Dinuclear Manganese(II) Complexes of 2,6-Bis[2-(dialkylamino)-ethyliminomethyl]-4-methylphenolate(1−): Synthesis, Structure, and Magnetism†

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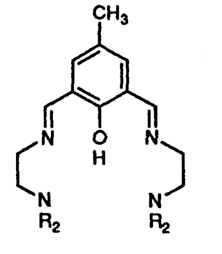
2,6-Bis[2-(dialkylamino)ethyliminomethyl]-4-methylphenolate(1−) [alkyl = methyl (L^1) or ethyl (L^2)] forms two types of dinuclear manganese(II) complexes $[Mn_2L(RCO_2)_2(NCS)]$ ($L = L^1$ or L^2, $R = CH_3$ or C_6H_5) and $[Mn_2LCl_3]$ ($L = L^1$ or L^2). The crystal structure of $[Mn_2L^1(CH_3CO_2)_2(NCS)]\cdot H_2O\cdot CH_3OH$ has been determined: monoclinic, space group $P2_1/n$, $a = 17.700(3)$, $b = 12.516(2)$, $c = 15.263(3)$ Å, $\beta = 107.16(1)°$ and $Z = 4$. The X-ray analysis reveals a dinuclear structure bridged by the phenolic oxygen of L^1 and two acetate groups. The thiocyanate group co-ordinates to one Mn, resulting in different co-ordination geometries about the two manganese ions, *i.e.* trigonal bipyramidal and pseudo-octahedral. Magnetic susceptibility measurements over the temperature range 4.2–300 K indicate weak antiferromagnetic interaction ($J = -2$ to -5 cm^{-1}) for $[Mn_2L(RCO_2)_2(NCS)]$ and no appreciable interaction for $[Mn_2LCl_3]$.

Multinuclear manganese cores are known to play integral roles in biological systems such as the oxygen-evolving complex of photosystem II of green plants,[1] manganese catalases,[2] and manganese ribonucleotide reductase.[3] It is known that there are four Mn atoms per oxygen-evolving complex,[4] but their precise arrangement has not been determined unambiguously.[5] The presence of two distinct Mn···Mn separations [2.72(3) and ≈3.3 Å] has been indicated by extended X-ray absorption fine structure (EXAFS) studies[6,7] and this finding has stimulated the synthesis of manganese complexes of 'dimer of dimer' type[8] as models of the active site of the oxygen-evolving complex. X-Ray structure analysis for the manganese catalase from *Thermus thermophilus*[9] has revealed the presence of a couple of manganese(III) ions with a Mn···Mn separation of *ca.* 3.6(3) Å. The catalase from *Lactobacillus plantarum* also has two manganese(III) ions in each subunit.[10] A μ-oxo-bis(μ-carboxylato)dimanganese(III) core structure is suggested for these catalases based on characteristic absorptions in the visible region.[11] The manganese content of ribonucleotide reductase has not been determined but this metal enzyme is also suggested to contain a μ-oxo-bis(μ-carboxylato)dimanganese(III) core.[11] Simple μ-oxo-bis(μ-carboxylato)dimanganese(III)[12] and μ-oxo-bis(μ-carboxylato)manganese(III)manganese(IV)[13] complexes have been obtained as models but the study of analogous dinuclear manganese complexes, such as those with a μ-phenoxo instead of the μ-oxo group, is also very important in order to gain insight into the dimanganese core effect in manganese enzymes.

In this study we carried out the syntheses of manganese complexes using 2,6-bis[2-(dialkylamino)ethyliminomethyl]-4-methylphenol [alkyl = methyl (HL^1) or ethyl (HL^2)]. Two types of dinuclear manganese(II) complexes, $[Mn_2L(RCO_2)_2(NCS)]$ ($L = L^1$ or L^2; $R = CH_3$ or C_6H_5) and $[Mn_2LCl_3]$ ($L = L^1$ or L^2), have been derived. The crystal structure of $[Mn_2L^1(CH_3CO_2)_2(NCS)]\cdot H_2O\cdot CH_3OH$ reveals a μ-phenoxo-bis(μ-carboxylato) bridging system. The cryomagnetic properties (4.2–300 K) of the two types of complexes are described.



