

Hexaaquamanganese(II) dipicrate dihydrate

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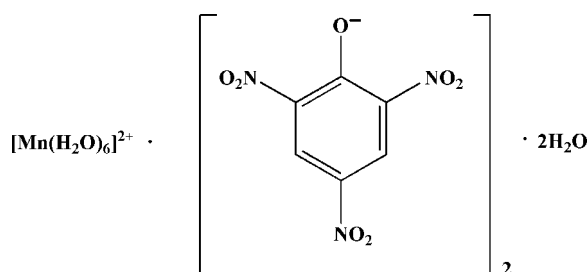
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.047; wR factor = 0.158; data-to-parameter ratio = 10.1.

In the title compound, $[\text{Mn}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, the manganese cation, on an inversion centre, is coordinated by six water molecules, but the picrate anion has no coordinative interaction with the manganese cation. The anions in the stack are linked *via* short intermolecular $\text{O} \cdots \text{C}$ (3.013 and 2.973 Å) and $\text{C} \cdots \text{C}$ (3.089 and 3.065 Å) contacts and hydrogen bonds.

Related literature

For related literature, see: Bibal *et al.* (2003); García *et al.* (2004); Harrowfield *et al.* (1995a,b); Honda *et al.* (2003); Ji & Chen (1996); Maartmann-Moe (1969); Olsher *et al.* (1996); Yang *et al.* (2001); Zhang *et al.* (2003).



Experimental

Crystal data

$[\text{Mn}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 655.28$
 Orthorhombic, *Pccn*
 $a = 25.344$ (6) Å
 $b = 7.1625$ (17) Å
 $c = 13.217$ (3) Å

$V = 2399.2$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.67$ mm⁻¹
 $T = 294$ (2) K
 $0.28 \times 0.24 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.835$, $T_{\text{max}} = 0.878$

11295 measured reflections
 2122 independent reflections

1643 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.158$
 $S = 1.11$
 2122 reflections
 211 parameters
 8 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.20$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.120 (3)	Mn1—O2	2.190 (2)
Mn1—O3	2.136 (3)		
O1—Mn1—O3	91.52 (11)	O3 ⁱ —Mn1—O2 ⁱ	86.83 (11)
O1—Mn1—O2 ⁱ	88.48 (11)	O1—Mn1—O2	86.98 (11)
O1—Mn1—O2 ⁱ	93.02 (11)	O3 ⁱ —Mn1—O2	93.17 (11)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A ⁱⁱ ···O11 ⁱⁱ	0.846 (10)	1.938 (12)	2.780 (4)	173 (4)
O1—H1B ⁱⁱⁱ ···O10 ⁱⁱⁱ	0.852 (10)	2.10 (2)	2.906 (4)	157 (4)
O2—H2A ^{iv} ···O10 ^{iv}	0.848 (10)	2.048 (12)	2.889 (4)	172 (4)
O2—H2A ^{iv} ···O9 ^{iv}	0.848 (10)	2.53 (4)	2.986 (4)	115 (3)
O3—H3A ^v ···O11 ^v	0.832 (10)	1.951 (12)	2.782 (4)	176 (5)
O3—H3B ^{vi} ···O6 ^{vi}	0.841 (10)	2.047 (12)	2.884 (4)	174 (5)
O11—H11A ^{vii} ···O2 ^{vii}	0.847 (10)	2.213 (19)	3.006 (4)	156 (4)
O11—H11B ^{viii} ···O10 ^{viii}	0.846 (10)	2.17 (2)	2.938 (4)	151 (4)
O11—H11B ^{viii} ···O4 ^{viii}	0.846 (10)	2.27 (3)	2.913 (4)	133 (4)
O2—H2B ^{ix} ···O4 ^{ix}	0.841 (10)	2.143 (19)	2.930 (4)	156 (4)

Symmetry codes: (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x, y - 1, z$; (vi) $-x + \frac{1}{2}, y - 1, z + \frac{1}{2}$; (vii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (viii) $-x + 1, -y + 2, -z + 1$; (ix) $-x + 1, -y + 1, -z + 1$.

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WW2104).

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supplementary materials

Acta Cryst. (2008). E64, m270-m271 [doi:10.1107/S1600536807064276]

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Comment

Picrate is commonly used as an accompanying ion in many systems involving extraction and transport of metal ions to improve the extractability and selectivity (Zhang *et al.*, 2003; Bibal *et al.*, 2003; García *et al.*, 2004). In many structures, picrate interacts as monodentate, bidentate and tridentate ligand (Olsher *et al.*, 1996). Besides, picrate is a penta-dentate ligand when it coordinates with sodium or potassium cation by chelating pairs of oxygen atoms from *p*-nitro groups of adjacent picrates, and with successive cation linking the array into two or three-dimensional network (Harrowfield *et al.*, 1995*a*; Maartmann-Moe, 1969). Furthermore, the picrate interacts as a heptadentate ligand through all its available oxygen donor atoms to coordinate with caesium (Harrowfield *et al.*, 1995*a*).

Fig. 1 shows the structure and the atomic numbering schemes of the crystal structure of the title manganese picrate complex (I). This situation is similar to the crystal structure of iron (II) picrate (Honda *et al.*, 2003) and Magnesium (II) picrate (Harrowfield *et al.*, 1995*b*) and the picrate anion adopts a keto form with C6—O10 bond distance of 1.257 (4) Å, C1—C6 and C5—C6 bond distance of 1.447 (5) and 1.456 (5) Å, respectively, which is longer than the other C—C bond lengths (between 1.374 (5) to 1.460 (4) Å) in the benzene ring. The Mn—O distance ranges from 2.120 (2) to 2.190 (2) Å. The bond angle C1—C6—C5 is 111.9 (3)°, which is the case in some picrate complexes, while the corresponding bond angle of picric acid is 116.4 (5)° (Yang *et al.*, 2001). Selected bond lengths and angles are given in Table 1.

