Crystal Structure and Magnetic Properties of a New Hetero-Dinuclear $Cu^{II}Mn^{II}$ Schiff Base Complex

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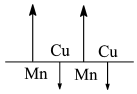
Z. Naturforsch. **58b,** 271 – 277 (2003); received November 15, 2002

$Mn[Cu(L)(O_2CMe)_2]\cdot H_2O$ (L = N,N'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane) was synthesized and the crystal structure determined. $(C_{23}H_{26}CuMnN_2O_8).H_2O$, monoclinic, space group $P2_1/c$, $a = 12.017(3)$, $b = 8.217(3)$, $c = 24.786(4)$ Å, $\beta = 92.10(2)^\circ$, $V = 2446(1)$ Å^3, $Z = 4$. The crystal structure consists of ordered dinuclear units with Cu^{II} and Mn^{II} ions bridged by two oxygen atoms of the Schiff base ligand. The Cu^{II} coordination sphere is a slightly distorted square-plane formed by the N_2O_2 donor set of the Schiff base ligands. The average Cu—O and Cu—N distances are 1.920(1) and 1.957(4) Å, respectively. The coordination around the Mn^{II} ion is a distorted tetrahedron with the donor oxygen atoms of the Schiff base ligands and oxygen atoms of the acetate anions. The Cu···Mn separation is 3.327(4) Å. There is also one non-coordinating water molecule in the crystal structure. The χ and χT versus T plots, χ being the molar magnetic susceptibility per $Cu^{II}Mn^{II}$ unit and T the temperature, has been measured in the 4.9 – 301 K temperature range. The values of the interaction parameters are $J = -28.3$ cm^{-1}, $g_{Mn} = 2.01$, $g_{Cu} = 2.07$. This indicates an intramolecular antiferromagnetic interaction between Cu^{II} and Mn^{II} ions.

Key words: Hetero-Dinuclear $Cu^{II}Mn^{II}$ Complex, Super-Exchange Interactions, Antiferromagnetic Interaction

Introduction

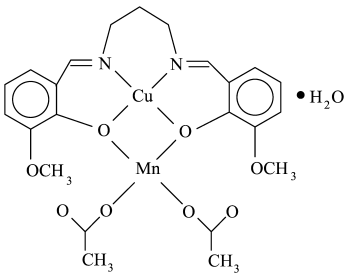
Hetero-dinuclear metal complexes have been less studied compared with homo-dinuclear complexes, in spite of the great interest in their properties arising from the presence of two dissimilar metal ions in close proximity. So far, considerable attention has been paid to magnetic interactions between two different metal ions, and such studies have served for understanding the spin-exchange mechanism in antiferro- or ferromagnetic coupling [1,2]. One of the first mechanisms to design molecular ferromagnets has been suggested by McConnell as early as 1963 [3]. This mechanism is the following: A molecular magnetic entity may exhibit a region 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 coupling. McConnel when proposing this approach had in mind purely organic compounds. The noncompensation of the spin densities may then arise from spin polarization effects [4]. However, the molecular units we refer to can be inorganic complexes as well. The antiferromagnetically coupled heterobinuclear species are obvious examples of molecular entities with noncompensating spin densities, as emphasized by a polarized neutron diffraction study of a $Ni^{II}Cu^{II}$ pair [5]. This noncompensation is particularly pronounced for the strongly coupled $Cu^{II}Mn^{II}$ entities with the local spins $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$. In this case, the ground state may be schematically drawn as:



In the absence of any interaction, a 1 D magnetic ordering is expected at 0 K, with a divergence of the

product χT, χ being here the molar susceptibility per $Cu^{II}Mn^{II}$ unit. This behavior may be defined as an one-dimensional ferrimagnetism. In fact, when the molecular entities with a magnetic ground state or the ferromagnetic chains are assembled within the crystal structure, intermolecular or interchain interactions are created. Even if these interactions are very weak as compared to the intramolecular or intrachain interactions, they lead to the onset of a magnetic order at non-zero temperatures. This order may be antiferromagnetic or ferromagnetic; most often it is antiferromagnetic. The problem at hand is to succeed in favoring the ferromagnetic ordering. Achieving an intermolecular or interchain ferromagnetic interaction is obviously very problematic. The factors governing the molecular packing are extremely subtle and difficult to control.

