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Triaqua(2,2′-bipyridine-κ^2N,N')-(nitrato-κO)manganese(II) nitrate

Xiaofeng Zhang, Deguang Huang, Wenguo Wang, Changneng Chen and Qiutian Liu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: lqt@ms.fjirsm.ac.cn

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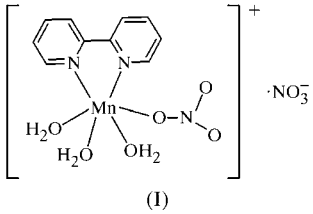
The crystal structure of the title compound, $[Mn(NO_3)(C_{10}H_8N_2)(H_2O)_3]NO_3$, contains a monomeric $[Mn(NO_3)(bpy)(H_2O)_3]^+$ cation (bpy is 2,2′-bipyridine) and a nitrate anion. The Mn^{II} ion is coordinated by one chelating bpy [Mn—N 2.241 (3) and 2.259 (3) Å], three water molecules [Mn—O 2.120 (3)–2.188 (3) Å] and a nitrate ligand [Mn—O 2.228 (2) Å] in a distorted octahedral geometry. There are O···H—O hydrogen-bonding interactions between the ligated water molecules and the ligated and unligated nitrate anions, resulting in double columns of stacked cations and anions.

Comment

Manganese complexes have attracted considerable interest recently, because of the frequent occurrence of such metal centres in biological systems (Wieghardt, 1989), especially in the oxygen evolving centre (OEC) of photosystem II (PSII) in green plants. It is thought that the coordination environment of Mn in the OEC contains O- and N-donors. The binding of a water ligand to the Mn site may be important in the oxidation



(I)

of the water for the evolution of dioxygen. In recent years, manganese–bpy (bpy is 2,2′-bipyridine) complexes have been extensively studied as model compounds for simulating the OEC in PSII (Vincent *et al.*, 1987, 1989). The complex behaviour of bpy with the Mn^{II} ion gives rise to a wide variety of Mn–bpy coordination complexes, of which most of the mononuclear compounds contain the $[Mn(bpy)_2]^{2+}$ core. In an attempt to synthesize Mn–Ca–bpy bimetallic complexes, we isolated the title complex, $[Mn(NO_3)(bpy)(H_2O)_3]NO_3$, (I), the cation of which contains three coordinated water molecules and only one bpy ligand.

The crystal structure of (I) consists of a discrete $[Mn(NO_3)(bpy)(H_2O)_3]^+$ cation and one nitrate anion. As illustrated in Fig. 1, the Mn^{II} ion is located in a very distorted octahedral environment, with three *trans* angles ranging from 164.58 (11) to 169.30 (12)°. The two chelating N atoms (N1 and N2) of the bpy ligand and two coordinated O atoms (O2 and O3) of two water molecules form an equatorial plane, with the largest deviation from the least-squares plane being 0.018 (3) Å for atom N2. The Mn^{II} ion lies out of this plane by 0.018 (8) Å. The axial positions are occupied by two other O atoms, namely atom O4 from the nitrate ligand and the third

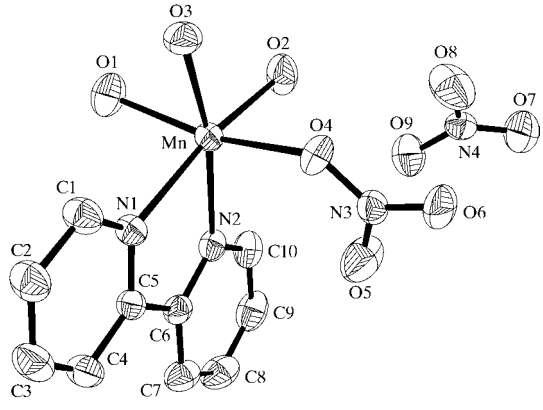


Figure 1
A view of the structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

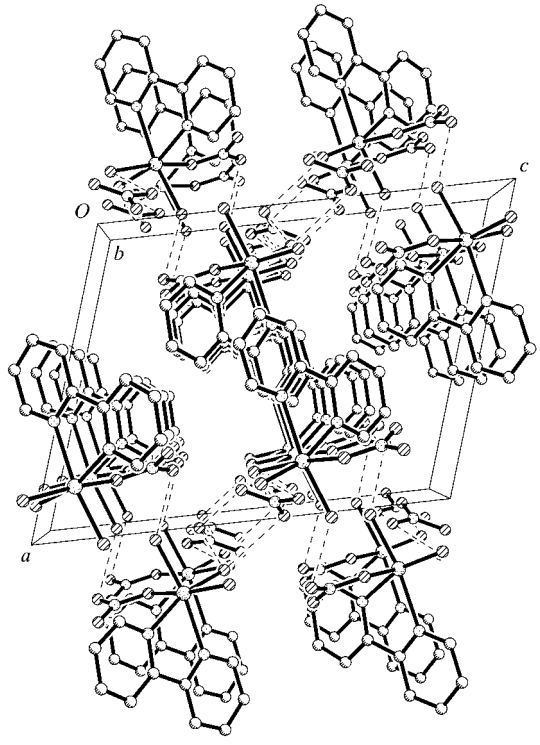


Figure 2
A packing diagram for (I), with hydrogen bonds shown as dashed lines.

