

## The Crystal Structure of $\alpha$ -Rubidium Iodate

BY N.W. ALCOCK

*Department of Molecular Sciences, University of Warwick, Coventry, CV4 7AL England*

(Received 3 June 1972)

The crystal structure of one form of  $\text{RbIO}_3$  has been determined. The crystals are rhombohedral,  $a = 4.5377(4) \text{ \AA}$ ,  $\alpha = 89.71(1)^\circ$  space group  $R3m$ . Refinement on 923 observed reflexions reached  $R = 2.3\%$ . The structure is a distortion of the perovskite structure in which the environment of the iodine atom is unsymmetrical with three near oxygen atoms (I–O  $1.807 \text{ \AA}$ , O–I–O  $99.63^\circ$ ) and three at a further distance (I–O  $2.753 \text{ \AA}$ ). The rubidium ion has twelve neighbours, Rb–O between  $3.103$  and  $3.377 \text{ \AA}$ . Revised unit-cell dimensions are presented for  $\text{KIO}_3$ ,  $\beta\text{-RbIO}_3$ ,  $\text{CsIO}_3$ ,  $\text{AgIO}_3$  and  $\text{TlIO}_3$ .

### Introduction

The alkali metal iodates and some related compounds were originally reported to have ideal perovskite structures, with each iodine atom surrounded by a regular octahedron of oxygen atoms, and to have primitive cubic unit cells of side *ca.*  $4.5 \text{ \AA}$ . However, reinvestigations have found that the unit cells of these iodates are distortions of the simple cubic cells (Alcock, 1963, and see Appendix) and in all compounds so far examined as single crystals, the iodine atom's environment consists of three near oxygen atoms, defining a pyramidal  $\text{IO}_3^-$  group, and three more distant oxygen atoms completing a distorted octahedron. This grouping is of considerable interest because of the possibility of a directed weak bond between the iodine atom and the distant atoms (Alcock, 1972). On X-ray powder photographs, samples of rubidium and caesium iodate showed no detectable departure from cubic unit cells, but had a very weak super-lattice corresponding to  $a \approx 9.0 \text{ \AA}$ . Because these symmetrical unit cells are unexpected for distorted perovskite structures, single-crystal investigations were started. Optical examination shows that the symmetry is not cubic, as both crystals show extinction. Caesium iodate appears to be multiply twinned on a microscopic scale within the small cubes formed by crystallization at room temperature, and so only rubidium iodate has been examined further. It was discovered that it can exist in two modifications of which the  $\beta$  form shows a super-lattice; the three-dimensional structure of the  $\alpha$  form has been determined.

### Experimental

Rubidium iodate was prepared by mixing a solution of 10 g rubidium chloride in 50 ml water with a solution of 10 g iodic acid in 50 ml water. Some of the resulting precipitate was recrystallized once from water to give small crystals, most of which could be seen to be twinned on optical examination. This was later shown to be  $\beta\text{-RbIO}_3$ . To obtain larger crystals, some of the precipitate was dissolved in water and evaporated slowly at  $60^\circ\text{C}$  in an oven. Many of the resulting crystals were

twinned and others consisted of several components in slightly different orientations, but after X-ray examinations of several, an irregular fragment was found suitable for crystal structure determination. Preliminary photographs showed that the unit cell was cubic (to the observable accuracy), but unexpectedly showed no super-lattice reflexions even on very long exposures. The exact reflecting positions of twelve high-angle reflexions of forms  $\{600\}$  and  $\{620\}$  were determined on the Picker FACS-1 diffractometer and the unit-cell constants refined by the least-squares program assuming the crystal to be triclinic. The resulting unit-cell axes were identical to within the accuracy of this refinement ( $\sigma = 0.001 \text{ \AA}$ ) as were the cosines of the interaxial angles ( $\sigma = 0.0005$ ). This suggested that the true symmetry was rhombohedral, and so the measurements were refined with the appropriate constraints for this symmetry. The sum of the squared deviations of observed and calculated angles was  $0.0120$ , compared to  $0.0093$  for the triclinic refinement (five and nine parameters respectively), and thus the triclinic refinement does not give significantly better agreement. The root-mean-square deviation of an individual measurement was  $0.02^\circ$ . The rhombohedral symmetry was confirmed by orienting the crystal under the polarizing microscope with the supposed threefold axis parallel to the direction of observation. The crystal then appeared isotropic, although when viewed in other directions it showed a marked extinction.

