

tion: *DREAM* (Blessing, 1986). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *XRAY* (Stewart, 1978). Molecular graphics: *CHEM3D* (Rubenstein & Rubenstein, 1987).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71727 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1056]

References

- Blessing, R. H. (1986). *Crystallogr. Rev.* **1**, 3–58.
 Calvo, C. (1968). *Bull. Soc. Chim. Fr.* pp. 1744–1747.
 Forsyth, J. B., Wilkinson, C., Paster, S. & Wanklyn, B. M. (1989). *J. Phys. Condens. Matter*, **1**, 169–178.
 Krishnamachari, N. & Calvo, C. (1972). *Acta Cryst.* **B28**, 2883–2885.
 Łukaszewicz, K. (1967). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **15**, 47–51.
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 Masse, B., Guitel, A. & Durif, A. (1979). *Mater. Res. Bull.* **14**, 337–341.
 Pietraszko, A. & Łukaszewicz, K. (1968). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **16**, 183–187.
 Robertson, B. E. & Calvo, C. (1967). *Acta Cryst.* **22**, 665–672.
 Robertson, B. E. & Calvo, C. (1968). *Can. J. Chem.* **46**, 605–612.
 Rubenstein, M. & Rubenstein, S. (1987). *CHEM3D. The Molecular Modeling System*. Cambridge Scientific Computing, Inc., Cambridge, Massachusetts, USA.
 Stefanidis, T. & Nord, A. G. (1984). *Acta Cryst.* **C40**, 1995–1998.
 Stewart, J. M. (1978). Editor. *The XRAY System of Crystallographic Programs*. (Version of 1980.) Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

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Isomorphous Crystals: K₂HPO₄ and K₅Na(HPO₄)₃

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Abstract

The crystals of dipotassium hydrogenphosphate, K₂HPO₄, are almost isomorphous with crystals of pentapotassium sodium tris(hydrogenphosphate), K₅Na-

(HPO₄)₃. In both, the three crystallographically independent HPO₄²⁻ anions are held together by O11—H11···O33 and O31—H31···O23 hydrogen bonds, forming chains. These chains are joined by symmetry-related hydrogen bonds, O24—H24···O21ⁱ and O21—H21···O24ⁱⁱ in K₂HPO₄ and K₅Na(HPO₄)₃, respectively, forming infinite helical chains running parallel to the *c* axis. The K⁺ cations have different numbers of neighbours (from six to eleven) and the Na⁺ cations are six-coordinated. The P—O(H) distances range from 1.596 (5) to 1.625 (3) Å and the P—O(terminal) distances range from 1.502 (3) to 1.536 (3) Å.

Comment

Usually dipotassium hydrogenphosphate crystallizes from an aqueous solution in three forms depending on temperature (Galecki, 1964). It crystallizes as a hexahydrate (K₂HPO₄·6H₂O) below 287 K, as a trihydrate (K₂HPO₄·3H₂O) in the temperature range 287–322 K, and as an anhydrite (K₂HPO₄) above 322 K. Only the crystal structure of the trihydrate salt has been determined previously (Baran, Lis & Ratajczak, 1989). In this paper the structure of the anhydrous salt and the isomorphous K₅Na(HPO₄)₃ salt are reported.

The crystal of K₂HPO₄ consists of three crystallographically independent HPO₄²⁻ anions and K⁺ cations. The crystallographically independent HPO₄²⁻ anions are held together by O11—H11···O33 and O31—H31···O23 hydrogen bonds. These chains are joined by symmetry-related O24—H24···O21ⁱ hydrogen bonds to form infinite chains running parallel to the *c* axis. The crystal structure of K₂HPO₄ and the numbering scheme are shown in Fig. 1, views of the structure of K₅Na(HPO₄)₃ are presented in Figs. 2 and 3, and data for the hydrogen bonds for both crystals are summarized in Table 5.

