The Crystal Structure of Synthetic Lautarite, Ca(IO₃)₂

By Subrata Ghose and Che'ng Wan

Department of Geological Sciences, University of Washington, Seattle, Washington, USA

and Oscar Wittke

Laboratorio de Cristalografía, Departmento de Fisica, Universidad de Chile, Casilla 5487, Santiago, Chile

Synthetic lautarite, $Ca(IO_3)_2$, is monoclinic, space group $P2_1/n$, with cell dimensions $a = 7 \cdot 143$ (1), $b = 11 \cdot 297$ (3), $c = 7 \cdot 2804$ (9) Å, $\beta = 106 \cdot 35$ (1)°, $Z = 4$. The structure has been determined by the heavy-atom method and refined by the full-matrix least-squares method to an R factor of 0·055 for 2044 reflections, measured on an automatic single-crystal diffractometer. The Ca atom is eight-coordinated (av. Ca–O distance 2·492 Å), the CaO_8 polyhedron being a distorted hexagonal bipyramid. The average I–O bond lengths (and O–I–O bond angles) within the $I(1)O_3$ and $I(2)O_3$ groups are 1·807 Å (101·7°) and 1·804 Å (97·0°) respectively. I(1) is weakly bonded to three further O atoms at an average distance of 2·964 Å, the $I(1)O_6$ polyhedron being a distorted octahedron. I(2) is further bonded to four O atoms at an average distance of 2·994 Å; the $I(2)O_7$ polyhedron is a trigonal antiprism, modified by an additional corner above a prism face. The structure of $Ca(IO_3)_2$ is a tightly bonded three-dimensional framework, formed by Ca polyhedral chains crosslinked by the iodate groups.

Introduction

Anhydrous calcium iodate, $Ca(IO_3)_2$, is known as the mineral lautarite from the nitrate deposits of Chile. We have previously described the crystal structure of two iodate minerals from Chile, namely salesite, $CuIO_3(OH)$ (Ghose, 1962), and bellingerite, $3Cu(IO_3)_2 \cdot 2H_2O$ (Ghose & Wan, 1974). In view of the current interest in the stereochemistry of iodine(V) [see Alcock (1972) for a review], we have made a precise structure determination of $Ca(IO_3)_2$, which provides the opportunity of studying the stereochemistry of two crystallographically independent I atoms not restricted by any space-group symmetry. While this structure determination was in progress, we learned of an independent determination of the structure of $Ca(IO_3)_2$ by Appleman & Mrose (1974), who believed that the true space group of this compound was most likely $P2_1$. If, indeed, $Ca(IO_3)_2$ were non-centrosymmetric, it could have potential application as a non-linear optical material [*cf.* $Ca(IO_3)_2 \cdot 6H_2O$: Morosin, Bergman & Crane, 1973]. However, our results indicate that $Ca(IO_3)_2$ is truly centrosymmetric (space group $P2_1/n$). Since our results differ from those of Appleman & Mrose (1974), we decided to publish our results independently.

Synthesis and crystal data

Because no specimen of the mineral lautarite was available, we decided to synthesize the mineral follow-ing the method of de Schulten (1898). Hydrated calcium iodate was dissolved in molten sodium nitrate in a platinum crucible, which was subsequently cooled slowly in the furnace at a programmed rate. Millimeter-size transparent white stubby prismatic crystals of $Ca(IO_3)_2$ were recovered from a portion of the solidified charge by dissolving the sodium nitrate in water.

The cell dimensions and space group of lautarite were previously determined by Gossner & Mussgnug (1930). The cell dimensions (Table 1) have been determined from a least-squares refinement of 15 strong reflections with 2θ values between 40 and 50° using Mo $K\alpha$ radiation on an automatic single-crystal diffractometer. The crystal morphology, as well as Wilson statistics of the measured diffraction intensities, indicates a centrosymmetric space group, confirmed by the structure determination. The results of an attempt to measure the pyroelectric constant on small synthetic $Ca(IO_3)_2$ crystals were inconclusive (Abrahams, 1975, private communication) owing to the small size of the crystals available.