### Crystal data

$\alpha\text{-RbIO}_3$ ,  $M = 260.37$ . Rhombohedral,  $a = 4.5377(4) \text{ \AA}$ ,  $\cos \alpha = 0.0050(1)$ ,  $\alpha = 89.71(1)^\circ$  at  $21^\circ\text{C}$ ,  $U = 93.27 \text{ \AA}^3$ ,  $Z = 1$ ,  $d_x = 4.63$ ,  $\mu(\text{Mo } K\alpha) = 221.5 \text{ cm}^{-1}$ ,  $F(000) = 138$ . The unit cell was determined as above, and the standard deviations (bracketed) are those determined by the least-squares refinement. Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) was used throughout. For the space group see below. The absence of super-lattice reflexions was surprising and therefore a powder photograph was taken with a Hagg–Guinier 5 cm camera. This confirmed the small cell and also showed that many of the

high-angle lines were split (as would be expected for the observed value of  $\alpha$ ), in disagreement with the results of Alcock (1963). The discrepancy was resolved by a photograph of the precipitate at the first stage of the preparation which showed super-lattice lines and had no high-angle splitting. This material can then be identified at  $\beta$ -RbIO<sub>3</sub>. The phase relationship between the two forms is not very certain, and the  $\beta$ -form may be metastable in the temperature range 20–60°C, as photographs of crystals obtained by slow evaporation at 45 and 20°C showed both to be the  $\alpha$ -form. Measurement of Guinier photographs gives  $a=9.080$  (2) Å at 18°C as the pseudo-cubic cell constant for  $\beta$ -RbIO<sub>3</sub>, but careful examination of the photographs suggests that its true symmetry may also be rhombohedral. Even though there are no split lines, some of the high-angle lines are broader than others, and the pattern of broad and narrow lines corresponds to that of split and unsplit lines in  $\alpha$ -RbIO<sub>3</sub>, as can be seen from Table 1. A comparison of the half-widths of microdensitometer traces for the lines {220} and {400} for the two forms suggests that the splitting for  $\alpha$ -RbIO<sub>3</sub> is 2.2 times that for  $\beta$ -RbIO<sub>3</sub>. The observation of broadening for all except {h00} lines is consistent only with rhombohedral symmetry. The following crystal data are therefore proposed for  $\beta$ -RbIO<sub>3</sub>: rhombohedral,  $a=9.080$  (2),  $\cos \alpha=0.0023$  (5),  $\alpha=89.86$  (3)°,  $Z=8$ .

Table 1. Guinier powder photograph lines

Index form (small cell)	$\alpha$ -RbIO <sub>3</sub>	$\beta$ -RbIO <sub>3</sub>
{100}	Singlet	Very sharp
{211}	Multiplet, one weak line resolved at low angle	Broad, shoulder at low angle
{220}	Equal weight doublet	Broad, apparently almost resolved
{320}	Widely separated 'doublet' with strong high angle line and weak low angle line	Possibly resolved on weak photographs but low angle line barely visible
{321}	Broad multiplet with one weak line resolved at low angle	Very broad, shoulder at low angle
{400}	Single	Very sharp

### Structure determination

Reflexions were collected from one complete hemisphere of reciprocal space ( $h > 0$ ) because of uncertainty about the Laue group and to confirm the crystal symmetry. This was done on the Picker FACS-1 with Mo  $K\alpha$  radiation and a graphite monochromator in perpendicular geometry, using an  $\omega$ -scan of 2° with background counts of 20 sec at each end of the scan, to  $2\theta=70^\circ$ . No attenuators were used. The crystal was randomly oriented, rigidly mounted on a Supper translation-only head. Two reflexions, 010 and 060, were monitored after every 40 measurements and showed no change with time. Lorentz and polarization corrections were applied assuming the monochromator to be

ideally mosaic. 923 independent reflexions were measured of which all had  $I/\sigma(I) > 3$  and were considered to be observed. The crystal was measured by the method of Alcock (1970) relative to the standard diffractometer axes with all circles set to zero. The bounding planes, after conversion to crystal-related orthogonal axes ( $X=a^*$ ,  $Y$  in the  $a^*-b^*$  plane,  $Z=c$ ), are shown in Table 2.

