Crystal structure of aquachloro[*N,N'*-bis(3-ethoxysalicylidene)propylenediiminato]manganese(III) dihydrate, $[Mn(C_{21}H_{24}N_2O_4)Cl(H_2O)] \cdot 2H_2O$

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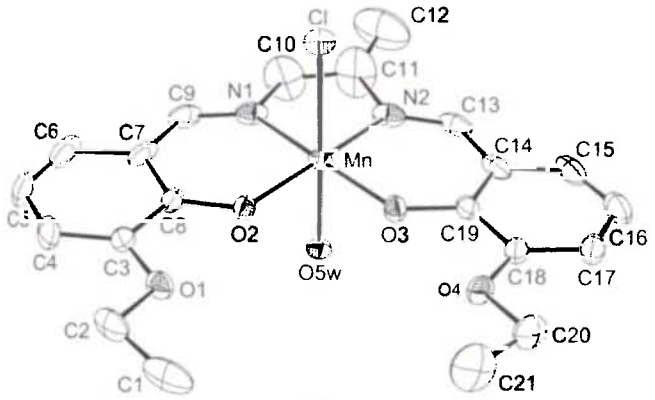

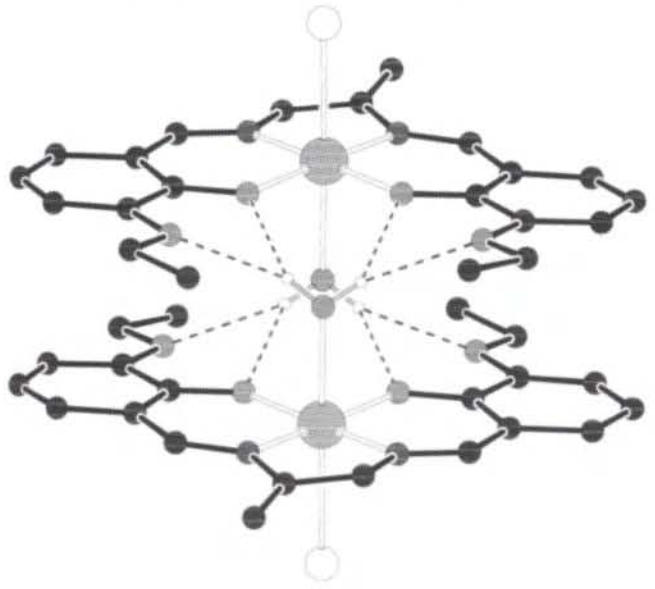

Abstract

$C_{21}H_{30}ClMnN_2O_7$, triclinic, $P\bar{1}$ (no. 2), a = 10.029(2) Å, b = 11.561(2) Å, c = 11.689(2) Å, α = 106.331(3)°, β = 107.874(3)°, γ = 99.092(3)°, V = 1192.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.071, $wR_{ref}(F^2)$ = 0.238, T = 293 K.

Source of material

To an ethanolic solution (25 ml) of 3-ethoxysalicylaldehyde (1.00 g, 6.02 mmol) was added 1,2-diaminopropane (0.25 ml, 2.93 mmol), and stirred for 6 h. The solid (*N,N'*-bis(3-ethoxysalicylidene)propylenediimine, $C_{21}H_{26}N_2O_4$) which precipitated was collected by filtration, washed with diethyl ether and dried in vacuo. For the synthesis of the Mn complex, $Mn(CH_3COO)_3 \cdot 2H_2O$ (0.50 g, 1.86 mmol), NaCl (0.11 g, 1.88 mmol) and $C_{21}H_{26}N_2O_4$ (0.70 g, 1.89 mmol) in EtOH (70 ml) and H_2O (5 ml) were stirred for 3 h at room temperature and then filtered. The solvent was removed in vacuo, the residue washed with acetone/diethyl ether and dried, to give a brown powder (0.97 g). Crystals suitable for X-ray diffraction measurement were obtained via slow evaporation from a water solution.

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Experimental details

The H atoms of the two solvent H_2O molecules could neither be located from Fourier difference maps nor added geometrically. The H atoms of the water ligand were localized from Fourier difference maps. The large R values and the large anisotropies of some atoms (C1, C10, C11, C12, C21) are connected with the disorder of the hydrate water, ethyl and propyl units.

