

Fig. 2. Coordination of Na sites. Symmetry codes are shown in Table 2, (x) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (xi) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$.

face in common, and the distance between the Na sites is extremely short (Table 2). It is noticeable that, in spite of these facts, 12% of the neighboring Na sites are really occupied simultaneously. If their simultaneous occupations were forbidden, the Na content of the compound could not exceed

Na_{0.50}V₂O₅. The Na ion exhibits a large, anisotropic apparent thermal motion toward the neighboring Na site (Fig. 2), which suggests that the distance between the neighboring Na sites is longer than 2.35 Å when both of them are occupied, and that it is shorter than 2.35 Å when only one is occupied.

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Structure of Calcium Manganese(II) Tetrabromide Octahydrate

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Abstract. CaMnBr₄.8H₂O, *M_r* = 558.75, monoclinic, *C2/m*, *a* = 9.062 (1), *b* = 9.582 (1), *c* = 9.405 (1) Å, *β* = 112.96 (1)°, *V* = 752.0 (2) Å³, *Z* = 2, *D_x* = 2.47 Mg m⁻³, Mo *Kα* radiation, *λ* = 0.71069 Å, *μ* = 11.57 mm⁻¹, *F*(000) = 530, room temperature, *R* = 0.062 (*wR* = 0.062) for 543 unique observed [*I* > 3σ(*I*)] reflections. Mn is octahedrally coordinated by four Br atoms (⟨Mn—Br⟩ = 2.71 Å) and two O_w (Mn—O = 2.18 Å). Ca is eightfold coordinated by six O_w (⟨Ca—O⟩ = 2.43 Å) and a Br and an O_w atom from an Mn(H₂O)₂Br₄ octahedron [Ca—Br = 3.073 (5), Ca—O = 3.01 (1) Å]. The structure thus consists of (H₂O)₆Ca(H₂O)BrMnBr₃H₂O molecular groups linked by hydrogen bonds. Since the Mn atom lies at a crystallographic center of symmetry, the Ca(H₂O)₆ groups are disordered on either side of the Mn(H₂O)₂Br₄ ion. Precession photographs show evidence of a superstructure with *b*' ≈ 5*b*.

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Introduction. The compound CaMnBr₄.8H₂O was first reported by Duhlev & Balarew (1987) as the only double salt found in the equilibrium CaBr₂–MnBr₂–H₂O system at 298 K. The size and hardness of the ions were considered to be the main factors affecting the molecular structure (Balarew & Duhlev, 1984), and the structure CaMnX₄.8H₂O (*X* = Cl or Br) was predicted (Balarew & Duhlev, 1983; Duhlev, 1984) to consist of Mn(H₂O)₂Br₄ and Ca(H₂O)₇Br groups sharing ligands. The aim of the present X-ray study was to check the correctness of this prediction.

Experimental. CaMnBr₄.8H₂O crystallizes as rose-colored extremely hygroscopic crystals from a saturated aqueous solution of CaBr₂ and MnBr₂ in a molar ratio 1.6:1. An approximately cylindrical crystal with diameter 0.22 mm and length 0.27 mm was coated with liquid paraffin and sealed in a thin-walled capillary under dry nitrogen. Precession photographs showed that, in addition to the reflections used in this study, most peaks had satellite

peaks displaced by approximately $\pm 2b^*/5$ corresponding to a modulated structure. Unit-cell parameters were determined using a Syntex $P2_1$ diffractometer from 15 well centered strong reflections in the range $19 < 2\theta < 31^\circ$. Intensities were measured for 876 reflections with $-10 \leq h \leq 9$, $0 \leq k \leq 11$, $0 \leq l \leq 11$ and $2\theta \leq 50^\circ$ and were corrected for Lorentz and polarization effects. Empirical absorption corrections were derived from ψ scans of 26 reflections (maximum correction factor of 1.91 for the intensity of reflection 001). The intensities of the $40\bar{4}$ and 404 reflections were monitored after every 48 measurements and showed variations of 1.5 and 1.1% respectively. Equivalent reflections were averaged ($R_{\text{int}} = 0.007$) to give 710 unique reflections, 543 of which, with $I > 3\sigma(I)$, were used for the refinement. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). The positions of five of the seven independent H atoms were located from peaks in the difference electron density map and were not refined.

