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## Key indicators

Single-crystal X-ray study

T = 295 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.032

wR factor = 0.081

Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## A dimeric manganese(II) complex bridged by 4-aminobenzoate

The dimeric Mn<sup>II</sup> title complex, di- $\mu$ -4-aminobenzoato-bis[(4-aminobenzoato)(2,2'-diamino-4,4'-bithiazole)manganese(II)] dihydrate,  $[\text{Mn}_2(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)_2(\text{C}_7\text{H}_6\text{NO}_2)_4] \cdot 2\text{H}_2\text{O}$ , bridged by aminobenzoate anions, is located on an inversion center. Each Mn<sup>II</sup> atom is coordinated by one diaminobithiazole and three aminobenzoate ligands with a distorted octahedral geometry.

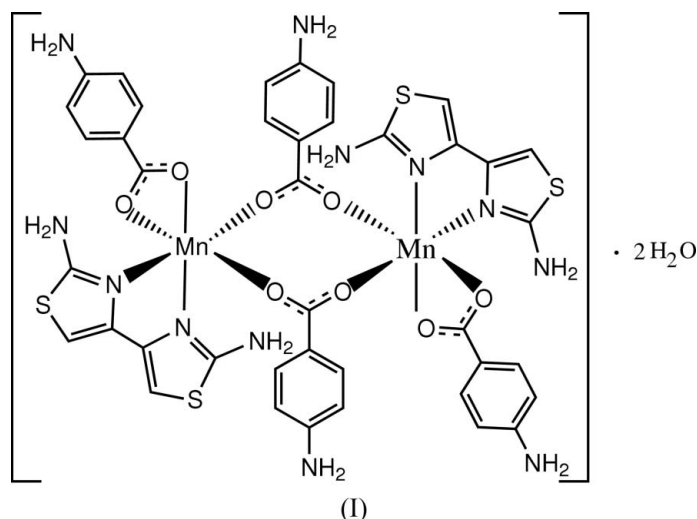
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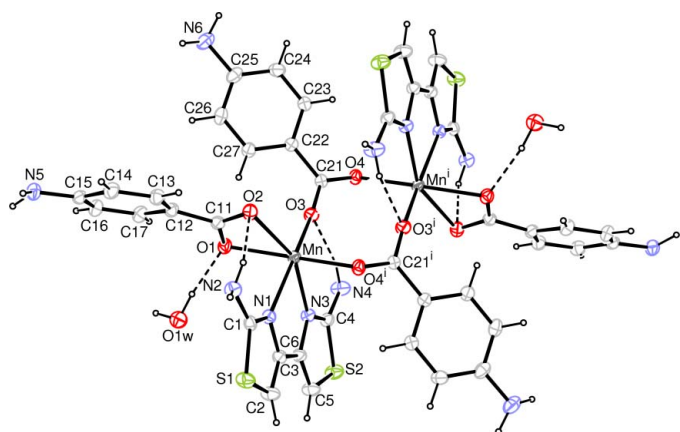
## Comment

As part of an ongoing investigation on the nature of  $\pi$ - $\pi$  stacking in metal complexes (Fu *et al.*, 2005), the title Mn<sup>II</sup> complex, (I), was recently prepared and its X-ray crystal structure is presented here.

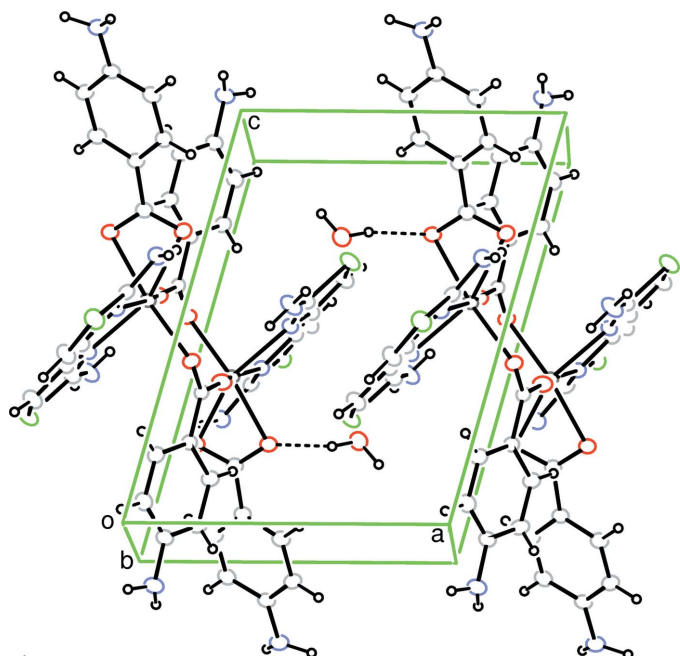


The dimeric molecule of (I) is located on an inversion center (Fig. 1). Each Mn<sup>II</sup> atom is coordinated by three aminobenzoate anions and one diaminobithiazole ligand, in a distorted octahedral geometry (Table 1). The diaminobithiazole chelating the Mn<sup>II</sup> atom displays a nearly planar configuration, with a dihedral angle of  $3.75(15)^\circ$  between the two thiazole mean planes; this differs from the twisted configuration [dihedral angle =  $20.02(8)^\circ$ ] found in a diaminobithiazole complex of Co<sup>II</sup> reported previously (Liu & Xu, 2005).