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ligated water molecule, atom O1. The bpy ligand exhibits its usual acute N···N bite distance of 2.669 (4) Å and N—Mn—N bite angle of 72.75 (10)°. These values are very close to those found in $[MnCl_2(bpy)_2]$ (Lumme & Lindell, 1988), $[Mn(NCS)_2(bpy)_2]$ (Veidis *et al.*, 1981) and $[MnCl(bpy)_2(H_2O)]$ (Chen *et al.*, 1995).

Strong hydrogen bonds (Table 2) between the ligated NO_3^- anion and water molecules link neighbouring $[Mn(NO_3)(bpy)(H_2O)_3]^+$ cations. There are also three strong hydrogen bonds between ligated water molecules and the NO_3^- counter-ion, also listed in Table 2. Double columns of stacked cations and stacked anions occur in the structure of (I) (Fig. 2). Interestingly, although there is no hydrogen-bonding interaction between two series of such double columns, the alternate stacking of the rings of the bpy ligands results in the ring separation ranging from 3.8 to 4.7 Å, which is slightly larger than the sum of the van der Waals radii of two C atoms (Hunter & Sanders, 1990), exhibiting weak $\pi\cdots\pi$ interactions. It is believed that these hydrogen-bonding and $\pi\cdots\pi$ interactions may play an important role in stabilizing the crystal structure of (I).

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.153 (3)	Mn—O4	2.228 (2)
Mn—O2	2.120 (3)	Mn—N1	2.241 (3)
Mn—O3	2.188 (3)	Mn—N2	2.259 (3)
O2—Mn—O1	91.82 (13)	O3—Mn—N1	91.81 (10)
O2—Mn—O3	98.65 (13)	O4—Mn—N1	91.95 (10)
O1—Mn—O3	87.04 (13)	O2—Mn—N2	96.76 (12)
O2—Mn—O4	87.93 (11)	O1—Mn—N2	93.05 (12)
O1—Mn—O4	165.33 (12)	O3—Mn—N2	164.58 (11)
O3—Mn—O4	78.50 (10)	O4—Mn—N2	101.55 (9)
O2—Mn—N1	169.30 (12)	N1—Mn—N2	72.77 (10)
O1—Mn—N1	90.99 (12)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···O8^{i}	0.827 (19)	2.12 (2)	2.890 (5)	156 (4)
O2—H2*C*···O6^{i}	0.85 (2)	2.02 (2)	2.868 (4)	173 (5)
O3—H3*C*···O9^{ii}	0.84 (6)	2.07 (3)	2.870 (4)	159 (7)
O3—H3*B*···O9^{iii}	0.84 (4)	2.02 (2)	2.848 (4)	169 (5)

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

Experimental

A mixture of $Mn(NO_3)_2{\cdot}4H_2O$ (0.50 g, 2.0 mmol), $Ca(NO_3)_2{\cdot}4H_2O$ (0.24 g, 1.0 mmol), 2,2′-bipyridine (0.31 g, 1.98 mmol) and $ClCH_2COOH$ (0.28 g, 2.96 mmol) in CH_3OH (20 ml) was refluxed for 22 h. After filtration, the filtrate was allowed to stand for one month, yielding yellow crystals of (I).

Crystal data

$[Mn(NO_3)(C_{10}H_8N_2)(H_2O)_3]NO_3$
M_r = 389.19
Monoclinic, $P2_1/c$
a = 11.5797 (5) Å
b = 9.5007 (4) Å
c = 14.8683 (6) Å
β = 107.8990 (10)°
V = 1556.57 (11) Å^3
Z = 4
D_x = 1.661 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2683 reflections
θ = 1.9–25.1°
μ = 0.90 mm^{-1}
T = 293 (2) K
Block, yellow
0.42 × 0.34 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.615, T_{max} = 0.805
5036 measured reflections
2708 independent reflections
2032 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.1°
$h = -8 \rightarrow 13$
$k = -6 \rightarrow 11$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.135
S = 0.93
2708 reflections
241 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

H atoms bonded to C atoms were inserted at calculated positions with C—H = 0.93 Å, and treated as riding atoms. H atoms associated with water molecules were located from difference maps and refined freely.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL* (Siemens, 1994); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1358). Services for accessing these data are described at the back of the journal.

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