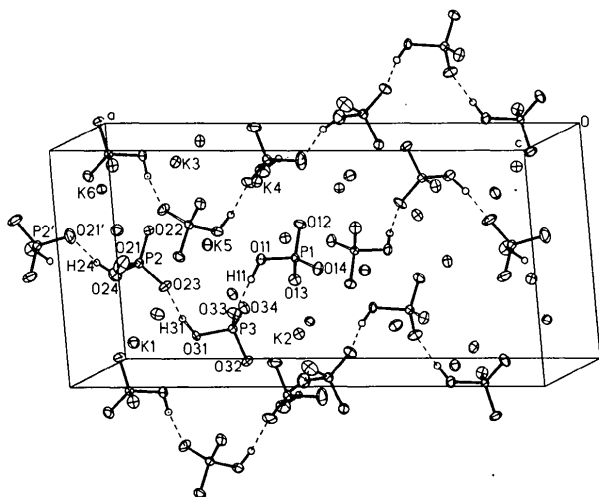


Fig. 1. The crystal structure and numbering scheme of K₂HPO₄.

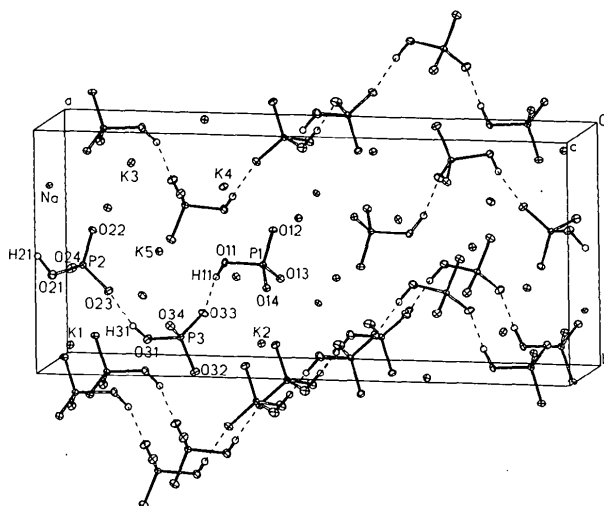


Fig. 2. The packing arrangement in the crystal of $K_5Na(HPO_4)_3$ viewed approximately along c .

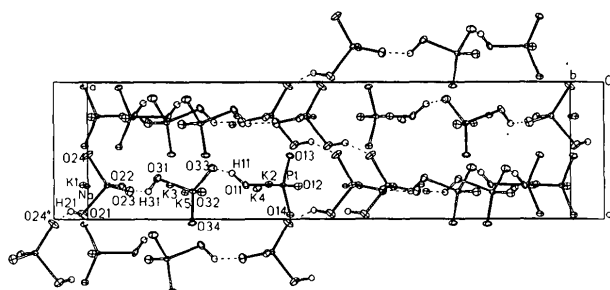


Fig. 3. The crystal structure of $K_5Na(HPO_4)_3$ viewed approximately along b .

Differences between the structures are visible in the localization of the hydroxyl group at the P2 atom. In the K_2HPO_4 crystal, the H atom is bonded to O24, while in the $K_5Na(HPO_4)_3$ crystal the respective H atom is bonded to O21. Consequently, in the latter crystal the helical chains are formed by $O21-H21 \cdots O24^{ii}$ hydrogen bonds. The P, K and Na atoms alternate in planes perpendicular to the c axis at approximately $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The K^+ cations are surrounded by different numbers of O atoms (from six to eleven). In the K_2HPO_4 crystal, the shortest $K \cdots O$ distances are observed for the K6 cation, which in $K_5Na(HPO_4)_3$ is replaced by the Na^+ cation. Both have slightly distorted octahedral environments. The remaining K^+ cations have a different number of neighbours (from eight to eleven) which form rather irregular polyhedrons. In both crystals the P—O(H) bonds are longer than the P—O(terminal) bonds. The values of the O—P—O angles that involve the P—O(H) bond are smaller than the ideal tetrahedral angle; the values of the O—P—O angles that do not involve the P—O(H) bond are larger than the ideal tetrahedral angle. The small and systematic shortening of the P—O bond lengths in the

K_2HPO_4 crystal is probably the effect of thermal vibrations.

