Significant Antiferromagnetic Coupling in a Terephthalate (ta)-bridged Manganese(II) Compound: Preparation, Crystal Structure and Magnetic Properties of the Chain $[Mn_2(bipy)_4(ta)][ClO_4]_2$ (bipy = 2,2′-bipyridine)†

Juan Cano,[a] **Giovanni De Munno,**[*,b] **José Sanz,**[a] **Rafael Ruiz,**[a] **Francesc Lloret,**[*,a] **Juan Faus**[a] **and Miguel Julve**[a]

[a] *Departament de Química Inorgànica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot (València), Spain*

[b] *Dipartimento di Chimica, Università degli Studi della Calabria, 87030 Arcavacata di Rende (Cosenza), Italy*

A new manganese(II) compound $[Mn_2(bipy)_4(ta)][ClO_4]_2$ **1** (bipy = 2,2′-bipyridine, ta = terephthalate dianion) has been synthesised and its crystal structure determined by single-crystal X-ray diffraction. It crystallizes in the triclinic system, space group $P\bar{1}$, with a = 9.516(2), b = 11.613(3), c = 11.615(3) Å, α = 70.92(2), β = 80.16(2), γ = 76.64(2)° and Z = 1. The structure consists of cationic terephthalate-bridged $[Mn_2(bipy)_4(ta)]^{2+}$ chains and non-co-ordinated perchlorate anions. Each terephthalate is bound to four manganese atoms through carboxylate oxygens with the sym-sym bridging mode, affording manganese(II) pairs which are linked by the terephthalate group to yield a one-dimensional chain running along the a axis. The intrachain Mn ··· Mn separations through the double carboxylate and terephthalate bridges are 4.643(1) and 9.637(2) Å, respectively. The manganese(II) ion displays a severely distorted octahedral co-ordination being linked to four nitrogen atoms of two bipy ligands and to two oxygen atoms of two carboxylate groups from two terephthalate ligands. The magnetic susceptibility of **1** as a function of temperature (4.2–290 K) exhibits a sharp maximum at 6.0 K which is consistent with a significant antiferromagnetic coupling between the metal centres. This magnetic behaviour has been interpreted in terms of a dimer with a molecular field approximation, the values obtained for J, g and zJ' being −1.35 cm^{-1}, 1.97 and −0.04 cm^{-1}, respectively. In the light of the structural data, it can be concluded that the double-carboxylate bridge between the manganese(II) pairs provides a more efficient exchange pathway than that of terephthalate and most likely is responsible for the observed J value.

The study of magnetic exchange interaction through extended bridging ligands has been of major interest in the field of molecular magnetism in the past few years.[1] In this context, both the achievement of strong magnetic interactions between paramagnetic metal centres and the search for the limiting distance for interaction between them[2] led magnetochemists to focus on dinuclear copper(II) complexes bridged by oxalate[3] and oxalate-type ligands,[4–7] end-to-end azide,[8] croconate (4,5-dihydroxycyclopent-4-ene-1,2,3-trionate),[9] 2,5-dihydroxy-1,4-benzoquinone and its derivatives,[10] squarate (3,4-dihydroxycyclobut-3-ene-1,2-dionate),[11] 4,4′-bipyridine[12] and terephthalate.[13] In this series, the intramolecular metal–metal separation is tuned from 5 to 11 Å. Moreover, the plasticity of the co-ordination sphere of Cu^{II} and the presence of only one unpaired electron on each metal centre makes these systems easy candidates to investigate the influence of the relative orientation of the magnetic orbitals on the exchange interaction through the bridging group. In spite of the available information on these systems, the ability of terephthalate to mediate exchange coupling, going from 4 to −140 cm^{-1} in its copper(II) complexes,[13d,e] requires further theoretical and experimental studies. In fact, for such a large intramolecular metal–metal separation (*ca.* 11 Å), the intermolecular interactions could be predominant.

In the present paper we report the synthesis, crystal structure and magnetic properties of the manganese(II) complex $[Mn_2(bipy)_4(ta)][ClO_4]_2$ **1** where bipy and ta correspond to 2,2′-bipyridine and terephthalate (dianion of benzene-1,4-dicarboxylic acid). This compound provides us with the possibility to analyse the influence of the number and symmetry of the magnetic orbitals on the exchange interaction through terephthalate (five magnetic orbitals for high spin Mn^{II} *versus* only one for Cu^{II}). The structure of **1** is the first reported for a terephthalate-bridged manganese(II) complex.

