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Zinc Bromide Dihydrate $ZnBr_2.2H_2O$: a Double-Salt Structure

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Abstract. $[Zn(H_2O)_6][Zn_2Br_6] = (ZnBr_2.2H_2O)_3$, M_r = 783·66, orthorhombic, *Immm* {Hall symbol $\bar{I}22$ [Hall (1981). *Acta Cryst.* A**37**, 517–525]}, a = 10·435 (1), b = 10·367 (1), c = 7·961 (1) Å, V = 861·2 (2) Å^3, Z = 2, D_x = 3·02 Mg m^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 17·68 mm^{-1}, $F(000)$ = 720, room temperature, R = 0·045 (wR = 0·046) for 327 unique observed [$I > 2\sigma(I)$] reflections. Prepared from a saturated aqueous solution of $ZnBr_2$ at 297 K. The compound is isostructural with $MgZn_2Br_6.6H_2O$ and consists of independent octahedral $Zn(H_2O)_6^{2+}$ complexes (ave. Zn—O = 2·07 Å) and dimeric tetrahedral $Zn_2Br_6^{2-}$ complexes [Zn—Br = 2·48 (bridging) and 2·36 Å (terminal)], linked together by O—H···Br hydrogen bonds.

Introduction. Although $ZnBr_2.2H_2O$ is a well known material its crystal structure has not previously been reported. Brehler (1961) reported the space group to be *I2mm*, with a = 10·4, b = 10·4, c = 7·94 Å, Z = 6. In their review of the structures of $MX_2.nH_2O$ salts, Balarew, Duhlev & Spassov (1984) pointed out that $ZnBr_2.2H_2O$ has different lattice parameters and hence probably a different structure from other $MX_2.2H_2O$ (M = Ca, Mn, Fe, Co, Ni, Cu; X = F, Cl, Br) compounds which are all composed of infinite chains of $MX_4(H_2O)_2$ octahedra sharing X—X edges.

Duhlev & Balarew (1986), in a study of solubility phase diagrams and X-ray powder diffraction patterns, found a continuous series of mixed crystals between $ZnBr_2.2H_2O$ and the double salt $MgZn_2Br_6.6H_2O$, suggesting that the two end members were isostructural. Using a method (Balarew & Duhlev, 1984) based on the relative softness and size of the ions, Duhlev & Balarew (1986) predicted that the structures of $MgZn_2Br_6.6H_2O$ and $ZnBr_2.2H_2O$ are composed of independent $Mg(H_2O)_6$ [or $Zn(H_2O)_6$] octahedra and $ZnBr_4$ tetrahedra, the latter either sharing corners to link into infinite chains $(ZnBr_3)_\infty$ or sharing edges to form discrete Zn_2Br_6 dimers. Further modelling of the structures (Duhlev, Faggiani & Brown, 1987) showed that the $[Mg(H_2O)_6][Zn_2Br_6]$ (or $[Zn(H_2O)_6][Zn_2Br_6]$) motifs fit well into the cell reported by Brehler (1961). These results are confirmed by the X-ray analysis of $MgZn_2Br_6.6H_2O$ (Duhlev, Faggiani & Brown, 1987) and $ZnBr_2.2H_2O$ (present work).

The successful prediction of the $ZnBr_2.2H_2O$ structure shows how unconventional sources such as solubility studies of three-component systems can sometimes be used to predict crystal structures.

Experimental. $ZnBr_2.2H_2O$ was obtained as colourless extremely hygroscopic crystals from saturated aqueous $ZnBr_2$ solution at room temperature. A crystal with dimensions 0·47 × 0·37 × 0·27 mm was coated with liquid paraffin, sealed in a thin-walled capillary under dry nitrogen and mounted on a Syntex $P2_1$ diffractometer. Unit-cell parameters were determined from 15 well centered strong reflections in the range $25 < 2\theta < 38°$. Intensities were measured for 891 reflections with $0 \leq h \leq 12$, $0 \leq k \leq 12$, $-9 \leq l \leq 9$, $2\theta < 50°$ and were corrected for Lorentz and polarization effects. The intensities of the $07\bar{1}$ and $25\bar{1}$

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Table 1. *Atomic positions and equivalent isotropic atomic displacement factors* (Å^2)

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ or U_{iso} (for H atoms).

	x	y	z	U_{eq}
Zn(1)	$\frac{1}{2}$	0·1602 (2)	0	0·0466
Zn(2)	0	0	0	0·0372
Br(1)	$\frac{1}{2}$	0	0·2318 (3)	0·0505
Br(2)	0·31230 (16)	0·28752 (16)	0	0·0579
O(1)	0·1425 (12)	0	0·1768 (16)	0·070
O(2)	0	0·2013 (15)	0	0·079
H(1)	0·163 (10)	0·069 (12)	0·219 (16)	0·11 (5)
H(2)	0·066 (17)	0·237 (19)	0	0·11 (8)

