Acta Cryst. (1970). B26, 1969

The Crystal Structure of Dipotassium Fumarate Dihydrate

BY M. P. GUPTA AND B. N. SAHU

Department of Physics, University of Ranchi, Ranchi-8, Bihar, India

(*Received* 16 *January* 1970)

Dipotassium fumarate, $K_2C_4H_2O_4.2H_2O$, is monoclinic with $a=6{\cdot}35_4$, $b=18{\cdot}22_8$, $c=7{\cdot}27_2$ Å, $\beta=98°20'$, space group $P2_1/c$, with four formula units in the unit cell. The structure has been refined from three-dimensional data with anisotropic temperature factors to give an R index of 0·111. Chains of fumarate groups are aligned parallel to the [010] axis at heights zero and $\frac{1}{2}c$. The chains are linked by bonds between the two water molecules, one of them linking the chains at heights approximately 0 and $\frac{1}{2}c$, separated by the [100] axis translation, through hydrogen bonds of 2·78 and 2·81 Å, and the other linking the chains at 0 and $\frac{1}{2}c$, *i.e.* one above the other, through hydrogen bonds of 2·90 and 2·81 Å. K^+–O distances range from 2·71 to 2·85 Å with an average value of 2·79 Å. The two COOH groups in the molecule are both ionized as evidenced by nearly equal C–O bonds in both carboxyl groups of the same molecule.

Several salts of fumaric acid have been investigated by Gupta (1956), Gupta & Barnes (1961), Gupta & Roy (1967) and Gupta & Sahu (1970). A salt of unusual interest is the so-called acid potassium hydrogen fumarate (Gupta, 1956) whose chemical composition can be expressed either as $2KC_4H_3O_4+C_4H_4O_4$ or $2C_4H_4O_4+K_2C_4H_2O_4$. Regardless of which formula really represents the actual structure there is, in either case, an extra 'molecule of crystallization', in a triclinic unit cell, which occupies a centre of symmetry (Gupta, 1956). One way to establish the correct chemical composition would be to determine accurately the dimensions of the compounds $K_2C_4H_2O_4$ and $KC_4H_3O_4$ [those of $C_4H_4O_4$ have already been determined by Brown (1966) and Bednowitz & Post (1966)] and to compare these values with those already determined for potassium hydrogen fumarate (Gupta & Roy, 1967). The present work describes an attempt at determining accurately the dimensions of the compound $K_2C_4H_2O_4$, which is the neutral potassium salt of fumaric acid.

Crystal data

The crystals were grown following the method described by Gupta & Barnes (1961). The unit-cell data are:

$a=6{\cdot}35_4$ Å	ϱ calc = 1·819 g.ml^{-1}
$b=18{\cdot}228$ Å	ϱ meas = 1·817 g.ml^{-1}
$c=7{\cdot}272$ Å	
$\beta=98°20'$	$Z=4$
Space group $P2_1/c$	

Linear absorption coefficient for

Mo $K\alpha=10{\cdot}5$ cm^{-1}
Cu $K\alpha=100{\cdot}8$ cm^{-1} .

Intensity data were collected using precession photographs and unfiltered Mo K radiation ($hk0, 0kl, h0l, hk\bar{h}, hkh, hk2\bar{h}, hk2h$) and equi-inclination Weissenberg photographs using unfiltered Cu K radiation around the [001] axis ($hk0, hk1, hk2, hk3, hk4$). A total of 704 reflexions were found to have non-zero intensity values, the others being too weak to be observed. The intensities were estimated visually using an intensity scale with crystal reflected spots and a graded series of exposures. They were all brought to a nearly absolute scale using statistical methods, and F^2 values were derived after application of appropriate corrections, which did not include that for absorption.