Table 2. Bounding planes

No.	$ax$	$+ by$	$+ cz$	$= d$
1	0.206	0.689	1.025	0.00455 cm
2	0.085	1.057	0.007	0.00295
3	0.905	0.374	0.212	0.00153
4	1.129	1.431	1.236	0.00760
5	0.253	0.768	0.620	0.00503
6	0.905	0.374	0.212	0.00229

An absorption correction was applied by the analytical method with the program *ABSCOR* in the X-RAY 63 system; the maximum and minimum transmission factors were 0.466 and 0.295. No systematic absences were observed and so the lattice must be primitive with Laue group  $\bar{3}$  or  $\bar{3}m$ . The reflexions were sorted to bring all the potentially equivalent occurrences of each together (*cf.* Table 4). An examination showed that reflexions of form  $\{hkl\}$  and cyclic permutations agreed as well with those of form  $\{hkl\}$  and cyclic permutations as did each group within itself. This indicates Laue group  $\bar{3}m$  with possible space groups  $R32$ ,  $R3m$  or  $R\bar{3}m$  satisfying the lack of systematic absences. Of these, only  $R3m$  allows a satisfactory placing of one iodate group within the unit cell, while  $R32$  is also inconsistent with the observed piezoelectric effect (Bergman, Boyd & Ashkin, 1966).  $R3m$  was therefore chosen as the space group; this was finally confirmed by the successful refinement.

The space group  $R3m$  requires that the iodine and rubidium atoms be on sixfold special positions ( $a$ ) with coordinates  $x, x, x$ , while the one independent oxygen atom is on the twofold position ( $b$ )  $x, x, z$ .† A trial structure was set up with the iodine atom at 0,0,0, the rubidium atom at 0.5, 0.5, 0.5 and the oxygen atom suitably placed for the usual geometry of the iodate group. Least-squares refinement with unit weights and isotropic temperature factors for all atoms, including anomalous dispersion, and with the positional parameter of the iodine fixed at zero rapidly converged to  $R=4.8\%$ . A calculation with the coordinates reversed gave  $R=5.9\%$ , confirming the polarity of the particular crystal examined. Anisotropic refinement only

† For convenience, actual occupancies six times these values were used. It was discovered after the refinement had been completed that a further multiplicity factor of three had been applied because the program system in use required rhombohedral cells specified on rhombohedral axes to be named primitive and not rhombohedral. As a result, all  $F$ -values given in this paper are 18 times absolute scale.

improved  $R$  to 4.0% and examination of the data revealed severe extinction effects. A weighting analysis reflected these effects. A weighting scheme of the form  $\sigma^2(F) = 1/30(1000 + 0.01F^2)$  gave satisfactory weights at this stage to all reflexions except some 50 with  $F > 800$ . Because some of these might have been affected by the lack of attenuators as well as by extinction, all reflexions with  $\omega F^2 > 6.25$  during a particular cycle (initially corresponding to  $F > 800$ ) were excluded from the refinement for that cycle. This slowed down convergence but prevented these few high  $F$ 's from distorting the fit to the main bulk of the data. In the final cycle only 13 reflexions were omitted. The final  $R$  index is 2.3% and the extinction parameter  $r^*$  (Larson, 1970) is  $1.38(3) \times 10^{-5}$ . The final atomic parameters are in Table 3, and the observed and calculated structure factors are in Table 4.

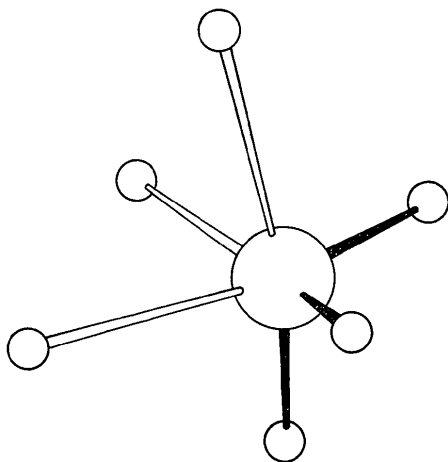


Fig. 1. Environment of the iodine atom. Large circle I, small circles O. Solid links 1.807 Å, open links 2.753 Å.

