



Synthesis, structure, and electrochemistry and magnetic properties of a novel 1D homochiral Mn^{III}(5-Brsalen) coordination polymer with left-handed helical character



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ARTICLE INFO

Article history:

Received 3 July 2015

Received in revised form

9 September 2015

Accepted 29 September 2015

Available online 3 October 2015

Keywords:

Spontaneous resolution

Chirality

Crystal structure

Electrochemistry

ABSTRACT

A novel homochiral manganese (III) Mn(5-Brsalen) coordination polymer with left-handed helical character by spontaneous resolution on crystallization by using Mn(5-Brsalen) and 4,4-bipyridine, [Mn^{III}(5-Brsalen)(4,4-bipy)]·ClO₄·CH₃OH (**1**) (4,4-bipy = 4,4-bipyridine) has been synthesized and structurally characterized by X-ray single-crystal diffraction, elemental analysis and infrared spectroscopy. In compound **1**, each manganese(III) anion is six-coordinate octahedral being bonded to four atoms of 5-Brsalen ligand in an equatorial plane and two nitrogen atoms from a 4,4-bipyridine ligand in axial positions. The structure of compound **1** can be described a supramolecular 2D-like structure which was formed by the intermolecular π -stacking interactions between the neighboring chains of the aromatic rings of 4,4-bipyridine and 5-Brsalen molecules. UV–vis absorption spectrum, electrochemistry and magnetic properties of the compound **1** have also been studied.

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1. Introduction

Chirality is an essential element for life, which plays a key role in biological system and pharmacy, as well as in advanced materials such as asymmetric catalysis, chiral separation and nonlinear optical devices [1–5]. The general approach to a chiral framework is using a chiral molecule as the primary linker or as an inducer of final chirality, which is the most effective method for the synthesis of chiral coordination polymers [6–9]. However, due to the limitation of the chiral pool and very often the high cost of chiral ligands, it is highly desirable to create chiral compounds from achiral precursors. Spontaneous resolution on crystallization without any chiral auxiliary usually yields chiral conglomerate, which has been proved as a constructive approach for the synthesis of individual chiral metal–organic coordination polymers [10–12]. However, the controllable generation of such chiral frameworks from totally achiral precursors is still of a great challenge since it may be significantly governed by several factors such as the flexibility of organic ligand, coordination geometry of the metal center, counteranion, solvent, reaction temperature, and pH value of the

solution [13–19]. Moreover, spontaneous resolution is relatively rare and cannot be predicted because its mechanism is not yet fully understood.

On the other hand, tetradentate H₂salen and salen derivatives are versatile ligands, which consisting of two nitrogen and two oxygen donors to form stable metal complexes, are very popular O- and N-donor linkers because of their excellent chelating capabilities. Salen-type N₂O₂ ligands coordinate to various kinds of transition-metal ions in a tetradentate fashion to produce stable complexes which have found versatile applications in a wide range of areas such as catalysis, biochemistry, electrochemistry, magnetic properties, and luminescent materials [20–26]. Among them, some manganese (III) complexes of salen type Schiff base ligands have been synthesized in the past decades [27–29]. However, to the best of our knowledge, the homochiral manganese (III) Mn(5-Brsalen) coordination polymer with left-handed helical character by spontaneous resolution on crystallization have not been reported so far. In this paper, we chose an achiral 5-BrsalenMn molecule as the building unit and successfully synthesized a homochiral Mn(5-Brsalen) coordination polymer with left-handed helical character, [Mn^{III}(5-Brsalen)(4,4-bipy)]·ClO₄·CH₃OH (**1**). The crystal structure, electrochemistry and magnetic properties of compound **1** have also been studied.

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2. Experimental section

2.1. General procedures

The reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed on an Elementar Vario ELIII analyzer. IR spectra were recorded using KBr pellets on a Vector 22 Bruker spectrophotometer in the 4000–400 cm^{-1} regions. The UV–Vis diffuse reflectance spectra were recorded with a JASCO V-570 UV–Vis–NIR spectrophotometer in the 300–800 nm. Cyclic voltammetry (CV) measurements were carried out on a BAS 100 W system in a three-electrode cell with a pure N_2 gas inlet and outlet. Temperature-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-5 magnetometer with an applied field of 1 kOe, and diamagnetic corrections were made with Pascal's constants.

2.2. Synthesis of the Schiff-base ligand *N,N*-bis(5-Bromosalicylidene)ethane-1,2-diamine (5-Brsalen)

The tetradentate Schiff base ligand was prepared by the condensation of 5-Bromosalicylaldehyde (2.01 g, 10 mmol) and 1,2-ethanediamine (0.30 g, 5 mmol) in methanol (10 mL) as reported earlier [30].

2.3. Synthesis of $[\text{Mn}^{\text{III}}(5\text{-Brsalen})(\text{H}_2\text{O})]\text{ClO}_4$ (5-BrsalenMn)

The manganese(III) complex was obtained by mixing manganese(III) acetate dihydrate (5.0 mmol, 1.34 g) and 5-Brsalen (5.0 mmol, 2.13 g) in methanol (200 mL) and anhydrous sodium perchlorate (7.5 mmol, 0.92 g) in water (80 mL). After evaporation to 40 mL and cooling, the resulting black crystals were collected by suction filtration [31]. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_7\text{Br}_2\text{ClMn}$: C, 32.22; H, 2.73; N, 4.70%. Found: C, 32.17; H, 2.70; N, 4.75%.

