

## Neutron Diffraction Studies of Polyiodides. II. Magnesium Octaiodide Hexahydrate

BY RUDOLF THOMAS

*Chemistry Department, University of Tasmania, Hobart, Tasmania 7001, Australia*

AND FRANK H. MOORE

*Australian Institute of Nuclear Science and Engineering, Lucas Heights, New South Wales 2232, Australia*

(Received 15 November 1980; accepted 7 May 1981)

### Abstract

The crystal structure of  $\text{MgI}_8 \cdot 6\text{H}_2\text{O}$  has been determined from neutron diffraction data, giving  $R_F = 0.086$  for 561 reflections. This compound crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 8.909$  (3),  $b = 9.719$  (3),  $c = 7.725$  (2) Å,  $\alpha = 114.46$  (2),  $\beta = 102.78$  (2),  $\gamma = 105.09$  (1)°,  $Z = 1$ . The structure consists of hexahydrated  $\text{Mg}^{2+}$  cations and  $\text{I}_8^{2-}$  anions, the latter made up of two asymmetric  $\text{I}_3^-$  units linked by an  $\text{I}_2$  molecule in a Z-shaped motif.

### Introduction

While the polyhalides of univalent cations, especially those of the alkali metals, have received considerable attention, only a few examples of this class of salts of divalent cations have been studied. These have usually been complexed transition-metal cations, e.g.  $\text{Ni}(\text{NH}_3)_4\text{I}_n$ ,  $n = 4, 6, 10, 14$  (Ephraim & Mosimann, 1921). Investigation of the polyiodides of the alkaline-earth cations, however, appears to have been neglected. Although the alkaline-earth metals (Mg, Ca, Sr) do not form unsolvated polyiodides, phase-equilibrium studies show that the hydrated cations are able to form relatively stable polyiodides. This series of divalent cations allows a study of the effect of cation size on the structure taken by the polyiodide anion. The next member of the series, Ba, does form salts with some interhalogen anions, such as  $\text{Ba}(\text{BrF}_4)_2$  (Sharpe & Emeleus, 1948), but an attempt to form a hydrated polyiodide was unsuccessful (Rivett & Packer, 1927).

### Experimental

The phase-equilibrium study of the system  $\text{MgI}_2$ – $\text{I}_2$ – $\text{H}_2\text{O}$  was conducted at 273 K and the only polyiodide of a hydrated Mg cation was determined to have the formula  $\text{MgI}_{11} \cdot 9\text{H}_2\text{O}$ . However, when a

50:27 mixture of iodine and magnesium iodide (as the hexahydrate) was dissolved in a minimum of water to give the saturated solution as required by the 273 K phase-equilibrium diagram, on evaporation at room temperature a compound precipitated which analysed as  $\text{MgI}_8 \cdot 6\text{H}_2\text{O}$  (Mg = 2.17,  $\text{I}_2 = 65.75$ ,  $\text{H}_2\text{O} = 9.95\%$ ;  $\text{MgI}_8 \cdot 6\text{H}_2\text{O}$  requires Mg = 2.11,  $\text{I}_2 = 66.39$ ,  $\text{H}_2\text{O} = 9.40\%$ ). By slow evaporation over sulphuric acid, a crystal  $2 \times 1.6 \times 12$  mm was obtained. This was mounted and protected from atmospheric moisture in a manner similar to that described in part I of this series (Thomas & Moore, 1980).

