An Unusual Isotactic Coordination Polymer Chain Assembled by Mn(II) and *O*-phthalate: [Mn(μ-phth)(phen)(H_2O)$_2$] • H_2O(phth = *o*-phthalato; phen = 1,10-phenanthroline)

Yugen Zhang,* Li Jianmin,*† Zhu Min,† Quanming Wang,†† and Xintao Wu††
Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China
†*Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*
††*State Key Laboratory of Structural Chemistry, Fujian Institute of Research of Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian 350002, P.R. China*

(Received July 7, 1998; CL-980513)

The complex [Mn(μ-phth)(phen)(H_2O)$_2$] •H_2O (phth = *o*-phthalato; phen = 1,10-phenanthroline), in which an unusual isotactic coordination polymer chain is assembled by Mn(II) and *o*-phthalate dianion, an amphiphilic channel which has hydrophilic inside and hydrophobic outside is formed *via* hydrogen bonds, has been isolated and structurally characterized.

The structure and properties of polymanganese complexes are currently of great interest, as they provide both molecular magnetism on account of its promising application to diverse areas of technology such as magnetic recording and magnetic optics[1] and model complexes for the study of the photosynthetic oxygen-evolving complexes (OEC).[2] The polynuclear structures in these complexes are key features to their special physical and chemical properties. Phthalate, terephthalate and isophthalate dianions, due to their versatile bonding mode with metal ions and the fact that the carboxylate groups are noncoplanar with themselves and with the benzene rings, have been widely used in synthesis of mimic polynuclear complexes,[3] supporting long-distance ferromagnetic exchange interactions[4] and construction of multi-dimensional supramolecular architectures.[1d,5] Here, we present a new polymanganese complex **(1)** possessing an unusual one dimensional supramolecular chain [Mn(μ-phth)(phen)(H_2O)$_2$]•H_2O (phth = *o*-phthalato; phen = 1,10-phenanthroline). In the chain structure of complex **1**, all hydrophobic aromatic rings are located at one side of the chain to form a isotactic coordination polymer structure. Supramolecular recognition through hydrogen interactions between two chains induces to form an amphiphilic channel which has hydrophilic inside and hydrophobic outside. It represents a novel structural model of polymanganese complexes.

An aqueous-alcohol (1:1) solution (20 ml) containing 1,10-phenanthroline (198 mg, 1 mmol), *o*-phthalic acid (166 mg, 1 mmol) and $MnSO_4$•H_2O (170 mg, 1 mmol) was kept at room temperature. After a few days, pale-orange single crystals of **1** were precipitated. The postulated composition was confirmed by IR and elemental analysis,[6] and the crystal structure was determined by the single crystal X-ray diffraction method.[7-9] The most salient feature of the IR spectrum of the compound was existence of several strong bands in the 1700-1200 cm^{-1} region, attributed to the $\nu_{as}(CO_2^-)$ (1665, 1560 cm^{-1}), $\nu_s(CO_2^-)$ (1457, 1382 cm^{-1}) stretching vibrations of different carboxylate groups.

The crystal structure of **1** is shown in Figure 1. This structure possesses an unsymmetric supramolecular chain. Mn(II) centers bridge by the carboxylate group of *o*-phthalate and saturate by phenanthroline and waters. The chain structure can be characterized by the following interesting features. Each *o*-phthalate dianion acts as bidentate ligand through one carboxylate group to bridge two Mn(II) atoms in this chain structure, another one carboxylate group bound to two coordinated H_2O molecules *via* hydrogen bonds. This is a new and unusual coordination model of *o*-phthalate ligand. All hydrophobic aromatic rings of *o*-phthalate and phenanthroline are located at one side of the chain to form an unsymmetric chain structure. It gives this chain an amphiphilic character which has hydrophilic one side and hydrophobic opposite side. The bond lengths of Mn(II) to two carboxylate oxygen atoms (2.182, 2.220 Å) are apparently longer than that in reported similar structures (2.075--2.145 Å).[3a,3b,4,10] It may due to the new coordination model of *o*-phthalate in chain structure. Locally, Mn is in a stretched octahedron with two long Mn-O

