the accuracy of the experiment, undistorted octahedra. The ions are held together by O—H···Br hydrogen bonds. The structure is composed of linear $[Mg(H_2O)_6]^{2+}[CdBr_6]^{4-}[Mg(H_2O)_6]^{2+}$ triplets with the three metal atoms lying on the same threefold axis and each $Mg(H_2O)_6^{2+}$ ion forming three hydrogen bonds to the adjacent $CdBr_6^{4-}$ ion along the threefold axis. The remaining hydrogen bonds link the $CdBr_6^{4-}$ ion to its six $Mg(H_2O)_6^{2+}$ neighbours lying in the *ab* plane. A projection of the structure viewed down the *c* axis is shown in Fig. 1. The present structure differs from the trigonal ones in the arrangements of the ions along the threefold axis. In the rhombohedral structure each $Mg(H_2O)_6^{2+}$ ion has four CdX_6^{4-} neighbours. In the trigonal structures one $Mg(H_2O)_6^{2+}$ ion has three, the other five CdX_6^{4-} neighbours.

We thank the Natural Science and Engineering Research Council of Canada for an operating grant.

References

BALAREW, CHR. & DUHLEV, R. (1984). *J. Solid State Chem.* **55**, 1–6.

BALAREW, CHR., DUHLEV, R. & PANAIOTOV, V. (1982). *Commun. Dep. Chem. Bulg. Acad. Sci.* **15**, 187–195.

CLARK, J. R., EVANS, H. T. JR. & ERD, R. C. (1980). *Acta Cryst.* B**36**, 2736–2739.

DUHLEV, R. (1984). PhD Thesis, Bulgarian Academy of Sciences, Sofia.

DUHLEV, R. & BALAREW, CHR. (1987). *Dokl. Bolg. Akad. Nauk*, **40**. In the press.

HALL, S. R. (1981). *Acta Cryst.* A**37**, 517–525.

International Tables for X-ray Crystallography (1974). Vol. IV. Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.

LECLAIRE, A. & BOREL, M. M. (1982). *Acta Cryst.* B**38**, 234–236.

LECLAIRE, A., BOREL, M. M. & MONIER, J. C. (1980). *Acta Cryst.* B**36**, 2734–2735.

LEDESERT, M. & MONIER, J. C. (1981). *Acta Cryst.* B**37**, 652–654.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). C**43**, 2046–2048

Structure of Magnesium Dizinc Hexabromide Hexahydrate, $MgZn_2Br_6.6H_2O$

BY R. DUHLEV,* R. FAGGIANI AND I. D. BROWN

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(*Received* 6 *May* 1987; *accepted* 1 *July* 1987)

Abstract. $[Mg(H_2O)_6][Zn_2Br_6]$, $M_r = 742{\cdot}59$, orthorhombic, *Immm* {Hall symbol $\bar{I}22$ [Hall (1981). *Acta Cryst.* A**37**, 517–525]}, $a = 10{\cdot}447\,(2)$, $b = 10{\cdot}325\,(1)$, $c = 7{\cdot}999\,(2)$ Å, $V = 862{\cdot}8$ Å^3, $Z = 2$, $D_x = 2{\cdot}86$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 16{\cdot}35$ mm^{-1}, $F(000) = 684$, room temperature, $R = 0{\cdot}057$ ($wR = 0{\cdot}056$) for 890 reflections. Prepared from a saturated aqueous solution of $MgBr_2$ and $ZnBr_2$ in a molar ratio of 1:2. The structure consists of independent octahedral $Mg(H_2O)_6^{2+}$ complexes (Mg—O = 2·04 Å) and dimeric tetrahedral $Zn_2Br_6^{2-}$ complexes [Zn—Br = 2·48 Å (bridging) and 2·36 Å (terminal)], linked together by H bonds.