In this study, we have synthesized a hetero-dinuclear $Cu^{II}Mn^{II}$ complex, $Mn[Cu(L)(O_2CMe)_2]\cdot H_2O$ (L=N,N'-bis(2-hydroxy-3- methoxybenzylidene)-1,3-diaminopropane) and determined its crystal structure by X-ray diffraction. We have measured magnetic susceptibilities in the temperature range 4.9 – 301 K using a SQUID magnetometer to investigate the relationship between the magnetic properties and the molecular structure, i.e. the magnetic interaction between the Cu^{II} and Mn^{II} ions.

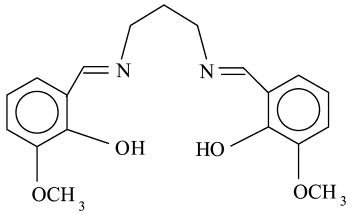


Experimental Section

Preparation

The hetero-dinuclear $Cu^{II}Mn^{II}$ complex, $Mn[Cu(L)(O_2CMe)_2]\cdot H_2O$ (L = N,N'-bis(2-hydroxy-3-meythoxybenzylidene)-1,3-diaminopropane) was prepared in two steps. At first, the Schiff base ligand was synthesized by reaction of 1,3-diaminopropane and 2-hydroxy-3-methoxy-benzaldehyde in a 1:2 molar ratio at room temperature. The Schiff base was obtained in the form of yellow crystals. The Schiff base ligand (1 mmol, 0.34 g) in hot methanol (50 ml) and a solution of $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol, 0.20 g) in hot methanol (40 ml) were then added. The green crystalline powder of [N,N'-bis(2-hydroxy-3-methoxybenzlidene)-1,3-diaminopropane]copper(II) (M) was filtered off and dried in an oven at 343 K.

In a second step, the powder of the Cu(II) monomer (M) (0.5 mmol, 0.02 g) was dissolved in 30 ml of dimethylformamide (dmf) and heated to the boiling point. $Mn(CH_3COO)_2$ (0.5 mmol, 0.008 g) in 30 ml of methanol was added and heated under reflux for 3 h. The resulting mixture was set aside for 3 d and the prismatic light green crystals which formed were filtered off and washed with cold ethanol.



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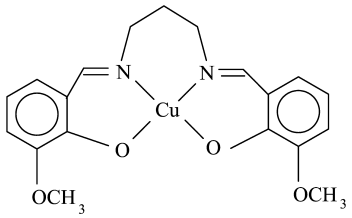


(M)

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [7] using a single crystal with dimension $0.30 \times 0.25 \times 0.20$ mm^3 with a graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections ($2.30 \leq \theta \leq 9.20$) carefully centered on the diffractometer. The standard reflections ($\bar{1}$ 0 0, 1 $\bar{2}$ 3, 1 $\bar{2}$, $\bar{3}$) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. A total of 5158 reflections was recorded, with Miller indices $h_{min} = -14$, $h_{max} = 1$, $k_{min} = -10$, $k_{max} = 0$, $l_{min} = -30$, $l_{max} = 30$. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [6]. The structure was solved by SHELXS-97 [7] and refined with SHELXL-97 [8]. The relatively high residual in the difference Fourier map can be attributed to the disorder of C10 in the propanediamine chelate ring in the compound. The C10 atoms were split into C10a and C10b with site occupation factors 0.58(2) and 0.42(2), respectively. Recently, we reported the crystal structures of [N,N'-bis(5-bromosalicylidene)-1,3-diaminopropane]nickel(II) and [N,N'-bis(5-chlorosalicylidene)-1,3-diaminopropane]copper(II) [9]. The same disorder as in the title compound was also observed in those

Table 1. Crystallographic data.