A weight $w = [\sigma^2(F_o) + kF_o^2]^{-1}$ was assigned, where $\sigma(F_o)$ is the uncertainty derived from counting statistics and k refined to 0.023. The scale factor, weighting factor (k), secondary-extinction coefficient and all variable (non-H-atom) positional and atomic displacement factors in the subcell listed in the *Abstract* were refined by least squares [function minimized = $\sum w(|F_o| - |F_c|)^2$] with *SHELX76* (Sheldrick, 1976). The final $R = 0.062$ ($wR = 0.062$), the goodness of fit $S = 0.52$ and the average shift/e.s.d. = 0.001 (max. = 0.004). The secondary-extinction coefficient (Larson, 1967) $g = 0.0032$ (6). The final difference electron density map has maximum and minimum values of $+1.38$ and -1.24 e \AA^{-3} respectively. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates and displacement parameters are given in Table 1 and the bond distances in Table 2.* Attempts to solve the modulated superstructure were not successful but as the disordered structure found in the subcell confirmed the expected chemical structure and provided sufficiently accurate bond distances and angles, the refinement was not taken further.

Discussion. $\text{Ca}(\text{H}_2\text{O})_6\text{MnBr}_4(\text{H}_2\text{O})_2$ contains discrete molecules in which an $\text{MnBr}_4(\text{H}_2\text{O})_2$ octahedron shares one Br and one H_2O with a $\text{Ca}(\text{H}_2\text{O})_7\text{Br}$ coordination polyhedron. The Ca, Mn and the two bridging atoms [O(1) and Br(1)] lie in the same

* Coordinates of the H atoms, anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52460 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3.$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$	Occupancy
Br(1)	0.4739 (2)	0	0.2026 (2)	0.0370	1.0
Br(2)		0.2811 (1)		0.0368	1.0
Mn		0		0.0262	1.0
Ca	0.1057 (6)	0	0.0671 (6)	0.0281	0.5
O(1)	0.2394 (10)	0	0.4149 (11)	0.0325	1.0
O(2)	0.2010 (51)	0	-0.1275 (51)	0.1901	0.5
O(3)	0.1800 (20)	0.2285 (18)	0.1705 (20)	0.0470	0.5
O(4)	-0.0877 (23)	0.1625 (21)	-0.1172 (21)	0.0562	0.5
O(5)	-0.1202 (39)	0	0.1578 (32)	0.0677	0.5

Table 2. Bond distances (\AA) and angles ($^\circ$)

Mn(H₂O)₂Br₄ octahedron				
Mn—O(1)	2.178 (9) × 2	O(1)—Mn—Br(1)	88.5 (3)	
Mn—Br(1)	2.713 (2) × 2	O(1)—Mn—Br(2)	90.0	
Mn—Br(2)	2.694 (2) × 2	Br(1)—Mn—Br(2)	90.0	
Ca(H₂O)₇Br polyhedron				
Ca—O(1)	3.01 (1)	Ca—O(4)	2.48 (2) × 2	
Ca—O(2)	2.31 (6)	Ca—O(5)	2.51 (4)	
Ca—O(3)	2.38 (2) × 2	Ca—Br(1)	3.073 (5)	
O(1)—Ca—O(2)	138.0 (10)	O(2)—Ca—Br(1)	69.3 (9)	
O(1)—Ca—O(3)	68.1 (4)	O(3)—Ca—O(3)	133.3 (6)	
O(1)—Ca—O(4)	129.4 (5)	O(3)—Ca—O(4)	73.6 (6)	
O(1)—Ca—O(5)	70.5 (6)	O(3)—Ca—O(5)	89.9 (6)	
O(1)—Ca—Br(1)	68.7 (2)	O(3)—Ca—Br(1)	75.0 (4)	
O(2)—Ca—O(3)	100.9 (6)	O(4)—Ca—O(4)	77.9 (6)	
O(2)—Ca—O(4)	79.9 (0)	O(4)—Ca—O(5)	77.8 (7)	
O(2)—Ca—O(5)	151.3 (11)	O(4)—Ca—Br(1)	130.1 (6)	
		O(5)—Ca—Br(1)	139.2 (6)	
Hydrogen bonds				
O—H...X	O...X	O—H	H...X	O—H...X
O(1)—H(1)...Br(2) (c)	3.332 (× 2)	0.92	2.48	154
O(2)...Br(1) (d)	3.265			
O(3)—H(31)...Br(1) (c)	3.285	0.93	2.36	169
O(3)—H(32)...Br(2) (a)	3.353	1.28	2.14	157
O(4)—H(41)...Br(1) (c)	3.582	1.04	2.59	176
O(4)—H(42)...Br(1) (b)	3.623	1.24	2.50	148
O(5)...Br(1) (b)	3.625			
O(5)...Br(2) (c)	3.650 (× 2)			
O(2)...O(3) (c)	2.897 (× 2)*			

