

Triaqua(2,2'-bipyridine- $\kappa^2N,N'$ )(3-carboxyphenoxyacetato- $\kappa O$ )manganese(II)  
3-carboxyphenoxyacetate monohydrateXian-Fa Zhang, Shan Gao,\*  
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## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(C-C) = 0.003$  Å  
 $R$  factor = 0.040  
 $wR$  factor = 0.091  
Data-to-parameter ratio = 15.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex,  $[Mn(C_9H_7O_5)(C_{10}H_8N_2)(H_2O)_3] \cdot (C_9H_7O_5) \cdot H_2O$  or  $[Mn(3-CPOAH^-)(2,2'-bipy)(H_2O)_3] \cdot (3-CPOAH^-) \cdot H_2O$  (where 3-CPOAH<sup>-</sup> is the 3-carboxyphenoxyacetate monoanion and 2,2'-bipy is 2,2'-bipyridine), the Mn<sup>II</sup> ion has a distorted octahedral geometry involving one O atom of the 3-CPOAH<sup>-</sup> group, two N atoms of the 2,2'-bipy ligand and three water molecules. A three-dimensional supramolecular network is constructed *via* O—H...O hydrogen-bonding and  $\pi$ – $\pi$  stacking interactions.

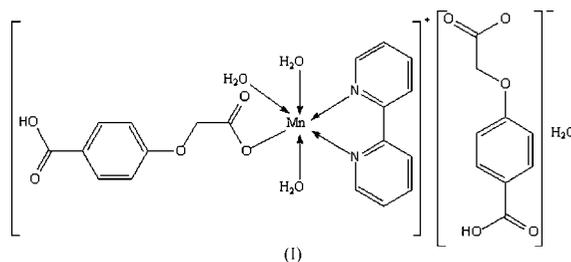
Received 26 October 2005

Accepted 28 October 2005

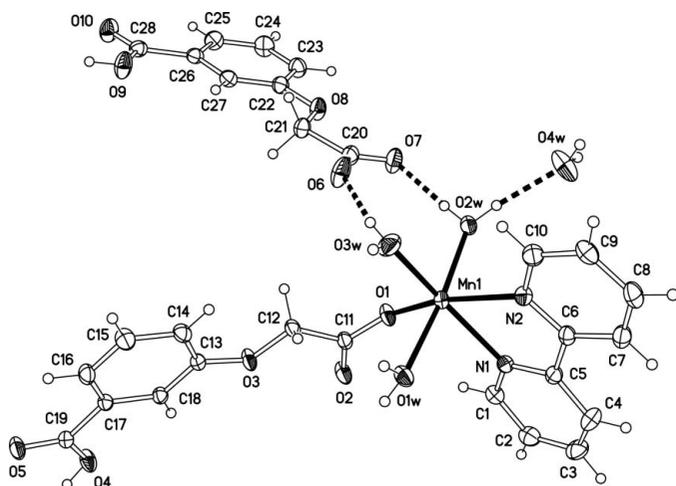
Online 5 November 2005

## Comment

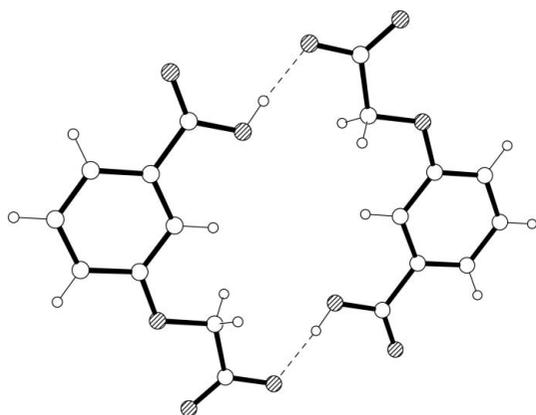
3-Carboxyphenoxyacetic acid (3-CPOAH<sub>2</sub>), with its multiple coordination sites and the capability of participating in hydrogen bonds as both a donor and an acceptor, can be regarded as an excellent candidate for the construction of supramolecular complexes (Zhao *et al.*, 2005). Recently, we reported the structure of an Mn<sup>II</sup> polymer constructed using 3-CPOAH<sub>2</sub> as ligand, namely  $[Mn(3-CPOA^{2-})_2(H_2O)_2]_n$ , in which each 3-CPOA<sup>2-</sup> anion acts in a bis-monodentate mode to connect two adjacent Mn<sup>II</sup> atoms, forming a one-dimensional chain structure (Gao *et al.*, 2005). In our further efforts to investigate the behaviour of Mn<sup>II</sup> salts with the 3-CPOAH<sub>2</sub> ligand, we synthesized the title new Mn<sup>II</sup> complex, (I), and report its structure here.