Determination and refinement of the structure

Patterson projections down the [001], [010] and [100] axes proved to be of no help in determining the positions of the potassium atoms. Trial and error methods based on considerations of packing and low-order reflexions showing large intensities proved fruitless. Inequality relations ($S_H \cdot S_K = S_{H+K}$) using only zonal reflexions ($hk0, 0kl, h0l$) proved equally useless. A three-dimensional unsharpened Patterson function was then computed, the solution of which led to the following assignment for the positions of the potassium atoms:

	x/a	y/b	z/c
K(I)	0·117	0	0·250
K(II)	0·400	133	$0{\cdot}\overline{250}$

Work was then concentrated on the [001] electron density projection which was the best projection. Reiterative normal Fourier refinements gave a value of $R(hk0)\simeq 0{\cdot}388$ and $R(0kl)\simeq 0{\cdot}30$. Four cycles of least-squares refinement for the zonal data, with an overall isotropic temperature factor and unit weight for all reflexions, brought the R value down to $R(hk0)=0{\cdot}155$ and $R(0kl)=0{\cdot}22$. A full-matrix three-dimensional refinement with anisotropic temperature factors was then undertaken at the TIFR, Colaba, using the CDC 3600 version of the program of Busing, Martin & Levy

(1962) as modified by Hamilton, Ibers, Srikanta and Johnson. Six cycles of least-squares refinement reduced the R value for all observed reflexions to 0·122. Four reflexions 042, 062, 102, 211, were corrected for extinction following the method of Srinivasan (1959). The final R value was 0·111 and the observed and calculated structure factors are given in Table 1. The contributions of the hydrogen atoms are not included. Reflexions not observed are excluded from the list. The atomic scattering factors as given in *International Tables for X-ray Crystallography* were used in the calculations. For the potassium atoms, values of the atomic scattering factor for K^+ were used.

Coordinates, bond-lengths and angles and intermolecular contacts

The final atomic coordinates together with their estimated standard deviations (in parenthesis) are given in Table 2(*a*) while the thermal parameters with their e.s.d.'s (in parenthesis) are listed in Table 2(*b*). The expressions used were of the type $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{31}hl+b_{12}hk)]$.

The bond lengths and angles for the fumarate group together with their e.s.d.'s are given in Table 3 where the symbols refer to the atoms as shown in Fig. 1. The K^+–O contacts less than 4 Å are listed in Table 4.

