

Aquabis(2,2'-bipyridine)(3-carboxylato-4-hydroxybenzenesulfonato)manganese(II) dihydrate

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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in main residue
 R factor = 0.048
 wR factor = 0.125
Data-to-parameter ratio = 14.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The Mn atom in the title compound, $[\text{Mn}(\text{C}_7\text{H}_4\text{O}_6\text{S})\text{-(C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$, is coordinated by the two *N*-heterocycles, a water molecule and a 3-carboxylato-4-hydroxybenzenesulfonate dianion through the carboxylate group, thus imposing an octahedral environment on the metal atom. The coordinated and uncoordinated water molecules, the carboxylate and sulfonate groups interact *via* hydrogen bonds, producing a three-dimensional network architecture.

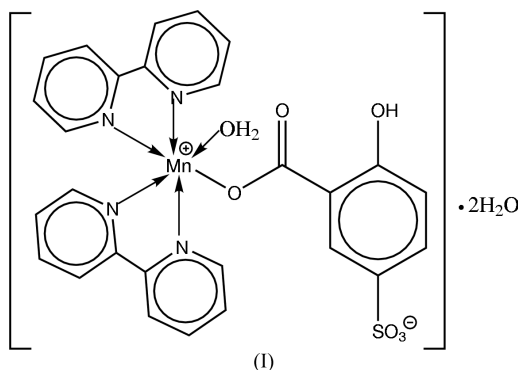
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Comment

A recent report (Gao *et al.*, 2005) mentions the small number of structurally authenticated examples of metal derivatives of sulfosalicylic (3-carboxy-4-hydroxybenzenesulfonic) acid; included among these are some complexes with *N*-heterocycles (Icbudak *et al.*, 2003; Li *et al.*, 2004; Wang *et al.*, 2004). Manganese 3-carboxy-4-hydroxybenzenesulfonate exists as a hexaaquamanganese salt (Ma *et al.*, 2003). Two 2,2'-bipyridine ligands probably limit the coordination sites available for coordination by water, so that in the present manganese derivative, (I), the fifth site is occupied by a water molecule and the remaining site by the negatively charged carboxylate O atom of the dianion (Fig. 1).



The inability of the sulfonate group to participate in hydrogen bonding is reflected in some disorder, the $-\text{SO}_3^-$ fragment adopting two orientations around the C–S axis. Nevertheless, the disordered fragment interacts with the uncoordinated water molecules through hydrogen bonds; the crystal structure appears to be tightly consolidated by extensive hydrogen bonds (Table 2).

Experimental

A mixture of manganese acetate tetrahydrate (0.050 g, 0.20 mmol), 5-sulfosalicylic acid dihydrate (0.051 g, 0.20 mmol), 2,2'-bipyridine (0.031 g, 0.20 mmol) and water (10 ml) was sealed in a 20 ml Teflon-lined stainless steel Parr bomb. The reactor was heated to 413 K for

24 h. The cooled colorless solution was set aside for a day to allow the solvent to evaporate. Pale yellow block-shaped crystals were obtained.

Crystal data

[Mn(C₇H₄O₆S)(C₁₀H₈N₂)₂·(H₂O)]·2H₂O
M_r = 637.52
 Triclinic, *P*1̄
a = 9.8406 (6) Å
b = 10.1729 (6) Å
c = 15.2354 (9) Å
 α = 73.5009 (13)°
 β = 84.7304 (14)°
 γ = 80.7830 (13)°
V = 1441.76 (15) Å³
Z = 2
D_x = 1.469 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3913 reflections
 θ = 2.5–25.9°
 μ = 0.59 mm⁻¹
T = 298 (2) K
 Block, pale yellow
 0.33 × 0.22 × 0.14 mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
T_{min} = 0.829, *T_{max}* = 0.922
 12401 measured reflections
 6350 independent reflections
 5289 reflections with *I* > 2σ(*I*)
R_{int} = 0.021
 θ_{max} = 27.5°
h = -12 → 12
k = -13 → 13
l = -19 → 19