Discussion

The crystal structure of the title compound consists of neutral complex $[Mn(C_{21}H_{24}N_2O_4)Cl(H_2O)]$ and two uncoordinated water molecules. Mn(III) ion is six-coordinated, $MnClN_2O_3$, and the environment around the Mn center is a distorted octahedral one (figure, top). Within the equatorial plane, the chelating angles lie in the range of 82.8(2)° – 92.1(2)° and the ∠O2–Mn–O3 bond angle is 92.8(1)°. The two Mn—N bond distances are nearly equivalent (1.978(4) Å and 1.984(4) Å) and longer than the Mn—O bond (1.865(3) Å and 1.874(3) Å). The apical ∠Cl–Mn–O5w bond angle is 173.26(7)° and the bond distance between the Mn atom and the O5w atom of the water ligand is considerably long with d(Mn—O5w) = 2.332(3) Å. The complex displays the intermolecular hydrogen bonds between the O5w atom and the O atoms of the chelate ligand with d(O5w···O^i) = 2.922 Å – 3.052 Å (symmetry code i: 2–x,1–y,–z). Moreover, there are intermolecular π-π interactions between the adjacent benzene rings. For Cg1 (the centroid of 6-membered ring C3-C8) and Cg2^i (ring C14-C19), the centroid-centroid distance is 3.637 Å and the dihedral angle between the ring planes is 2.2°. Two complex molecules are assembled through these hydrogen-bonding and π-π interactions (figure, bottom).

Table 1. Data collection and handling.

Crystal:	dark brown plate, size 0.10 × 0.25 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.08 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, ω/φ
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7351, 5211
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3499
$N(param)_{refined}$:	292
Programs:	SHELXS-97 [1], SHELXL-97 [2], ORTEP-III [3], PLATON [4]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(5WA)	2i	1.1681	0.5960	0.1336	0.090
H(5WB)	2i	1.1985	0.4990	0.0698	0.090
H(1A)	2i	0.5678	0.5951	–0.1945	0.163
H(1B)	2i	0.4143	0.6051	–0.1929	0.163
H(1C)	2i	0.4737	0.4946	–0.1641	0.163
H(2A)	2i	0.5991	0.7474	–0.0012	0.104
H(2B)	2i	0.4993	0.6497	0.0286	0.104
H(4)	2i	0.6767	0.8127	0.2129	0.115
H(5)	2i	0.8188	0.9033	0.4250	0.145
H(6)	2i	0.9942	0.8178	0.5146	0.129
H(9)	2i	1.1280	0.6588	0.4961	0.087
H(10A)	2i	1.3139	0.5421	0.4439	0.189
H(10B)	2i	1.2160	0.4782	0.5028	0.189

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(11)	2i	1.1557	0.3200	0.3744	0.216
H(12A)	2i	1.3058	0.2314	0.4163	0.318
H(12B)	2i	1.3623	0.3641	0.5240	0.318
H(12C)	2i	1.4300	0.3339	0.4183	0.318
H(13)	2i	1.2381	0.1863	0.1765	0.088
H(15)	2i	1.1977	0.0349	–0.0195	0.107
H(16)	2i	1.0703	–0.0681	–0.2283	0.129
H(17)	2i	0.8790	–0.0050	–0.3366	0.110
H(20A)	2i	0.6484	0.0366	–0.3796	0.106
H(20B)	2i	0.7436	0.1215	–0.4259	0.106
H(21A)	2i	0.5179	0.1806	–0.3456	0.192
H(21B)	2i	0.5151	0.1531	–0.4857	0.192
H(21C)	2i	0.6205	0.2758	–0.3750	0.192