Notes: (a) within the molecule; (b) within the [101] chain; (c) between chains related by $\pm \frac{1}{2}, \pm \frac{1}{2}, 0$; (d) between chains related by $\pm 1, 0, \bar{1}$.

* This distance is observed for antiparallel chains only and would probably be changed by atomic position relaxation. It probably does not represent a hydrogen bond.

mirror plane. In the subcell the molecule appears disordered by inversion in the crystallographic center of symmetry at the Mn atom. This leaves the $\text{MnBr}_4(\text{H}_2\text{O})_2$ moiety unchanged but results in the $\text{Ca}(\text{H}_2\text{O})_6$ group appearing in two places with half occupancy. The resulting molecule is oriented with its Mn—Ca vector pointing in the [101] (or $[\bar{1}0\bar{1}]$) direction (see Fig. 1).

If it is assumed that the molecule at the origin is oriented along [101], steric considerations require that the molecules on the [101] and $[\bar{1}0\bar{1}]$ corners of the cell must also be oriented in the same direction. Thus along the [101] direction the molecules are

linked (by O—H...Br bonds) into ordered chains. Each such chain is hydrogen bonded to six neighboring chains (displaced by $1,0,\bar{1}$; $\bar{1},0,1$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$) but there are no restrictions on the relative orientations of these chains other than those imposed by a few weak hydrogen bonds. The molecules in adjacent chains may be parallel (with their Mn—Ca vectors in the same direction) or antiparallel (with their Mn—Ca vectors in opposite directions). The regions in reciprocal space in which the superlattice reflections have their largest intensity indicate that the superstructure modulation is related to the ordering of these chains but we were unable to find a model of the superstructure that would fit the intensities in detail.

Details of the hydrogen bonding are given in Table 2. All the bonds are formed between H₂O and Br, and, since the Br atoms are in the same positions regardless of the chain orientation, each water molecule forms the same hydrogen bonds whatever the orientation of the neighboring chain. However, the bonds received by a given Br atom will depend on the neighboring chain orientations as indicated in Table 3. In particular the Br(1) that is not bonded to Ca is linked to the next molecule in the chain by three hydrogen bonds that are roughly equivalent in strength to the Ca—Br bond. Each Br(1) forms two hydrogen bonds [0.15–0.17 valence units (v.u.)] to either O(4) or O(3) in neighboring chains and, depending on the chain orientation, it may also form a strong hydrogen bond (0.22 v.u.) to O(2). Similarly, Br(2) may accept up to two weak (0.07 v.u.) hydrogen bonds from O(5) in neighboring chains. For all possible conformations the valence sums at Br are satisfactory (Table 3) which explains why the

