

Bis(4-carboxybenzenesulfonato)bis(1,10-phenanthroline)manganese(II)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.072
wR factor = 0.144
Data-to-parameter ratio = 11.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The mononuclear title compound, $[\text{Mn}(\text{C}_7\text{H}_5\text{O}_5\text{S})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$, was obtained as a second crop of crystals from the hydrothermal reaction of manganese sulfate, potassium hydrogen 4-carboxybenzenesulfonate and 1,10-phenanthroline. The coordination geometry of the Mn^{II} atom is octahedral; each 4-carboxybenzenesulfonate anion retains a proton on the carboxyl group as each coordinates to the metal atom through only one sulfonyl O atom. Intermolecular $\pi-\pi$ interactions and hydrogen bonds are observed in the crystal structure.

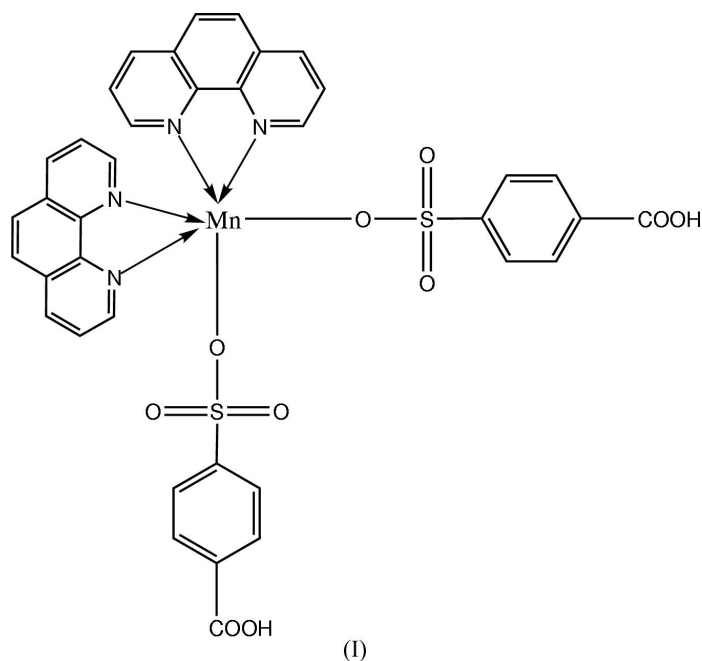
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Comment

4-Carboxylbenzenesulfonic acid (H_2cbs) has two coordination sites, and the $-\text{CO}_2\text{H}$ and $-\text{SO}_3\text{H}$ groups can be partially or fully deprotonated. To date, only six complexes of the acid have been structurally characterized (Yuan *et al.*, 2001; Xiong *et al.*, 2001; Fan, Xiao, Zhang, Cai & Zhu, 2004; Fan, Xiao, Zhang & Zhu, 2004; Fan, Zhang *et al.*, 2005); the two groups in these are deprotonated. The title complex, (I), is the first complex with the monodeprotonated Hcbs^- entity.



The title complex is a monomeric species and the Mn^{II} atom adopts an octahedral geometry made up of four N-atom donors from two 1,10-phenanthroline ligands and two sulfonato O atoms from two Hcbs^- ligands (Fig. 1). The geometry is similar to that of the Mn atom in $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{ssal})\cdot 4\text{H}_2\text{O}$ (ssal is the 5-sulfosalicylate dianion), (II)

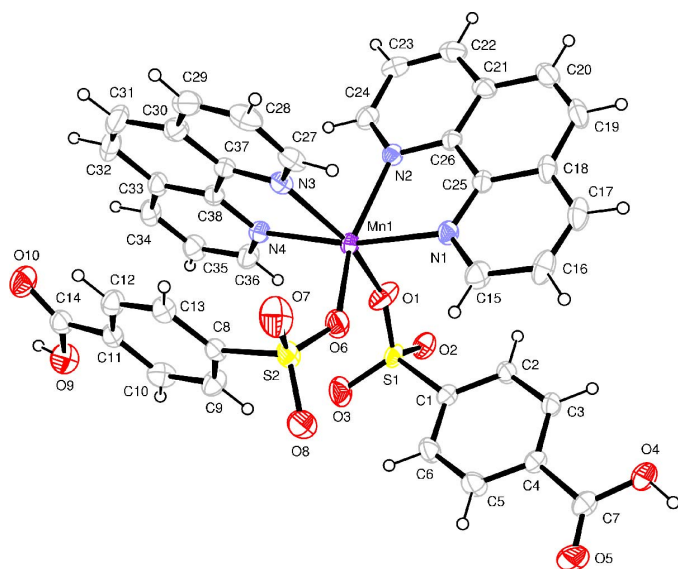


Figure 1
ORTEP-3 view (Farrugia, 1997) of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

