Structure of Magnesium Zinc Tetrachloride Hexahydrate MgZnCl₄.6H₂O

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Abstract. Hexaaquamagnesium tetrachlorozincate, $[Mg(H_2O)_6][ZnCl_4]$, $M_r = 339 \cdot 59$, triclinic, $P\bar{1}$, $a = 6 \cdot 562$ (1), $b = 6 \cdot 597$ (1), $c = 14 \cdot 101$ (1) Å, $\alpha = 88 \cdot 63$ (1), $\beta = 89 \cdot 43$ (1), $\gamma = 84 \cdot 83$ (1)°, $V = 607 \cdot 7$ (5) Å³, $Z = 2$, $D_x = 1 \cdot 86$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71073$ Å, $\mu = 3 \cdot 00$ mm⁻¹, $F(000) = 340$, $T = 290$ K, $R = 0 \cdot 029$ ($wR = 0 \cdot 031$) for 2585 unique observed $[I > 3\sigma(I)]$ reflections. The structure consists of $Mg(H_2O)_6^{2+}$ octahedra and $ZnCl_4^{2-}$ tetrahedra linked together by O—H⋯Cl hydrogen bonds and packed in a CsCl-like lattice. A comparison is made between the structures of $MZnX_4.nH_2O$ compounds (M = Mg, Ca, Mn; X = Cl, Br; n = 5, 6, 7). The correlation found between the number of water molecules (n) and the ratio of the radius of the complex cation to the radius of the complex anion is explained.

Introduction. In their study of the phase equilibrium in the system $MgCl_2$–$ZnCl_2$–H_2O at 297 K, Balarew & Spassov (1980) found a wide field of crystallization of a new double salt which was assigned the formula $MgZnCl_4.5H_2O$. It was interesting to solve the structure of this crystallohydrate to check the prediction of Duhlev (1984) and to compare the structure with that of $CaZnBr_4.5H_2O$ (Duhlev, Brown & Faggiani, 1988), where Ca is sevenfold coordinated by five water molecules and two Br atoms each from a different $ZnBr_4$ tetrahedron. An aqueous solution of $MgCl_2$ and $ZnCl_2$ in the molar ratio 1:1 was left in a desiccator until colourless, very hygroscopic crystals started to form. During the course of the X-ray study it became clear that the composition of the double salt was in fact $MgZnCl_4.6H_2O$. About ten different crystals were checked and they all showed the lattice parameters of the hexahydrate.

Experimental. A crystal with approximate dimensions $0 \cdot 1 \times 0 \cdot 2 \times 0 \cdot 1$ mm was separated from the mother liquor and immediately covered with a suspension of wax in toluene. In a few seconds, the organic solvent evaporated and the crystal, coated with a thin protective film of wax, was mounted on a glass capillary and investigated on an Enraf–Nonius CAD-4 diffractometer. ω–2θ scans. Unit-cell parameters were determined from 24 well centred strong reflections in the range $24 < \theta < 26°$. Intensities were measured for 2980 reflections with $0 \leq h \leq 8$, $-8 \leq k \leq 8$, $-18 \leq l \leq 18$ and $\theta < 28°$ and were corrected for Lorentz and polarization effects. The reflections 200, 020 and 006, serving as intensity standards, were monitored every 2 h and showed variations less than 2%. Empirical absorption correction coefficients were derived from ψ scans of nine reflections (transmission factor varied between 0·80 and 0·99). A small number of equivalent reflections were averaged ($R_{int} = 0 \cdot 023$) to give 2743 unique reflections, 2585 of which $[I > 3\sigma(I)]$ were used in the subsequent calculations. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The H-atom positions were found from the difference map and refined with a fixed $B_{iso} = 5$ Å². The scale factor, secondary-extinction coefficient, all positional parameters and all (non-H) anisotropic atomic displacement factors (a total of 149 parameters) were refined by least squares [function minimized $= \Sigma w(|F_o| - |F_c|)^2$]. The final cycle of refinement gave $R = 0 \cdot 029$ ($wR = 0 \cdot 031$) and goodness of fit $S = 0 \cdot 75$. The weight applied was defined as $w = F_o/43 \cdot 15$ if $F_o < 43 \cdot 15$ or $w = 43 \cdot 15/F$ if $|F_o| \geq 43 \cdot 15$. Empirical correction for secondary extinction $F(corr) = F/(1 + gI)$; g refined to $0 \cdot 127 \times 10^{-4}$. The average shift/e.s.d. $= 0 \cdot 01$ (max. $= 0 \cdot 03$). The final difference electron density has maximum and minimum values of $+0 \cdot 39$ and $-0 \cdot 36$ e Å⁻³, respectively. Atomic scattering factors and anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1.). PDP 11/44 computer with a locally modified CAD-4/*SDP* V3.0 software package were used. The

