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Magnesium diiodide, MgI$_2$

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Single crystals of magnesium diiodide have been grown and the structure solved for the first time from single-crystal X-ray diffraction data. This study confirms that MgI$_2$ is isostructural with CdI$_2$ (C6 or 2H structure type). The space group is $P\bar{3}m1$ with the Mg atom on a site with $3m$ symmetry (Wyckoff site $1a$) and the I atom on a site with m symmetry (Wyckoff site $2d$). Trends in the 2H structures of dihalides are discussed briefly.

Comment

MgI$_2$ belongs to the series of known dihalides (AX_2, where X = F, Cl, Br, I). Surprisingly, single-crystal growth of MgI$_2$ has never been reported and no refined structure exists. Seventy years ago, Blum (1933) derived a structural model from powder X-ray diffraction data. The conclusion reached was that MgI$_2$ crystallizes in a layered structure isotypic with CdI$_2$ (defined as C6 or 2H type). Here, the growth of good quality single crystals has allowed the structure of MgI$_2$ to be determined for the first time.

The single-crystal diffraction data set obtained confirms that MgI$_2$ crystallizes in the trigonal space group $P\bar{3}m1$, adopting the same hexagonal close-packed layered structure as CdI$_2$, with unit-cell parameters a = 4.1537 (7) Å, c = 6.862 (2) Å, V = 102.53 (4) Å^3, Z = 1, and c/a = 1.652. Within the structure, the I$^-$ anions are hexagonally close-packed, whilst the Mg^{2+} cations occupy all of the octahedral holes between alternate layers of close-packed anions. Hence, half of the available octahedral holes throughout the structure are occupied. The structure can also be thought of as being built up from layers of MgI$_6$ octahedra. Each such octahedron shares edges with six adjacent identical units within each MgI$_2$ layer (Fig. 1).

The six equal Mg—I bond distances of 2.9183 (5) Å and the I—Mg—I bond angles (φ) of 90.739 (17)° describe a slightly distorted MgI$_6$ octahedron. Interestingly, the only other example of a magnesium iodide in the literature with a refined crystal structure is the ternary compound CsMgI$_3$ (McPherson *et al.*, 1980), in which the Mg—I distance is 2.899 (4) Å, in good agreement with the value obtained in the present work. Apart from the original work of Blum (1933), the only other measurement of the Mg—I distance in MgI$_2$ was performed by Akishin & Spiridonov (1958), who used electron diffraction to determine the bond length in the gas phase. Unsurprisingly, the value of 2.52 Å in the triatomic structure is significantly shorter than the value observed here in the solid state. The $M—X$ distances differ slightly from the corresponding values in CdI$_2$ (2.989 Å; Pałosz & Salje, 1989), in which the octahedral CdI$_6$ unit is slightly more distorted than the MgI$_6$ octahedron, with I—Cd—I bond angles of 90.49°. Iodide anions in MgI$_2$ are separated by intraplanar distances of 4.1009 (11) and 4.1537 (7) Å across the thickness and along the length of the Mg–I layer, respectively. Magnesium cations are similarly separated within layers by 4.1537 (7) Å. Iodide ions in adjacent layers are separated by a longer interplanar distance of 4.2722 (12) Å.

The notable feature of the present diiodide and the structure type in general is the van der Waals interlayer gap between hexagonally close-packed I$^-$ ions. The interlayer gap (d) in MgI$_2$ [3.535 (2) Å] is significantly wider than the Mg–I layer thickness (t) [3.326 (2) Å]. The same trend is observed in CdI$_2$, but the difference between these two distances is far smaller. Furthermore, by contrast, the absolute value of d in CdI$_2$ is smaller than in MgI$_2$, whereas t is larger. The relevant structural information for both MgI$_2$ and CdI$_2$ appears in Table 2. The values for other isostructural dihalides are included for comparison. Note that the data for FeCl$_2$ represent the high-pressure polymorph at 6.4 Kbar (1 bar = 10^5 Pa) (Vettier & Yelon, 1975).