(Fan, Zhu *et al.*, 2005), and bond dimensions involving the Mn atom are similar in both complexes. The Hcbs[−] ligand, which has its carboxylic group retaining the acid proton, coordinates to the metal atom through one sulfonate O atom. The distances of the six S—O bonds fall within the typical range of S—O bond distances reported for the sulfonate anion (Onoda *et al.*, 2001); the S1—O1 and S2—O6 bonds are longer than the other four as atoms O1 and O6 are involved in bonding. The crystal structure shows π – π stacking between the Hcbs[−] anion and the 1,10-phenanthroline ligand; the distance between the two π -systems is about 3.42 Å and the dihedral angle is 5.2 (3)°. The crystal structure also features hydrogen bonds (Table 2) that give rise to the formation of a linear chain motif.

Experimental

A mixture of manganese 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 the autoclave, a yellow solution was obtained and, after 1 d, pale-yellow crystals separated from solution. The crystals were air-sensitive. The filtrate was set aside and the solvent allowed to evaporate at room temperature. After 10 d, pale-yellow block-shaped crystals were obtained; these crystals were air-stable and one specimen was used in the diffraction study.

Crystal data

[Mn(C₇H₅O₅S)₂(C₁₂H₈N₂)₂]

$M_r = 817.69$

Triclinic, $P\bar{1}$

$a = 9.5218$ (6) Å

$b = 13.5515$ (8) Å

$c = 13.6083$ (8) Å

$\alpha = 89.216$ (1)°

$\beta = 78.692$ (1)°

$\gamma = 82.348$ (1)°

$V = 1706.38$ (18) Å³

$Z = 2$

$D_x = 1.591$ Mg m^{−3}

Mo $K\alpha$ radiation

Cell parameters from 3743 reflections

$\theta = 2.4$ – 28.0°

$\mu = 0.58$ mm^{−1}

$T = 295$ (2) K

Block, pale yellow

0.35 × 0.22 × 0.17 mm

Data collection

Bruker SMART APEX area-

detector diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2002)

$T_{\min} = 0.823$, $T_{\max} = 0.908$

9038 measured reflections

5920 independent reflections

5509 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 25.0^\circ$

$h = -11 \rightarrow 11$

$k = -16 \rightarrow 14$

$l = -16 \rightarrow 14$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.072$

$wR(F^2) = 0.144$

$S = 1.25$

5920 reflections

502 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 2.6715P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.61$ e Å^{−3}

$\Delta\rho_{\min} = -0.33$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.094 (3)	Mn1—N2	2.287 (3)
Mn1—O6	2.155 (3)	Mn1—N3	2.248 (4)
Mn1—N1	2.241 (3)	Mn1—N4	2.321 (3)
O1—Mn1—O6	97.0 (2)	O6—Mn1—N4	108.7 (1)
O1—Mn1—N1	93.4 (1)	N1—Mn1—N2	73.2 (1)
O1—Mn1—N2	91.4 (1)	N1—Mn1—N3	106.4 (1)
O1—Mn1—N3	159.6 (1)	N1—Mn1—N4	165.7 (1)
O1—Mn1—N4	87.1 (1)	N2—Mn1—N3	89.5 (1)
O6—Mn1—N1	85.4 (1)	N2—Mn1—N4	92.5 (1)
O6—Mn1—N2	157.5 (1)	N3—Mn1—N4	72.4 (1)
O6—Mn1—N3	89.8 (1)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4 o ···O8 ⁱ	0.85 (5)	1.88 (4)	2.713 (4)	168 (6)
O9—H9 o ···O2 ⁱⁱ	0.84 (4)	1.83 (4)	2.653 (4)	165 (6)

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $1 - x, -y, 1 - z$.

H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [$C-H = 0.93$ Å and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$]. The carboxyl H atoms were located in a difference Fourier map and were refined with a distance restraint of $O-H = 0.85$ (1) Å and with fixed isotropic displacement parameters of 0.08 Å². Although the data were measured to a 2θ limit of 56.6° , only the intensities below 50° were used in the refinement; the use of all reflections gave a much higher R factor.

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: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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