



## ORIGINAL ARTICLE

Catena-[bis(o-aminobenzoato-κ<sup>3</sup> N,O:O')Mn(II)]

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## KEYWORDS

2-Aminobenzoic acid;  
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**Abstract** In the title complex, [C<sub>14</sub>H<sub>12</sub>MnN<sub>2</sub>O<sub>4</sub>]<sub>n</sub>, the Mn(II) cation octahedrally coordinated by two N and two O atoms from two o-aminobenzoate ligands and two O atoms from another two o-aminobenzoate ligands. The carboxylate groups of two o-aminobenzoate anions coordinate to the Mn(II) cation in a monodentate manner, whereas the other two o-aminobenzoate anions chelate the Mn(II) cations through the O-atom of the carboxylate group and the N-atom of the amino group. This complex adopts the syn-anti carboxylate bridging mode with the conformation syn(eq)-anti(eq). The title complex is a two-dimensional coordination polymer based on an infinite Mn—O—C—O—Mn chain. There is hydrogen bond interaction within the two dimensional network. The adjacent two-dimensional network is packed only by Van der Waals interactions.

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## 1. Introduction

In recent years research on coordination polymers has expanded rapidly because of their fascinating structural diversity and potential application as functional materials (Moulton and Zaworotko, 2001; Batten and Robson, 1998). Multifunctional carboxylate frameworks are of great interest due to their intriguing network topologies and their potential applications as microporous, magnetic, nonlinear optical and

fluorescent materials (Zaworotko, 2000; Ward et al., 1997; Fujita et al., 1995; Armentano et al., 2001; Lin et al., 1998; Tong et al., 1999). The carboxylate group cannot only bridge two or more metal centers to produce a wide variety of complexes ranging from zero-dimensional discrete molecules to three dimensional architectures, but also can adopt various types of bridging conformation modes, such as the so-called syn-syn, syn-anti, and anti-anti modes (Scheme 1).

In terms of constructing the extended structural motifs, either di- and multi-carboxylato ligands, or multifunctional carboxylate-containing ligands incorporating other coordination groups containing N and O,O' atoms, have been employed (Barthelet et al., 2002; Konar et al., 2002; Rueff et al., 2002). The N or O,O'-donor ligands adopt different coordination modes forming different kinds of building blocks, which are finally combined to generate different supramolecular architectures.

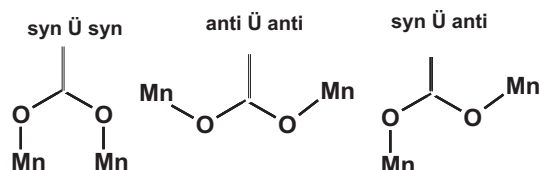
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**Scheme 1** Schematic representations of the coordination modes for the carboxylate bridges.

In this paper, we report the preparation and crystal structure of a new two dimensional coordination polymer formulated as  $[\text{Mn}(\text{2-aba})_2]_n$  (1).

## 2. Experimental

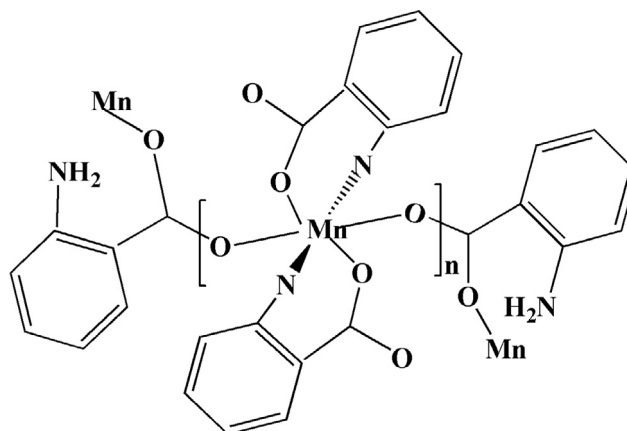
A mixture of  $\text{Mn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  (150 mg, 0.46 mmol),  $\text{H}_2\text{cp-Ala}$  [2-(carboxyphenyl) imino-2-propanoic acid] (90 mg, 0.43 mmol),  $\text{NaOH}$  (47 mg, 1.18 mmol), ethanol (15 ml) and dichloromethane (15 ml) was refluxed for 30 min. The turbid solution was then filtered after being cooled to room temperature and slowly evaporated at ambient temperature to afford pale brown crystals of  $[\text{Mn}(\text{2-aba})_2]_n$  after one month, Yield 23%.