Experimental

Materials.—2,2′-Bipyridine and manganese(II) perchlorate hexahydrate were obtained from Aldrich and used without further purification. The piperidinium salt of terephthalic acid was prepared by a literature method.[13a] Elemental analyses (C, H, N) were by the Microanalytical Service of the Universidad Autónoma de Madrid.

Preparation of $[Mn_2(bipy)_4(ta)][ClO_4]_2$ **1**.—A warm methanolic solution of 2,2′-bipyridine (312 mg, 2.0 mmol) was slowly added to a solution of manganese(II) perchlorate hexahydrate (362 mg, 1.0 mmol) in the same solvent with continuous stirring (final volume 50 cm^3). A methanolic solution (100 cm^3) of piperidinium terephthalate (169 mg, 0.5 mmol) was added dropwise. The light yellow powder which separated during the addition was filtered off and discarded. Small yellow prisms of complex **1** suitable for X-ray

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: emu = SI × $10^6/4\pi$.

investigation were obtained after 3 d by slow evaporation of the mother-liquor at room temperature. They were filtered off and air-dried. This compound is insoluble in common solvents (water, methanol, acetonitrile, acetone, dimethyl sulfoxide, dimethylformamide) (Found: C, 51.40; H, 3.10; N, 10.30. Calc. for $C_{48}H_{36}Cl_2Mn_2N_8O_{12}$: C, 52.50; H, 3.30; N, 10.20%). The most salient features of the IR spectra are those associated with the presence of perchlorate and terephthalate groups: absorptions at 1100s, 930w, 625m and 460m cm^{-1} suggests the presence of unco-ordinated perchlorate,[14] and $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ stretching vibrations at 1570s and 1385s cm^{-1} respectively (*cf.* 1565 and 1395 cm^{-1} for piperidinium terephthalate) indicate that bridging carboxylate co-ordination is involved.[15] These spectroscopic assignments are in agreement with the structure of **1**.

Physical Techniques.—Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–300 cm^{-1} region. Magnetic susceptibility measurements were carried out on a polycrystalline sample of complex **1** in the temperature range 4.2–290 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer[16] 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 diamagnetism were estimated from Pascal's constants[17] as -533×10^{-6} emu mol^{-1}.

Crystal Structure Determination and Refinement.—Diffraction data were collected at 298 K on a Siemens R3m/V automatic four-circle diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Details of the crystallographic data collection and structure refinement are in Table 1. The lattice parameters were determined from least-squares refinement of the setting angles of 25 reflections in the range $15 \leqslant 2\theta \leqslant 30°$. A total of 4658 reflections were collected by the ω–2θ scan method in the range 2θ 3–54 with index ranges *h* 0–8, *k* −14 to 14 and *l* −14 to 14; 4270 of them were unique, and from these 3069 were considered as observed $[I > 3\sigma(I)]$ and used for the refinement of the structure. Examination of three standard reflections, monitored after every 100, showed no sign of crystal deterioration. Lorentz-polarization and ψ-scan absorption corrections[18] were applied to the intensity data. The maximum and minimum transmission factors were 0.959 and 0.818, respectively.

The structure was solved by standard Patterson methods with the SHELXTL PLUS program[19] and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of bipy and terephthalate were set in calculated positions and refined as riding atoms. A common fixed isotropic thermal parameter was assigned to them. The final full-matrix least-squares refinement, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0010(F_o)^2]$ [with $\sigma(F_o)$ from counting statistics], converged at *R* and *R'* indices of 0.0417 and 0.0456, respectively. The number of reflections/number of variable parameters was 9.4. In the final difference map the residual maxima and minima were 0.54 and −0.39 e $Å^{-3}$. The largest and mean Δ/σ were 0.044 and 0.003. Solutions and refinement were performed with the SHELXTL PLUS system and the final geometrical calculations were carried out with the PARST program.[20] The graphical manipulations were performed using the XP utility of the SHELXTL PLUS system. The final atomic coordinates for non-hydrogen atoms and selected bond distances and angles are given in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure of Complex **1**.—The structure of complex **1** consists of polymeric cationic $[Mn_2(bipy)_4(ta)]^{2+}$ units and non-co-ordinated perchlorate anions. One of the units is shown in Fig. 1(*a*) together with the atom-numbering scheme. The terephthalate group acts as a tetrakis(monodentate) ligand which is bound on each side to two manganese(II) ions through the carboxylato oxygens in a sym-sym conformation yielding a chain which runs parallel to the *a* axis as depicted in Fig. 1(*b*). A crystallographic inversion centre is located at the centre of the benzene ring of the terephthalate ligand.

