ cm^3 K mol^{-1}). This behavior is strongly reminiscent of that previously reported for the trinuclear (Cu_2Fe) complexes.[17,18] It results from an intramolecular antiferromagnetic coupling of the two spin $^1/_2$ Cu(II) ions with

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(25) Inada, Y.; Sugimoto, K.; Ozutsumi, K.; Funahashi, S. *Inorg. Chem.* **1994**, *33*, 1875

Table 4. Parameters Resulting from Fitting of the Magnetic Data

compd	J	θ	g_{Cu}	g_{Mn}	R
1	−33.8(5)	−0.82(5)	2.11(1)	2.065(1)	1×10^{-4}
2	−31.8(6)	−1.13(9)	2.12(1)	2.079(2)	2×10^{-4}
3	−29.4(2)	−0.58(2)	2.02(1)	1.974(5)	2×10^{-4}
5	−32.8(3)	−1.2(1)	2.11(1)	2.060(2)	3×10^{-4}
6	−30.3(1)	0	2.03(1)	1.932(2)	3×10^{-4}

the spin $^5/_2$ Mn(II) ion to yield an $S = {}^3/_2$ ground state which is separated from the neighboring $S = {}^5/_2$ state by an energy gap equal to $^5/_2J$.

$\chi_M T$ is perfectly constant from 20 to 4 K in the case of **6** while a further decrease is observed below ca. 10 K for the other complexes. That behavior could be due to a splitting in zero field of the ground state. However, there is no obvious reason why this effect would not be detectable for complex **6**. Otherwise, the five complexes have very similar EPR spectra which at 90 and 4 K are devoid of any fine structure. Finally the decrease of $\chi_M T$ at low temperature most probably originates in small intermolecular interactions.

The experimental data are reasonably well represented by the following equation:[26]

$$\chi_M T = \frac{N\beta^2}{4k}\frac{T}{T-\theta}[35{g_{5/2,0}}^2 + 35{g_{5/2,1}}^2 \exp(-J/kT) + 10{g_{3/2,1}}^2 \exp(-7J/2kT) + 84{g_{7/2,1}}^2 \exp(5J/2kT)]/[3 + 3\exp(-J/kT) + 2\exp(-7J/2kT) + 4\exp(5J/2kT)]$$

N, β, and k have their usual meanings. J is the equivalent parameter characterizing the magnetic interaction between each copper ion and the manganese ion while a Weiss correction θ is introduced to account for any additional interaction. The Zeeman factors associated with the different spin states are expressed in terms of the local factors g_{Mn} and g_{Cu}: $g_{5/2,0} = g_{Mn}$; $g_{5/2,1} = (31g_{Mn} + 4g_{Cu})/35$; $g_{3/2,1} = (7g_{Mn} - 2g_{Cu})/5$; $g_{7/2,1} = (5g_{Mn} + 2g_{Cu})/7$. Least-squares fitting of the experimental $\chi_M T$ values provides an estimate of the parameters J, θ, g_{Mn}, and g_{Cu} and the agreement factor ($R = \sum(\chi_{obs}T - \chi_{calc}T)^2/\sum(\chi_{obs}T)^2$). They are quoted in Table 4.

The five complexes display similar J and θ values. The copper−manganese coupling constants (from −29.4 to −33.8 cm^{-1}) compare well with the values (from −23.4 to −36.6 cm^{-1}) previously reported for polynuclear complexes involving Cu(II) and Mn(II) ions bridged by oxamido or oxamato groups.[1,6,9−11,13,15,17]

The θ term is small and even equal to 0 (within the experimental uncertainty) for **6** so that the five complexes behave as if they involve quasi-isolated trinuclear units. That conclusion is reinforced by the fact that θ eventually comprises a contribution from the interaction between the terminal copper ions which is not explicitly included in the above equation. From a study of the complex (CuL)$_2$Zn,[19] that antiferromagnetic interaction is at best equal to 1 cm^{-1}. It may be noted that the structural data obtained for **(5)** point to short Cu···Cu intermolecular contacts leading to a (Cu−Mn−Cu−Cu−Mn−Cu)$_n$ chain structure[27] while the magnetic properties are well represented by a model involving quasi-isolated trinuclear units. This apparent inconsistency likely results from the absence of a bridging element between the trinuclear units so that the intermolecular interaction may be dipolar in nature and, owing to the interunit separation, of feeble intensity. Similarly the possibility of chain-like structure suggested by the spectroscopic data for **1**, **2**, and **3** is not supported by the magnetic results, which are in favor of isolated trinuclear (CuL)$_2$Mn species.

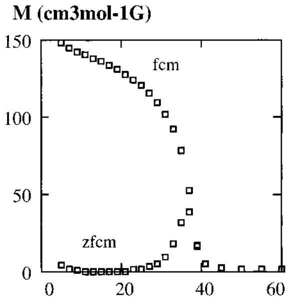

Figure 3. Zero-field-cooled magnetization ZFCM and field-cooled magnetization (fcm, H = 4 G) *vs* T for **4**.

