Macrocyclic Tetranuclear Manganese(II) Complexes of a New 'Dimer of Dimers' Type: Synthesis, Structure and Magnetism†

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The template reaction of 2,6-diformyl-4-methylphenol, 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = methyl or ethyl) and manganese(II) benzoate tetrahydrate in 1 : 1 : 2 molar ratio leads to the formation of a macrocyclic tetranuclear manganese(II) complex $[Mn_4(L^n)(PhCO_2)_6]$ where H_2L^n is a [2 + 2] macrocycle obtained by condensation of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dialkyl-3,6-diazaoctane [alkyl = methyl (L^2) or ethyl (L^3)]. An adduct of the L^2 complex, $[Mn_4L^2(PhCO_2)_6(Me_2CHOH)_2]\cdot 2CH_2Cl_2$, crystallizes in the orthorhombic space group *Pbca* with $a = 20.692(3)$, $b = 20.074(3)$, $c = 22.988(5)$ Å and $Z = 4$. The refinement converged to $R = 0.0899$ and $R' = 0.0942$ based on 3798 reflections with $|F_o| > 3\sigma(|F_o|)$. The complex molecule is centrosymmetric and contains two pairs of manganese ions bridged by a phenolic oxygen of L^2 and two benzoate groups. The manganese ions in each pair are inequivalent. One is bound to the phenolic oxygen, one imino nitrogen and two amino nitrogens of L^2 and assumes a six-co-ordinate geometry co-ordinating to two oxygens of the bridging benzoate groups. The other is bound to the bridging phenolic oxygen and an imino nitrogen of L^2, two bridging benzoate oxygens, one monodentate benzoate oxygen, and one propan-2-ol oxygen to assume a six-co-ordinate geometry. Magnetic susceptibility measurements over the temperature range of 4.2–300 K indicate a weak antiferromagnetic interaction between the manganese(II) ions in each pair ($J \approx -4$ cm^{-1} based on $\hat{H} = -2JS_1 \cdot S_2$) and no magnetic interaction between the two pairs.

In photosystem II of green plants oxygen-evolving complex (OEC) plays an important role in oxidizing water to molecular oxygen.[1] It is now known[2] that four Mn ions are involved in OEC but despite many studies the precise arrangement of the four Mn ions is still unclear. Recent extended X-ray absorption fine structure (EXAFS) studies[3] have proved the presence of two distinct Mn ··· Mn separations [2.72(3) and *ca.* 3.3 Å] in OEC and this finding has stimulated the design of tetramanganese clusters of 'dimer of dimers' type[4] as a model of OEC. A mechanistic scheme that invokes the conversion of two H_2O molecules (or OH^- or O^{2-} ions) to $O_2{}^{2-}$ prior to the release of molecular oxygen has been proposed[5] and a recent study[6] suggests that this conversion occurs at the $S_3 \longrightarrow S_4$ stage of Kok's four-electron scheme. In view of these facts it is valuable to prepare new 'dimer of dimers' type tetranuclear manganese complexes in which two OH^- (or O^{2-}) groups, each bridging a pair of manganese ions, are facing each other in close proximity to provide a stereochemical pathway for O–O bond formation.

The macrocycle (H_2L^1) derived from the 2 : 2 condensation of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-diazaoctane (trien) was first obtained in dinuclear lanthanoid complexes by Kahwa *et al.*[7] Recently we have reported that this macrocycle forms a tetranuclear copper(II) complex $[Cu_4L^1(OH)_2][ClO_4]_4$ in which a pair of copper(II) ions are bridged by a phenolic oxygen and a OH^- oxygen and in which the two bridging OH^- groups face each other at a close distance.[8] However, our attempts to prepare tetranuclear manganese complexes of $(L^1)^{2-}$ by similar template reactions were all in vain. In related reactions using 1,9-diamino-3,7-diazanonane as the tetraamine component and Pb^{II} as the template ion, we have found that an unusual condensation occurs through two secondary amino groups of the tetraamine and one formyl group of 2,6-diformyl-4-methylphenol to afford a macrocycle $(L^4)^{2-}$ having hexahydropyrimidine rings.[9] Similarly, in the 3 : 1 condensation product of 2,6-diformyl-4-methylphenol and trien $(L^5)^{2-}$, obtained as praseodymium(III) and neodymium(III) complexes, the formation of an imidazolidine ring is recognized.[10] Such an unusual condensation must be due to the use of trien as the tetraamine and Mn^{II} as the template ion. In order to avoid this unusual condensation it is recommended to use a trien derivative alkylated at the secondary amino nitrogens instead of trien. Indeed, in our preliminary study a macrocyclic analogue H_2L^2 was obtained as a dilead(II) complex when 1,8-diamino-3,6-dimethyl-3,6-diazaoctane was used instead of trien.[11]