Introduction. The title compound was first described by Duhlev & Balarew (1986) as one of the solid phases crystallizing in the ternary system $MgBr_2$–$ZnBr_2$–H_2O at 298 K. Using a method (Balarew & Duhlev, 1984) based on the relative softness of the ions (Pearson, 1963), Duhlev & Balarew (1986) predicted that the structure would contain independent $Mg(H_2O)_6$ octahedra and $ZnBr_4$ tetrahedra, the later sharing either corners to link into an infinite chain $(ZnBr_3)_\infty$ or edges to form discrete Zn_2Br_6 dimers.

Before the X-ray study was undertaken the structure was modelled using the cell reported by Brehler (1961) for the isostructural (Duhlev & Balarew, 1986) $ZnBr_2.2H_2O$ and the space group *Immm*. As a $(ZnBr_3)_\infty$ chain could not be fitted into this cell, the dimer was selected. With the aid of the program *STRUMO* (Brown, 1987) the model was refined to give atomic positions within 0·05 Å of those found.

Experimental. $MgZn_2Br_6.6H_2O$ forms colourless, extremely hygroscopic crystals. Therefore, a cylindrical crystal with diameter 0·2 mm and length 0·3 mm was sealed in a thin-walled capillary under dry nitrogen and mounted on a Nicolet *P*3 diffractometer. Unit-cell parameters were determined from 15 well centred strong reflections in the range $20 < 2\theta < 38°$. Empirical absorption corrections were derived from ψ-scans of 15 reflections (maximum correction factor of 1·70 for the intensity of reflection 222). Intensities were

---

* On leave from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria.

0108-2701/87/112046-03$01.50

measured for 890 reflections with $0 \leq h \leq 12$, $-5 \leq k \leq 12$, $-9 \leq l \leq 9$ and $2\theta < 50°$. The $07\bar{1}$ and $25\bar{1}$ reflections were used as standards and showed variations less than 2%. Equivalent reflections were averaged ($R_{\rm int} = 0{\cdot}020$) to give 460 unique reflections. The structure was solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The scale factor, weighting factor (k), 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 *SHELX*76 (Sheldrick, 1976). The positions of the H atoms were found from the difference map but since the coordinates did not refine well the atoms were placed at their expected positions and only the atomic displacement factors refined. The final refinement based on the use of all reflections with fixed hydrogen positions and a fixed $k = 0{\cdot}001$ in the weighting equation $w = [\sigma^2(F_o) + kF_o^2]^{-1}$ [where $\sigma(F_o)$ is the error derived from counting statistics] gave $R = 0{\cdot}057$, $wR = 0{\cdot}056$ and a goodness of fit $S = 1{\cdot}29$ [$R = 0{\cdot}045$, $wR = 0{\cdot}046$ and $S = 1{\cdot}32$ when 97 reflections with $F < 3\sigma(F)$ were omitted]. The average shift/e.s.d. $= 0{\cdot}001$ (max $= 0{\cdot}005$). The maximum height in the final difference electron density map is $+0{\cdot}78$, the minimum is $-0{\cdot}74$ e Å^{-3}. The secondary-extinction coefficient (Larson, 1967) $g = 0{\cdot}0022$ (3). Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.*

Discussion. The bond distances and angles are shown in Table 2. The structure found confirmed the prediction of Duhlev & Balarew (1986) and the detailed model developed with the aid of *STRUMO* (Brown, 1987). Although there are two crystallographically distinguishable kinds of O atoms around Mg, both form bonds with the same length to form a regular octahedron $Mg(H_2O)_6^{2+}$. Because the Br(1) atoms are bridging, the tetrahedral environment around Zn is distorted with respect to both the distances and the angles.

The $Mg(H_2O)_6^{2+}$ and $Zn_2Br_6^{2-}$ groups are linked together by O(2)—H(2)···Br(2) hydrogen bonds to form infinite chains $[Mg(H_2O)_6]^{2+}[Zn_2Br_6]^{2-}$ extended along the a axis and by 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 $Mg(H_2O)_6^{2+}$ and $Zn_2Br_6^{2-}$ complex ions are arranged in an NaCl-type structure with a and b axes rotated 45° with respect to the pseudo-cubic axes of 7·4 Å. Fig. 1 represents a view of the structure in the ab plane.

