

Tetrakis[(4-aminopyridinio)acetato- κ O]diaquamanganese(II) diperchlorate

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Received 24 October 2001

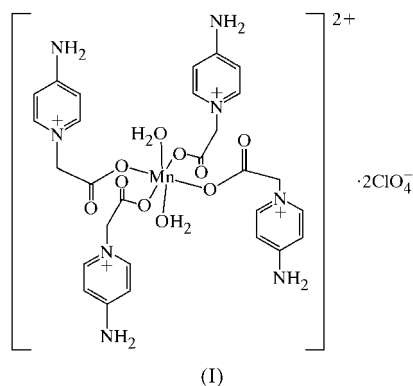
Accepted 7 January 2002

Online 28 February 2002

In the centrosymmetric title complex, $[\text{Mn}(\text{C}_7\text{H}_8\text{N}_2\text{O}_2)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, the Mn^{II} ion is in an octahedral environment, with the equatorial plane being defined by the O atoms of four monodentate carboxylate groups, and the octahedron being completed by two *trans*-coordinated water molecules. There are intramolecular hydrogen bonds between the coordinated water molecules and the non-coordinated O atoms of the carboxylate groups. Hydrogen bonds between the amino groups and the carboxylate groups of neighbouring molecules generate a layered hydrogen-bonded network.

Comment

Manganese complexes containing coordinated carboxylate have been extensively studied for their structural chemistry and biological function. Much research has focused on the



preparation of model compounds to mimic various manganese enzymes, such as manganese catalase (Christou, 1989) and the water-oxidizing oxygen-evolving complex (OEC) of photosystem II (Linburg *et al.*, 1999). A rich structural diversity of carboxylate-containing Mn complexes has been revealed. The carboxylate ligand can coordinate to Mn (in different oxidation states) in different coordination fashions, such as *syn* and

anti, and monodentate and bidentate (Iikura & Nagata, 1998). Here, we present the structure of a further such complex, the title compound, (I).

The structure described here shows (I) to be a centrosymmetric mononuclear species, with Mn at a crystallographic centre of symmetry. The Mn^{II} ion is in an octahedral environment, with the equatorial plane being defined by the O atoms of four monodentate carboxylate groups of the (4-aminopyridinio)acetate ligands, and the octahedron being completed by two *trans*-coordinated water molecules (Fig. 1). The perchlorate ions are not coordinated to Mn.

The bond lengths and angles in (I) are normal, and the unique angles in the octahedron are close to ideal (Table 1). In particular, the Mn–O1W distance (Mn–water) is 2.225 (2) Å, which is similar to the value of 2.218 (2) Å found in $[\text{Mn}(\text{HC}_4\text{O}_3\text{NH}_2)_2(\text{H}_2\text{O})_6]$ by Hosein *et al.* (1998). The C–O distances in (I) are normal, indicating that the coordination of Mn^{II} to acetate does not affect the geometry of the acetate.

The dihedral angles of the basal plane through atoms O2, O2A, O4 and O4A with the O2- and O4-containing acetate plane are 37.5 (2) and 56.5 (1)°, respectively. The dihedral angles between the N3- and N4-containing pyridyl rings and the C2- and C9-containing acetate planes are 77.8 (2) and 61.7 (2)°, respectively. The orientation of the pyridyl ring is defined by the torsion angles of 179.6 (3)° for C2–N3–C3–C4 and 178.4 (4)° for C9–N4–C14–C13.

The non-coordinated carboxylate O atoms (O1 and O3) and the water molecule (O1W) are *cis* with respect to the equatorial plane (Fig. 1), and each of O1 and O3 is the receptor in an intramolecular hydrogen bond from O1W (Table 2). In the

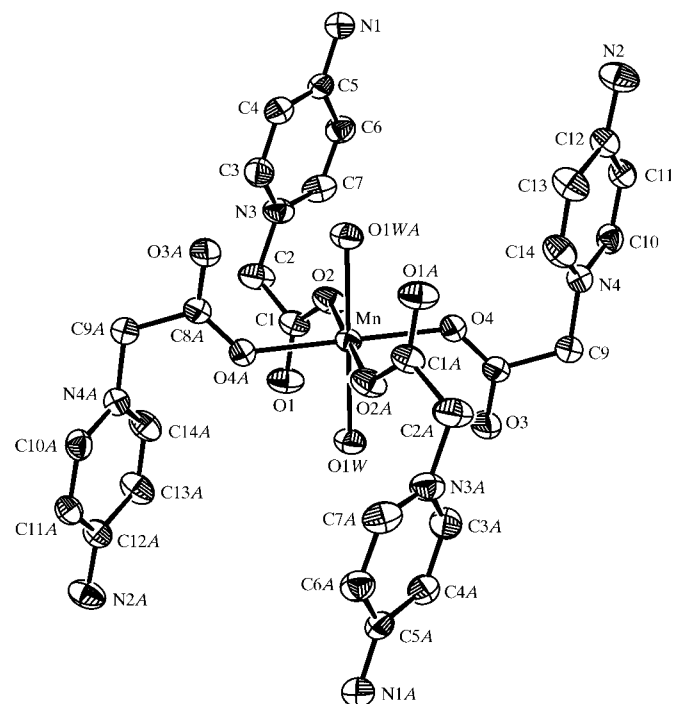


Figure 1
A view of the structure of (I) showing the atom-numbering scheme, with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

crystal, intermolecular hydrogen bonds between the amino group of the ligand and the O atoms of the carboxylate groups from neighbouring molecules, together with weak hydrogen bonds formed between the amino groups and a disordered perchlorate ion, form a layered hydrogen-bonded network.

