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Bis(μ -4-bromoisophthalato)bis[bis(1,10-phenanthroline)manganese(II)] tetrahydrate

In the title centrosymmetric compound, $[\text{Mn}_2(\text{C}_8\text{H}_3\text{BrO}_4)_2(\text{C}_{12}\text{H}_8\text{N}_2)_4] \cdot 4\text{H}_2\text{O}$, the Mn^{II} atom is surrounded by two O atoms from two 4-bromoisophthalate dianions and four N atoms from two phen (phen is 1,10-phenanthroline) heterocycles in a distorted octahedral geometry. Two bromoisophthalate dianions link two $[\text{Mn}(\text{phen})_2]^{2+}$ cations in bis-monodentate mode, resulting in a binuclear complex.

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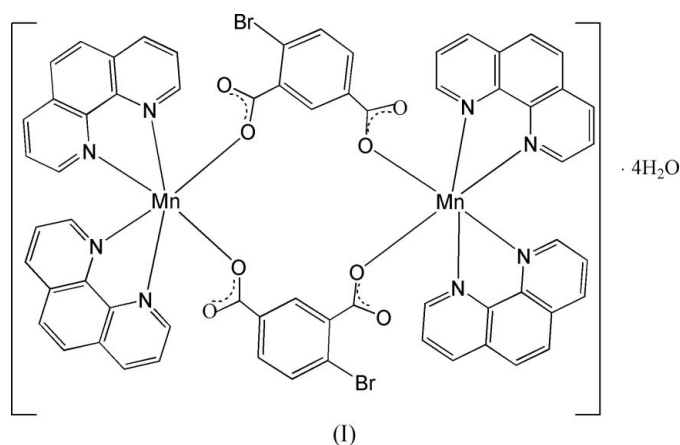
Key indicators

Single-crystal X-ray study
 $T = 298 \text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
 R factor = 0.075
 wR factor = 0.153
 Data-to-parameter ratio = 12.7

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

Comment

Many metal-organic coordination polymers constructed by using isophthalic acid (Hou *et al.*, 2003; Xiao *et al.*, 2004), 5-hydroxyisophthalic acid (Li *et al.*, 2004; Plater *et al.*, 2001) and 5-nitroisophthalic acid (Si *et al.*, 2004; Xiao *et al.*, 2005) have been reported. However, complexes formed from 4-bromoisophthalic acid are rather limited (Eddaoudi *et al.*, 2002), and the title complex, (I), represents one such example.



The asymmetric unit of (I) contains a $[\text{Mn}(\text{phen})_2]^{2+}$ cation (phen is 1,10-phenanthroline, a bridging 4-bromoisophthalate anionic ligand and two water molecules. In (I), two $[\text{Mn}(\text{phen})_2]^{2+}$ cations are linked by two 4-bromoisophthalate dianions in bis-monodentate mode to form a binuclear complex.

In the title centrosymmetric compound, each Mn^{II} atom is coordinated by four N atoms from two phen heterocycles and two O atoms from two 4-bromoisophthalate dianions to furnish a highly distorted octahedral coordination environment (Fig. 1). The Mn–N bond lengths are in the range 2.263 (4)–2.323 (4) Å. The *trans* angles of the octahedron are 158.12 (15), 162.08 (14) and 168.72 (14)°, and the other angles are in the range 72.28 (14)–102.12 (14)° (Table 1).

The mean planes through the two phen ligands form a dihedral angle of 85.80 (7)°, *i.e.* the two phen ligands are nearly perpendicular to each other. There are intermolecular

hydrogen-bonding interactions between the water molecules and uncoordinated carboxyl O atoms (Table 2). Weak π - π stacking interactions are observed between inversion-related phen rings; the shortest centroid-centroid distance of 3.591 (4) Å is observed between the N1-pyridine ring at (x , y , z) and its inversion-related equivalent at ($1 - x$, $2 - y$, $-z$). All these interactions link the binuclear units into a three-dimensional network structure.

Experimental

Compound (I) was synthesized by the hydrothermal method from a mixture of 4-bromoisophthalic acid (0.3 mmol), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.3 mmol), 1,10-phenanthroline (0.5 mmol) and water (8.0 ml) in a 15.0 ml Teflon-lined stainless steel reactor. The solution was heated at 423 K for 5 d. After reaction, the vessel was cooled slowly to room temperature to give yellow crystals.

