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trans-Diaqua(bipyridyl)(salicylato)manganese(III) Perchlorate Monohydrate

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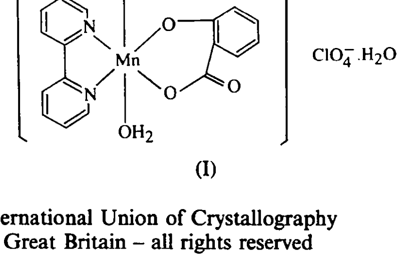
Abstract

The mononuclear manganese(III) complex $[Mn(sal)(bpy)(H_2O)_2]ClO_4.H_2O$ (sal = salicylate, $C_7H_4O_3^{2-}$; bpy = bipyridyl, $C_{10}H_8N_2$) has been prepared and characterized by X-ray analysis. The manganese(III) ion displays elongated octahedral coordination with mutually *trans* water molecules occupying axial sites. The equatorial plane, defined by two sal O atoms and two bpy N atoms, nearly coincides with the sal and bpy ligand planes and with the metal ion.

Comment

The chemistry of manganese is currently receiving much attention owing to its participation in many biological systems (Christou, 1989). Of particular importance has been the realisation that manganese plays an essential and specific role in the water-oxidizing complex of photosystem II (Christou, 1989; Wieghardt, 1989). We now report the preparation and structure of the title mononuclear manganese(III) complex, (I), which contains a salicylate ligand whose phenoxide and carboxylate functions act as convenient models for the side groups of the amino acids tyrosine and aspartic and glutamic acid.



(I)

The asymmetric unit (Fig. 1) consists of the complex cation $[Mn(sal)(bpy)(H_2O)_2]^+$, a ClO_4^- anion and a water molecule. The Mn^{III} ion is hexacoordinate and possesses an N_2O_4 ligand environment by virtue of the bidentate salicylate and bipyridyl ligands which form the equatorial plane (O11, O12, N201 and N208) and the two axial water molecules which complete an octahedron round the metal ion. The phenolate and carboxylate O atoms O11 and O12 are *cis*. The equatorial Mn—O11 and Mn—O12 bond lengths [1.830 (2) and 1.871 (4) Å, respectively] are similar to those in the complex $[Mn(EtOH)_4][Mn_2(sal)_4(py)_2]$ (py = pyridine) (Vincent, Huffman & Christou, 1986) in which the Mn^{III}—N bond lengths lie in the range 1.863 to 1.911 Å. The Mn—N bond lengths in the title complex [2.034 (3) and 2.041 (4) Å] are longer, but agree with the values observed for $Mn^{III}(hgn)_3$ (hgn = 8-hydroxyquinolinate) (2.057–2.058 Å). The axial Mn—O distances [2.225 (4) and 2.240 (4) Å] are distinctly longer than those in the equatorial plane. Such marked axial elongation is typical for high spin d^4 systems. With the exceptions of the internal bpy angle N201—Mn—N208 [79.2 (1)°], which is restricted by the five-membered chelate ring, and O12—Mn—N201 [171.0 (2)°], the bond angles at Mn [86.2 (1) to 95.6 (1), and 174.0 (1)°] are reasonably close to those for an ideal octahedron (90 and 180°, respectively). The deviation of the Mn atom from the N_2O_2 equatorial plane is 0.012 Å; the Mn atom and all bpy and salicylate atoms are approximately coplanar. The ClO_4^- anion is linked to a coordinated water molecule by the hydrogen bond O2—Hw21···O41 (O2···O41 2.824 Å, O2—Hw21···O41 173°).