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.048
wR (*F*²) = 0.125
S = 1.03
 6350 reflections
 435 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.2944P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.37 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.0998 (17)	Mn1—N2	2.2681 (19)
Mn1—O1w	2.1200 (19)	Mn1—N3	2.311 (2)
Mn1—N1	2.259 (2)	Mn1—N4	2.254 (2)
O1—Mn1—O1w	90.98 (8)	O1w—Mn1—N4	95.07 (8)
O1—Mn1—N1	162.14 (7)	N1—Mn1—N2	71.94 (7)
O1—Mn1—N2	90.20 (7)	N1—Mn1—N3	93.90 (7)
O1—Mn1—N3	86.13 (7)	N1—Mn1—N4	93.04 (7)
O1—Mn1—N4	103.90 (7)	N2—Mn1—N4	155.34 (8)
O1w—Mn1—N1	93.16 (8)	N2—Mn1—N3	89.21 (7)
O1w—Mn1—N2	104.96 (8)	N3—Mn1—N4	72.00 (7)
O1w—Mn1—N3	165.57 (8)		

Table 2

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>
O3—H3O...O2	0.86 (3)	1.734 (18)	2.535 (3)	155 (4)
O1w—H1w1...O2w	0.85 (3)	1.82 (3)	2.667 (3)	173 (3)
O1w—H1w2...O3w	0.84 (3)	1.87 (3)	2.696 (3)	166 (3)
O2w—H2w1...O4 ⁱ	0.85 (3)	1.967 (16)	2.793 (4)	165 (4)
O2w—H2w1...O4 ⁱⁱ	0.85 (3)	1.85 (2)	2.671 (10)	162 (4)
O2w—H2w2...O5 ⁱⁱⁱ	0.85 (3)	2.00 (3)	2.750 (13)	148 (4)
O3w—H3w1...O6 ⁱⁱⁱ	0.84 (3)	1.986 (12)	2.827 (4)	174 (4)
O3w—H3w1...O6 ⁱⁱⁱ	0.84 (3)	1.98 (3)	2.738 (11)	149 (4)
O3w—H3w2...O2	0.84 (4)	1.99 (4)	2.824 (3)	172 (4)

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) 1 + *x*, *y* - 1, *z*; (iii) *x*, *y* - 1, *z*.

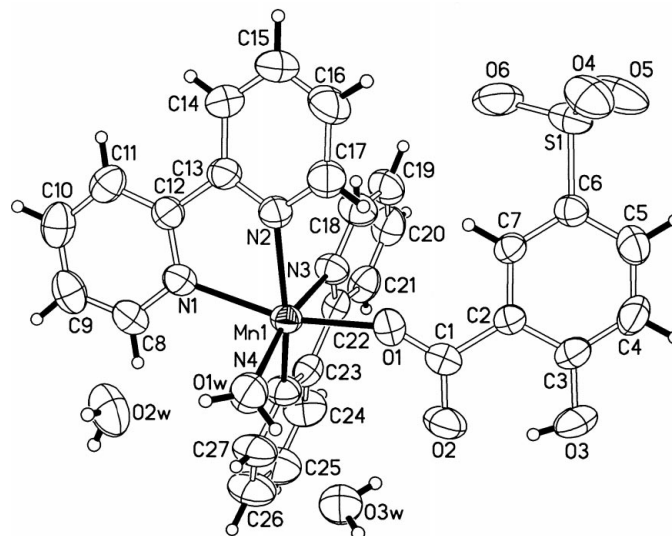


Figure 1 ORTEPII (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level. The minor disorder component is not shown.

The aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)]. The water and hydroxy H atoms were located in a difference Fourier map and were refined with a distance restraint of O—H = 0.85 (1) Å. The sulfonate group is disordered; the structure was refined with the six S—O distances restrained to be equal within 0.01 Å. The site occupancy factors for the disordered atoms O4, O5, O6 are 0.744 (8) and 0.256 (8).

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: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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