A study of the exchange interaction through phenolato, oximato and oxamidato bridges in $Mn^{II}Cu^{II}$ dimers. Crystal structure of $[Cu(salen)Mn(hfa)_2]$

Rafael Ruiz, Francesc Lloret, Miguel Julve* and Juan Faus
Departament de Química Inorgànica, Facultat de Química, Universitat de València, Dr. Moliner 50, 46100 Burjassot (València) (Spain)

M. Carmen Muñoz
Departamento de Física Aplicada, Universidad Politécnica de València, Camino de Vera s/n, 46071 València (Spain)

Xavier Solans
Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia de la Universitat de Barcelona, 08028 Barcelona (Spain)

(Received March 17, 1993; revised May 14, 1993)

Abstract

Three new heterodinuclear $Cu^{II}Mn^{II}$ complexes of formula $[Cu(salen)Mn(hfa)_2]$ (**1**), $[Cu(pdmg)Mn(phen)_2](ClO_4)_2 \cdot 2.5H_2O$ (**2**) and $[Cu(apox)Mn(bpy)_2](ClO_4)_2 \cdot 0.5H_2O$ (**3**) (salen = *N,N'*-ethylenebis(salicylideneiminate), hfa = hexafluoroacetylacetonate, pdmg = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximate, phen = 1,10-phenanthroline, apox = *N,N'*-bis(3-aminopropyl)oxamidate and bipy = 2,2'-bipyridyl) have been synthesized. The crystal and molecular structure of **1** has been determined by X-ray diffraction methods. It crystallizes in the triclinic system, space group $P\bar{1}$ with cell constants $a = 15.584(4)$, $b = 12.039(3)$, $c = 9.470(2)$ Å, $\alpha = 113.83(2)$, $\beta = 107.17(3)$, $\gamma = 84.28(3)°$; $V = 1552(1)$ Å^3, D (calc., $Z = 2$) = 1.708 g cm^{-3}, $M_r = 798.89$, $F(000) = 792$, λ (Mo Kα) = 0.71069 Å, $\mu = 12.63$ cm^{-1} and $T = 298$ K. A total of 3129 reflections was collected over the range $2 \leqslant \theta \leqslant 25$; of these, 2584 (independent and with $I \geqslant 2.5\sigma(I)$) were used in the structural analysis. The final value of R and R_w residuals was 0.069. The structure of **1** is made up of neutral $[Cu(salen)Mn(hfa)_2]$ units. Imine-nitrogen and phenolate-oxygen atoms from salen are bound to the copper atom forming a four-folding surrounding slightly deviating from planarity whereas six oxygen atoms (two from salen and four from the two hfa ligands) define a distorted octahedral environment around the manganese atom. The CuO_2Mn bridging network is bent, the dihedral angle being 14.6°. The magnetic properties of **1**–**3** have been investigated in the 4.2–300 K temperature range. They correspond to what is expected for an antiferromagnetically coupled $Cu^{II}Mn^{II}$ pair with $S_{Cu} = 1/2$ and $S_{Mn} = 5/2$ local spins. Based on the spin Hamiltonian $\hat{H} = -J\hat{S}_{Cu} \cdot \hat{S}_{Mn}$, the coupling constant J was evaluated as -22.4, -50.3 and -24.5 cm^{-1} for **1**–**3**, respectively. The larger value of $|J|$ for **2** confirms the great efficiency of the oximate bridge to transmit the electronic effects between metal centers separated by more than 3.5 Å.

Introduction

The study of the exchange interaction between metal centers through extended bridges has been one of the most active research fields in magnetism [1–3]. The fundamental understanding of the factors that govern the magnetic properties, the design of new materials which can fulfill specific tasks and the biological relevance of the exchange-coupled polynuclear systems are at the origin of the increasing interest in this phenomenon.

In our current research work, we are particularly interested in extended bridging systems which can mediate a strong antiferromagnetic coupling between paramagnetic centers. Along this line, bridging ligands such as oxalate [4], oxamidate [5] and oximate [6] have been used and singlet–triplet energy gaps from -380, -580 and about -1000 cm^{-1} were found in oxalato–, oxamidato– and oximato–copper(II) dinuclear complexes, respectively. The interest in the $Mn^{II}Cu^{II}$ unit which has played a key role in the design of molecular-based ferromagnets [7] moved us to investigate the relative ability of mono and polyatomic bridges to mediate magnetic exchange interactions between both metal ions.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

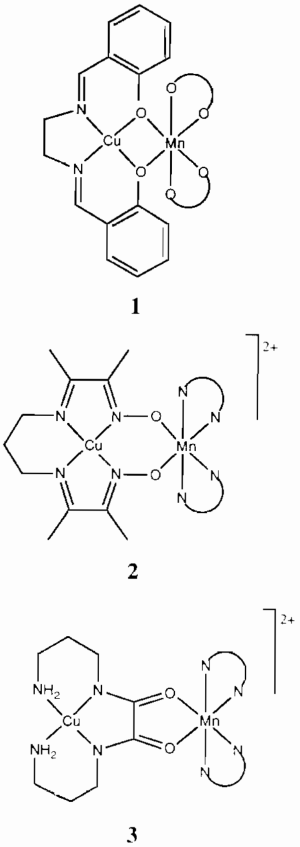
In the present paper we report the synthesis and magnetic characterization of three copper(II)–manganese(II) heterodinuclear complexes of formula [Cu(salen)Mn(hfa)$_2$] (**1**), [Cu(pdmg)Mn(phen)$_2$]-$(ClO_4)_2 \cdot 2.5H_2O$ (**2**) and [Cu(apox)Mn(bipy)$_2$]$(ClO_4)_2 \cdot 0.5H_2O$ (**3**) (salen-dianion of *N,N′*-ethylenebis(salicylideneimine), hfa = hexafluoroacetylacetonate anion, pdmg = dianion of 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime, phen = 1,10-phenanthroline, apox = dianion of *N,N′*-bis(3-aminopropyl)oxamide, bipy = 2,2′-bipyridyl) (see Scheme 1) in which the intramolecular metal–metal separation follows the trend **1** < **2** < **3**. The crystal structure of **1** is also reported.