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

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

	x	y	z	$U_{\rm eq}$
Zn	$\frac{1}{2}$	0·16139 (16)	0	0·0472
Br(1)	$\frac{1}{2}$	0	0·2302 (2)	0·0533
Br(2)	0·3120 (13)	0·28803 (11)	0	0·0588
Mg	0	0	0	0·036
O(1)	0·1408 (10)	0	0·1765 (12)	0·070
O(2)	0	0·1975 (12)	0	0·079
H(1)	0·1748	0·0611	0·2190	0·34 (16)
H(2)	0·0603	0·2457	0	0·08 (5)

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

Zn—Br(1)	2·484 (2) (× 2)	Br(1)—Zn—Br(1)	95·66 (7)
		Br(1)—Zn—Br(2)	111·76 (2)
Zn—Br(2)	2·359 (2) (× 2)	Br(2)—Zn—Br(2)	112·59 (8)
Mg—O(1)	2·039 (10) (× 4)	O(1)—Mg—O(1)	92·3 (4)
		O(1)—Mg—O(2)	89·94 (0)
Mg—O(2)	2·039 (12) (× 2)	O(2)—Mg—O(2)	179·85 (4)

O—H···Br	O—H	H···Br	O···Br	∠OHBr	∠HOH
O(1)—H(1)···Br($2^{\rm i}$)	0·80	2·74	3·425 (7)	145	104
O(2)—H(2)···Br(2)	0·80	2·67	3·392 (4)	151	103

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

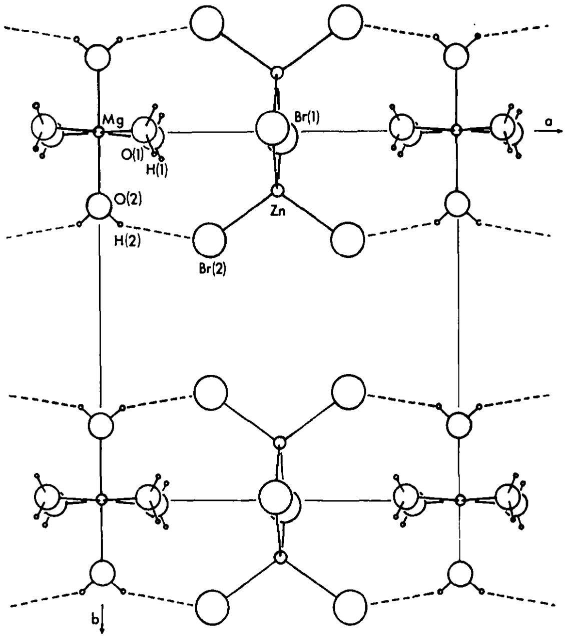

Fig. 1. Projection of the structure of $[Mg(H_2O)_6][Zn_2Br_6]$ down the c axis. The H(1) atoms hydrogen bond to the Br(2) atoms from the Zn_2Br_6 groups located above (or below) the $Mg(H_2O)_6$ octahedra.

---

* Lists of structure factors and anisotropic atomic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44210 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This work is supported by an operating grant from the Natural Science and Engineering Research Council of Canada.

References

BALAREW, CHR. & DUHLEV, R. (1984). *J. Solid State Chem.* **55**, 1–6.

BREHLER, B. (1961). *Fortschr. Mineral.* **39**, 338.

BROWN, I. D. (1987). *Phys. Chem. Minerals.* In the press.

DUHLEV, R. & BALAREW, CHR. (1986). *Rev. Chim. Miner.* **23**, 116–124.

