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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.040
 wR factor = 0.107
 Data-to-parameter ratio = 14.0

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

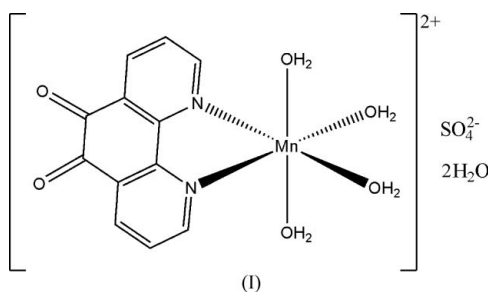
**Tetraaqua(1,10-phenanthroline-5,6-dione- $\kappa^2\text{N,N}'$)-
 manganese(II) sulfate dihydrate**

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The title compound, $[\text{Mn}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2)(\text{H}_2\text{O})_4]\text{SO}_4 \cdot 2\text{H}_2\text{O}$, was obtained by the reaction of manganese(II) sulfate with an equivalent of 1,10-phenanthroline-5,6-dione in aqueous solution. Mn(II) is hexacoordinated in a distorted octahedral geometry by the two N atoms from the phenanthroline-dione ligand and the O atoms from four coordinated water molecules. Both the cation and anion lie about mirror planes. The structure is stabilized by an extensive network of O—H···O hydrogen bonds.

Comment

1,10-Phenanthroline-5,6-dione is a versatile ligand for the assembly of metal-organic materials (Calderazzo *et al.*, 2002). It seems always to utilize the imine N atoms to bind metal ions, leaving the diketone O atoms uncoordinated, as found in the crystal structures of its complexes with Cu(I or II) (Galet *et al.*, 2005), Ru(II) (Fujihara *et al.*, 2003a, 2004; Yokoyama, Wakabayashi *et al.*, 2006; Rusanova *et al.*, 2002) and Ni(II) (Hadadzadeh *et al.*, 2006) while keeping the diketone unit uncoordinated. Owing to its redox activity, the dione in a metal-free state and in complexes with transition metals shows strong electrocatalytic activity (Hilt *et al.*, 1997; Yokoyama *et al.*, 2005, Yokoyama, Asakura *et al.*, 2006; Fujihara *et al.*, 2003b). We report here the preparation and structure of the title compound, (I), the first phenanthroline-dione complex of Mn(II) (Fig. 1 and Table 1).



Both the complex cation and the sulfate anion lie about mirror planes, hence the asymmetric unit consists of one half-cation, one half-anion, and a water molecule. As expected, the phenanthroline-dione ligand coordinates to the central Mn(II) atom *via* its imine N atoms with the dione O atoms not involved in coordination to the metal. The C=O double-bond length [1.209 (3) Å] is the same as the value reported for the metal-free phenanthroline-dione (Calderazzo *et al.*, 1999) and comparable to other phenanthroline-dione complexes.

The structure is stabilized by an extensive network of O—H···O hydrogen bonds, involving both coordinated and

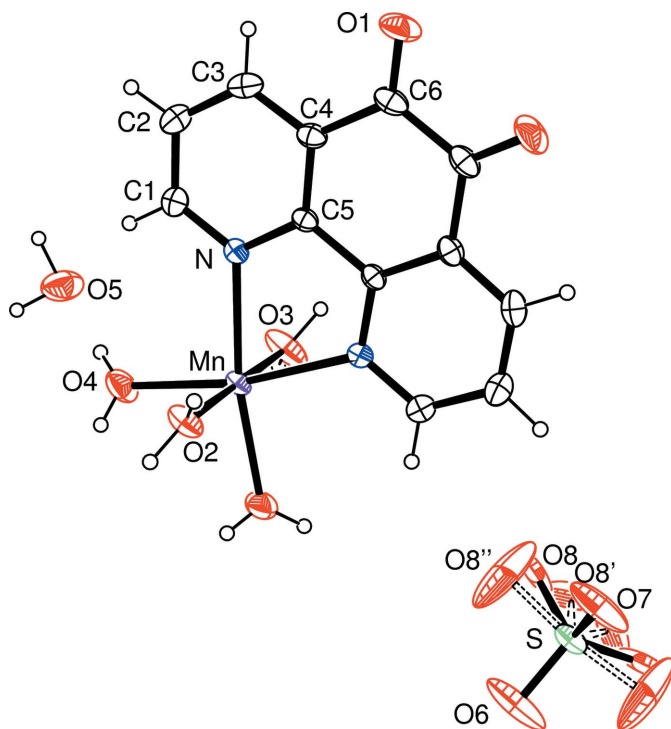


Figure 1

The structure of the components of the title compound, with displacement ellipsoids drawn at the 30% probability level and only the non-H atoms in the asymmetric unit labelled. The O8' and O8'' disorder components are linked to the sulfur with dashed lines. The symmetry codes relating the labelled to the unlabelled atoms are $x, -y, z$ for the cation and $x, 1 - y, z$ for the anion.