HL^1 $R = CH_3$
HL^2 $R = C_2H_5$

Experimental

Materials.—2,6-Diformyl-4-methylphenol was prepared by a modification[14] of the method of Denton and Suschitzky.[15] All the chemicals were of reagent grade and used as purchased.

Measurements.—Elemental analyses of C, H and N were obtained at the Service Centre of Elemental Analysis, Kyushu University. Analyses of Mn were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were recorded on KBr disks with a JASCO IR-810 spectrophotometer. Molar conductances were measured on a DKK AOL-10 conductivity meter at room temperature. Electronic spectra were recorded on a Shimadzu MPS-2000 spectrophotometer at room temperature. Magnetic susceptibilities were measured on a HOXAN HSM-D SQUID susceptometer in the temperature range 4.2–80 K and a Faraday balance in the range 80–300 K. Calibrations were made with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$ for the SQUID magnetometer and with $[Ni(en)_3][S_2O_3]$ (en = ethane-1,2-diamine) for the Faraday balance.[16] Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A T)^{\frac{1}{2}}$, where χ_A is the atomic magnetic susceptibility corrected for diamagnetism of the constituting atoms using Pascal's constants.[17]

Preparations.—$[Mn_2L^1(CH_3CO_2)_2(NCS)]$ **1**. A solution of 2,6-diformyl-4-methylphenol (0.164 g, 1.0 mmol) and *N,N*-dimethylethane-1,2-diamine (0.176 g, 2.0 mmol) in methanol (5

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† *Supplementary data available* (No. SUP 56921, 7 pp.): temperature dependences of susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Atomic coordinates ($\times 10^4$) of non-hydrogen atoms in $[Mn_2L^1(CH_3CO_2)_2(NCS)]\cdot H_2O\cdot CH_3OH$

Atom	*x*	*y*	*z*
Mn(1)	4399(1)	3737(2)	2231(1)
Mn(2)	3983(1)	6326(2)	1932(1)
O(1)	4036(5)	5031(7)	2907(5)
N(1)	4847(6)	3125(8)	3611(8)
N(2)	4873(8)	2054(10)	2047(10)
N(3)	2950(6)	6769(9)	2367(7)
N(4)	3425(6)	7732(8)	951(8)
C(1)	3852(7)	5063(10)	3675(8)
C(2)	4180(7)	4330(10)	4389(8)
C(3)	3991(8)	4410(11)	5214(8)
C(4)	3475(8)	5152(11)	5392(9)
C(5)	3143(8)	5849(11)	4685(9)
C(6)	3316(7)	5829(10)	3843(8)
C(7)	3286(10)	5182(14)	6284(10)
C(8)	4697(7)	3454(10)	4341(9)
C(9)	5358(10)	2189(13)	3726(11)
C(10)	5521(13)	1936(16)	2861(16)
C(11)	4351(15)	1223(19)	2109(23)
C(12)	5070(30)	1915(22)	1290(21)
C(13)	2878(8)	6628(11)	3176(9)
C(14)	2452(9)	7599(13)	1794(11)
C(15)	2963(10)	8331(13)	1429(11)
C(16)	4031(12)	8449(15)	838(13)
C(17)	2951(13)	7401(15)	59(12)
O(A1)	5214(6)	4408(8)	1699(7)
O(A2)	4950(5)	6125(8)	1400(7)
C(A1)	5992(10)	5333(14)	945(12)
C(A2)	5323(8)	5291(12)	1379(9)
O(B1)	3320(5)	3459(7)	1264(7)
O(B2)	3306(6)	5186(7)	925(6)
C(B1)	2212(11)	4142(16)	134(16)
C(B2)	3017(8)	4298(12)	826(10)
S(T)	5399(5)	8988(5)	4182(4)
N(5)	4713(7)	7394(10)	2970(8)
C(T)	4977(9)	8074(11)	3451(10)
O(M)	7686(5)	2519(9)	2532(6)
C(M)	8510(19)	3247(30)	2673(20)
O(W)	6185(6)	9089(9)	1389(10)