Table 1. $Ca(IO_3)_2$: *crystal data*

Monoclinic, $2/m$	Space group: $P2_1/n$
$a = 7 \cdot 1432$ (13) Å	$D_m = 4 \cdot 50$ g cm⁻³
$b = 11 \cdot 2969$ (31)	$D_c = 4 \cdot 48$
$c = 7 \cdot 2804$ (9)	$\mu(Mo\ K\alpha) = 121 \cdot 12$ cm⁻¹
$\beta = 106 \cdot 35$ (1)°	$\lambda(Mo\ K\alpha) = 0 \cdot 71069$ Å
$V = 563 \cdot 73$ (20) Å³	
Cell content: $4[Ca(IO_3)_2]$	

Experimental

A small single crystal of lautarite was ground to a sphere with a diameter of 0·23 (1) mm using a sphere grinder (Bond, 1951). The crystal sphere was mounted on the computer-controlled Syntex $P\bar{1}$ single-crystal diffractometer. The intensities of all reflections with 2θ values below 65° were measured by the 2θ–θ scan method. Mo $K\alpha$ radiation (50 kV, 10 mA), mono-chromatized by reflection from a graphite 'single' crystal, and a solid-state detection system were used for the intensity measurements. The variable-scan method was used, the minimum scan rate being 1° min^{-1} and the maximum 24° min^{-1}. The intensities were corrected for Lorentz, polarization, and absorption factors. For $I < 0·7\sigma(I)$, where $\sigma(I)$ is the standard error of measurement, I was set to $0·7\sigma(I)$, regardless of whether I was positive or negative. 2044 reflections were measured, out of which 29 had intensities below $3\sigma(I)$.

Determination and refinement of the structure

The positions of two I and one Ca atom were determined from the three-dimensional Patterson synthesis. A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an R factor of 0·18. Three-dimensional Fourier and difference Fourier syntheses yielded the positions of the remaining six O atoms. The full-matrix least-squares program *RFINE* (Finger, 1969) was used for the refinement of the structure. The structure factors (F_o) were weighted as $F_o/\sigma^2(F_o)$ where $\sigma(F_o)$ is the standard error of measurement as determined from the counting statistics. The scattering factors of the non-ionized atoms Ca, I and O were taken from Cromer & Mann (1968). Dispersion corrections were applied according to Cromer & Waber (1965). Three cycles of least-squares refinement using isotropic temperature factors, followed by three more cycles using anisotropic temperature factors, yielded an R factor of 0·055 for 2044 reflections. Thirty-nine very strong low-angle

reflections, most likely affected by extinction, were excluded from the refinement. The R factor excluding these reflections is 0·039.

Table 3. $Ca(IO_3)_2$: *interatomic distances* (Å) *and angles* (°) *(with standard deviations in parentheses)*

Symmetry code

None x,y,z
(i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ (v) $\frac{1}{2}-x, \frac{1}{2}-y, -1+(\frac{1}{2}+z)$
(ii) $1+x,y,z$ (vi) $-1+(\frac{1}{2}+x), \frac{1}{2}-y, \frac{1}{2}+z$
(iii) $1-x, -y, -z$ (vii) $-1+(\frac{1}{2}+x), \frac{1}{2}-y, -1+(\frac{1}{2}+z)$
(iv) $-x, -y, 1-z$ (viii) $2-(\frac{1}{2}+x), -(\frac{1}{2}-y), 1-(\frac{1}{2}+z)$

