

Jian-Fang Ma,* Jin Yang and
Jing-Fu LiuDepartment of Chemistry, Northeast Normal
University, Changchun 130024, People's
Republic of China

Correspondence e-mail: jfma@public.cc.jl.cn

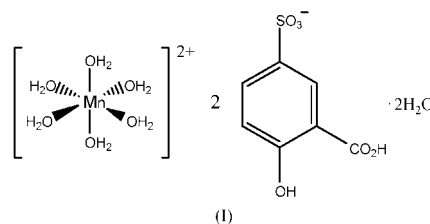
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.031
 wR factor = 0.089
Data-to-parameter ratio = 12.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexaaquamanganese(II) 3-carboxy-4-
hydroxybenzenesulfonate dihydrate

In the title compound, $[\text{Mn}(\text{H}_2\text{O})_6]L_2 \cdot 2\text{H}_2\text{O}$, where HL is 3-carboxy-4-hydroxybenzenesulfonic acid ($\text{C}_7\text{H}_6\text{O}_6\text{S}$), each Mn^{II} cation lies on an inversion center and is octahedrally coordinated by six water molecules. The L^- anions do not coordinate to manganese, but act as counter-anions. The crystal structure is composed of alternating layers of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations and sulfonate anions. The $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations, water molecules and L^- anions are connected through a complex pattern of H-bonding interactions.

Comment

Metal phosphonate chemistry has been developed rapidly. By contrast, the coordination chemistry of transition metal sulfonates is not well explored or rationalized, owing to the preconception that sulfonates are weakly coordinating ligands (Yu & Enright, 2001). In some cases, a sulfonate group can compete with water molecules in coordinating to a metal ion (Shimizu *et al.*, 1998; Smith *et al.*, 1998; Sundberg & Sillanpaa, 1993). Squattrito and co-workers have studied the structures of some transition metal sulfonates, in which the metal is coordinated by water molecules, the sulfonate anions remaining uncoordinated (Gunderman *et al.*, 1997; Kosnic *et al.*, 1992; Shubnell *et al.*, 1994). We have determined the crystal structures of five transition metal (Mn, Co, Ni, Cu and Zn) 3-carboxy-4-hydroxybenzenesulfonates. The crystal structure of the manganese compound, (I), is presented here, and the crystal structures of the other four related compounds are reported in the following papers.



The Mn atom is located on an inversion center, and all other atoms are in general positions. Selected bond lengths and angles are given in Table 1. Fig. 1 shows the asymmetric unit, together with the complete coordination environment of the Mn^{II} cation. Each Mn^{II} cation is coordinated by six water molecules, giving an octahedral coordination geometry. The average Mn—O distance of 2.173 \AA is similar to values in other manganese compounds (Wu *et al.*, 1995). Owing to the weak coordinating ability of sulfonate ions toward transition metal ions, the sulfonate ions are non-coordinating. The

Received 28 April 2003

Accepted 11 June 2003

Online 24 June 2003

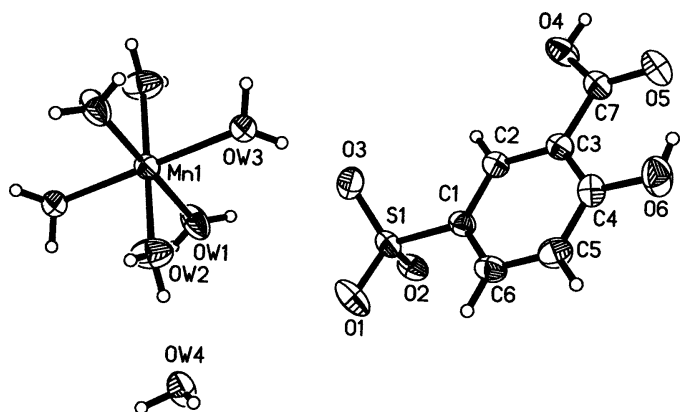


Figure 1
View of the asymmetric unit, expanded to show the complete coordination of Mn^{II}, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

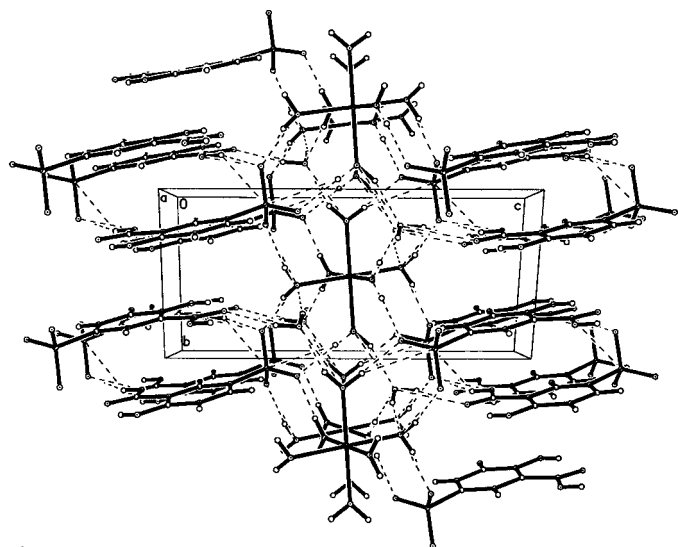


Figure 2
View of the alternating layers of cations and anions, along the *a* axis.

crystal structure of (I) is composed of alternating layers of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations and sulfonate anions, as shown in Fig. 2. Within the sulfonate layer, there are rows of anions with alternating orientations of the organic group.