### 2.1. Crystal data

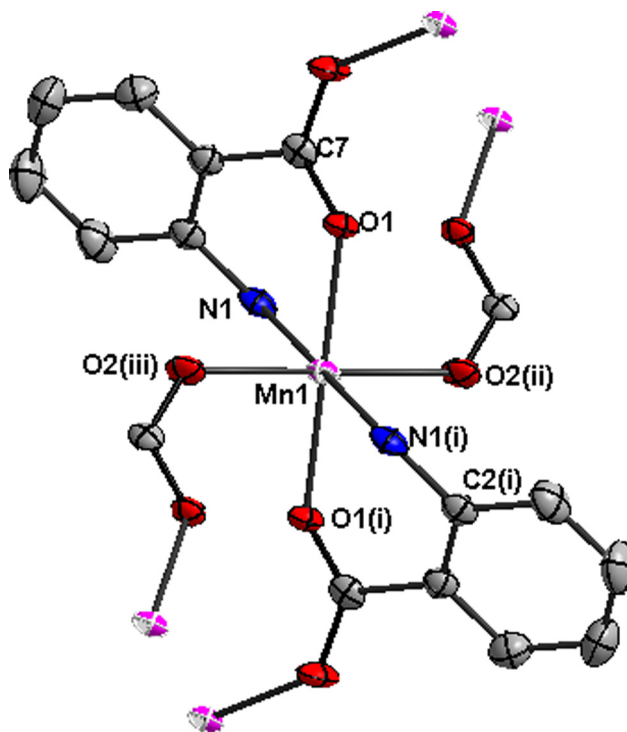
$\text{C}_{14} \text{H}_{12} \text{Mn} \text{N}_2 \text{O}_4$	$V = 660.97(126) \text{ \AA}^3$
$M_r = 327.2$	$Z = 2$
Monoclinic, $P 1 2_1/c 1$	Mo $K\alpha$ radiation
$a = 13.9391(9) \text{ \AA}$	$\mu = 1.016$
$b = 5.2369(3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 9.5015(5) \text{ \AA}$	$F(000) = 334$
$\beta = 107.64(1)^\circ$	
<b>Data collection</b>	
Oxford Gemini-S diffractometer	2551 measured reflections
Absorption correction: multi-scan	1309 independent reflections
CrysAlis PRO SHELXL-97 (Oxford Diffraction Ltd., 2009)	1060 reflections with $I > 2_\sigma(I)$
Sheldrick (1997)	Rint = 0.0362
<b>Refinement</b>	
$wR2, R1$ (all data) = 0.0858, 0.0596	1309 reflections
$wR2, R1$ [ $I \geq 2\sigma(I)$ ] = 0.0817, 0.0436	121 parameters
$S = 1.085$	0 restraints
$\Delta\rho_{\text{max}} = 0.326 \text{ e \AA}^{-3}$	$\Delta\rho_{\text{min}} = -0.337 \text{ e \AA}^{-3}$

## 3. Results and discussion

The title coordination polymer was prepared by reacting  $\text{Mn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  with  $\text{Ala}[2\text{-(carboxyphenyl)-imino-2-propanoic acid}]$  in the presence of base.



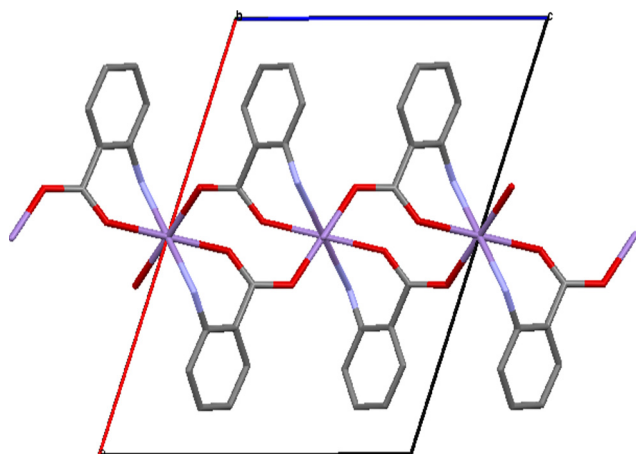
The symmetric unit of (1) contains one manganese cation and four o-aminobenzoate ions. The Mn(II) atom is six-coordinate, forming a slightly distorted octahedral with  $\text{MnN}_2\text{O}_4 \sim$  chromophore. In the coordination polyhedron, the equatorial plane is occupied by four O (O1, O1', O2'' and O2''') atoms from four o-aminobenzoate anions and the axial sites situated two N (N1 and N1') atoms from two o-aminobenzoate anions already associated with the equatorial plane (Fig. 1). The Mn(II) center is coordinated by two types of o-aminobenzoate anions, one behaves in a chelating mode



**Figure 1** The ORTEP drawing of the title compound (1). Displacement ellipsoids are drawn at 50% probability level, symmetry codes: (i)  $-x + 1, -y, -z + 2$ , (ii)  $-x + 1, y - 0.5, -z + 5/2$ .