I(1) polyhedron

I(1)–O(1)	1·825 (4)	O(1)–I(1)–O(2)	103·94 (19)
I(1)–O(2)	1·796 (4)	O(1)–I(1)–O(3)	99·67 (20)
I(1)–O(3)	1·801 (4)	O(2)–I(1)–O(3)	101·43 (20)
Mean	1·807	Mean	101·68
I(1)–O(1^{iv})	2·920 (4)	O(1)–O(2)–O(3)	58·89 (15)
I(1)–O(4^{vi})	2·811 (5)	O(2)–O(3)–O(1)	61·78 (15)
I(1)–O(5^{vi})	3·160 (4)	O(3)–O(1)–O(2)	59·33 (15)
Mean	2·964	Mean	60·00
O(1)–O(2)	2·852 (6)	O(1^{iv})–I(1)–O(1)	73·25 (18)
O(2)–O(3)	2·784 (6)	O(1^{iv})–I(1)–O(2)	93·96 (17)
O(3)–O(1)	2·771 (6)	O(1^{iv})–I(1)–O(5^{vi})	75·52 (12)
Mean	2·964	O(1^{iv})–I(1)–O(4^{vi})	88·46 (12)
		O(2)–I(1)–O(5^{vi})	122·37 (16)
O(1^{iv})–O(1)	2·964 (9)	O(5^{vi})–I(1)–O(4^{vi})	53·54 (11)
O(1^{iv})–O(2)	3·532 (6)	O(4^{vi})–I(1)–O(1)	81·47 (15)
O(1^{iv})–O(5^{vi})	3·728 (6)	O(3)–I(1)–O(5^{vi})	98·48 (16)
O(1^{iv})–O(4^{vi})	3·998 (6)	O(3)–I(1)–O(4^{vi})	76·49 (16)
O(2)–O(5^{vi})	2·964 (6)	O(3)–I(1)–O(1^{iv})	164·29 (16)
O(5^{vi})–O(4^{vi})	2·707 (6)		
O(4^{vi})–O(1)	3·116 (6)		
O(3)–O(5^{vi})	3·887 (6)		
O(3)–O(4^{vi})	2·963 (6)		

I(2) polyhedron

I(2)–O(4)	1·814 (4)	O(4)–I(2)–O(5)	97·18 (20)
I(2)–O(5)	1·795 (4)	O(5)–I(2)–O(6)	93·57 (21)
I(2)–O(6)	1·804 (4)	O(6)–I(2)–O(4)	100·33 (18)
Mean	1·804	Mean	97·03
I(2)–O(1^{ii})	2·862 (4)	O(4)–O(5)–O(6)	62·81 (15)
I(2)–O(3)	3·164 (4)	O(5)–O(6)–O(4)	60·08 (15)
I(2)–O(3^{i})	3·051 (4)	O(6)–O(4)–O(5)	57·11 (16)
I(2)–O(4^{i})	2·902 (4)	Mean	60·00
Mean	2·994		
O(4)–O(5)	2·707 (6)	O(3^{i})–I(2)–O(1^{ii})	110·54 (11)
O(5)–O(6)	2·623 (6)	O(3^{i})–I(2)–O(4^{i})	61·39 (12)
O(6)–O(4)	2·778 (6)	O(3^{i})–I(2)–O(5)	103·61 (17)
Mean	2·703	O(3^{i})–I(2)–O(6)	76·39 (14)
		O(3^{i})–I(2)–O(3)	91·18 (12)
O(3^{i})–O(1^{ii})	4·012 (6)	O(1^{ii})–I(2)–O(4^{i})	65·45 (12)
O(3^{i})–O(4^{i})	4·612 (6)	O(4^{i})–I(2)–O(5)	66·09 (16)
O(3^{i})–O(5)	3·887 (6)	O(1^{ii})–I(2)–O(5)	91·99 (18)
O(3^{i})–O(6)	3·158 (6)	O(6)–I(2)–O(3)	63·67 (15)
O(3^{i})–O(3)	4·440 (2)	O(3)–I(2)–O(1^{ii})	107·93 (12)
O(1^{ii})–O(4^{i})	3·116 (6)	O(4)–I(2)–O(1^{ii})	70·48 (16)
O(4^{i})–O(5)	3·431 (6)	O(4)–I(2)–O(4^{i})	131·58 (18)
O(6)–O(3)	2·864 (6)	O(4)–I(2)–O(3)	69·34 (16)
O(3)–O(1^{ii})	2·771 (6)	O(4)–I(2)–O(3^{i})	91·18 (12)
O(4)–O(1^{ii})	2·831 (6)		
O(4)–O(4^{i})	4·324 (2)		
O(4)–O(3)	3·042 (6)		

Table 2. $Ca(IO_3)_2$: *atomic positional and thermal parameters* *(with standard deviations in parentheses)*

Fractional coordinates are $\times 10^5$.