cm^3) was refluxed for 10 min. To the resulting yellow solution was added manganese(II) acetate tetrahydrate (0.490 g, 2.0 mmol) and the mixture was refluxed for 30 min. The addition of NaSCN (0.162 g, 2.0 mmol) yielded a yellow crystalline precipitate. Yield: 0.28 g (48%) (Found: C, 44.80; H, 5.60; Mn, 18.8; N, 12.00. Calc. for $C_{22}H_{33}Mn_2N_5O_5S$: C, 44.85; H, 5.65; Mn, 18.6; N, 11.90%).

$[Mn_2L^2(CH_3CO_2)_2(NCS)]$ **2**. This complex was prepared as yellow microcrystals by a method similar to that for **1** using *N*,*N*-diethylethane-1,2-diamine instead of *N*,*N*-dimethylethane-1,2-diamine. Yield: 0.40 g (62%) (Found: C, 48.10; H, 6.40; Mn, 17.2; N, 10.95. Calc. for $C_{26}H_{41}Mn_2N_5O_5S$: C, 48.35; H, 6.40; Mn, 17.0; N, 10.85%).

$[Mn_2L^1(C_6H_5CO_2)_2(NCS)]$ **3**. This was prepared as yellow microcrystals by a method similar to that for complex **1** using manganese(II) benzoate dihydrate instead of manganese(II) acetate tetrahydrate. Yield: 0.57 g (80%) (Found: C, 53.85; H, 5.25; Mn, 15.7; N, 9.80. Calc. for $C_{32}H_{37}Mn_2N_5O_5S$: C, 53.85; H, 5.25; Mn, 15.4; N, 9.80%).

$[Mn_2L^2(C_6H_5CO_2)_2(NCS)]$ **4**. This was prepared as yellow microcrystals by the method similar to that for complex **2**. Manganese(II) benzoate dihydrate was used instead of manganese(II) acetate tetrahydrate. Yield: 0.39 g (50%) (Found: C, 56.20; H, 5.90; Mn, 14.9; N, 9.00. Calc. for $C_{36}H_{45}Mn_2N_5O_5S$: C, 56.20; H, 5.90; Mn, 14.3; N, 9.10%).

$[Mn_2L^1Cl_3]$ **5**. A mixture of 2,6-diformyl-4-methylphenol (0.164 g, 1.0 mmol) and of *N*,*N*-dimethylethane-1,2-diamine (0.176 g, 2.0 mmol) in methanol (5 cm^3) was refluxed for 10 min to form a yellow solution. Then, manganese(II) chloride tetrahydrate (0.396 g, 2.0 mmol) was added, and the mixture refluxed for 30 min and concentrated to 2 cm^3 to give a yellow precipitate. Yield: 0.26 g (50%) (Found: C, 39.25; H, 5.20; Mn, 21.2; N, 10.80. Calc. for $C_{17}H_{27}Cl_3Mn_2N_4O$: C, 39.30; H, 5.25; Mn, 21.1; N, 10.80%).

$[Mn_2L^2Cl_3]$ **6**. This complex was prepared as a yellow crystalline powder by a method similar to that for **5**, using *N*,*N*-diethylethane-1,2-diamine instead of *N*,*N*-dimethylethane-1,2-diamine. Yield: 0.04 g (6.8%) (Found: C, 43.30; H, 6.05; Mn, 18.8; N, 9.60. Calc. for $C_{21}H_{35}Cl_3Mn_2N_4O\cdot 0.5H_2O$: C, 43.15; H, 6.20; Mn, 18.8; N, 9.60%).

X-Ray Structural Analysis of $[Mn_2L^1(CH_3CO_2)_2(NCS)]\cdot H_2O\cdot CH_3OH$.—*Crystal data.* $C_{23}H_{39}Mn_2N_5O_7S$, $M = 639.53$, monoclinic, space group $P2_1/n$, $a = 17.700(3)$, $b = 12.516(2)$, $c = 15.263(3)$ Å, $\beta = 107.16(1)°$, $U = 3231(1)$ Å^3, $Z = 4$, $D_c = 1.32$ g cm^{-3}, $F(000) = 1336$, μ(Mo-Kα) = 8.54 cm^{-1}.

