

Novel Cyclic Tetranuclear Manganese(II) Complex containing Two Phthalato Bridging Ligands; X-ray Crystal Structure of $[\text{Mn}_4(\mu\text{-phth})_2(\text{bpy})_8](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ (H_2phth = phthalic acid; bpy = 2,2'-bipyridyl)

Zong-Hui Jiang,^a Shu-Lin Ma,^a Dai-Zheng Liao,^a Shi-Ping Yan,^a Geng-Lin Wang,^a Xin-Kan Yao^b and Ru-Ji Wang^b

^a Department of Chemistry, Nankai University, Tianjin, 300071, China

^b Central Laboratory, Nankai University, Tianjin, 300071, China

A novel cyclic tetranuclear Mn^{II} complex containing two phthalato bridging ligands and the X-ray structure of $[\text{Mn}_4(\mu\text{-phth})_2(\text{bpy})_8](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ are reported.

The structure and properties of polymanganese complexes are currently of great interest, as they provide both background chemistry and model complexes for the study of the photosynthetic oxygen-evolving complexes (OEC).^{1,2} The biological active site is now generally believed to contain four manganese ions bridged by oxygen donors.^{3,4} The development of the chemistry of related complexes will help to define the likely properties and structure of the OEC.

On the other hand, studies on novel ferromagnetically-coupled magnetic systems involving magnetic centres separated from each other *via* multiatom-bridging units are significant. Phthalate dianions, due to their versatile bonding mode with metal ions⁵ and the fact that the carboxylate groups are noncoplanar with themselves and with the benzene ring, could be good candidates in supporting long-distance ferromagnetic exchange interactions. Phthalato-bridged binuclear

