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Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
H-atom completeness 88%
Disorder in main residue
 R factor = 0.050
 wR factor = 0.145
Data-to-parameter ratio = 11.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**cis-Diaquabis(1,10-phenanthroline)manganese(II)
4-sulfonatobenzoate 6.5-hydrate**

In the title complex salt, $[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_7\text{H}_4\text{O}_5\text{S}) \cdot 6.5\text{H}_2\text{O}$, the coordination geometry about the Mn^{II} atom is distorted octahedral, defined by four N atoms from two 1,10-phenanthroline ligands and two O atoms from two water molecules. $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions among cations, anions, and solvent water molecules generate a three-dimensional network and enhance the stability of the crystal structure.

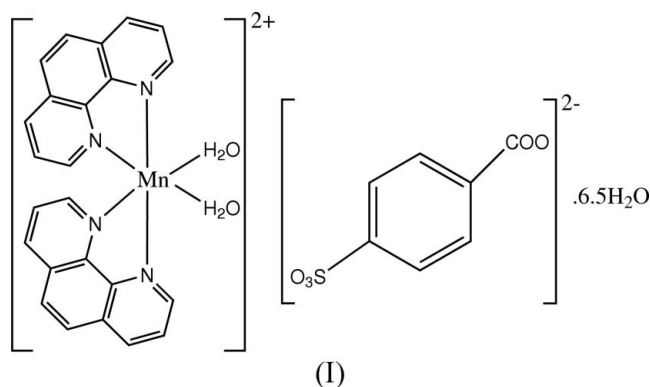
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Comment

4-Sulfobenzoate metal complexes exhibit interesting coordination modes and structural topologies, for example, cyclic dimers (Fan *et al.*, 2004; Fan *et al.*, 2005; Zhang & Zhu, 2005*a*), a monodentate 4,4'-bipyridine metal complex (Zhang & Zhu, 2005*b*) and a seven-coordinate manganese complex (Zhang & Zhu, 2005*c*). In our previous work we successfully observed the conversion reaction of an air-sensitive complex to an air-stable complex and reported the crystal structure of the air-stable complex (Zhang & Zhu, 2005*d*). In the conversion process, the fully deprotonated 4-sulfobenzoate anion was protonated. Here, we present the structure of the title air-sensitive 4-sulfobenzoate manganese(II) complex, (I).



Complex (I) consists of an $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation (phen is 1,10-phenanthroline), a 4-sulfobenzoate anion and water molecules (Fig. 1 and Table 1). In the cation, the coordination geometry about the Mn^{II} atom is best considered as distorted octahedral, defined by four N donors from two phen ligands and two O atoms of two *cis*-arranged water molecules. The $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation can be found in several previously reported complexes (Geraghty *et al.*, 1998; Marek *et al.*, 2003; Zhang *et al.*, 2003; Zheng *et al.*, 2001), with a similar coordination geometry.

In the crystal structure of (I), $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions between anions and solvent water molecules generate a three-dimensional architecture. The cations inter-

act with this anionic three-dimensional network *via* hydrogen bonds to form a host-guest assembly (Table 2).

Experimental

A mixture of manganese(II) sulfate monohydrate (0.085 g, 0.49 mmol), potassium hydrogen 4-sulfobenzoate (0.120 g, 0.5 mmol), 1,10-phenanthroline (0.098 g, 0.5 mmol) and water (15 ml) was heated at 423 K for 26 h in a 30 ml Teflon-lined stainless steel autoclave. After cooling, a yellow solution was obtained and this was allowed to evaporate. After 1 d, pale-yellow crystals of (I) were formed and these were filtered off. The crystal used for X-ray analysis was coated in oil.

