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catena-Poly[benzylmethylammonium [[diaquadichloromanganate(II)]-μ-chloro]]

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Key indicators

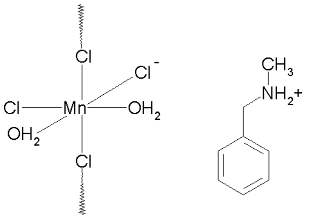
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.009 Å
R factor = 0.047
wR factor = 0.127
Data-to-parameter ratio = 15.8

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

In the structure of the title compound, $\{(C_8H_{12}N)[MnCl_2(\mu\text{-}Cl)(H_2O)_2]\}_n$, adjacent chains of $[MnCl_4(H_2O)_2]$ octahedra running parallel to the *c* axis are connected through O—H···Cl hydrogen bonds to forms sheets perpendicular to the *a* axis. These sheets are separated by benzylmethylammonium cations, and an extensive network is formed *via* O—H···Cl hydrogen bonds within the chains, and N—H···Cl hydrogen bonds between the chains and the cations.

Comment

Organic–inorganic materials provide opportunities for fundamental studies and applications as they combine the specific properties of the organic and inorganic moieties within a single system. In particular, organic–inorganic hybrids with low-dimensional structures are of interest because of their magnetic, optical and electrical properties, which can be tuned in relation to their low-dimensional structure. The title compound, (I), belongs to a family of organic–inorganic solids with the general formula $AMX_3\cdot 2H_2O$, in which *A* is an organic ammonium cation, *M* is a divalent metal ion and *X* is an halogen (Cl or Br). Compounds of this family with *M* = Mn are good candidates for use in studying the magnetic properties of linear chain systems containing Mn^{II} ions. Previous systems reported with *M* = Mn include $[CH_3NH_3]MnCl_3\cdot 2H_2O$ (Depmeier & Klaska, 1980; Caputo & Willett, 1981*a*), $[(CH_3)_2NH_2]MnCl_3\cdot 2H_2O$ (Caputo & Willett, 1981*b*; Stepanov *et al.*, 1994), $[(CH_3)_3NH]MnCl_3\cdot 2H_2O$ (Caputo *et al.*, 1976) and $[(CH_3)_2CHNH_3]MnCl_3\cdot 2H_2O$ (Willett, 1979).



(I)

The structure of (I) contains extended linear chains of $[MnCl_4(H_2O)_2]$ octahedra running parallel to the *c* axis, in which the octahedra are corner-linked *via* Cl atoms. The basal plane of the octahedron contains two Cl atoms and the two water molecules in *cis* positions. As already observed in similar compounds (Depmeier & Klaska, 1980; Caputo & Willett, 1981*a*), the octahedra are distorted, with the bonds between atom Mn1 and the bridging Cl4 atoms longer [2.5629 (13) and 2.5902 (13) Å] than the bonds to the terminal Cl atoms [2.4737 (12) and 2.5061 (12) Å]. These extended chains of octahedra are linked through hydrogen bonds

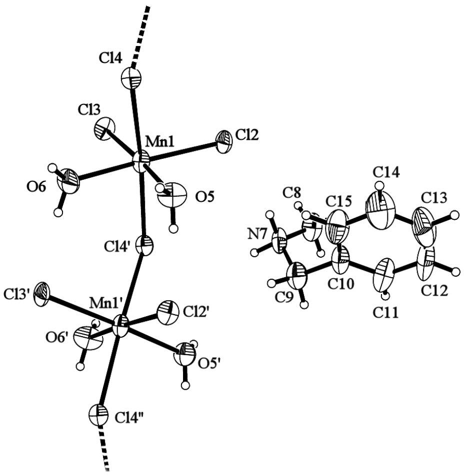


Figure 1
Part of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are represented by spheres of arbitrary radii. Atoms labeled with a single prime (′) and double primes (″) are related by the symmetry operators $(x, \frac{1}{2} - y, z - \frac{1}{2})$ and $(x, y, -1 + z)$, respectively.

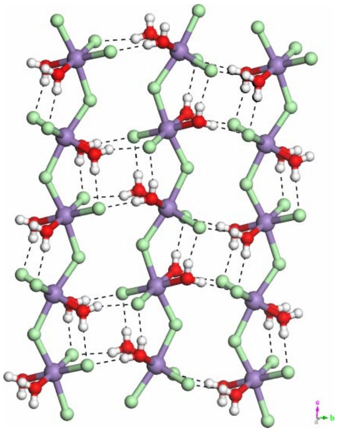


Figure 2
View of the hydrogen-bonded plane of $MnCl_4(H_2O)_2$ chains perpendicular to the *a* axis. Hydrogen bonds are shown as dashed lines.