Data collection and reduction. Single crystals were obtained by recrystallization of the complex from methanol–water (9:1). A crystal with approximate dimensions 0.3 × 0.3 × 0.2 mm sealed in a glass tube was used for the X-ray diffraction study. Intensities and lattice parameters were obtained on a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at 20 ± 1 °C. Lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 25 2θ values in the range $28 < 2\theta < 29°$. For the intensity data collections the ω–2θ scan mode was used at a scan rate of 2° min^{-1}. The octant measured was $+h$, $+k$, $\pm l$. Three standard reflections were monitored every 100 and showed no systematic decrease in intensity. The intensity data were corrected for Lorentz and polarization factors, but not for absorption. 2891 Independent reflections with $F > 3\sigma(F)$ in the range $2.5 \leqslant 2\theta \leqslant 48°$ were assumed to be observed.

The structure was solved by direct methods. Refinement was carried out by the block-diagonal least-squares method, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and equal weights ($w = 1$) were adopted for all reflections. Atomic scattering factors were taken from ref. 18. Hydrogen atoms were fixed at the calculated positions and were not refined. The final values of R and R' were 0.0931 and 0.1039, respectively. All the calculations were carried out on a FACOM M-1800/20 computer in the Computer Centre of Kyushu University by the use of local versions[19] of the UNICS III[20] and ORTEP[21] programs. The final positional parameters of the non-hydrogen atoms with their estimated standard deviations are listed in Table 1.

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

Results and Discussion

Synthesis and General Properties.—The two types of dinuclear manganese complexes $[Mn_2L(RCO_2)_2(NCS)]$ **1** ($L = L^1$, $R = CH_3$), **2** ($L = L^2$, $R = CH_3$), **3** ($L = L^1$, $R = C_6H_5$), **4** ($L = L^2$, $R = C_6H_5$) and $[Mn_2LCl_3]$ **5** ($L = L^1$) and **6** ($L = L^2$) are air-stable both in the solid state and in solution. Relevant IR spectral data are summarized in Table 2. All the complexes show two strong peaks at ≈1640 cm^{-1} attributable to the C=N stretching mode, suggesting that two C=N linkages of L^1 and L^2 are not equivalent in the crystal lattice. The spectrum of **1** shows antisymmetric and symmetric ν(COO) vibrations of the acetate group at 1595 and 1405 cm^{-1}, respectively. Similarly, **2**–**4** show ν_{asym}(COO) and ν_{sym}(COO) vibrations of the carboxylate group at 1585–1565 and 1410–1395 cm^{-1}, respectively. The separation between ν_{asym}(COO) and ν_{sym}(COO) is useful in the diagnosis of the co-ordination mode of the carboxylate group. That is, a symmetrically bridging carboxylate group gives a $\Delta\nu$ [$=\nu_{asym}$(COO) $-$ ν_{sym}(COO)] value smaller than 200 cm^{-1}, whereas monodentate carboxylate gives $\Delta\nu > 200$ cm^{-1}.[22] The $\Delta\nu$ values of **1**, **2**, **3** and **4**

Table 2 Selected IR spectral, molar conductance, and visible spectral data for complexes 1–6

	IR ($\tilde{\nu}$/cm^{-1})					
		carboxylate				
Complex	imine	ν_{asym}(COO)	ν_{sym}(COO)	thiocyanate	Λ_M[a]	VIS($\tilde{\nu}_{max}$/cm^{-1})[b]
1 $[Mn_2L^1(CH_3CO_2)_2(NCS)]$	1650 1630	1595	1405	2060	54	26 100 (7800)
2 $[Mn_2L_2(CH_3CO_2)_2(NCS)]$	1650 1630	1585	1410	2060	57	26 100 (8000)
3 $[Mn_2L^1(C_6H_5CO_2)_2(NCS)]$	1655 1630	1565	1395	2085	60	26 200 (8000)
4 $[Mn_2L^2(C_6H_5CO_2)_2(NCS)]$	1655 1640	1565	1395	2045	58	26 200 (7600)
5 $[Mn_2L^1Cl_3]$	1645 1630				21	25 700 (6400)
6 $[Mn_2L^2Cl_3]$	1645 1625				25	25 100 (7200)