In this study we carried out the template synthesis of tetranuclear manganese(II) complexes of macrocyclic analogues $(L^2)^{2-}$ and $(L^3)^{2-}$ using 1,8-diamino-3,6-dimethyl-3,6-diazaoctane and 1,8-diamino-3,6-diethyl-3,6-diazaoctane, respectively. Manganese(II) complexes of formula $[Mn_4L^n(PhCO_2)_6]$ ($L^n = L^2$ or L^3) have been obtained and the structure of $[Mn_4L^2(PhCO_2)_6(Me_2CHOH)_2]\cdot 2CH_2Cl_2$ was determined by single-crystal X-ray diffraction. Further, cryomagnetic properties of the complexes were studied in the temperature range 4.2–300 K.

Experimental

Measurements.—Elemental analyses of carbon, hydrogen, and nitrogen were obtained from the Elemental Analysis Service Centre of Kyushi University. Analyses of manganese were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared (IR) spectra were recorded with a JASCO IR-810 spectrophotometer. Molar conductances were measured in *N,N*-dimethylformamide (dmf) (10^{-3} mol dm^{-3}) on a DKK AOL-10 conductivity meter at 20 °C. Electronic absorption spectra were recorded in dmf with a Shimadzu MPS-2000 spectrophotometer at room temperature, proton NMR spectra (400 MHz) on a JEOL JNM-GX 400 spectro-

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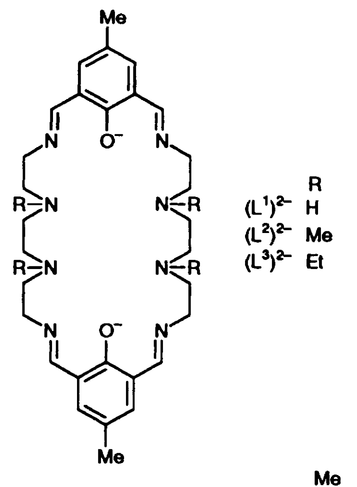
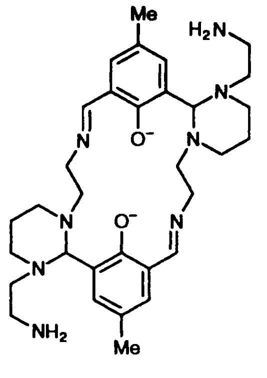
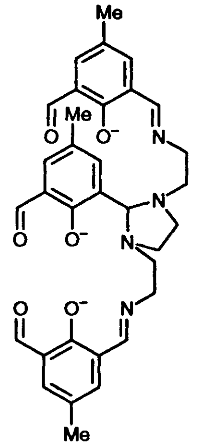
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-S.I. unit employed: mmHg ≈ 133 Pa.





$(L^4)^{2-}$



$(L^5)^{2-}$

meter in $CDCl_3$ using tetramethylsilane as the internal standard and fast atom bombardment (FAB) mass spectra on a JEOL JMS-SX102A/102A tandem mass spectrometer. 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 $[NH_4]_2[Mn(SO_4)_2]\cdot6H_2O$ for the SQUID susceptometer and with $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine) for the Faraday balance.[12] Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A T)^{\frac{1}{2}}$, where χ_A is the magnetic susceptibility corrected for diamagnetism of the constituting atoms using Pascal's constants.[13]

Materials.—2,6-Diformyl-4-methylphenol was prepared by a modification[14] of the method of Denton and Suschitzky.[15] *N*-(Toluene-*p*-sulfonyl)aziridine was prepared by the literature method.[16] All the chemicals were of reagent grade and used as purchased.

Preparations.—1,8-*Diamino*-3,6-*dimethyl*-3,6-*diazaoctane*. This reagent has been prepared previously[17] but a new, widely applicable method was developed in this study. To a hot solution of *N*,*N*′-dimethylethylenediamine (0.44 g) in acetonitrile (150 cm³) a solution of *N*-(toluene-*p*-sulfonyl)aziridine (2.00 g) in acetonitrile was added dropwise, and the mixture was refluxed for 2 h. On concentrating the reaction mixture to a small volume, crude *N*,*N*′-bis(toluene-*p*-sulfonyl)-1,8-diamino-3,6-dimethyl-3,6-diazaoctane was obtained as a yellow oily substance. This was dissolved in a mixture of acetic acid (180 cm³) and hydrobromic acid (47%, 320 cm³), and the solution was refluxed for 90 h. The solution was then concentrated to *ca.* 10 cm³ and made alkaline by addition of aqueous KOH. The resulting 1,8-diamino-3,6-dimethyl-3,6-diazaoctane was extracted with chloroform and purified by vacuum distillation as a colourless liquid boiling at 90 °C (1 mmHg). Yield: 1.42 g (87%). ^1H NMR($CDCl_3$): δ 2.78–2.75 (t, 4 H), 2.49–2.42 (m, 8 H) and 2.24 (s, 6 H). Selected IR data: 2970–2760, 1600, 1460, 1355, 1300 and 1030 cm⁻¹.