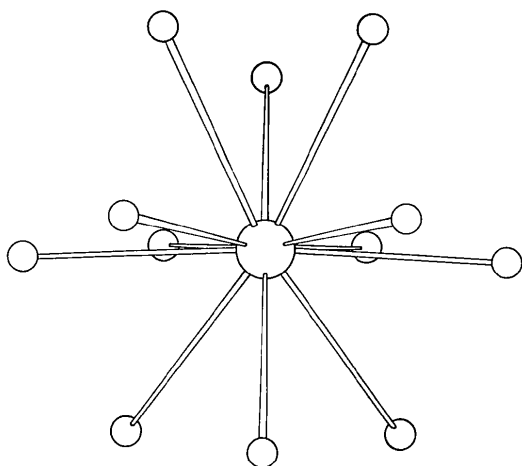


Fig. 2. The rubidium ion coordination viewed from close to 11T. Large circle Rb, small circles O. The three oxygen atoms of one  $\text{IO}_3^-$  group are at the top and centre rear.

Table 3. Atomic parameters with standard deviations in parentheses

The temperature factors are of the form

$$\exp[-8\pi^2(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$$

	Position	Parameters
I	$x, x, x$	$x = 0$ . Fixed $U_{11} = U_{22} = U_{33} = 0.01036(9)$ $U_{12} = U_{13} = U_{23} = -0.00058(9)$
Rb	$x, x, x$	$x = 0.4850(3)$ $U_{11} = U_{22} = U_{33} = 0.0346(8)$ $U_{12} = U_{13} = U_{23} = -0.0009(3)$
O	$x, x, z$	$x = -0.0361(5)$ $z = 0.3955(6)$ $U_{11} = U_{22} = 0.0347(9)$ $U_{33} = 0.0098(9)$ $U_{12} = -0.0016(11)$ $U_{13} = U_{23} = -0.0006(6)$

Correlation matrix.

The parameters are in the order: scale factor, extinction factor, then atom parameters in order as above. Only the upper triangle is given with diagonal elements omitted and slashes separating lines. All elements are multiplied by  $10^3$ .

823, 791, -321, 389, 558, 331, -177, -143, 158, 132, -35, -63 / 639, -196, 256, 362, 206, -108, -91, 102, 98, -28, -51 / 146, -166, 62, -209, 64, 65, 105, 141, -22, -65 / 854, -830, -793, 369, 319, -39, -63, -12, 2 / 932, 932, -406, -365, 75, 26, -8, -20 / 893, -400, -353, 105, 64, -14, -31 / -395, -351, 65, 18, -5, -7 / 131, -43, 4, -12, 11 / -81, 52, -19, 35 / -413, -15, -38 / 17, 114 / 10 /.

Calculations were performed using the X-RAY 63 and X-RAY program systems with *CRYLSQ* used to refine the independent parameters of which the actual atomic parameters are functions. Scattering factors and anomalous dispersion factors for  $\text{Rb}^+$ , neutral I and O were taken from *International Tables for X-ray Crystallography* (1962). Bond lengths and angles are given in Table 5. The standard deviations given are only approximate as no satisfactory error function program was available. The correlation between the two unit cell parameters is unknown but the correlation matrix for the other parameters is given in Table 3.

## Discussion

The iodine has the expected environment (Fig. 1) of three near oxygen atoms (1.807 Å) forming a pyramidal iodate group, with three further oxygen atoms (2.753 Å) completing a distorted octahedron. This coordination geometry, common to almost all iodates, is fully discussed in Alcock (1972); here a comparison is made (Table 6) only with the two closely related compounds  $\text{LiIO}_3$  (de Boer, van Bolhuis, Olthof-Hazekamp & Vos, 1966) and  $\text{NH}_4\text{IO}_3$  (Keve, Abrahams & Bernstein, 1971).\* The only systematic difference between

\* The coordination reported in the structure of  $\text{NaIO}_3$  (MacGillavry & van Eck, 1943) is rather irregular, probably because one or more of the oxygen atoms is not located very accurately.

the iodine environment is the decreasing length of the I...O long interaction. This is probably a consequence of the changing cation coordination discussed below. The high O-I-O angle in NH4IO3 may be a result of the hydrogen bonding in this compound.