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Table 1. *Atomic positions and equivalent isotropic displacement parameters*

$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2)$
$+ ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$

	x	y	z	B_{eq} (Å^2)
Zn	0·47483 (6)	0·41040 (6)	0·25981 (2)	2·269 (6)
Cl(1)	0·1429 (1)	0·5459 (1)	0·25993 (6)	3·05 (1)
Cl(2)	0·4661 (1)	0·0633 (1)	0·26492 (6)	3·23 (2)
Cl(3)	0·6284 (1)	0·4811 (1)	0·12043 (6)	3·94 (2)
Cl(4)	0·6334 (1)	0·5170 (1)	0·38648 (5)	3·28 (2)
Mg(1)	0	0	0	2·33 (3)
Mg(2)	0	0	½	2·07 (2)
O(11)	0·1640 (5)	−0·2469 (4)	0·0566 (2)	6·37 (7)
O(12)	0·0776 (5)	0·1665 (5)	0·1129 (2)	6·50 (7)
O(13)	0·2542 (5)	0·0703 (4)	−0·0742 (2)	6·95 (7)
O(21)	0·0906 (4)	0·2799 (3)	0·4585 (2)	3·21 (5)
O(22)	0·0816 (4)	0·0457 (3)	0·6390 (2)	3·17 (4)
O(23)	0·2914 (3)	−0·1232 (4)	0·4716 (2)	3·65 (5)

final atomic coordinates and temperature factors are given in Table 1.*

Discussion. The bond distances and angles are shown in Table 2. The molecular structure, which is similar to that of [Mn(H$_2$O)$_6$][ZnBr$_4$] (Villella, Faggiani & Brown, 1986), is in agreement with the prediction based on the method of Balarew & Duhlev (1984): the harder metal ion, Mg^{2+}, coordinates the harder H$_2$O ligands while the softer Zn^{2+} is bonded to the softer Cl$^-$ ligands. Zn, in a general position, is tetrahedrally coordinated by four chlorines with Zn—Cl distances between 2·24 and 2·30 Å which are typical for this bond. There are two crystallographically distinct Mg atoms placed at the centres of symmetry, each surrounded by six water molecules in a regular octahedron [bond lengths Mg(1)—O = 2·02–2·05 Å and Mg(2)—O = 2·05–2·07 Å]. The Mg(H$_2$O)$_6^{2+}$ and ZnCl$_4^{2-}$ complex ions are linked by an extensive network of O—H⋯Cl hydrogen bonds (Table 2 and Fig. 1). The four Cl atoms participate in 12 hydrogen bonds which, as one can expect from the low symmetry of the cell, are not distributed uniformly among the Cl atoms. Cl(4), which forms the shortest bond to Zn, accepts only two hydrogen bonds; Cl(2) forms the longest Zn—Cl bond and accepts four hydrogen bonds while Cl(1) and Cl(3) participate in three hydrogen bonds each. In addition to these strong hydrogen bonds, most H atoms also participate in weak O—H⋯Cl hydrogen bonds with H⋯Cl distances between 2·91 and 3·54 Å and O—H—Cl angles between 84 and 132°.

If we compare this structure with those of MnZnBr$_4$.6H$_2$O (Villella, Faggiani & Brown, 1986) and MgZnBr$_4$.7H$_2$O (Duhlev & Brown, 1989), we

* Lists of structure factors, H-atom positions and anisotropic atomic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53974 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Octahedron Mg(1)(H$_2$O)$_6$

Mg(1)	O(11)	O(12)	O(13)
O(11)	2·022 (3)	2·864 (4)	2·854 (4)
O(12)	89·37 (12)	2·050 (3)	2·931 (4)
O(13)	89·16 (12)	91·43 (12)	2·043 (3)

Octahedron Mg(2)(H$_2$O)$_6$

Mg(2)	O(21)	O(22)	O(23)
O(21)	2·060 (2)	2·949 (4)	2·862 (3)
O(22)	90·96 (9)	2·073 (2)	2·914 (4)
O(23)	88·24 (9)	89·93 (9)	2·049 (2)

Tetrahedron ZnCl$_4$

Zn	Cl(1)	Cl(2)	Cl(3)	Cl(4)
Cl(1)	2·2787 (8)	3·6626 (10)	3·7245 (11)	3·6835 (11)
Cl(2)	106·34 (3)	2·2951 (8)	3·6193 (11)	3·7386 (11)
Cl(3)	110·30 (3)	105·23 (3)	2·2577 (9)	3·7653 (11)
Cl(4)	109·30 (3)	111·14 (3)	113·79 (3)	2·2353 (8)