Sum formula	$(C_{23}H_{26}CuMnN_2O_8)\cdot H_2O$
f_w (g.mol^{-1})	595.01
Space group	$P2_1/c$
$a = 12.017(3)$ Å	$\alpha = 90^\circ$
$b = 8.217(3)$ Å	$\beta = 92.10(2)^\circ$
$c = 24,\ 786(4)$ Å	$\gamma = 90^\circ$
Vol [Å^3]	2446(1)
Z	4
D_{calc}(g.cm^{-3})	1.616
μ[cm^{-1}]	1.368
$F(000)$	1224
Index ranges	$-14 \le h \le 1,\ -10 \le k \le 0,$ $-30 \le l \le 30$
Reflection collected	5158
Independent reflection	4783 $[R(\text{int}) = 0.027]$
Data / restraints / parameters	3116 / 0 / 337
Goodness-of-fit on F^2	1.025
Final R indices $[I > 2\sigma(I)]$	$R = 0.0456$, $wR = 0.1193$
Final R indices for all data	$R = 0.0681$, $wR = 0.1312$
Largest diff. peak and hole	0.845 and -0.617 e.Å^3

compounds. C10a and C10b atoms were refined isotropically. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. The hydrogen atoms of the water molecule were located in the difference Fourier maps calculated at the end of the refinement process as a small positive electron density and were not refined. The final positional parameters are presented in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 195386 [10].

Susceptibility measurements

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 in the temperature range 4.9 – 301 K. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constant [11]. The applied field was 2 T. The effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828\chi T^{1/2}$, where χ is the magnetic susceptibility per $Cu^{II}Mn^{II}$.

Discussion

X-ray crystal structure

An ORTEP representation of the structure including the atomic numbering scheme is given in Fig. 1 [12]. Selected bond lengths and angles are summarized in Table 3. The Cu(II) and Mn(II) ions are bridged by

Table 2. Atomic coordinates and equivalent isotropic displacement parameters.

Atom	x	y	z	$U(eq)$
C1	0.6916(4)	0.4351(7)	0.4945(2)	0.0689(14)
C2	0.8750(4)	0.3230(5)	0.49803(17)	0.0462(10)
C3	0.8984(4)	0.3827(6)	0.54901(19)	0.0585(12)
C4	0.9997(5)	0.3447(7)	0.57524(19)	0.0658(14)
C5	1.0759(4)	0.2525(6)	0.55032(19)	0.0590(12)
C6	1.0543(4)	0.1957(5)	0.49743(17)	0.0473(10)
C7	0.9529(3)	0.2300(5)	0.47093(15)	0.0412(9)
C8	1.1415(4)	0.1088(6)	0.4722(2)	0.0499(11)
C9	1.2517(4)	−0.0208(7)	0.4110(2)	0.0697(14)
C10a	1.2499(8)	−0.1276(13)	0.3646(4)	0.069(4)
C10b	1.2719(11)	−0.0084(18)	0.3490(5)	0.064(5)
C11	1.2086(6)	−0.0706(12)	0.3144(3)	0.123(3)
C12	1.0403(5)	−0.0619(7)	0.2643(2)	0.0658(14)
C13	0.9268(4)	−0.0384(5)	0.24832(18)	0.0549(12)
C14	0.8922(5)	−0.0833(6)	0.1950(2)	0.0665(14)
C15	0.7848(6)	−0.0670(7)	0.1781(2)	0.0735(16)
C16	0.7067(5)	−0.0038(7)	0.21168(19)	0.0644(14)
C17	0.7385(4)	0.0455(6)	0.26320(18)	0.0533(11)
C18	0.8488(4)	0.0259(5)	0.28244(17)	0.0478(10)
C19	0.5574(4)	0.1440(9)	0.2826(2)	0.0863(18)
C20	0.7192(5)	0.5012(7)	0.3422(2)	0.0686(15)
C21	0.7080(6)	0.6697(7)	0.3186(2)	0.0826(18)
C22	0.5952(4)	−0.0115(7)	0.4254(2)	0.0612(12)
C23	0.5540(5)	−0.1657(7)	0.4476(3)	0.0839(18)
N1	1.1440(3)	0.0549(5)	0.42343(15)	0.0484(9)
N2	1.0889(4)	−0.0311(5)	0.31034(17)	0.0639(11)
O1	0.7773(3)	0.3472(4)	0.46924(12)	0.0569(8)
O2	0.9273(2)	0.1792(4)	0.42142(11)	0.0456(7)
O3	0.8741(2)	0.0699(4)	0.33296(11)	0.0530(7)
O4	0.6692(3)	0.1124(5)	0.29970(13)	0.0641(9)
O5	0.8112(4)	0.4298(5)	0.33999(16)	0.0849(12)
O6	0.6437(4)	0.4351(5)	0.36450(19)	0.0955(14)
O7	0.5264(5)	0.0885(7)	0.4095(3)	0.145(2)
O8	0.6946(3)	0.0078(6)	0.42281(15)	0.0874(13)
O9	0.4313(4)	0.3898(8)	0.4072(2)	0.1036(18)
Cu1	1.01525(4)	0.05985(6)	0.37243(2)	0.04384(17)
Mn1	0.75950(5)	0.20787(8)	0.38384(3)	0.0463(2)

