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PII: S1878-5352(15)00114-8

DOI: <http://dx.doi.org/10.1016/j.arabjc.2015.04.012>

Reference: ARABJC 1627

To appear in: *Arabian Journal of Chemistry*

Received Date: 11 July 2013

Accepted Date: 13 April 2015

Please cite this article as: R.G. Abuhmaiera, R.M. El-Mehdawi, F.A. Treish, M.M. Ben Younesa, D. Poleti, J. Rogan, Catena-[bis(o-Aminobenzoato- $\kappa^3$  N,O:O')Mn(II)], *Arabian Journal of Chemistry* (2015), doi: <http://dx.doi.org/10.1016/j.arabjc.2015.04.012>

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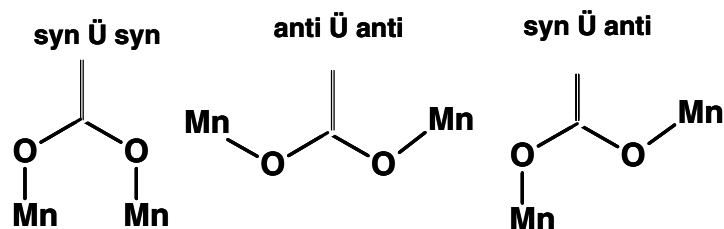
**Keywords:** 2-aminobenzoic acid, Crystal structure, Carboxylate, octahedral

### Abstract

In the title complex,  $[C_{14}H_{12}MnN_2O_4]_n$ , 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 oaminobenzoate ligands. The carboxylate groups of two o-aminobenzoate anions coordinates 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 twodimensional network. The adjacent two-dimensional network are packed only by Van der Waals interactions.

### 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 & Zaworotko, 2001; Batten & 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 *et al.*, 2000; Ward *et al.*, 1997; Ogura *et al.*, 1995; Armentano *et al.*, 2001; Wang *et al.*, 1998; Tong *et al.*, 1999). The carboxylate group can not only bridge two or more metal centers to produce a wide variety of complexes ranging from zero-dimensional discrete molecules to threedimensional 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).



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

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.*, 2000; Rueff, 2000). 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.

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, 0.46mmol),  $\text{H}_2\text{cp-Ala}$  [2-(carboxyphenyl) imino-2-propanoic acid] (90 mg, 0.43 mmol), NaOH (47 mg, 1.18mmol), ethanol (15 ml) and dichloromethane (15 ml) were 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

$\text{C}_{14}\text{H}_{12}\text{MnN}_2\text{O}_4$

$M_r = 327.2$

Monoclinic, P 1 21/c 1

$a = 13.9391(9) \text{ \AA}$

$b = 5.2369(3) \text{ \AA}$

$c = 9.5015(5) \text{ \AA}$

$\beta = 107.64(1)^\circ$

$V = 660.97(126) \text{ \AA}^3$

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 1.016$

$T = 293\text{K}$

$F(000) = 334$

### Data collection

Oxford Gemini-S diffractometer

Absorption correction: multi-scan

(CrysAlis PRO SHELXL-97

(Sheldrick, 1997)

2551 measured reflections

1309 independent reflections

1060 reflections with  $I > 2_\sigma(I)$

$R_{\text{int}} = 0.0362$

### Refinement

$wR_2, R_1$  (all data) = 0.0858, 0.0596

$wR_2, R_1 [I \geq 2\sigma(I)] = 0.0817, 0.0436$

$S = 1.085$

$\Delta\rho_{\text{max}} = 0.326 \text{ e \AA}^{-3}$

1309 reflections

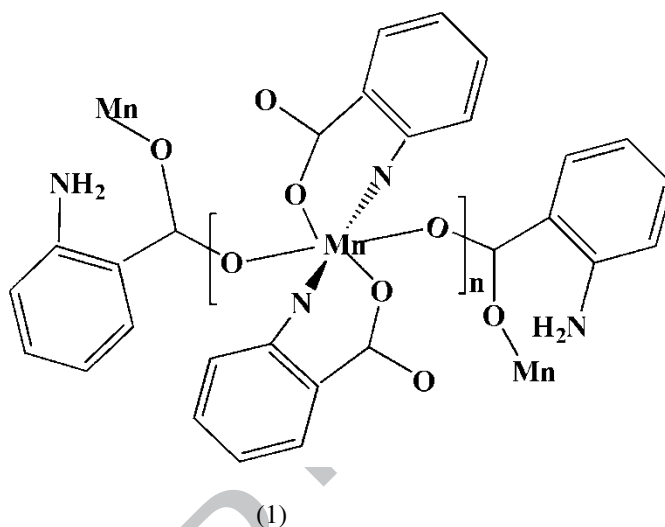
121 parameters

0 restraints

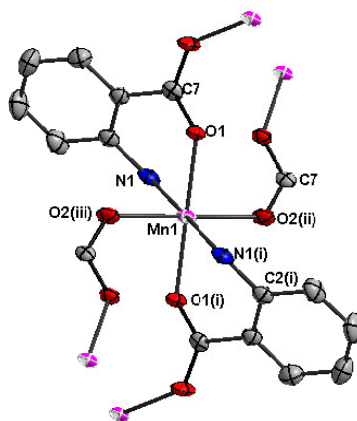
$\Delta\rho_{\text{min}} = -0.337 \text{ e \AA}^{-3}$

### 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 Ala[2-(carboxyphenyl)-imino-2-propanoic acid in the presence of base .