There is one additional uncoordinated water molecule in the asymmetric unit. The $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations, water molecules and L^- anions are connected through a complex pattern of hydrogen-bonding interactions. Selected hydrogen-bond parameters are listed in Table 2. There are 10 H atoms available for hydrogen bonding in the asymmetric unit. Some of the water molecules play a role as both acceptor and donor, while the hydroxyl and carboxyl OH groups are only donors, and the sulfonate and carboxyl O atoms are necessarily only acceptors.

Experimental

A mixture of 3-carboxy-4-hydroxybenzenesulfonic acid (0.44 g, 2 mmol) and MnCO_3 (0.12 g, 1 mmol) in water (10 ml) was stirred at room temperature for 30 min. Colorless crystals of compound (I)

were obtained after leaving the solution to stand at room temperature for several days. Analysis calculated for $\text{C}_{14}\text{H}_{26}\text{MnO}_{20}\text{S}_2 \cdot \text{C}$: C 26.55, H 4.14%; found: C 26.62, H 4.18%.

Crystal data

$[\text{Mn}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_5\text{O}_6\text{S})_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 633.41$
 Triclinic, $P\bar{1}$
 $a = 7.0608$ (19) Å
 $b = 7.1535$ (19) Å
 $c = 13.836$ (3) Å
 $\alpha = 90.49$ (2)°
 $\beta = 90.49$ (2)°
 $\gamma = 119.118$ (17)°
 $V = 610.4$ (3) Å³

$Z = 1$
 $D_x = 1.723$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 19 reflections
 $\theta = 5.5\text{--}9.9^\circ$
 $\mu = 0.81$ mm⁻¹
 $T = 293$ (2) K
 Block, colorless
 $0.50 \times 0.32 \times 0.28$ mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.645$, $T_{\text{max}} = 0.798$
 3086 measured reflections
 2384 independent reflections
 1961 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -1 \rightarrow 8$
 $k = -8 \rightarrow 8$
 $l = -17 \rightarrow 17$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.089$
 $S = 1.04$
 2384 reflections
 194 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.0568P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.264 (10)

Table 1

Selected geometric parameters (Å, °).

C4—O6	1.343 (3)	O3—S1	1.4511 (19)
C7—O5	1.218 (3)	OW1—Mn1	2.1556 (18)
C7—O4	1.311 (3)	OW2—Mn1	2.1534 (19)
O1—S1	1.4544 (17)	OW3—Mn1	2.2110 (17)
O2—S1	1.4716 (16)		
O5—C7—O4	123.1 (2)	OW2—Mn1—OW1	90.52 (8)
O3—S1—O1	114.68 (12)	OW2—Mn1—OW3	88.95 (8)
O3—S1—O2	110.54 (11)	OW1—Mn1—OW3	93.83 (7)
O1—S1—O2	110.72 (10)		

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>
OW1—H1A...OW4 ⁱ	0.881 (17)	1.938 (19)	2.781 (3)	160 (3)
OW1—H1B...O1 ⁱ	0.892 (17)	1.908 (18)	2.796 (3)	174 (3)
OW2—H2B...O1 ⁱⁱ	0.879 (18)	1.958 (18)	2.836 (3)	177 (3)
OW2—H2A...OW4	0.876 (17)	1.903 (18)	2.777 (3)	176 (3)
OW3—H3B...O2 ⁱⁱⁱ	0.879 (17)	1.898 (19)	2.763 (2)	168 (3)
OW3—H3A...O3	0.871 (17)	1.863 (18)	2.722 (3)	169 (3)
OW4—H4A...O5 ^{iv}	0.873 (17)	2.028 (19)	2.855 (2)	158 (3)
OW4—H4B...OW3 ⁱⁱ	0.866 (18)	2.133 (19)	2.980 (3)	166 (3)
O4—H4...O2 ^v	0.82	1.91	2.693 (2)	159
O6—H6A...O5	0.82	1.90	2.619 (3)	146

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

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the carboxyl group and hydroxyl group were also positioned

geometrically and refined as riding atoms, with $O-H = 0.82 \text{ \AA}$ and $U_{iso}(H) = 1.5U_{eq}(O)$. The water H atoms were located in a difference Fourier map and refined with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Fok Ying Tung Education Foundation and the Ministry of Education of China.

References

- Gunderman, B. J., Kabell, I. D., Squattrito, P. J. & Dubey, S. N. (1997). *Inorg. Chim. Acta*, **258**, 237–246.
- Kosnic, E. J., McClymont, E. L., Hodder, R. A. & Squattrito, P. J. (1992). *Inorg. Chim. Acta*, **201**, 143–151.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shimizu, G. K. H., Enright, G. D., Ratcliffe, C. I., Rego, G. S., Reid, J. L. & Ripmeester, J. A. (1998). *Chem. Mater.* **10**, 3282–3283.
- Shubnell, A. J., Kosnic, E. J. & Squattrito, P. J. (1994). *Inorg. Chim. Acta*, **216**, 101–112.
- Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Smith, G., Cloutt, B. A., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1998). *Inorg. Chem.* **37**, 3236–3242.
- Sundberg, M. R. & Sillanpaa, R. (1993). *Acta Chem. Scand.* **47**, 1173–1178.
- Wu, L. P., Yamamoto, M., Kuroda-Sowa, T., Maekawa, M., Fukui, J. & Munakata, M. (1995). *Inorg. Chim. Acta*, **239**, 165–169.
- Yu, J. O., Cote A. P., Enright, G. D. & Shimizu G. K. H. (2001). *Inorg. Chem.* **40**, 582–583.