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

Zn(1)–Br(1)	2·483 (2)	(× 2)	Br(1)–Zn(1)–Br(1^{i})	95·96 (9)
			Br(1)–Zn(1)–Br(2)	111·87 (3)
Zn(1)–Br(2)	2·362 (2)	(× 2)	Br(2)–Zn(1)–Br(2^{ii})	111·99 (11)
Zn(2)–O(1)	2·047 (12)	(× 4)	O(1)–Zn(2)–O(1^{iii})	93·1 (5)
			O(1)–Zn(2)–O(2)	90·00
Zn(2)–O(2)	2·086 (15)	(× 2)	O(2)–Zn(2)–O(2)	180·00

O–H···Br	O–H	H···Br	O···Br	∠OHBr	∠HOH
O(1)–H(1)···Br(2^{iv})	0·82 (13)	2·70 (13)	3·420 (10)	148 (11)	122 (12)
O(2)–H(2)···Br(2)	0·80 (19)	2·63 (19)	3·379 (4)	163 (17)	124 (21)

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

reflections were monitored after every 48 measurements and showed variations less than 1·5%. Empirical absorption corrections were derived from ψ scans of 26 reflections (maximum correction factor of 3·22 for the intensity of reflection 811). Equivalent reflections were then averaged ($R_{int} = 0·029$) to give 461 unique reflections, 327 of which, with $I > 2\sigma(I)$, were used for the refinement. The heavy-atom coordinates for the isostructural $[Mg(H_2O)_6][Zn_2Br_6]$ (Duhlev, Faggiani & Brown, 1987) were used as the initial model. The positions of the H atoms were found from the difference map. A weight $w = [\sigma^2(F_o) + kF_o^2]^{-1}$ was used in the least-squares refinement, where $\sigma(F_o)$ is the uncertainty derived from counting statistics and k was refined to 0·000532. The scale factor, weighting factor (k), secondary-extinction coefficient and all variable positional and atomic displacement parameters were refined by least squares [function minimized $= \sum w(|F_o| - |F_c|)^2$] with *SHELX*76 (Sheldrick, 1976). The coordinates of O(1) and H(1) were strongly correlated and were refined in alternate cycles. The final cycle of the refinement gave $R = 0·045$ ($wR = 0·046$) and a goodness of fit $S = 1·65$. The average shift/e.s.d. = 0·001 (max. = 0·002). The secondary-extinction coefficient (Larson, 1967) $g = 0·0005$ (2). The final difference electron density has maximum and minimum values of +0·95 and −0·99 e Å^{-3} respectively. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates and temperature factors are given in Table 1.*

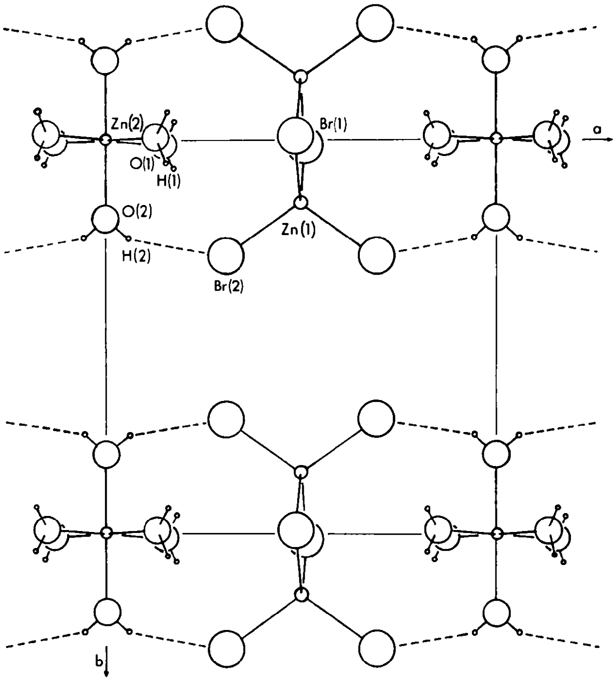

Fig. 1. Projection of the structure of $[Zn(H_2O)_6][Zn_2Br_6]$ down the c axis. The H(1) atoms hydrogen bond to the Br(2) atoms from the Zn_2Br_6 groups located above (or below) the $Zn(H_2O)_6$ octahedra.

Discussion. The bond distances and angles are shown in Table 2. The structure found confirms the prediction of Duhlev & Balarew (1986). $ZnBr_2.2H_2O$ is isostructural with $[Mg(H_2O)_6][Zn_2Br_6]$ (Duhlev, Faggiani & Brown, 1987). There are two different kinds of Zn atoms in the structure. Zn(1) is tetrahedrally coordinated by four Br atoms and forms dimeric $Zn_2Br_6^{2-}$ groups with *mmm* crystallographic symmetry. The bridging function of Br(1) distorts both the bond distances and the angles around Zn(1) from an ideal tetrahedron. Zn(2) forms $Zn(H_2O)_6^{2+}$ octahedra also with crystallographic *mmm* symmetry. These are linked to the $Zn_2Br_6^{2-}$ groups through O(2)–H(2)···Br(2) hydrogen bonds to form infinite chains $[Zn(H_2O)_6]^{2+}$-$[Zn_2Br_6]^{2-}$ extended along the a axis and through O(1)–H(1)···Br(2) hydrogen bonds into layers in the bc plane (Table 2). The bridging Br(1) does not participate in the hydrogen bonding. The $Zn(H_2O)_6^{2+}$ and $Zn_2Br_6^{2-}$ complex ions are arranged in an NaCl-type structure with a and b axes rotated 45° with

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* Lists of structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51086 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

respect to the pseudo-cubic axes of 7·4 Å. Fig. 1 represents a view of the structure in the *ab* plane.

