position spéciale du groupe d'espace. Par conséquent, les distances interatomiques du groupe linéaire N–C–S sont susceptibles d'erreurs importantes.

Les facteurs de température isotropes pour chaque atome sont très élevés. On peut supposer que les vraies positions des atomes sont décalées par rapport aux positions moyennes pour accommoder le groupe NCS désordonné.

La structure du [Ir(NCS) (NH$_3$)$_5$]Cl$_2$ est isotype de celle de [Co(NCS) (NH$_3$)$_5$]Cl$_2$ (Snow & Boomsma, 1972), qui montre aussi les facteurs de température très élevés.

Cette détermination fait partie d'une étude sur les structures cristallines et moléculaires des complexes thiocyanato et isothiocyanato d'iridium et de rhodium (III) et fait suite à la première publication (Flack & Parthé, 1973).

Nous tenons à remercier ici le Professeur C. K. Jørgensen qui nous a suggéré ce problème et nous a donné les monocristaux ainsi que le Professeur E. Parthé pour ses nombreuses discussions critiques.

Références

BUSING, W. R., MARTIN, K. O., LEVY, H. A., ELLISON, R. D., HAMILTON, W. C., IBERS, J. A., JOHNSON, C. K. & THIESSEN, W. E. (1971). *ORXFLS3: Crystallographic Structure Factor Least-Squares Program.* Oak Ridge National Laboratory, Oak Ridge, Tennessee.

FLACK, H. D. & PARTHÉ, E. (1973). *Acta Cryst.* B**29**, 1099–1102.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1970). *ORTEP.* Report ORNL-3794 (Second Revision), Oak Ridge National Laboratory, Oak Ridge, Tennessee.

SNOW, M. R. & BOOMSMA, R. F. (1972). *Acta Cryst.* B**28**, 1908–1913.

WYCKOFF, R. W. G. (1965). *Crystal Structures.* 2nd ed. Vol. 3, p. 783. New York: Interscience.

Magnesium Arsenate, Mg$_3$As$_2$O$_8$

BY NARASIMHAN KRISHNAMACHARI AND CRISPIN CALVO

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

Abstract. Tetragonal, $a = 6·783$ (2), $c = 18·963$ (4) Å, $V = 842·47$ Å^3, $D_m = 3·9$ (1) g cm^{-3}, $Z = 6$, $D_c = 4·03$ g cm^{-3}, space group $I\bar{4}2d$. Crystals were obtained from a melt (m.p. 1450°C) starting with MgCO$_3$ and As$_2$O$_5$. 744 unique reflexions were used in a full-matrix least-squares refinement yielding a final R of 0·043. The structure contains two distinct AsO$_4$ groups with average As–O bond lengths of 1·678 and 1·690 Å. Two of the three Mg ions are octahedrally coordinated and the third occupies a site of $\bar{4}$ symmetry.

Introduction. Data were collected from a crystal of dimensions $0·02 \times 0·01 \times 0·01$ cm. 744 unique reflexions were collected with a Syntex P$\bar{1}$ automatic diffractometer (graphite monochromated, Mo Kα, scintillation counter, check reflexion after every 50, backgrounds measured at either side of the peak, variable scan, $2\theta \leq 80°$). 133 reflexions with positive measure had intensity less than 3σ, where σ was based on counting statistics for the peak and backgrounds. Absorption corrections were not applied ($\langle \mu R \rangle \simeq 1·0$). Conditions

Table 1. *Atomic parameters for* Mg$_3$As$_2$O$_8$

U_{ij}'s in Å^2 are computed from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where $T = \exp\{-[\beta_{11}h^2 + 2\beta_{12}hk + \ldots]\}$ appears in the structure-factor expression and b_j are reciprocal-lattice cell vectors.