1,8-*Diamino*-3,6-*diethyl*-3,6-*diazaoctane*. This was prepared by a method similar to that of 1,8-diamino-3,6-dimethyl-3,6-diazaoctane using *N*,*N*′-diethylethylenediamine instead of *N*,*N*′-dimethylethylenediamine. Yield: 0.34 g (40%), b.p. 107 °C (1 mmHg). ^1H NMR($CDCl_3$): δ 2.74–2.71 (t, 4 H), 2.57–2.49 (m, 12 H) and 1.04–1.00 (t, 6 H). Selected IR data: 2960–2810, 1600, 1455, 1380, 1325, 1160, 1095, 815 and 660 cm⁻¹.

$[Mn_4L^2(PhCO_2)_6]\cdot2MeOH$ **1**. A solution of 2,6-diformyl-4-methylphenol (0.164 g, 1.0 mmol) and manganese(II) benzoate dihydrate (0.666 g, 2.0 mmol) in methanol (10 cm³) was refluxed for 5 min. To the resulting yellow solution was added 1,8-diamino-3,6-dimethyl-3,6-diazaoctane (0.174 g, 2.0 mmol) and the mixture was refluxed for 20 min to give a yellow crystalline precipitate (0.62 g, 77% yield) (Found: C, 57.95; H, 5.40; Mn, 13.6; N, 6.95. Calc. for $C_{78}H_{88}Mn_4N_8O_{16}$: C, 58.05; H, 5.50; Mn, 13.6; N, 6.95%). Selected IR data (KBr disk): 3050–2800, 1635, 1608, 1564, 1545, 1400, 1060–980, 810 and 715 cm⁻¹. Mass spectrum (positive-ion FAB): *m*/*z* 1579 $(M - MeOH)^+$ and 1548 $(M - 2MeOH)^+$. Molar conductance (dmf): 9 S cm² mol⁻¹. UV/VIS (dmf): λ_{max} 390 nm (ε = 12 300 dm³ mol⁻¹ cm⁻¹).

$[Mn_4L^3(PhCO_2)_6]\cdot2MeOH$ **2**. This complex was prepared as yellow microcrystals by the same method as that for **1** using 1,8-diamino-3,6-diethyl-3,6-diazaoctane instead of 1,8-diamino-3,6-diethyl-3,6-diazaoctane. Yield: 0.34 g (40%) (Found: C, 58.90; H, 5.75; Mn, 13.6; N, 6.70. Calc. for $C_{82}H_{96}Mn_4N_8O_{16}$: C, 59.00; H, 5.80; Mn, 13.2; N, 6.70%). Selected IR data (KBr disk): 3050–2800, 1635, 1605, 1564, 1540, 1400, 1060–1020 and 715 cm⁻¹. Molar conductance (dmf): 23 S cm² mol⁻¹. UV/VIS (dmf): λ_{max} 405 nm (ε = 18 000 dm³ mol⁻¹ cm⁻¹).

X-Ray Structural Analysis of $[Mn_4L^2(PhCO_2)_6(Me_2CHOH)_2]\cdot2CH_2Cl_2$ **1′**.—*Crystal data*. $C_{86}H_{104}Cl_8Mn_4N_8O_{16}$, *M* = 2009.14, orthorhombic, space group *Pbca*, *a* = 20.692(3), *b* = 20.074(3), *c* = 22.988(5) Å, *U* = 9548(3) Å³, *Z* = 4, D_c = 1.40 g cm⁻³, *F*(000) = 4160, μ(Mo-Kα) = 7.84 cm⁻¹.

Data collection and reduction. Single crystals were obtained by the diffusion of propan-2-ol into a dichloromethane solution of the complex. A crystal with approximate dimensions 0.20 × 0.25 × 0.30 mm sealed in a glass tube was used for X-ray diffraction study. The intensities and lattice parameters were obtained on a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at 20 ± 1 °C. Lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 20 reflections in the range $25 < 2\theta < 36°$. Crystal data are summarized in Table 1. For the intensity data collections, the ω–2θ scan mode was used at a scan rate of 2° min⁻¹. The octant measured was $+h, +k, +l$. Three standard reflections were monitored every 100 reflections and showed no systematic decrease in the intensity. The intensity data were corrected for Lorentz and polarization factors but not for absorption. 3798 Independent reflections with $|F_o| > 3\sigma(|F_o|)$ in the range $2.5 \leqslant 2\theta \leqslant 48°$ were assumed to be observed.