$ZnBr_2.2H_2O$ and $MgZn_2Br_6.6H_2O$ are not only isostructural but almost exactly isometric. There are small differences in the unit cell (~0·2%) but all the atomic positional and displacement parameters are the same within the limits of experimental uncertainty. The only change that occurs when Mg is substituted for Zn is a reduction in the (Mg, Zn)—O bond lengths but this is only marginally significant.

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Structures of Oxonium Pentafluorozirconate Mono- and Dihydrates

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Abstract. (I) $[ZrF_5^-.H_3O^+.2H_2O]$, $M_r = 241\cdot27$, monoclinic, $C2$, $a = 10\cdot171$ (9), $b = 6\cdot603$ (1), $c = 18\cdot156$ (10) Å, $\beta = 106\cdot29$ (7)°, $V = 1170$ (2) Å^3, $Z = 8$, $D_x = 2\cdot738$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 19\cdot03$ cm^{-1}, $F(000) = 928$, $T = 293$ K, $R = 0\cdot045$ for 977 unique observed reflections. (II) $[ZrF_5^-.H_3O^+.H_2O]$, $M_r = 223\cdot25$, orthorhombic, *Cmmm*, $a = 6\cdot620$ (3), $b = 9\cdot858$ (3), $c = 8\cdot066$ (2) Å, $V = 526\cdot4$ (5) Å^3, $Z = 4$, $D_x = 2\cdot817$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 20\cdot92$ cm^{-1}, $F(000) = 424$, $T = 293$ K, $R = 0\cdot022$ for 323 unique observed reflections. Both structures consist of two-dimensional networks of $(ZrF_5)^{n-}$ connected by oxonium ions and water molecules *via* O—H···O and O—H···F hydrogen bonds. The two structures have nearly identical $(ZrF_5)^{n-}$ layers but differ principally in the packing of these layers and in the hydrogen bonding between them.

Introduction. Hydrates of ZrF_4 have been of interest in research work on fluorine glasses; during the synthesis of $ZrF_4.H_2O$ two distinct fluorohydrates have been isolated and crystallized. Several fluorohydrates have already been mentioned (Waters, 1960; Gaudreau, 1965) but, in the absence of crystal structure determinations, the number of water molecules was still questionable. The present paper reports the structure of $ZrF_4.HF.3H_2O$ (I) (given by Gaudreau as $ZrF_4.HF.4H_2O$) and $ZrF_4.HF.2H_2O$ (II) (given by Waters as $ZrF_4.HF.3H_2O$): as was previously shown for the Ti compound, $TiF_5^-.OH_3^+$ (Cohen, Selig & Gut, 1982), we establish the ionic formulation and the presence of oxonium ions.

Experimental. Enraf–Nonius CAD-4 diffractometer, graphite monochromator; unit-cell parameters refined from 25 reflections in the range $8 < \theta < 12°$; three standard reflections monitored at 100 reflections intervals; scans by $\omega/2\theta$ method; sphere up to $\theta = 25°$; Lorentz and polarization corrections; structure solved by Patterson function for Zr, remaining atoms located by difference Fourier technique; full-matrix least-squares refinement on F; scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); calculations on a PDP 11/23 Plus using the *SDP Plus* suite of programs (Frenz, 1983). (I) prepared by dissolving ZrF_4 in 40% aqueous HF and evaporating slowly at ambient temperature (Gaudreau, 1965); colourless crystal, 1·0 × 0·6 × 0·4 mm; loss of 19·3% in 16 h, linearly corrected; 1231 reflections collected, 1122 unique, 977 with $I \geq 3\sigma(I)$; $0 \leq h \leq 12$, $0 \leq k \leq 7$, $-21 \leq l \leq 21$; empirical absorption correction using the program *DIFABS* (Walker & Stuart, 1983), max. and min. transmissions, 2·0–0·78; anisotropic thermal parameters for Zr; $R = 0\cdot045$, $wR = 0\cdot049$ ($w = 1$), $(\Delta/\sigma)_{\max} = 0\cdot10$, $S = 4\cdot5$. In final difference Fourier synthesis, no peaks greater than 0·9 e Å^{-3}; no correction for extinction. (II) ZrF_4 in 40% aqueous HF and evaporat-

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