The coordination of the cations changes very markedly in the series. Li+ in LiIO3 has six oxygen neighbours at 2.12 Å (average) in an almost regular octahedron. Both the other compounds have distorted perovskite structures. In the ideal form of this, the smaller cation (here iodine) is octahedrally coordinated and the larger one has twelve neighbours. In NH4IO3, the distortion of the unit cell and the movement of the oxygen and nitrogen atoms gives the latter four neighbours arranged approximately tetrahedrally. In RbIO3, the rubidium from retains twelve neighbours at distances 3.103 to 3.377 Å. The environment (Fig. 2) is not seriously distorted from the ideal, and is still qualitatively that of an atom in a close-packed structure. The shortest O-O distances are quite variable, from 2.761 to 3.636 Å but this probably does not affect the electrostatic energy of the RbO12 group very much.

This changing cation coordination suggests the cause of the different unit cells found for MIO3 compounds (Appendix). In the perovskite structure, an iodine atom forming short I-O bonds of 1.80 Å and long I-O bonds of 2.80 Å, with angles at iodine of about 90°, will define a cell of side 4.6 Å and the oxygen to cation distance will be about 4.6/√2=3.25 Å. This should be almost correct for caesium (Cs+ + O2- = 3.09 Å, six-coordinate radii from Wells, 1962) and rather large for rubidium (Rb+ + O2- = 2.88 Å). These can be expected to fit in without much distortion, when the difference between 12-coordinate and six-coordinate radii is allowed for, particularly as angular displacements of the oxygen atoms should not influence the electrostatic energy appreciably. For the ammonium ion, the tendency to form hydrogen bonds can be expected to produce further distortion and this will also be expected for the somewhat smaller thallium and potassium ions. There is a substantial decrease in radius on going from potassium to sodium and so it is not surprising that the perovskite structure is no longer stable for NaIO3 and LiIO3. Its absence in AgIO3 can be attributed to inter-

Table 4. Observed and final calculated structure factors

The columns are h, k, l, F0, Fc, |WAF|, A, B. The 13 reflections excluded from refinement are those with |WAF| > 2.5. The difference between Fc and |(A2 + B2)| is due to the inclusion of the extinction correction in the calculation of Fc.

Table with multiple columns containing numerical data for structure factors. The columns correspond to h, k, l, F0, Fc, |WAF|, A, B as defined in the caption. The table contains numerous rows of data, representing different reflections.

Table 4 (cont.)

Table 4 (cont.) containing multiple columns of numerical data, likely representing bond lengths and angles for various chemical environments.

Table 4 (cont.)

Table 4 (cont.) containing multiple columns of numerical data, likely representing bond lengths and angles for various chemical environments.

Table 5. Bond lengths and angles with standard deviations

Table 5. Bond lengths and angles with standard deviations. Lists bond lengths (i, ii, iii, iv) and angles (I-O-I, O-I-O, O-I-I-O, O-II-O, Rb-O-I, Rb-O-II, Rb-O-III, Rb-O-IV) with their respective values and standard deviations.

Table 6. Comparison of iodate environments

Table 6. Comparison of iodate environments. Compares Li+, NH4+\*, and Rb+ environments with I-O, I...O, O-I-O, and O-I...O bond lengths and angles.

\* Averaged values.

Table 7. *Unit cells of iodates*  $\text{MIO}_3$ 

	System	<i>a</i>	<i>b</i>	<i>c</i>	Angle	References
$\text{LiIO}_3$	Hexagonal	5.478 (3) Å		5.170 (2) Å		1
$\text{NaIO}_3$	Orthorhombic	5.74	6.37 Å	8.11		2
$\text{KIO}_3$	Monoclinic	8.985 (4)	8.981 (3)	8.945 (3)	$\beta = 91.06 (5)^\circ$	3
$\text{RbIO}_3\text{-}\alpha$	Rhombohedral	4.5377 (4)			$\alpha = 89.68 (1)$	4
$\text{RbIO}_3\text{-}\beta$	Rhombohedral (?)	9.080 (2)			$\alpha = 89.86 (3)$	3, 4
$\text{CsIO}_3$	(Pseudo-cubic)	9.3467 (9)				3
$\text{NH}_4\text{IO}_3$	Orthorhombic	6.4115 (5)	9.1706 (5)	6.3740 (5)		5
	(Alternative cell)	9.0415	9.1706	9.0415	$\beta = 89.70$	
$\text{AgIO}_3$	Orthorhombic	15.17 (2)	5.772 (5)	7.265 (5)		3, 6
$\text{TlIO}_3$	Rhombohedral	4.5108 (4)			$\alpha = 89.316 (9)$	3, 7

1. de Boer, van Bolhuis, Olthof-Hazekamp & Vos (1966).

