bromide complexes, the Cr—X bonds to the bridging halogens, 2·48 Å, are considerably longer than those to the terminal halogens, 2·38 Å. The chromium atoms are displaced away from one another across the shared octahedral face, resulting in a Cr—Cr separation of 3·17 Å, cf. 2·88 Å for chromium atoms centrally located in the octahedra.

It was of interest to compare the bond lengths in the mixed-halide complex with those for the pure end members. An excellent refinement has been reported for $Cs_3Cr_2Br_9$ (Saillant et al., 1971). However, for $Cs_3Cr_2Cl_9$, the reported atom positions were determined from electron density maps and were not refined, so e.s.d.'s were not given for the interatomic distances (Wessel & IJdo, 1957). We carried out a least-squares refinement of the structure of $Cs_3Cr_2Cl_9$, using the $h0l$ structure-factor data reported by Wessel & IJdo (1957). Refinement of coordinates and an overall temperature factor converged at $R = 0·12$. The final coordinates and e.s.d.'s are given in Table 3. Relevant bond lengths and angles for the chloride and bromide complexes are compared with those for $Cs_3Cr_2Br_3Cl_6$ in Table 2. For the latter compound the bond lengths associated with the bridging halogen, Cr—X(1) and X(1)—X(1), agree closely with the corresponding values for $Cs_3Cr_2Cl_9$, whereas the distances associated with the terminal halogens, Cr—X(2) and X(2)—X(2), are intermediate between the corresponding values for the chloride and bromide complexes. This is consistent with ordering of bromine in the terminal halogen sites as determined from the refinement. The question of whether the bromines are ordered in the three terminal sites at one end of the binuclear anions or statistically distributed over all six terminal sites has not been resolved. As discussed above, refinement of the ordered model in $P6_3mc$ was unsuccessful. However, it is

Table 3. *Atomic coordinates for $Cs_3Cr_2Cl_9$ from refinement of data of Wessel & IJdo (1957)*

	x	y	z
Cs(1)	0	0	$\frac{1}{4}$
Cs(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·0773 (3)
Cr	$\frac{1}{3}$	$\frac{2}{3}$	0·8375 (9)
Cl(1)	0·514 (2)	0·028	$\frac{1}{4}$
Cl(2)	0·822 (1)	0·644	0·0928 (5)

possible that the ordering occurs in microdomains and the X-ray intensity data correspond to an averaged model over all microdomains. The ordered model with three bromine atoms at one end (3–0 configuration) maintains the local threefold symmetry of the binuclear units (C_{3v}) whereas the statistical model includes configurations of the type 2–1 (two bromines at one end and one at the other) and the local threefold symmetry would be lost (highest point symmetry C_s). An analysis of vibrational and electronic spectra has been made to distinguish between these models and the results are consistent with the 3–0 configuration. These studies will be reported elsewhere.

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Structure of Hexaaquamanganese(II) Tetrabromozincate

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Abstract. $[Mn(H_2O)_6][ZnBr_4]$, $M_r = 548·02$, orthorhombic, *Pbam* {Hall symbol $\bar{P}22_{ab}$ [*Acta Cryst.* (1981), A**37**, 517–525]}, $a = 12·444$ (3), $b = 12·952$ (3), $c = 8·002$ (1) Å, $V = 1289·7$ Å^3, $Z = 4$, $D_x = 2·82$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 16·04$ mm^{-1}, $F(000) = 1020$, $T = 208$ K, $R = 0·052$ for 897 reflections. Prepared from a saturated equimolar aqueous solution of $MnBr_2$ and $ZnBr_2$. The crystal consists of octahedral $Mn(H_2O)_6^{2+}$ [av. Mn—O $= 2·18$ (1) Å] and tetrahedral $ZnBr_4^{2-}$ [av. Zn—Br $= 2·413$ (3) Å] ions linked by hydrogen bonds (3·30–3·68 Å).

Introduction. Recent studies of the binary bromides crystallized from saturated solution has highlighted how little is known about the structures of these compounds.

The current work was undertaken to confirm the correctness of the prediction of Balarew & Duhlev (1984) that Br will bond preferentially to the Zn and the H_2O to Mn.