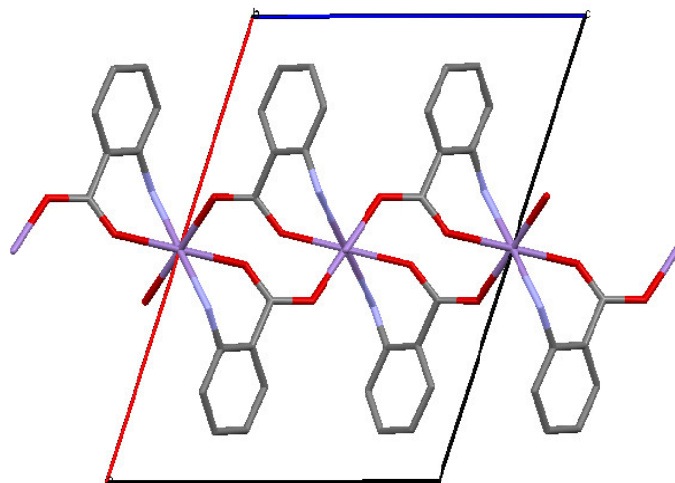
The symmetric unit of (1) contains one manganese cation and four o-aminobenzoate ions. The Mn(II) atom is six-coordinate, forming a slightly distorted octahedral with  $\text{MnN}_2\text{O}_4$  chromophore . In the coordination polyhedron, the equatorial plane is occupied by four O (O1, O1<sup>i</sup>, O2<sup>ii</sup> and O2<sup>iii</sup>) atoms from four o-aminobenzoate anions and at the axial sites are situated two N (N1 and N1<sup>i</sup>) atoms from two o-aminobenzoate anions already associated with the equatorial plane (Fig. 1) . The Mn(II) center is coordinate by two types of o-aminobenzoate anions, one behaves in a chelating mode [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 analogues ( Haendler *et al.*, 1983; Haendler *et al.*, 1975 ) (Fig. 2).



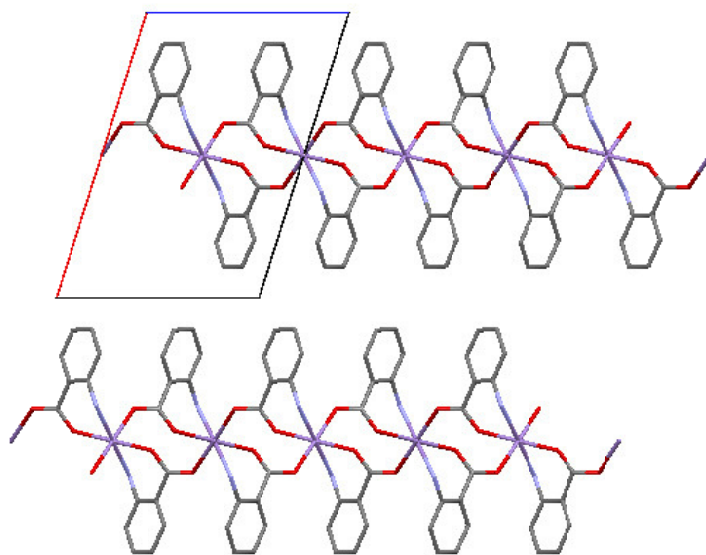
**Figure 1**

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)  $-x+1, y-0.5, -z+5/2$

The bond angles between the cis-donors around Mn(II) lying in the ranges  $79.59(8)$  to  $90.87(8)^\circ$ . The length of two manganese-carboxylate distances are 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  $[\text{Mn}(3\text{-aba})_2]_n$  complex (Hong *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  $\mu_2, n^2$ -carboxylate group (1). The double syn-anti mode  $\mu_{1,3}$ -carboxylato-O,O bridges coming from two 2-aba ligands exist between neighbouring 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  $[\text{Mn}(3\text{-aba})_2]_n$  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  $\text{N1}-\text{H2}\cdots\text{O1}$  and  $\text{N1}-\text{H1}\cdots\text{O2}$  of (1) are within the range compared with  $2.998$  and  $2.954$  Å for 2-aba complexes of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions respectively (Fu-Pei *et al.*, 2006). The hydrogen bond geometry are listed in (Table 2). No hydrogen bonds are observed between 2D network. The adjacent two-dimensional network are packed only by Van der Waals interactions.

**Figure 2**

View of the coordination environment around Mn(ii)

**Figure 3**

View of a pack diagram along the b axis showing the two-dimensional network.

**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.

**Table 2**

## Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N <sub>1</sub> —H <sub>2</sub> ...O <sub>1</sub> <sup>ii</sup>	0.90(4)	2.11(4)	2.989(4)	164(3)
N <sub>1</sub> —H <sub>1</sub> ...O <sub>2</sub> <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.

**4- Conclusion**

From all of these we conclude that by employing aromatic amino acids with different substituent position (namely, ortho, meta 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 chelating 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 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 organization 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. (Fu-Pei *et al.*, 2006).

**Supplementary material**

Crystallographic data for the structural analyses have been deposited to the Cambridge Crystallographic Data Center, CCDC No. 805344.

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336033; Email: deposit@ccdc.cam.ac.uk, or <http://www.ccdc.cam.ac.uk>).

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