Experimental

Reagents

The starting materials [Cu(salen)], Cu(Hpdmg)$(ClO_4) \cdot H_2O$, [Cu(apox)] and [Mn(hfa)$_2$$(H_2O)_2$] were prepared by literature methods [8–11]. Perchlorate salts were used as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Universidad Autónoma de Madrid (Spain).

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. We used only small amounts of material in the syntheses described herein (the preparations were carried out at the millimole scale) and the starting perchlorate salts were hydrates. The resulting solutions were handled with care and evaporated slowly at room temperature.



1

2

3

Scheme 1.

Synthesis of the complexes

[Cu(salen)Mn(hfa)$_2$] (1)

[Mn(hfa)$_2$$(H_2O)_2$] (258 mg, 0.5 mmol) dissolved in the minimum amount of methanol was added to a solution of [Cu(salen)] (115 mg, 0.5 mmol) in chloroform (50 cm^3) under continuous stirring. The resulting solution was then heated at reflux for 0.5 h. Slow evaporation of the filtered solution overnight produced small, well-shaped prismatic red crystals of **1** which were suitable for X-ray analysis. *Anal.* Calc. for $C_{26}H_{16}F_{12}N_2O_6CuMn$ (**1**): C, 39.09; H, 2.02; N, 3.51. Found: C, 39.28; H, 1.88; N, 3.46%.

[Cu(pdmg)Mn(phen)$_2$]$(ClO_4)_2 \cdot 2.5H_2O$ (2)

Separated methanolic solutions (10 cm^3) of $Mn(CH_3COO)_2 \cdot 4H_2O$ (123 mg, 0.5 mmol) and phen (198 mg, 1.0 mmol) were successively added to a hot methanolic solution (15 cm^3) of Cu(Hpdmg)$(ClO_4) \cdot H_2O$ (210 mg, 0.5 mmol) and the mixture was refluxed under continuous stirring for 0.5 h. A stoichiometric amount of sodium perchlorate (70 mg, 0.5 mmol) was added to the resulting solution while warm and it was left in a hood to evaporate at room temperature. Black crystals of **2**, which were not suitable for X-ray analysis, were deposited in a few hours. *Anal.* Calc. for $C_{35}H_{39}Cl_2N_8O_{12.5}CuMn$ (**2**): C, 43.74; H, 4.09; N, 11.66. Found: C, 43.63; H, 3.89; N, 11.52%.

[Cu(apox)Mn(bpy)$_2$]$(ClO_4)_2 \cdot 0.5H_2O$ (3)

Large apricot pink crystals of **3** were obtained by slow evaporation of acetonitrile solutions of its dihydrate form which was prepared as previously reported [12]. The crystals of **3** rapidly lose solvent molecules and decompose when separated from the mother liquor. *Anal.* Calc. for $C_{28}H_{33}Cl_2N_8O_{10.5}CuMn$ (**3**): C, 40.08; H, 3.96; N, 13.36. Found: C, 39.95; H, 3.80; N, 13.42%.

Magnetic measurements

Variable-temperature magnetic susceptibility measurements were carried out in the range 4.2–300 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. The apparatus was calibrated with Hg[Co(NCS)$_4$]. Corrections for the diamagnetism of **1**–**3** were estimated from Pascal's constants [13] as -351×10^{-6}, -511×10^{-6} and -413×10^{-6} cm^3 mol^{-1}, respectively.

X-ray structure determination of 1

A prismatic crystal of **1** of approximate dimensions $0.10 \times 0.10 \times 0.20$ mm was mounted on a Philips PW-1100 four-circle diffractometer and used for data collection. A summary of the pertinent crystallographic data and structure refinements is given in Table 1. Unit-cell dimensions were determined and refined from least-squares fitting of 25 carefully centered reflections in the range $4 \leqslant \theta \leqslant 12°$. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed during data collection. The θ range for data collection was 2–25°, the octants of data collected being $-17 \leqslant h \leqslant 17$, $-13 \leqslant k \leqslant 13$ and $0 \leqslant l \leqslant 11$. Intensities were corrected for Lorentz and polarization effects but not for absorption. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu and Mn were taken from ref. 14.

On the basis of the centric distribution of E values, the $P\bar{1}$ space group was assumed and later confirmed by the successful refinement of the structure. Location of copper and manganese atoms were determined by Patterson synthesis, while the remaining non-hydrogen atoms were located from a subsequent Fourier synthesis. The structure was refined by full-matrix least-squares methods, using the SHELX-76 computer program [15]. Six (F(1), F(2), F(3), F(10), F(11) and F(12)) of the twelve fluorine atoms were located in disorder positions, each atom being distributed in two peaks to which an occupancy factor of 0.50 was assigned according to the Fourier map height of the respective peak. Hydrogen atoms could not be located. All non-hydrogen atoms except the fluorine ones were refined anisotropically. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ ($|F_o|$ and $|F_c|$ are the observed and calculated structure factors) with $w = \sigma^{-2}|F_o|$. At final convergence the final R (R_w) factor was 0.069 (0.069) for all observed reflections. Maximum and minimum peaks in final difference synthesis were 0.4 and -0.3 e Å^{-3}, respectively. Max. shift/e.s.d. is 0.1. Final atomic coordinates for non-hydrogen atoms with equivalent isotropic temperature factors and bond distances and angles concerning metal surroundings are listed in Tables 2 and 3, respectively. The molecular plot was drawn using the SCHAKAL program [16].

