Synthesis, Crystal Structure and Heterogeneous Catalysis of a New Chiral Manganese Coordination Polymer Based on the Schiff-base Ligand Postprint

Authors: Qing-Chun XIA, LI Zi-Jian, LIU Yan, Bai-Zhan Liu, CUI Yong

Date: 2017-11-05T00:00:00+00:00

Abstract

A homochrial manganese(III) complex (1) derived from chiral salen ligand (1R,2R)-(-)-1,2-diphenylethane-1,2-diamine-N,N -bicarboxyl-salicylidene) has been synthesized through solvothermal procedure and characterized by IR, elemental analysis, TGA, circular dichroism (CD), powder and single-crystal X-ray crystallography. It crystallizes in orthorhombic, space group P212121 with a = 9.108(3), b = 16.431(5), c = 26.531(6) Å, V = 3970.4(19) Å3, Z = 4, Dc = 1.248 g/cm3, F(000) = 1568, Mr = 745.73, = 0.383 mm-1, the final GOOF = 0.957, R = 0.0631 and wR = 0.1079 for 13250 observed reflections with I > 2 (I). The coordination polymer 1 possesses a 1D infinite zigzag chain architecture constructed by the dicarboxyl-functionalized metallosalen ligand (Mn-salen), and the polymeric chains are further assembled into a 3D supramolecular network structure via strong intermolecular hydrogen bonding interactions between adjacent zigzag chains. As a heterogeneous catalyst, 1 was used as an efficient heterogeneous catalyst for the asymmetric olefin epoxidation.

Full Text

Preamble

Synthesis, Crystal Structure and Heterogeneous Catalysis of a New Chiral Manganese Coordination Polymer Based on the Schiff-base Ligand

XIA Qing-Chun(1)(夏庆春); LI Zi-Jian(1)(李子建); LIU Yan(1)(刘燕); LIU Bai-Zhan(3)(刘百战); CUI Yong(1, 2)(崔勇)

(1) State Key Laboratory of Metal Matrix Composites; School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China;
(2) Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China;
(3) China Tobacco, Shanghai 200240, China

ABSTRACT

A homochiral manganese(III) complex (1) derived from chiral salen ligand (1R,2R)-(-)-1,2-diphenylethane-1,2-diamine-N,N -bicarboxyl-salicylidene) has been synthesized through solvothermal procedure and characterized by IR, elemental analysis, TGA, circular dichroism (CD), powder and single-crystal X-ray crystallography. It crystallizes in orthorhombic, space group P212121 with a = 9.108(3), b = 16.431(5), c = 26.531(6) Å, V = 3970.4(19) Å^3, Z = 4, Dc = 1.248 g/cm^3, F(000) = 1568, Mr = 745.73, = 0.383 mm ^{1}, the final GOOF = 0.957, R = 0.0631 and wR = 0.1079 for 13250 observed reflections with I > 2 (I). The coordination polymer 1 possesses a 1D infinite zigzag chain architecture constructed by the dicarboxyl-functionalized metallosalen ligand (Mn-salen), and the polymeric chains are further assembled into a 3D supramolecular network structure via strong intermolecular hydrogen bonding interactions between adjacent zigzag chains. As a heterogeneous catalyst, 1 was used as an efficient heterogeneous catalyst for the asymmetric olefin epoxidation.

Keywords: manganese(III) complex; crystal structure; salen; asymmetric catalysis;

DOI: 10.14102/j.cnki.0254-5861.2011-1640

1 INTRODUCTION

Chiral salen ligands and their metal complexes have been widely applied in asymmetric synthesis [?]. Derivatives of salen ligands, such as salan, salalen and N-methyl substituted salan ligands, have also been developed [?]. Metal-salen coordination polymers have attracted great attention in heterogeneous catalysis because of their advantages over other immobilized catalyst systems such as crystalline structures, with high catalyst loadings, more uniform, isolated and accessible active sites and enhanced catalytic activity in some cases by providing confined spaces for reactants [?]. We have recently reported a series of chiral coordination polymers based on chiral salen ligands with their properties in asymmetric catalysis, separation and sensing [?]. In this study, we report the synthesis of a dicarboxyl-functionalized Mn-salen ligand to build a 1D infinite zigzag polymeric chain, and such chains are further assembled into a 3D supramolecular network structure via strong intermolecular hydrogen bonds, which can be used as an efficient heterogeneous catalyst for asymmetric olefin epoxidation.