The structure was solved by the direct method. Refinements were 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 calculated positions and were not refined. The final values of *R* and *R*′ were 0.0899 and 0.0942, 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 a local version[19] of the UNICS III[20] and ORTEP[21]

Table 1 Atomic coordinates (× 10^4) for non-hydrogen atoms of complex **1′**

Atom	*x*	*y*	*z*
Mn(1)	835(1)	5829(1)	1081(1)
Mn(2)	172(1)	7109(1)	249(1)
O(1)	872(4)	6349(3)	234(3)
N(1)	953(5)	7657(5)	−241(4)
N(2)	−290(5)	8134(5)	24(4)
N(3)	−451(5)	6863(5)	−623(4)
N(4)	−825(5)	5014(4)	−434(4)
C(1)	1348(5)	6231(5)	−130(4)
C(2)	1547(6)	5554(5)	−245(5)
C(3)	2055(6)	5425(6)	−618(5)
C(4)	2423(6)	5930(6)	−867(5)
C(5)	2993(7)	5768(8)	−1240(6)
C(6)	2237(6)	6567(6)	−762(5)
C(7)	1702(6)	6742(7)	−437(5)
C(8)	1493(6)	7440(6)	−428(5)
C(9)	812(7)	8358(6)	−347(7)
C(10)	264(7)	8590(6)	22(7)
C(11)	−749(8)	8332(7)	478(7)
C(12)	−601(7)	8091(6)	−553(6)
C(13)	−921(7)	7427(6)	−650(6)
C(14)	−35(7)	6860(7)	−1142(6)
C(15)	−849(6)	6239(5)	−601(5)
C(16)	−434(6)	5615(5)	−546(5)
C(17)	−1176(6)	5025(6)	14(5)
O(A1)	−198(4)	5774(4)	1162(4)
O(A2)	−603(4)	6657(4)	704(3)
C(A1)	−644(6)	6174(6)	1059(5)
C(A2)	−1278(6)	6082(5)	1350(5)
C(A3)	−1343(6)	5566(6)	1741(5)
C(A4)	−1937(7)	5475(7)	2032(5)
C(A5)	−2443(7)	5903(7)	1930(6)
C(A6)	−2370(7)	6421(7)	1543(7)
C(A7)	−1785(7)	6502(7)	1260(6)
O(B1)	791(4)	6710(4)	1597(3)
O(B2)	507(5)	7563(4)	1036(4)
C(B1)	734(6)	7318(5)	1493(5)
C(B2)	961(6)	7796(6)	1962(5)
C(B3)	1162(7)	7561(6)	2492(6)
C(B4)	1364(8)	7999(7)	2921(6)
C(B5)	1343(8)	8658(7)	2818(6)
C(B6)	1138(9)	8912(6)	2290(7)
C(B7)	944(8)	8475(5)	1859(6)
O(C1)	977(4)	5065(4)	1748(3)
O(C2)	2042(4)	4921(5)	1761(5)
C(C1)	1481(6)	4750(6)	1874(5)
C(C2)	1395(6)	4083(6)	2184(5)
C(C3)	811(7)	3914(7)	2436(6)
C(C4)	749(8)	3298(8)	2717(6)
C(C5)	1268(9)	2883(7)	2711(7)
C(C6)	1848(8)	3042(7)	2461(8)
C(C7)	1921(7)	3640(7)	2194(6)
O(P)	1940(4)	5961(4)	1121(4)
C(P1)	2279(7)	7090(7)	952(6)
C(P2)	2292(7)	6520(7)	1364(6)
C(P3)	2984(6)	6302(7)	1502(6)
Cl(D1)	2328(3)	8911(3)	404(4)
Cl(D2)	1364(4)	9908(3)	454(4)
C(D)	2067(11)	9670(10)	690(9)
Cl(E1)	−358(4)	8619(6)	−2097(4)
Cl(E2)	644(6)	9403(5)	−1733(4)
C(E)	151(10)	9192(10)	−2254(9)

