Crystal structure of calciumpermanganate tetrahydrate, $Ca(MnO_4)_2{\cdot}4H_2O$, $CaH_8Mn_2O_{12}$

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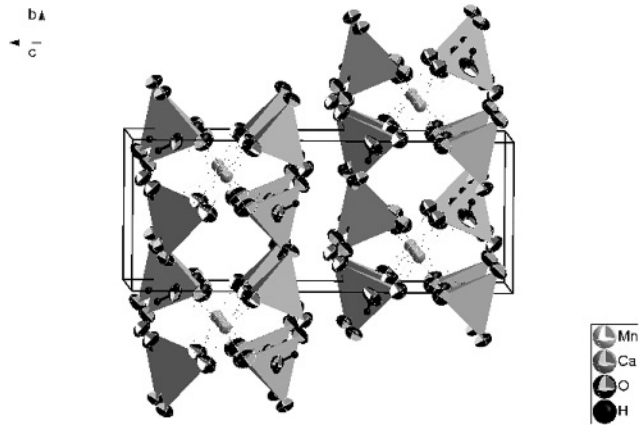

Abstract

$CaH_8Mn_2O_{12}$, orthorhombic, *Pccn* (no. 56), a = 13.9791(19) Å, b = 5.5404(8) Å, c = 13.3908(18) Å, V = 1037.1(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0318, $wR_{ref}(F^2)$ = 0.0659, T = 293 K.

Table 1. Data collection and handling.

Crystal:	violet needles, size 0.1×0.1×0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.79 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD 1K, ω
$2\theta_{max}$:	66.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13335, 1917
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1462
$N(param)_{refined}$:	85
Programs:	OLEX2 [1], SHELX [2]

Source of material

The title compound was synthesized by adding 0.9072 g, 4 mmol of $Ag(MnO_4)$ [4] to a solution of 0.3409 g, 2 mmol of $CaCl_2{\cdot}2H_2O$ in 25 ml deionised water. The AgCl was separated by centrifugation. The solution was concentrated in vacuum to a volume of 10ml and transferred into a 20 ml scintillation vial with a 1mm hole in the cap. Crystals large enough for a single crystal diffraction experiment were formed after 25 days. A suitable crystal was selected and sealed in a Mark-tube together with mother liquor to prevent loss of crystal water.The data collection was performed at room temperature on a Bruker SMART Platform diffractometer equipped with a CCD-Detector. Attempts to perform measurements at low temperatures were not successful since the crystals were destroyed while cooling. Using Olex2 [1], the structure was solved with the XS [2] structure solution program using Direct Methods and refined with the XL [2] refinement package using a Full-Matrix-Least-Squares refinement.

Discussion

The chemistry of permanganates is well known [5] and many of them have structurally been characterized. However, for some of them only the unit cell parameters are known. The crystal structure of calcium permanganate tetrahydrate consists of $^1{}_\infty[Ca(H_2O)_4(MnO_4)_{4/2}]$-chains extending along the *c*-axis. The coordination polyhedron of the Mn^{7+}ion in the permanganate anion is a slightly distorted tetrahedron. The calcium cations are eight-foldly coordinated by four oxygen atoms of the water molecules and four oxygen atoms belonging to four different permanganate anions. The resulting coordination polyhedron is best described by a distorted square antiprism. The $Ca–O_{(water)}$ distances are with 2.393(2) Å and 2.36(2) Å clearly shorter than the $Ca–O_{(permanganate)}$ with 2.520(2) Å and 2.504(2) Å. When allowing for a maximum O–O distance in OH···O of 3 Å, the structure can be described as slabs of $^1{}_\infty[Ca(H_2O)_4(MnO_4)_{4/2}]$-chains linked via hydrogen bonds. The slabs are stacked along the crystallographic *a*-axis. In the lithium permanganate $^1{}_\infty[Li(H_2O)_{6/2}]MnO_4$, described by Hoppe and Fischer [6] cations are not directly coordinated by the permanganate ions, as we observe it in this calcium permanganate, but exclusively surrounded by water molecules. $^1{}_\infty[Li(H_2O)_{6/2}]$-chains are linked via hydrogen bonds (maximum OH···O-distance of slightly less than 3 Å) to the permanganate anions.

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

Atom	Site	x	y	z	U_{iso}
H(5A)	8*e*	0.382(2)	–0.023(4)	0.459(2)	0.031(7)
H(5B)	8*e*	0.431(2)	0.078(5)	0.397(2)	0.041(8)
H(6A)	8*e*	0.379(2)	0.544(6)	0.246(2)	0.05(1)
H(6B)	8*e*	0.386(3)	0.615(7)	0.327(3)	0.11(2)

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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	8*e*	0.13153(2)	0.51163(5)	0.09716(2)	0.0238(1)	0.0221(1)	0.0182(1)	0.0011(1)	0.0001(1)	–0.0004(1)
Ca	4*c*	¼	¼	0.34954(4)	0.0225(2)	0.0232(2)	0.0174(2)	0.0019(2)	0	0
O(1)	8*e*	0.0860(1)	0.7809(3)	0.1013(1)	0.0456(8)	0.0299(7)	0.0343(7)	0.0118(6)	–0.0043(7)	–0.0021(7)
O(2)	8*e*	0.0484(1)	0.3168(3)	0.0897(1)	0.0417(9)	0.0426(9)	0.063(1)	–0.0159(7)	0.0110(8)	–0.0122(9)
O(3)	8*e*	0.1999(1)	0.4892(3)	0.0008(1)	0.0446(9)	0.0422(8)	0.0278(7)	–0.0038(7)	0.0119(6)	–0.0083(7)
O(4)	8*e*	0.1924(1)	0.4674(3)	0.1970(1)	0.055(1)	0.051(1)	0.0271(7)	0.0136(8)	–0.0112(7)	0.0057(7)
O(5)	8*e*	0.3845(1)	0.0191(3)	0.4054(1)	0.0275(7)	0.0405(9)	0.0291(7)	0.0062(6)	0.0002(6)	0.0072(8)
O(6)	8*e*	0.3741(2)	0.5115(4)	0.2971(1)	0.055(1)	0.053(1)	0.0289(8)	–0.0267(9)	–0.0069(8)	0.0109(9)

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