TABLE 1. Crystallographic data for 1

Chemical formula	$C_{26}H_{16}F_{12}N_2O_6CuMn$
Formula weight	798.89
Crystal system	triclinic
a (Å)	15.584(4)
b (Å)	12.039(3)
c (Å)	9.470(2)
α (°)	113.83(2)
β (°)	107.17(3)
γ (°)	84.28(3)
V (Å^3)	1552(1)
Z	2
Space group	$P\bar{1}$
T (°C)	25
D_{calc} (g cm^{-3})	1.708
Radiation	graphite monochromated Mo Kα ($\lambda = 0.71069$ Å)
$F(000)$	792
μ (cm^{-1})	12.6
Scan technique	ω-scan
Scan speed (° min^{-1})	1.8
Scan width (°)	0.8
No. collected reflections	3129
Cutoff observed data	$2.5\sigma(I)$
No. observed reflections	2584
No. refined parameters	397
R^a	0.069
$R_w{}^b$	0.069

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

Results and discussion

Description of the structure of 1

The crystals of **1** are built up of neutral [Cu(salen)Mn(hfa)$_2$] dinuclear units (Fig. 1). The two metal-containing fragments, Cu(salen) and Mn(hfa)$_2$ are joined through the phenolic oxygen atoms O(1) and O(2) to form a dimeric compound. In fact, Cu(salen) acts as a bidentate ligand toward Mn(hfac)$_2$. An analogous situation was previously found in three related compounds of formula [Cu(salen)M(hfa)$_2$] with M = Co(II) [17], Cu(II) [18] and Ni(II) [19].

The copper atom is in a slightly distorted square-planar environment formed by the two imine-nitrogen (N(1) and N(2)) and the two phenolate-oxygen (O(1) and O(2)) atoms from the salen ligand. The small distortion from planar toward tetrahedral stereochemistry around the copper atom of this four donor set of atoms is characterized by a twisting angle of 8.2° (i.e. the dihedral angle between the CuN(1)N(2) and CuO(1)O(2) planes). The copper–nitrogen and copper–oxygen bond lengths are very close and they lie in the range 1.880(8)–1.927(10) Å. The bond angles around the copper atom show significant deviations from 90°, two of them being contracted (84.8(5) and 85.4(3)° for N(1)–Cu–N(2) and O(1)–Cu–O(2)) with respect to the other two (96.2(4) and 94.0(4)° for N(1)–Cu–O(1) and N(2)–Cu–O(2)). The salen ligand as a whole is far from being planar. It has a convex shape, as was the case in the parent [Cu(salen)Co(hfa)$_2$] complex [17] (the dihedral angles between the two phenyl rings are 19.9 and 36.4° for **1** and CuCo, respectively). The manganese atom is coordinated to six oxygen atoms situated at the corners of a slightly distorted octahedron with the manganese–oxygen bond lengths ranging in the narrow range 2.138(10)–2.187(8) Å. In this respect, the manganese environment ap-

TABLE 2. Final atomic coordinates for non-hydrogen atoms[a] and equivalent isotropic displacement parameters[b] for **1**

Atom[c]	*x/a*	*y/b*	*z/c*	B_{eq} (Å^2)
Cu	0.5013(1)	0.2579(1)	0.2261(2)	4.10(8)
Mn	0.2916(1)	0.2497(2)	0.1094(2)	3.80(9)
O(1)	0.4119(6)	0.1793(7)	0.0306(9)	4.57(43)
O(2)	0.4062(5)	0.2972(6)	0.3209(9)	3.70(37)
O(3)	0.1897(7)	0.1930(8)	−0.1211(10)	5.66(49)
O(4)	0.2851(6)	0.4156(7)	0.0691(10)	4.89(44)
O(5)	0.2472(6)	0.0934(7)	0.1269(10)	4.65(44)
O(6)	0.1981(7)	0.3430(7)	0.2417(10)	5.12(47)
N(1)	0.6013(8)	0.2128(9)	0.1370(14)	4.93(59)
N(2)	0.5884(7)	0.3568(8)	0.4199(13)	2.62(47)
C(1)	0.4260(10)	0.0999(10)	−0.1106(15)	4.47(70)
C(2)	0.3511(10)	0.0427(10)	−0.2401(15)	4.85(68)
C(3)	0.3647(14)	−0.0393(12)	−0.3909(16)	6.83(92)
C(4)	0.4545(13)	−0.0624(14)	−0.4049(17)	6.45(93)
C(5)	0.5247(11)	−0.0053(12)	−0.2775(17)	5.57(79)
C(6)	0.5141(11)	0.0797(11)	−0.1258(16)	5.02(75)
C(7)	0.5981(10)	0.1379(13)	−0.0009(20)	5.23(80)
C(8)	0.6915(10)	0.2603(13)	0.2588(16)	5.97(76)
C(9)	0.6708(9)	0.3771(11)	0.3868(17)	5.68(73)
C(10)	0.5775(9)	0.4015(10)	0.5631(16)	4.63(63)
C(11)	0.4983(9)	0.3754(12)	0.5919(15)	4.69(65)
C(12)	0.5116(10)	0.4063(13)	0.7619(16)	5.85(78)
C(13)	0.4418(11)	0.3739(11)	0.8043(15)	5.21(72)
C(14)	0.3611(10)	0.3184(11)	0.6897(14)	5.22(70)
C(15)	0.3504(10)	0.2903(10)	0.5269(15)	5.09(71)
C(16)	0.4203(8)	0.3211(10)	0.4784(14)	3.90(59)
C(17)	0.1377(10)	0.2602(12)	−0.1729(17)	5.58(75)
C(18)	0.1404(10)	0.3825(14)	−0.1303(19)	6.41(86)
C(19)	0.2157(11)	0.4528(11)	−0.0058(18)	5.44(76)
C(20)	0.0527(17)	0.1808(26)	−0.3305(28)	10.89(169)
C(21)	0.2316(19)	0.6074(20)	0.0640(32)	14.24(192)
C(22)	0.1765(10)	0.0843(13)	0.1570(17)	5.73(80)
C(23)	0.1190(9)	0.1754(12)	0.2202(18)	5.43(75)
C(24)	0.1368(10)	0.2959(13)	0.2597(16)	5.15(74)
C(25)	0.1601(14)	−0.0631(20)	0.1088(31)	11.52(157)
C(26)	0.0820(13)	0.4026(32)	0.3569(31)	13.58(208)
F(1)	0.0101(14)	0.2532(18)	−0.3949(25)	8.12(16)
F(2)	0.1008(16)	0.1039(23)	−0.4350(28)	10.16(20)
F(3)	0.0149(16)	0.1297(24)	−0.2799(29)	9.55(19)
F(1)′	0.0704(14)	0.1784(20)	−0.4529(25)	8.18(16)
F(2)′	0.0500(14)	0.0736(19)	−0.3335(25)	7.85(16)
F(3)′	−0.0148(20)	0.2473(27)	−0.3114(35)	12.31(26)
F(4)	0.1495(11)	0.6296(14)	−0.0309(19)	6.56(12)
F(5)	0.2353(11)	0.6522(15)	0.1957(21)	6.27(13)
F(6)	0.2856(12)	0.6213(16)	−0.0055(22)	6.99(14)
F(7)	0.0748(11)	−0.0638(14)	0.1215(18)	5.92(11)
F(8)	0.1451(11)	−0.1155(14)	−0.0396(20)	5.69(12)
F(9)	0.2187(11)	−0.0935(14)	0.2016(19)	5.96(12)
F(10)	−0.0091(17)	0.3402(22)	0.3037(31)	8.17(23)
F(11)	0.1230(15)	0.4579(22)	0.5034(29)	8.19(18)
F(12)	0.0651(17)	0.4922(22)	0.3190(32)	8.85(20)
F(10)′	0.0361(18)	0.4410(25)	0.2538(31)	10.04(24)
F(11)′	0.1000(23)	0.4037(29)	0.4958(39)	11.99(30)
F(12)′	0.0126(21)	0.3493(26)	0.3685(38)	10.10(28)