2 EXPERIMENTAL

2.1 Materials and measurements

(1R,2R)-(-)-1,2-diphenylethane-1,2-diamine-N,N -bicarboxyl-salicylidene (H4L) was synthesized according to the procedure of literature by replacing chiral 1,2-diamino-cyclohexane with 1,2-phenylendiamine. All reagents and solvents used in these studies are commercially available and used without further purification [?]. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400–4000 cm ^{1} region) on a Nicolet Magna 750 FT-IR spectrometer. The CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in an air atmosphere at a heating rate of 10 °C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu-K radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single-crystal reflection data. The NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at the resonance frequency of 400 MHz. Analytical high performance liquid chromatography (HPLC) was performed on a LC-2010HAT HPLC with UV detection at 200 or 254 nm. Analytical CHIRALCEL OD-H, AD-H, AS-H and OJ-H column (4.6mm × 25cm) from Daicel was used. X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS Ultra DLD surface analysis instrument.

2.2 Synthesis of 1

A mixture of Mn(OAc) ·4H O (15.0 mg, 0.06 mmol), H4L (18 mg, 0.03 mmol), DMF (3 mL), EtOH (3 mL) and HAc (0.5 mL) in a capped vial was heated at 80 °C for 12 h. Red crystals of 1 were filtered, washed with MeOH and Et O respectively, and dried at room temperature. Yield: 8.3 mg, 37%. The products can be best formulated as Mn(HL)·DMF on the basis of microanalysis, IR, TGA and single-crystal diffraction.

Elemental analysis and IR for 1: Anal. Calcd. for C H MnN O (%): C, 66.04; H, 5.91; N, 5.63. Found (%): C, 65.82; H, 6.21; N, 5.59.

IR(KBr pellet, /cm ^{1}): 3436 (s), 3148 (s), 2958 (s), 1658 (s), 1602 (s), 1562 (m), 1495 (w), 1455 (w), 1395(s), 1385 (s), 1311 (m), 1283 (m), 1240 (m), 1220 (m), 1167 (w), 1139 (w), 1108 (w), 1006 (w), 931(w), 849 (w), 727 (m), 699 (w), 686 (w), 573 (m).

2.3 Crystallographic measurements and structure determination

Single-crystal XRD data for 1 were collected on a Bruker D8 VENTURE CMOS photon 100 diffractometer with Helios mx multilayer monochromator Mo-K radiation (= 0.71073 Å) at 259 K. The structure was solved by direct methods with SHELXS-2014 and refined with SHELXL-2014 using OLEX 2.0 [?]. All the non-hydrogen atoms except the guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, and treated as riding atoms. For 1, the final R = 0.0631, and wR = 0.1079 ($w = 1/[\ ^{2}(Fo^{2}) + (0.1071P)^{2}]$, where $P = (Fo^{2} + 2Fc^{2})/3$), S = 0.957, (Δ/)max = 0.001, (Δ)max = 0.373 and (Δ)min = -0.252 e/Å^{3}. The selected bond lengths and bond angles are given in Table 1 .

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Mn(1)-O(1)	Mn(1)-N(1)	Angle	Dist.
1.882(3)	1.986(4)	O(1)-Mn(1)-N(1)	91.91(16)
Mn(1)-O(2)	Mn(1)-N(2)	Angle	O(1)-Mn(1)-N(2)
1.877(4)	1.981(5)	81.7(2)	170.7(2)
Mn(1)-O(5) #1	Mn(1)-O(6)	Angle	O(2)-Mn(1)-O(6)
2.145(5)	2.323(5)	92.3(2)	92.67(16)
O(1)-Mn(1)-O(6)	O(2)-Mn(1)-N(1)	N(2)-Mn(1)-N(1)	O(1)-Mn(1)-O(5)#1
88.10(19)	172.3(2)	82.50(18)	95.44(17)
O(2)-Mn(1)-N(2)	N(2)-Mn(1)-O(5)#1	O(2)-Mn(1)-O(5)#1	O(5)#1-Mn(1)-O(6)
92.13(18)	92.7(2)	88.32(17)	176.36(19)

Symmetry transformations used to generate the equivalent atoms: #1 x-1/2, -y-3/2, -z; #2: x+1/2, -y-3/2, -z

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°)