The structure was determined from neutron diffraction data collected on a four-circle diffractometer provided by the Australian Institute of Science and Engineering (AINSE) at the Australian Atomic Energy Commission (AAEC) research establishment. The wavelength of the neutrons,  $\lambda = 0.9882$  Å, was obtained from diffraction measurements of a LiF crystal ( $a = 4.0262$  Å). The cell dimensions were calculated from the orientation angles of some 60 selected reflections. The density, determined by the displacement of paraffin oil saturated with iodine, was found to be  $3.40$  (5)  $\text{Mg m}^{-3}$ , compared to a calculated density of  $3.49$   $\text{Mg m}^{-3}$  for  $Z = 1$ . On the basis of intensity statistics, the centrosymmetric space group  $P\bar{1}$  was chosen. The linear absorption coefficient ( $\mu = 0.093$   $\text{mm}^{-1}$ ) was calculated from the sum of the values for the absorption and scattering cross sections of Mg, O and I ( $3.7, 4.2, 7.5 \times 10^2$   $\text{fm}^2$  respectively at  $\lambda = 1.0$  Å) (Bacon, 1975), and the value for the slow-neutron cross section for H in water (Melkonian, 1949) ( $35 \times 10^2$   $\text{fm}^2$  at  $\lambda = 1.0$  Å). Two sets of equivalents were collected for  $2\theta < 45^\circ$ , analysed and combined to give 561 independent reflections.

### Structure determination and refinement

*MULTAN* 76 (Main, Woolfson, Lessinger, Germain & Declercq, 1976) was used to solve the structure. The

values used for the coherent neutron scattering lengths (Shull, 1972) were 5.32, 5.80, 5.28 and -3.74 fm for Mg, O, I and H respectively. In the  $E$  map produced, the Mg atom, which has to be on a centre of symmetry, and the O atoms were recognizable, while the positions of the I atoms were obtained from a Fourier map. The positions of these atoms were refined isotropically with *LINUS* (Coppens & Hamilton, 1970), and the positions of the H atoms were then determined from a difference map. The introduction of anisotropic temperature factors for all atoms gave  $R = \sum |F_o^2| - |F_c^2| / \sum |F_o^2| = 0.137$ . Structure factor calculations with the data where  $F^2 > 3\sigma(F^2)$  gave  $R_{F^2} = 0.127$  and

$R_F = 0.086$ .\* The positional and thermal parameters are listed in Table 1, bond lengths and angles in Table 2.

### Discussion

The structure consists of hexahydrated  $Mg^{2+}$  ions arranged in the normal octahedral manner and  $I_8^{2-}$  ions in sheets (Fig. 1). The  $I_8^{2-}$  ion (Fig. 2) consists of two asymmetrical  $I_3^-$  units linked by an  $I_2$  molecule in a Z-shaped motif, and is similar to the only other example of this anion, observed in  $Cs_2I_8$  (Havinga, Boswijk & Wiebenga, 1954). Although the bond lengths of the  $I_3^-$  unit and the distance to the  $I_2$  molecule are almost identical, the angle between these two moieties in this structure is some  $18^\circ$  larger. This difference has resulted in a smaller covalent interaction on the  $I_2$  molecule, which consequently has a slightly shorter I—I bond than in  $Cs_2I_8$ . The  $I_8^{2-}$  units are symmetrically interlocked (Fig. 1), the minimum distance between the two units being 3.840 Å. This distance is considerably

Table 1. *Positional parameters and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )
Mg	0.0	0.0	0.0	3.21 (26)
O(1)	0.1895 (10)	0.2138 (7)	1.0816 (12)	5.82 (28)
O(2)	0.1785 (7)	-0.0770 (8)	0.0922 (14)	6.07 (32)
O(3)	-0.0099 (7)	0.1065 (10)	0.2887 (10)	5.82 (30)
I(1)	-0.3592 (5)	0.2545 (5)	0.2908 (6)	3.96 (19)
I(2)	-0.3710 (5)	0.5661 (5)	0.3034 (6)	3.54 (19)
I(3)	-0.3836 (5)	0.8677 (5)	0.3299 (6)	4.43 (20)
I(4)	0.1024 (6)	0.5731 (5)	0.2044 (8)	6.43 (23)
H(1)	0.310 (2)	0.224 (3)	0.130 (5)	32.8 (2.1)
H(2)	0.179 (3)	0.298 (3)	0.094 (4)	20.3 (1.3)
H(3)	0.227 (2)	-0.128 (3)	0.005 (3)	20.0 (1.3)
H(4)	0.228 (2)	-0.051 (3)	0.242 (3)	22.2 (1.3)
H(5)	-0.105 (3)	0.034 (3)	0.331 (4)	32.9 (2.1)
H(6)	0.044 (3)	0.195 (3)	0.393 (4)	21.4 (1.6)

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Symmetry code: (') -x, -y, -z.