	x	y	z	$^*B_{eq}$ (Å^2)
Ca	77440 (15)	9843 (9)	640 (14)	0·715 (15)
I(1)	23138 (5)	7390 (3)	46486 (4)	0·686 (9)
I(2)	76040 (4)	28536 (3)	44618 (4)	0·643 (9)
O(1)	−2904 (60)	9112 (38)	34813 (56)	0·247 (59)
O(2)	30628 (66)	−3936 (37)	32746 (58)	1·328 (60)
O(3)	32176 (66)	20510 (36)	37796 (63)	1·365 (63)
O(4)	65225 (61)	24528 (40)	19753 (58)	1·302 (59)
O(5)	93334 (64)	39066 (41)	40685 (63)	1·553 (67)
O(6)	59174 (61)	39804 (35)	47438 (56)	1·057 (54)

* Equivalent isotropic temperature factor, calculated from β_{ij}'s.

Table 3 (cont.)

Ca polyhedron

Ca—O(1ii)	2·490 (4)	O(1ii)—Ca—O(2iii)	154·03 (15)
Ca—O(2iii)	2·429 (4)	O(1ii)—Ca—O(3v)	108·03 (15)
Ca—O(3v)	2·468 (4)	O(1ii)—Ca—O(4)	69·49 (13)
Ca—O(4)	2·476 (4)	O(1ii)—Ca—O(5vii)	123·78 (15)
Ca—O(5vii)	2·341 (4)	O(1ii)—Ca—O(6v)	79·10 (14)
Ca—O(6v)	2·343 (4)	O(1ii)—Ca—O(6viii)	79·09 (14)
Ca—O(6viii)	2·446 (4)	O(2iii)—Ca—O(3v)	83·52 (15)
Ca—O(5viii)	2·939 (5)	O(2iii)—Ca —O(4)	136·44 (15)
Mean of 7	2·428	O(2iii)—Ca—O(5vii)	76·80 (15)
Mean of 8	2·492	O(2iii)—Ca—O(6v)	82·45 (15)
		O(2iii)—Ca—O(6viii)	77·38 (14)
O(1ii)—O(3v)	4·012 (6)	O(3v)—Ca—O(4)	73·62 (14)
O(1ii)—O(4)	2·831 (6)	O(3v)—Ca—O(5vii)	94·42 (17)
O(1ii)—O(5vii)	4·262 (6)	O(3v)—Ca—O(6v)	72·99 (14)
O(1ii)—O(6viii)	3·143 (6)	O(3v)—Ca—O(6viii)	139·53 (14)
O(1ii)—O(6v)	3·080 (6)	O(4)—Ca—O(5vii)	68·79 (14)
O(2iii)—O(3v)	3·262 (6)	O(4)—Ca—O(6v)	79·10 (14)
O(2iii)—O(4)	4·555 (6)	O(4)—Ca—O(6viii)	141·42 (14)
O(2iii)—O(5vii)	2·964 (6)	O(5vii)—Ca—O(6v)	156·88 (15)
O(2iii)—O(6viii)	3·047 (6)	O(5vii)—Ca—O(6viii)	114·98 (15)
O(2iii)—O(6v)	3·146 (6)	O(6v)—Ca—O(6viii)	69·39 (15)
O(3v)—O(4)	2·963 (6)		
O(4)—O(5vii)	2·724 (6)		
O(5vii)—O(6viii)	4·038 (6)		
O(6)—O(6viii)	2·727 (8)		

The atomic positional and thermal parameters are listed in Table 2. Table 3 lists the bond lengths and angles. The average standard error in Ca—O and I—O bond lengths is ±0·004 Å, and those in O—Ca—O and O—I—O angles are ±0·15 and ±0·20° respectively.*

Description of the structure and discussion

The structure of Ca(IO₃)₂ consists of CaO₈, I(1)O₆ and I(2)O₇ polyhedra connected into a three-dimensional framework (Figs. 1 and 2).