Table 1. *Observed and calculated structure factors*

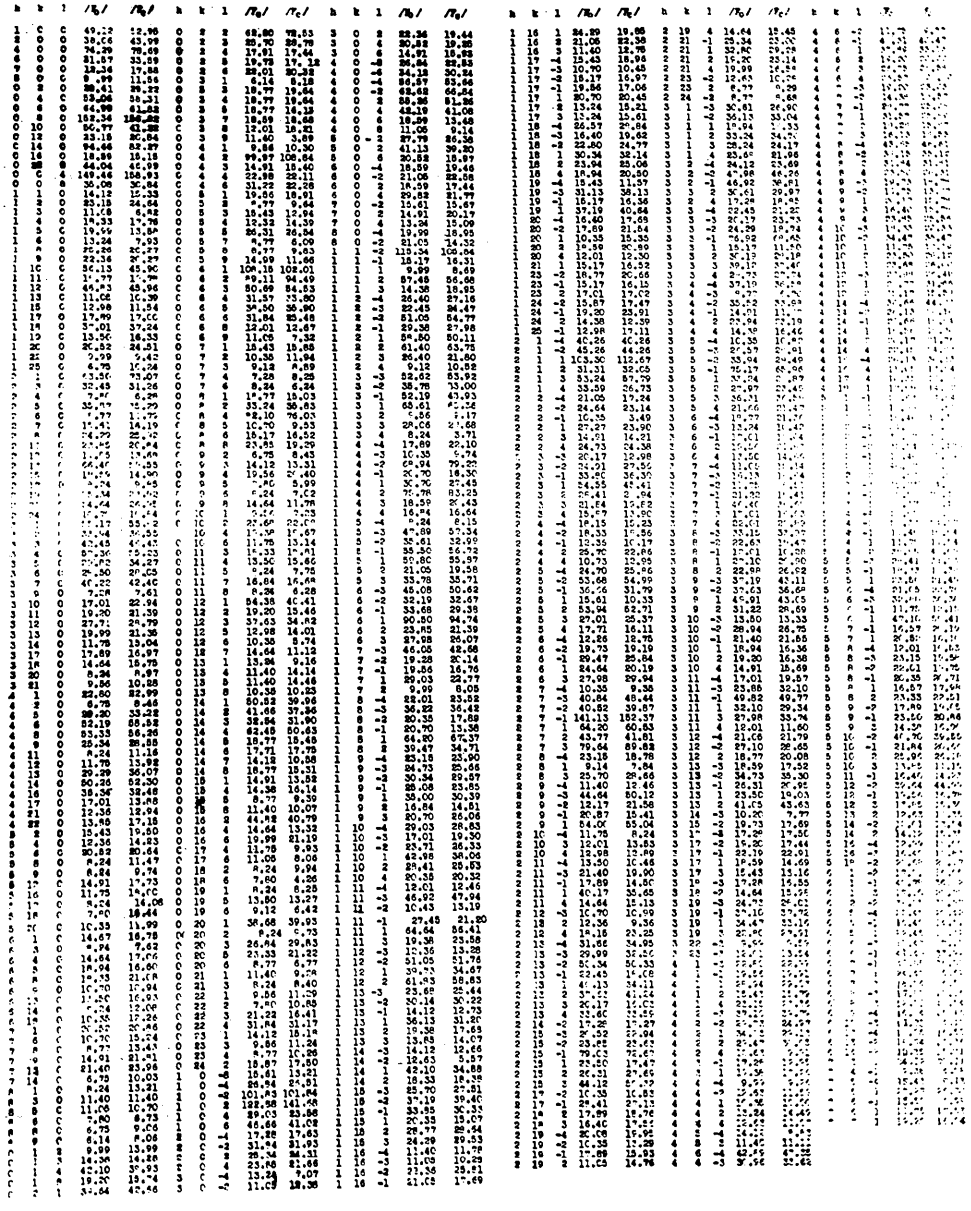

Table 2. *Final parameters*

(*a*) Fractional coordinates ($\times 10^5$)

	x	*y*	*z*
K(I)	12410 (87)	473 (23)	26094 (84)
K(II)	39906 (82)	13481 (24)	76456 (93)
C(1)	−8810 (378)	13479 (116)	2709 (391)
C(2)	−15883 (352)	21507 (103)	3752 (373)
C(3)	−4684 (441)	27308 (111)	23 (409)
C(4)	−11367 (436)	35096 (111)	1140 (328)
O(1)	−22977 (255)	8970 (74)	703 (279)
O(2)	10471 (252)	12507 (82)	1257 (253)
O(3)	3254 (259)	39856 (74)	2270 (288)
O(4)	−31096 (256)	36522 (83)	27847 (317)
O(5) (H_2O) (I)	56687 (253)	2035 (82)	27847 (317)
O(6) (H_2O) (II)	39871 (256)	21397 (72)	26203 (293)

(*b*) Thermal parameters ($\times 10^4$ Å^2)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
K(I)	137 (13)	5 (1)	148 (14)	4 (3)	34 (11)	3 (3)
K(II)	103 (12)	11 (1)	178 (17)	4 (4)	35 (11)	−1 (4)
C(1)	135 (56)	8 (5)	151 (78)	−5 (17)	−41 (59)	−8 (16)
C(2)	135 (57)	5 (4)	139 (69)	−9 (16)	−44 (52)	1 (15)
C(3)	288 (93)	9 (5)	120 (64)	7 (19)	16 (70)	24 (16)
C(4)	280 (80)	10 (5)	9 (47)	7 (19)	89 (60)	16 (13)
O(1)	146 (45)	6 (3)	259 (60)	−21 (11)	47 (44)	−3 (11)
O(2)	106 (39)	11 (4)	161 (51)	1 (12)	3 (37)	11 (11)
O(3)	143 (51)	7 (3)	257 (59)	2 (12)	56 (46)	11 (13)
O(4)	147 (45)	7 (4)	344 (71)	9 (13)	−5 (46)	−4 (13)
O(5) (H_2O) (I)	114 (43)	12 (4)	388 (70)	−16 (11)	44 (46)	0 (14)
O(6) (H_2O) (II)	107 (39)	9 (3)	280 (61)	14 (13)	−1 (39)	15 (14)

The symbol ^{a}O(2) refers to the oxygen atom derived from O(2) by a unit translation along [100], *etc.*; a symbol such as ^a_gO(4) indicates an atom derived from the oxygen atom O(4) by a unit **a** translation followed by a glide operation, and so on; the primed symbols refer to centrosymmetrically related atoms. The average value for the K^+–O contacts is 2·79 Å and there is fourfold coordination of the oxygen atoms around the potassium atom K(II) and fivefold coordination around the potassium atom K(I) if only the contacts less than 2·9 Å are taken into account.

