Refinement of crystal structure of tetraaquamanganese(II) dichloride, $Mn(H_2O)_4Cl_2$

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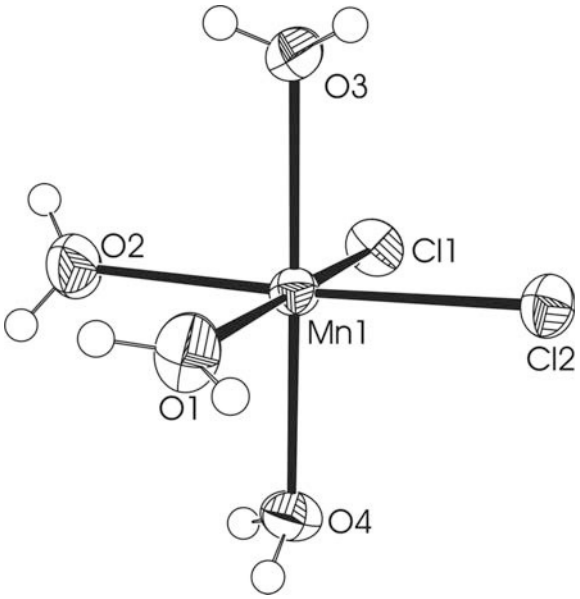

Abstract

$Cl_2H_8MnO_4$, monoclinic, $P2_1/n$ (no. 14), a = 6.186(3) Å, b = 9.514(4) Å, c = 11.194(5) Å, β = 99.776(7)°, V = 649.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.046, T = 293 K.

Source of material

The single crystals of the title complex were unexpectedly obtained as a by-product of an attempted preparation of an Mn(II) complex by reacting $MnCl_2 \cdot 4H_2O$ (0.28 g, 1.41 mmol) and 1,5-bis(2′-pyridylmethyleneamino)-3-aminopentane (0.40 g, 1.42 mmol) in EtOH. Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH_3CN solution of the brown reaction product.

Discussion

The X-ray structure analysis of the title complex was previously carried out by Zalkin et al. [1], but they did not give a complete description of the hydrogen bonding because of an error in the use of a computer program [2,3]. Using the results of the X-ray data of Zalkin et al., Baur [2] deduced new hydrogen bonds in the complex by consideration of the electrostatic energy of the crystal. The published and our crystal structures are essentially the same, however, the geometric properties and parameters presented here are slightly different and more accurate, respectively.

In the title complex the Mn^{2+} ion is six-coordinated in a somewhat distorted octahedral environment by two Cl atoms and four O atoms of four water molecules, and the Cl atoms are in *cis* position. This results in non-linear *trans* axes (∠O1–Mn1–Cl1 = 173.74(3)°, ∠O2–Mn1–Cl2 = 169.06(4)° and ∠O3–Mn1–O4 = 177.48(4)°). As a result of the different *trans* effects of the Cl and O atoms, the Mn—O bonds *trans* to the Cl atom (lengths: 2.196(1) and 2.179(1) Å; mean length: 2.188 Å) are slightly shorter than bond lengths to mutually *trans* O atoms (lengths: 2.215(1) and 2.213(1) Å; mean length: 2.214 Å). The O—H bond lengths lie in the range of 0.74(2) - 0.82(2) Å and the H–O–H angles in the water molecules vary from 106(2)° to 115(2)°. The O—H bond lengths are considerably shorter than the values obtained from the neutron-diffraction analysis (0.923 - 0.971 Å) [3]. Zalkin et al. [1] reported that only four of the eight crystallographically different H atoms from hydrogen bonds, whereas Baur [2] and El Saffar et al. [3] showed that all of the H atoms are involved in hydrogen bonds. Our crystal structure confirms that all the H atoms participate in intermolecular O–H···Cl or O–H···O hydrogen bonds with d(O···Cl) = 3.174(2) - 3.319(2) Å and d(O···O) = 2.926(2) and 2.966(2) Å.

Table 1. Data collection and handling.

Crystal:	colorless octahedron, size 0.15 × 0.18 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	27.79 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	54.32°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3837, 1422
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1331
$N(param)_{refined}$:	96
Programs:	SHELXS-97 [4], SHELXL-97 [5], ORTEP-III [6]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.862(3)	0.543(2)	0.363(2)	0.057(6)
H(1B)	4*e*	0.822(3)	0.432(2)	0.423(2)	0.062(7)
H(2A)	4*e*	0.853(4)	0.565(3)	0.114(2)	0.070(8)
H(2B)	4*e*	1.054(4)	0.563(3)	0.111(2)	0.078(8)
H(3A)	4*e*	1.377(4)	0.360(2)	0.370(2)	0.064(7)
H(3B)	4*e*	1.353(4)	0.463(2)	0.300(2)	0.059(7)
H(4A)	4*e*	0.552(3)	0.298(2)	0.193(2)	0.056(6)
H(4B)	4*e*	0.610(4)	0.299(2)	0.092(2)	0.052(6)

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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(1)	4*e*	0.98654(3)	0.32877(2)	0.23295(2)	0.0211(1)	0.0233(1)	0.0231(1)	–0.00028(7)	0.00444(8)	0.00022(7)
Cl(1)	4*e*	1.09410(6)	0.19266(4)	0.06116(3)	0.0348(2)	0.0357(2)	0.0256(2)	0.0042(1)	0.0076(1)	–0.0053(1)
Cl(2)	4*e*	1.03564(5)	0.13369(3)	0.38155(3)	0.0342(2)	0.0269(2)	0.0259(2)	–0.0002(1)	0.0045(1)	0.0039(1)
O(1)	4*e*	0.8676(2)	0.4612(1)	0.3688(1)	0.0490(7)	0.0325(6)	0.0360(6)	0.0031(5)	0.0193(5)	–0.0006(5)
O(2)	4*e*	0.9590(2)	0.5260(1)	0.1325(1)	0.0385(7)	0.0350(6)	0.0495(7)	0.0056(5)	0.0146(6)	0.0153(5)
O(3)	4*e*	1.3324(2)	0.3870(1)	0.3007(1)	0.0278(5)	0.0280(6)	0.0352(6)	–0.0051(4)	0.0013(4)	0.0025(4)
O(4)	4*e*	0.6441(2)	0.2715(1)	0.1571(1)	0.0233(5)	0.0408(6)	0.0275(5)	0.0010(4)	0.0037(4)	0.0044(4)

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