While the C11 carboxyl group chelates to the Mn<sup>II</sup> atom, the C22 carboxyl bridges Mn<sup>II</sup> atoms to form the dimeric complex molecule. Although the larger Mn—O3—C21 angle of  $157.73(14)^\circ$  implies poor overlap between atomic orbitals of the Mn and O3 atoms, the shorter Mn—O3 bond distance (Table 1) shows the normal bonding interaction between them. This is consistent with the situation found in an Mn<sup>II</sup> complex with salicylate (Su & Xu, 2005) and in a Mn<sup>II</sup> complex with benzenedicarboxylate (Nie *et al.*, 2001), and clearly



**Figure 1**  
The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonds [symmetry code: (i)  $2 - x, 1 - y, 1 - z$ ].



**Figure 2**  
The packing in (I).

suggests a significant electrostatic contribution to the Mn—O bond.

As shown in Fig. 2, a partially overlapping arrangement of parallel benzene rings, related by an inversion center, occurs in the crystal structure of (I), but the face-to-face separation of 4.0068 (13) Å shows that there is no  $\pi$ - $\pi$  stacking between aminobenzoate ligands. An extensive hydrogen-bonding network occurs in the crystal structure of (I) (Table 2).

### Experimental

An aqueous solution (20 ml) containing diaminothiazole (1 mmol) and  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  (1 mmol) was mixed with another aqueous solution (10 ml) of 4-aminobenzoic acid (4 mmol) and NaOH (4 mmol). The mixture was refluxed for 10 h. After cooling to room temperature, the solution was filtered. Yellow single crystals of (I) were obtained from the filtrate after 15 d.

### Crystal data

$[\text{Mn}_2(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)_2(\text{C}_7\text{H}_6\text{NO}_2)_4] \cdot 2\text{H}_2\text{O}$   
 $M_r = 1086.96$   
 Triclinic,  $P\bar{1}$   
 $a = 9.1429$  (8) Å  
 $b = 10.6796$  (9) Å  
 $c = 12.0826$  (12) Å  
 $\alpha = 89.916$  (2)°  
 $\beta = 74.203$  (2)°  
 $\gamma = 84.889$  (2)°  
 $V = 1130.39$  (18) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.597$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 4228 reflections  
 $\theta = 2.2$ – $24.0$ °  
 $\mu = 0.82$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Prism, yellow  
 $0.32 \times 0.28 \times 0.18$  mm

### Data collection

Rigaku R-Axis RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\text{min}} = 0.775, T_{\text{max}} = 0.862$   
 5976 measured reflections

3923 independent reflections  
 3582 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.013$   
 $\theta_{\text{max}} = 25.0$ °  
 $h = -4 \rightarrow 10$   
 $k = -12 \rightarrow 12$   
 $l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.081$   
 $S = 1.07$   
 3923 reflections  
 307 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.3658P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Mn—O1	2.2053 (14)	Mn—O4 <sup>i</sup>	2.1532 (13)
Mn—O2	2.3233 (15)	Mn—N1	2.3154 (15)
Mn—O3	2.1361 (13)	Mn—N3	2.2321 (16)

Symmetry code: (i)  $-x + 2, -y + 1, -z + 1$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1A <sup>i</sup> ···O1	0.90	1.91	2.774 (2)	161
O1W—H1B <sup>i</sup> ···N6 <sup>ii</sup>	0.97	1.96	2.923 (3)	168
N2—H2A <sup>i</sup> ···O2	0.88	2.23	3.011 (2)	148
N2—H2B <sup>i</sup> ···O4 <sup>iii</sup>	0.90	2.15	3.006 (2)	159
N4—H4A <sup>i</sup> ···O3	0.86	2.16	2.967 (2)	157
N4—H4B <sup>i</sup> ···O1W <sup>iv</sup>	0.91	2.09	2.940 (2)	155
N5—H5A <sup>i</sup> ···O1W <sup>v</sup>	0.94	2.12	3.034 (2)	165
N5—H5B <sup>i</sup> ···N2 <sup>v</sup>	0.98	2.38	3.310 (3)	157
N6—H6B <sup>i</sup> ···O2 <sup>vi</sup>	0.92	2.47	3.287 (2)	149
C2—H2 <sup>i</sup> ···N5 <sup>vii</sup>	0.93	2.49	3.418 (3)	172
C27—H27 <sup>i</sup> ···O1	0.93	2.46	3.353 (2)	162

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

H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.93 Å, and included in the final cycles of refinement in the riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Other H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{carrier})$ .

Data collection and cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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## References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fu, X.-D., Lin, D.-D. & Xu, D.-J. (2005). *Acta Cryst.* **E61**, m1823–m1825.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Liu, J.-G. & Xu, D.-J. (2005). *J. Coord. Chem.* pp. 735–740.
- Nie, J.-J., Liu, L.-J., Luo, Y. & Xu, D.-J. (2001). *J. Coord. Chem.* **53**, 365–371.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSK (2002). *CrystalStructure*. Version 3.00. Rigaku/MSK, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Su, J.-R. & Xu, D.-J. (2005). *Acta Cryst.* **C61**, m256–m258.