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32953 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The Ca polyhedron

The Ca atom is coordinated to seven O atoms at an average distance of 2·428 Å with a maximum variation of 0·087 Å and to an eighth, O(5'), at a distance of 2·939 Å. The coordination polyhedron can be described as a distorted hexagonal bipyramid, where O(3), O(4), O(5), O(5'), O(6') and O(6) form a distorted hexagonal plane, O(1) and O(2) forming the apices (Fig. 1). If the long Ca—O(5') bond is neglected, the CaO₇ polyhedron becomes a distorted, but more regular pentagonal bipyramid. In contrast, the [CaO₂(H₂O)₆] polyhedron in Ca(IO₃)₂.6H₂O is a square antiprism, with Ca—O distances ranging from 2·43 to 2·57 Å.

Stereochemical configuration of the iodate groups

The two crystallographically independent IO₃ groups are trigonal pyramids. I(1) is closely bonded to three O atoms at an average distance of 1·807 Å, the average O—I—O angle being 101·4°. I(1) is further bonded to three O atoms at an average distance of 2·964 Å. The I(1)O₆ polyhedron is a highly distorted octahedron (Fig. 3a).

I(2), likewise, is bonded to three O atoms at an average distance of 1·804 Å, the average O—I—O angle being 97·0°. I(2) is further bonded to four O atoms at an average distance of 2·994 Å. The I(2)O₇ polyhedron can be considered as a trigonal antiprism, modified by an additional corner, O(4'), above a prism face (Fig. 3b).

Both iodate groups deviate significantly from the highest possible point symmetry 3m. Thus, within each IO₃ group, one I—O bond is significantly longer than the other two I—O bonds and one O—I—O angle is significantly larger than the other two O—I—O angles (Table 3). The deviation from 3m symmetry in both iodate groups is most pronounced in terms of the configuration of the weak I—O bonds (Fig. 3).

All the O atoms are bonded strongly to one Ca and one I atom each, except O(6), which is bonded to two Ca atoms and one I atom. O(1), O(3) and O(4) in
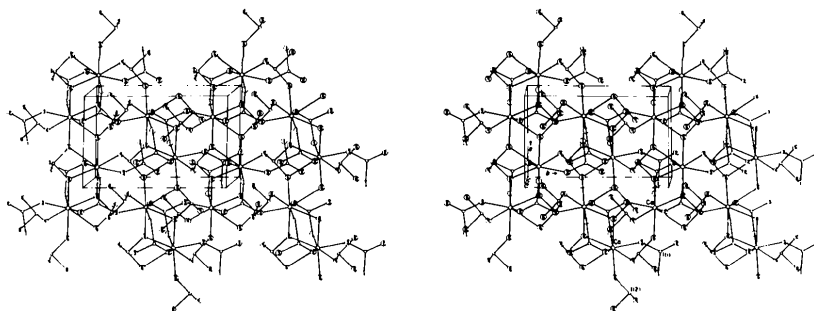

Fig. 1. A stereoview of the Ca(IO₃)₂ structure nearly along the c axis, showing the Ca polyhedral chains parallel to the a axis, crosslinked by (IO₃) groups.
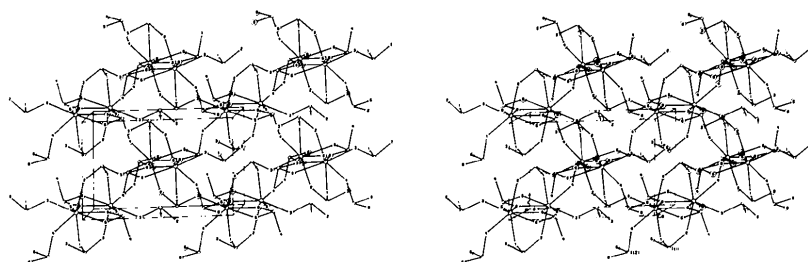
Fig. 2. A stereoview of the $Ca(IO_3)_2$ structure along the a axis, showing the space filling by the iodate polyhedra.
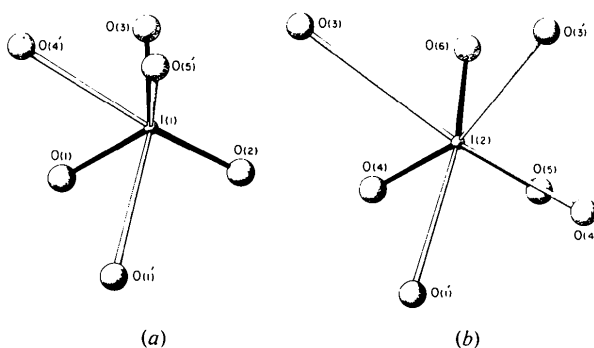