the phenolic oxygens atoms, O2 and O3. The Cu…Mn separation is 3.327(4) Å.

The copper ion is coordinated by two imine N atoms and two phenolate O atoms from the imine-phenolate ligand in a slightly distorted square-planar coordination geometry. The atom with the greatest deviation from the coordination plane Cu1, N1, O2, N2 and O3 is O2 at 0.112(2) Å. The deviation of Cu1 from the least-squares plane of N_2O_2 is only −0.034(2) Å. The average Cu – O and Cu – N distances are 1.920(1) and 1.957(4) Å, respectively. These distances are in the range of those of conventional Schiff base copper(II) complexes of square-planar coordination [9, 13, 14].

The Mn(II) ion has a distorted tetrahedral coordination, which is not common for Mn(II) complexes. Generally, monomeric and dimeric Mn(II) complexes

Table 3. Selected bond length [Å] and angles [°].

Cu1—N1	1.962(4)	Mn1—O2	2.202(4)
Cu1—N2	1.952(4)	Mn1—O3	2.213(4)
Cu1—O2	1.910(3)	Mn1—O5	2.223(4)
Cu1—O3	1.929(3)	Mn1—O8	2.073(4)
O2—Cu1—O3	78.7(1)	O2—Cu1—N2	167.3(2)
O3—Cu1—N2	91.9(2)	O2—Cu1—N1	92.4(1)
O3—Cu1—N1	170.3(1)	N2—Cu1—N1	97.5(2)
O8—Mn1—O5	174.1(1)	O2—Mn1—O3	66.9(1)
O3—Mn1—O8	96.4(1)		
Cu1—O2—Mn1	107.8(1)	Cu1—O3—Mn1	106.7(1)
Cu1—O2—Mn1	107.8(1)	Cu1—O2—Mn1	107.8(1)

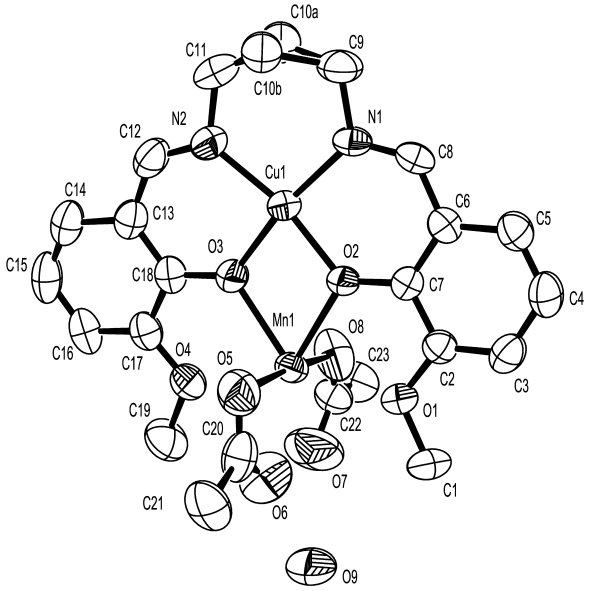


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms have been omitted for clarity.

possess a distorted octahedral coordination [15 – 18]. The average distance between the Mn(II) ion and O atoms of the Schiff base ligand is 2.208(1) Å. The bond distances Mn1–O5 and Mn1–O6 are 2.223(4) and 2.073(4) Å, respectively. The Cu1–O2–Mn1 and Cu1–O3–Mn1 bridging angles are 107.8(1) and 106.7(1)^o, respectively. The bridging plane containing Cu1, O2, Mn1, O3 is planar. The torsion angles N1–Cu1–O2–Mn1 and N2–Cu1–O3–Mn1 are −176.6(4) and −171.0(4)°. The coordination bond distances and angles are in good agreement with the values found in similar complexes [19, 20].