HALL, S. R. (1981). *Acta Cryst.* A**37**, 517–525.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2.B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PEARSON, R. G. (1963). *J. Am. Chem. Soc.* **85**, 3533–3539.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). C**43**, 2048–2050

Octachlorure de Tris[tétrammineplatine(II)] et de Bis[triamminechloroplatine(II)]

PAR P. TOFFOLI, P. KHODADAD ET N. RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, Rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France

ET B. VIOSSAT

Laboratoire de Chimie Minérale, UFR de Médecine et de Pharmacie, 34 *Rue du Jardin des Plantes,* 86034 *Poitiers CEDEX, France*

(*Reçu le* 19 *février* 1987, *accepté le* 23 *juin* 1987)

Abstract. $2[\mathrm{PtCl(NH_3)_3}]^+.3[\mathrm{Pt(NH_3)_4}]^{2+}.8\mathrm{Cl}^-$, $M_r = 1636{\cdot}5$, tetragonal, $P4_2/nme$, $a = 10{\cdot}566\ (2)$, $c = 16{\cdot}703\ (4)$ Å, $V = 1864{\cdot}8\ (7)$ Å^3, $Z = 2$, $D_m = 2{\cdot}85\ (3)$, $D_x = 2{\cdot}914$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 19{\cdot}6$ mm^{-1}, $F(000) = 1480$, $T = 295\ (1)$ K. Final $R = 0{\cdot}031$ for 703 independent reflections. There are six $[\mathrm{Pt(NH_3)_4}]^{2+}$, four $[\mathrm{Pt(NH_3)_3Cl}]^+$ and 16 Cl^- ions per unit cell. The coordination around the three Pt atoms is square planar. Along the $\bar{4}$ axes, the $[\mathrm{Pt(NH_3)_4}]^{2+}$ cations form square columns of approximately constant section. In these columns, groups of three cations are separated by a vacancy. Around the vacancy, there are four $[\mathrm{Pt(NH_3)_3Cl}]^+$ ions, the geometry of which has not hitherto been described. Several N—H···Cl hydrogen bonds are involved in the cohesion of the structure.

Introduction. Selon Kurnakow & Andrejewsky (1930), le chlorure de tétrammineplatine(II) mis en solution dans l'ammoniaque, donne naissance, au bout de quelques jours, à des cristaux incolores dont ils représentent la composition par la formule $(\mathrm{PtCl_2,2NH_3})(\mathrm{PtCl_2,4NH_3})_4$. Les mêmes auteurs indiquent que ces cristaux appartiennent au système quadratique et que le rapport c/a des axes de la maille est égal à 1,1107.

La détermination de la structure de ce composé a été entreprise dans le cadre de l'étude des composés de coordination formés par le platine avec l'ammoniac et les amines aliphatiques. Le produit utilisé a été préparé selon la méthode indiquée par Kurnakow & Andrejewsky. Les résultats de l'analyse élémentaire sont en bon accord avec la formule globale trouvée par ces derniers.

Partie expérimentale. Cristal parallélépipédique: 0,33 × 0,33 × 0,17 mm. Masse volumique par flottaison. Dimensions de la maille déterminées sur monocristal avec 25 réflexions telles que $7{,}71 \le \theta \le 16{,}54°$. Diffractomètre Enraf–Nonius CAD-4. Scan $\theta/2\theta$ d'amplitude $s(°) = 0{,}90 + 0{,}35\ \mathrm{tg}\ \theta$. $0{,}05 \le (\sin\theta)/\lambda \le 0{,}66$ Å^{-1}. $0 \le h \le 9$, $0 \le k \le 13$, $0 \le l \le 22$, $(h \le k)$. Réflexions de contrôle: 040, 400 et $6\bar{2}0$. $\sigma(I)/I$ moyen (contrôle): 0,0023. 1243 réflexions indépendantes mesurées, 540 inobservées $[I \le 3\sigma(I)]$. Corrections d'absorption (Coppens, Leiserowitz & Rabinovich, 1965). Valeurs maximale et minimale du coefficient de transmission: 0,109 et 0,050. Programme *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) et série de Fourier des ΔF. H non localisés. Affinement sur F. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974). $R = 0{,}030$, $wR = 0{,}041$, $w = 1$ pour toutes les réflexions, $S = 1{,}35$, $(\Delta/\sigma)_{\max} = 0{,}25$, $|\Delta\rho|_{\max} = 1{,}9\ (3)$ e Å^{-3}. Programmes de calcul du système *SDP*

0108-2701/87/112048-03$01.50