2.4. Synthesis of $[\text{Mn}^{\text{III}}(5\text{-Brsalen})(4,4\text{-bipy})]\text{ClO}_4\cdot\text{CH}_3\text{OH}$ (1)

A solution of $[\text{Mn}^{\text{III}}(5\text{-Brsalen})(\text{H}_2\text{O})]\text{ClO}_4$ (0.1 mmol, 0.060 g) and 4,4-bipyridine (0.1 mmol, 0.016 g) in CH_3OH solution (20 mL) was stirred for 2 h at room temperature, and then filtered, and the filtrate was left at room temperature in the dark room for evaporation. After one week, the dark-brown crystals were collected by suction filtration, washed with water, and air-dried. Yield: 43%. Elemental analysis for compound **1**: Calc (found) for $\text{C}_{27}\text{H}_{24}\text{Br}_2\text{ClMnN}_4\text{O}_7$: %C 42.30 (42.36), %N 7.31 (7.35), %H 3.16 (3.18). IR (solid KBr pellet ν/cm^{-1}): 3441 br, 3082 w, 3048 w, 2965 w, 2826 w, 2854 w, 2802 w, 1624 s, 1532 w, 1451 s, 1407 m, 1371 m, 1277 m, 1179 w, 1092 s, 1005 w, 975 w, 832 w, 807 w, 690 w, 621 w, 479 w, 463 w.

2.5. X-ray crystallography

The data were collected at a temperature of 293 ± 2 K on a Bruker Smart APEX II X–diffractometer equipped with graphite monochromated Mo– $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. Indexing and unit cell refinement were based on all observed reflections from those 72 frames. The structure was solved in the space group $P4_32_12$ by direct method and refined by the full–matrix least–squares fitting on F^2 using SHELXTL–97 [32]. All non–hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically in theoretical positions. The final cycle of full–matrix least–squares refinement was based on number of observed reflections ($I > 2\sigma(I)$). The crystal data and structure refinement of compound **1** is summarized in Table 1. Selected bond lengths (Å) and bond angles ($^\circ$) for **1** is listed in

Table 1
Crystallographic data and structure refinement for compound **1**.

Formula	$\text{C}_{27}\text{H}_{24}\text{Br}_2\text{ClMnN}_4\text{O}_7$
Fw	766.71
Crystal system	Tetragonal
Space group	$P4_32_12$
<i>a</i> , Å	16.5697(5)
<i>c</i> , Å	21.9035(15)
<i>V</i> , Å ³	6013.7(5)
<i>Z</i>	8
<i>D_c</i> , g/cm ³	1.694
μ (Mo $K\alpha$), mm ^{−1}	3.237
Crystal size, mm ³	$0.40 \times 0.10 \times 0.08$
θ_{min} , θ_{max} , $^\circ$	1.54, 27.50
No. total reflns.	26816
No. uniq. reflns (R_{int})	6847 (0.0653)
No. obs. [$I \geq 2\sigma(I)$]	4304
No. params	379
Completeness to theta = 27.50, %	99.2
<i>R</i> 1, <i>wR</i> 2 [$I \geq 2\sigma(I)$]	0.0817, 0.2047
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1308, 0.2395
Absolute structure parameter	−0.02(2)
GOF	1.015

$$R_1 = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|; wR_2 = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$$

Table 2. CCDC 1026479 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Email: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Crystal structures

Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the tetragonal chiral space group $P4_32_12$. The crystal structure comprised one $[\text{Mn}^{\text{III}}(5\text{-Brsalen})(4,4\text{-bipy})]^+$ cation, one uncoordinated methanol molecule and one perchlorate anion. As shown in Fig. 1, each manganese (III) anion is six-coordinate octahedral being bonded to four atoms of 5-Brsalen ligand in an equatorial plane and two nitrogen atoms from a 4,4-bipyridine ligand in axial positions. Each 4,4-bipyridine molecule links the $\text{Mn}^{\text{III}}(5\text{-Brsalen})$ moieties result in the one-dimensional polymeric structure. The bond lengths in the equatorial plane fall in the range of 1.889(5)–1.895(6) Å for Mn–O, 1.978(6)–1.978(7) Å for Mn–N, while axial Mn–N distances are in the range of 2.346(6)–2.362(6) Å. Selected bond lengths and angles are summarized in Table 2. The axial bonds are significantly longer than the equatorial bonds, as expected for the Jahn–Teller distortion of Mn ions with a +3 oxidation state. The intrachain Mn···Mn distance is

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for complex **1**.

Mn(1)–O(1)	1.889(5)	Mn(1)–N(2)	1.978(6)
Mn(1)–O(2)	1.895(6)	Mn(1)–N(3)	2.346(6)
Mn(1)–N(1)	1.978(7)	Mn(1)–N(4)#1	2.362(6)
Br(1)–C(4)	1.907(10)	Br(2)–C(13)	1.910(9)
O(1)–Mn(1)–O(2)	97.8(2)	N(2)–Mn(1)–N(3)	95.0(2)
O(1)–Mn(1)–N(2)	172.2(3)	N(1)–Mn(1)–N(3)	91.6(3)
O(2)–Mn(1)–N(2)	89.4(3)	O(1)–Mn(1)–N(4)#1	86.6(2)
O(1)–Mn(1)–N(1)	91.0(2)	O(2)–Mn(1)–N(4)#1	88.6(2)
O(2)–Mn(1)–N(1)	171.2(3)	N(2)–Mn(1)–N(4)#1	90.7(2)
N(2)–Mn(1)–N(1)	81.8(3)	N(1)–Mn(1)–N(4)#1	91.7(3)
O(1)–Mn(1)–N(3)	88.0(2)	N(3)–Mn(1)–N(4)#1	173.7(2)
O(2)–Mn(1)–N(3)	88.9(2)		

Symmetry transformations used to generate equivalent atoms: #1 $y + 1, x, -z$.

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