Each manganese atom has a distorted-octahedral co-ordination sphere comprised of two carboxylate-oxygen atoms [O(1) and O(2b)] from two terephthalate ligands which occupy *cis* positions and four nitrogen atoms [N(1), N(2), N(3) and N(4)] from two chelating bipy groups. The Mn–N(bipy) bond lengths lie in the range 2.262(3)–2.305(3) Å, values which are significantly longer than that of the Mn–O(carboxylate) (average 2.118 Å). These bond distances are in agreement with those reported for other bipy- and carboxylato-containing manganese(II) complexes.[21] Large deviations from the idealized orthogonal geometry are found at the metal atom in the five-membered Mn(1)N(1)C(9)C(10)N(2) and Mn(1)N(3)-C(19)C(20)N(4) chelate rings [72.1(1) and 71.4(1)° for N(1)–Mn(1)–N(2) and N(3)–Mn(1)–N(4), respectively] as expected due to the small bite distance of the bipy ligand.[22] The

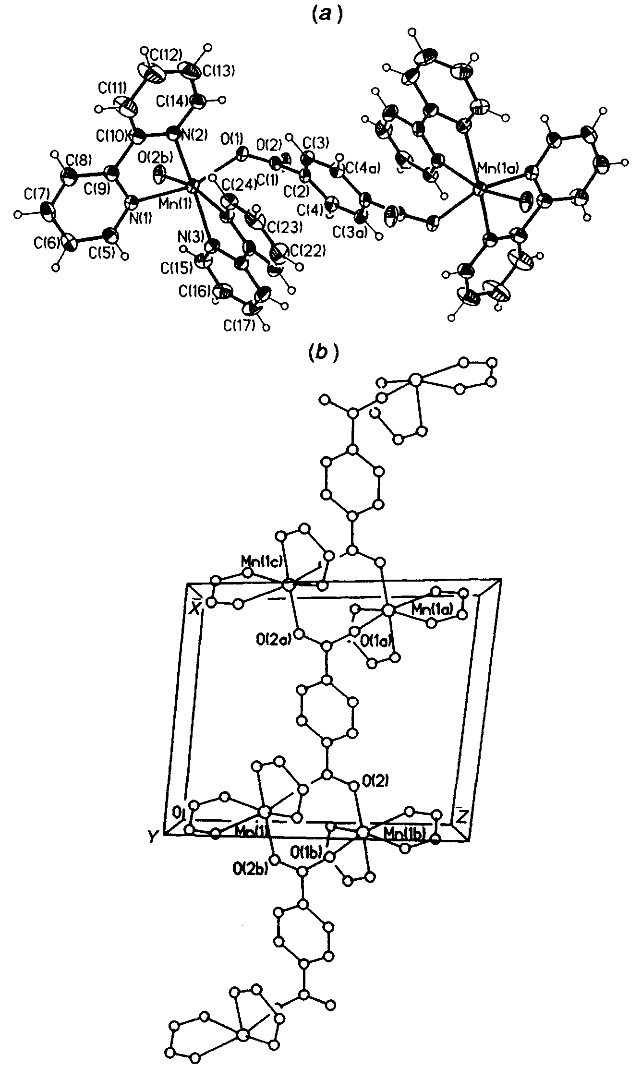


Fig. 1 (*a*) A perspective view of the cationic unit $[Mn_2(bipy)_4(ta)]^{2+}$ of complex **1** showing the atom labelling; thermal ellipsoids are drawn at the 30% probability level. (*b*) A view of the polymerization of **1** through sym-sym carboxylato bridges; part of the bipy ligands has been omitted for clarity