D–H···A	d(D–H)	d(H···A)	d(D···A)
O(3)-H(3)···O(7)	2.530(7)	3.239(9)	3.379(7)
C(4)-H(4)···O(7)	2.735(7)	3.019(9)	2.952(9)
C(6)-H(6)···O(3)	2.984(7)	3.438(8)	3.005(9)
C(7)-H(7)···O(3)	2.670(3)	3.304(18)	-
C(26)-H(26B)···O(2)	-	-	-
C(32)-H(32A)···O(1)	-	-	-
C(34)-H(34B)···O(2)	-	-	-
C(36)-H(36)···O(4)	-	-	-
C(37)-H(37C)···O(1)	-	-	-
C(39)-H(39C)···O(6)	-	-	-

D-H···A	d(D-H)	d(H···A)	d(D···A)
C(40)-H(40A)···O(5)	-	-	-

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization

As outlined in Scheme 1, the dicarboxyl-functionalized salen ligand (1R,2R)-(-)-1,2-diphenylethane-1,2-diamine-N,N -bicarboxyl-salicylidene (H4L) was synthesized in 93% yield by the 1:1 condensation of 1,2-phenylendiamine with 3-tert-butyl-5-formyl-4-hydroxybenzoic acid according to literature. Heating Mn(OAc) ·4H O and H4L (2:1 molar ratio) in N,N-dimethylformamide (DMF), ethanol and acetic acid at 80 °C afforded brown block-like crystals 1 in good yield.

The phase purity of 1 was supported by the powder X-ray diffraction (XRD) pattern of the bulk sample, which is consistent with the calculated pattern (Fig. 1 [Figure 1: see original paper]). The thermal stability of 1 was investigated on crystalline samples under a N atmosphere from 50 to 800 °C. The solid-state circular dichroism (CD) spectra of 1 made from R and S enantiomers of H4L showed the mirror images of each other, indicating their enantiomeric nature (Fig. 2 [Figure 2: see original paper]). TGA revealed that there are almost no guest molecules and it is stable up to 270 °C. IR spectra reveal the presence of hydroxyl group with the strong peak at 3436 and 3148 cm ^{1}, which demonstrates the existence of uncoordinated carboxyl group. The absorption at 1658, 1602 and 1562 cm ^{1} can be assigned to the symmetry and anti-symmetry stretching vibrations of COO and C=O in DMF. The characteristic peaks at 1395 and 1385 cm ^{1} may come from C=N vibration (Fig. 3 [Figure 3: see original paper]). The manganese ion in 1 is in the +3 oxidation state, as suggested by the Mn 2p3/2 and 2p1/2 peaks around 642.58 and 655.52 eV, respectively, in X-ray photoelectron spectroscopy (XPS) spectrum (Fig. 4 [Figure 4: see original paper]).

3.2 Structural description

The single-crystal X-ray diffraction analysis reveals that 1 has a one-dimensional coordination framework that crystallizes in the orthorhombic chiral space group P212121 and the asymmetric unit contains one MnHL unit and one coordinated N,N-dimethylformamide molecule. In the MnHL unit, the Mn(III) center adopts a distorted octahedral coordination geometry with the equatorial plane occupied by the N O donors of one L ligand and the apical position by two oxygen atoms from a DMF molecule and a monodentate carboxylate oxygen atom of another L ligand (Fig. 5a [Figure 5: see original paper]). The Mn-N and Mn-O bond lengths range from 1.981(5) to 1.986(4) and from 1.877(4) to 2.323(5) Å, respectively. The dicarboxyl-functionalized metallosalen ligand (MnL unit) uses one monodentate carboxylate group to bind another Mn center but remains a carboxylate group uncoordinated, and thus adjacent Mn centers are linked by metallosalen ligands to generate a 1D zigzag chain (Fig. 5b). The adjacent zigzag chains are further linked up together to generate a 3D supramolecular structure through intermolecular O–H···O hydrogen bonds, which plays an irreplaceable role in the chain assembly and further promotes the stability of the structure (Fig. 5c).

3.3 Enantioselective catalysis

To a suspension of 1 (0.5 mol%) in dry DCM (1.0 mL), alkene (0.1 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (2 mg, 0.006 mmol) were added. The same amount of oxidant was added 18 more times at 15 min intervals. The reaction was carried out overnight at 0 °C. After that, the mixture was centrifuged at 9000 rpm for 5 min, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ^{1}H NMR to give the conversion and by HPLC to give the ee value.

