

Structure of Magnesium Zinc Tetrabromide Heptahydrate, $\text{MgZnBr}_4 \cdot 7\text{H}_2\text{O}$

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(Received 13 October 1988; accepted 8 November 1988)

Abstract. $[\text{Mg}(\text{H}_2\text{O})_6][\text{ZnBr}_4] \cdot \text{H}_2\text{O}$, $M_r = 535.41$, monoclinic, $P2_1/n$ {Hall symbol $-P2_1^n$ [Hall (1981), *Acta Cryst.* A37, 517–525]}, $a = 8.327(1)$, $b = 12.596(3)$, $c = 14.048(2)$ Å, $\beta = 97.92(1)^\circ$, $V = 1459.4(5)$ Å³, $Z = 4$, $D_x = 2.44$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 12.41$ mm⁻¹, $F(000) = 1008$, room temperature, $R = 0.047$ ($wR = 0.046$) for 1073 unique observed [$I > 2\sigma(I)$] reflections. The structure consists of independent octahedral $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ (ave. Mg–O = 2.05 Å), tetrahedral ZnBr_4^{2-} (ave. Zn–Br = 2.41 Å) complexes and an uncoordinated H_2O molecule, linked together by O–H...Br and O–H...O hydrogen bonds.

Introduction. In their study of the equilibrium phase diagram of the system MgBr_2 – ZnBr_2 – H_2O at 298 K, Duhlev & Balarew (1986) found two new double salts, $\text{MgZnBr}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgZn}_2\text{Br}_6 \cdot 6\text{H}_2\text{O}$, as well as mixed crystals formed between $\text{MgZn}_2\text{Br}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$. After reporting the structures of $\text{MgZn}_2\text{Br}_6 \cdot 6\text{H}_2\text{O}$ (Duhlev, Faggiani & Brown, 1987) and $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$ (Duhlev, Brown & Faggiani, 1988), we now report the structure of $\text{MgZnBr}_4 \cdot 7\text{H}_2\text{O}$. From a method (Balarew & Duhlev, 1984) which considers the softness and size of the ions to be the most important factors determining the molecular structure, this struc-

ture was predicted (Duhlev, 1984) to contain independent octahedral $\text{Mg}(\text{H}_2\text{O})_6$ and tetrahedral ZnBr_4 groups and an uncoordinated water molecule. The aim of this X-ray analysis is to check the validity of this prediction.

Experimental. $\text{MgZnBr}_4 \cdot 7\text{H}_2\text{O}$ crystallizes as colourless extremely hygroscopic crystals from saturated aqueous solution containing MgBr_2 and ZnBr_2 in a molar ratio 1:1. A crystal with dimensions $0.53 \times 0.30 \times 0.12$ mm was coated with liquid paraffin, sealed

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Table 1. Atomic positions and equivalent isotropic atomic displacement factors (Å²)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zn	0.4736 (2)	0.30477 (14)	0.31979 (13)	0.0424
Br(1)	0.4328 (2)	0.21811 (15)	0.46769 (12)	0.0547
Br(2)	0.4978 (2)	0.49239 (13)	0.34010 (11)	0.0506
Br(3)	0.7242 (2)	0.23437 (13)	0.27473 (12)	0.0551
Br(4)	0.2477 (2)	0.26131 (14)	0.20138 (12)	0.0586
Mg(1)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.0430
Mg(2)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.0387
O(1)	0.3880 (14)	0.5639 (9)	0.1092 (7)	0.063
O(2)	0.3606 (16)	0.3664 (10)	−0.0006 (8)	0.075
O(3)	0.6687 (14)	0.4325 (9)	0.1032 (8)	0.062
O(4)	0.1374 (17)	0.3695 (10)	0.5444 (10)	0.092
O(5)	−0.2033 (13)	0.4190 (9)	0.5254 (8)	0.064
O(6)	−0.0328 (18)	0.4433 (12)	0.3634 (8)	0.097
O(7)	−0.0042 (15)	0.4811 (10)	0.1706 (9)	0.084