Experimental

K_2HPO_4

Crystal data

$M_r = 174.18$
Orthorhombic
 $Pna2_1$
 $a = 22.535 (15) \text{ \AA}$
 $b = 10.322 (5) \text{ \AA}$
 $c = 5.923 (3) \text{ \AA}$
 $V = 1377.7 (14) \text{ \AA}^3$
 $Z = 12$
 $D_x = 2.519 (3) \text{ Mg m}^{-3}$
 $D_m = 2.504 \text{ Mg m}^{-3}$
 D_m measured by flotation in $CHCl_3/CCl_4$ mixture

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$
Cell parameters from 15 reflections
 $\theta = 11-14^\circ$
 $\mu = 2.3 \text{ mm}^{-1}$
 $T = 300 (1) \text{ K}$
Irregularly shape
 $0.5 \times 0.3 \times 0.3 \text{ mm}$
Colourless

Data collection

Syntex $P2_1$ diffractometer
 $\omega/2\theta$ scans
Absorption correction:
DIFABS (Walker & Stuart, 1983)
 $T_{\min} = 0.85$, $T_{\max} = 1.05$
4815 measured reflections
2950 independent reflections
2166 observed reflections
 $[F > 6.0\sigma(F)]$

$R_{\text{int}} = 0.0244$

$\theta_{\text{max}} = 35^\circ$

$h = -36 \rightarrow 36$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 9$

2 standard reflections monitored every 50 reflections
intensity variation: 6%

Refinement

Refinement on F

$R = 0.0320$

$wR = 0.0290$

$S = 2.08$

2166 reflections

201 parameters

All H-atom parameters refined

Calculated weights

$$w = 1/\sigma^2(F_o)$$

$(\Delta/\sigma)_{\text{max}} = 0.12$

$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

$K_5Na(HPO_4)_3$

Crystal data (at 298 K in square brackets)

$M_r = 506.43$

Orthorhombic

$Pna2_1$

$a = 22.402 (15)$

[22.498 (9)] \AA

$b = 9.979 (5)$ [9.996 (5)] \AA

$c = 5.822 (3)$ [5.858 (2)] \AA

$V = 1301.5 (13)$

[1317.4 (10)] \AA^3

$Z = 4$

$D_x = 2.584 (3)$

[2.553 (3)] Mg m^{-3}

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10-15^\circ$

$\mu = 2.1 \text{ mm}^{-1}$

$T = 100 (1)$ [298 (1)] K

Irregularly shape

$0.2 \times 0.1 \times 0.1 \text{ mm}$

Colourless

Data collection

Kuma KM-4 automated
four-circle κ -axis diffrac-
tometer

$\omega/2\theta$ scans

Absorption correction:

DIFABS (Walker & Stu-
art, 1983)

$T_{\min} = 0.94$, $T_{\max} = 1.04$

3225 measured reflections

3145 independent reflections

2335 observed reflections

$[I > 3\sigma(I)]$

Refinement

Refinement on F^2

$R = 0.0256$

$wR = 0.0298$

$S = 1.07$

2286 reflections

201 parameters

All H-atom parameters
refined

Calculated weights

$$w = 1/[\sigma^2(F_o) + 0.00017F_o^2]$$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for K₂HPO₄