**Table 1** Selected bond lengths (Å).

Mn1—O1	2.1288(17)	Mn1—O2 <sup>ii</sup>	2.1801(19)
Mn1—N	2.311(2)	O1—C7	1.259(3)
O2—C7	1.256(3)	N1—C2	1.415(4)
N1—H1	0.87(3)	N1—H2	0.90(3)

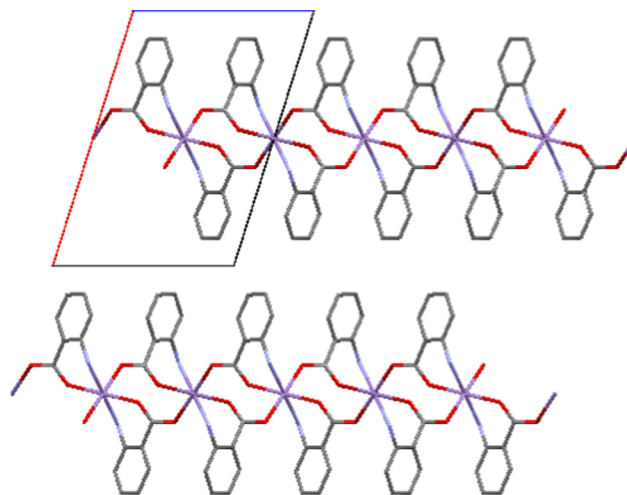
Symmetry codes: (ii)  $1 - x, -0.5 + y, 2.5 - z$ .**Figure 2** View of the coordination environment around Mn(ii).

[Mn—O1 = 2.1288(17) Å and Mn—N1 = 2.311(2) Å], the other one acts as a monodentate [Mn—O2 = 1.1801(19) Å] (Table 1) which is isostructural with Zn and Cu analogs (Haendler et al., 1983; Haendler and A Ibanese, 1975) (Fig. 2).

The bond angles between the cis-donors around Mn(II) lie in the ranges 79.59(8)–90.87(8)°. The length of two manganese–carboxylate distances is none equivalent (Mn—O, 2.1288(17) and 2.1801(19) Å), while the manganese amino-bond (Mn—N, 2.311(2) Å) is slightly longer (Table 1). These bond angles and bond distances are slightly different from those observed in the [Mn(3-aba)<sub>2</sub>]<sub>n</sub> complex (Ruihu et al., 2006). Hence the difference in Mn—O bond length in (1) may be attributed to the packing forces rather than differing in oxygen basicity. The 2-aba ligand acts as an exo-tridentate bridging mode through the amino nitrogen atom and  $\mu_2, \eta^2$ -carboxylate group (1). The double syn-anti mode  $\mu_{1,3}$ -carboxylato—O,O bridges coming from two 2-aba ligands exist between neighboring Mn(II) ions forming an infinite Mn—O—C—O chain with the C—O—Mn bond angles being 128.09(17) and 132.461(17). The closest Mn···Mn distance within the chain is 5.4246(2) Å and the shortest inter-chain Mn···Mn distance is 5.2369(3) Å. The inter-chain distance is much smaller than the observed value of 8.129 Å between the Mn-atoms in the case of the related [Mn(3-aba)<sub>2</sub>]<sub>n</sub> complex, while the Mn···Mn distance within the chain of (1) is longer than the observed value of 4.607 Å in the same complex. This may be related to the mode of bonding of the carboxylate group syn–syn versus syn–anti. There exist hydrogen-bonding interactions in the two-dimensional network between the hydrogens of the amino group of one molecule and the oxygen of the carboxylate group of another molecule. The average D···A distances for N1—H2···O1 and N1—H1···O2 of (1) are within the range compared with 2.998 and 2.954 Å for 2-aba complexes of Co<sup>2+</sup> and Ni<sup>2+</sup> ions respectively (Wel You-Huan

**Table 2** Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···O1 <sup>ii</sup>	0.90(4)	2.11(4)	2.989(4)	164(3)
N1—H1···O2 <sup>i</sup>	0.87(3)	2.30(3)	3.134(3)	161(3)

Symmetry codes: (i)  $x, -0.5 - y, -0.5 + z$ ; (ii)  $1 - x, -0.5 + y, 2.5 - z$ .**Figure 3** View of a pack diagram along the b axis showing the two-dimensional network.

et al., 2006). The hydrogen bond geometry is listed in (Table 2). No hydrogen bonds are observed between 2D networks. The adjacent two-dimensional network is packed only by Van der Waals interactions (see Fig. 3).

#### 4. Conclusion

From all of these we conclude that by employing aromatic amino acids with different substituent positions (namely, ortho, metha or para) in addition to the type of metal cation one can easily vary the resultant supramolecular organization. By using 2-aminobenzoate as a ligand with different metal ions such as Mn<sup>2+</sup> and Ca<sup>2+</sup> or Sr<sup>2+</sup> one can get different coordination modes especially with the amino group. In the case of Mn<sup>2+</sup> ion (1) the amino group chelates the metal ion while in the case of Ca<sup>2+</sup> and Sr<sup>2+</sup> ions the amino group does not take part in the coordination in the former and while in the latter coordinates to the neighboring Sr<sup>2+</sup> ion (Murugavel et al., 2000). By changing the position of the amino group in the aminobenzoate from 2 to 3 different supramolecular organizations will result, for example the 3-aminobenzoate ligand coordinates to the Mn<sup>2+</sup> ion in different way compared to the title complex, but similar to Co<sup>2+</sup> and Ni<sup>2+</sup> complexes (Wel You-Huan et al., 2006).

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