Experimental. A crystal $0.02 \times 0.02 \times 0.25$ mm was mounted in a sealed glass capillary on a Nicolet $P2_1$ diffractometer and cooled to 208 K using the Nicolet LT1 temperature controller. Lattice parameters from 15 well centered reflections in the range $20° < 2\theta < 30°$. Absorption corrections using the program *DIFABS* (Walker & Stuart, 1983). Intensities of 2524 reflections with $0 \le h \le 14, 0 \le k \le 15, -9 \le l \le 9$ and $2\theta < 59°$. The $54\overline{2}$ and $16\overline{2}$ reflections as standards (< 1% variation). After averaging $(R = 0.046)$ 1192 unique reflections remained. Structure from *MULTAN80* (Main *et al.*, 1980), refined by least squares using *SHELX76* (Sheldrick, 1976) to give $R = 0.077$ at this stage. Weighting factor $w = [\sigma^2(F) + kF_o^2]^{-1/2}$ where $\sigma(F)$ is the error derived from counting statistics. Most of the reflections with $w||F_o| - |F_c|| > 2$ were very weak and, in spite of the assigned values of $\sigma(F)$, had intensities that were probably not significantly above background. Therefore, in the final round of refinement 295 reflections with $F < 3\sigma(F)$ were omitted to give $R = 0.052$ $(wR = 0.053)$. Weighting factor $k = 0.00115$ and the goodness of fit S was 0.601. Average shift/e.s.d. was 0.25 (max. $= 0.78$). A difference map calculated at this stage failed to show the positions of H atoms above the background (maximum difference electron density $= \pm 2.4$ e Å^{-3}). Scattering curves for Mn, Zn, Br and O from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.* A view down **c** is shown in Fig. 1.

Discussion. The bond distances and angles in $[Mn(H_2O)_6][ZnBr_4]$ (Table 2) all lie in the expected ranges. The anisotropic displacement parameters indicate that each of the complex ions is undergoing a small libration about its center of mass. Although the two $Mn(H_2O)_6$ groups are crystallographically independent their surroundings are remarkably similar. The equatorial oxygens [O(2), O(4)] form normal hydrogen bonds to the $ZnBr_4$ ion so that each Br is involved in two such bonds. The axial oxygens [O(1), O(3)] form rather weak bonds to Br(3) and to the equatorial O atoms in the adjacent $Mn(H_2O)_6$ complex.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42811 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positions* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(Å^2 \times 10^4)$

$$U_{eq} = \tfrac{1}{3}Tr\ U \times 10^4.$$

	x	y	z	U_{eq}
Mn(1)	5000	5000	5000	216
Mn(2)	0	5000	5000	199
Zn(1)	2641 (2)	3029 (2)	0	245
Br(1)	4557 (1)	3421 (1)	0	294
Br(2)	1550 (2)	4567 (1)	0	297
Br(3)	2348 (1)	2206 (1)	2637 (1)	307
O(1)	5019 (12)	6672 (10)	5000	445
O(2)	3770 (7)	4968 (7)	3080 (10)	313
O(3)	−1728 (10)	5427 (10)	5000	381
O(4)	212 (7)	6206 (7)	3118 (11)	344
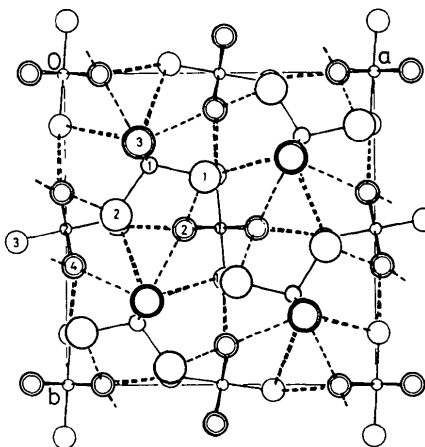
Fig. 1. $[Mn(H_2O)_6][ZnBr_4]$ viewed down the *c* axis.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Mn(1)—O(1)	2.166 (13) (×2)	O(1)—Mn(1)—O(2)	91.5 (4)
Mn(1)—O(2)	2.169 (8) (×4)	O(2)—Mn(1)—O(2)	90.2 (3)
Mn(2)—O(3)	2.220 (13) (×2)	O(3)—Mn(2)—O(4)	93.5 (3)
Mn(2)—O(4)	2.186 (9) (×4)	O(4)—Mn(2)—O(4)	92.9 (3)
Zn—Br(1)	2.437 (3)	Br(1)—Zn—Br(2)	112.3 (1)
Zn—Br(2)	2.411 (3)	Br(1)—Zn—Br(3)	104.0 (1)
Zn—Br(3)	2.392 (1) (×2)	Br(2)—Zn—Br(3)	106.4 (1)
		Br(3)—Zn—Br(3)	123.8 (1)

Possible H-bonded distances

O(2)—H⋯Br(3)	3.24 (1)	O(1)—H⋯Br(3)	3.57 (1) (×2)
O(2)—H⋯Br(1)	3.32 (1)	O(1)—H⋯O(4)	3.14 (1) (×2)
O(4)—H⋯Br(3)	3.32 (1)	O(3)—H⋯Br(3)	3.68 (1) (×2)
O(4)—H⋯Br(2)	3.47 (1)	O(3)—H⋯O(2)	3.01 (1) (×2)
O(4)—H⋯Br(2)	3.67 (1)		

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