		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg(1)	8d	0·2416 (6)	¼	⅛	0·008 (1)	0·005 (1)	0·008 (1)	—	—	−0·000 (1)
Mg(2)	8c	0	0	0·2284 (2)	0·011 (1)	0·007 (1)	0·007 (1)	−0·003 (1)	—	—
Mg(3)	4b*	0	0	½	0·014 (5)	U_{11}	0·013 (4)	—	—	—
As(1)	8d	−0·3446 (1)	¼	⅛	0·0050 (3)	0·0045 (3)	0·0053 (3)	—	—	−0·0005 (3)
As(2)	4a	0	0	0	0·0036 (6)	U_{11}	0·0053 (4)	—	—	—
O(1)	16e	0·0566 (7)	0·2074 (7)	0·0438 (2)	0·009 (2)	0·004 (1)	0·010 (2)	0·000 (1)	−0·004 (1)	−0·002 (1)
O(2)	16e	0·4937 (9)	0·2883 (9)	0·1925 (2)	0·007 (2)	0·023 (3)	0·010 (1)	−0·001 (2)	0·005 (2)	−0·010 (2)
O(3)	16e	0·2206 (8)	0·5464 (8)	0·1017 (3)	0·009 (2)	0·006 (2)	0·017 (2)	−0·003 (1)	−0·003 (2)	0·000 (1)

* Site is half occupied.

limiting possible reflexions ($h+k+l=2n$ in general and $2h+l=4n$ for hhl) restricts the space group to $I4_1md$ and $I\bar{4}2d$. For arsenic atoms in fully occupied sites it was not possible to locate these atoms without condensed AsO_4 groups in space group $I4_1md$ but a solution of the Patterson function was found consistent with space group $I\bar{4}2d$. The structure was refined with a full-matrix least-squares program written for the CDC 6400 by J. S. Stephens with atomic scattering factors taken from Cromer & Waber (1965) and corrected for dispersion (Cromer, 1965). Weights, $w=$

$[10 \cdot 0 + 0 \cdot 008|F_o| + 0 \cdot 0005|F_o|^2]^{-1}$, were chosen so that ΔF would be independent of F_o. Unobserved reflexions ($I<3\sigma$) whose F_c was less than the measured value were given zero weight. A parameter, g, to correct for the effects of secondary extinction (Larson, 1967), was refined with the positional and thermal parameters of atoms. The g value found was $8 \cdot 09 \times 10^{-5}$. The refinement was terminated when all the calculated shifts were less than $0 \cdot 1\sigma$. The final $R=0 \cdot 043$, and $R_w=[\sum|F_o-F_c|^2/\sum F_o^2]^{1/2}=0 \cdot 056$. The final positional and thermal parameters are listed in Table 1.* Selected bond lengths and angles are given in Table 2.

Discussion. The structure contains sheets of polyhedra (Fig. 1). Edge-shared pairs of MgO_6 octahedra are bridged by corner-sharing with $Mg(2)O_6$ octahedra and edge-sharing with MgO_8 groups forming undu-

Table 2. *Bond distances and angles in* $Mg_3As_2O_8$ *with estimated standard deviations in parentheses*

Distance

As(1) –O(2^i)	1·705 (5) Å	2×
As(1) –O(3^ii)	1·676 (5)	2×
As(2) –O(1^i, iii, v, vii)	1·678 (5)	4×
Mg(1)–O(1^i, iv)	2·007 (5)	2×
Mg(1)–O(2^i, iv)	2·151 (6)	2×
Mg(1)–O(3^i, iv)	2·063 (5)	2×
Mg(2)–O(1^ii, iv)	2·065 (5)	2×
Mg(2)–O(2^xiii, xv)	2·077 (6)	2×
Mg(2)–O(3^ii, iv)	2·155 (6)	2×
Mg(3)–O(2^vi, viii, x, xii)	2·240 (6)	4×
Mg(3)–O(3)	2·722 (5)	4×