[a] Molar conductance (S cm^2 mol^{-1}) measured at 10^{-3} mol dm^{-3}. [b] Absorption coefficient (dm^3 mol^{-1} cm^{-1}) given in parentheses.

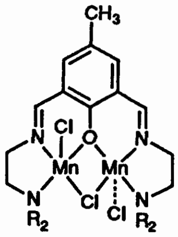

Fig. 1 Proposed structure of the chloride complexes 5 and 6

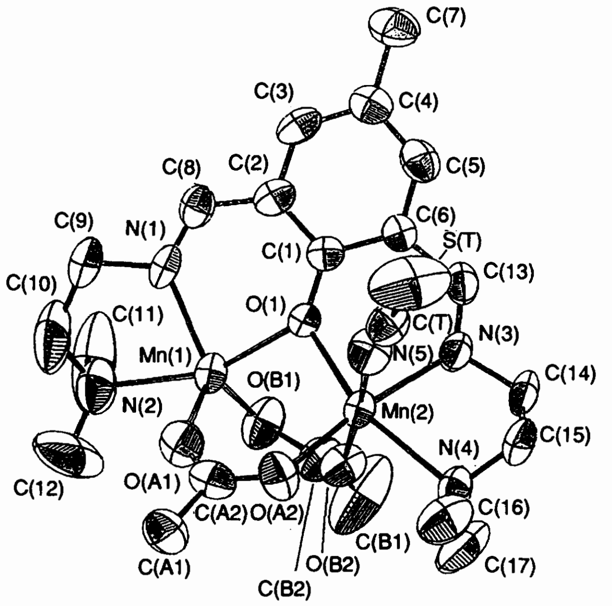

Fig. 2 An ORTEP view of complex 1 with the atom numbering scheme

are 190, 175, 170 and 170 cm^{-1}, respectively, suggesting a bridging function of the carboxylate groups between the two manganese(II) ions. The spectra of complexes 1-4 show a strong peak at ≈2060 cm^{-1}, which is characteristic of ν(CN) of the thiocyanate group. However, the ν(CS) and δ(NCS) modes of the thiocyanate group could not be assigned unambiguously.

Molar conductance data are listed in Table 2. The carboxylate complexes 1–4 are 1:1 electrolytes in dimethylformamide (dmf),[23] suggesting that the thiocyanate ion is dissociated. On the other hand, the chloride complexes 5 and 6 are essentially non-electrolytes in dmf.[23] We presume that one chloride ion acts as a bridge between a pair of manganese(II) ions and the remaining two chloride ions each co-ordinates singly to each manganese (see Fig. 1).[24,25]

Table 3 Selected bond distances (Å) and angles (°) for $[Mn_2L^1(CH_3CO_2)_2(NCS)]\cdot H_2O\cdot CH_3OH$