The unique half of the Schiff base ligands of the complex is reasonably planar. The maximum deviation from the plane defined by atoms C1, O1, C2–C9, N1 and O2 is 0.092(4) Å for C9 and for the atoms C19, O4, C11–C18, N2 and O2 it is 0.047(5) Å for C19. However, the entire ligand is not exactly planar since the two halves are twisted with respect to one another. The least-squares planes through each half of the molecule are inclined at an angle of 8.7(2)° in the complex. The atoms Cu1, N1, C9, C10 (C10 is disordered atom, split to C10a and C10b), C11 and N2 form a six-membered chelate ring of chair conformation. The atom with the greatest deviation from the CuN_2O_2 plane is C10a at −0.544(8) Å. There is a non-coordinating water molecule in the crystal structure. This molecule and the complex are linked *via* intermolecular hydrogen bonds O9–H···O6 [2.824(7) Å] and O9–H···O7 [2.726(8) Å] between the O atom of the water molecule and the O atoms of the acetate anions.

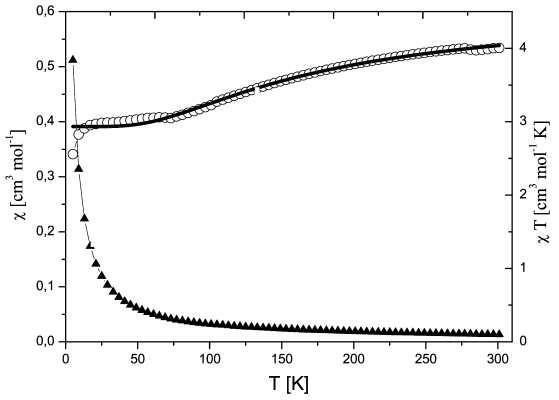


Fig. 2a. The magnetic susceptibilities χ (▲) and χT (○) product *versus* T plots.

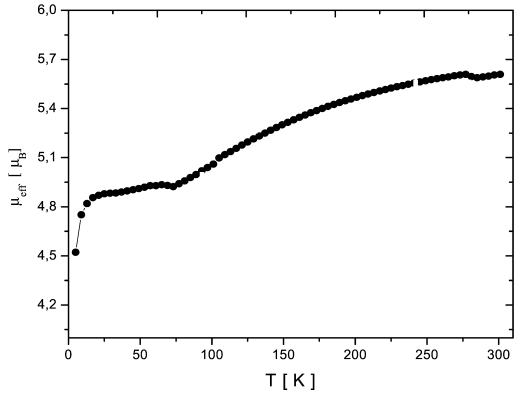


Fig. 2b. Magnetic moment per $Cu^{II}Mn^{II}$ *vs.* temperature curve.

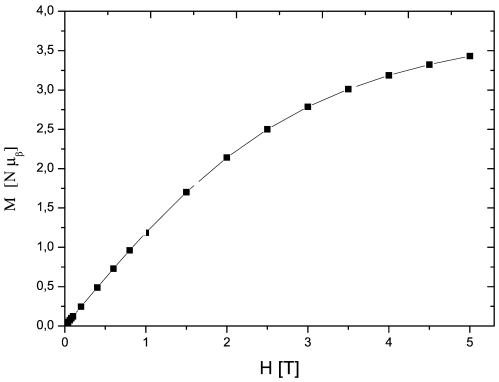
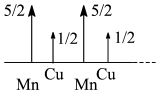


Fig. 3. The magnetization *versus* field curve at 4.2 K.

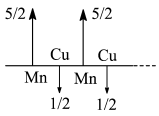
Magnetic properties

The magnetic susceptibilities and χT product are shown as a function of temperature in Fig. 2a. The magnetic moments are shown as a function of temperature in Fig. 2b. The field dependence of magnetization measured at 4.2 K is given in Fig 3.