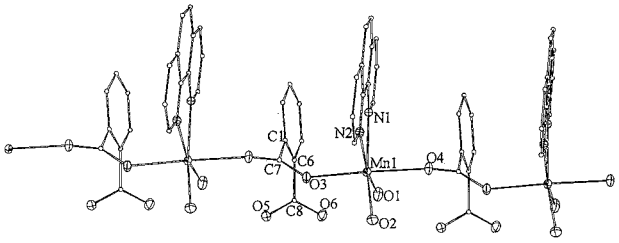

Figure 1. ORTEP diagram of **1** with labeling scheme. Selected bond length (Å) and angles (°): Mn1-O2 2.139(2), Mn1-O1 2.168(2), Mn1-O3 2.182(2), Mn1-O4 2.220(2), Mn1-N1 2.274(2), Mn1-N2 2.288(2),O2-Mn1-O1 103.68(9), O2-Mn-O3 96.55(7), O1-Mn1-O3 92.26(7), O2-Mn1-O4 87.38(7), O1-Mn1-O4 82.97(7), O3-Mn1-O4 174.41(6), O2-Mn1-N1 164.57(9), O1-Mn1-N1 90.61, O3-Mn1-N1 88.55(7), O4-Mn1-N1 88.67(7), O2-Mn1-N2 92.17(8), O1-Mn1-N2 161.39(8), O3-Mn1-N2 95.60(7), O4-Mn1-N2 88.20(7), N1-Mn1-N2 72.80(8).

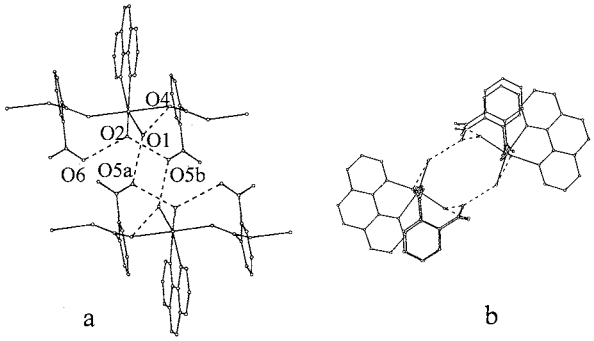

Figure 2. Hydrogen interactions between two molecule chains (a) and the cross section of this molecule tube (b). Length of hydrogen bonds (Å): O1---O4 2.906, O1---O5a 2.703, O2---O5b 2.677, O2---O6 2.725, a: 1-x, -y, 2-z; b: 1+x, y, z.

(phth) bonds (2.182, 2.220 Å) and two short Mn-O (H_2O) bonds (2.139, 2.168 Å) and two Mn-N (phen) bonds (2.274, 2.288 Å).

It is very interesting that every two supramolecular chains recognize each other through hydrogen interactions to form one dimensional microtubular structure, see Figure 2. The dimensions of the tubular cavity is 6.78 × 5.14 Å. The hydrophilic sides of two chains stagger joint *via* hydrogen bonds. It assembles an amphiphilic channel which has hydrophilic inside and hydrophobic outside, Figure 2 (b). And, maybe it is the multiply strong hydrogen bonds which enforced by polar solvent that induce to form the unusual unsymmetric coordination polymer chain. Although the strength of hydrogen bond is much weaker than that of coordination bond, complex **1** shows us a good example of multiply bonds co-constructing supramolecular architecture. It tells us that molecule recognition is not only between small molecules or small guest and supramolecular host, but also between supramolecular structures, that induces high-class supramolecular recognition and construction of more complex assemblies. Furthermore, molecule tubes in **1** assemble back-to-back (hydrophobic side to hydrophobic side) *via* π-packing interactions (face-to-face

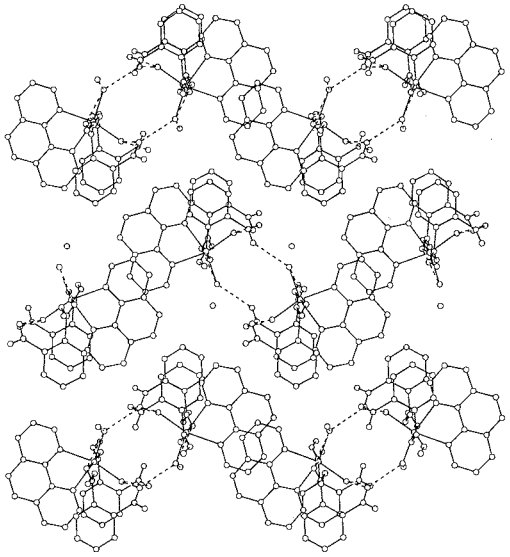

Figure 3. Packing of molecule tubes in **1**.

distance: 3.45 Å) to form a two dimensional wavy sheet, Figure 3. Here, it is seen that supramolecule structure of **1** is self-assembled in three classes. Firstly, chain structure is assembled by coordination bonds; second, molecule tube is assembled between supramolecular chains through hydrogen interactions; Third, two dimensional sheet is packed *via* π interactions between aromatic rings. It shows us that weak interactions can play a very important part in constructing secondary or third-class structures in supramolecules, in fact, that is a general rule in nature. Does complex **1** possesses some new magnetic and molecule recognition properties based on its new structural model? Further work are in progress.

