

Locking the Absolute Configuration of Achiral Amine Ligand: A Strategy for Helicity Introduction in Coordination Polymers

SUN Jian-Ke JIN Xu-Hui LI Wei ZHANG Jie

(State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the
Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, China)

ABSTRACT A novel coordination polymer $\{[\text{Mn}(m\text{-cpdba})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ **1** has been synthesized and characterized. Single-crystal X-ray diffraction analysis reveals that compound **1** contains one-dimensional single-stranded helical chains, in which the chirality of a stereochemically labile amine of the ligands can be locked by the Mn(II) ion via coordination bonds and transferred to the whole coordination polymeric chain, exhibiting an identical absolute configuration. Crystal data for **1**: $\text{C}_{14}\text{H}_{17}\text{Mn}_1\text{N}_3\text{O}_{13}$, $M_r = 490.25$, space group $C2/c$, $a = 18.5177(18)$, $b = 6.6194(5)$, $c = 31.563(4)$ Å, $\beta = 105.046(5)^\circ$, $Z = 8$, $V = 3736.2(7)$ Å³, $D_c = 1.743$ g/cm³, $F(000) = 2008$ and $\mu = 0.786$ mm⁻¹.

Keywords: amine derivative, helix, manganese, carboxylate, crystal structure

1 INTRODUCTION

Chirality has attracted considerable attention in the last few years^[1]. As the intrinsic character of chirality, helicity is not only ubiquitous in nature and as the foundation of genetic codes, but also the best example of chirality that can be introduced by metal-ligand coordination^[2]. Many strategies have been made to introduce helices, such as using chiral ligands or employing well-designed asymmetric bridging ligands^[3]. Especially the latter are of greater interest because such ligands are usually easy to be synthesized and modified^[4]. Although much success has been made, it remains a challenge to obtain predictable chirality without a chiral auxiliary unit. Our interest is focused on the use of asymmetric polycarboxylic acid ligand with prochiral

amine core, with the idea that the chirality of the stereochemically labile amine core can be locked via the coordination of metal ions with the terminal carboxylate groups and transferred to the whole coordination framework to direct the formation of chiral skeletons^[5]. As our continuing work in this area, we develop an asymmetric amine-containing ligand 4-(3-carboxyphenylamino)-3,5-dinitrobenzoic acid (*m*-H₂cpdba) for our synthetic strategy. Herein we report the successful self-assembly of a manganese(II) coordination complex consisting of single-stranded helical chain, $\{[\text{Mn}(m\text{-cpdba})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ **1**.

2 EXPERIMENTAL

2.1 Materials and measurements

Received 24 July 2009; accepted 10 September 2009 (CCDC 753198)

This work was supported by the National Natural Science Foundation of China (No. 20973171/20671090) and the Key Project from CAS (No. KJXC2.YW.H01)

Corresponding author. Zhang Jie, born in 1968, professor, majoring in functional coordination chemistry.

Tel: +86 591 83792871, Fax: +86 591 83710051, E-mail: zhangjie@fjirsm.ac.cn

4-(3-carboxyphenylamino)-3,5-dinitrobenzoic acid was prepared according to the literature method^[6-7]. All other reagents and solvents were commercially purchased and used as received. Elemental analyses for the C, H and N atoms were carried out on an Elementar Vario ELIII elemental analyzer. IR spectra were measured as KBr disk on a Bomem MB-102 FT-IR spectrometer.

2.2 Synthesis of $\{[\text{Mn}(m\text{-cpdba})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$

1.2 mL DMSO containing $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.2 mmol, 40 mg) was added to 10 mL aqueous solution of *m*- H_2cpdba (0.2 mmol, 69 mg) and NaOH (0.4 mmol, 16 mg). The resulting solution was allowed to stand at room temperature for slow evaporation. A few days later, yellow prism crystals of **1** were obtained in 55% yield on the basis of manganese. Anal. Calcd. (%) for $\text{C}_{14}\text{H}_{17}\text{Mn}_1\text{N}_3\text{O}_{13}$ ($M_r = 490.25$): C, 34.30; H, 3.50; N, 8.57. Found (%): C, 34.62; H, 3.36; N, 8.67. FT-IR (KBr, cm^{-1}): 3291 m, 1625 s, 1600 s, 1544 s, 1529 m, 1447 s, 1388 s, 1271 s, 1178 w, 1099 w, 926 w, 895 w, 780 w, 753 w, 728 w, 698 w, 682 w, 659 w, 573 w, 503 w.