Table 1 Crystallographic data for $[Mn_2(bipy)_4(ta)][ClO_4]_2$ **1**

Formula	$C_{48}H_{36}Cl_2Mn_2N_8O_{12}$
M	1097.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.516(2)
b/Å	11.613(3)
c/Å	11.615(3)
α/°	70.92(2)
β/°	80.16(2)
γ/°	76.64(2)
U/Å^3	1173.9(5)
Z	1
D_c/kg m^{-3}	1.553
F(000)	560
Crystal size/mm	0.46 × 0.22 × 0.12
μ(Mo-Kα)/cm^{-1}	7.26
No. of collected reflections	4658
No. of unique reflections	4270
No. of independent reflections[a]	3069
No. of refined parameters, N_p	325
$R[=\Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|]$	0.0417
$R'\{=[\Sigma(\|\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$	0.0456
S[b]	1.318

[a] $I > 3\sigma(I)$. [b] Goodness of fit $= [\Sigma w(\|F_o\| - \|F_c\|)^2/(N_o - N_p)]^{\frac{1}{2}}$.

Table 2 Final atomic coordinates for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Mn(1)	0.0504(1)	0.1466(1)	0.3147(1)
O(1)	0.1502(2)	−0.0254(2)	0.4308(2)
O(2)	0.1615(2)	−0.1077(2)	0.6322(2)
C(1)	0.2146(3)	−0.0541(3)	0.5259(3)
C(2)	0.3614(3)	−0.0259(3)	0.5129(2)
C(3)	0.4590(4)	−0.0359(3)	0.4103(3)
C(4)	0.4052(4)	0.0098(3)	0.6019(3)
N(1)	−0.0395(3)	0.2947(2)	0.1445(2)
C(5)	−0.1255(4)	0.4025(3)	0.1460(3)
C(6)	−0.2025(4)	0.4790(3)	0.0493(3)
C(7)	−0.1936(5)	0.4404(4)	−0.0507(3)
C(8)	−0.1042(5)	0.3298(3)	−0.0545(3)
C(9)	−0.0276(4)	0.2595(3)	0.0435(3)
C(10)	0.0740(4)	0.1402(3)	0.0448(3)
C(11)	0.1304(6)	0.1073(4)	−0.0594(3)
C(12)	0.2244(7)	−0.0044(5)	−0.0511(4)
C(13)	0.2634(6)	−0.0789(4)	0.0612(4)
C(14)	0.2052(4)	−0.0412(3)	0.1619(3)
N(2)	0.1125(3)	0.0663(2)	0.1559(2)
N(3)	0.0350(3)	0.2696(2)	0.4359(2)
C(15)	−0.0811(4)	0.2917(3)	0.5155(3)
C(16)	−0.0749(5)	0.3396(3)	0.6080(3)
C(17)	0.0546(6)	0.3633(4)	0.6209(3)
C(18)	0.1737(5)	0.3420(3)	0.5407(3)
C(19)	0.1603(4)	0.2968(3)	0.4468(3)
C(20)	0.2817(4)	0.2825(3)	0.3498(3)
C(21)	0.4083(5)	0.3239(3)	0.3399(4)
C(22)	0.5107(5)	0.3170(4)	0.2418(4)
C(23)	0.4843(4)	0.2698(3)	0.1552(4)
C(24)	0.3572(4)	0.2272(3)	0.1726(3)
N(4)	0.2564(3)	0.2324(2)	0.2680(2)
Cl(1)	0.4710(1)	0.3453(1)	0.7398(1)
O(3)	0.4019(8)	0.2555(6)	0.8130(7)
O(4)	0.5558(6)	0.2972(5)	0.6513(5)
O(5)	0.5612(5)	0.3735(4)	0.8060(4)
O(6)	0.3712(4)	0.4517(4)	0.6874(4)

Table 3 Selected interatomic distances (Å) and bond angles (°) for complex **1** with e.s.d.s in parentheses *