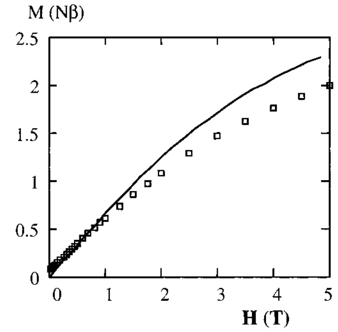

Figure 4. Field dependence of the magnetization for **4** at 5 K. The solid line corresponds to a $S_T = {}^3/_2$ ground state with a g-factor equal to 2.

Interestingly the magnetic behavior of **4** differs widely from that of the related complexes **1**, **2**, and **3**. The temperature dependence of $\chi_M T$ is represented in Figure 2C. At a temperature of 250 K and an applied field of 1000 G, $\chi_M T$ is equal to 4.87 cm^3 K mol^{-1}. This value is slightly lower than the one (5.12 cm^3 K mol^{-1}) expected for three isolated ions (2 Cu, 1 Mn). Upon cooling down, $\chi_M T$ slowly decreases to reach a rounded minimum of 2.96 cm^3 K mol^{-1} at 48 K. The data obtained in the 250−50 K temperature range are well represented by the model used previously used for complexes **1**, **2**, **3**, **5**, and **6** i.e., insulated trinuclear (Cu, Mn, Cu) units with antiferromagnetic exchange coupling between the Mn and Cu ions ($J = -30.4$ cm^{-1}, $g_{Cu} = 2.11$, $g_{Mn} = 2.06$, $R = 5 \times 10^{-4}$). Below 48 K, $\chi_M T$ increases sharply, suggesting the onset of a ferromagnetic order. At 30 K, $\chi_M T$ shows a maximum value of 14.65 cm^3 K mol^{-1}, which is large compared with the corresponding value (7.87 cm^3 K mol^{-1}) expected for the largest total spin ($S_T = {}^7/_2$) of a (Cu, Mn, Cu) unit.

To confirm the magnetic phase transition the temperature dependence of the magnetization was investigated. The results are represented in Figure 3. The field-cooled magnetization data (fcm) at 4 G shows the usual feature of a ferromagnetic transition,[28] i.e., an abrupt increase of M below 40 K and a break in the curve around $T_c = 37$ K. We have also measured M by cooling the sample down to 4 K in zero field, then applying the field of 4 G and heating up (zero-field-cooled magnetization, zfcm). The zfcm exhibits a maximum around T_c as expected for a polycrystalline ferromagnet.[29] The field dependence of the magnetization at 5 K (cf. Figure 4) shows that saturation is not completely reached in the maximum field available (5 T).

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(26) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(27) An example of a (Cu−Mn−Cu−Cu−Mn−Cu)$_n$ polynuclear complex has been reported: Pei, Y.; Kahn, O.; Sletten, J. *J. Am. Chem. Soc.* **1986**, *108*, 3143.

(28) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.

(29) Hitzfeld, M.; Ziemann, P.; Buckel, W. *Phys. Chem. Rev.* **1984**, *29*, 5023.

However extrapolation of the experimental data suggests that the magnetization saturation is, at best, equal to $2.2N\beta$ and therefore significantly smaller than the value expected for a $S_T = {}^3/_2$ system. Finally cycling the magnetic field between 7000 and −7000 G yields a characteristic hysteresis loop with a very feeble remnant magnetization of $0.025N\beta$ and a coercive field of 400 G.

Considered together, the experimental data obtained for **4** confirm that a magnetic transition occurs in the low-temperature range ($T_c = 37$ K). In addition they support the view of a canting process in the ordered magnetic state leading to weak ferromagnetism. Otherwise the magnetic behavior of **4** in the high temperature regime is almost identical to those displayed by **1**, **2**, **3**, **5**, and **6** in the whole temperature range.

The lack of structural data prevents any conclusive discussion to be done about the origin of the magnetic behavior of **4**. Indeed as mentioned previously, thermogravimetric and spectroscopic arguments could suggest that the ordering in **4** originates in an antiferromagnetic interaction between Cu^{2+} and Mn^{2+} ions of different (Cu, Mn, Cu) units through oxygen atoms from the ligand. However, the packing observed in **5** (Figure S1, Supporting Information) would seemingly favor another possibility, i.e., a ferromagnetic interaction between copper ions belonging to different trinuclear units. Such interactions have been previously mentioned in the literature.[30]

Acknowledgment. We thank Dr. A. Mari for his contribution to the magnetic measurements and Dr. A. Bousseksou for providing the fitting program used in this work. The suggestion provided by one of the reviewers, concerning the magnetic behavior of complex **4**, is also gratefully acknowledged.

Supporting Information Available: A PLUTON drawing (Figure S1) depicting the linear chain running in the direction of the *c*-axis (1 page). The X-ray crystallographic file for $(CuL)_2Mn\cdot 2dmso$, in CIF format, is available. Ordering and access information is given on any current masthead page.

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(30) Villa, J. F.; Hatfield, W. E. *J. Chem. Phys.* **1971**, *55*, 4758.