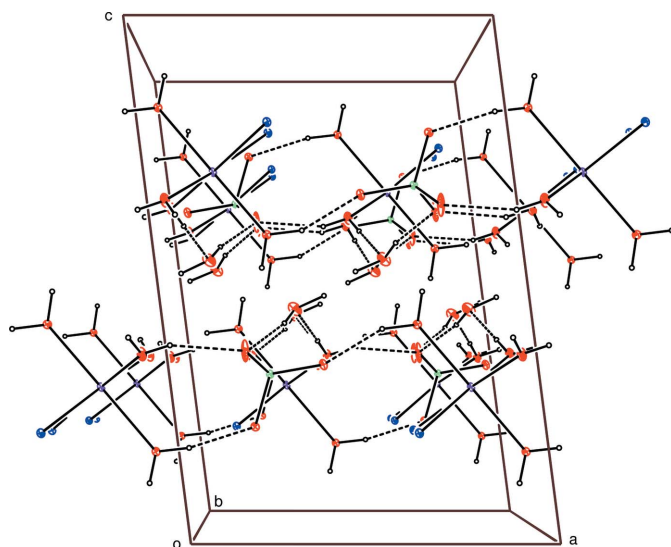


Figure 2

View of the packing along [010], with hydrogen bonds shown as dashed lines. The 1,10-phenanthroline-5,6-dione ligands and O8' and O8'' disorder components are omitted for clarity.

solvent water and sulfate anions. Indeed, only the carbonyl atom O1 is not involved in any hydrogen-bond formation (Table 1, Fig. 2). There are no obvious π - π stacking interactions between adjacent dione ligands.

Experimental

1,10-Phenanthroline-5,6-dione (0.5 mmol) was dissolved in a hot aqueous solution (20 ml) and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.5 mmol) added. The mixture was stirred for 30 min and filtered. Orange single crystals of the title complex were obtained from the filtrate at room temperature in a week.

Crystal data

$[\text{Mn}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2)(\text{H}_2\text{O})_4](\text{SO}_4) \cdot 2\text{H}_2\text{O}$	$V = 1842.41 (14) \text{ \AA}^3$
$M_r = 469.28$	$Z = 4$
Monoclinic, $C2/m$	$D_x = 1.692 \text{ Mg m}^{-3}$
$a = 9.6237 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.9117 (6) \text{ \AA}$	$\mu = 0.90 \text{ mm}^{-1}$
$c = 13.8744 (6) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 97.317 (3)^\circ$	Block, orange
	$0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	2205 independent reflections
φ and ω scans	1906 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.028$
10376 measured reflections	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 3.5719P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
2205 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
158 parameters	
H-atom parameters constrained	

Table 1

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H41 \cdots O5	0.90	1.80	2.697 (3)	178
O2—H21 \cdots O7 ⁱ	0.87	1.80	2.659 (4)	169
O3—H31 \cdots O6 ⁱⁱ	0.92	1.79	2.656 (4)	156
O3—H32 \cdots O8 ⁱⁱⁱ	0.87	1.91	2.747 (8)	163
O3—H32 \cdots O8 ^{iv}	0.87	1.91	2.747 (8)	163
O4—H42 \cdots O8 ⁱ	0.75	1.92	2.639 (8)	158
O4—H42 \cdots O8 ⁱⁱ	0.75	1.98	2.705 (9)	160
O5—H51 \cdots O8 ^v	0.95	1.67	2.537 (13)	151
O5—H51 \cdots O8 ^{vi}	0.95	1.74	2.654 (8)	162
O5—H52 \cdots O5 ^{vi}	0.95	1.97	2.798 (5)	145

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

Water H atoms were located in a difference map while carbon-bound H atoms were positioned geometrically. All H atoms were refined as riding on the attached O or C atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O or C})$; $\text{O}-\text{H} = 0.75\text{--}0.92$ and $\text{C}-\text{H} = 0.93 \text{ \AA}$. The O atoms of the sulfate anion have high displacement parameters and the positional disorder for the O8 was resolved into three positions, O8, O8' and O8''. The occupancy factors refined to 0.35 (2), 0.331 (14) and 0.319 (15) respectively.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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