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

Mn(1)–O(1)	2.212(7)	Mn(1)–N(4′)	2.252(9)
Mn(1)–O(A1)	2.150(8)	Mn(1)–O(B1)	2.133(8)
Mn(1)–O(C1)	2.188(8)	Mn(1)–O(P)	2.303(8)
Mn(2)–O(1)	2.105(7)	Mn(2)–N(1)	2.257(10)
Mn(2)–N(2)	2.326(10)	Mn(2)–N(3)	2.433(10)
Mn(2)–O(A2)	2.118(9)	Mn(2)–O(B2)	2.141(9)
Mn(1) ··· Mn(2)	3.487(2)		
O(1)–Mn(1)–N(4′)	76.9(3)	O(1)–Mn(1)–O(A1)	97.7(3)
O(1)–Mn(1)–O(B1)	95.8(3)	O(1)–Mn(1)–O(C1)	160.7(3)
N(1)–Mn(1)–O(P)	87.0(3)	N(4′)–Mn(1)–O(A1)	90.5(3)
N(4′)–Mn(1)–O(B1)	172.0(3)	N(4′)–Mn(1)–O(C1)	86.4(3)
N(4′)–Mn(1)–O(P)	97.0(3)	O(A1)–Mn(1)–O(B1)	87.2(3)
O(A1)–Mn(1)–O(C1)	92.1(3)	O(A1)–Mn(1)–O(P)	171.9(3)
O(B1)–Mn(1)–O(C1)	101.3(3)	O(B1)–Mn(1)–O(P)	85.7(3)
O(C1)–Mn(1)–O(P)	85.4(3)	O(1)–Mn(2)–N(1)	81.5(3)
O(1)–Mn(2)–N(2)	157.0(3)	O(1)–Mn(2)–N(3)	101.7(3)
O(1)–Mn(2)–O(A2)	102.6(3)	O(1)–Mn(2)–O(B2)	95.7(3)
N(1)–Mn(2)–N(2)	75.7(4)	N(1)–Mn(2)–N(3)	93.9(4)
N(1)–Mn(2)–O(A2)	176.0(4)	N(1)–Mn(2)–O(B2)	89.0(4)
N(2)–Mn(2)–N(3)	77.3(3)	N(2)–Mn(2)–O(A2)	100.3(4)
N(2)–Mn(2)–O(B2)	86.8(4)	N(3)–Mn(2)–O(A2)	85.4(3)
N(3)–Mn(2)–O(B2)	162.6(3)	O(A2)–Mn(2)–O(B2)	90.6(3)

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

Crystal Structure of **1′**.—The crystal structure of complex **1′** reveals a centrosymmetric complex molecule and two dichloromethane molecules captured in the crystal lattice. The ORTEP view of the complex molecule is shown in Fig. 1, together with the atom numbering scheme. Selected bond distances and angles are given in Table 2.

The complex molecule consists of the tetranucleating macrocycle L^2, four Mn ions, six benzoate groups, and two propan-2-ol molecules. The macrocycle contains two pairs of Mn ions. In each pair Mn(1) and Mn(2) are bridged by a phenolic oxygen of L^2 and two benzoate groups, affording a μ-phenoxo-bis(μ-carboxylato)dimanganese(II) core. The two manganese ions in each pair are not equivalent with respect to their co-ordination environments. The geometry about Mn(1) is distorted octahedral with co-ordination to the phenolic oxygen O and the imino nitrogen N(4′) of L^2, O(A1) and O(B1) of the bridging benzoate groups, O(C1) of the monodentate benzoate group and O(P) of the propan-2-ol molecule. The geometry about Mn(2) is also distorted octahedral with co-ordination to the phenolic oxygen O, the imino nitrogen N(1), two amino nitrogens N(2) and N(3) and the two benzoate oxygens O(A2) and O(B2). A similar inequivalence in the two manganese geometries of the μ-phenoxo-bis(μ-carboxylato)dimanganese(II) core is found for the related $[Mn_2L^6(RCO_2)_2(NCS)]$[22] (L^6 = 2,6-bis{*N*-[2-(dialkylamino)ethyl]iminomethyl}-4-methylphenolate(1 −), R = Me or Et) and $[Mn_2(L^7)(MeCO_2)_2(NCS)]$[23] {$L^7$ = 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenolate(1 −)}.

The Mn–O distances [2.105(7)–2.212(7) Å] fall in the range commonly found for manganese(II) complexes.[24] The Mn(1)–N(4′) and Mn(2)–N(1) distances are 2.252(9) and 2.26(1) Å, respectively, which are normal for Mn^{II}–N(imine) bonds.[24] The Mn(2)–N(2) distance [2.33(1) Å] is typical for Mn^{II}–N(amine) bonds[24] but the Mn(2)–N(3) distance [2.43(1) Å] is slightly elongated. This elongation may be due to intramolecular steric repulsion between the *N*-substituents attached to the amino nitrogen N(3) and the aromatic part of the ligand L^2. The Mn(1) ··· Mn(2) distance within a pair is 3.487(2) Å, which is typical for μ-phenoxo-bis(μ-carboxylato)dimanganese(II) core structures.[5] The two dinuclear units are separated significantly. The Mn(1) ··· Mn(1′), Mn(1) ··· Mn(2′) and