2.3 X-ray crystal structure determination

A yellow prism single crystal with approximate dimensions of 0.20 mm \times 0.10 mm \times 0.15 mm was selected for X-ray diffraction studies. The crystal data were collected on a Rigaku Mercury-CCD diffractometer at 293 K with a graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods with SHELXL-97 and refined by full-matrix least-squares fitting on F^2 by SHELXL-97^[8,9]. Data were corrected for absorption with the CrystalClear programs. A total of 13752 reflections were collected in the range of $3.03^\circ < \theta < 27.48^\circ$ by using an ω - 2θ scan mode, of which 4301 were independent ($R_{\text{int}} = 0.0247$) and 3750 observed reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were fixed at their ideal positions, and those to O atoms were located in a difference Fourier map. The final refinement converged at $R = 0.0328$ and $wR = 0.0799$. The selected bond distances and bond angles are shown in Table 1 and hydrogen bonds are given in Table 2.

Table 1. Selected Bond Lengths (\AA) and Bond Angles ($^\circ$)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn(1)–O(1)	2.1282(12)	Mn(1)–O(2W)	2.1316(14)	Mn(1)–O(3)#1	2.1735(12)
Mn(1)–O(3W)	2.1904(13)	Mn(1)–O(4W)	2.2454(13)	Mn(1)–O(5W)	2.2691(13)
Angle	($^\circ$)	Angle	($^\circ$)	Angle	($^\circ$)
O(1)–Mn(1)–O(2W)	96.36(6)	O(2W)–Mn(1)–O(3)#1	166.92(5)	O(3)#1–Mn(1)–O(4W)	90.73(5)
O(1)–Mn(1)–O(3)#1	90.12(5)	O(2W)–Mn(1)–O(3W)	83.83(6)	O(3)#1–Mn(1)–O(5W)	107.06(5)
O(1)–Mn(1)–O(4W)	157.82(5)	O(2W)–Mn(1)–O(4W)	87.54(6)	O(3W)–Mn(1)–O(5W)	166.32(6)
O(1)–Mn(1)–O(3W)	110.86(5)	O(2W)–Mn(1)–O(5W)	85.39(5)	O(3W)–Mn(1)–O(4W)	91.24(5)
O(1)–Mn(1)–O(5W)	78.69(5)	O(3)#1–Mn(1)–O(3W)	83.25(5)	O(4W)–Mn(1)–O(5W)	79.89(5)

Symmetry transformation: #1: 0.5–*x*, –0.5+*y*, 0.5–*z*

3 RESULTS AND DISCUSSION

3.1 Description of the structure

The single-crystal X-ray diffraction reveals that compound **1** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit consists of one *m*- cpdba^{2-} ligand, one Mn(II) ion, four coordinated water molecules and one lattice water molecule. Each Mn(II) ion is coordinated by six oxygen atoms

from four water molecules and two carboxylate groups of different *m*- cpdba^{2-} ligands, resulting in a slightly distorted octahedral geometry (Fig. 1). The *m*- cpdba^{2-} ligand adapts a twisted nonplanar conformation, with the dihedral angle of 56.87° between the two phenyl rings on the two sides of the amine nitrogen atom. The 3-nitro group of *m*- cpdba^{2-} ligand is approximately coplanar with its parent benzene ring and forms strong intramolecular hy-

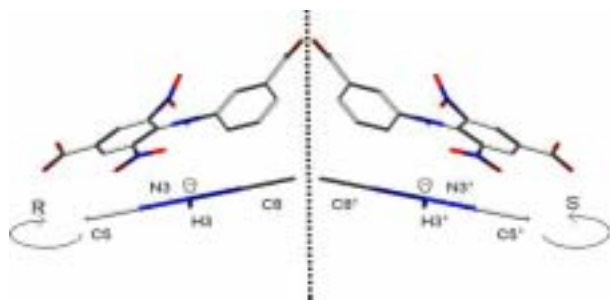


Fig. 3. R- and S-enantiomers of the chiral organic structure unit in **1**. The R and L helical chains show S and R configurations, respectively