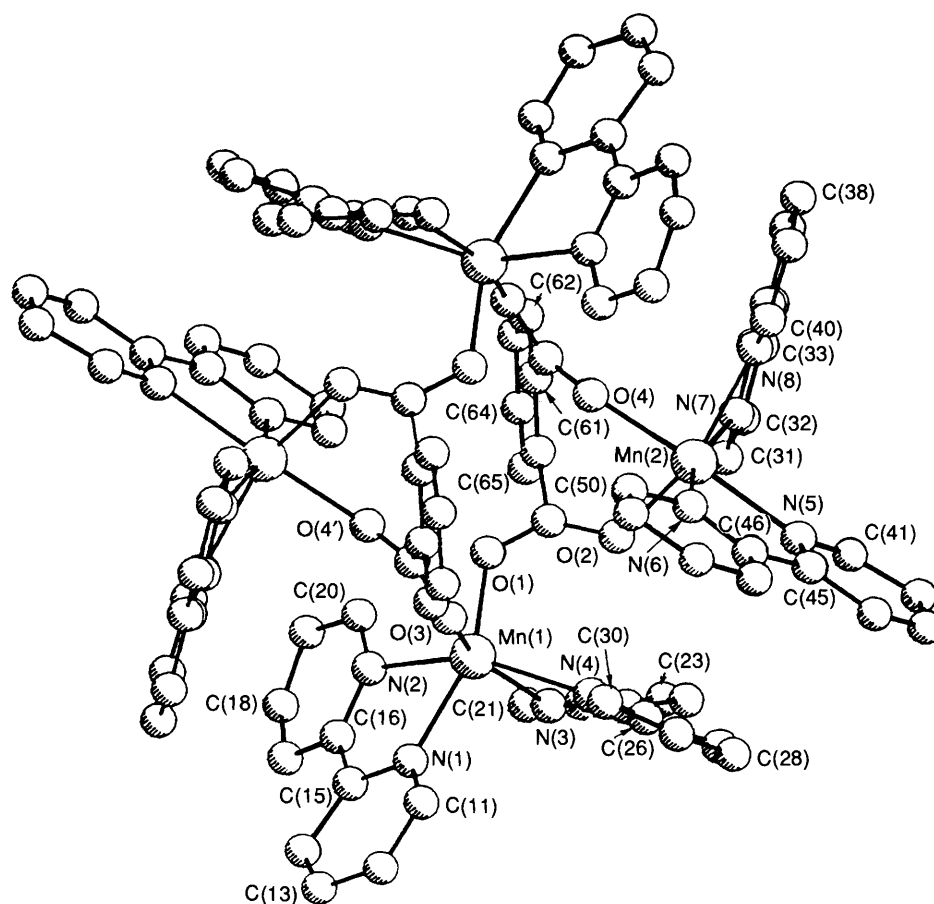


Fig. 1 Perspective view of the cation $[\text{Mn}_4(\mu\text{-phth})_2(\text{bpy})_8]^{14+}$. Selected interatomic distances (Å) and angles ($^\circ$); Mn(1)–Mn(2) 5.160, Mn(1)–Mn(1') 7.337, Mn(2)–Mn(2') 7.598, Mn(1)–O(1) 2.075, Mn(1)–O(3) 2.129, Mn(1)–N(1) 2.227, Mn(1)–N(2) 2.313, Mn(1)–N(3) 2.382, Mn(1)–N(4) 2.289, Mn(2)–O(2) 2.082, Mn(2)–O(4) 2.167, Mn(2)–N(5) 2.267, Mn(2)–N(6) 2.248, Mn(2)–N(7) 2.284, Mn(2)–N(8) 2.274; O(1)–Mn(1)–N(1) 155.7(3) O(3)–Mn(1)–N(3) 156.6(3), N(2)–Mn(1)–N(4) 151.2(3), O(2)–Mn(2)–N(8) 156.2(3), O(4)–Mn(2)–N(5) 161.8(2), N(5)–Mn(2)–N(7) 163.4(3).

copper(II) complexes have been reported,⁶ but polynuclear manganese(II) complexes bridged by phthalato dianions have not been reported.

We now report a novel cyclic tetranuclear manganese(II) complex containing two phthalato bridging ligands, $[\text{Mn}_4(\mu\text{-phth})(\text{bpy})_8](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ **1**; the crystal structure of **1** has been determined by direct X-ray methods.[†] To our knowledge, this is the first example of a sixteen-membered macrocyclic complex containing four manganese atoms.

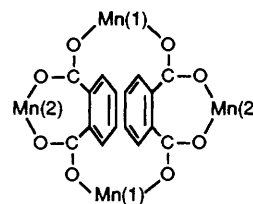


Fig. 2 Binding mode of phthalate ligand

[†] *Crystal data* for $[\text{Mn}_4(\mu\text{-phth})_2(\text{bpy})_8](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$, yellow, crystal dimensions $0.2 \times 0.3 \times 0.3$ mm, triclinic, $a = 14.276(6)$, $b = 14.369(9)$, $c = 15.54(1)$ Å, $\alpha = 70.22(5)$, $\beta = 61.73(6)$, $\gamma = 66.38(5)^\circ$, $V = 2527$ Å³, space group $P\bar{1}$, $Z = 1$, $F(000) = 1120$. Determination of the unit cell and data collection were performed with Mo-K α radiation ($\lambda = 0.71073$ Å) on a CAD4 diffractometer equipped with a graphite monochromator. A total of 6368 independent reflections was collected by the $\omega - 2\theta$ scan technique in the range $2 \leq \theta \leq 22^\circ$, in which 2076 reflections [$I \geq 3\sigma(I)$] were considered to be observed. Intensity data were corrected for LP factors and empirical absorption. The structure of the complex was obtained by direct methods (MULTAN 82). Two manganese atoms were located from an E-map. The other non-hydrogen atoms were determined with successive difference Fourier syntheses. The final refinement by full-matrix least-squares method with anisotropic thermal parameters for the manganese and chlorine atoms, and isotropic thermal parameters for the other non-hydrogen atoms converged to $R = 0.086$ and $R_w = 0.094$, respectively (unit weights for all observed reflections). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Complex **1** was prepared by adding a methanolic solution of the phthalate piperidinium salt to a methanolic solution of manganese(II) perchlorate and bipyridine and refluxing for 4 h. On cooling the product was filtered off as a yellow powder in ca. 32.9% yield. Crystals suitable for X-ray crystallography were obtained from a dimethylformamide and methanol solution (1 : 1).

The structure of the cation of the complex is shown in Fig. 1. It has a centre of symmetry. The four manganese atoms are bridged by phth dianions, coordinated in bidentate modes, through the oxygen atoms of their carboxylate groups. In the complex each carboxylate group bridges two Mn^{II} ions and each Mn^{II} ion links two oxygen atoms which belong to two carboxylate groups, respectively. Thus, a sixteen-membered macrocycle containing tetramanganese bridged by two phth dianions is derived (Fig. 2). This compound is different from other phthalate- and dicarboxylate-bridged species. In phthalate-bridged dinuclear iron(III) compounds,⁷ the two carboxylate groups coordinate to the two iron centres independently in a monodentate fashion. In contrast, the bridging of the two