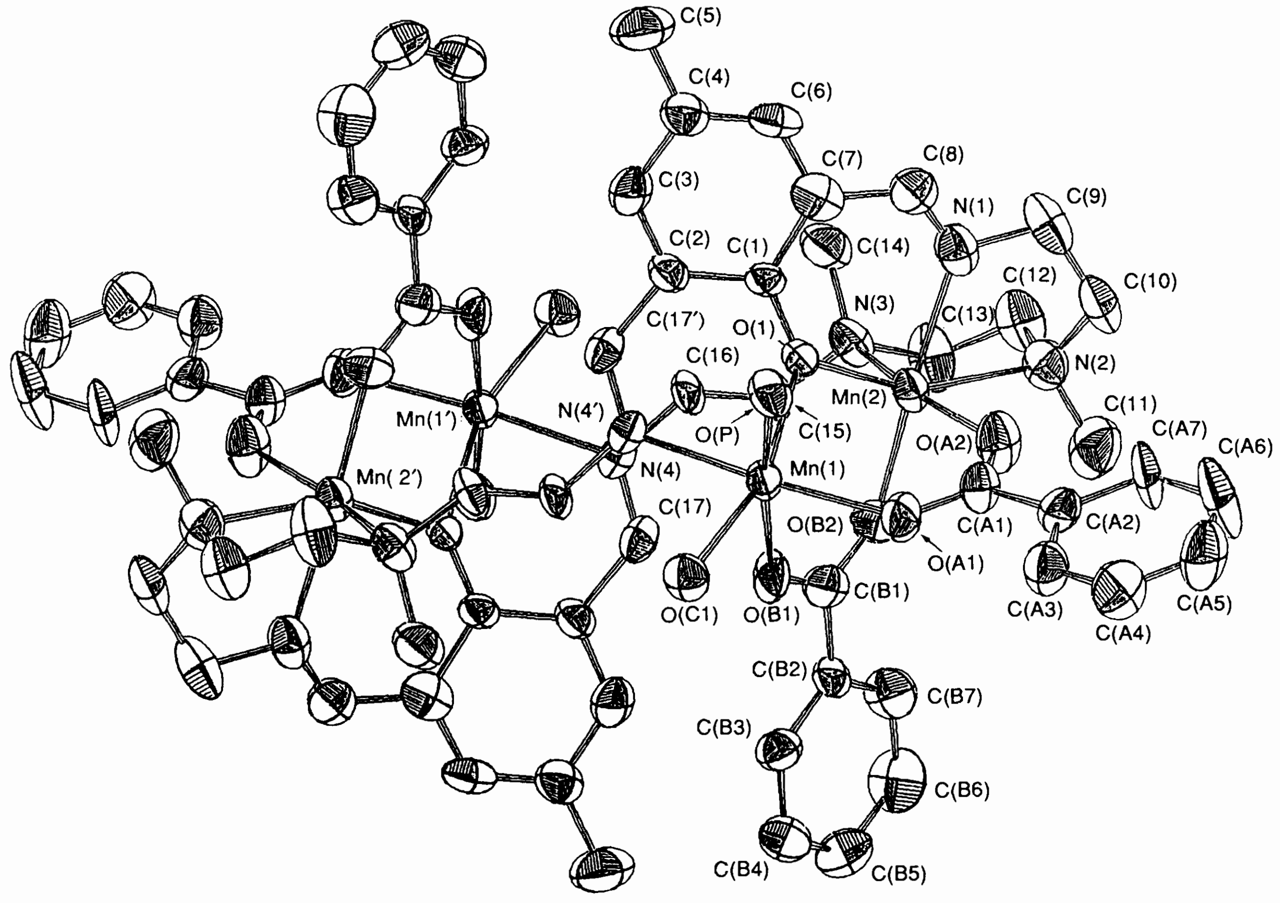
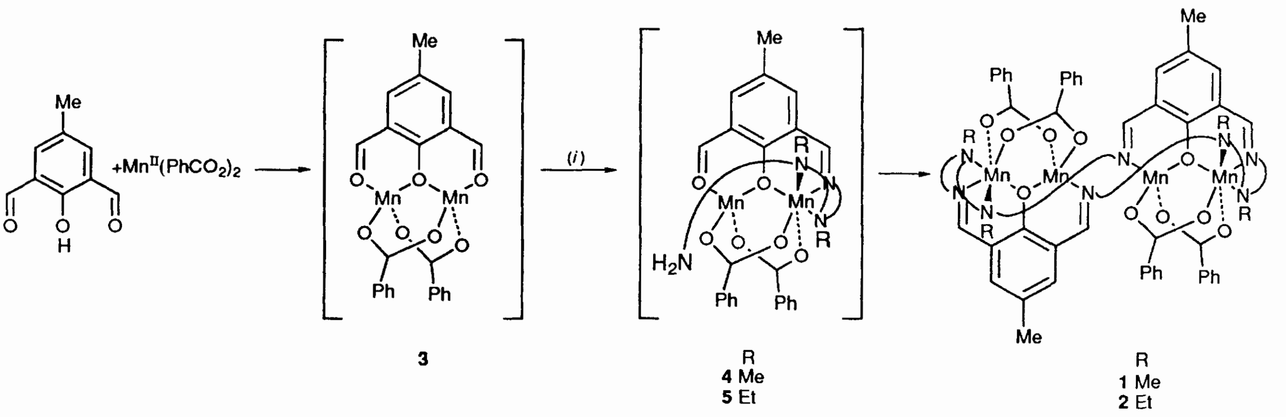