	$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$		
	x	y	z
P1	0.59381 (4)	0.54499 (9)	0.7486 (4)
P2	0.92500 (5)	0.56748 (9)	0.7576 (4)
P3	0.74427 (5)	0.84955 (9)	0.7896 (3)
O11	0.66533 (11)	0.5495 (3)	0.7431 (8)
O12	0.57822 (13)	0.4028 (3)	0.7536 (9)
O13	0.57239 (18)	0.6129 (4)	0.5369 (7)
O14	0.57393 (18)	0.6167 (5)	0.9581 (7)
O21	0.97935 (17)	0.5911 (5)	0.8994 (8)
O22	0.90108 (13)	0.4323 (3)	0.7821 (9)
O23	0.87842 (14)	0.6701 (3)	0.7953 (9)
O24	0.94533 (17)	0.5853 (4)	0.5014 (7)
O31	0.81227 (13)	0.8689 (3)	0.7119 (7)
O32	0.71811 (13)	0.9841 (3)	0.7856 (7)
O33	0.71583 (16)	0.7626 (3)	0.6126 (6)
O34	0.74408 (15)	0.7870 (3)	1.0188 (6)
K1	0.94999 (4)	0.90187 (8)	3/4
K2	0.59868 (4)	0.86597 (9)	0.7395 (4)
K3	0.82825 (4)	0.13691 (8)	0.7453 (3)
K4	0.66394 (4)	0.22474 (9)	0.7796 (4)
K5	0.78228 (4)	0.49409 (9)	0.7933 (3)
K6	0.98734 (4)	0.25243 (8)	0.7399 (4)
H11	0.685 (2)	0.622 (3)	0.671 (8)
H24	0.980 (2)	0.530 (5)	0.493 (12)
H31	0.843 (2)	0.803 (5)	0.710 (14)

Table 2. Selected geometric parameters (\AA , $^\circ$) for K₂HPO₄

P1—O11	1.613 (3)	P2—O23	1.508 (3)
P1—O12	1.509 (3)	P2—O24	1.596 (5)
P1—O13	1.515 (4)	P3—O31	1.612 (3)
P1—O14	1.513 (4)	P3—O32	1.509 (3)
P2—O21	1.505 (4)	P3—O33	1.522 (4)
P2—O22	1.502 (3)	P3—O34	1.503 (4)
O11—P1—O12	105.1 (2)	O22—P2—O23	112.9 (3)
O11—P1—O13	106.8 (2)	O22—P2—O24	107.6 (3)

$R_{\text{int}} = 0.0259$

$\theta_{\text{max}} = 35^\circ$

$h = -1 \rightarrow 36$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 9$

3 standard reflections

monitored every 100

reflections

intensity variation: 2%

$(\Delta/\sigma)_{\text{max}} = 0.17$

$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Table*

for *X-ray Crystallogra-*

phy (1974, Vol. IV, Table

2.2B)

O11—P1—O14	107.3 (3)	O23—P2—O24	105.1 (3)
O12—P1—O13	113.1 (3)	O31—P3—O32	104.7 (2)
O12—P1—O14	113.0 (3)	O31—P3—O33	106.1 (2)
O13—P1—O14	111.0 (3)	O31—P3—O34	108.3 (2)
O21—P2—O22	112.9 (3)	O32—P3—O33	111.6 (2)
O21—P2—O23	111.7 (3)	O32—P3—O34	114.1 (2)
O21—P2—O24	106.2 (3)	O33—P3—O34	111.6 (2)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for K₅Na(HPO₄)₃ at 100 K

