

Tris(1*H*-benzimidazole- κN^3)(iminodiacetato- $\kappa^2 O, O'$)manganese(II) dihydrateJian-Rong Su,^a Kai-Liang Yin^b and Duan-Jun Xu^{a*}^aDepartment of Chemistry, Zhejiang University, People's Republic of China, and ^bKey Laboratory of Fine Chemical Engineering, Jiangsu Polytechnic University, People's Republic of China

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Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.042
 wR factor = 0.111
Data-to-parameter ratio = 15.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[Mn(C_4H_5NO_4)(C_7H_6N_2)_3] \cdot 2H_2O$, the Mn^{II} atom is surrounded by one iminodiacetate dianion and three benzimidazole molecules in a distorted octahedral geometry. The tridentate iminodiacetate dianion chelates the Mn^{II} atom in the facial mode. Extensive intermolecular, $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonding and $C-H \cdots \pi$ (arene) interactions are present in the crystal structure.

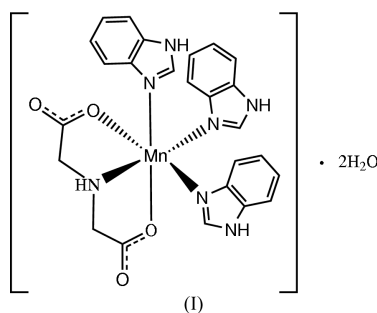
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Comment

As part of investigations of the non-covalent interactions between aromatic rings in metal complexes, the title benzimidazole (BZIM) complex of Mn^{II} , (I), has been prepared and its crystal structure is presented here.



The molecular structure of (I) is illustrated in Fig. 1. The Mn^{II} atom is surrounded by one iminodiacetate dianion (IDA) and three benzimidazole molecules (BZIM) in a distorted octahedral coordination geometry, similar to that found in the Ni^{II} analogue (Su *et al.*, 2004). The IDA chelates, in a tridentate fashion, the Mn^{II} atom in a facial configuration. Of the two five-membered chelating rings, the O1-containing ring is nearly planar, the maximum deviation being 0.061 (2) Å (for atom C2), whereas the O3-containing ring displays an envelope conformation, the Mn atom lying in the flap position and out of the mean plane formed by the other four atoms by 0.867 (4) Å. Such a facial configuration of IDA agrees with the situation found in other reported IDA complexes (Yasui *et al.*, 1987; Castineiras *et al.*, 1993).

The carboxyl groups of IDA coordinate, in a monodentate fashion, to the Mn^{II} atom, whereas uncoordinated carboxy O atoms (O2 and O4) are hydrogen bonded to water molecules and to BZIM of neighboring complex molecules, as shown in Fig. 2 and Table 1.

A *PLATON* analysis (Spek, 1980) gave the following $H \cdots C_g$ distances and $C-H \cdots C_g$ angles (C_g is the ring centroid), suggesting weak $C-H \cdots \pi$ (arene) interactions in the crystal structure, as shown in Fig. 3 (Nishio *et al.*, 1998):

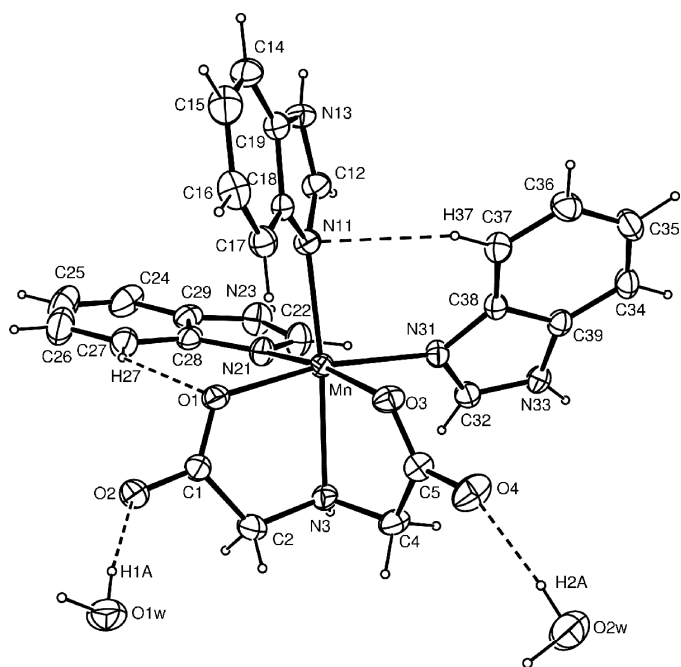


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding, including possible weak intramolecular C—H...O and C—H...N interactions.

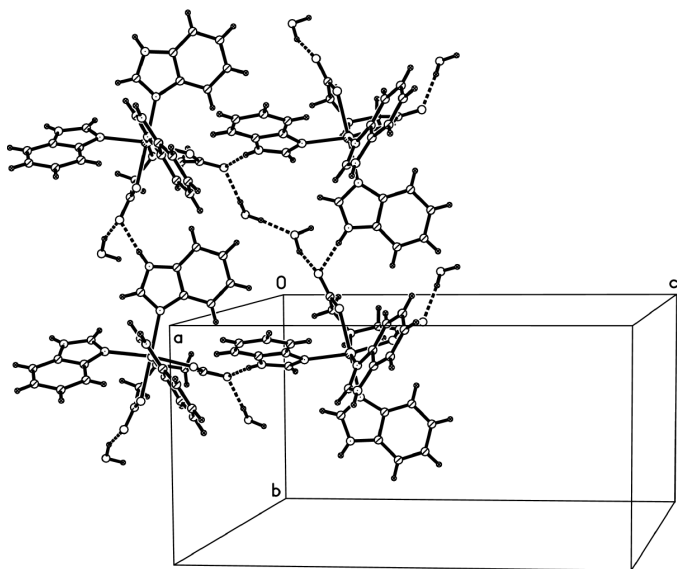


Figure 2
A partial packing diagram of (I), showing the hydrogen bonding (dashed lines).