Manganese environment			
Mn(1)–O(1)	2.123(2)	Mn(1)–N(2)	2.262(3)
Mn(1)–O(2b)	2.113(2)	Mn(1)–N(3)	2.278(3)
Mn(1)–N(1)	2.297(2)	Mn(1)–N(4)	2.305(3)
O(1)–Mn(1)–O(2b)	94.0(1)	O(2b)–Mn(1)–N(3)	96.6(1)
O(1)–Mn(1)–N(1)	161.0(1)	N(1)–Mn(1)–N(4)	88.3(1)
O(1)–Mn(1)–N(2)	88.9(1)	N(1)–Mn(1)–N(2)	72.1(1)
O(1)–Mn(1)–N(3)	99.6(1)	N(1)–Mn(1)–N(3)	99.1(1)
O(1)–Mn(1)–N(4)	94.6(1)	N(2)–Mn(1)–N(4)	91.8(1)
O(2b)–Mn(1)–N(1)	87.1(1)	N(2)–Mn(1)–N(3)	161.6(1)
O(2b)–Mn(1)–N(4)	166.3(1)	N(3)–Mn(1)–N(4)	71.4(1)
O(2b)–Mn(1)–N(2)	99.1(1)		
Terephthalate bridge			
C(1)–O(1)	1.266(4)	C(2)–C(3)	1.399(4)
C(1)–O(2)	1.264(3)	C(2)–C(4)	1.386(5)
C(1)–C(2)	1.479(5)	C(3)–C(4a)	1.368(5)
O(1)–C(1)–O(2)	123.6(3)	C(1)–C(2)–C(4)	120.9(3)
O(1)–C(1)–C(2)	118.8(2)	C(3)–C(2)–C(4)	118.8(3)
O(2)–C(1)–C(2)	117.5(3)	C(2)–C(3)–C(4a)	120.3(3)
C(1)–C(2)–C(3)	120.2(3)	C(2)–C(4)–C(3a)	120.9(3)

* Symmetry codes: a $1 - x, -y, 1 - z$; b $-x, -y, 1 - z$.

best equatorial plane is defined by atoms N(2), O(2b), N(3) and N(4) [largest deviation from the mean plane 0.014(3) Å for N(3)] and the manganese atom is 0.156(1) Å out of this plane toward O(1).

The six-membered rings of the two bipy ligands are planar as expected with deviations from the mean planes not greater than ±0.015(4) Å. However, the bipy ligands as a whole exhibit relevant deviations from planarity [dihedral angles between the pyridyl rings in each bipy ligand 11.5(1) and 17.6(1)°]. Average carbon–carbon and –nitrogen bond distances are close to those reported for unco-ordinated bipy.[22] Concerning the terephthalate ligand, the most remarkable structural feature is its unprecedented tetrakis(monodentate) co-ordinating character. Co-ordination of terephthalate to two [bis(monodentate) and bis(chelating) co-ordination modes] and three [tris(monodentate)] metal centres has been reported in previous structural works dealing with terephthalato-containing first-row transition-metal ions.[13,23,24] Its eight carbon atoms in complex **1** are strictly coplanar [largest deviation from the mean plane 0.002(3) Å]. The O(1) and O(2) atoms of the carboxylate groups are respectively 0.645(2) and −0.672(3) Å above and below this plane. The dihedral angle between the benzene ring and the carboxylate plane is 143.8(1)°. The weak overlapping between this benzene ring and the N(4)C(20)C(21)C(22)C(23)-C(24) pyridyl group [the separation between them is 3.478(3) Å] is at the origin of such a large dihedral angle. The dihedral angle between the equatorial plane and the benzene ring is 17.3(1)°, whereas that formed by the carboxylate group and the O(1)O(2b)N(1)N(4) mean plane is 35.5(1)°.

The perchlorate groups have their expected tetrahedral geometry [average values for Cl–O and intra-ion O–Cl–O bond angle 1.379(6) Å and 109.4(3)°, respectively].

The intrachain metal–metal separations are 4.643(1) and 9.637(2) Å for Mn(1)···Mn(1b) and Mn(1)···Mn(1a), respectively the shortest corresponding to the doubly carboxylate-bridged manganese(II) pair. This kind of carboxylate bridging in terephthalato complexes was previously observed in $[Cu(3Me\text{-}py)_2(ta)]\cdot0.5(3Me\text{-}py)\cdot0.5MeOH$ (3Me-py = 3-methylpyridine).[13h] The shortest intrachain metal–metal separation is 9.516(2) Å for Mn(1)···Mn(1c) (symmetry code: c $1 + x, y, z$).