Crystal data

$[\text{Mn}_2(\text{C}_8\text{H}_3\text{BrO}_4)_2(\text{C}_{12}\text{H}_8\text{N}_2)_4] \cdot 4\text{H}_2\text{O}$	$Z = 1$
$M_r = 1388.79$	$D_x = 1.572 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.2104 (14) \text{ \AA}$	Cell parameters from 2167 reflections
$b = 12.1592 (16) \text{ \AA}$	$\theta = 2.3\text{--}21.0^\circ$
$c = 13.9932 (19) \text{ \AA}$	$\mu = 1.87 \text{ mm}^{-1}$
$\alpha = 66.705 (2)^\circ$	$T = 298 (2) \text{ K}$
$\beta = 70.878 (2)^\circ$	Prism, yellow
$\gamma = 70.700 (2)^\circ$	$0.27 \times 0.13 \times 0.08 \text{ mm}$
$V = 1466.6 (3) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	5245 independent reflections
φ and ω scans	4112 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.633$, $T_{\text{max}} = 0.865$	$\theta_{\text{max}} = 25.2^\circ$
10 863 measured reflections	$h = -12 \rightarrow 12$
	$k = -14 \rightarrow 14$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.3548P]$
$R[F^2 > 2\sigma(F^2)] = 0.075$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.20$	$\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$
5245 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
412 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.073 (3)	Mn1—N1	2.298 (4)
Mn1—O3 ⁱ	2.114 (3)	Mn1—N2	2.302 (4)
Mn1—N4	2.263 (4)	Mn1—N3	2.323 (4)
O1—Mn1—O3 ⁱ	90.08 (14)	N4—Mn1—N2	95.87 (13)
O1—Mn1—N4	102.00 (15)	N1—Mn1—N2	72.30 (14)
O3 ⁱ —Mn1—N4	102.12 (14)	O1—Mn1—N3	100.59 (15)
O1—Mn1—N1	91.14 (15)	O3 ⁱ —Mn1—N3	168.72 (14)
O3 ⁱ —Mn1—N1	95.19 (14)	N4—Mn1—N3	72.28 (14)
N4—Mn1—N1	158.12 (15)	N1—Mn1—N3	88.28 (14)
O1—Mn1—N2	162.08 (14)	N2—Mn1—N3	86.05 (14)
O3 ⁱ —Mn1—N2	84.80 (14)		

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

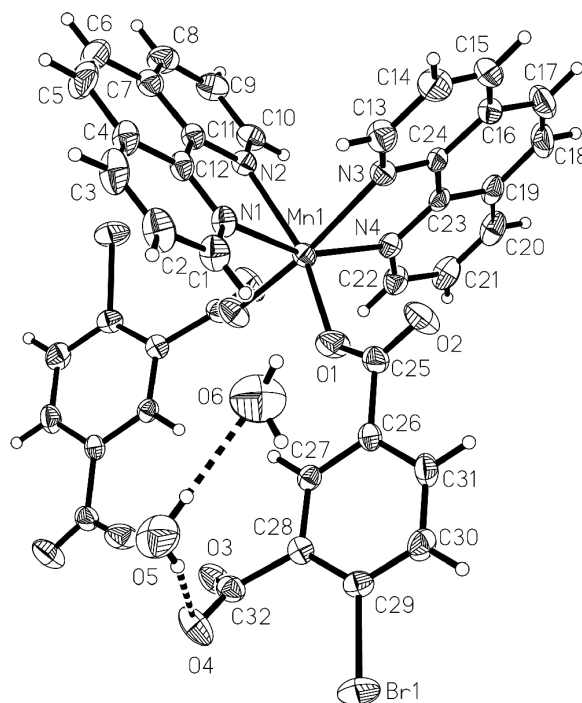


Figure 1

The coordination environment of the Mn atom in (I), with atomic numbering, showing displacement ellipsoids at the 30% probability level. The unlabelled atoms are generated by the symmetry code ($1 - x, 1 - y, 1 - z$). The dashed lines indicate hydrogen bonds.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O5—H5A \cdots O4	0.86 (7)	2.01 (7)	2.852 (8)	165 (6)
O5—H5B \cdots O6	0.84 (8)	2.06 (8)	2.900 (11)	177 (8)
O6—H6B \cdots O2 ⁱⁱ	0.86 (2)	2.08 (7)	2.707 (7)	129 (7)

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

The water H atoms were located in a difference map and refined isotropically. O—H and H \cdots H distances involving atom O6 were restrained to 0.85 (2) and 1.39 (2) Å, respectively and $U_{\text{iso}}(\text{H6B})$ was set at $1.5U_{\text{eq}}(\text{O6})$. H atoms attached to C atoms were placed in calculated positions and included in the refinement in the riding-model approximation [$\text{C—H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

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: SHELXTL (Bruker, 2002); software used to prepare material for publication: SHELXL97.

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