(a)   (b)

Fig. 3. Stereochemical configurations of the $I(1)O_6$ and $I(2)O_7$ groups in $Ca(IO_3)_2$.

addition are involved in two weak I—O bonds each, whereas O(5) is involved in only one weak I—O bond. O(2) does not seem to participate in any weak I—O bond, if we accept 3·2 Å as a cut-off limit for these bonds. Commensurate with these environments, the I(1)—O(2) (1·796 Å) and I(2)—O(5) (1·795 Å) bonds are the shortest found in this structure.

The three-dimensional framework

The Ca polyhedra share two edges [O(5)—O(5′) and O(6)—O(6′)] with two adjacent Ca polyhedra and form zigzag chains parallel to the a axis. These polyhedral chains are cross-linked through the edge and/or corner-sharing (IO_3) groups into a three-dimensional framework (Fig. 1). Alternatively, if we consider the weak I—O bonds, the structure of $Ca(IO_3)_2$ can be considered as a close packing of $I(1)O_6$ and $I(2)O_7$ polyhedra, the interstices of which are filled by Ca atoms (Fig. 2).

In terms of space filling, the structure of $Ca(IO_3)_2$ closely resembles that of $\alpha\text{-}Cu(IO_3)_2$ (Liminga, Abrahams & Bernstein, 1975a) and bellingerite, $3Cu(IO_3)_2.2H_2O$ (Ghose & Wan, 1974), where a similar packing of iodate polyhedra and Cu octahedra gives rise to a tightly bonded framework structure. The structure of the chemically related compound $Ca(IO_3)_2.6H_2O$ is quite different, where chains of $[IO_4(H_2O)_2]$ octahedra are held together by $[CaO_2(H_2O)_6]$ polyhedra and hydrogen bonds

(Braibanti, Manotti-Lanfredi, Pellinghelli & Tiripicchio, 1971; Morosin et al., 1973).

Coordination of iodine (V)

From a survey of the available data on iodates to date, Ghose & Wan (1974) have shown that the I—O coordination varies from five to eight; the coordination polyhedron is a distorted trigonal bipyramid for fivefold coordination, a distorted octahedron for sixfold coordination, a distorted pentagonal bipyramid or irregular for sevenfold coordination, and a distorted square antiprism for eightfold coordination. The coordination number of I seems to depend on the coordination number of the associated cation. Sixfold coordination is commonly found in iodates, where the cation coordination number is six (e.g. Li^+, Na^+, Cu^{2+}, etc.); likewise, eightfold coordination is found in iodates where the cation coordination number is eight (e.g. Ce^{4+}, Zr^{4+}, etc.). Sevenfold coordination is transitional between these two categories. Besides $Ca(IO_3)_2$, it has been found in $Sr(IO_3)_2.H_2O$ (Manotti-Lanfredi, Pellinghelli, Tiripicchio & Camellini, 1972), bellingerite, $3Cu(IO_3)_2.2H_2O$ (Ghose & Wan, 1974), $\alpha\text{-}Cu(IO_3)_2$ (Liminga, et al., 1975a) and $Nd(IO_3)_3.H_2O$ (Liminga et al., 1975b).

References

ALCOCK, N. W. (1972). Adv. Inorg. Chem. Radiochem. 15, 1–58.
APPLEMAN, D. E. & MROSE, M. E. (1974). Am. Crystallogr. Assoc. Program Abstr. 2, 270.
BOND, W. L. (1951). Rev. Sci. Instrum. 22, 344–345.
BRAIBANTI, A., MANOTTI-LANFREDI, A. M., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1971). Inorg. Chim. Acta, 5, 590–594.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104–109.

FINGER, L. (1969). Carnegie Inst. Washington Yearb. 67, 216–217.

GHOSE, S. (1962). Acta Cryst. 15, 1105–1109.

GHOSE, S. & WAN, C. (1974). Acta Cryst. B30, 965–974.