2. MacGillavry & van Eck (1943).

3. Alcock (1963).

4. Present work.

5. Keve, Abrahams & Bernstein (1971).

6. Santana (1948).

7. Smith & Welch (1960).

See also: Rosenzweig & Morosin (1966) ( $\text{LiIO}_3$ ); Náray-Szábo & Kálmán (1961); Ozerov *et al.* (1962); Smith & Welch (1960) ( $\text{KIO}_3$ ); Rivoir & Abbad (1947) ( $\text{TlIO}_3$ ).

action between cation and anion, as occurs in other silver salts.

I thank Professor C. Ballhausen and Dr K. Watson for hospitality and use of equipment, and Fru E. Bang for taking high resolution Guinier photographs.

## APPENDIX

### *Unit cells of iodates* $\text{MIO}_3$

The unit cells of the iodates of univalent cations were reported in Alcock (1963) on the basis of powder photographs taken with a Nonius Guinier camera. The refinement was by least-squares fitting of calculated and observed  $\sin^2 \theta$  values and quoted errors were the standard deviations given by the computer program.  $\text{Cu } K\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation was used, with internal calibration ( $\text{NaCl}$ ,  $a_0 = 5.6394 \text{ \AA}$ ). Some of these results have been superseded by single-crystal studies, and the best values are given in Table 7. Several phases have been reported for most of these compounds, but these results apply to samples recrystallized at room temperature (except  $\alpha\text{-RbIO}_3$ ).

The five salts:  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ti}^+\text{IO}_3^-$  have very similar powder patterns, approximating to those for a cubic cell of side 4.5–4.6 Å. However, all except  $\text{TlIO}_3$  and  $\alpha\text{-RbIO}_3$  show weak super-lattice lines from a true cell with sides of approximately 9.0 Å and all except  $\beta\text{-RbIO}_3$  and  $\text{CsIO}_3$  have some lines split; the latter two are optically anisotropic and so cannot have cubic symmetry. For  $\text{CsIO}_3$ , the true symmetry is un-

known as all the crystals examined have been poly-synthetic twins, but  $\beta\text{-RbIO}_3$  is probably rhombohedral (see above).

## References

- ALCOCK, N. W. (1963). Ph. D. thesis, Cambridge.  
 ALCOCK, N. W. (1970). *Acta Cryst.* A **26**, 437.  
 ALCOCK, N. W. (1972). *Advances in Inorganic Chemistry and Radiochemistry*. Vol. 15. In the press.  
 BERGMAN, J. G., BOYD, G. D. & ASHKIN, A. (1966). *J. Appl. Phys.* **40**, 2860.  
 BOER, J. L. DE, VAN BOLHUIS, F., OLTHOF-HAZEKAMP, R. & VOS, A. (1966). *Acta Cryst.* **21**, 841.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 KEVE, E. T., ABRAHAMS, S. C. & BERNSTEIN, J. L. (1971). *J. Chem. Phys.* **54**, 2556.  
 LARSON, A. (1970). In *Crystallographic Computing*. pp. 291–294. Edited by F. R. AHMED. Copenhagen: Munksgaard.  
 MACGILLAVRY, C. H. & VAN ECK, C. L. P. (1943). *Rec. Trav. Chim. Pays-Bas*, **62**, 729.  
 NÁRAY-SZÁBO, I. & KÁLMÁN, A. (1961). *Acta Cryst.* **14**, 791.  
 OZEROV, R. P., RANNER, N. V., PAKHOMOV, N. I., REX, I. S. & ZHDANOV, G. S. (1962). *Kristallografiya*, **7**, 620.  
 RIVOIR, L. & ABBAD, M. (1947). *Anal. Soc. Esp. Fis. Quím.* **43**, 1051.  
 ROSENZWEIG, A. & MOROSIN, B. (1966). *Acta Cryst.* **20**, 758.  
 SANTANA, P. (1948). *Anal. Soc. Esp. Fis. Quím.* **44**A, 557.  
 SMITH, A. J. & WELCH, A. J. E. (1960). *Acta Cryst.* **13**, 653.  
 WELLS, A. F. (1962). *Structural Inorganic Chemistry*, 3rd ed. p. 71. Oxford: Univ. Press.