Crystal data

$[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_7\text{H}_4\text{O}_5\text{S}) \cdot 6.5\text{H}_2\text{O}$	$Z = 2$
$M_r = 769.15$	$D_x = 1.46 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.4689 (10) \text{ \AA}$	Cell parameters from 4511 reflections
$b = 13.0731 (11) \text{ \AA}$	$\theta = 2.5\text{--}28.2^\circ$
$c = 13.3104 (11) \text{ \AA}$	$\mu = 0.51 \text{ mm}^{-1}$
$\alpha = 106.408 (2)^\circ$	$T = 295 (2) \text{ K}$
$\beta = 101.908 (1)^\circ$	Block, pale yellow
$\gamma = 114.895 (1)^\circ$	$0.51 \times 0.50 \times 0.49 \text{ mm}$
$V = 1751.1 (3) \text{ \AA}^3$	

Data collection

Bruker APEX area-detector diffractometer	6101 independent reflections
φ and ω scans	5105 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.059$
$T_{\text{min}} = 0.782$, $T_{\text{max}} = 0.789$	$\theta_{\text{max}} = 25.0^\circ$
8888 measured reflections	$h = -14 \rightarrow 14$
	$k = -15 \rightarrow 13$
	$l = -15 \rightarrow 13$

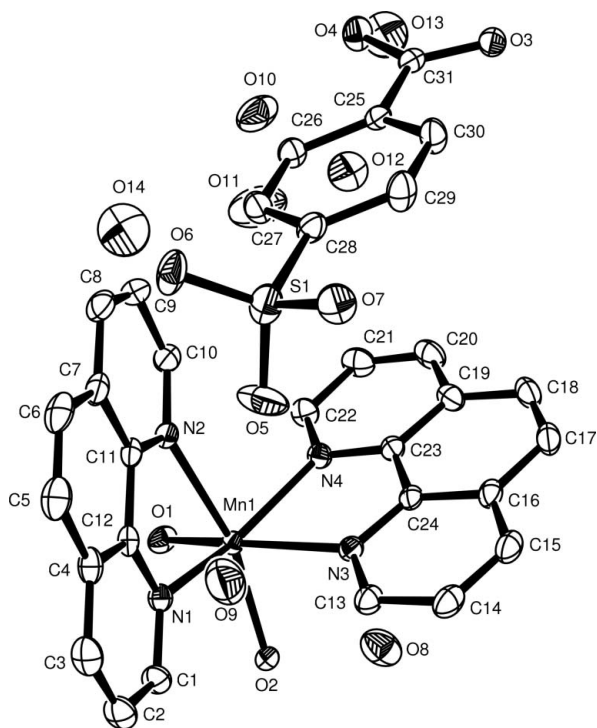


Figure 1

The asymmetric unit of (I). Displacement ellipsoids are drawn at the 40% probability level. H atoms, and the minor components of the disordered sulfonate and water molecules, have been omitted for clarity.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0852P)^2 + 0.1951P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$
6101 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
544 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn1—O1	2.116 (2)	Mn1—N2	2.303 (2)
Mn1—O2	2.1570 (19)	Mn1—N3	2.284 (2)
Mn1—N1	2.269 (2)	Mn1—N4	2.278 (2)
O1—Mn1—O2	84.02 (8)	N1—Mn1—N3	89.43 (8)
O1—Mn1—N1	110.56 (9)	N4—Mn1—N3	72.99 (9)
O2—Mn1—N1	93.02 (9)	O1—Mn1—N2	94.97 (9)
O1—Mn1—N4	91.09 (9)	O2—Mn1—N2	164.63 (8)
O2—Mn1—N4	105.67 (8)	N1—Mn1—N2	72.91 (8)
N1—Mn1—N4	152.91 (9)	N4—Mn1—N2	89.67 (8)
O1—Mn1—N3	157.91 (9)	N3—Mn1—N2	100.04 (8)
O2—Mn1—N3	85.67 (8)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1A \cdots O7 ⁱ	0.84 (4)	1.69 (2)	2.521 (11)	168 (4)
O1—H1A \cdots O7 ⁱ	0.84 (4)	1.98 (1)	2.821 (8)	175 (3)
O1—H1B \cdots O8 ⁱ	0.85 (4)	1.83 (4)	2.674 (3)	175 (3)
O2—H2A \cdots O3 ⁱⁱ	0.85 (3)	1.89 (2)	2.704 (3)	162 (3)
O2—H2B \cdots O3 ⁱⁱⁱ	0.84 (3)	1.89 (3)	2.713 (3)	166 (3)
O8—H8B \cdots O4 ^{iv}	0.85 (3)	1.89 (2)	2.721 (3)	165 (3)
O8—H8A \cdots O9	0.85 (4)	1.96 (4)	2.804 (4)	174 (4)
O9—H9A \cdots O5	0.87 (3)	1.81 (1)	2.641 (5)	158 (3)