It has been documented that metallosalen complexes are among the best catalysts and privileged ligands for asymmetric synthesis [?], and MOFs based on M-salen have been explored as catalysts for asymmetric transformations, where M is Mn/Ru/Co/Fe/VO/Cu/Cr [?]. Chiral manganese salen complexes are active asymmetric catalysts for various types of organic reaction [?]. Based on the pioneering work, the catalytic activity of 1 toward asymmetric epoxidation was examined with 2,2-dimethyl-2H-chromene as substrate and 2-(tert-butylsulfonyl)iodosylbenzene (a soluble compound) as oxidant in CH Cl at 0 °C, and the best result with 69% conversion and 81% ee of desired epoxide after 12 h. When the electron-withdrawing group (6-CN) and electron-donating group (6-OMe) in the chroman were employed, 73% and 64% conversions together with 83% and 79% ee were obtained.

Table 3. 1 Catalyzed Enantioselective Epoxidation of Alkenes

Entry	Conv.(%)	ee(%)
1	69	81
2	73	83
3	64	79

Calculated based on ^{1}H NMR spectroscopy;   Determined by HPLC

4 CONCLUSION

In summary, we have synthesized one novel Mn(salen)-based metallosalan coordination polymer 1 from dicarboxyl-functionalized salen ligand. It was characterized by single-crystal and powder X-ray diffraction, CD, TGA and XPS. In addition, the coordination polymer shows efficient enantioselective abilities to catalyze the oxidation olefin to epoxide.

REFERENCES

(1) Cozzi, P. G. Metal-Salen Schiff base complexes in catalysis: practical aspects. Chem. Soc. Rev. 2004, 33, 410–421.

(2) Ford, D. D.; Nielsen, L. P. C.; Zuend, S. J.; Musgrave, C. B.; Jacobsen, E. N. Mechanistic basis for high stereoselectivity and broad substrate scope in the (salen)Co(III)-catalyzed hydrolytic kinetic resolution. J. Am. Chem. Soc. 2013, 135, 15595–15608.

(3) Huang, Y.; Iwama, T.; Rawal, V. H. Design and development of highly effective Lewis acid catalysts for enantioselective Diels-Alder reactions. J. Am. Chem. Soc. 2002, 124, 5950–5951.

(4) Sawada, Y.; Matsumoto, K.; Kondo, S.; Watanabe, H.; Ozawa, T.; Suzuki, K.; Saito, B.; Katsuki, T. Rational design of a well-defined soluble calcium hydride complex. Angew. Chem. Int. Ed. 2006, 45, 3478–3480.

(5) Berkessel, A.; Brandenburg, M.; Schfer, M. Mass-spectrometric and kinetic studies on the mechanism and degradation pathways of titanium salalen catalysts for asymmetric epoxidation with aqueous hydrogen peroxide. Adv. Synth. Catal. 2008, 350, 1287–1294.

(6) Egami, H.; Katsuki, T. Fe(salan)-catalyzed asymmetric oxidation of sulfides with hydrogen peroxide in water. J. Am. Chem. Soc. 2007, 129, 8940–8941.

(7) Zhang, F. W.; Zhou, Y. F.; Dong, J. Q.; Liu, B. Z.; Zheng, S. J.; Cui, Y. Synthesis and crystal structure of a novel chiral 3D metal-organic framework based on an N-methyl substituted salan ligand. Chin. J. Struc. Chem. 2014, 33, 1154–1158.

(8) Wei, G. Y.; Zhu, C. F.; Zha, M. Q.; Xuan, W. M.; Li, X.; Cui, Y. Synthesis and characterization of a homochrial manganese(II) complex constructed from (1R,2R)-(-)-diaminocyclohexane-N,N -bicarboxyl-salicylidene). Chin. J. Struct. Chem. 2011, 30, 164–169.

(9) Xi, X. B.; Dong, T. W.; Li, G.; Cui, Y. Controlled structures of a 1D chiral metallosalen polymer by photo- and solvent-induced partial depolymerization. Chem. Commun. 2011, 47, 3831–3833.

(10) Li, G.; Zhu, C. F.; Xi, X. B.; Cui, Y. Selective binding and removal of organic molecules in a flexible polymeric material with stretchable metallosalen chains. Chem. Commun. 2009, 2118–2120.