Fig. 1 An ORTEP view of [$Mn_4L^2(PhCO_2)_6(Me_2CHOH)_2$] with the atom numbering scheme



Scheme 1 Mechanism for the formation of complexes **1** and **2**. (*i*) $H_2N(CH_2)_2NR(CH_2)_2NR(CH_2)_2NH_2$, R = Me or Et

Mn(2)$\cdots$Mn(2') separations are 12.460(3), 11.457(3) and 14.435(3) Å, respectively.

Synthetic Mechanism.—The success in the template synthesis of complexes **1** and **2** depended upon the operating conditions employed. When 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = methyl or ethyl) and manganese(II) benzoate dihydrate were mixed first in methanol and 2,6-diformyl-4-methylphenol then added to the resulting reddish brown solution, no crystalline complex was obtained. A similar reaction under anaerobic conditions led to formation of orange solutions from which, however, desired macrocyclic complexes could not be obtained. When manganese(II) benzoate dihydrate and 2,6-diformyl-4-methylphenol were mixed first in methanol and then the tetraamine was added to this mixture under aerobic conditions, the reaction mixture assumed an orange colour and formed the macrocyclic complexes **1** and **2** in good yields. Based on these facts and the confirmation of the structure of complex **1'** by X-ray crystallography, a synthetic mechanism for the formation of the macrocyclic complexes **1** and **2** is proposed (Scheme 1). It is presumed that manganese(II) benzoate reacts with 2,6-diformyl-4-methylphenol to form an air-stable μ-phenoxo-bis(μ-benzoato)dimanganese(II) core structure **3**. Upon treatment with the tetraamine this complex forms the 1 : 1 Schiff-base complex **4** (R = Me) or **5** (R = Et), in which one of the formyl groups of **3** and one of the primary amino groups of the tetraamine remain intact. Dimerization of complex **4** affords the macrocyclic tetranuclear manganese(II) structure as found for **1'**. It should be noted that the essential structure of the dinuclear unit of **1'** is constructed in the intermediate **4**. The conformation of the 1:1 type Schiff base in **4** seems to be energetically preferred, irrespective of the nature of

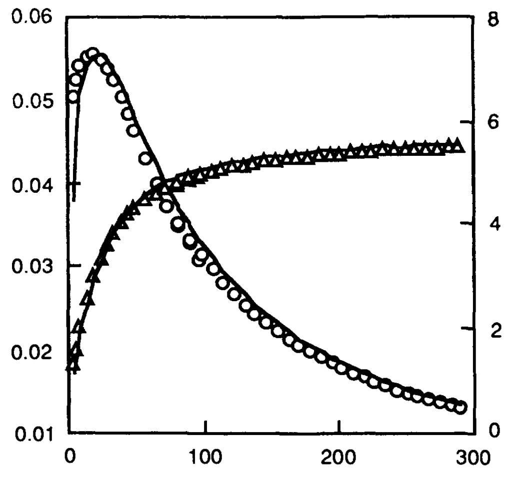


Fig. 2 Temperature dependences of χ_A (○) and μ_{eff} (△) of **1**. Solid curves are drawn based on the equation in the text, using $J = -2.8$ cm^{-1}, $g = 1.96$ and $N\alpha = 0$ cm^3 mol^{-1}