We thank the National Nature Science Foundation of China; Chinese Academy of Science; the State Key Laboratory of Structural Chemistry, Fujian Institute of Research of Structure of Matter, for financial support.

References and Notes

1 a) S. M. J. Aubin, Z. Sun, H. A. Guzei, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Chem. Commun.*, **1997**, 2239; b) E. M. Chudnovsky, *Science*, **274**, 938(1996); c) R. Sessoli, D.Gatteschi, A. Caneschi, and M. A. Novak, *Nature*, **365**, 141(1993); d) J. L. Manson, C. Campana, and J. S. Miller, *Chem. Commun.*, **1998**, 251; e)M. Osawa, K. Fujisawa, N. Kitajima, and Y. Moro-oka, *Chem. Lett.*, **1997**, 919.

2 a) M. Tyler Caudle, J. W. Kampf, M. L. Kirk, P. G. Rasmussen, and V. L. Pecoraro, *J. Am. Chem. Soc.*, **119**, 9297(1997); b) W. Ruttinger and G. C. Dismukes, *Chem. Rev.*, **97**, 1(1997); c) V. K. Yachandra, V. J. DeRose, M. J. Latimer, I. Mukerji, K. Sauer, and M. P. Klein, *Science*, **260**, 675(1993); d) G. Christou, *Acc. Chem. Res.*, **22**, 328(1989).

3 a) X. S. Tan, J. Sun, D. F. Xiang, and W. X. Tang, *Inorg. Chim. Acta*, **255**, 157(1997); b) J. Cano, G. De Munno, J. Sanz, R. Ruiz, F. Lioret, J. Faus, and M. Julve, *J. Chem. Soc., Dalton Trans.*, **1994**, 3465; c) S. K. Shakhatreh, E. G. Bakalbassis, I. Brudgam, H. Hartl, J. Mrozinski, and C. A. Tsipis, *Inorg. Chem.*, **30**, 2801(1991); d) P. Chaudhuri, K. Oder, K. Wieghardt, S. Gehring, W. Haase, B. Nuber, and J. Weiss, *J. Am. Chem. Soc.*, **110**, 3657(1988).

4 Z. Jiang, S. Ma, D. Liao, S. Yan, G. Wang, X. Yao, and R. Wang, *Chem. Commun.*, **1993**, 745.

5 a) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 2186(1998); b) W. Mori, F. Inoue, K. Yoshida, H. Nakayama, S. Takamizawa, and M. Kishita, *Chem. Lett.*, **1997**, 1219; c) A. D. Burrows, S. Menzer, D. M. P. Mingos, A. J. P. White, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, **1997**, 4237.

6 Analysis found: C, 55.13; H, 3.75; N, 6.76 %. Calcd. for $C_{20}H_{16}MnN_2O_6$: C, 55.17; H, 3.68; N, 6.44 %.

7 Crystal data: $C_{20}H_{18}MnN_2O_7$, M = 453.30, monoclinic, $P2_1/n$, a = 6.4633(1), b = 14.1345(2), c = 21.2253(3) Å, β = 97.859(1) °, V = 1920.84(5) Å^3, $F(000)$ = 932, Z = 4, Dc = 1.568 g/cm^3, T = 293 K, λ(Mo-Ka) = 0.71073 Å. A crystal of approximate dimensions 0.30 × 0.30 × 0.20 mm was mounted a siemens SMART/CCD diffractometer using graphite monochromated Mo-Kα radiation. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range $1.74 < \theta < 25.4°$, measured by the computer controlled diagonal slit method of centering. Scattering factors were taken from Cromer and Waber.[8] The ω-2θ scan mode with a maximum 2θ value being 50.0° were used to collect intensity data. A total of 3398 reflections were collected, of which 2835 had $I > 2\sigma(I)$ with 271 parameters. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares calculation (SHELXL-93). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined. All calculations were performed on INDY workstation using MolEN/PC.[9] Final R = 0.036, Rw = 0.105, goodness of fit = 1.119.

8 D. T. Cromer and J. T. Waber, " International Tables for X-ray Crystallography, " The Kynoch Press, Birmingham, England (1974), Vol. IV.

9 Molen, " An Interactive Structure Solution Procedure, " Enraf-Nonius, Delft (1990).

10 a) J. Cano, G. De Munno, J. Sanz, R. Ruiz, J. Faus, F. Lioret, M. Julve, and A. Canischi, *J. Chem. Soc., Dalton Trans.*, **1997**, 1915; b) X. S. Tan, D. F. Xiang, W. X. Tang, and K. B. Yu, *Polyhedron*, **16**, 1411(1997).