Experimental

Mn(ClO₄)₂·6H₂O (1.00 mmol) was mixed with 4-amino-*N*-pyridine acetate (4.00 mmol) in a thick Pyrex tube, and pyridine (0.10 ml) and *n*-butanol (2.50 ml) were then added. The solution was heated at 363 K for 2 d, and was then kept at ambient temperature for one week for crystallization to occur. Colourless prismatic crystals of (I) were formed.

Crystal data

[Mn(C ₇ H ₈ N ₂ O ₂) ₄ (H ₂ O) ₂](ClO ₄) ₂	<i>Z</i> = 1
<i>M_r</i> = 898.49	<i>D_x</i> = 1.583 Mg m ⁻³
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 9.049 (2) Å	Cell parameters from 2867 reflections
<i>b</i> = 10.507 (3) Å	<i>θ</i> = 1.4–27.8°
<i>c</i> = 10.779 (3) Å	<i>μ</i> = 0.58 mm ⁻¹
<i>α</i> = 71.79 (4)°	<i>T</i> = 293 (2) K
<i>β</i> = 89.52 (4)°	Prism, colourless
<i>γ</i> = 76.13 (4)°	0.3 × 0.2 × 0.2 mm
<i>V</i> = 942.7 (4) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	3275 independent reflections
<i>φ</i> and <i>ω</i> scans	2834 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: empirical (<i>SADABS</i> ; Sheldrick, 1997)	<i>R</i> _{int} = 0.043
<i>T</i> _{min} = 0.870, <i>T</i> _{max} = 0.901	<i>θ</i> _{max} = 25°
4859 measured reflections	<i>h</i> = -8 → 10
	<i>k</i> = -11 → 12
	<i>l</i> = -10 → 12

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0923P)^2 + 0.2644P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.05	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
3275 reflections	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$
295 parameters	
H-atom parameters constrained	

All H atoms were placed in geometrically calculated positions, with C–H = 0.93–0.97 Å and N–H = 0.86 Å, and refined as riding atoms, with *U*_{iso}(H) = 1.2*U*_{eq}(parent atom). The occupancy factor for a second orientation of the perchlorate ion refined to a value close to 0.5, so the occupancies of the perchlorate O atoms were set to 0.5 for the final refinement.

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

Table 1

Selected geometric parameters (Å, °).

Mn–O4	2.133 (2)	N2–C12	1.322 (4)
Mn–O2	2.151 (2)	C2–N3	1.469 (5)
Mn–O1W	2.225 (2)	C3–C4	1.344 (5)
O1–C1	1.238 (4)	N3–C7	1.337 (5)
O2–C1	1.240 (4)	N4–C10	1.349 (5)
O3–C8	1.238 (4)	N4–C14	1.349 (5)
O4–C8	1.240 (4)	N4–C9	1.459 (5)
N1–C5	1.330 (5)	C5–C6	1.411 (5)
O4–Mn–O2	90.15 (11)	O1–O1W–O3	111.15 (13)
O4–Mn–O1W	91.80 (10)	N3–C2–C1	113.1 (3)
O2–Mn–O1W	89.49 (9)	C7–N3–C2	120.3 (3)
C1–O2–Mn	127.5 (2)	N1–C5–C4	122.5 (3)
C8–O4–Mn	130.8 (2)	O3–C8–O4	126.6 (3)
O1–C1–O2	127.5 (3)	O3–C8–C9	116.3 (3)
O1–C1–C2	115.6 (3)	N2–C12–C11	121.9 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1W–H1WA···O3	0.90	1.93	2.787 (4)	160
O1W–H1WB···O1	0.90	2.05	2.856 (4)	158
N1–H1A···O3 ⁱ	0.86	2.05	2.879 (5)	163
N2–H2A···O2 ⁱⁱ	0.86	2.35	3.072 (5)	142
N2–H2A···O4 ⁱⁱ	0.86	2.51	3.205 (5)	138
N2–H2B···O1 ⁱⁱⁱ	0.86	2.35	3.038 (5)	137

Symmetry codes: (i) *x*, *y*, *z* – 1; (ii) 1 – *x*, –*y*, 1 – *z*; (iii) 1 + *x*, *y* – 1, *z*.

This work was funded by the National Natural Science Foundation of China (grant Nos. 29871017 and 29823001). The authors thank Mr Yong-Jiang Liu (Coordination Chemistry Institute, Nanjing University) for the X-ray structure determination.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1355). Services for accessing these data are described at the back of the journal.

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