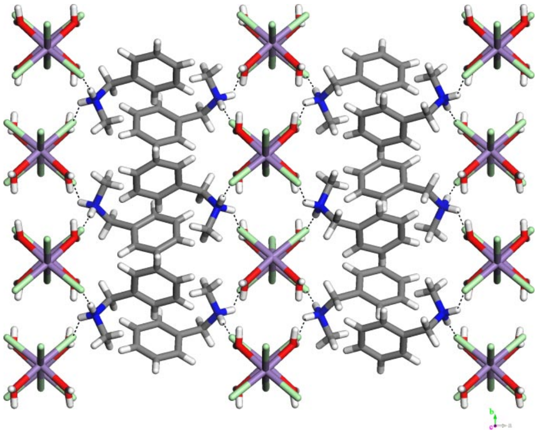


Figure 3
Packing diagram of (I), viewed along the *c* axis, showing the hydrogen bonds (as dashed lines) between the ammonium cations and the inorganic chains.

between Cl atoms and water molecules along the *b* axis (Fig. 2). Each water molecule is involved in two O—H···Cl hydrogen bonds. One bond involves a Cl atom of the adjacent octahedron within the same chain; the other involves a Cl atom from the neighboring chain (see Table 2 and Fig. 2). The inorganic chains define layers perpendicular to the *a* axis that have the same disposition as those in $[(CH_3)_2NH_2]MnCl_3\cdot 2H_2O$ (Caputo & Willett, 1981*b*; Stepanov *et al.*, 1994).

Notably, the relative positions of the Mn—Cl—Mn—Cl backbones between adjacent chains are similar, with the Cl atoms tipped toward or away from one another. As a result, the Mn—Cl—Mn—Cl backbones of the adjacent zigzag chains do not run in the same way as is observed in the methylammonium trichloromanganate dihydrate $(CH_3NH_3)MnCl_3\cdot 2H_2O$ (Caputo & Willett, 1981*a*). The arrangement of the $[MnCl_4(H_2O)_2]$ octahedra also differs from the structure of trimethylammonium manganese(II) chloride dihydrate $[(CH_3)_3NH]MnCl_3\cdot 2H_2O$ (Caputo *et al.*, 1976), in which the water molecules are *trans* and the $[MnCl_4(H_2O)_2]$ octahedra share edges. A completely different structural organization, based on centrosymmetric $[Mn_2Cl_6(H_2O)_4]$ anionic dimers, was found for $[(CH_3)_2CHNH_3]MnCl_3\cdot 2H_2O$ (Willett, 1979).

The benzylmethylammonium ions are located between the layers, linked by two N—H···Cl hydrogen bonds with Cl atoms of the octahedral chains (Fig. 3). Despite the constraint imposed by this hydrogen bond, packing of the phenyl ring of the cation can be satisfied through a distorted conformation for the ammonium arm, as shown by the C8—N7—C9—C10 torsion angle [57.5 (6)°]. Compared with $[(CH_3)_2NH_2]MnCl_3\cdot 2H_2O$, the larger size of the ammonium cation results in an increase of the distance separating the layers of the paired chains [12.500 (1) *versus* 8.604 (4) Å].

Experimental

Crystals were grown by slow evaporation of an equimolar aqueous solution of C_6H_5–CH_2–NH-CH_2, HCl and $MnCl_2\cdot 4H_2O$. Needle-like crystals were obtained when the solution was allowed to stand at room temperature for a couple of days.

Crystal data

$(C_8H_{12}N)[MnCl_3(H_2O)_2]$
$M_r = 319.51$
Orthorhombic, *Pbca*
$a = 24.959$ (2) Å
$b = 11.951$ (1) Å
$c = 9.192$ (2) Å
$V = 2741.8$ (7) Å^3
$Z = 8$
$D_x = 1.548$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 12 699 reflections
$\theta = 1.0$–13.3°
$\mu = 1.53$ mm^{-1}
$T = 110$ (2) K
Needle, colorless
0.50 × 0.20 × 0.15 mm

Data collection

Nonius DIP2000 diffractometer
ω scans
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.520$, $T_{\max} = 0.800$
12 699 measured reflections
2356 independent reflections
1732 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.04$
$\theta_{\max} = 24.8°$
$h = -30 \rightarrow 30$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.127$
$S = 1.07$
2356 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 6.9025P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0082 (6)

Table 1
Selected geometric parameters (Å, °).