O(2^i)——As(1) –O(2^iv)	99·9 (3)°
O(2^i)——As(1) –O(3^ii)	104·5 (3)
O(1^i)——As(2) –O(1^iii)	120·7 (2)
O(1^i)——Mg(1)–O(1^iv)	102·6 (3)
O(1^i)——Mg(1)–O(2^i)	166·0 (3)
O(1^i)——Mg(1)–O(2^iv)	91·3 (2)
O(1^i)——Mg(1)–O(3^iv)	88·9 (2)
O(1^i)——Mg(1)–O(3^i)	86·1 (2)
O(1^i)——Mg(2)–O(1^iv)	156·5 (3)
O(1^i)——Mg(2)–O(2^xiii)	104·8 (2)
O(1^i)——Mg(2)–O(2^xv)	92·2 (2)
O(1^i)——Mg(2)–O(3^ii)	82·4 (2)
O(1^i)——Mg(2)–O(3^iv)	81·1 (2)
O(2^vi)——Mg(3)–O(2^viii)	121·7 (2)
O(3)——Mg(3)–O(3)	89·8 (3)
O(2^vi)——Mg(3)–O(3)	162·8 (2)
O(2^vi)——Mg(3)–O(3)	75·1 (3)
O(3^ii)——As(1) –O(3^iii)	119·8 (3)
O(3^iii) –As(1) –O(2^iv)	113·3 (3)
O(1^i)——As(2) –O(1^v)	104·2 (2)
O(2^i)——Mg(1)–O(2^iv)	74·7 (2)
O(2^i)——Mg(1)–O(3^iv)	92·6 (2)
O(2^i)——Mg(1)–O(3^i)	93·7 (2)
O(3^i)——Mg(1)–O(3^iv)	172·1 (3)
O(2^xiii)–Mg(2)–O(2^xv)	87·5 (3)
O(2^xiii)–Mg(2)–O(3^ii)	172·7 (2)
O(2^xiii)–Mg(2)–O(3^iv)	91·5 (2)
O(3^ii)——Mg(2)–O(3^iv)	90·4 (2)
O(2^vi)——Mg(3)–O(2^x)	103·7 (3)
O(3)——Mg(3)–O(3)	120·1 (3)
O(2^vi)——Mg(3)–O(3)	74·6 (2)
	64·4 (2)

Atom transformations

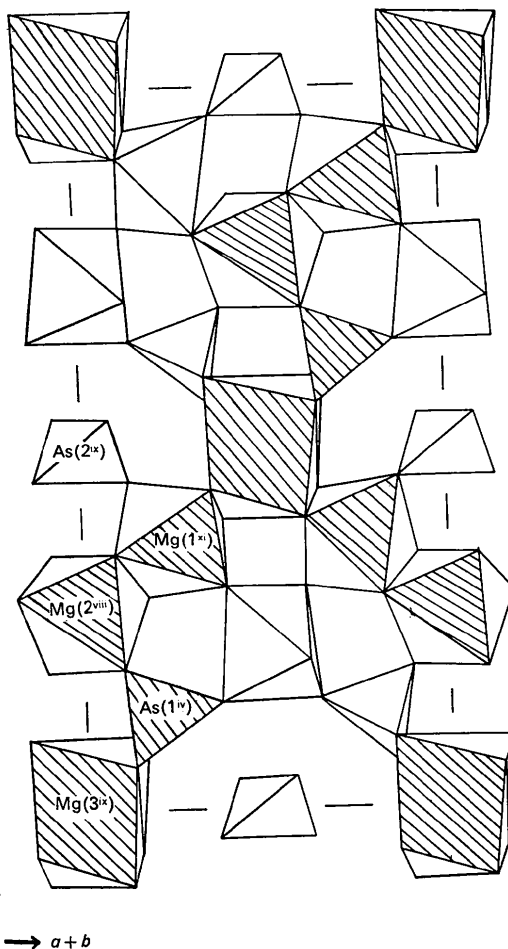|					
i	x,y,z	ii	$x,\frac{1}{2}-y,\frac{1}{4}-z$	iii	$-x,\frac{1}{2}+y,\frac{1}{4}-z$
iv	$-x,-y,z$	v	$-y,x,-z$	vi	$y,-x,-z$
vii	$\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$			viii	$\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}-z$
ix	$\frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}+z$			x	$\frac{1}{2}+x,-y,\frac{3}{4}-z$
xi	$y,\frac{1}{2}+x,\frac{1}{4}+z$			xii	$-y,\frac{1}{2}-x,\frac{1}{4}+z$
xiii	$\frac{1}{2}-x,y,\frac{3}{4}-z$			xiv	$\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z$
xv	$\frac{1}{2}+y,x,\frac{3}{4}+z$				
xvi	$\frac{1}{2}-y,-x,\frac{3}{4}+z$				

Fig. 1. A slice of the structure of $Mg_3As_2O_8$.