Mn(1)–O(1)	2.119(9)	Mn(2)–N(3)	2.192(12)
Mn(1)–N(1)	2.161(11)	Mn(2)–N(4)	2.333(10)
Mn(1)–N(2)	2.315(13)	Mn(2)–O(A2)	2.117(11)
Mn(1)–O(A1)	2.035(11)	Mn(2)–O(B2)	2.178(9)
Mn(1)–O(B1)	2.069(9)	Mn(2)–N(5)	2.181(11)
Mn(2)–O(1)	2.183(9)	Mn(1) • • • Mn(2)	3.325(3)
O(1)–Mn(1)–N(1)	82.7(4)	O(1)–Mn(2)–O(B2)	84.2(3)
O(1)–Mn(1)–N(2)	158.1(4)	O(1)–Mn(2)–N(5)	93.6(4)
O(1)–Mn(1)–O(A1)	103.4(4)	N(3)–Mn(2)–N(4)	76.8(4)
O(1)–Mn(1)–O(B1)	97.3(4)	N(3)–Mn(2)–O(A2)	171.1(4)
N(1)–Mn(1)–N(2)	75.8(5)	N(3)–Mn(2)–O(B2)	92.6(4)
N(1)–Mn(1)–O(A1)	115.8(4)	N(3)–Mn(2)–N(5)	89.6(5)
N(1)–Mn(1)–O(B1)	129.2(4)	N(4)–Mn(2)–O(A2)	94.6(4)
N(2)–Mn(1)–O(A1)	90.1(5)	N(4)–Mn(2)–O(B2)	90.1(3)
N(2)–Mn(1)–O(B1)	93.0(4)	N(4)–Mn(2)–N(5)	93.0(4)
O(A1)–Mn(1)–O(B1)	113.5(4)	N(4)–Mn(2)–O(B2)	89.4(4)
O(1)–Mn(2)–N(3)	81.6(4)	N(4)–Mn(2)–N(5)	88.8(5)
O(1)–Mn(2)–N(4)	157.3(4)	N(4)–Mn(2)–N(5)	176.6(4)
O(1)–Mn(2)–O(A2)	107.2(4)		

All the complexes show no appreciable absorption in the region below 22 000 cm^{-1} in dmf solution, indicating the electronic configuration of Mn^{II} to be of high spin. An intense band around 26 300 cm^{-1} (see Table 2) is assigned to the azomethine π–π* transition.[26]

Structure of Complex 1.—The crystal structure of $[Mn_2L^1(CH_3CO_2)_2(NCS)]\cdot H_2O\cdot CH_3OH$ has been determined by single-crystal X-ray methods. A perspective view of the complex molecule with the atom numbering scheme is depicted in Fig. 2. Selected bond distances and angles with their estimated standard deviations are listed in Table 3.

The complex molecule consists of the dinucleating ligand L^1, two Mn ions, two acetate groups, and one thiocyanate group. The water and the methanol molecules involved in the crystal are free from co-ordination and captured in the lattice. The ions Mn(1) and Mn(2) are bridged by the phenolic oxygen of L^1 and two acetate groups, affording a μ-phenoxo-bis(μ-carboxylato)dimanganese(II) core structure. The thiocyanate group co-ordinates to Mn(2) to afford a different geometrical environment. The environment around Mn(1) is regarded as trigonal bipyramidal with the imino nitrogen N(1) and the two acetate oxygens O(A1) and O(B1) in the basal plane and the phenolic oxygen O(1) and the amino nitrogen N(2) at the apices. The surroundings of Mn(2) are pseudo-octahedral with

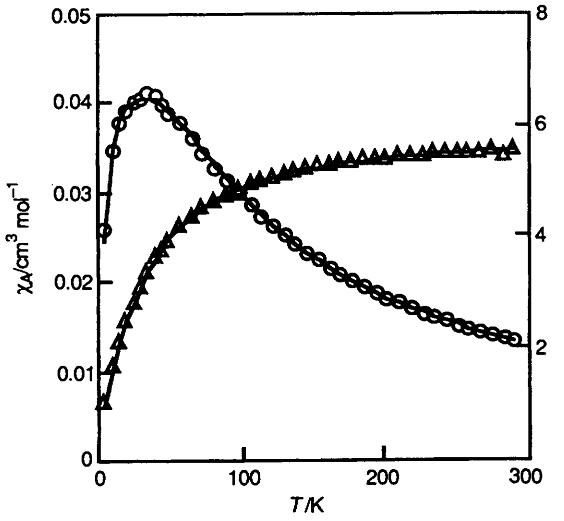

Fig. 3 Temperature dependences of χ_A (○) and μ_{eff} (△) of complex **1**. Solid curves based on equation (1), using $J = -4.0$ cm^{-1}, $g = 2.00$ and $N\alpha = 0$

O(1), N(3) and N(4) of L^1, O(A2) and O(B2) of the bridging acetate groups, and N(5) of the thiocyanate group. Similar asymmetry in the dimanganese(II) structure has been found by Mikuriya *et al.*[27] for a related complex $[Mn_2L'(CH_3CO_2)_2(NCS)]$ of 4-methyl-2,6-bis[2-(2-pyridylethyl)iminomethyl]phenolate (L′). In this complex the geometry of the five-co-ordinate manganese is regarded as square pyramidal.