The molecular structure of the asymmetric unit of complex (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The asymmetric unit of (I) consists of one  $[Mn(3-CPOAH^-)(2,2'-bipy)(H_2O)_3]^+$  cation, one free 3-CPOAH<sup>-</sup> anion and one uncoordinated water molecule. The Mn<sup>II</sup> ion displays a distorted octahedral geometry involving one O atom of the 3-CPOAH<sup>-</sup> group, two N atoms of the chelating 2,2'-bipy ligand and three water molecules. The Mn—O(water) bond distances are slightly longer than the Mn—O(carboxylate) bond length, which in turn are somewhat shorter than the Mn—N bond distances (Table 1). Both 3-CPOAH<sup>-</sup> groups are almost planar, with torsion angles of 170.97 (15) (C13—O3—C12—C11) and 179.33 (16)° (C22—O8—C21—C20).


**Figure 1**

A plot of (I), with 30% probability displacement ellipsoids. The O—H...O hydrogen bonds are denoted by dashed lines (see Table 2 for details).

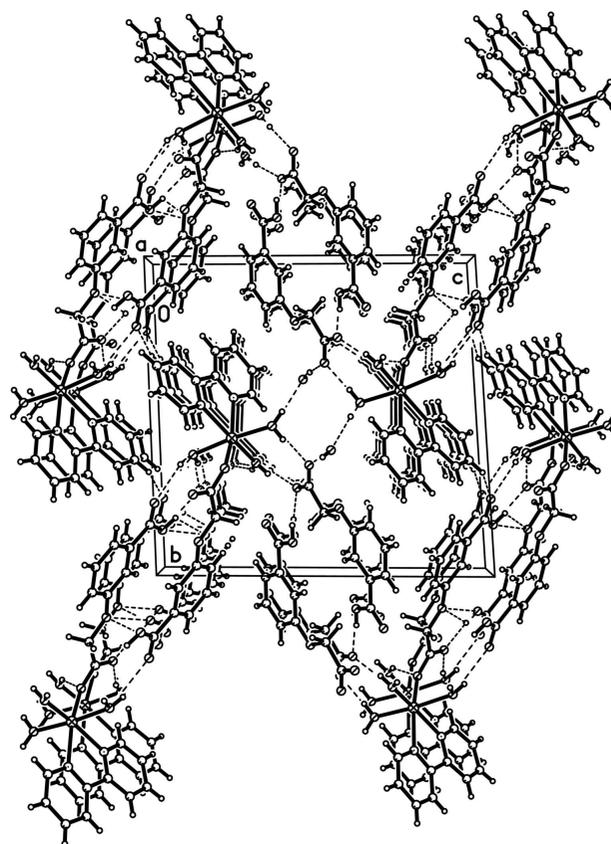

**Figure 2**

The hydrogen-bonded dimer of two uncoordinated 3-carboxyphenoxyacetate anions. Hydrogen bonds are denoted by dashed lines.

The uncoordinated 3-carboxyphenoxyacetate anions are linked by hydrogen bonds to form a centrosymmetric dimer (Fig. 2). These dimer motifs are linked by the  $[\text{Mn}(\text{3-CPOAH}^-)(2,2'\text{-bipy})(\text{H}_2\text{O})_3]^+$  cations and water molecules *via* extended hydrogen bonds to form a two-dimensional layer structure. Furthermore, there are  $\pi$ – $\pi$  stacking interactions between the 2,2'-bipy rings, the centroid-centroid distance being 3.618 (3) Å. As a result, a three-dimensional supramolecular network is constructed *via* hydrogen-bonding and  $\pi$ – $\pi$  stacking interactions (Table 2, Fig. 3).

## Experimental

Complex (I) was prepared by the addition of stoichiometric amounts of  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  (10 mmol), 2,2'-bipy (10 mmol) and 3-CPOAH<sub>2</sub> (15 mmol) to a hot aqueous solution, and the pH value was adjusted to *ca* 5 using NaOH (0.2 M) solution. Pale-yellow crystals of (I) were obtained from the filtered solution at room temperature over several days. Analysis, calculated for  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_{14}\text{Mn}$ : C 49.94, H 4.49, N 4.16%; found: C 49.98, H 4.46, N 4.18%.