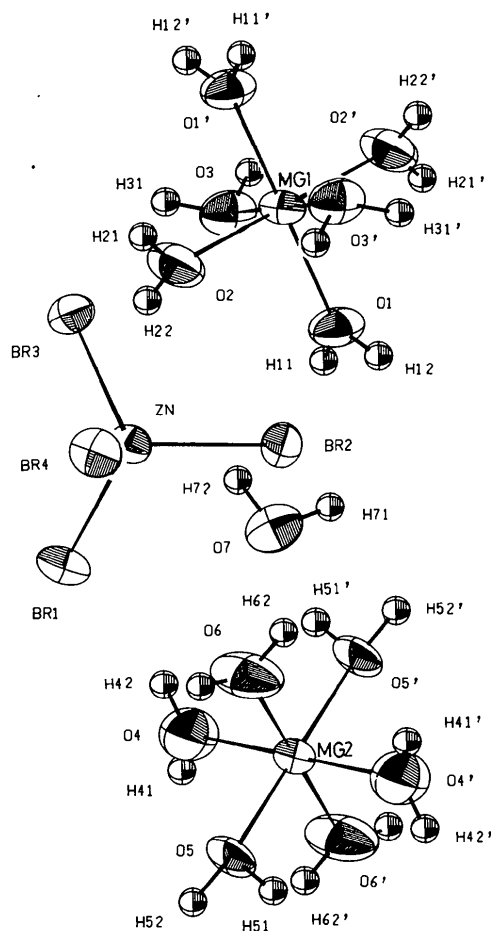


Fig. 1. Molecular structure of $\text{MgZnBr}_4 \cdot 7\text{H}_2\text{O}$ with thermal ellipsoids.

in a thin-walled capillary under dry nitrogen and mounted on a Syntex P_2 diffractometer. Unit-cell parameters were determined from 15 well centred strong reflections in the range $19 < 2\theta < 28^\circ$. Intensities were measured for 3150 reflections with $0 \leq h \leq 8$, $-10 \leq k \leq 13$, $-15 \leq l \leq 15$ and $2\theta \leq 45^\circ$ and were corrected for Lorentz and polarization effects. Empirical absorption corrections were derived from ψ scans of 17 reflections (maximum correction factor of 1.77 for the intensities of reflections $25\bar{1}$, $2\bar{4}2$ and $2\bar{5}2$). The intensities of the 117 and 400 reflections were monitored after every 48 measurements and showed variations less than 2.2 and 1.8% respectively. Equivalent reflections were averaged ($R_{\text{int}} = 0.012$) to give 1919 unique reflections, 1073 of which, with $I > 2\sigma(I)$, were used for the refinement. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). The positions of the H atoms, determined from the difference map and from chemical considerations, were held fixed. A weight $w = [\sigma^2(F_o) + kF_o^2]^{-1}$ was used, where $\sigma(F_o)$ is the uncertainty derived from counting statistics and k was refined to 9.47×10^{-4} . The scale factor, weighting factor (k), secondary-extinction coefficient and all variable (non-hydrogen) positional and atomic displacement factors were refined by least squares [function minimized = $\sum w(|F_o| - |F_c|)^2$] with *SHELX76* (Sheldrick, 1976). The final cycle of the refinement gave $R = 0.047$ ($wR = 0.046$) and a

Table 2. *Interatomic distances* (Å) *and angles* ($^\circ$)