The c/a ratio observed here for MgI$_2$ is in close agreement with that previously reported (1.66; Blum, 1933). The t/d ratio obtained previously for MgI$_2$ can only be inferred as 1 assuming the z position for I is $\frac{1}{4}$ as reported. Table 2 reveals that the vast majority of dihalides with the CdI$_2$ structure have c/a values in the range $1.6 \leq c/a \leq 1.65$. PbI$_2$ is perhaps the

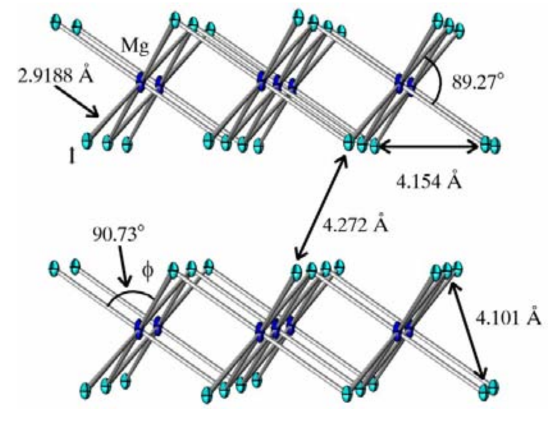

Figure 1
The coordination environment of Mg^{2+} (dark ellipsoids) and I$^-$ (light ellipsoids) within octahedral layers. Displacement ellipsoids are drawn at the 50% probability level.

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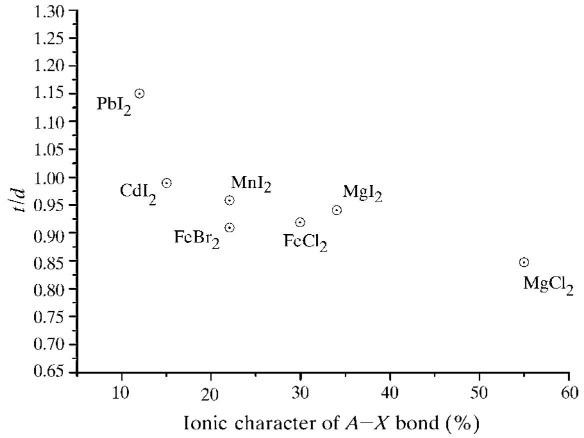

Figure 2
Plot of the layer thickness/interlayer gap ratio (t/d) *versus* ionic character (ionicity) of the A—X bond. Data are taken from Table 2.

most notable exception in this respect, in that it has the largest a parameter and A—X bond length, and consequently the smallest c/a ratio reported (Pałosz *et al.*, 1990). Interestingly, PbI_2 is the only dihalide with $t/d > 1$. In fact, only a select number of the dihalide 2H structures reported in the literature and depicted in Table 2 have been refined. In the remainder of cases, the halide z coordinate, $z(X)$, is assumed to be 0.25. A number of trends are nonetheless evident from the pool of refined data. As might be expected, the t/d ratio increases with increasing A—X bond length and decreasing X—A—X bond angle (φ). Bonding in the essentially ionic layers (manifested in t) generally plays a more significant role here than the weaker anion replusion between layers (influencing d). Naturally, the halide z coordinate (2d site; $\frac{1}{3}$, $\frac{2}{3}$, z) follows the same trends with A—X and φ. Interestingly, again here, PbI_2 also possesses the most covalent A—X bond, thus minimizing interlayer repulsion. It is, therefore, not so unexpected that $d < t$ in this compound. In fact, there is a good correlation between the ionic character of the A—X bond, as defined by Pauling (1960), and the t/d ratio (Fig. 2). A similar correspondance obviously exists between $z(X)$ and the bond ionicity. The c/a ratio is broadly constant across the structure type (and invariant with A—X and φ) but, within the observed range, increases slightly with decreasing t/d [$z(X)$].

As the number of accurately refined metal dihalide structures increases, the relationships between the various structural variables should become clearer to the point where it should become possible to predict (interpolate) $z(X)$, and hence bond length, on the basis of the A—X bond ionicity or the c/a ratio. The continuing advances made in structure determination from powder data should facilitate and expediate this process.

Experimental

The title MgI_2 crystals were produced during the attempted reaction of MgI_2 (Aldrich, anhydrous beads 99.9%, ground into a polycrystalline powder) with Mg_3N_2. Mg_3N_2 powder was prepared by the reaction of pure magnesium (Strem Chemicals, 99.9% purity) with dry nitrogen gas at 973 K. Due to the air sensitivity of the reactants and products involved, all manipulations were carried out in glove-boxes (either recirculating nitrogen-filled or evacuable argon-filled). Stoichiometric ratios of the reactants were thoroughly mixed and ground together, then pressed to form a pellet (*ca* 1 g). The pellet was placed in a molybdenum foil liner and transferred to a stainless steel crucible, which was subsequently welded shut under an argon atmosphere. The sealed crucibles were heated in a tube furnace (1323 K, 5 d) under flowing argon to prevent oxidation of the steel crucibles. The furnace was cooled slowly (20 K h^{-1}). The crucibles were opened in an N_2-filled glove-box. Opaque irregular crystals were observed on the molybdenum foil. Crystals were selected in a recirculating N_2-filled glove-box under an optical microscope and placed under RS3000 perfluoropolyether (Riedel de Haën) on a microscope slide prior to mounting on the diffractometer. The moisture-free viscous perfluoropolyether protects the crystals from atmospheric oxygen and moisture without interfering with the diffraction experiment.