Principal hydrogen bonds

O—H⋯X	O—H	H⋯X	O⋯X	O—H⋯X	H—O—H
O(11)—H(11)′⋯Cl(1^i)	0·77 (4)	2·39 (4)	3·154 (3)	173 (4)	118 (5)
O(11)—H(11)″⋯Cl(3^{ii})	0·66 (4)	2·57 (5)	3·196 (3)	157 (5)	
O(12)—H(12)′⋯Cl(3^{iii})	0·75 (5)	2·78 (5)	3·451 (3)	150 (5)	106 (4)
O(12)—H(12)″⋯Cl(2)	0·95 (4)	2·42 (4)	3·359 (3)	169 (3)	
O(13)—H(13)′⋯Cl(3^{iv})	0·85 (5)	2·33 (5)	3·176 (3)	171 (4)	103 (5)
O(13)—H(13)″⋯Cl(2^{ii})	0·67 (5)	2·75 (5)	3·332 (3)	147 (5)	
O(21)—H(21)′⋯Cl(1)	0·76 (4)	2·59 (4)	3·300 (3)	157 (4)	108 (4)
O(21)—H(21)″⋯Cl(4^v)	0·72 (4)	2·53 (4)	3·242 (3)	172 (4)	
O(22)—H(22)′⋯Cl(2^{vi})	0·91 (4)	2·40 (4)	3·288 (3)	167 (4)	124 (4)
O(22)—H(22)″⋯Cl(1^{vii})	0·75 (4)	2·59 (4)	3·300 (2)	158 (5)	
O(23)—H(23)′⋯Cl(4^{ii})	0·67 (4)	2·63 (4)	3·246 (2)	156 (5)	125 (5)
O(23)—H(23)″⋯Cl(2)	0·77 (4)	2·60 (5)	3·367 (3)	170 (4)	

Symmetry codes: (i) x, $y-1$, z; (ii) $1-x$, $-y$, $-z$; (iii) $x-1$, y, z; (iv) $1-x$, $1-y$, $-z$; (v) $1-x$, $1-y$, $1-z$; (vi) $1-x$, $-y$, $1-z$; (vii) $-x$, $1-y$, $1-z$.
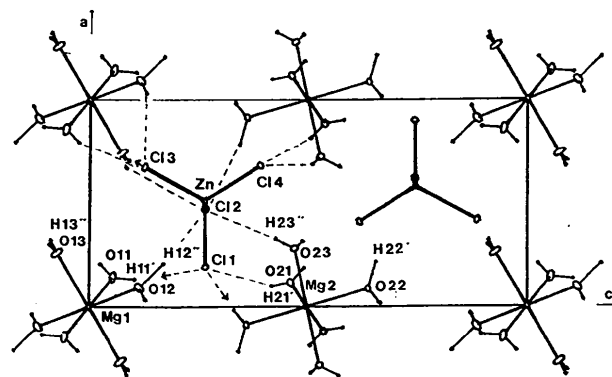

Fig. 1. Projection of the structure of [Mg(H$_2$O)$_6$][ZnCl$_4$] down the b axis. The labels correspond to the atomic positions from Table 1. The ZnCl$_4$ groups are centred around the level $y = 0·5$. The hydrogen bonds involving the four labelled Cl atoms are shown by a dashed line (a dashed arrow points to an H atom from one unit cell above).

find similarities in molecular structure and lattice spacings (Table 3). Both MgZnCl$_4$.6H$_2$O and MnZnBr$_4$.6H$_2$O show a distorted CsCl-type structure with the complex ions M(H$_2$O)$_6^{2+}$ (M = Mg,Mn) and ZnX$_4^{2-}$ (X = Cl, Br) occupying the simple ions' sites. Each ZnX$_4^{2-}$ has eight nearest M(H$_2$O)$_6^{2+}$ neighbours [four M(1)(H$_2$O)$_6^{2+}$ and four M(2)(H$_2$O)$_6^{2+}$] and each

Table 3. *Crystal data for compounds containing $[M(H_2O)_6][M'X_4]$ motifs*

Compound	Ref.	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z	V/Z (Å³)
$[Mg(H_2O)_6][ZnCl_4]$	(a)	$P\bar{1}$	6·6	6·6	2 × 7·0	89	89	85	2	304
$[Mn(H_2O)_6][ZnBr_4]$	(b)	$Pbam$	2 × 6·2	2 × 6·5	8·0	90	90	90	4	322
$[Mg(H_2O)_6][ZnBr_4].H_2O^*$	(c)	$P2_1/c$	2 × 6·3	2 × 7·0	8·3	98	90	90	4	365
			2 × 6·3	7·7	8·6	119	90	90	2	

References: (a) This paper; (b) Villella, Faggiani & Brown (1986); (c) Duhlev & Brown (1989).