Octahedron Mg(1)O ₆					
Mg(1)	O(1)	O(2)	O(3)		
O(1)	2.065 (11)	2.920 (16)	2.875 (17)		
O(2)	90.5 (5)	2.044 (11)	2.894 (16)		
O(3)	88.4 (4)	89.7 (5)	2.058 (10)		
Octahedron Mg(2)O ₆					
Mg(2)	O(4)	O(5)	O(6)		
O(4)	2.050 (12)	2.881 (18)	2.890 (18)		
O(5)	89.3 (5)	2.050 (10)	2.860 (18)		
O(6)	90.1 (6)	89.0 (5)	2.031 (11)		
Tetrahedron ZnBr ₄					
Zn	Br(1)	Br(2)	Br(3)	Br(4)	
Br(1)	2.412 (2)	3.963 (3)	3.884 (3)	3.883 (2)	
Br(2)	111.32 (9)	2.386 (2)	3.929 (3)	3.935 (2)	
Br(3)	106.63 (9)	109.27 (10)	2.430 (3)	3.974 (3)	
Br(4)	107.65 (10)	110.68 (9)	110.78 (9)	2.396 (2)	
Hydrogen bonds and angles					
O—H...X	O—H	H...X	O...X	O—H...X	H—O—H
O(1)—H(11)...Br(2)	0.97	2.41	3.370 (10)	176	112
O(1)—H(12)...Br(1 ⁱ)	0.98	2.40	3.358 (11)	164	
O(2)—H(21)...Br(3 ⁱⁱ)	0.91	2.57	3.446 (11)	161	113
O(2)—H(22)...Br(4)	0.86	2.59	3.380 (12)	154	
O(3)—H(31)...Br(3)	1.00	2.87	3.456 (11)	118	98
O(3)—H(31)...Br(1 ⁱⁱⁱ)	1.00	3.04	3.635 (12)	119	
O(3)—H(32)...O(7 ^{iv})	1.00	1.88	2.825 (16)	156	
O(4)—H(41)...Br(3 ^v)	0.92	2.59	3.472 (14)	160	160
O(4)—H(42)...Br(1)	0.91	2.52	3.403 (14)	166	
O(5)—H(51)...Br(2 ^{vi})	1.02	2.85	3.469 (11)	119	104
O(5)—H(51)...Br(2 ^{vii})	1.02	2.77	3.479 (12)	126	
O(5)—H(52)...Br(4 ^{viii})	1.01	2.42	3.423 (12)	174	
O(6)—H(61)...Br(3 ^{vii})	0.89	2.56	3.446 (14)	172	113
O(6)—H(62)...O(7)	0.97	1.98	2.792 (17)	140	
O(7)—H(71)...Br(1 ⁱ)	0.97	2.72	3.655 (13)	162	110
O(7)—H(72)...Br(4)	0.96	2.70	3.464 (13)	137	

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

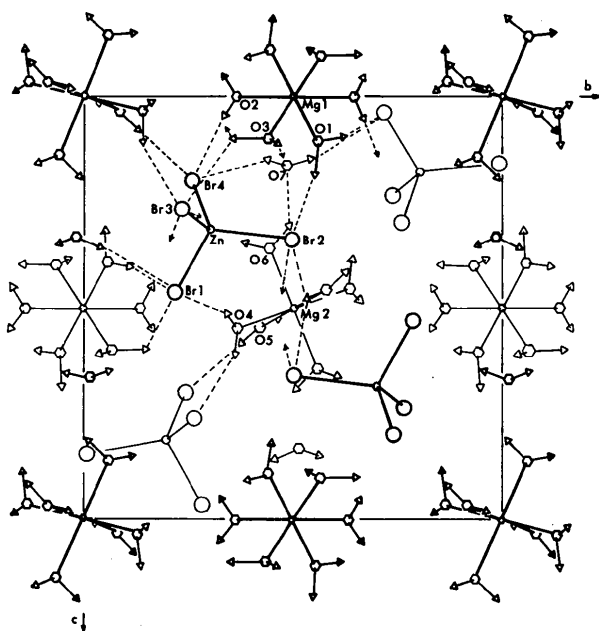


Fig. 2. Projection of the $\text{MgZnBr}_4 \cdot 7\text{H}_2\text{O}$ structure down the a axis. The groups centred around the level $x = 0.5$ are drawn with thick pen, while those around $x = 0$ with thin pen. Hydrogen bonds involving labelled atoms are shown by a dashed line (a dashed arrow pointing to an atom represents a hydrogen bond to the atom from one unit cell above).

goodness of fit $S = 1.17$. The average shift/e.s.d. = 0.001 (max. = 0.004). The secondary-extinction coefficient (Larson, 1967) $g = 0.00114$ (16). The final difference electron density has maximum and minimum values of +0.79 and -0.75 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 temperature factors are given in Table 1.*

Discussion. The structure found (Fig. 1) confirms the prediction of Duhlev (1984). Zn is surrounded by four Br atoms in an almost regular tetrahedron. The centres of symmetry are occupied by two crystallographically distinct kinds of Mg atoms, both of them coordinated by six water molecules in $\text{Mg}(\text{H}_2\text{O})_6$ octahedra which are regular within the accuracy of the experiment. The

* Lists of structure factors, anisotropic atomic displacement factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51598 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

seventh water molecule is uncoordinated and lies between the $\text{Mg}(\text{H}_2\text{O})_6$ and ZnBr_4 groups. The structure can be described (Fig. 2) as formed by sheets containing two kinds of parallel chains extended along the b axis: one formed by the alternation of $[\text{Mg}(1)(\text{H}_2\text{O})_6]$ and $[\text{Mg}(2)(\text{H}_2\text{O})_6]$ octahedra, the other of $[\text{ZnBr}_4]$ and uncoordinated H_2O molecules.

