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Redetermination of Cs[$MnCl_3(H_2O)_2$]

Werner Massa,[a]* Olga V. Yakubovich[b] and Olga V. Dimitrova[b]

[a]Fachbereich Chemie, Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany, and [b]Department of Geology, Moscow Lomonosov State University, Vorob'evy Gory, 119992 Moscow, Russian Federation

Correspondence e-mail:
massa@chemie.uni-marburg.de

The structure of the one-dimensional antiferromagnet caesium diaquatrichloromanganate(II) was re-refined based on area-detector data, including the positions of H atoms. The Mn^{II} atom, on a twofold rotation axis, is in a distorted octahedral coordination by two bridging Cl ligands in *trans* positions, two terminal Cl ligands and two aqua ligands, both in *cis* positions. Hydrogen bonds of the type O—H···Cl connect octahedra along the chain and link the chains into layers which are separated by the Cs ions (also on twofold axes). The structure is discussed in comparison with non-isotypic related compounds of the morphotropic series $AMCl_3(H_2O)_2$ (A = Cs, Rb, K and M = Mn, Fe, Co).

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–O) = 0.004 Å
R factor = 0.034
wR factor = 0.068
Data-to-parameter ratio = 27.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Cs[$MnCl_3(H_2O)_2$] aroused interest in the field of magnetochemistry due to its one-dimensional antiferromagnetic properties (Skalyo *et al.*, 1970; Nishihara *et al.*, 1975). Its crystal structure, important for understanding magneto-structural correlations, was reported in 1962 (Jensen *et al.*, 1962). As that determination was from film data, the precision was inevitably rather poor (R = 0.093–0.101) and no H atoms

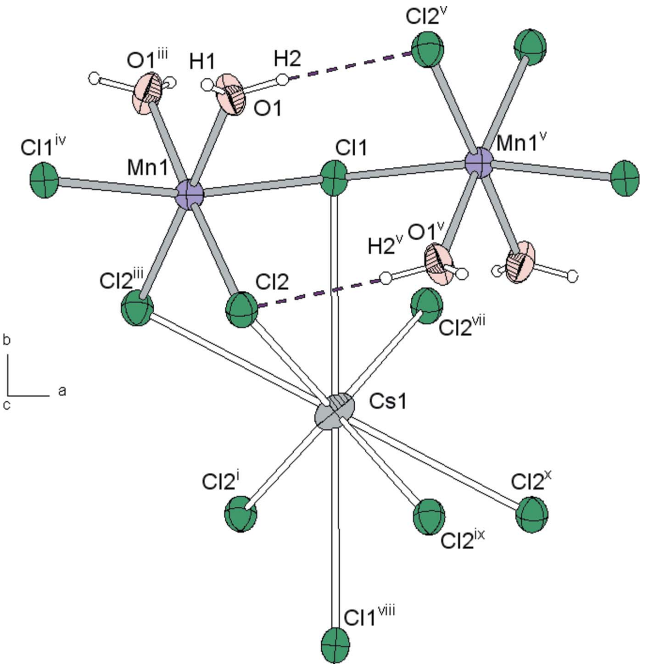

Figure 1
The main structural elements of the title compound, with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (iii) $-x, y, -z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + 1, -z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, -y + 1, z$; (vii) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (viii) $x, y - 1, z$; (ix) $-x + \frac{1}{2}, -y, z$; (x) $x + \frac{1}{2}, -y, -z + \frac{1}{2}$.]

were located. As we obtained single crystals of this compound in the course of attempts to prepare new manganese borates by hydrothermal syntheses, we found it worthwhile to refine the structure anew and to compare it with analogous compounds.

In the structure (Fig. 1), the Mn^{2+} ions on a twofold axis show distorted octahedral coordination by two *cis* aqua ligands, and two terminal and two *trans*-bridging Cl ligands, with the formation of bent chains parallel to the *a* axis. Although the structure of Jensen *et al.* (1962) is confirmed in principle, the bond lengths (Table 1) differ by up to 0.1 Å.