The χT product of the complex at room temperature is approximately 4.0 cm^3 mol^{-1} K and decreases as the temperature is lowered. It reaches an approximate plateau between 73 and 23 K with about χT = 3.1 cm^3 mol^{-1} K and finally decreases rapidly upon further cooling. This behavior indicates an antiferromagnetic interaction between the Cu(II) and Mn(II) ions. The plateau indicates that only the quintet ground state is thermally populated below 73 K, and the rapid decrease below 23 K may be due to secondary effects such as an antiferromagnetic interaction and/or the zero-field splitting effect, which are operative only at very low temperature. Indeed, according to this qualitative approach when extrapolating χT towards high temperatures, one obtains the paramagnetic limit corresponding to uncoupled Mn(II) and Cu(II) ions. Upon cooling down from 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 χT 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



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

The magnetic data were fitted on the basis of the isotropic Heisenberg model $\mathbf{H} = -\mathbf{2JS_1.S_2}$, where J is the interaction parameter between two spin carriers. The molar magnetic susceptibility for Cu(II) – Mn(II) complexes is expressed as

$$\chi T = \frac{2N\mu_B^2}{k}\frac{[5g_2^2 + 14g_3^2\exp(6J/kT)]}{[5 + 7\exp(6J/kT)]} \qquad (1)$$

where the g_S (S = 2, 3) factors for the total spin-states $S_T = 2$ and 3, g_2 and g_3 are derived arithmetically [21,22] as $g_2 = (7g_{Mn} - g_{Cu})/6$, and $g_3 = (5g_{Mn} + g_{Cu})/6$. The best-fit parameters which were obtained with eq. (1) by using a standard least-squares program were $J = -28.3$ cm^{-1}, $g_{Mn} = 2.01$, $g_{Cu} = 2.07$, with the agreement factor defined as $R(\chi) = [\Sigma(\chi_{obsd} - \chi_{calcd})^2/[\Sigma(\chi_{obsd})^2]$, $R = 3.10^{-4}$. The copper(II) - manganese(II) coupling constant $J = -28.3$ cm^{-1} interaction parameter) compares 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 [23–29]. The magnetic moments were obtained from the relation $\mu_{eff} = 2.828\ (\chi T)^{1/2}$. The magnetic moment at 301 K is about 5.6 μ_B, and 4.5 μ_B at 4.9 K.

We measured also the variation of the magnetization (M) at 4.2 K as a function of the field (H) up to 5 T. The field dependence of the magnetization at 4.2 K (Fig. 3) shows that saturation is not completely reached in the maximum field available (5 T). However, extrapolation of the experimental data suggests that the magnetization saturation is, at best, equal to $3.71N\mu_B$. The M *versus* T curve is typical of what is expected for a powdered ferromagnet with a very large zero-field susceptibility $(dM/dH)_{H=0}$ and then a rapid saturation. The saturation magnetization M_s is $3.71N\mu_B$, which confirms that all the Cu(II) spins are along the opposite

direction, or all the S = 2 molecular spins per $Cu^{II}Mn^{II}$ units are aligned in a parallel fashion. This means a phase transition from a weak ferromagnet to a ferromagnet with applied magnetic field [4, 30].

The antiferromagnetic interaction between Cu(II) and Mn(II) ions can be easily understood in terms of the non-zero overlap between the magnetic orbitals around Cu(II) and Mn(II) ions [1]. It has been demonstrated that, for oxalato-, oxamido-, or oxamato- and alkoxo-bridged copper(II) complexes, the magnitude of the magnetic interaction can be tuned by the coordination geometry around the metal ions [31 – 35]. The most important structural features for the dinuclear copper(II) complexes are (i) the dihedral angle between the two coordination planes, (ii) the planarity of the bonds around the bridging atom, and (iii) the Cu–O–Cu bridging angle [37,38]. Therefore, one can derive important structural information from the *J* parameter. However, the variation of the strength of the super-exchange interaction cannot be explained completely by the structural features of hetero/homonuclear complexes.

Acknowledgments

This work was supported by the Research Fund of the University of Ankara under grant number 98-05-05-02 and by the Fonds der Chemischen Industrie.

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