Table 3. Bond-valence analysis of hydrogen-bond acceptors

	Br(1) (bonded to Ca)	Br(1) (not bonded to Ca)
Br(1)—Mn	0.31	0.31
Br(1)—Ca	0.22	
Br(1)...H—O(4) in same chain		0.11 × 2
Br(1)...H—O(5) in same chain		0.09
Br(1)...H—O(3) antiparallel A chain	0.17 × 2	0.17 × 2
parallel A chain	0.15 × 2	
Br(1)...H—O(4) antiparallel A chain		0.15 × 2
parallel A chain		
Br(1)...H—O(2) antiparallel B chain	0.22	
parallel B chain		0.22
Valence-sum range around Br(1)	0.83–1.09	0.92–1.18
Br(2)—Mn	0.33	
Br(2)...H—O(3) same molecule	0.16	
Br(2)...H—O(1) A chains	0.14 × 2	
Br(2)...H—O(5) A chains	0.07 × 0, 1 or 2	
Valence-sum range around Br(2)	0.77–0.98	

Notes: Four A chains are related by $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$. Two B chains are related by $1,0,\bar{1}$; $\bar{1},0,1$. Bond valences are calculated using the method of Brown & Altermatt (1985) with $r_0 = 2.28$ for Mn—Br and 2.507 for Ca—Br. The valence sums around Mn are 1.98, around Ca 2.04 and around O range from 2.00 to 2.13.

disorder can be present. The only problematic contact (2.90 Å) between atoms in adjacent chains occurs between O(2) and O(3) of antiparallel chains. In principle this could be a hydrogen bond from O(2) to O(3) but O(3) has a full complement of hydrogen bonds and the O(2)—O(3) vector lies in a position that is unfavorable for hydrogen bonding at either atom. Significantly, O(2) has a very large atomic displacement parameter suggesting that in the supercell structure it is displaced by more than 0.5 Å from the mirror plane. The only other anomaly is a moderately large atomic-displacement parameter for O(5) perpendicular to the mirror plane. This atom has three potential acceptor Br atoms at equal distances and in the disordered structure it lies very close to O(2). For neither O(2) nor O(5) could individual H atoms be seen in the difference electron density map.

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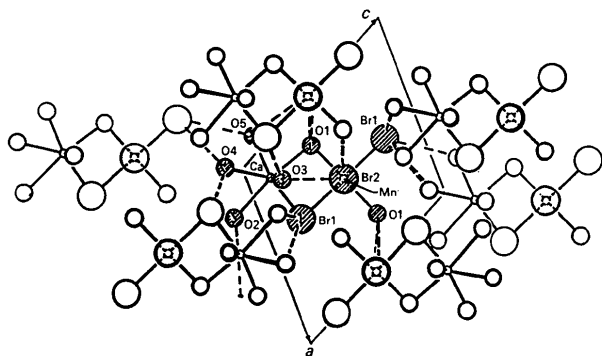


Fig. 1. The hydrogen-bonding environment (dashed lines) around one $\text{Ca}(\text{H}_2\text{O})_6\text{MnBr}_4(\text{H}_2\text{O})_2$ molecule (shaded). Large circles = Br, medium circles = O, small circles = Ca (solid), Mn (broken). All atoms lie on mirror planes except Br(2), O(3) and O(4) which occur both above and below the molecular plane. In the refined structure there is a crystallographic center of symmetry at Mn. The figure shows a possible ordering scheme with a parallel (top) and an antiparallel (bottom) chain relative to the central [101] chain (horizontal).

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Structure of Dilead(II) Hydrogenarsenate(III) Dichloride

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Abstract. $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$, $M_r = 609.21$, monoclinic, $P2_1/m$, $a = 6.410$ (2), $b = 5.525$ (1), $c = 9.293$ (3) Å, $\beta = 90.69$ (2)°, $V = 329.1$ (2) Å³, $Z = 2$, $D_x = 6.15$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 54.9$ mm⁻¹, $F(000) = 512$, room temperature, $R(F) = 0.044$ for 1410 independent reflections with $F_o > 3\sigma F_o$ and 47 variables. The As atom is trigonal-pyramidally coordinated by two O atoms and one OH group. From consideration of the nearest neighbours around the Pb atoms, $\text{Pb}(1)\text{O}_4$ and $\text{Pb}(2)\text{O}_2\text{Cl}$ pyramids are combined into rows along [010]. The AsO_2OH anion and the hydrogen bridge $\text{O} \cdots \text{H} \cdots \text{Cl}$ are within the same row. These rows are interconnected by additional Pb—O and Pb—Cl bonds. Crystals of the title compound were synthesized under hydrothermal conditions.