Hydrogen bonds of the type $O1—H2\cdots Cl2^{vi}$ provide additional connection along the chain and are probably responsible for the low bridging angle Mn—Cl—Mn = 126.54 (8)°. Additional $O1—H1\cdots Cl2^{vii}$ hydrogen bonds link the chains along the *c* axis to form anionic $[MnCl_3(H_2O)_2]^-$ layers parallel to the *ac* plane (Fig. 2). In the *b* direction, these layers are connected by layers of Cs^+ cations surrounded by six Cl2 and two Cl1 atoms at distances of between 3.4856 (15) and 3.6405 (18) Å (Figs. 1 and 2). Given the long distances involved (>3.7 Å) and the H-atom positions, no serious $Cs\cdots OH_2$ bonding interaction needs to be taken into account.

Four isostructural compounds have been confirmed so far: $Cs[CoCl_3(H_2O)_2]$ (Thorup & Soling, 1969), $Cs[FeCl_3(D_2O)_2]$, $Rb[FeCl_3(D_2O)_2]$ (Basten *et al.*, 1978) and $Rb[MnCl_3(H_2O)_2]$ (Jensen, 1967). Another structure type is realised in antiferromagnetic $Rb[CoCl_3(H_2O)_2]$ (Harkema & van der Graaf, 1975), which shows *trans*-connected octahedral anionic chains like the title compound, but with *trans* instead of *cis* positions for the aqua ligands. Although H atoms were not located in that study, a similar connection of the chains *via* hydrogen bonds to layers parallel to the *bc* plane seems probable. In contrast with the simple translational stacking in the CsMn compound, deriving from the tetragonal rod packing scheme (Fig. 2), the RbCo structure shows alternating stacking along the *a* axis, according to the *C*-centring (Fig. 3). The arrangement of chains is now related to the hexagonal rod packing scheme. In both structures, remarkable compression is observed in the direction of the hydrogen bonds.

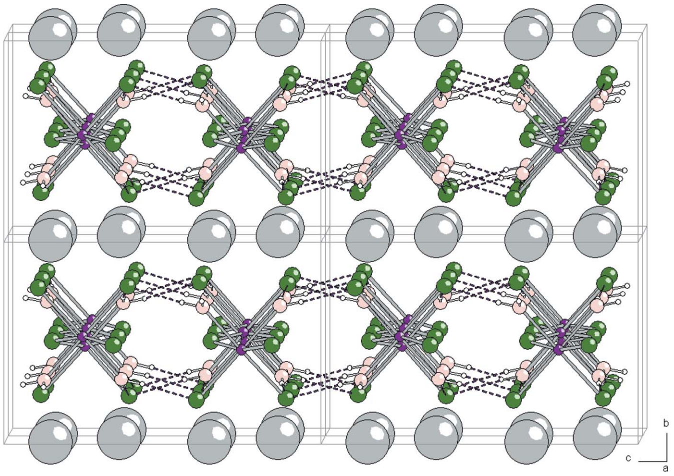

Figure 2
A view along the chains of the Mn octahedra parallel to the *a* axis, linked by hydrogen bonds along the *c* axis and separated by layers of Cs^+ ions (large spheres)

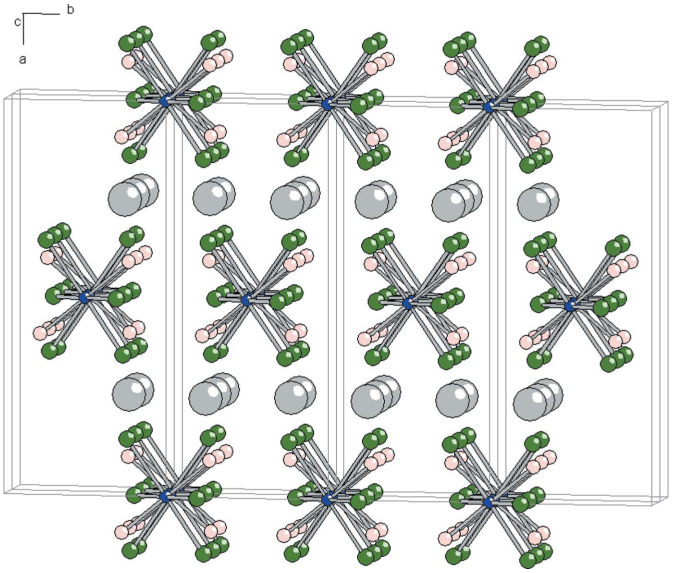

Figure 3
Compressed hexagonal chain packing in the structure of $Rb[CoCl_3(H_2O)_2]$. Small pink spheres O, large grey spheres Rb.