	$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$		
	x	y	z
P1	0.58750 (3)	0.55130 (7)	0.7512 (3)
P2	0.92531 (3)	0.57079 (7)	0.7492 (3)
P3	0.74120 (4)	0.85633 (8)	0.7984 (3)
O11	0.65946 (9)	0.5460 (3)	0.7496 (7)
O12	0.56731 (10)	0.4058 (3)	0.7568 (6)
O13	0.56805 (15)	0.6252 (4)	0.5354 (5)
O14	0.56843 (14)	0.6281 (4)	0.9677 (5)
O21	0.97065 (15)	0.5941 (4)	0.9619 (6)
O22	0.90553 (9)	0.4258 (3)	0.7575 (7)
O23	0.87537 (11)	0.6705 (3)	0.7928 (6)
O24	0.95955 (16)	0.6043 (4)	0.5301 (6)
O31	0.80858 (11)	0.8764 (3)	0.7010 (5)
O32	0.71499 (11)	0.9962 (3)	0.8044 (6)
O33	0.70869 (13)	0.7680 (3)	0.6248 (6)
O34	0.74659 (13)	0.7890 (3)	1.0305 (5)
K1	0.95035 (3)	0.90155 (6)	3/4
K2	0.59255 (3)	0.87856 (6)	0.7462 (3)
K3	0.83271 (3)	0.14825 (6)	0.7471 (3)
K4	0.65788 (3)	0.23223 (6)	0.7734 (3)
K5	0.77984 (3)	0.50195 (7)	0.8032 (3)
Na	0.98594 (5)	0.24682 (11)	0.7554 (4)
H11	0.681 (3)	0.613 (5)	0.661 (11)
H21	0.999 (5)	0.522 (9)	0.939 (19)
H31	0.830 (4)	0.815 (8)	0.799 (15)

Table 4. Selected geometric parameters (\AA , $^\circ$) for K₅Na(HPO₄)₃ at 100 K

P1—O11	1.613 (2)	P2—O23	1.518 (2)
P1—O12	1.521 (2)	P2—O24	1.526 (4)
P1—O13	1.521 (3)	P3—O31	1.625 (3)
P1—O14	1.536 (3)	P3—O32	1.515 (3)
P2—O21	1.618 (4)	P3—O33	1.526 (3)
P2—O22	1.513 (2)	P3—O34	1.514 (3)
O11—P1—O12	105.4 (2)	O22—P2—O23	113.9 (2)
O11—P1—O13	107.3 (2)	O22—P2—O24	112.6 (2)
O11—P1—O14	107.4 (2)	O23—P2—O24	111.5 (2)
O12—P1—O13	113.3 (2)	O31—P3—O32	104.7 (2)
O12—P1—O14	112.1 (2)	O31—P3—O33	106.5 (2)
O13—P1—O14	110.9 (2)	O31—P3—O34	107.0 (2)
O21—P2—O22	107.3 (2)	O32—P3—O33	111.3 (2)
O21—P2—O23	103.9 (2)	O32—P3—O34	114.8 (2)
O21—P2—O24	107.0 (2)	O33—P3—O34	111.9 (2)

Table 5. The geometry of the hydrogen bonds in K₂HPO₄ and K₅Na(HPO₄)₃ (\AA , $^\circ$)

D	H	A	D...A	H...A	D—H...A
K ₂ HPO ₄					
O11	H11	O33	2.594(4)	1.64(4)	165(4)
O24	H24	O21 ⁱ	2.562(6)	1.64(5)	156(6)
O31	H31	O23	2.584(4)	1.67(5)	156(6)
K ₅ Na(HPO ₄) ₃					
O11	H11	O33	2.579(4)	1.68(5)	152(5)
O21	H21	O24 ⁱⁱ	2.554(5)	1.65(10)	153(9)
O31	H31	O23	2.597(3)	1.76(8)	143(7)

Symmetry codes: (i) $2 - x, 1 - y, z - \frac{1}{2}$; (ii) $2 - x, 1 - y, \frac{1}{2} + z$.

Colorless crystals of the title compounds were of commercial-grade material (Merck). They are hygroscopic and were held in a capillary. Oscillation and Weissenberg photographs, as well as preliminary diffractometer data collection suggested the isomorphism of the crystals. The structure of $K_5Na(HPO_4)_3$ was solved by direct methods and a satisfactory solution was obtained in the non-centrosymmetric space group $Pna2_1$. The refinement for K_2HPO_4 was started by using the coordinates for the heavy atoms of $K_5Na(HPO_4)_3$. In both structures the H atoms were found from difference maps and refined with constraints ($O-H = 0.97 \text{ \AA}$). *SHELX76* (Sheldrick, 1976) was used for the refinements.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71731 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1064]