Mg—O(1)	2.045 (12)	I(3)—I(2)	2.886 (10)
Mg—O(2)	2.038 (11)	I(2)—I(1)	3.020 (10)
Mg—O(3)	2.068 (13)	I(1)—I(4)	3.448 (12)
O(1)—H(1)	1.02 (5)	I(4)—I(4)	2.776 (20)
O(1)—H(2)	0.81 (5)	I(3)···I(1)	3.849 (10)
O(2)—H(3)	0.92 (5)	H(1)—I(1)	2.81 (5)
O(2)—H(4)	1.03 (6)	H(2)—I(4)	2.77 (5)
O(3)—H(5)	1.15 (5)	H(3)—I(1)	2.78 (5)
O(3)—H(6)	0.81 (5)	H(4)—I(3)	2.80 (5)
		H(5)—I(3)	2.58 (6)
		H(6)—I(2)	2.87 (5)
O(2)—Mg—O(1)	88.0 (6)	I(3)—I(2)—I(1)	177.8 (4)
O(2)—Mg—O(3)	92.1 (6)	I(2)—I(1)—I(4)	98.0 (3)
O(1)—Mg—O(3)	90.1 (6)	I(1)—I(4)—I(4')	178.4 (3)
H(1)—O(1)—H(2)	115 (3)	I(2)—I(1)—I(3')	169.0 (3)
H(3)—O(2)—H(4)	116 (3)		
H(5)—O(3)—H(6)	104 (3)		

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36093 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

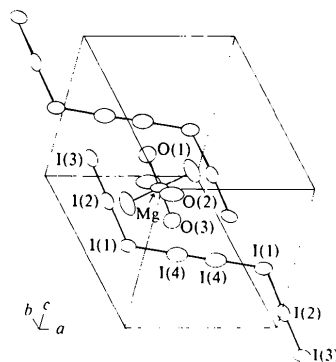


Fig. 1. The structure of magnesium octaiodide hexahydrate. The H-atom ellipsoids are omitted.

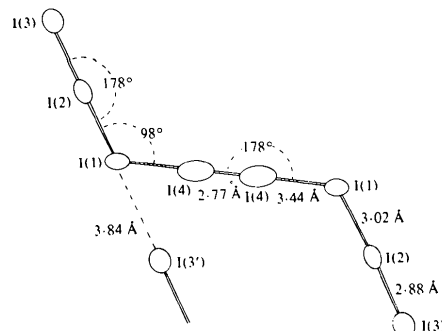


Fig. 2. The  $I_8^{2-}$  ion in magnesium octaiodide hexahydrate.

shorter than twice the van der Waals radius for I (4.30 Å), which indicates that there is a small interaction between the  $I_8^{2-}$  units. This view is supported by the black lustre of the crystals, in contrast to the pale yellow of tetraphenylarsonium triiodide, in which the triiodide units are 5.29 Å apart (Runsink, Swen-Walstra & Migchelsen, 1972).

The  $Mg^{2+}$  ions are situated at the vertices of the cell, each with six equidistant water molecules ( $Mg-O = 2.04-2.06$  Å) in a slightly distorted octahedral arrangement (Fig. 3). The O-H lengths are influenced by the relatively high thermal parameters of the H atoms and are rather short [O-H = 0.81 (5)-1.15 (5) Å]. When averaged over thermal motion (ORFFE, Busing, Martin & Levy, 1964) these become 1.00 (6)-1.44 (6) Å.