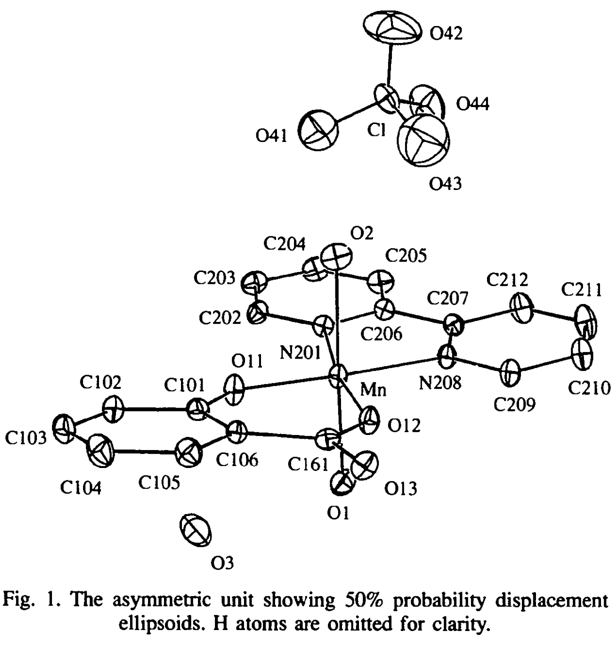


Fig. 1. The asymmetric unit showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

A solution of (^{n}Bu$_4$N)MnO$_4$ (2 mmol) in 1:1 MeOH/MeCN (15 ml) and a solution of 2,2-bipyridyl (3.5 mmol) in 1:1 MeOH/MeCN (15 ml) were simultaneously added dropwise to a stirred solution of manganese(III) acetate (5 mmol) and NaHsal (5 mmol) in 1:1 MeOH/MeCN (30 ml). The solution gradually turned black. After stirring for 3 h it was filtered. Block-shaped crystals were obtained by vapour diffusion of Et$_2$O into the deep green filtrate for three weeks. The products were purified by dissolution in EtOH (30 ml) followed by filtration and addition of Et$_2$O (15 ml) to the filtrate. After a week, deep green prismatic crystals suitable for X-ray diffraction studies were obtained in 45% yield.

Crystal data

[Mn(C$_7$H$_4$O$_3$)(C$_{10}$H$_8$N$_2$)-(H$_2$O)$_2$]ClO$_4$.H$_2$O
$M_r = 500.73$
Triclinic
$P\bar{1}$
$a = 7.611\,(2)$ Å
$b = 11.808\,(2)$ Å
$c = 12.609\,(2)$ Å
$\alpha = 103.86\,(1)^\circ$
$\beta = 103.12\,(1)^\circ$
$\gamma = 103.48\,(1)^\circ$
$V = 1020.9\,(4)$ Å^3
$Z = 2$
$D_x = 1.629$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.4\text{–}13.6^\circ$
$\mu = 0.809$ mm^{-1}
$T = 294\,(1)$ K
Prismatic
0.3 × 0.2 × 0.2 mm
Deep green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans
$T_{\min} = 0.904$, $T_{\max} = 0.999$
3751 measured reflections
3373 independent reflections