$\text{H16} \cdots \text{Cg}(\text{C34}^{\text{vii}} \text{ ring}) = 2.78 \text{ \AA}$, $\text{C16} - \text{H16} \cdots \text{Cg}(\text{C34}^{\text{vii}} \text{ ring}) = 139^\circ$; $\text{H36} \cdots \text{Cg}(\text{C26}^{\text{vii}} \text{ ring}) = 2.79 \text{ \AA}$, $\text{C36} - \text{H36} \cdots \text{Cg}(\text{C26}^{\text{vii}} \text{ ring}) = 148^\circ$ [symmetry code: (vii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$].

Experimental

All reagents were commercially available and of analytical grade. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.24 g, 1 mmol), H_2IDA (0.13 g, 1 mmol), BZIM (0.24 g, 2 mmol) and Na_2CO_3 (0.11 g, 1 mmol) were dissolved in a water (6 ml)–ethanol (2 ml) mixture. The solution was stirred at room temperature until the bubbles of CO_2 disappeared. The solution was then refluxed for 4 h and a small amount of precipitate

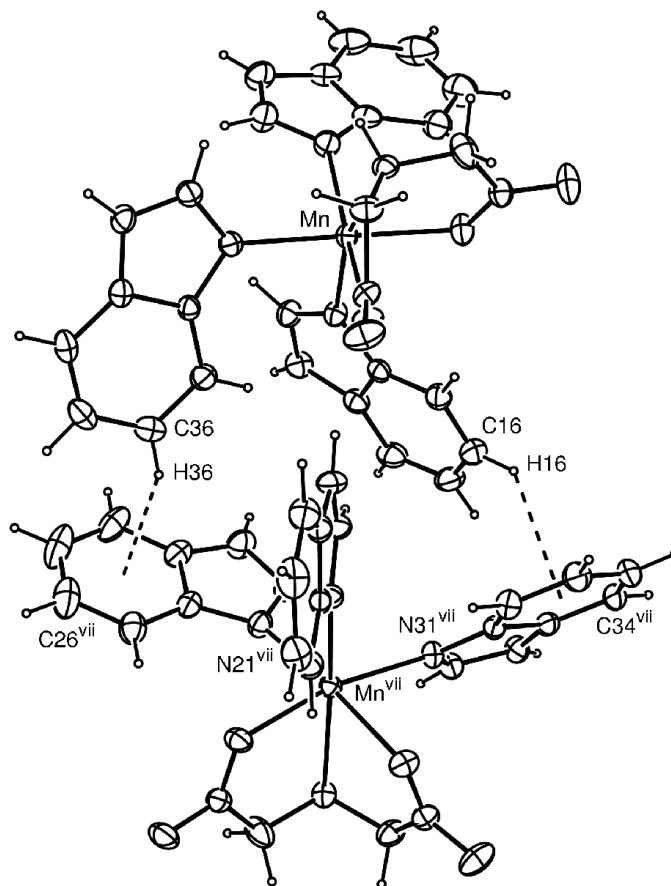


Figure 3
A diagram showing the intermolecular C—H... π interactions (dashed lines). [Symmetry code: (vii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

appeared. The solution was filtered into hot water (10 ml), then kept at room temperature. Colorless single crystals were obtained from the filtrate after 2 d.

Crystal data

$[\text{Mn}(\text{C}_4\text{H}_5\text{NO}_4)(\text{C}_7\text{H}_6\text{N}_2)_3] \cdot 2\text{H}_2\text{O}$
 $M_r = 576.48$
Monoclinic, $P2_1/c$
 $a = 13.5852(7) \text{ \AA}$
 $b = 10.4183(4) \text{ \AA}$
 $c = 19.5622(7) \text{ \AA}$
 $\beta = 104.065(2)^\circ$
 $V = 2685.7(2) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.426 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 16 558 reflections
 $\theta = 2.0\text{--}25.0^\circ$
 $\mu = 0.55 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
Prism, colorless
 $0.27 \times 0.21 \times 0.11 \text{ mm}$

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.86$, $T_{\text{max}} = 0.94$
21 886 measured reflections

5333 independent reflections
4315 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\text{max}} = 26.1^\circ$
 $h = -16 \rightarrow 16$
 $k = -12 \rightarrow 12$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.111$
 $S = 1.05$
5333 reflections
352 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.7438P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bonding 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—H1A···O2	0.84	2.00	2.822 (3)	164
O1W—H1B···O2W ⁱ	0.95	1.89	2.814 (3)	163
O2W—H2A···O4	0.96	1.90	2.797 (3)	155
O2W—H2B···O2 ⁱⁱ	0.95	2.10	3.001 (3)	159
N3—H3···O1W ⁱⁱⁱ	0.91	2.14	3.025 (3)	164
N13—H13···O3 ^{iv}	0.86	2.19	3.037 (3)	167
N23—H23···O4 ^v	0.86	1.93	2.770 (3)	165
N33—H33···O2 ^{vi}	0.86	1.98	2.819 (3)	166

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

H atoms of water molecules were located in a difference Fourier map and included in the structure-factor calculations with fixed positional and isotropic displacement parameters of $U_{\text{iso}}(\text{H}) = 0.08 \text{ \AA}^2$. Other H atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.97 Å (methylene) and N—H = 0.86 (imidazole) or 0.91 Å (imino), and were included in the final cycles of refinement in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atoms})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Shel-

drick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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