[a] e.s.d.s are given in parentheses. [b] $B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$. [c] Primed atoms denote disorder position of the noted atom.

TABLE 3. Selected interatomic distances (Å) and bond angles (°) for **1**

Cu–O(1)	1.895(8)	Mn–O(2)	2.166(7)
Cu–O(2)	1.880(8)	Mn–O(3)	2.172(9)
Cu–N(1)	1.916(11)	Mn–O(4)	2.167(8)
Cu–N(2)	1.927(10)	Mn–O(5)	2.150(8)
Mn–O(1)	2.187(8)	Mn–O(6)	2.138(10)
N(1)–Cu–O(1)	96.2(4)	O(1)–Mn–O(6)	165.7(3)
N(1)–Cu–N(2)	84.8(5)	O(2)–Mn–O(3)	172.4(3)
N(1)–Cu–O(2)	176.7(4)	O(2)–Mn–O(4)	98.8(3)
N(2)–Cu–O(2)	94.0(4)	O(2)–Mn–O(5)	96.7(3)
N(2)–Cu–O(1)	172.6(4)	O(2)–Mn–O(6)	94.1(3)
O(1)–Cu–O(2)	85.4(3)	O(3)–Mn–O(4)	81.0(3)
Cu–O(1)–Mn	99.6(3)	O(3)–Mn–O(5)	85.3(3)
Cu–O(2)–Mn	100.8(3)	O(3)–Mn–O(6)	93.5(4)
O(1)–Mn–O(2)	72.0(3)	O(4)–Mn–O(5)	159.5(3)
O(1)–Mn–O(3)	100.4(3)	O(4)–Mn–O(6)	82.0(3)
O(1)–Mn–O(4)	96.7(3)	O(5)–Mn–O(6)	83.7(3)
O(1)–Mn–O(5)	100.7(3)		

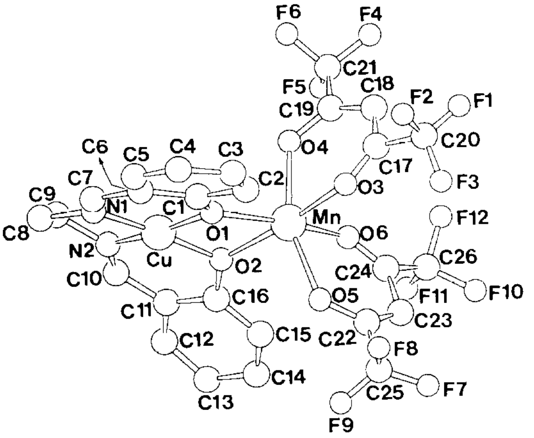


Fig. 1. Perspective drawing of **1** showing the atom numbering.

proaches more closely to octahedral symmetry than do the six-coordinated cobalt(II) and nickel(II) surroundings in the parent Cu(II)Co(II) [17] and Cu(II)Ni(II) [19] complexes. The octahedral distortion of the hfa-coordinated copper(II) from the [Cu(salen)Cu(hfa)$_2$] complex [18] is much more pronounced, as expected because of the Jahn-Teller effect of Cu(II). Concerning the bond angles around the manganese atom, the O(1)–Mn–O(2) angle is the smallest (72.0(3)°), the others ranging from 81.0(3) to 100.7(3)°. The bridging angles at the phenolato bridges are practically identical (99.6(3) and 100.8(3)° for Cu–O(1)–Mn and Cu–O(2)–Mn, respectively). The dihedral angle between the mean equatorial plane of manganese (MnO(1)O(2)O(3)O(6)) and the mean basal plane of copper (CuN(1)N(2)O(1)O(2)) is 17.5°, a value very similar to that reported for the parent Cu(II)Co(II) compound (18.1°). However, the bending of the CuO(1)O(2)Mn core around the O(1)–O(2) axis is significantly reduced with respect to that observed in the Cu(II)Ni(II) compound (38.6° for CuO$_2$Ni) and consequently, the intramolecular metal–metal separation is very different (3.123(2) and 2.897(1) Å in