Table 3. *Bond lengths and angles in the fumarate group*

	Length, *l*	$\sigma(l)$
C(1)–O(1)	1·245 Å	0·029 Å
C(1)–O(2)	1·264	0·028
C(4)–O(3)	1·264	0·028
C(4)–O(4)	1·295	0·031

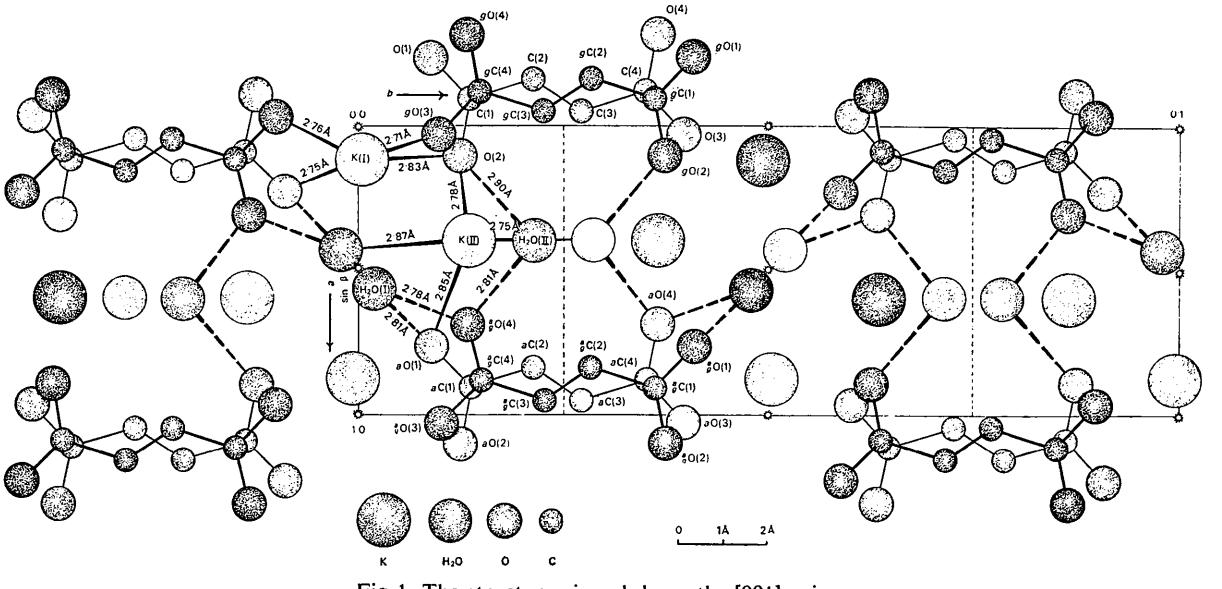

Fig. 1. The structure viewed down the [001] axis.

Table 3 (*cont.*)

	Length, l	$\sigma(l)$
C(1)–C(2)	1·489	0·028
C(3)–C(4)	1·487	0·029
C(2)=C(3)	1·324	0·030
	Angle, θ	$\sigma(\theta)$
O(1)–C(1)–O(2)	123·9°	1·2°
O(1)–C(1)–C(2)	116·9	1·2
O(2)–C(1)–C(2)	118·5	1·6
C(1)–C(2)–C(3)	124·9	1·5
C(2)–C(3)–C(4)	125·8	1·6
C(3)–C(4)–O(4)	118·8	1·4
C(3)–C(4)–O(3)	116·5	1·4
O(3)–C(4)–O(4)	124·5	1·2

Table 4. K^+–O *contact distances less than* 4 Å

	Distance
K(I)—O(1)	3·109 Å
K(I)—O(2)	2·832
K(I)—$_g$O(3)	2·718
K(I)—O(1′)	2·754
K(I)—$_g$O(4′)	3·129
K(I)—O(2′)	3·290
K(I)—$_g$O(3′)	2·769
K(I)—H_2O(I)	2·811
K(II)–O(2)	2·785
K(II)–^{a}O(1)	2·854
K(II)–(H_2O) (II)	3·894
K(II)–(H_2O) (I)	3·741
K(II)–(H_2O) (I′)	2·857
K(II)–$_g$(H_2O) (II)	2·756

Significant intermolecular contacts less than 4 Å are listed in Table 5.