An extensive network of $\text{O}-\text{H}\cdots\text{Br}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds holds the different groups together. Although there are 14 H atoms in the asymmetric unit, they participate in 16 hydrogen bonds (Table 2) since two of the H atoms form bifurcated $\text{O}-\text{H}\begin{matrix} \nearrow \text{Br} \\ \searrow \text{Br} \end{matrix}$ bonds.

The environment around O(7), the oxygen of the uncoordinated water molecule, is tetrahedral, with angles varying between 90 and 122° (ave. 108.6°). O(7) participates in two donor hydrogen bonds, to Br(1') and Br(4), and in two acceptor ones, from O(3) and O(6).

We gratefully acknowledge Mr Romolo Faggiani's help in the data collection and financial support from

the Natural Science and Engineering Research Council of Canada through an operating grant to IDB.

References

- BALAREW, CHR. & DUHLEV, R. (1984). *J. Solid State Chem.* **55**, 1–6.
 DUHLEV, R. (1984). PhD Thesis. Bulgarian Academy of Sciences, Sofia.
 DUHLEV, R. & BALAREW, CHR. (1986). *Rev. Chim. Miner.* **23**, 116–124.
 DUHLEV, R., BROWN, I. D. & FAGGIANI, R. (1988). *Acta Cryst.* **C44**, 1696–1698.
 DUHLEV, R., FAGGIANI, R. & BROWN, I. D. (1987). *Acta Cryst.* **C43**, 2046–2048.
 HALL, S. R. (1981). *Acta Cryst.* **A37**, 517–525.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1989). **C45**, 699–701

A Mixed-Valence Niobium Phosphate with an Empty Nasicon Structure: $\text{Nb}_2(\text{PO}_4)_3$

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(Received 14 October 1988; accepted 14 November 1988)

Abstract. Niobium(IV) niobium(V) phosphate, $M_r = 470.73$, trigonal, $R\bar{3}c$, $a = 8.6974$ (7), $c = 22.123$ (2) Å, $V = 1449.3$ (3) Å³, $Z = 6$, $D_x = 3.24$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.824$ mm⁻¹, $T = 294$ K, $F(000) = 223$, $R = 0.0347$ and $wR = 0.03706$ for 435 observed reflections. The niobium has a mixed valence (IV)–(V). The framework is built up from NbO_6 octahedra sharing corners with PO_4 tetrahedra and belongs to the empty Nasicon-type structure.

Introduction. The introduction of mixed-valence transition elements in oxides characterized by a mixed framework of octahedra and tetrahedra can be used to generate particular physical properties. Two classes of materials can be distinguished according to whether the octahedra share their corners forming infinite chains or layers, or whether they are only linked to the tetrahedra. The crystal chemistry of phosphates which

shows the great ability of PO_4 tetrahedra and MO_6 octahedra to adapt to each other allows both families to be synthesized. The first class of oxides, which is represented by the large family of phosphate tungsten bronzes (Raveau, 1986), allows anisotropic metallic or semi-metallic conductivity to be generated owing to the delocalization of electrons along the octahedral chains or layers. Conversely, the second class in which the MO_6 octahedra are isolated from each other does not present such electron-transport properties but is of interest for the study by local structural methods of the environment of such ions in the crystalline matrix and for the study of their distribution, ordered or not, in the lattice; it also raises the question of the possible electron transfer between two centers which each have a different oxidation state. Few compounds corresponding to this latter family have been isolated up to now. Those that have include the molybdenum phosphates $\text{AMo}_3\text{P}_6\text{Si}_2\text{O}_{25}$ ($A = \text{K, Rb, Tl, Cs}$) (Leclaire, Monier &