(11) Ye, C. C.; Zhu, C. F.; Gong, T. F.; Sheng, E. H.; Xuan, W. M.; Cui, Y.; Liu, B. Z. A novel Cu-based metallosalan complex: synthesis, structure and chiral sensor study. Chin. J. Struct. Chem. 2013, 32, 1076–1082.

(12) Zhu, C. F.; Ban, F. J.; Sheng, E. H.; Zheng, S. J.; Liu, B. Z.; Cui,

Y. Synthesis, structure and photoluminescence of one zinc-based metal-metallosalen framework. Chin. J. Struct. Chem. 2013, 32, 205–210.

(13) Dong, T. W.; Mo, K.; Li, G.; Zhu, C. F.; Xi, X. B.; Cui, Y. Synthesis, characterization and crystal structure of one Ni (salen) complex. Chin. J. Struct. Chem. 2011, 30, 247–251.

(14) Yuan, G. Z.; Zhu, C. F.; Liu, Y.; Cui, Y. Nano- and microcrystals of a Mn-based metal-oligomer framework showing size-dependent magnetic resonance behaviors. Chem. Commun. 2011, 47, 3180–3182.

(15) Zhu, C. F.; Chen, X.; Yang, Z. W.; Du, X.; Liu, Y.; Cui, Y. Chiral microporous Ti(salan)-based metal-organic frameworks for asymmetric sulfoxidation. Chem. Commun. 2013, 49, 7120–7122.

(16) Sheldrick, G. M. SHELXS-97, Program for X-ray Crystal Structure Solution. University of Göttingen, Germany 1997.

(17) Cho, S. H.; Ma, B. Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation. Chem. Commun. 2006, 2563–2565.

(18) Falkowski, J. M.; Wang, C.; Liu, S.; Lin, W. Actuation of asymmetric cyclopropanation catalysts: reversible single-crystal to single-crystal reduction of metal-organic frameworks. Angew. Chem. Int. Ed. 2011, 50, 8674-8678.

(19) Zhu, C. F.; Yuan, G. Z.; Chen, X.; Yang, Z. W.; Cui, Y. Chiral nanoporous metal-metallosalen frameworks for hydrolytic kinetic resolution of epoxides. J. Am. Chem. Soc. 2012, 134, 8058-8061.

(20) Yang, Z. W.; Zhu, C. F.; Li, Z. J.; Liu, Y.; Liu, G. H.; Cui, Y. Engineering chiral Fe(salen)-based metal-organic frameworks for asymmetric sulfide oxidation. Chem. Commun. 2014, 50, 8775-8778.

(21) Zhu, C. F.; Xia, Q. C.; Chen, X.; Du, X.; Liu, Y.; Cui, Y. Chiral metal-organicframework as a platform for cooperative catalysis in asymmetric cyanosilylation of aldehydes. ACS Catal. 2016, 6, 7590-7596.

(22) Liu, Y.; Li, Z. J.; Yuan, G. Z.; Xia, Q. C.; Yuan, C.; Cui, Y. Chiral Cu(salen)-based metal-organic framework for heterogeneously catalyzed aziridination and amination of olefins. Inorg. Chem. 2016, 55, 12500-12503.

(23) Xia, Q. C.; Liu, Y.; Li, Z. J.; Gong, W.; Cui, Y. A Cr(salen)-based metal-organic framework as a versatile catalyst for efficient asymmetric transformations. Chem. Commun. 2016, 52, 13167-13170.

(24) Chang, S.; Galvin, J. M.; Jacobsen, E. N. Effect of chiral quaternary ammonium salts on (salen)Mn-catalyzed epoxidation of cis-olefins. A highly enantioselective, catalytic route to trans-epoxides. J. Am. Chem. Soc. 1994, 116, 6937-6938.

(25) Sun, W.; Wang, H. W.; Xia, C. G.; Li, J. W.; Zhao, P. Q. Chiral-Mn(Salen)-complex-catalyzed kinetic resolution of secondary alcohols in water. Angew. Chem. Int. Ed. 2003, 42, 1042-1044.

(26) Brown, M. K.; Blewett, M. M.; Colombe, J. R.; Corey, E. J. Mechanism of the enantioselective oxidation of racemic Secondary alcohols catalyzed by chiral Mn(III)-Salen complexes. J. Am. Chem. Soc. 2010, 132, 11165-11170.

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.