Table 5. *Intermolecular contacts less than* 4 Å

	Distance
C(1)–$_g$C(4)	3·553 Å
C(2)–$_g$C(3)	3·423
C(4)–$_g$C(1)	3·735
O(2)–$_g$C(4)	3·792
O(3)–$_g$C(1)	3·908
O(4)–$_g$C(1)	3·729
O(2)–$_g$O(3)	3·826
O(3)–$_g$O(2)	3·551
O(1)–$_g$O(3)	3·883
O(4)–$_g$O(2)	3·966
(H_2O) (I)—$_g^a$O(3)	3·545
(H_2O) (I)—$_g^a$O(3′)	3·525
(H_2O) (I)—O(2)	3·789
(H_2O) (I)—$_g$O(4′)	3·657
(H_2O) (I)—O(1′)	3·410
(H_2O) (I)—(H_2O) (I′)	4·084
(H_2O) (II)–$_g$(H_2O) (II)	3·865
(H_2O) (II)–$_a$O(4)	3·842
(H_2O) (II)–$_g$O(3)	3·809
(H_2O) (II)–$_a$O(1)	3·924
(H_2O) (II)–$_g$O(2)	4·049
$_g$(H_2O) (II)–O(3)	3·805
K(I)—O(1)	3·108
K(I)—$_g$O(4′)	3·129
K(I)—O(2′)	3·290
K(II)–(H_2O) (II)	3·894
K(II)–(H_2O) (I)	3·741
K(I)—C(1)	3·146
K(II)–C(1)	3·864

Planarity of the atoms in the fumarate group

The equation to the best plane passing through all the atoms in the fumarate group, derived by the method of least-squares, is given by

$$X-1{\cdot}980\ Y-31{\cdot}773\ Z+15{\cdot}544=0$$

and the deviations of the atoms from this plane with e.s.d.'s are given in Table 6. The fumarate group is definitely not planar. The two halves of the fumarate group, *i.e.* the groups containing the atoms C(1), C(2), O(1), O(2) and the atoms C(3), C(4), O(3), O(4) are in two different but nearly parallel planes, the angle between them being 176·3°. The equations to the two planes are given below:

$$X-7{\cdot}623\ Y+60{\cdot}025\ Z+11{\cdot}733=0$$
[C(1), C(2), O(1), O(2)]

$$X+2{\cdot}262\ Y-20{\cdot}226\ Z-11{\cdot}563=0$$
[C(3), C(4), O(3), O(4)].

The deviations of the plane-defining atoms from the plane and their e.s.d.'s are given in Table 7. Although fumaric acid is itself planar (Brown, 1966; Post *et al.*, 1966), the fumarate groups in the salts are not planar (Gupta & Roy, 1967; Gupta & Sahu, 1970; Pedone & Sirigu, 1967). The lack of planarity in the molecule is not surprising since accurate structure determinations of fumaric acid itself by Brown (1966) and Bednowitz & Post (1966), has shown an absence of conjugation in the C–CH–CH–C bond system, with the central C–C bond being a real double C=C bond. This, therefore, leaves scope for the COOH group to twist around the single C–C bond, presumably to conform with packing considerations, the metal–oxygen linkages and the local balancing of opposite charges.

Table 6. *Deviations of atoms from the plane of the fumarate group*

	Deviation	E.s.d.
C(1)	0·117 Å	0·030 Å
C(2)	−0·056	0·028
C(3)	0·164	0·031
C(4)	−0·014	0·024
O(1)	0·284	0·020
O(2)	0·271	0·019
O(3)	−0·118	0·021
O(4)	−0·154	0·022

Table 7. *Deviations of atoms from the planes of the two halves of the fumarate group*

	Deviation	E.s.d.
C(1)	0·061 Å	0·031 Å
C(2)	−0·049	0·029
O(1)	0·013	0·031
O(2)	0·007	0·025
C(3)	−0·031	0·033
C(4)	0·025	0·033
O(3)	0·085	0·023
O(4)	−0·093	0·024