In this polyiodide, in contrast to the other structures studied in this series, all the minimum  $H \cdots I$  distances [2.58 (5)-2.87 (5) Å] are significantly less than the sum of the van der Waals radii (3.15 Å, Bondi, 1964). Similar distances have been observed for  $H \cdots I$  in the X-ray structures of iminodiacetic acid hydroiodide, 2.8 (1) Å (Oskarsson, 1974), and  $NaI(pak)_2 \cdot 2H_2O$ , 2.2 (3) Å (Phillips & Truter, 1975), in both of which the H is bonded to O. In (*o*-phenanthroline)bis-(thiourea)copper(I) iodide-*o*-phenanthroline, in which the H is bonded to N, an  $H \cdots I$  distance of 2.80 (6) Å was observed (Hall, Kepert, Raston & White, 1977). A neutron structure containing this bond is that of  $PH_4I$  in which the  $H \cdots I$  distance is 2.87 (1) Å (Sequeira &

Hamilton, 1967). A hydrogen bond is said to exist if the H to heavy-atom distance is 0.2 Å or more shorter than the sum of the van der Waals radii (Hamilton & Ibers, 1968). Thus the observed  $H \cdots I$  distances, which are 0.3 to 0.5 Å shorter, represent weak hydrogen bonds. Hydrogen bonds are, however, normally regarded as formed only where an H atom is bonded to two highly electronegative elements such as O, F or even Cl, and this weak interaction to an I atom is probably due more to the polarizability of the I atom.

One of us (RT) is grateful for a series of grants from the Australian Institute of Science and Engineering.

### References

- BACON, G. E. (1975). *Neutron Diffraction*, 3rd ed. Oxford: Clarendon Press.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441-451.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORFFE. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71-83.
- EPHRAIM, F. & MOSIMANN, P. (1921). *Chem. Ber.* **54**, 385-396.
- HALL, S. R., KEPERT, D. L., RASTON, C. L. & WHITE, A. H. (1977). *Aust. J. Chem.* **30**, 1955-1963.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- HAVINGA, E. F., BOSWIJK, K. H. & WIEBENGA, E. H. (1954). *Acta Cryst.* **7**, 487-490.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1976). *MULTAN 76. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MELKONIAN, E. (1949). *Phys. Rev.* **76**, 1750-1759.
- OSKARSSON, A. (1974). *Acta Cryst.* **B30**, 780-783.
- PHILLIPS, S. E. V. & TRUTER, M. R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1066-1070.
- RIVETT, A. C. & PACKER, J. (1927). *J. Chem. Soc.* pp. 1342-1349.
- RUNSINK, J., SWEN-WALSTRA, S. & MIGCHELSON, T. (1972). *Acta Cryst.* **B28**, 1331-1335.
- SEQUEIRA, A. & HAMILTON, W. C. (1967). *J. Chem. Phys.* **47**, 1818-1822.
- SHARPE, A. G. & EMELEUS, H. J. (1948). *J. Chem. Soc.* pp. 2135-2138.
- SHULL, C. G. (1972). Private communication.
- THOMAS, R. & MOORE, F. H. (1980). *Acta Cryst.* **B36**, 2869-2873.

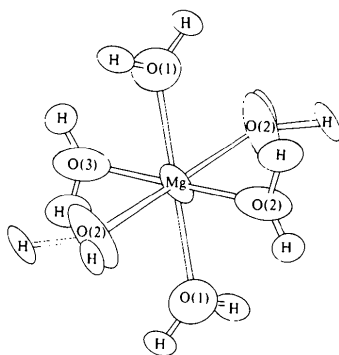


Fig. 3. A perspective view of the hydrated  $Mg^{2+}$  ion in magnesium octaiodide hexahydrate. The ellipsoids are at 50% probability except for those of the H atoms which are one-third of this scale.