Cu(II)Mn(II) and Cu(II)Ni(II), respectively). In fact, in the Cu(II)Ni(II) compound two CuNi units are related through a symmetry center, leading to an exceptional bis-heterodinuclear entity (the intermolecular copper–copper separation is 3.43 Å), in contrast to what is observed in **1**. For this compound, such a situation does not occur (see Fig. 2) and the shortest intermolecular copper–copper separation is as large as 6.04 Å.

Magnetic properties

The magnetic behavior of **1** is shown in Fig. 3 in the form of a $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature, $\chi_M T$ is equal to 4.34 cm^3 mol^{-1} K, a value which is slightly below what is expected for isolated Mn(II) and Cu(II) ions. Upon cooling down, $\chi_M T$ continuously decreases and finally reaches a plateau around 15 K with $\chi_M T = 2.68$ cm^3 mol^{-1} K. This plateau is kept down to 4.2 K. This behavior closely follows what is expected for an isolated Cu$^{\text{II}}$Mn$^{\text{II}}$ pair, with local spins $S_{\text{Cu}} = 1/2$ and $S_{\text{Mn}} = 5/2$. The antiferromagnetic interaction within the pair gives rise to a ground spin quintet and an excited spin septet. The plateau below 15 K corresponds to the temperature range where only the ground state is populated. Consequently, the magnetic data are interpreted with the theoretical law appropriate for an isolated Cu(II)Mn(II) pair (eqn. (1))

$$\chi_M T = (2N\beta^2/k)[5g_2^2 + 14g_3^2 \exp(3J/kT)]/[5 + 7\exp(3J/kT)] \quad (1)$$

where the symbols N, β and k have their usual meaning, J is the interaction parameter occurring in the spin Hamiltonian $-JS_{\text{Cu}} \cdot S_{\text{Mn}}$, and g_2 and g_3 are the Zeeman factors associated with the quintet and septet spin states, respectively. The least-squares fitting of the experimental data through eqn. (1) minimizing the reliability factor P $(P = \Sigma[(\chi_M T)^{\text{obs}} - (\chi_M T)^{\text{calc}}]^2 / \Sigma[(\chi_M T)^{\text{obs}}]^2)$ leads to $J = -22.0$ cm^{-1}, $g_2 = 1.89$ and $g_3 = 2.01$ $(P = 1.1 \times 10^{-5})$. The energy gap between quintet and septet pair states is equal to $3J = -66.0$ cm^{-1}. The values of g_2 and g_3 may be related to the local Zeeman factors g_{Mn} and g_{Cu}, assumed to be isotropic, through eqn. (2) [20, 21]

$$g_2 = (7g_{\text{Mn}} - g_{\text{Cu}})/6 \qquad g_3 = (5g_{\text{Mn}} + g_{\text{Cu}})/6 \quad (2)$$

The values of g_{Mn} and g_{Cu} deduced from eqn. (2) are equal to 1.95 and 2.31, respectively.

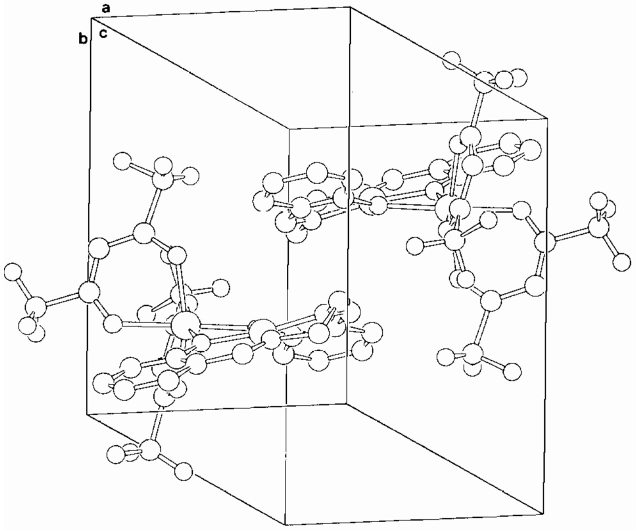


Fig. 2. Perspective view showing the packing of **1** in the crystal.

The thermal dependence of $\chi_M T$ for **2** and **3** in the temperature range 4.2–100 K is shown in Fig. 4. The magnetic behavior of both complexes is qualitatively similar. The $\chi_M T$ value at room temperature for **2** and **3** is 4.00 and 4.32 cm^3 mol^{-1} K, respectively. The first $\chi_M T$ value is significantly reduced with respect to what is expected for magnetically non-interacting Mn(II) and Cu(II) ions, supporting the occurrence of a stronger antiferromagnetic interaction within the Cu(II)Mn(II)

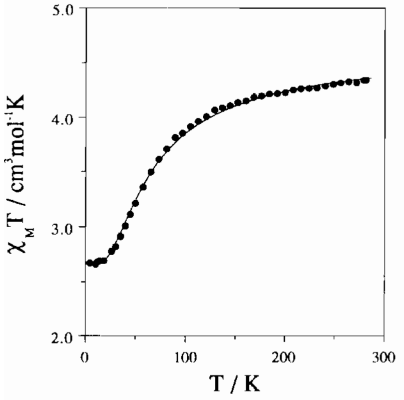


Fig. 3. Thermal dependence of $\chi_M T$ for **1**. The solid line corresponds to the best theoretical fit (see text).