Magnetic Properties.—The magnetic behaviour of complex **1** represented by plots of χ_m [molar magnetic susceptibility per two manganese(II) ions] and χ_mT *versus* T is depicted in Fig. 2. At 290 K, χ_mT = 8.32 cm^3 K mol^{-1}, a value somewhat smaller than expected for two uncoupled manganese(II) ions (8.75 cm^3

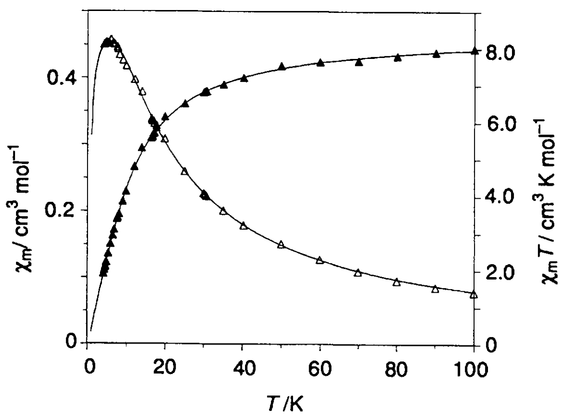
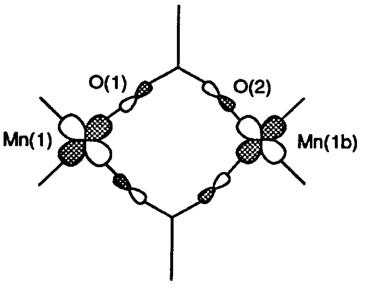


Fig. 2 Thermal dependence of the molar magnetic susceptibility χ_m (Δ) and $\chi_m T$ (▲) (per two manganese atoms). The solid line corresponds to the best theoretical fit (see text)



Scheme 1

K mol^{-1}); $\chi_m T$ continuously decreases upon cooling and reaches a value of 1.91 cm^3 K mol^{-1} at 4.2 K. Such a behaviour is characteristic of an antiferromagnetic interaction between two high-spin manganese(II) ions. The occurrence of a sharp susceptibility maximum around 6.0 K is the signature of an antiferromagnetic interaction with a singlet ground state.

We have attempted to reproduce theoretically the experimental susceptibility of complex **1** by use of the Heisenberg–Dirac–Van Vleck $S_A = S_B = \frac{5}{2}$ spin-coupled dimer model ($\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$) with a molecular field correction[25] to account for the actual nature of the compound. Values of -1.35 cm^{-1}, 1.97 and -0.04 cm^{-1} were obtained for J, g and zJ', respectively with a very good R value of 5.9×10^{-5} {R is the agreement factor defined as $\Sigma[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2/\Sigma[(\chi_m T)_{obs}]^2$}. An inspection of the computed curves (Fig. 2) shows that a satisfactory match to the experimental data is achieved. In the light of the structure of **1** two exchange pathways are possible within the chain: the double carboxylate bridge in the sym-sym conformation and the extended terephthalate group which leads to metal–metal separations of 4.643(1) and 9.637(2) Å, respectively. The much shorter metal–metal separation through the carboxylate together with the fact that the value of $-J$ found agrees well with those reported for other triply ($-J$ 3.5–4.4 cm^{-1})[21a,c] and doubly bridged carboxylate manganese(II) complexes ($-J = 1.9$ cm^{-1})[21f], allows us to propose this bridging network as responsible for this significant antiferromagnetic coupling. This exchange pathway involving the overlapping between the two $d_{x^2-y^2}$ magnetic orbitals centred on Mn(1) and Mn(1b) [the x and y axes are roughly defined by the O(1)···N(1) and O(2b)···N(4) vectors, respectively] through sym-sym carboxylate bridges is illustrated by Scheme 1. Consequently, the weak antiferromagnetic coupling J' most likely accounts for the interaction between manganese(II) ions through the more extended terephthalate bridge. In this regard, it is worthwhile noting that very weak exchange interactions either antiferro- or ferro-magnetic have been reported for most terephthalato-bridged copper(II) complexes[13d,f,h,i] and only a few cases exhibiting a moderately strong antiferromagnetic interaction are known.[13b,e] The synthesis, structural and magnetic characterization of other examples of terephthalate-bridged manganese(II) compounds will be the subject of further work in order to explore the influence of the symmetry of the magnetic orbitals with respect to the terephthalate bridge and check the possible σ- and π-exchange pathways.