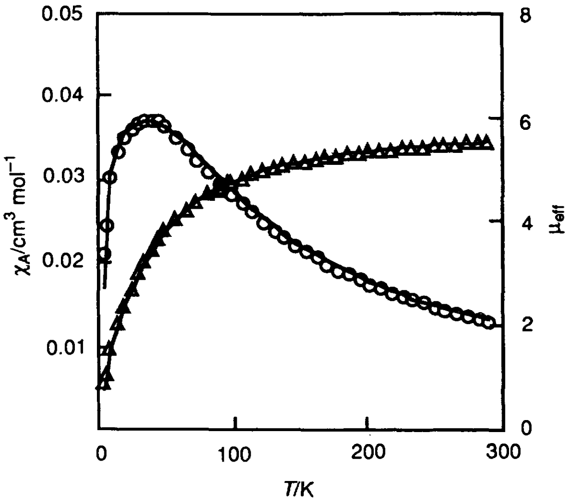


Fig. 3 Temperature dependences of χ_A (○) and μ_{eff} (△) of **2**. Solid curves are drawn based on the equation in the text, using $J = -4.4$ cm^{-1}, $g = 2.00$ and $N\alpha = 0$ cm^3 mol^{-1}

the template ion. For example, the dinuclear lead(II) complex of H_2L^2, $[Pb_2(H_2L^2)(dmf)_4(ClO_4)_2][ClO_4]_2$, bears a marked structural resemblance to **1′** except that two co-ordination sites are occupied by protons.[11] In this case the intermediate must be a mononuclear lead(II) complex of the 1:1 type Schiff base (protonated form) in the preferred conformation.

Physicochemical Properties.—The tetranuclear manganese complexes **1** and **2** are stable towards molecular oxygen both in the solid state and in solution. Both complexes are essentially non-electrolytes in dmf,[25] indicating that the benzoate groups are not dissociated in this solvent. Both **1** and **2** show an intense absorption band (at 390 and 405 nm, respectively), which is assigned to the azomethine π–π^* transition.[26] Except for this band no appreciable absorption is observed in the visible region, in accord with high-spin electronic configuration of the manganese(II) ions.

The IR spectrum of **1** shows antisymmetric and symmetric $\nu(CO_2)$ vibrations of the benzoate group at 1564 and 1400 cm^{-1}, respectively. Similarly, the IR spectrum of **2** shows $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ vibrations of the benzoate group at 1564 and 1400 cm^{-1}, respectively. The separation between the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ vibrations of less than 200 cm^{-1} is typical of bridging carboxylate groups.[27] However, $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes of the monodentate benzoate group could not be assigned unambiguously.

Magnetic susceptibility measurements were made on powder samples in the temperature range 4.2–300 K. The temperature dependences of the magnetic susceptibility (χ_A) and effective magnetic moment (μ_{eff}) per Mn for **1** and **2** are shown in Figs. 2 and 3, respectively. The room-temperature μ_{eff} values of **1** and **2** are 5.49 and 5.49 respectively, and decrease with decreasing temperature down to 1.29 and 0.86 at 4.2 K, respectively. Such magnetic behaviour suggests the operation of an antiferromagnetic interaction between the high-spin manganese(II) ions within a molecule. As the first approximation the magnetic interaction between the two dinuclear units can be neglected owing to their large separation (>11 Å). Thus, magnetic analyses for **1** and **2** were performed employing the magnetic susceptibility expression [equation (1)] for a ($S_1 = \frac{5}{2}$)–($S_2 = \frac{5}{2}$)

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

system based on the Heisenberg model $\hat{H} = -2JS_1 \cdot S_2$, where $x = \exp(-J/kT)$. In this expression χ_A is the magnetic susceptibility per Mn, N is the Avogadro constant, g is the Zeeman splitting factor, β is the Bohr magneton, J is the exchange integral, k is the Boltzman constant, T is the absolute temperature and $N\alpha$ is the temperature independent paramagnetism. The cryomagnetic properties of **1** could be well simulated by this equation, using the magnetic parameters $g = 1.96$, $J = -2.8$ cm^{-1} and $N\alpha = 0$ cm^3 mol^{-1}. The discrepancy factor defined as $R(\chi) = [\Sigma(\chi_{obs} - \chi_{cal})^2/\Sigma(\chi_{obs})^2]$ was 5.7×10^{-3}. Similarly, a good magnetic simulation was attained for **2**, using the magnetic parameters $g = 2.00$, $J = -4.4$ cm^{-1} and $N\alpha = 0$ cm^3 mol^{-1}. The $R(\chi)$ value was 8.0×10^{-4}. Thus, it is proved that the two dimanganese(II) units in a molecule are magnetically independent of each other and a weak antiferromagnetic interaction operates within each μ-phenoxo-bis(μ-benzoato)dimanganese(II) core. The exchange integrals J for **1** and **2** can be compared to the values ($J = -2$ to -5 cm^{-1}) found for the μ-phenoxo-bis(μ-carboxylato)dimanganese(II) complexes $[Mn_2L^6(RCO_2)_2(NCS)]$ (R = Me or Et)[22] and $[Mn_2L^7(MeCO_2)_2(NCS)]$.[23]

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