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Bis[4-bromo-2-(pyridin-2-ylmethyliminomethyl)phenolato]manganese(III) nitrate

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Key indicators

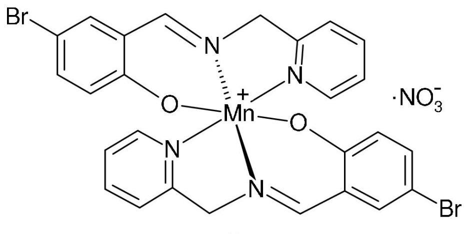
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.046
wR factor = 0.125
Data-to-parameter ratio = 16.1

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

The title compound, $[Mn(C_{13}H_{10}BrN_2O)_2]NO_3$, consists of a mononuclear manganese(III) complex cation and a nitrate anion. In the cation, the Mn^{III} atom is coordinated by four N atoms and two O atoms from two tridentate Schiff base ligands, forming an octahedral complex.

Comment

Manganese is a metal with a number of oxidation states (II–IV) under normal conditions, which results in its presence in naturally occurring processes and in magnetic materials. Examples include the photosynthetic water-oxidizing complex (WOC) of green plants (Zouni *et al.*, 2001; Wieghardt, 1989; Bruckner *et al.*, 1993; Vincent & Christou, 1989) and cyanobacteria containing an Mn_4 unit (Law *et al.*, 1998; Yocum & Pecoraro, 1999). Single-molecule magnets are derived from Mn_{12} complexes, with slow-relaxation magnetization and quantum tunnelling of magnetization (Sessoli *et al.*, 1993; Thomas *et al.*, 1996). In order to mimic the behaviour of these manganese clusters, a number of manganese complexes have been synthesized, among which some crystal structures revealed the existence of significant electrostatic interaction between the Mn atom and the ligand (Nie *et al.*, 2001; Hu *et al.*, 2002; Liu & Xu, 2003). We report here a new manganese(III) complex, (I) (Fig. 1).



(I)

In the cation of (I), the Mn^{III} atom displays an octahedral geometry and is coordinated by two Schiff base ligands. Each Schiff base acts as a tridentate ligand and ligates to the Mn atom through one phenolate O atom, one imine N atom, and one pyridine N atom. The three *trans* angles at Mn are all close to 180° (Table 1). The other angles are close to 90°, ranging from 83.05 (14) to 98.51 (14)°, which indicates a slightly distorted octahedral geometry of the Mn atom. The six bond lengths around the Mn atom are similar, ranging from 1.883 (3) to 1.958 (3) Å. The average Mn—O bond length [1.892 (3) Å] and $Mn—N_{imine}$ bond length [1.892 (3) Å] are comparable to other values observed in Schiff base manganese(III) complexes (Zhang *et al.*, 1999, 2000). The N1—Mn1—N2 and N3—Mn1—N4 bond angles deviate from 90° by

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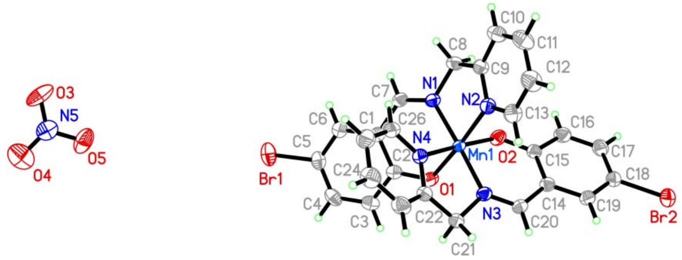

Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the major component of the disordered nitrate anion is shown.

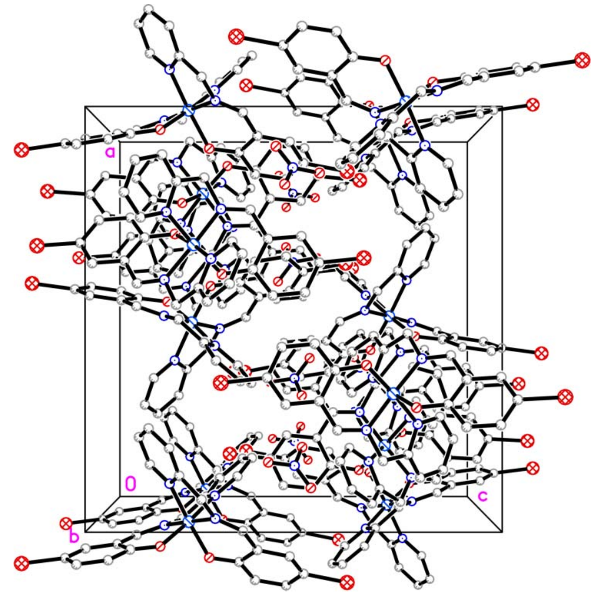

Figure 2
The crystal packing of (I) viewed along the *b* axis. H atoms have been omitted. Only the major components of the disordered nitrate anions are shown.

6.59 (14) and 6.95 (14)°, respectively, because of the strain created, respectively, by the Mn1/N1/C8/C9/N2 and Mn1/N3/C21/C22/N4 five-membered chelate rings. In the crystal structure, there are no obviously short contacts (Fig. 2).

Experimental

5-Bromosalicylaldehyde (0.1 mmol, 20.1 mg) and 2-aminomethylpyridine (0.1 mmol, 10.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred for 1 h to give a yellow solution, which was added to a stirred aqueous solution (5 ml) of $Mn(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 28.7 mg). The mixture was stirred at room temperature for 30 min, then filtered. The filtrate was kept in air for 12 d, forming brown block-shaped crystals.

Crystal data

$[Mn(C_{13}H_{10}BrN_2O)_2]NO_3$
$M_r = 697.23$
Tetragonal, $P4_2/n$
$a = 17.608$ (3) Å
$c = 17.224$ (3) Å
$V = 5340.2$ (16) Å^3
$Z = 8$
$D_x = 1.734$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 8655 reflections
$\theta = 2.3$–21.7°
$\mu = 3.53$ mm^{-1}
$T = 298$ (2) K
Block, brown
0.23 × 0.21 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.466$, $T_{max} = 0.548$
60512 measured reflections
6135 independent reflections
3995 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.5°$
$h = -22 \rightarrow 22$
$k = -22 \rightarrow 22$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.125$
$S = 1.02$
6135 reflections
380 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 7.176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.90$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.883 (3)	Mn1—O2	1.901 (3)
Mn1—N1	1.892 (3)	Mn1—N2	1.954 (3)
Mn1—N3	1.893 (3)	Mn1—N4	1.958 (3)
O1—Mn1—N1	92.39 (13)	N3—Mn1—N2	98.51 (14)
O1—Mn1—N3	85.68 (13)	O2—Mn1—N2	88.75 (13)
N1—Mn1—N3	177.65 (14)	O1—Mn1—N4	90.54 (13)
O1—Mn1—O2	91.62 (13)	N1—Mn1—N4	95.65 (14)
N1—Mn1—O2	87.88 (13)	N3—Mn1—N4	83.05 (14)
N3—Mn1—O2	93.50 (13)	O2—Mn1—N4	175.78 (13)
O1—Mn1—N2	175.77 (13)	N2—Mn1—N4	89.37 (14)
N1—Mn1—N2	83.41 (14)		

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The O atoms of the nitrate anion are disordered over two distinct sites, with occupancies of 0.512 (8) and 0.488 (8). The N—O and O···O distances in both disordered components were restrained to be equal.

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

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