Acknowledgements

Financial support from the Dirección General de Investigación Científica Técnica (DGICYT) (Spain) through Project PB91-0807-C02-01 and from the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica is gratefully acknowledged. Two of us (J. C. and R. R.) are indebted to the Ministerio de Educación y Ciencia and to the Conselleria de Cultura, Educació i Ciència de la Generalitat Valenciana for predoctoral grants.

References

1 *Magneto-Structural Correlations in Exchange Coupled Systems*, eds. R. D. Willet, D. Gatteschi and O. Kahn, NATO ASI Series, Reidel, Dordrecht, 1985.
2 R. E. Coffman and G. R. Buettner, *J. Phys. Chem.*, 1979, **83**, 2387.
3 T. R. Felthouse, E. J. Laskowski and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 1077; M. Julve, M. Verdaguer, O. Kahn, A. Gleizes and M. Philoche-Levisalles, *Inorg. Chem.*, 1984, **23**, 3808; L. Soto, J. García, E. Escrivá, J.-P. Legros, J.-P. Tuchagues, F. Dahan and A. Fuertes, *Inorg. Chem.*, 1989, **28**, 3378; S. Alvarez, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 4500; A. Gleizes, M. Julve, M. Verdaguer, J. A. Real, J. Faus and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1992, 3209.
4 M. Julve, G. De Munno, G. Bruno and M. Verdaguer, *Inorg. Chem.*, 1988, **27**, 3160; M. Julve, M. Verdaguer, G. De Munno, J. A. Real and G. Bruno, *Inorg. Chem.*, 1993, **32**, 795.
5 M. Verdaguer, O. Kahn, M. Julve and A. Gleizes, *Nouv. J. Chim.*, 1985, **9**, 325; Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.*, 1985, **24**, 4063; H. Okawa, N. Matsumoto, M. Koikawa, K. Takeda and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1990, 1383; J. Ribas, A. García, R. Costa, M. Monfort, S. Alvarez, C. Zanchini, X. Solans and M. V. Domenech, *Inorg. Chem.*, 1991, **30**, 841; 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 J. J. Girerd, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem.*, 1978, **17**, 3034; R. Veit, J. J. Girerd, O. Kahn, F. Robert, Y. Jeannin and N. El Murr, *Inorg. Chem.*, 1984, **23**, 4448; R. Veit, J. J. Girerd, O. Kahn, F. Robert and Y. Jeannin, *Inorg. Chem.*, 1986, **25**, 4175.
7 R. Vicente, J. Ribas, S. Alvarez, A. Seguí, X. Solans and M. Verdaguer, *Inorg. Chem.*, 1987, **26**, 4004.
8 J. Commarmond, P. Plumeré, J. M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn and I. Morgenstern-Badarau, *J. Am. Chem. Soc.*, 1982, **104**, 6330; I. Bkouche-Waksman, M. L. Boillot, O. Kahn and S. Sikorav, *Inorg. Chem.*, 1984, **23**, 4454; P. Chaudhuri, K. Oder, K. Wieghardt, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 2818.
9 I. Castro, J. Sletten, J. Faus, M. Julve, Y. Journaux, F. Lloret and S. Alvarez, *Inorg. Chem.*, 1992, **31**, 1989; A. Cornia, A. C. Fabretti, A. Giusti, F. Ferraro and D. Gatteschi, *Inorg. Chim. Acta*, 1993, **212**, 87.
10 C. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2367; M. Verdaguer, A. Michalowicz, J. J. Girerd, N. Alberding and O. Kahn, *Inorg. Chem.*, 1980, **19**, 3271; F. Tinti, M. Verdaguer, O. Kahn and J. M. Savariault, *Inorg. Chem.*, 1987, **26**, 2380; J. V. Folgado, R. Ibáñez, E. Coronado, D. Beltrán, J. M. Savariault and J. Galy, *Inorg. Chem.*, 1988, **27**, 19; P. Chaudhuri and K. Oder, *J. Chem. Soc., Dalton Trans.*, 1990, 1597.
11 X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775.
12 M. Julve, M. Verdaguer, J. Faus, F. Tinti, J. Moratal, A. Monge and E. Guitérrez-Puebla, *Inorg. Chem.*, 1987, **26**, 3520.
13 (*a*) M. Verdaguer, J. Gouteron, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem.*, 1984, **23**, 4291; (*b*) E. G. Bakalbassis, C. A. Tsipis and J. Mrozinski, *Inorg. Chem.*, 1985, **24**, 4231; (*c*) E. G. Bakalbassis, J. Mrozinski and C. A. Tsipis, *Inorg. Chem.*, 1986, **25**, 3684; (*d*) E. G. Bakalbassis, A. P. Bozopoulos, J. Mrozinski, P. J. Rentzeperis and C. A. Tsipis, *Inorg. Chem.*, 1988, **27**, 529; (*e*) P. Chaudhuri, K. Oder, K. Wieghardt, S. Ghering, W. Haase, B. Nuber and