2695 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.029$
$\theta_{\max} = 25^\circ$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 1.79%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.048$
$S = 1.094$
2695 reflections
280 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = 0.14$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Mn	0.78205 (9)	0.01646 (6)	0.79932 (5)	2.40 (1)
O1	1.0091 (4)	−0.0716 (3)	0.7897 (3)	3.90 (8)
O2	0.5669 (4)	0.1176 (3)	0.7993 (2)	3.80 (7)
O3	0.8139 (6)	−0.3070 (4)	0.6469 (4)	6.9 (1)
Cl	0.6064 (2)	0.3726 (1)	0.6764 (1)	4.20 (3)
O41	0.652 (1)	0.3583 (5)	0.7846 (5)	16.0 (3)
O42	0.5383 (9)	0.2571 (5)	0.6018 (5)	10.7 (2)
O43	0.4888 (8)	0.4383 (6)	0.6845 (9)	16.1 (3)
O44	0.7689 (6)	0.4405 (4)	0.6620 (5)	8.7 (2)
O12	0.7594 (4)	−0.0075 (3)	0.9375 (2)	2.96 (6)
C161	0.6321 (5)	−0.0858 (3)	0.9581 (3)	2.48 (8)
C106	0.4834 (5)	−0.1837 (3)	0.8615 (3)	2.46 (8)
C105	0.3452 (6)	−0.2656 (4)	0.8865 (4)	3.5 (1)
C104	0.2066 (7)	−0.3619 (4)	0.8014 (4)	4.3 (1)
C103	0.2052 (6)	−0.3795 (4)	0.6881 (4)	3.9 (1)
C102	0.3386 (6)	−0.3004 (4)	0.6607 (4)	3.3 (1)
C101	0.4781 (5)	−0.2003 (4)	0.7464 (3)	2.70 (9)
O13	0.6393 (4)	−0.0781 (3)	1.0584 (2)	3.20 (7)
O11	0.6006 (4)	−0.1280 (3)	0.7109 (2)	3.34 (7)
N201	0.8314 (4)	0.0703 (3)	0.6638 (3)	2.51 (7)
C202	0.7382 (6)	0.0066 (4)	0.5538 (3)	3.1 (1)
C203	0.7820 (7)	0.0477 (4)	0.4662 (4)	3.9 (1)
C204	0.9264 (7)	0.1541 (5)	0.4932 (4)	4.1 (1)
C205	1.0223 (6)	0.2195 (4)	0.6065 (4)	3.6 (1)
C206	0.9702 (5)	0.1764 (4)	0.6906 (3)	2.62 (9)
C207	1.0575 (6)	0.2395 (4)	0.8142 (3)	2.69 (9)
C209	1.0526 (6)	0.2294 (4)	0.9966 (3)	3.2 (1)
C210	1.1845 (7)	0.3429 (4)	1.0472 (4)	4.1 (1)
C211	1.2550 (7)	0.4047 (5)	0.9796 (4)	4.7 (1)
C212	1.1924 (7)	0.3533 (4)	0.8621 (4)	4.1 (1)
N208	0.9877 (4)	0.1796 (3)	0.8820 (3)	2.58 (7)

Table 2. *Selected geometric parameters* (Å, °)

Mn—O1	2.225 (4)	N208—C207	1.354 (6)
Mn—O2	2.240 (4)	O12—C161	1.292 (5)
Mn—O12	1.871 (4)	O13—C161	1.234 (5)
Mn—O11	1.830 (2)	O11—C101	1.341 (5)
Mn—N201	2.041 (4)	C106—C161	1.481 (4)
Mn—N208	2.034 (3)	C206—C207	1.473 (5)
O1—Mn—O2	174.0 (1)	O1—Mn—O12	95.6 (1)
O1—Mn—O11	90.7 (1)	O1—Mn—N201	86.2 (1)
O1—Mn—N208	88.4 (1)	O2—Mn—O12	89.6 (1)
O2—Mn—O11	91.9 (1)	O2—Mn—N201	88.3 (1)
O2—Mn—N208	88.4 (1)	O12—Mn—O11	94.1 (1)
O12—Mn—N201	171.0 (2)	O12—Mn—N208	91.9 (1)
O11—Mn—N201	94.9 (1)	O11—Mn—N208	174.0 (1)
N201—Mn—N208	79.2 (1)	O12—C161—C106	119.5 (4)
O12—C161—O13	119.1 (3)	C106—C161—O13	121.4 (4)
C161—C106—C101	123.0 (4)	C106—C101—O11	124.7 (3)
C102—C101—O11	116.2 (4)	N201—C206—C207	114.7 (4)
C206—C207—N208	114.5 (4)		

Data collection and cell refinement: CAD-4 diffractometer software (Enraf–Nonius, 1988). Program used to solve structure: *MULTAN* (Germain, Main & Woolfson, 1971). Program used to refine structure: *SDP-Plus* (Frenz, 1985). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and a packing diagram, have been deposited with the IUCr (Reference: MU1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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