The Mn–O distances [2.03(1)–2.183(9) Å] fall within the range commonly found for manganese(II) complexes.[28] The Mn–N distances, except for Mn(1)–N(2) and Mn(2)–N(4), fall in the range 2.16(1)–2.19(1) Å, which is normal for manganese(II) complexes.[28] The distances Mn(1)–N(2) and Mn(2)–N(4) are 2.31(1) and 2.33(1) Å, respectively, which are slightly elongated. This may be due to the intramolecular steric repulsion between the methyl groups attached to the amino nitrogen and the bridging acetate groups.

Magnetic Properties.—Magnetic susceptibility measurements were made on powdered samples in the temperature range 4.2–300 K. The temperature dependences of the magnetic susceptibility (χ_A) and effective magnetic moments (μ_{eff}) per Mn for **1** are shown in Fig. 3. Corresponding data for complexes **2**–**6** have been deposited as SUP 56921. The μ_{eff} values of the carboxylate complexes **1**–**4** at room temperature are in the range 5.53–5.67 (see Table 4) and decrease with decreasing temperature. The results suggests that the manganese(II) ion is high spin in all the complexes and there is an antiferromagnetic interaction within a pair of manganese(II) ions. The magnetic susceptibility equation (1) is based on the Heisenberg model [$\mathcal{H} = -2JS_1{\cdot}S_2$ ($S_1 = S_2 = \frac{5}{2}$)] where $x = \exp(-J/kT)$ and other symbols have their usual meanings.

$$\chi_A = \frac{Ng^2\beta^2}{kT} \cdot \frac{x^{28} + 5x^{24} + 14x^{18} + 30x^{10} + 55}{x^{30} + 3x^{28} + 5x^{24} + 7x^{18} + 9x^{10} + 11} + N\alpha \quad (1)$$

The cryomagnetic properties of **1** are well simulated by this equation, using the magnetic parameters $g = 2.00$, $J = -3.98$ cm^{-1}, and $N\alpha = 0$. Similarly, good magnetic simulations have been attained for **2**–**4**. The best-fitting parameters obtained for these complexes are summarized in Table 4. The exchange integrals J fall in the range -2 to -5 cm^{-1} compared to the value ($J = -2.5$ cm^{-1}) of the μ-phenoxo-bis(μ-carboxylato)dimanganese(II) complex derived from 4-methyl-2,6-bis[2-(2-pyridylethyl)iminomethyl]phenolate(1−).[27]

Table 4 Magnetic data for complex **1**–**6**

Complex	μ_{eff} at room temperature	J/cm^{-1}	g	$N\alpha$
1	5.57	−4.0	2.00	0
2	5.67	−2.9	2.00	0
3	5.54	−4.6	2.00	0
4	5.53	−4.8	2.00	0
5	5.83			
6	5.77			

The chloride complexes **5** and **6** exhibit a larger magnetic moment at room temperature (see Table 4) and each moment shows only a small reduction with decreasing temperature. Our magnetic analyses based on equation (1) gave the exchange integrals of -0.4 and -0.3 cm^{-1} for **5** and **6**, respectively. For the related chloride dimanganese(II) complex of *N,N,N′,N′*-tetrakis[(1-methylbenzimidazol-2-yl)methyl]-1,3-diaminopropan-2-olate(1−) the magnetic interaction is reported to be weakly ferromagnetic ($J \approx 1$ cm^{-1}).[25] However, for those dimanganese(II) complexes the contribution of the zero-field splitting of the manganese(II) ion cannot be neglected. Therefore, we conclude that the chloride complexes **5** and **6** show no appreciable magnetic interaction within each molecule.

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