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X-ray Structure Analysis Online

Crystal Structure of Aqua[*N*,*N*′-bis(3-methoxysalicylidene)propane-1,2-diaminato]methanolmanganese(III) Perchlorate

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The title compound, a hydrogen-bonded pseudo-dimer, $Mn(C_{19}H_{18}N_2O_4)(CH_4O)(H_2O)]ClO_4$, (I), has been structurally characterized. Complex (I) affords an elongated octahedral coordination environment, with axial Mn–O(CH_3OH) = 2.296(5) and Mn–O(water) = 2.208(3)Å.

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Manganese-Schiff base complexes have been of great interest in recent years because of their important role in the development of coordination chemistry as well as inorganic biochemistry, catalysis and optical and magnetic materials.[1–3] Recently, we reported a hydrogen-bonded zigzag chain manganese(III) complex.[4] As an extension of the research on the structural characterization of Mn^{III} compounds, here the crystal structure of the title compound, (I), which is a hydrogen-bonded linear chain of a pseudodimers Schiff-base Mn^{III} complex having elongated axial Mn–O bonds to two aqua ligands, is reported.

The ligand was prepared by the reaction of 1,2-diaminopropane (1 mmol) with 3-methoxysalicylaldehyde (2 mmol) in hot ethanol (100 mL). A yellow compound was precipitated from the solution upon cooling. The title compound was prepared by the addition of manganese(III) acetate dihydrate (1 mmol) in 70 mL of hot ethanol to the ligand (1 mmol) in 140 mL of hot methanol. The resulting solution was stirred for 10 min. After the solution had been filtered, a methanol solution of sodium perchlorate monohydrate (1.71 mmol) was added to the filtrate. The solution was warmed to 50°C; then, 20 cm^3 of hot water was added, and the solution was filtered rapidly. A deep-green solution was obtained, and then allowed to stand at room temperature. Several weeks of standing had led to the growth of deep-green crystals of the title compound, suitable for X-ray analysis. *Anal*. Calcd for $C_{20}H_{24}ClMnN_2O_{10}$: C, 44.25; H, 4.46; N, 5.16%. Found: C, 44.50; H, 4.33; N, 5.35%.

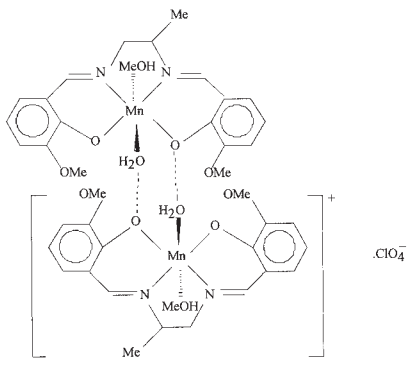

Fig. 1 Schematic diagram of the title compound.

Diffraction measurements were made on three-circle CCD diffractometers using graphite-monochromated Mo-K_α radiation at 100 K. The intensity data were integrated using the SAINT program. The structure was solved by direct methods, and refined using full-matrix least squares against F^2 using SHELXTL. All non-hydrogen atoms were refined anisotropically. There is disorder in the perchlorate anion, which is a commonly observed phenomenon in the X-ray structures of perchlorate salts because of the spherical nature of this anion. The perchlorate was modelled using the SHELXTL program. The O8 atom was split into O8A and O8B with 67% and 33% occupancy, respectively. The O10 atom was split into O10A and O10B with 65% and 35% occupancy, respectively. After refinement, the displacement parameters for perchlorate O10 atoms were still somewhat anisotropic, and the Cl–O distances showed variations, but further attempts with more disordered positions did not converge. Atom C18 also showed

Table 1 Crystal and experimental data

CCDC	662985
Formula	$C_{20}H_{24}ClMnN_2O_{10}$
Formula weight	542.80
Crystal system	monoclinic
Space group	$P2_1/c$ Z=4
Unit cell dimensions	a = 13.359(3)Å
	b = 13.338(3)Å β = 118.09(3)°
	c = 14.185(3)Å
Volume	2229.7(8)Å^3
D_{cal}	1.617 Mg/m^3
No. of reflections used	4092
θ range for data collection	2.23 to 27.48° with Mo K_α
μ	0.773 mm^{-1}
R	0.0886
Largest diff. peak and hole	1.364/–1.244 eÅ^{-3}
Measurement	Bruker SMART APEX CCD area detector
Program system	SAINT
Structure determination	SHELXTL
Refinement method	full-matrix least-squares on F^2

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Table 2 Selected geometric parameters [Å, °]