Introduction. Protonated oxoanions are well known from structure determinations of inorganic compounds (Ferraris & Ivaldi, 1984). However, the $\text{As}^{\text{III}}\text{O}_2\text{OH}$ anion has so far only been determined for trigonite, $\text{Pb}_3\text{Mn}(\text{AsO}_3)_2(\text{AsO}_2\text{OH})$ (Pertlik, 1987*a*). In connection with investigations of the stereochemistry of As^{III} atoms and with examinations of the interconnection of AsO_3 pyramids (Pertlik, 1979; Hawthorne, 1985), the crystal structure of $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$ was investigated in detail.

The crystal structures of the following lead(II) arsenate(III) compounds have so far been determined: isolated arsenate(III) pyramids have been found in finnemanite, $\text{Pb}_5(\text{AsO}_3)_3\text{Cl}$ (Effenberger & Pertlik, 1979); As_2O_5 dimers (two AsO_3 groups connected over a common O-atom corner) occur in paulmooreite, $\text{Pb}_2\text{As}_2\text{O}_5$ (Araki, Moore & Brunton, 1980) and in gebhardtite, $\text{Pb}_8\text{OCl}_6(\text{As}_2\text{O}_5)_2$ (Klaska & Gebert, 1982; Medenbach, Gebert & Abraham, 1983). PbAs_2O_4 (Dinterer, Effenberger, Kugler, Pertlik, Spindler & Wildner,

1988) contains As_4O_8 rings and $\text{Pb}(\text{AsO}_2)\text{Cl}$ and $\text{Pb}_2(\text{AsO}_2)_3\text{Cl}$ (Pertlik, 1988) contain AsO_2 chains. In some ways $\text{Pb}_6\text{Cu}(\text{AsO}_3)_2\text{Cl}_7$ (Pertlik, 1986) and free-dite, $\text{Pb}_8\text{Cu}(\text{AsO}_3)_2\text{Cl}_5\text{O}_3$ (Pertlik, 1987*b*) also belong to this type of compound but $\text{Cu}^{\text{I}}-\text{As}^{\text{III}}$ interactions are assumed.

Experimental. Single crystals suitable for X-ray investigations were synthesized by hydrothermal treatment of a mixture of native lead (powder, GR) and As_2O_3 (GR) in the molar ratio $\sim 2:1$. 1 g was inserted into a teflon-lined steel vessel with approximately 6 ml capacity; the remaining reaction space was filled to 80% with 1M HCl (GR). After heating to 393 K for three days, crystals of the title compound were formed along with PbCl_2 . For $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$ the crystallographic forms {100}, {010} and {001} were determined exclusively. Crystals form needles which are elongated along [010], their diameter is up to 0.05 mm, their length is up to 0.5 mm, and they are colourless.

Synthetic crystal, $0.035 \times 0.30 \times 0.040$ mm, Stoe four-circle diffractometer AED2, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 40 reflections with $30 \leq 2\theta \leq 40^\circ$, $2\theta-\omega$ scan mode; minimum of 35 steps per reflection increased for $\alpha_1-\alpha_2$ splitting, step width 0.03° , step time 0.5 to 1.5 s per step, five points each side for background correction; three standard reflections, interval 2 h, intensity variation 7.2%; 3191 reflections measured, $4 \leq 2\theta \leq 70^\circ$ (h : $-10 \rightarrow 10$, k : $0 \rightarrow 8$, l : $-15 \rightarrow 15$); 1597 reflections in unique data set ($R_{\text{int}} = 0.053$), 1410 reflections with $F_o > 3\sigma F_o$ used for refinement; absorption correction from 108 ψ -scan data (transmission factors from 0.036 to 0.089); corrections for Lorentz and polarization effects. Complex neutral atomic scattering functions (*International Tables for X-ray Crystallography*,