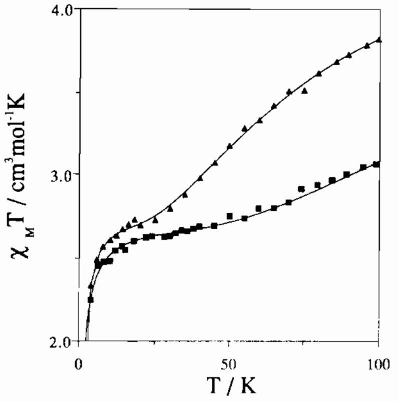


Fig. 4. Temperature dependence of $\chi_M T$ for **2** (■) and **3** (▲). The solid lines correspond to the best theoretical fits (see text).

framework in **2**. Again, $\chi_M T$ continuously decreases upon cooling down for both compounds and reaches a plateau at 35 K ($\chi_M T = 2.66$ cm^3 mol^{-1} K) and at 20 K ($\chi_M T = 2.70$ cm^3 mol^{-1} K) for **2** and **3**, respectively. $\chi_M T$ decreases again for temperatures lower than 25 (**2**) and 20 (**3**) K. Least-squares fit of the data down to 25 (**2**) and to 20 (**3**) K through eqn. (1) led to $J = -50.3$ cm^{-1}, $g_2 = 1.88$ and $g_3 = 1.98$ ($P = 3.8 \times 10^{-5}$) for **2** and to $J = -24.5$ cm^{-1}, $g_2 = 1.89$ and $g_3 = 2.01$ ($P = 5 \times 10^{-5}$) for **3**. The values of g_{Mn} and g_{Cu} calculated through eqn. (2) are equal to 1.93 and 2.22 for **2** and 1.95 and 2.31 for **3**.

The magnetic behavior of **2** and **3** in the lower temperature region is difficult to interpret unambiguously. Antiferromagnetic intermolecular interactions and/or zero-field splitting of the ground state could account for it. Assuming that the decrease of $\chi_M T$ on cooling to liquid helium temperature is mainly due to the zero-field splitting of the quintet ground state, the experimental data could be treated by eqn. (3) [22]

$$\chi_M = (\chi_\parallel + 2\chi_\perp)/3 \tag{3}$$

where $\chi_\parallel$ and $\chi_\perp$ correspond to eqns. (4) and (5)

$$\begin{aligned}\chi_\parallel = {} & (2N\beta^2/kT)[g_2^2(\exp(D/kT) + 4\exp(-2D/kT)) \\ & + 14g_3^2 \exp(3J/kT)]/[\exp(2D/kT) \\ & + 2\exp(D/kT) + 2\exp(-2D/kT) \\ & + 7\exp(3J/kT)]\end{aligned} \tag{4}$$

$$\begin{aligned}\chi_\perp = {} & 2N\beta^2[(g_2^2/3D)(9\exp(2D/kT) - 7\exp(D/kT) \\ & - 2\exp(-2D/kT)) + (14g_3^2/kT) \\ & \exp(3J/kT)]/[\exp(2D/kT) \\ & + 2\exp(D/kT) + 2\exp(-2D/kT) \\ & + 7\exp(3J/kT)]\end{aligned} \tag{5}$$

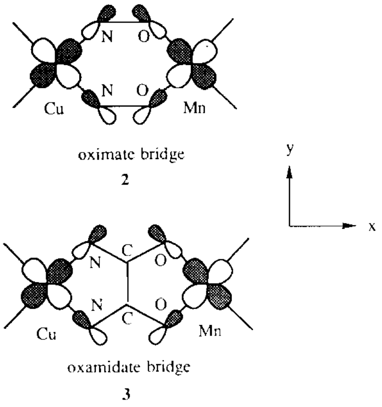
D being the axial zero-field splitting parameter for the quintet spin state. The least-squares fit of the experimental data with eqn. (3) led to $J = -49.8$ cm^{-1}, $g_2 = 1.88$, $g_3 = 1.98$ and $D = 3.8$ cm^{-1} ($P = 1.0 \times 10^{-4}$) for **2** and to $J = -26.0$ cm^{-1}, $g_2 = 1.90$, $g_3 = 2.04$ and $D = 3.0$ cm^{-1} ($P = 5 \times 10^{-5}$) for **3**. These fits correspond to the solid lines in Fig. 4.

The J values and the intramolecular copper–manganese separation for **1–3** are listed in Table 4. Two points deserve to be commented on in the light of these data: (i) the close J values for **1** and **3** in spite of the different metal–metal separation through phenolate and oxamidate bridges, and (ii) the stronger antiferromagnetic coupling in **2** with respect to **3**.

TABLE 4. J values and intermetal distances for complexes **1–3**

Compound	Bridge	$-J$ (cm^{-1})	Cu···Mn (Å)
1	phenolate	22.0	3.123
2	oximate	50.3	>3.7[a]
3	oxamidate	24.5 (21.5)[c]	>5.3[b]

[a] Estimated value from related dinuclear complexes in ref. 6a. [b] Estimated value from parent dinuclear complexes in refs 5c, 23 and 24. [c] Value from ref 12.



Scheme 2.

Dealing with the first point, a decrease of the exchange coupling when going from **1** to **3** would be expected due to the increasing intramolecular Cu(II)–Mn(II) separation in this series. However, the observed trend is oximate > oxamidate ≈ phenolate. This sequence confirms, once again, that the separation between the magnetic centers is in no way a determinant factor for the magnitude of the interaction [4a, 5a, 25–27]. The bending of the CuO_2Mn core in **1** accounts for the reduced value of J as previously observed in other $Cu(TSB)Mn(hfa)_2$ complexes, where TSB represents a tetradentate Schiff base [28, 29].