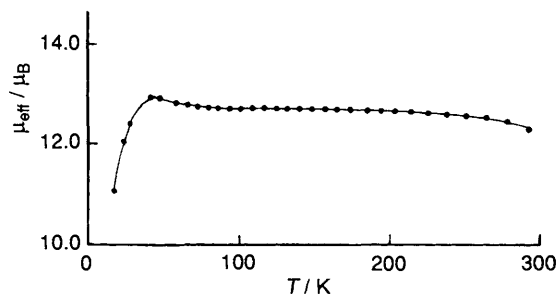


Fig. 3 Plot of μ_{eff} against T for the complex 1

Fe^{III} ions by maleate only involves one bridging bidentate carboxylate group, with the other one uninvolved in coordination. In phthalate-bridged binuclear copper(II) complexes⁶ two carboxylate groups coordinate in both uni- and bi-dentate ways to the two copper centres, respectively, and infinite chains of polymeric cations are derived. In the case of the new manganese complex, the most striking feature is the binding of the bridging phthalate which displays both coordination modes. The structure around manganese(II) could be described as a distorted octahedron. Owing to the centre of symmetry only two Mn^{II} ions are independent in the macrocycle molecule. The two manganese environments are similar: the coordination atoms around Mn include both the four nitrogen atoms of the two bipyridines as well as two oxygen atoms from the carboxylate group of the phth bridge; the two oxygen atoms are coordinated in a *cis*-fashion. The difference between the two manganese environments is that the two oxygen atoms coordinated to Mn(1) belong to two different carboxylate groups from two different phth ligands but the two oxygen atoms coordinated to Mn(2) belong to the carboxylate groups from the same phth. Owing to unequal Mn–O and Mn–N bond distances (see Fig. 1) and the deviation of the O–Mn–N and N–Mn–N angles from 180° (Fig. 1), the local geometry around Mn^{II} could be regarded as a severely distorted octahedral.

The distances, Mn(1)–Mn(2), Mn(1)–Mn(1') and Mn(2)–Mn(2') are 5.160, 7.337 and 7.598 Å, respectively. The shortest intermolecular Mn–Mn distance is 8.018 Å. The ClO_4^- anions are noncoordinated.

The magnetic property of the complex is shown in Fig. 3 (μ_{eff} vs. T , μ_{eff} being the molecular magnetic moment). The observed magnetic moment of the complex at room temperature is greater than the spin-only value (11.83 μ_{B}), and when the temperature decreases from room temperature (300 K) to 41 K the magnetic moment increases slightly from 12.3 to 13.0 μ_{B} ; below 41 K μ_{eff} decreases upon cooling. The magnetic behaviour above 41 K indicates a weak ferromagnetic coupling between the Mn^{II} ions in the complex, however, the magnetic behaviour below 41 K is more difficult to interpret unambiguously. A detailed analysis of the magnetic properties of the complex is in progress.

This project was supported by the National Natural Science Foundation of China.

Received, 14th September 1992; Com. 2/04916C

Received in revised form 16th February 1993

References

- J. B. Vincent, C. Christmas, H. R. Chang, Q. Li, P. O. W. Boyd, J. C. Hutmman, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1989, **111**, 2086.
- See for example: J. S. Bashkin, Hsiu-Rong Chang, W. E. Streib, J. C. Huffman, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1987, **109**, 6502; K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1153; A. R. Schake, E. A. Schmitt, A. J. Conti, W. E. Streib, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1991, **30**, 3192.
- G. C. Dismukes, *Photochem. Photobiol.*, 1986, **43**, 99.
- See for example; G. W. Brudvig and R. H. Crabtree, *Proc. Natl. Acad. Sci. USA*, 1986, **83**, 4586; J. B. Vincent and G. Christou, *Inorg. Chim. Acta*, 1987, **136**, L41.
- M. C. Biagini, A. M. Manotti Lanfredi, A. Tiripicchio and C. M. Tiripicchio, *Acta Crystallogr., Sect. B*, 1981, **37**, 2159; I. Krstanovic, Lj. Karanovic, Dj. Stojakovic and Lj. Go'c, *Cryst. Struct. Commun.*, 1982, **11**, 1747; C. K. Prout, J. R. Carruthers and F. J. C. Rossotti, *J. Chem. Soc., A*, 1971, 3350.
- S. K. Shakhtrah, E. G. Bakalbassis, I. Brudgam, H. Hartl, J. Mrozinski and C. A. Tsipis, *Inorg. Chem.*, 1991, **30**, 2801.
- R. E. Norman, R. C. Holz, S. M'enage, C. J. O'Connor, J. H. Zhang and L. Que, Jr., *Inorg. Chem.*, 1990, **29**, 4629.