In the case of planarity of picrate anion, the *ortho* nitro group are twisted relative to the plane of the benzene ring, (between 19.01 and 27.69°), while *para*-positioned nitro group is deviated 13.02° off the benzene ring. The picrate ions are stacked head-to-tail, presumably as a result of charge-transfer interactions. The anion in the stack are linked *via* short intermolecular O...C and C...C contacts of 3.013, 2.973, 3.089 and 3.065 Å for O6...C1^x, O7...C5^{xi}, C2...C2^x and C4...C4^{xi} [symmetry codes: (x) 1/2 - x, 3/2 - y, z; (xi) 1/2 - x, 5/2 - y, z] respectively (Fig.2). The picrate anions are not parallel to one another, and the dihedral angles between neighbouring benzene planes are 25.01°, 25.25° and 3.48° respectively.

Experimental

The title compound (I) was obtained by the reaction of 3.20 g (13.96 mmol) picric acid with 0.80 g (6.98 mmol) manganese carbonate in water (350 ml), according to Ji *et al.*, 1996. Heating has been continued for another 1 h and filtered while it was still hot. The filtrate was partially evaporated and left to stand in open atmosphere for a few days, during which time, yellow crystals suitable for X-Ray determination were obtained. Analysis, calculated for C₁₂H₂₀N₆O₂₂Mn: C 21.98, H 3.05, N 12.80, Mn 8.40%; Found: C 22.35, H 3.34, N 12.46, Mn 8.68%.

Refinement

All H atoms of water were located from difference map and then refined with O—H distances restrained to 0.85 (1) Å. All other H atoms were positioned geometrically and refined using a riding mode with the C—H bond lengths of 0.93 Å and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{carrier atom})$.

Figures

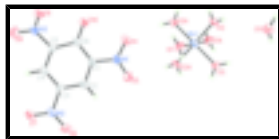


Fig. 1. The molecular structure of (I), with displacement ellipsoids at the 50% probability level and the atomic labeling scheme.

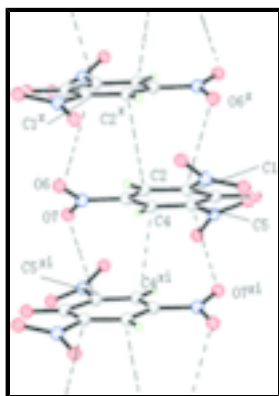


Fig. 2. The crystal structure of (I), projected along the *c* axis. The dashed lines indicate short intermolecular contacts with N...O, C...C and O...C distances less than 3.0, 3.2 and 3.0 Å, respectively. [Symmetry mode: (x) $1/2 - x, 3/2 - y, z$; (xi) $1/2 - x, 5/2 - y, z$]

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Crystal data

$[\text{Mn}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$

$M_r = 655.28$

Orthorhombic, *Pccn*

Hall symbol: -P 2ab 2ac

$a = 25.344 (6) \text{ \AA}$

$b = 7.1625 (17) \text{ \AA}$

$c = 13.217 (3) \text{ \AA}$

$V = 2399.2 (9) \text{ \AA}^3$

$Z = 4$

$F_{000} = 1340$

$D_x = 1.814 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3819 reflections

$\theta = 3.0\text{--}26.9^\circ$

$\mu = 0.67 \text{ mm}^{-1}$

$T = 294 (2) \text{ K}$

Prism, yellow

$0.28 \times 0.24 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294(2) \text{ K}$

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.835, T_{\max} = 0.878$

11295 measured reflections

2122 independent reflections

1643 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

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

$\theta_{\text{min}} = 3.0^\circ$

$h = -30 \rightarrow 20$

$k = -6 \rightarrow 8$

$l = -14 \rightarrow 15$

Fig. 1

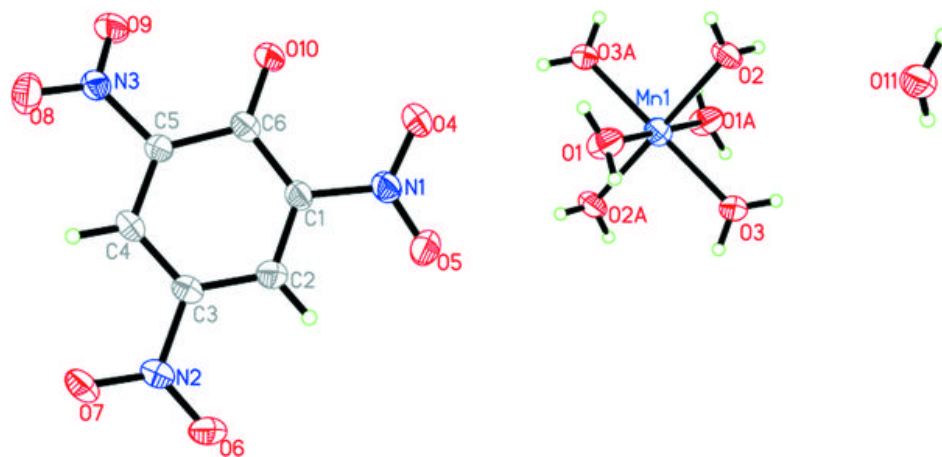


Fig. 2