Crystal data

MgI_2
$M_r = 278.11$
Trigonal, $P\bar{3}m1$
$a = 4.1537$ (7) Å
$c = 6.862$ (2) Å
$V = 102.53$ (4) Å^3
$Z = 1$
$D_x = 4.504$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 529 reflections
$\theta = 3.0$–27.3°
$\mu = 15.24$ mm^{-1}
$T = 150$ (2) K
Plate, colourless
0.20 × 0.20 × 0.08 mm

Table 1
Selected geometric parameters (Å, °).

Mg—I	2.9183 (5)
Mg^{i}—I—Mg	90.739 (17)

Symmetry code: (i) $1 + x, y, z$.

Table 2
Selected structural data (Å, °) for MX_2 dihalides with the CdI_2 (2H) structure.

MX_2	M—X^a	φ^a	c/a	t	d	t/d^b	$z(X)$
CdI_2[i]	2.989	90.49	1.62	3.4211	3.443	0.99	0.2492
PbI_2[ii]	3.227	90.16	1.53	3.738	3.248	1.15	0.2675 (2)
MgI_2	2.9183 (5)	90.739 (17)	1.65	3.3267	3.5353	0.94	0.24237 (6)
MnI_2[iii]	2.92	90.44	1.65	3.346	3.482	0.96	0.245 (2)
$MnBr_2$[iv]	2.729	90.27	1.62	3.136	3.136	1.00	0.25
$TiBr_2$[v]	2.65	93.59	1.79	3.246	3.246	1.00	0.25
$FeBr_2$[vi]	2.636	91.47	1.65	2.965	3.261	0.91	0.238 (5)
VCl_2[vii]	2.538	90.32	1.62	2.915	2.915	1.00	0.25
$TiCl_2$[viii]	2.527	90.40	1.65	2.937	2.937	1.00	0.25
$MgCl_2$[ix]	2.505	93.21	1.63	2.726	3.2	0.85	0.23
$TiCl_2$[x]	2.499	93.35	1.78	3.05	3.05	1.00	0.25
$FeCl_2$[xi]	2.483	92.41	1.6	2.744	2.99	0.92	0.2393 (2)
CaI_2[xii]	3.12	93.313	1.55	3.48	3.48	1	0.25

† Notes: (a) in some cases, s.u. values are not reported in the literature; (b) where $t/d = 1$, the literature assumes that $z(X) = \frac{1}{4}$, where t = thickness of layer and d = interlayer gap. References: (i) Pałosz & Salje (1989); (ii) Pałosz *et al.* (1990); (iii) Cable *et al.* (1962); (iv) Wollan *et al.* (1958); (v) Ehrlich *et al.* (1961); (vi) Haberecht *et al.* (2001); (vii) Ehrlich & Seifert (1959); (viii) Baenziger & Rundle (1948); (ix) Bassi *et al.* (1982); (x) Gal'perin & Sandler (1962); (xi) Vettier & Yelon (1975); (xii) Blum (1933).

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Bruker, 2001)
$T_{\min} = 0.093$, $T_{\max} = 0.505$
623 measured reflections
115 independent reflections
112 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.081$
$\theta_{\max} = 27.3°$
$h = -5 \rightarrow 4$
$k = -5 \rightarrow 4$
$l = -8 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.063$
$S = 1.13$
115 reflections
7 parameters
$w = 1/[\sigma^2(F_o^2) + (0.037)^2 + 0.102P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.86$ e Å^{-3}
$\Delta\rho_{\min} = -0.91$ e Å^{-3}

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1998); software used to prepare material for publication: *enCIFer* (CCDC, 2003), *PLATON* (Spek, 1990, 2002) and *WinGX* (Farrugia, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1028). Services for accessing these data are described at the back of the journal.

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