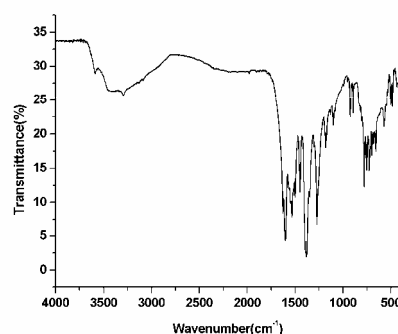


Fig. 4. IR spectrum of compound **1**

The adjacent single helical chains are connected with each other via hydrogen bonds built by coordinated water and lattice water as well as the carboxylate group with the O···O distance ranging from 2.685 to 2.867 Å. The abutting chains are related in an inversion center and show opposite hands, so that the whole 3D supramolecular framework is racemic.

3.2 IR spectrum of **1**

The IR spectrum shows typical antisymmetric (1625 and 1600 cm^{-1}) and symmetric (1447 cm^{-1}) stretching bands of carboxylate groups. The bands appearing at 1544 and 1345 cm^{-1} are attributed to the antisymmetric and symmetric stretching bands of nitro groups, respectively^[10].

REFERENCES

- (a) Zhang, J.; Chen, S. M.; Valle, H.; Wong, M.; Austria, C.; Cruz, M.; Bu, X. H. *J. Am. Chem. Soc.* **2007**, 129, 14168–14169. (b) Yao, Q. X.; Xuan, W. M.; Zhang, H.; Tu, C. Y.; Zhang, J. *Chem. Commun.* **2009**, 59–61. (c) Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J. L.; Palacios, J. C. *Chem. Commun.* **2000**, 887–892.
- (a) Cui, Y.; Ngo, H. L.; Lin, W. B. *Chem. Commun.* **2003**, 1388–1389. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, 101, 1629–1658. (c) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, 97, 2005–2062. (c) Sailaja, S.; Rajasekharan, M. V. *Inorg. Chem.* **2000**, 39, 4586–4590.
- (a) Xue, D. X.; Zhang, W. X.; Chen, X. M.; Wang, H. Z. *Chem. Commun.* **2008**, 1551–1553. (b) Ma, Y.; Han, Z.; He, Y.; Yang, L. *Chem. Commun.* **2007**, 4107–4109. (c) Prins, L. J.; Huskens, J.; Jong, F.; Timmerman, P.; Reinhoudt, D. N. *Nature* **1999**, 398, 498–502. (d) Hirschberg, J. H. K. K.; Brunsveld, L.; Ramzi, A.; Sijbesma, J. A. J. M. R. P.; Meijer, E. W. *Nature* **2000**, 407, 167–170. (e) Gangopadhyay, P.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed.* **2001**, 40, 2451–2455.
- (a) Wang, Y. T.; Tong, M. L.; Fan, H. H.; Wang, H. Z.; Chen, X. M. *J. Chem. Soc., Dalton Trans.* **2005**, 130, 424–426. (b) Wang, L.; Yang, M.; Li, G. H.; Shi, Z.; Feng, S. H. *Inorg. Chem.* **2006**, 45, 2474–2478.
- Li, W.; Ju, Z. F.; Yao, Q. X.; Zhang, J. *CrystEngComm.* **2008**, 10, 1325–1327.
- Clemons, G. R. *J. Chem. Soc.* **1950**, 1481–1485.
- Etter, M. C.; Frankenbach, G. M.; Bernstein, J. *Tetra. Lett.* **1989**, 30, 3617–3619.
- Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany **1997**.
- Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany **1997**.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley & Sons: New York **1986**, 221–224.

4 CONCLUSION

In conclusion, an interesting single helical chain compound $\{[\text{Mn}(m\text{-cpdba})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ **1** has been synthesized based on asymmetric ligand in the mixed solvents. During the assembly process, the prochiral amine core of the ligand can be locked and transferred into the 1D helical chain. Although the resultant compound is racemic, it still provides an opportunity to get an enantiomer via controlling the chirality of amine core. Further work in this area is continuing.