* The crystal axes for $[Mg(H_2O)_6][ZnBr_4].H_2O$ are listed on the first line in the order b, c, a for the actual cell corresponding to (c) and on the second line in the order b', a', c' for the CsCl-like cell (see text).

$M(1)(H_2O)_6^{2+}$ or $M(2)(H_2O)_6^{2+}$ has eight nearest ZnX_4^{2-} neighbours.

The presence of an additional interstitial water molecule in $MgZnBr_4.7H_2O$ (Duhlev & Brown, 1989) introduces a severe distortion from the CsCl-type of arrangement for the complex ions $Mg(H_2O)_6^{2+}$ and $ZnBr_4^{2-}$. A CsCl-like cell is achieved by rotating the actual cell 45° around b and has $a' = 7·66$, $b' = b/2 = 6·30$, $c' = 8·65$ Å and $\beta' = 118·9°$. $ZnBr_4^{2-}$ is displaced quite far from the expected position in a CsCl-like cell and is surrounded by six nearest $Mg(H_2O)_6^{2+}$ ions [three $Mg(1)(H_2O)_6^{2+}$ and three $Mg(2)(H_2O)_6^{2+}$] in a trigonal prism. Each kind of $Mg(H_2O)_6^{2+}$ is in an octahedral environment of six nearest $ZnBr_4^{2-}$ ions.

Brown & Duhlev (1991), considering the crystal structures of double salts as close-packed complex ions with radii $R = L + 0·55$ Å (where L is the metal—ligand bond length),* were able to estimate the cell dimensions taking into account the predicted complex ions' compositions (Balarew & Duhlev, 1984; Duhlev, 1984; Duhlev, Brown & Balarew, 1991). For $MgZnCl_4.6H_2O$, a CsCl-type structure was expected with a lower symmetry. The predicted and observed cells are compared in Table 4.

Fig. 2 represents a plot of R_c/R_a, the ratio of the radii of complex cations (R_c) and anions (R_a), against the number of water molecules (n) in the formula for $CaZnBr_4.5H_2O$ (Duhlev, Brown & Faggiani, 1988), $MgZnCl_4.6H_2O$, $MnZnBr_4.6H_2O$ (Villella, Faggiani & Brown, 1986) and $MgZnBr_4.7H_2O$ (Duhlev & Brown, 1989). The trend observed indicates that below or above a certain value of the ratio R_c/R_a, typical for the CsCl-type structure, the complex ions can either move apart to make space for an interstitial water or penetrate each other with elimination of a water molecule (as in the case of $CaZnBr_4.5H_2O$).

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* In the paper by Brown & Duhlev (1991), L was calculated from the predicted bond valences using the method of Brown & Altermatt (1985) while in this paper L is assumed to be equal to the sum of Pauling ionic radii.

Table 4. *Comparison of the observed and predicted cells for $MgZnCl_4.6H_2O$*

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Observed cell:	6·56	6·60	14·10	88·6	89·4	84·4
Predicted cell:	6·58	6·58	13·16	90·0	90·0	90·0

The length of a cubic Cs-Cl-type is $a_0 = 2(R_c + R_a)/\sqrt{3}$, where R_c and R_a, the radii of the complex cation and complex anion, are defined as $R = L + 0·55$ Å (see text) and L is the metal—ligand bond length calculated as a sum of Pauling ionic radii.
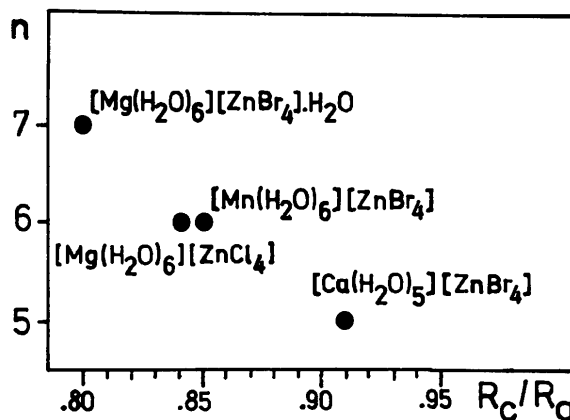

Fig. 2. Relationship between the ratio of the radii of the complex cation and complex anion (R_c/R_a) and the number of water molecules (n) for $MZnX_4.nH_2O$ compounds. See the footnote to Table 4 for the definition of R_c and R_a.

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