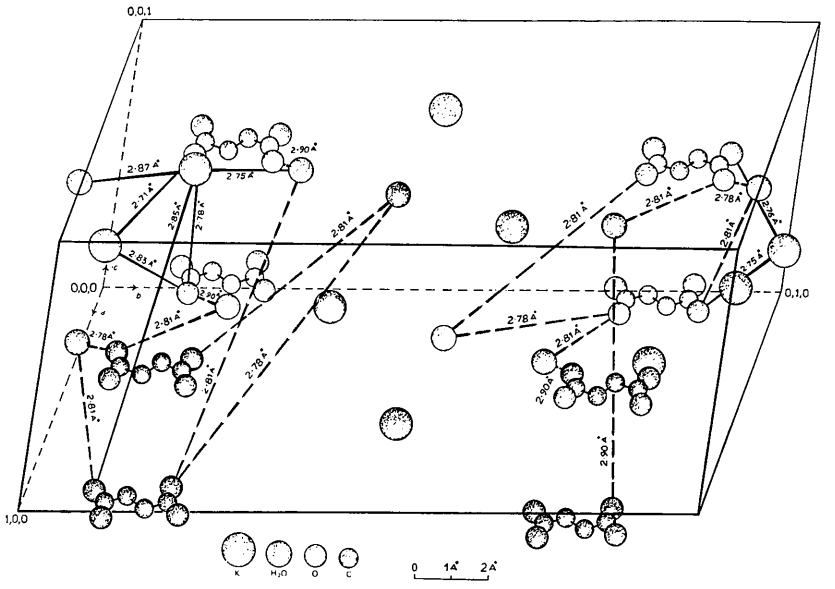

Fig. 2. A three-dimensional view of the structure.

Description of the structure

The nearly equal bond-length values for the C–O distances in the carboxyl groups indicate that the COOH groups are fully ionized as would be expected. Fig. 1 shows a view of the structure looking down the [001] axis while Fig. 2 is a three-dimensional view of the structure. In the crystal, fumarate groups are aligned parallel to the [010] axis at heights approximately zero and $\frac{1}{2}c$ from the basal plane (001). The chains are linked by weak van der Waals contacts of 4·0 Å between oxygen atoms O(1)---O(2′) and O(2)---O(1′). Stronger bonding is, however, provided by the water molecules. The water molecule (H_2O)(I) links the chain at zero with the one immediately above it derived by the glide operation, the H-bonds being 2·81 Å, (H_2O)(I)---^{a}O(1), and 2·78 Å, (H_2O)(I)---$^{a}_{g}$O(4) respectively (Fig. 1) and the angle ^{a}O(1)---(H_2O)(I)---$^{a}_{g}$O(4) being 98·2°. The second water molecule (H_2O)(II) binds the two chains of fumarate groups which are separated by a unit **a** translation and are at heights zero and $\frac{1}{2}c$ from the basal plane (001), through hydrogen bonds of 2·81 Å, (H_2O)(II)---$^{a}_{g}$O(4) and 2·90 Å, (H_2O)(II)---O(2), the angle O(2)---(H_2O)(II)---$^{a}_{g}$O(4) being 100·5°. In other words, one of the water molecules (H_2O)(I), binds the chains placed immediately above and below while the second water molecule (H_2O)(II), cross links the chains separated by the unit **a** translation. The short distances of 2·81, 2·78, 2·81 and 2·90 Å and nearly tetrahedral values for the O---(H_2O)---O angles indicate that they are real hydrogen bonds.

No attempt has been made to locate the hydrogen atoms in this structure, although projections of difference Fourier syntheses indicate peaks in the expected positions.

One of us (BNS) gratefully acknowledges the award of a research scholarship by the University of Ranchi during the tenure of which this work was done. Grateful acknowledgment is made of the computing facilities at the TIFR, Colaba, on the CDC – 3600.

References

BEDNOWITZ, A. L. & POST, B. (1966). *Acta Cryst.* **21**, 566.
BROWN, C. J. (1966). *Acta Cryst.* **21**, 1.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program.* Oak Ridge National Laboratory Report ORNL-TM-305.
GUPTA, M. P. (1956). *Acta Cryst.* **9**, 263.
GUPTA, M. P. & BARNES, W. H. (1961). *Canad. J. Chem.* **39**, 1739.
GUPTA, M. P. & ROY, P. K. (1967). *Indian J. Phys.* **41** (9), 787.
GUPTA, M. P. & SAHU, R. G. (1970). *Acta Cryst.* B**26**, 61.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
PEDONE, C. & SIRIGU, A. (1967). *Acta Cryst.* **23**, 759.
SRINIVASAN, R. (1959). *Proc. Indian Acad. Sci.* **6**, 340.