GOSSNER, B. & MUSSGNUG, F. (1930). Z. Kristallogr. 75, 410.

LIMINGA, R., ABRAHAMS, S. C. & BERNSTEIN, J. L. (1975a). J. Chem. Phys. 62, 4388–4399.

LIMINGA, R., ABRAHAMS, S. C. & BERNSTEIN, J. L. (1975b). J. Chem. Phys. 62, 755–763.

MANOTTI-LANFREDI, A. M., PELLINGHELLI, M. A., TIRIPICCHIO, A. & CAMELLINI, M. (1972). Acta Cryst. B28, 679–682.

MOROSIN, B., BERGMAN, J. G. & CRANE, G. R. (1973). Acta Cryst. B29, 1067–1072.

SCHULTEN, A. DE (1898). Bull. Soc. Fr. Minéral. 21, 144.

A Low-Temperature Neutron Diffraction Study of α-UO₂(NH₂O)₂.4H₂O

BY H. W. W. ADRIAN AND A. VAN TETS

Atomic Energy Board, Private Bag X256, Pretoria, Republic of South Africa

To locate the H atoms in α-UO₂(NH₂O)₂.4H₂O a single-crystal neutron diffraction analysis was carried out at −150°C. Space group P1̄, $a = 6·287$ (8), $b = 6·000$ (16), $c = 5·634$ (15) Å, $\alpha = 96·2$ (4), $\beta = 90·8$ (2), $\gamma = 105·1$ (2)°. The U, O and N atom positions were confirmed, and all the H atoms were found.

Introduction

Crystals of uranyl dihydroxylamide tetrahydrate are polymorphic. The structure of the α modification described here is similar to that of the trihydrate (Adrian & Van Tets, 1977). Although strong hydrogen bonding occurs in all these compounds, the α-tetrahydrate shows an unusual vibrationally 'free' H atom in the crystal water which distinguishes it from other compounds in the same group (Scheuermann & Van Tets, 1977).

Medium-sized single crystals of α-tetrahydrate can be grown in a desiccator from hydrochloric acid solutions which are slowly neutralized with ammonia vapour.

Structure determination

The X-ray crystal structure of the compound has been reported (Van Tets & Adrian, 1977). The crystal data are given in Table 1. The crystal selected for neutron diffraction possessed the triclinic shape of the unit cell and had a mass of 1·26 (5) mg. With $D_m = 3·27$ Mg m⁻³ this gave a volume of 0·385 mm³ for the crystal.

The neutron beam was monochromated by pyrolytic graphite ($\lambda = 1·451$ Å). The κ–φ configuration neutron single-crystal diffractometer (De Vries & Adrian, 1975) was used. Reflections were step-scanned in ω (interval $= 0·072°$) and the step width was 2·88° over the 2θ

range of 108°. The duration of the count at each step was determined by a monitor counter. After every 25 reflections a standard reflection was measured. Its intensity was found to vary negligibly during the course of the experiment.

An Enraf–Nonius universal low-temperature device was used to blow a stream of evaporated nitrogen over the sample. The temperature was monitored near the crystal and was constant to ±2°C during the experiment. The actual temperature of the sample (−150°C) was determined by replacing the crystal with a thermocouple. Condensation on the glass capillary (0·01 mm wall thickness) containing the crystal was within acceptable limits and deposits of ice were removed at regular intervals.

610 reflections were measured, of which 332 were significant ($I > 3\sigma$). Lorentz corrections were applied but absorption was disregarded.

Table 1. Crystal data

Molecular formula UO₂(NH₂O)₂.4H₂O
M_r (calculated) = 406·13
M_r (gravimetric) = 405
Space group P1̄
$D_m = 3·27$, $D_c = 3·305$ Mg m⁻³ for $Z = 1$
$\mu_{X-ray} = 1·83$, $\mu_{neutron} = 0·037$ m⁻¹

$a = 6·287$ (8) Å	$\alpha = 96·2$ (4)°
$b = 6·000$ (16)	$\beta = 90·8$ (2)
$c = 5·634$ (15)	$\gamma = 105·1$ (2)
$V = 204·0$ Å³	