O9—H9A \cdots O5 ^v	0.87 (3)	2.21 (2)	3.066 (16)	165 (4)
O9—H9B \cdots O6 ^v	0.85 (2)	1.97 (1)	2.781 (7)	161 (3)
O10—H10A \cdots O4	0.86 (3)	1.99 (3)	2.846 (4)	178 (4)
O10—H10B \cdots O6 ^{vi}	0.85 (4)	1.95 (2)	2.762 (5)	158 (4)
O10—H10B \cdots O6 ^{vi}	0.85 (4)	2.07 (2)	2.853 (10)	154 (4)
O13—H13A \cdots O9 ^{vii}	0.85 (1)	2.45 (7)	2.964 (12)	120 (7)

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

All aromatic H atoms were positioned geometrically and refined as riding atoms, with $C\text{---}H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. The water H atoms were located in difference Fourier maps and refined with a distance restraint of $O\text{---}H = 0.85 (1) \text{ \AA}$ and a fixed isotropic displacement parameter of $U_{\text{iso}}(H) = 0.08 \text{ \AA}^2$. The sulfonate O atoms are disordered over two positions in the ratio 0.610 (13):0.390 (13), for atoms O5/O6/O7 and O5'/O6'/O7', respectively. The water atoms O12 and O14 are disordered over two sites in the ratios 0.587 (12):0.413 (12) for O12 and O12', and 0.663 (18):0.337 (18) for O14 and O14', respectively. The occupancy of atom O13 was initially refined to 0.76 (1), and was fixed at 0.50 in the final cycles of refinement.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References

- Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Fan, S.-R., Xiao, H.-P., Zhang, L.-P. & Zhu, L.-G. (2004). *Acta Cryst.* **E60**, m1833–m1835.
- Fan, S.-R., Zhang, L.-P., Xiao, H.-P., Cai, G.-Q. & Zhu, L.-G. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 69–70.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Geraghty, M., McCann, M., Casey, M. T., Curran, M., Devereux, M., McKee, V. & McCrea, J. (1998). *Inorg. Chim. Acta*, **277**, 257–262.
- Marek, J., Travnicek, Z. & Kopel, P. (2003). *Acta Cryst.* **C59**, m429–m431.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Zhang, L.-P. & Zhu, L.-G. (2005a). *Acta Cryst.* **E61**, m1439–m1440.
- Zhang, L.-P. & Zhu, L.-G. (2005b). *Acta Cryst.* **E61**, m1768–m1770.
- Zhang, L.-P. & Zhu, L.-G. (2005c). *Acta Cryst.* **E61**, m1036–m1038.
- Zhang, L.-P. & Zhu, L.-G. (2005d). *Acta Cryst.* **E61**, m705–m707.
- Zhang, X.-F., Huang, D.-G., Chen, F., Chen, C.-N. & Liu, Q.-T. (2003). *Chin. J. Struct. Chem.* **22**, 525–528.
- Zheng, Y.-Q., Lin, J.-L. & Sun, J. (2001). *Z. Anorg. Allg. Chem.* **627**, 1059–1065.