References

- Baran, J., Lis, T. & Ratajczak, H. (1989). *J. Mol. Struct.* **195**, 159–174.
 Galecki, J. (1964). *Preparatyka nieorganiczna*, p. 578. Warszawa: Wydawnictwo Naukowo-Techniczne. (In polish.)
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1994). **C50**, 487–488

LiGaSi₂O₆

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Abstract

The structure of gallium lithium metasilicate, $LiGaSi_2O_6$, has been determined from diffractometer data. The structure is similar to that of spodumene ($LiAlSi_2O_6$).

Comment

The structure of the title compound is isostructural with $LiAlSi_2O_6$ and $LiFeSi_2O_6$ (Clark, Appleman & Papike, 1969), $LiScSi_2O_6$ (Hawthorne & Grundy, 1977) and $LiInSi_2O_6$ (Grotepass, Behruzi & Hahn, 1983). This structure ($C2/c$) takes the high-temperature form of $LiFeSi_2O_6$ and $LiCrSi_2O_6$, which transform to the low-temperature form ($P2_1/c$)

at 228 and 343 K, respectively (Behruzi, Hahn, Pre-witt & Baldwin, 1984).

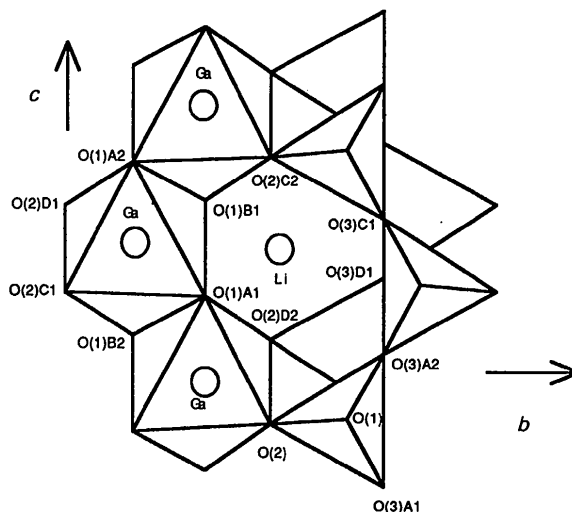


Fig. 1. a^* -axis projection of $LiGaSi_2O_6$. Atom nomenclature follows that used by Clark, Appleman & Papike (1969).

Experimental

The title compound was prepared according to the procedure described by Ohashi, Osawa & Sato (1989).

Crystal data

$LiGaSi_2O_6$

$M_r = 228.83$

Monoclinic

$C2/c$

$a = 9.561 (1) \text{ \AA}$

$b = 8.569 (1) \text{ \AA}$

$c = 5.268 (1) \text{ \AA}$

$\beta = 110.244 (3)^\circ$

$V = 404.90 (5) \text{ \AA}^3$

$Z = 4$

$D_x = 3.75 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 22 reflections

$\theta = 33-37^\circ$

$\mu = 7.29 \text{ mm}^{-1}$

$T = 298 \text{ K}$

$0.20 \times 0.15 \times 0.11 \text{ mm}$

Colourless

Data collection

Enraf-Nonius CAD-4

diffractometer

ω -2 θ scans

Absorption correction:

by integration from crystal shape

$T_{\min} = 0.371$, $T_{\max} = 0.501$

1309 measured reflections

1309 independent reflections

1268 observed reflections

$[I > 1.5\sigma(I)]$

$\theta_{\max} = 40^\circ$

$h = 0 \rightarrow 17$

$k = 0 \rightarrow 15$

$l = -9 \rightarrow 9$

3 standard reflections

monitored every 100

reflections for orientation and every 240 min for intensity

intensity variation: -0.8%

Refinement

Refinement on F

$R = 0.017$

Extinction correction:

isotropic secondary