As far as the second point is concerned, the most interesting result of this study concerns the greater efficiency of oximato with respect to oxamidato to transmit electronic effects between paramagnetic centers (-50.3 versus -24.5 cm^{-1} for oximato and oxamidato bridges, respectively). The value of J in **3** agrees well with that reported previously for oxamidato-bridged Cu(II)Mn(II) complexes [30]. However, as far as we are aware, no magnetic study concerning the oximato-bridged Cu(II)Mn(II) unit was reported in the literature. This remarkable efficiency of oximato versus oxamidato can be qualitatively explained taking into account the overlapping between the d_{xy} magnetic orbitals of Cu(II) and Mn(II) through the corresponding bridge (Scheme 2). Both orbitals are delocalized toward the N–O (oxime) and N–C–O (oxamide) fragments and the resulting antiferromagnetic coupling issues from the net overlapping between them. The closer vicinity of the interacting ions in **2** with respect to **3** most likely causes a larger overlapping in the former and consequently a stronger antiferromagnetic coupling.

To conclude this paper, we will comment briefly on the synthetic strategy that we have used to prepare complexes **1**–**3**. Although the use of dissymmetric polynucleating ligands has been the way preferred by synthetic chemists to design heteropolymetallic species [31], another known strategy which consists of using 'complexes as ligands' [32] has been used herein. In fact, [Cu(salen)], [Cu(apox)] and [Cu(pdmg)] mononuclear complexes can act as chelating ligands toward metal ions M through phenolate-, oxamidate- and oximate-oxygen atoms. The fact that compounds with a controlled degree of nuclearity can be obtained by monitoring the Cu/M molar ratio and the nature of the ligands which can be previously fixed on M [4a, 5c, 6a, 23, 24, 29, 32f, 33] makes it invaluable for chemists.

Supplementary material

Tables of thermal parameters, non-essential bond distances and angles, least-squares planes (5 pp) as well as a listing of observed and calculated structure factors (11 pp) are available from the authors on request.

Acknowledgements

Financial support from the Comisión Interministerial de Ciencia y Tecnología (Project PB91-0807-C02-01) is gratefully acknowledged. We are indebted to A. Derory for the magnetic susceptibility measurements. R.R. acknowledges the Conselleria de Cultura, Educació i Ciència de la Generalitat Valenciana for a doctoral grant.

References

1 R.D. Willett, D. Gatteschi and O. Kahn (eds.), *Magneto-Structural Correlations in Exchange Coupled Systems,* NATO ASI Series, Vol. 140, Reidel, Dordrecht, 1985.

2 P. Delhaes and M. Drillon (eds.), *Organic and Inorganic Low-Dimensional Crystalline Materials,* NATO ASI Series, Vol. 168, Plenum, New York, 1987.

3 D. Gatteschi, O. Kahn, J.S. Miller and F. Palacio (eds.), *Magnetic Molecular Materials,* NATO ASI Series, Vol. 198, Kluwer, Dordrecht, 1991.

4 (a) M. Julve, M. Verdaguer, O. Kahn, A .Gleizes and M. Philoche-Levisalles, *Inorg. Chem., 23* (1984) 3808; (b) M. Julve, J. Faus, M. Verdaguer and A. Gleizes, *J. Am. Chem. Soc., 106* (1984) 8306; (c) S. Alvarez, M. Julve and M. Verdaguer, *Inorg. Chem., 29* (1990) 4501; (d) A. Gleizes, M. Julve, M. Verdaguer, J.A. Real, J. Faus and X. Solans, *J. Chem. Soc., Dalton Trans.,* (1992) 3209.

5 (a) M. Verdaguer, O. Kahn, M. Julve and A. Gleizes, *Nouv. J. Chim., 9* (1985) 325; (b) A. Bencini, C. Benelli, A.C. Fabretti, G. Franchini and D. Gatteschi, *Inorg. Chem., 25* (1986) 1063; (c) Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem., 24* (1985) 4063; (d) F. Lloret, M. Julve, J. Faus, Y. Journaux, M. Philoche-Levisalles and Y. Jeannin, *Inorg. Chem., 28* (1989) 3702; (e) H. Okawa, N. Matsumoto, M. Koikawa, K. Takeda and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1990) 1383; (f) J.A. Real, M. Mollar, R. Ruiz, J. Faus, F. Lloret, M. Julve and M. Philoche-Levisalles, *J. Chem. Soc., Dalton Trans.,* (1993) 1483.

6 (a) D. Luneau, H. Oshio, H. Okawa, M. Koikawa and S. Kida, *Bull. Chem. Soc. Jpn., 63* (1990) 2212; (b) R. Ruiz, J. Sanz, B. Cervera, F. Lloret, M. Julve, C. Bois, J. Faus and M.C. Muñoz, *J. Chem. Soc., Dalton Trans.,* (1993) 1623.

7 (a) O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard and J. Sletten, *J. Am. Chem. Soc., 110* (1988) 782; (b) K. Nakatani, J.Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J.P. Renard, Y. Pei, J. Sletten and M. Verdaguer, *J. Am. Chem. Soc., 111* (1989) 5739; (c) Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathonière and J. Sletten, *J. Am. Chem. Soc., 113* (1991) 6558; (d) O. Kahn, Y. Pei, K. Nakatani, Y. Journaux and J. Sletten, *New J. Chem., 16* (1992) 269; (e) F. Lloret, M. Julve, R. Ruiz, Y. Journaux, K. Nakatani, O. Kahn and J. Sletten, *Inorg. Chem., 32* (1993) 27.