J. Weiss, *J. Am. Chem. Soc.*, 1988, **110**, 3657; (*f*) E. G. Bakalbassis, O. Kahn, P. Bergerat, S. Jeannin, Y. Jeannin and Y. Dromzee, *J. Chem. Soc., Chem. Commun.*, 1990, 1771; (*g*) E. G. Bakalbassis, C. A. Tsipis, A. P. Bozopoulos, W. Dreissig, H. Hartl and J. Mrozinski, *Inorg. Chim. Acta*, 1991, **186**, 113; (*h*) E. G. Bakalbassis, P. Bergerat, O. Kahn, S. Jeannin, Y. Jeannin, Y. Dromzee and M. Guillot, *Inorg. Chem.*, 1992, **31**, 625; (*i*) C. E. Xanthopoulos, M. P. Sigalas, G. A. Katsoulos, C. A. Tsipis, A. Terzis, M. Mentzafos and A. Hountas, *Inorg. Chem.*, 1993, **32**, 5433.

14 M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.

15 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley-Interscience, New York, 1986, p. 231.

16 J. C. Bernier and P. Poix, *Actual. Chim.*, 1978, **2**, 7.

17 A. Earshaw, *Introduction to Magnetochemistry*, Academic Press, London and New York, 1968.

18 A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

19 SHELXTL PLUS, Version 4.21/V, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.

20 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.

21 (*a*) K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols and J. J. Girerd, *J. Am. Chem. Soc.*, 1988, **110**, 7398; (*b*) D. Deguenon, G. Bernardelli, J. P. Tuchagues and P. Castan, *Inorg. Chem.*, 1990, **29**, 3031; (*c*) S. Ménage, S. E. Vitols, P. Bergerat, E. Codjovi, O. Kahn, J. J. Girerd, M. Guillot, X. Solans and T. Calvet, *Inorg. Chem.*, 1991, **30**, 2666; (*d*) Z. H. Jiang, S. L. Ma, D. Z. Liao, S. P. Yan, G. L. Wang, X. K. Yao and R. J. Wang, *J. Chem. Soc., Chem. Commun.*, 1993, 745; (*e*) M. Andruh, H. W. Roesky, M. Noltemeyer and H. G. Schmidt, *Polyhedron*, 1993, **12**, 2901; (*f*) H. Oshio, E. Ino, I. Mogi and T. Ito, *Inorg. Chem.*, 1993, **32**, 5697.

22 L. L. Merrit and E. D. Schroeder, *Acta Crystallogr.*, 1956, **9**, 801.

23 S. Cueto, V. Gramlich, W. Peter, F. Rys and P. Rys, *Acta Crystallogr., Sect. C*, 1991, **47**, 75.

24 Z. L. Deng, J. Shi, Z. H. Jiang, D. Z. Liao, S. P. Yang, G. L. Wang, H. G. Wang and R. J. Wang, *Polyhedron*, 1992, **11**, 885.

25 A. P. Ginsberg and M. E. Lines, *Inorg. Chem.*, 1972, **11**, 2289.

Received 18*th March* 1994; *Paper* 4/01629G