lating strips running parallel to the $a+b$, c planes. These strips are joined by AsO_4 tetrahedra which share edges with MgO_8 groups in one strip and corners with $Mg(2)O_6$ groups in the next. Similar sheets are generated normal to those in Fig. 1 by the symmetry of the crystal and provide the three-dimensional bonding. Two of the three Mg atoms have distorted octahedral environments of oxygen atoms with average Mg(1)–O and Mg(2)–O distances of 2·074 and 2·099 Å respectively. The third Mg atom lies at a site of $\bar{4}$ symmetry, with fractional occupancy of $\frac{1}{2}$, and is bonded to four oxygen atoms at 2·240 Å and an additional four at 2·722 Å. From Brown & Shannon's (1973) relationship between bond length, R, and bond strength S_i:

$$\ln S_i = 5\cdot0 \ln \frac{2\cdot098}{R} - 0\cdot0996,$$

it is found that a total bond strength of 0·956 is contributed by the four nearest oxygen atoms in agreement with a value of 1 expected for the fractionally occupied Mg^{2+}. The longer bond lengths contribute an additional 0·408 to the $\sum S_i$ value, however.

As(1) lies on a twofold axis and As(2) lies at a site with $\bar{4}$ symmetry. In the former case the two unique sets of As–O bond lengths differ significantly and in both cases the AsO_4 groups show substantial angular distortion with bond angles ranging from about 104 to 121°. In the case of $As(2)O_4$ this arises from a compression along the $\bar{4}$ axis. The $As(1)O_4$ group, on the other hand, shares three of its edges with three different Mg polyhedra [the O(2)–O(2′) edge is shared with an $Mg(1)O_6$ group while the O(2)–O(3) and O(2′)–O(3′) edges are shared with two different $Mg(3)O_n$ polyhedra] and the three smallest angles of the $As(1)O_4$ group correspond to the three angles subtended by these shared edges.

Robijn (1967) has postulated, on the basis of chemical analyses of various samples of $Mg_3As_2O_8$, that a range of stable non-stoichiometric compositions might exist. The structure of $Mg_3As_2O_8$ suggests that two additional Mg ions could be accommodated in the unit cell by filling the fractionally occupied Mg(3) site. A composition $Mg_{20}As_{11\cdot2}O_{48}$ can thus be obtained by the removal of arsenic ions in order to maintain electrical neutrality. Refinement of the population parameters of the arsenic and magnesium ion sites in the present case did not indicate significant deviations from the composition $Mg_3As_2O_8$.

The X-ray powder pattern of $Mg_3As_2O_8$ has been reported independently by three groups of workers (Ide, Kawai & Yamazaki, 1962; Robijn, 1967; Travniçek, Kröger, Botden & Zalm, 1952). One of these attempted to index the pattern on a hexagonal cell (Robijn, 1967). The powder pattern of the sample used in this study agrees well with those previously reported, indicating that the hexagonal assignment was incorrect.

References

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
IDE, H., KAWAI, N. & YAMAZAKI, S. (1962). *Denki Kagaku*, **30**, 233–235.
LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
ROBIJN, P. (1967). *Ind. Chim. Belge*, **32**, 601–606.
TRAVNIÇEK, M., KRÖGER, F. A., BOTDEN, T. P. J. & ZALM, P. (1952). *Physica*, **18**, 33–43.

Refinement of the Crystal Structure of Caesium Dichloroiodide

BY F. VAN BOLHUIS AND P. A. TUCKER*

Laboratorium voor Structuurchemie, Rijksuniversiteit te Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands

Abstract. $CsICl_2$, trigonal, space group $R\bar{3}m$ with $a=$ 5·469 (2) Å, $\alpha=70\cdot67$ (3)°, $Z=1$. The atomic positions have been determined by least-squares refinement of counter intensities, the final R being 0·031 for 256 reflexions. The I–Cl bond length is 2·548 Å.

* Present address: Department of Chemistry, University of Leicester, Leicester LE1 7RH, England.

Experimental. The orange-yellow crystals commonly develop the forms {100}, {110}, and {1$\bar{1}$0}, referred to rhombohedral axes, and are elongated along [111]. The material slowly loses halogen and the crystals were mounted with grease in thin-walled glass capillaries.

The cell constants were obtained from Weissenberg photographs superimposed with NaCl reflexions. The intensities for the 756 reflexions in one quadrant of