**Figure 3**

A perspective view along the *a* axis of the crystal packing of complex (I), with the O—H...O hydrogen bonds denoted by dashed lines.

### Crystal data

$[\text{Mn}(\text{C}_9\text{H}_7\text{O}_5)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3] \cdot (\text{C}_9\text{H}_7\text{O}_5) \cdot \text{H}_2\text{O}$   
 $M_r = 673.48$   
 Triclinic,  $P\bar{1}$   
 $a = 6.0749$  (12) Å  
 $b = 15.428$  (3) Å  
 $c = 16.028$  (3) Å  
 $\alpha = 86.59$  (3)°  
 $\beta = 86.42$  (3)°  
 $\gamma = 81.19$  (3)°  
 $V = 1479.7$  (5) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.512$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 13697 reflections  
 $\theta = 3.0$ – $27.5^\circ$   
 $\mu = 0.52$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Prism, pale yellow  
 0.35 × 0.26 × 0.19 mm

### Data collection

Rigaku R-Axis RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.839$ ,  $T_{\max} = 0.907$   
 14322 measured reflections

6667 independent reflections  
 5008 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -20 \rightarrow 20$   
 $l = -19 \rightarrow 20$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.091$   
 $S = 1.03$   
 6667 reflections  
 436 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.2859P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.20$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Mn1—O1	2.1171 (15)	Mn1—N2	2.2599 (17)
Mn1—O2W	2.1373 (15)	Mn1—O1W	2.2697 (16)
Mn1—O3W	2.1710 (17)	Mn1—N1	2.2772 (16)
O1—Mn1—O2W	88.01 (6)	O3W—Mn1—O1W	83.97 (6)
O1—Mn1—O3W	104.00 (7)	N2—Mn1—O1W	91.50 (6)
O2W—Mn1—O3W	89.28 (7)	O1—Mn1—N1	91.40 (6)
O1—Mn1—N2	162.55 (5)	O2W—Mn1—N1	100.72 (6)
O2W—Mn1—N2	89.77 (6)	O3W—Mn1—N1	161.99 (7)
O3W—Mn1—N2	93.28 (7)	N2—Mn1—N1	72.02 (6)
O1—Mn1—O1W	92.75 (6)	O1W—Mn1—N1	86.03 (6)
O2W—Mn1—O1W	173.19 (5)		

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O2 <sup>i</sup>	0.85 (2)	1.88 (2)	2.706 (2)	162 (2)
O1W—H1W2...O5 <sup>ii</sup>	0.84 (2)	2.15 (2)	2.879 (2)	144 (2)
O2W—H2W1...O4W	0.84 (2)	1.85 (2)	2.681 (2)	169 (2)
O2W—H2W2...O7	0.84 (2)	1.87 (2)	2.708 (2)	177 (2)
O3W—H3W1...O6	0.84 (2)	1.91 (2)	2.741 (2)	170 (3)
O3W—H3W2...O1 <sup>i</sup>	0.84 (2)	2.50 (3)	3.268 (3)	152 (2)
O4W—H4W1...O6 <sup>iii</sup>	0.84 (3)	2.29 (3)	3.068 (3)	154 (3)
O4W—H4W2...O7 <sup>iv</sup>	0.85 (3)	1.97 (3)	2.803 (3)	169 (3)
O4—H29...O2 <sup>v</sup>	0.85 (2)	1.80 (2)	2.641 (2)	174 (3)
O4—H29...O3 <sup>v</sup>	0.85 (2)	2.51 (2)	2.918 (2)	110 (2)
O9—H30...O6 <sup>vi</sup>	0.85 (2)	1.70 (2)	2.549 (2)	173 (3)

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y + 2, -z$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $-x + 2, -y + 1, -z + 1$ ; (v)  $-x + 2, -y + 2, -z$ ; (vi)  $-x + 1, -y + 2, -z + 1$ .

The water and carboxylic acid H atoms were located in difference Fourier maps and refined with a distance restraint of 0.85 (1) Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The remaining H atoms were placed in calculated positions and treated as riding, with aromatic C—H = 0.93 Å and aliphatic C—H = 0.97 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *RAPID AUTO* (Rigaku, 1998); cell refinement: *RAPID AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (grant No. 20101003), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (grant No. 1054 G036) and Heilongjiang University for supporting this work.

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