Experimental

Colourless plate-like crystals of $CsMnCl_3(H_2O)_2$ of up to 0.5 mm were obtained by hydrothermal synthesis in the system $MnCl_2$–Cs_2CO_3–B_2O_3–H_2O [*T* = 553 K, 70 bar (1 bar = 100 000 Pa), 20 d, ratio $MnCl_2/Cs_2CO_3/B_2O_3/H_2O$ = 2:1:1:20] in a PTFE-lined stainless steel autoclave. The presence of Cs, Mn and Cl in the samples was confirmed by qualitative X-ray spectroscopic analysis (CamScan 4DV plus EDA Link AN 1000).

Crystal data

$Cs[MnCl_3(H_2O)_2]$
$M_r = 330.23$
Orthorhombic, *Pcca*
$a = 9.0307 (12)$ Å
$b = 7.2636 (8)$ Å
$c = 11.4312 (13)$ Å
$V = 749.83 (15)$ Å^3

$Z = 4$
$D_x = 2.925$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 7.52$ mm^{-1}
$T = 293 (2)$ K
Irregular fragment, colourless
0.10 × 0.06 × 0.04 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.596$, $T_{max} = 0.625$ (expected range = 0.706–0.740)

9154 measured reflections
1002 independent reflections
529 reflections with $I > 2\sigma(I)$
$R_{int} = 0.099$
$\theta_{max} = 29.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.068$
$S = 0.78$
1002 reflections
36 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.38$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Cs1—Cl2^{i}	3.4856 (15)	Cs1—O1^{iii}	3.710 (5)
Cs1—Cl2	3.5371 (18)	Mn1—O1	2.183 (4)
Cs1—Cl1	3.6321 (4)	Mn1—Cl2	2.5255 (18)
Cs1—Cl2^{ii}	3.6405 (18)	Mn1—Cl1	2.5422 (10)
O1—Mn1—O1^{iv}	88.7 (3)	O1^{iv}—Mn1—Cl1	84.64 (13)
O1—Mn1—Cl2^{iv}	178.37 (13)	Cl2^{iv}—Mn1—Cl1	93.69 (5)
O1—Mn1—Cl2	90.45 (13)	Cl2—Mn1—Cl1	93.96 (5)
Cl2^{iv}—Mn1—Cl2	90.47 (8)	Cl1—Mn1—Cl1^{v}	169.13 (5)
O1—Mn1—Cl1	87.59 (13)	Mn1^{vi}—Cl1—Mn1	126.54 (8)

Symmetry codes: (i) $x+\frac{1}{2}, -y, -z+\frac{1}{2}$; (ii) $x, -y, z-\frac{1}{2}$; (iii) $-x, y-1, -z+\frac{1}{2}$; (iv) $-x, y, -z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+1, -z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, -y+1, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl2^{vii}	0.85	2.32	3.164 (5)	175
O1—H2···Cl2^{vi}	0.85	2.31	3.158 (5)	175

Symmetry codes: (vi) $-x+\frac{1}{2}, -y+1, z$; (vii) $-x, -y+1, -z+1$.

The positions of the two independent H atoms were obtained by difference Fourier techniques and they were refined using common isotropic displacement parameters. The O—H bond lengths were constrained to 0.85 Å and the H—O—H angle to 109.8°, but the rotational angle around the Mn—O bond direction was refined. The maximum residual electron density is 0.91 Å from Cs1.

Data collection: *EXPOSE* (Stoe & Cie, 1999); cell refinement: *CELL* (Stoe & Cie, 1999); data reduction: *INTEGRATE* (Stoe & Cie, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Version 1.0c; Westrip, 2006).

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