Mn1—O5	2.180 (3)	N7—C9	1.503 (7)
Mn1—O6	2.187 (3)	C9—C10	1.497 (7)
Mn1—Cl3	2.4737 (12)	C10—C11	1.358 (8)
Mn1—Cl2	2.5061 (12)	C10—C15	1.393 (8)
Mn1—Cl4	2.5629 (13)	C11—C12	1.369 (9)
Mn1—Cl4^{i}	2.5902 (13)	C12—C13	1.375 (11)
Cl4—Mn1^{ii}	2.5902 (13)	C13—C14	1.328 (10)
N7—C8	1.465 (6)	C14—C15	1.379 (8)
O5—Mn1—O6	86.82 (16)	Cl2—Mn1—Cl4^{i}	93.49 (4)
O5—Mn1—Cl3	176.70 (11)	Cl4—Mn1—Cl4^{i}	171.44 (3)
O6—Mn1—Cl3	90.05 (12)	Mn1—Cl4—Mn1^{ii}	126.81 (4)
O5—Mn1—Cl2	88.82 (11)	C8—N7—C9	115.1 (4)
O6—Mn1—Cl2	175.63 (12)	C10—C9—N7	112.9 (5)
Cl3—Mn1—Cl2	94.32 (4)	C11—C10—C15	118.9 (5)
O5—Mn1—Cl4	88.33 (10)	C11—C10—C9	121.0 (6)
O6—Mn1—Cl4	86.83 (11)	C15—C10—C9	120.2 (5)
CL3—Mn1—Cl4	92.55 (4)	C10—C11—C12	121.2 (6)
Cl2—Mn1—Cl4	92.84 (4)	C11—C12—C13	118.8 (6)
O5—Mn1—Cl4^{i}	86.05 (11)	C14—C13—C12	121.4 (6)
O6—Mn1—Cl4^{i}	86.41 (11)	C13—C14—C15	120.3 (7)
Cl3—Mn1—Cl4^{i}	92.71 (4)	C14—C15—C10	119.5 (6)
O5—Mn1—Cl4—Mn1^{ii}	135.82 (11)	C8—N7—C9—C10	57.5 (6)
O6—Mn1—Cl4—Mn1^{ii}	−137.27 (13)	N7—C9—C10—C11	−101.3 (7)
Cl3—Mn1—Cl4—Mn1^{ii}	−47.37 (7)	N7—C9—C10—C15	78.3 (7)
Cl2—Mn1—Cl4—Mn1^{ii}	47.09 (7)	C9—C10—C15—C14	−179.0 (6)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N7—H71···Cl3^{iii}	0.92	2.51	3.208 (4)	133
N7—H71···Cl4^{i}	0.92	2.78	3.263 (4)	114
N7—H72···Cl2	0.92	2.24	3.149 (4)	171
O5—H51···Cl2^{i}	0.89 (2)	2.26 (3)	3.133 (4)	167 (7)
O5—H52···Cl3^{iv}	0.89 (2)	2.24 (2)	3.132 (4)	178 (7)
O6—H61···Cl3^{i}	0.90 (2)	2.27 (2)	3.156 (4)	169 (7)
O6—H62···Cl2^{iv}	0.90 (2)	2.34 (3)	3.221 (4)	165 (6)

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $2-x, -y, 1-z$; (iv) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$.

The H atoms of the benzylmethylammonium cation were placed in idealized positions (C—H = 0.95–0.99 Å and N—H = 0.92 Å) and refined in the riding-model approximation, with isotropic displacement parameters fixed at $1.2U_{\rm eq}$ ($1.5U_{\rm eq}$ for the methyl group) of the atoms to which they are bonded. H atoms of the water molecules were found in a difference Fourier map and refined with restraints on the distances (0.8–0.9) and $U_{\rm iso}$ values [$1.5U_{\rm eq}$(O)].

Data collection: *XPRESS* (MacScience, 1989); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997) and *Material Studio* (Accelrys, 2002); software used to prepare material for publication: *PLATON* (Spek, 2002).

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