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	2i	1.00301(6)	0.40988(6)	0.17143(5)	0.0416(4)	0.0490(4)	0.0345(3)	0.0131(3)	0.0050(2)	0.0182(3)
Cl	2i	0.8217(1)	0.2801(1)	0.2363(1)	0.0574(7)	0.0720(8)	0.0622(7)	0.0146(6)	0.0212(6)	0.0311(6)
O(1)	2i	0.6913(4)	0.6178(3)	0.0425(3)	0.062(2)	0.067(2)	0.086(2)	0.037(2)	0.042(2)	0.042(2)
O(2)	2i	0.8877(3)	0.5181(3)	0.1378(3)	0.052(2)	0.049(2)	0.040(1)	0.021(1)	0.014(1)	0.012(1)
O(3)	2i	0.9299(3)	0.3057(3)	–0.0004(3)	0.052(2)	0.047(2)	0.046(2)	0.021(1)	0.014(1)	0.012(1)
O(4)	2i	0.7826(4)	0.1906(3)	–0.2405(3)	0.083(2)	0.050(2)	0.040(2)	0.002(2)	0.015(2)	0.002(1)
O(5W)	2i	1.1865(3)	0.5291(3)	0.1362(3)	0.053(2)	0.055(2)	0.045(2)	0.014(1)	0.014(1)	0.023(1)
N(1)	2i	1.1028(5)	0.5187(4)	0.3538(4)	0.068(3)	0.077(3)	0.036(2)	–0.003(2)	–0.000(2)	0.023(2)
N(2)	2i	1.1457(4)	0.3145(5)	0.2199(4)	0.048(2)	0.092(3)	0.076(3)	0.028(2)	0.014(2)	0.055(3)
C(1)	2i	0.4998(6)	0.5815(7)	–0.1539(8)	0.053(3)	0.143(7)	0.175(8)	0.047(4)	0.035(4)	0.118(7)
C(2)	2i	0.5686(6)	0.6596(6)	–0.0126(7)	0.071(4)	0.105(5)	0.145(6)	0.064(4)	0.065(4)	0.086(5)
C(3)	2i	0.7717(6)	0.6764(4)	0.1718(5)	0.076(3)	0.050(3)	0.067(3)	0.024(2)	0.045(3)	0.027(2)
C(4)	2i	0.7502(9)	0.7787(6)	0.2483(8)	0.137(6)	0.070(4)	0.147(6)	0.056(4)	0.114(6)	0.053(4)
C(5)	2i	0.833(1)	0.8320(7)	0.3746(9)	0.21(1)	0.065(4)	0.122(7)	0.043(5)	0.126(8)	0.018(4)
C(6)	2i	0.938(1)	0.7806(7)	0.4274(7)	0.162(8)	0.068(4)	0.078(4)	–0.016(4)	0.081(5)	–0.009(3)
C(7)	2i	0.9654(7)	0.6689(5)	0.3523(4)	0.095(4)	0.059(3)	0.040(2)	–0.015(3)	0.036(3)	–0.002(2)
C(8)	2i	0.8747(5)	0.6182(4)	0.2174(4)	0.062(3)	0.041(2)	0.049(2)	0.008(2)	0.032(2)	0.009(2)
C(9)	2i	1.0729(7)	0.6172(6)	0.4092(4)	0.087(4)	0.072(4)	0.031(2)	–0.010(3)	0.007(2)	0.011(2)
C(10)	2i	1.224(1)	0.480(1)	0.4228(7)	0.159(8)	0.160(9)	0.077(5)	0.057(7)	–0.051(5)	0.026(5)
C(11)	2i	1.233(1)	0.363(1)	0.3543(9)	0.169(9)	0.22(1)	0.101(6)	0.121(9)	–0.041(6)	0.041(7)
C(12)	2i	1.342(1)	0.319(1)	0.435(1)	0.144(9)	0.27(2)	0.30(2)	0.10(1)	0.06(1)	0.20(2)
C(13)	2i	1.1649(6)	0.2210(6)	0.1418(7)	0.057(3)	0.090(4)	0.117(5)	0.043(3)	0.044(3)	0.077(4)
C(14)	2i	1.0859(6)	0.1666(5)	0.0096(6)	0.067(3)	0.063(3)	0.114(4)	0.038(3)	0.058(3)	0.061(3)
C(15)	2i	1.1203(8)	0.0615(6)	–0.0615(9)	0.108(5)	0.070(4)	0.160(7)	0.056(4)	0.098(6)	0.073(5)
C(16)	2i	1.046(1)	0.0009(6)	–0.1848(9)	0.169(8)	0.067(4)	0.162(8)	0.067(5)	0.126(7)	0.060(5)
C(17)	2i	0.9315(9)	0.0394(5)	–0.2497(6)	0.155(6)	0.047(3)	0.089(4)	0.017(4)	0.082(5)	0.013(3)
C(18)	2i	0.8933(6)	0.1426(4)	–0.1886(5)	0.085(4)	0.043(3)	0.063(3)	0.013(2)	0.044(3)	0.014(2)
C(19)	2i	0.9713(5)	0.2078(4)	–0.0567(4)	0.060(3)	0.041(2)	0.062(3)	0.016(2)	0.034(2)	0.023(2)
C(20)	2i	0.6905(7)	0.1222(6)	–0.3690(5)	0.103(5)	0.067(4)	0.051(3)	–0.015(3)	0.011(3)	–0.001(3)
C(21)	2i	0.5759(9)	0.1888(8)	–0.3963(7)	0.105(6)	0.116(6)	0.076(4)	–0.022(5)	–0.021(4)	–0.004(4)
O(6W)	2i	0.5018(8)	0.1256(7)	0.2423(7)	0.173(7)	0.141(6)	0.192(7)	0.024(5)	0.088(6)	0.045(5)
O(7W)	2i	0.3835(5)	0.8699(5)	0.0711(4)	0.074(3)	0.115(4)	0.097(3)	0.019(3)	0.027(2)	0.020(3)

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