8 R.H. Bailes and M. Calvin, *J. Am. Chem. Soc., 69* (1947) 1886.

9 R.R. Gagné, *J. Am. Chem. Soc., 98* (1976) 6709.

10 H. Ojima and K. Nonoyama, *Z. Anorg. Allg. Chem., 389* (1972) 75.

11 R.L. Bedford, D.E. Martell and M. Calvin, *J. Inorg. Nucl. Chem., 2* (1956) 11.

12 Z.M. Liu, D.Z. Liao, Z.H. Jiang and G.L. Wang, *Synth. React. Inorg. Met.-Org. Chem., 21* (1991) 289.

13 A. Earshaw, *Introduction to Magnetochemistry,* Academic Press, London, 1968.

14 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 99–100, 149.

15 G.M. Sheldrick, *SHELX,* a computer program for the crystal structure determination, University of Cambridge, UK, 1976.

16 E. Keller, *SCHAKAL,* a FORTRAN program for the graphic representation of molecular and crystallographic models, University of Freiburg, Germany, 1987.

17 N.B. O'Bryen, T.O. Maier, I.C. Paul and R.S. Drago, *J. Am. Chem. Soc., 95* (1973) 6640.

18 K.A. Leslie, R.S. Drago, G.D. Stucky, D.J. Kitko and J.A. Breese, *Inorg. Chem., 18* (1979) 1885.

19 Y. Journaux, O. Kahn, I. Morgenstern-Badarau, J. Galy, J. Jaud, A. Bencini and D. Gatteschi, *J. Am. Chem. Soc., 107* (1985) 6305.

20 O. Kahn, *Angew. Chem., Int. Ed. Engl., 24* (1985) 834.

21 R.P. Scaringe, D. Hodgson and W.E. Hatfield, *Mol. Phys., 35* (1978) 701.

22 Y. Journaux, O. Kahn, J. Zarembowitch, J. Galy and J. Jaud, *J. Am. Chem. Soc., 105* (1983) 7585.

23 Z.Y. Zhang, D.Z. Liao, Z.H. Jiang, X.K. Hao, H.G. Wang and G.L. Wang, *Inorg. Chim. Acta, 173* (1990) 201.

24 A. Escuer, R. Vicente, J. Ribas, R. Costa and X. Solans, *Inorg. Chem., 31* (1992) 2627.

25 F. Tinti, M. Verdaguer, O. Kahn and J.M. Savariault, *Inorg. Chem., 26* (1987) 2380.

26 P. Chaudhuri, K. Oder, K. Wieghardt, S. Gehring, W. Haase, B. Nuber and J. Weiss, *J. Am. Chem. Soc., 110* (1988) 3657.

27 M.A.S. Aquino, F.L. Lee, E.J. Gave, C. Bensimon, J.E. Greedan and R.J. Crutchley, *J. Am. Chem. Soc., 114* (1992) 5130.

28 C.J. O'Connor, D.P. Freyberg and E. Sinn, *Inorg. Chem., 18* (1979) 1077.

29 G.A. Brewer and E. Sinn, *Inorg. Chem., 26* (1987) 1529.

30 (a) Y. Pei, K. Nakatani, O. Kahn, J. Sletten and J.P. Renard, *Inorg. Chem., 28* (1989) 3170; (b) K. Nakatani, J. Sletten, S. Halut-Desporte, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem., 30* (1991) 30.

31 (a) U. Casellato and P.A. Vigato, *Coord. Chem. Rev., 23* (1977) 31; (b) E. Groh, *Isr. J. Chem., 15* (1976/77) 277; (c) R.L. Lindvedt and N. Ahmad, *Inorg. Chem., 21* (1982) 2356; (d) S.L. Lambert, C.L. Spiro, R.P. Gagné and D.N. Hendrickson, *Inorg. Chem., 21* (1982) 68.

32 (a) S.J. Gruber, C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem., 30* (1968) 1805; (b) N.B. O'Brien, T.O. Maier, I.C. Paul and R.S. Drago, *J. Am. Chem. Soc., 95* (1973) 6640; (c) D. Coucouvanis, N.C. Baenziger and S.M. Johnson, *Inorg. Chem., 13* (1974) 1191; (d) F. Hollander and D. Coucouvanis, *Inorg. Chem., 13* (1974) 2381; (e) K.A. Leslie, R.S. Drago, G.D. Stucky, D.J. Kitko and J. A. Breese, *Inorg. Chem., 18* (1979) 1885; (f) E. Sinn, in K.D. Karlin and J. Zubieta (eds.), *Biological and Inorganic Copper Chemistry,* Adenine Press, New York, 1985, p. 195; (g) Y. Pei, Y. Journaux and O. Kahn, *Inorg. Chem., 27* (1988) 399; (h) H. Ojima and K. Nonoyama, *Coord. Chem. Rev., 92* (1988) 85; (i) P. Chaudhuri, M. Winter, B.P.C. Della Védova, E. Bill, S.G. Trautwein, P. Fleischhauer, B. Nuber and J. Weiss, *Inorg. Chem., 30* (1991) 2148; (j) F. Lloret, M. Julve, J. Faus, R. Ruiz, I. Castro, M. Mollar and M. Philoche-Levisalles, *Inorg. Chem., 31* (1990) 784.

33 (a) A. Bencini, C. Benelli, A. Dei and D. Gatteschi, *Inorg. Chem., 24* (1985) 695; (b) A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem., 25* (1986) 572; (c) Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem., 25* (1986) 439; (d) P. Chadhuri, M. Winter, P.P. Fleischhauer, W. Haase, U. Flörke and H. Haupt, *J. Chem. Soc., Chem. Commun.,* (1990) 1728; (e) H. Okawa, M. Koikawa, S. Kida, D. Luneau and H. Oshio, *J. Chem. Soc., Dalton Trans.,* (1990) 469; (f) Z.J. Zhong, H. Okawa, N. Matsumoto, H. Sakiyama and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1991) 497; (g) D. Laroque, I. Morgenstern-Badarau, H. Winkler, E. Bill, A.X. Trautwein and M. Julve, *Inorg. Chim. Acta, 192* (1992) 107.