Mn(1)-N(1)	1.974 (4)	Mn(1)-O(2)	1.869 (4)
Mn(1)-N(2)	1.990 (5)	Mn(1)-O(5)	2.208 (3)
Mn(1)-O(1)	1.870 (4)	Mn(1)-O(6)	2.296 (5)
O(2)-Mn(1)-O(1)	92.54 (2)	N(1)-Mn(1)-O(5)	89.70 (2)
O(1)-Mn(1)-N(1)	91.89 (2)	N(2)-Mn(1)-O(5)	88.15 (2)
O(2)-Mn(1)-N(2)	92.24 (2)	O(2)-Mn(1)-O(6)	88.40 (2)
O(2)-Mn(1)-N(1)	175.37 (2)	O(1)-Mn(1)-O(6)	94.40 (2)
O(1)-Mn(1)-N(2)	174.38 (2)	N(1)-Mn(1)-O(6)	89.90 (2)
N(1)-Mn(1)-N(2)	83.30 (2)	N(2)-Mn(1)-O(6)	82.80 (2)
O(2)-Mn(1)-O(5)	91.28 (2)	O(5)-Mn(1)-O(6)	170.90 (2)
O(1)-Mn(1)-O(5)	94.69 (2)		

Table 3 Hydrogen bonding geometry (Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
O5–H5B···O1^{i}	0.89 (7)	2.25 (1)	2.969 (6)	139 (9)
O5–H5B···O3^{i}	0.89 (7)	2.13 (7)	2.898 (6)	145 (8)
O5–H5C···O2^{i}	0.89 (7)	2.29 (1)	2.916 (6)	127 (7)
O5–H5C···O4^{i}	0.89 (7)	2.03 (6)	2.883 (6)	161 (9)
O6–H6B···O10A^{ii}	0.92 (1)	2.10 (1)	2.871 (2)	141 (1)

Symmetry codes: (i)[–*x*+1, –*y*+1, –*z*], (ii)[*x*+1, *y*, *z*]

high anisotropy and a possibility of disorder. Two sets of positions (A & B) were refined with occupancies 0.68(A) & 0.32(B). The disorders of the structure resulted is short intermolecular contacts between atoms C20 and O8A^{iii} [symmetry code: (iii) –*x*+1, –*y*+1, –*z*+1] with the distance of 2.51 Å and between atoms C8 and O10B^{vi} [symmetry code: (iii) –*x*, *y*+1/2, *z*+1/2] with a distance of 2.87 Å. Residual density greater than 1 e Å^{-3} is located 1.37 and 1.22 Å from atom O7. The peaks indicate that there is a slight disorder of this O7 atom, which has not been allowed for.

In complex (I), the molecule comprises a manganese(III) centre coordinated by the nearly planar Schiff-base ligand [the angle between the least-squares planes of the aromatic rings of the ligands is 9.15°] with Mn–O_{phenol} bond lengths of 1.870(4)Å and 1.869(4)Å, together with Mn–N_{imin}, bond lengths of 1.974(4) and 1.990(5)Å. The coordination sphere of the manganese centre is completed by a methanol molecule [Mn–O_{metoh} 2.296(5)Å] and a water molecule [Mn–O_{water} 2.208(3)Å]. The central Mn^{III} ion adopts an elongated octahedral coordination geometry, with the displacement of the Mn1 ion from the O1/N1/N2/O2 least-squares plane is 0.035(2)Å. In the crystal structure of (I), adjacent molecules are linked by hydrogen bonds [O5···O1^{i} = 2.969 Å, O5···O2^{i} = 2.916 Å, O5···O3^{i} = 2.898 Å and O5···O4^{i} = 2.883 Å; symmetry code, (i) [–*x*+1, –*y*+1, –*z*], to form hydrogen-bonded pseudo-dimers, with additional face-to-face π-π stacking interactions between the benzene groups (C6···C10 = 3.697 Å and C5···C11 = 3.950 Å); symmetry code, (i) [–*x*+1, –*y*+1, –*z*]. Moreover, hydrogen bonds [O6–O10A^{ii} = 2.871 Å] (ii) [*x*+1, *y*, *z*] are formed between the axial methanol ligand and the perchlorate ion.

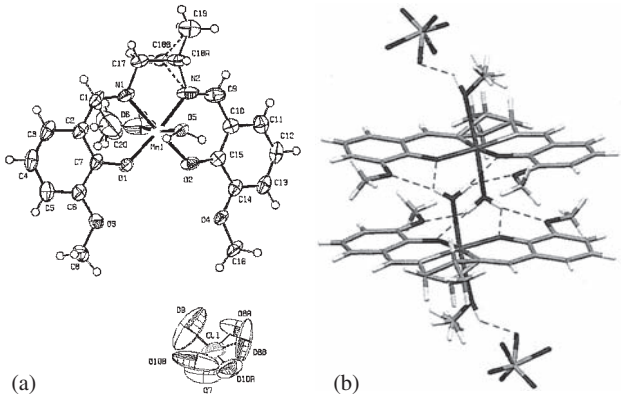

Fig. 2 (a) ORTEP drawing of the title compound with atom labeling; (b) Stick representation of the hydrogen-bonded (dashed lines) pseudo-dimer formed in (I).

Acknowledgements

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