

- MEZ, H. C. & DONOHUE, J. (1969). *Z. Kristallogr.* **130**, 376–387.
- NAQVI, R. R. & WHEATLEY, P. J. (1970). *J. Chem. Soc. (A)*, pp. 2053–2058.
- OMEL'CHENKO, YU. A., KONDRASHEV, YU. D., GINZBURG, S. L. & NEIGAUZ, M. G. (1973). *J. Struct. Chem.*, **14**, 533–535 (574–576 in original).
- ORVILLE-THOMAS, W. J. (1966). *The Structure of Small Molecules*, pp. 44–50, 83–89. London: Elsevier.
- OTTERSON, T. (1973a). *Acta Chem. Scand.* **27**, 797–813.
- OTTERSON, T. (1973b). *Acta Chem. Scand.* **27**, 835–845.
- PAOLONI, L., GRAMACCIONI, P. & VACIAGO, A. (1966). *Theor. Chim. Acta*, **5**, 102–111.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. pp. 232–240. Ithaca: Cornell Univ. Press.
- RØ, G. & SØRUM, H. (1972). *Acta Cryst.* **B28**, 991–998.
- SABELLI, C., TANGOCCI, P. & ZANAZZI, P. F. (1969). *Acta Cryst.* **B25**, 2231–2236.
- SABELLI, C. & ZANAZZI, P. F. (1972). *Acta Cryst.* **B28**, 1173–1177.
- SABESAN, M. N. & VENKATESAN, K. (1971). *Acta Cryst.* **B27**, 986–993.
- SASAKI, T., KANEMATSU, K. & OCHIAI, S. (1972). *Tetrahedron Lett.* pp. 1885–1886.
- SCHILLING, J. W. & NORDMAN, C. E. (1972). *Acta Cryst.* **B28**, 2177–2182.
- SECCOMBE, R. C. & KENNARD, C. H. L. (1973). *J. Chem. Soc. Perkin II*, pp. 1–3, 4–6, 9–11, 11–14.
- SECCOMBE, R. C., TILLACK, J. V. & KENNARD, C. H. L. (1973). *J. Chem. Soc. Perkin II*, pp. 6–8.
- SHARMA, B. D. & MCCONNELL, J. F. (1965). *Acta Cryst.* **19**, 797–806.
- SIM, G. A. & SUTTON, L. E. (1973). (Editors). *Molecular Structure by Diffraction Methods*, Vol. I, Ch. 2, pp. 67, 73, 84. London: The Chemical Society.
- SINHA, U. C. (1970). *Acta Cryst.* **B26**, 889–895.
- SLETTEN, J., SLETTEN, E. & JENSEN, L. H. (1968). *Acta Cryst.* **B24**, 1692–1698.
- STALS, J. (1970). *Rev. Pure Appl. Chem.* **20**, 1–20.
- STREITWEISER, A. (1961). *Molecular Orbital Theory*, pp. 165–172. New York: John Wiley.
- TAKUSAGAWA, F., HIGUCHI, T., SHIMADA, A., TAMURA, C. & SASADA, Y. (1974). *Bull. Chem. Soc. Japan*, **47**, 1409–1413.
- TUCKER, P. A., HOEKSTRA, A., TEN CATE, J. M. & VOS, A. (1975). *Acta Cryst.* **B31**, 733–737.
- VINCENT, A. T. & WHEATLEY, P. J. (1972a). *J. Chem. Soc. Perkin II*, pp. 687–690.
- VINCENT, A. T. & WHEATLEY, P. J. (1972b). *J. Chem. Soc. Perkin II*, pp. 1567–1571.
- WATSON, D. G., SWEET, R. M. & MARSH, R. E. (1965). *Acta Cryst.* **19**, 573–580.
- WETHERINGTON, J. B., HOLMES, K. D. & MONCRIEF, J. W. (1974). *Acta Cryst.* **B30**, 246–249.
- WHEATLEY, P. J. (1954). *Acta Cryst.* **7**, 68–72.
- WHEATLEY, P. J. (1955). *Acta Cryst.* **8**, 224–226.

Acta Cryst. (1976). **B32**, 3224

The Crystal Structure of Trisguanidinium Hydrogen Pyrophosphate

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The structure of $[\text{C}(\text{NH}_2)_3]_3\text{HP}_2\text{O}_7$ has been determined from microdensitometer data. The space group is $P2_12_12_1$ with $a=9.29$ (2), $b=17.01$ (2), $c=9.47$ (2) Å, $Z=4$. The guanidinium C–N bonds are all within 3σ of the usual 1.33 Å. The P–O–P bridge is symmetrical with P–O bonds of 1.62 Å; the angle is 128.2 (4)°. The remaining P–O lengths vary from 1.478 (8) to 1.550 (7) Å. There is a short O–H...O hydrogen bond [2.47 (1) Å] linking pyrophosphate groups into infinite chains. Eighteen of the nineteen H atoms in each formula unit are involved in the hydrogen bonding.

Introduction

The structural study of the title compound was undertaken as part of an investigation into systems containing multiple hydrogen bonds to oxygen (the ratio of H:O is almost 3:1 in this case). Guanidinium compounds are especially useful in this respect since they invariably form five or six hydrogen bonds per unit charge (Adams & Small, 1976; Adams & Pritchard, 1976).

Experimental

The sample was prepared by addition of guanidinium carbonate to pyrophosphoric acid, followed by slow evaporation. Small, colourless, needle-shaped crystals

formed which were examined by oscillation and Weissenberg photographs. Symmetry and systematic absences gave the space group as $P2_12_12_1$ and high- θ reflexions were used to obtain the cell parameters (Table 1). Equi-inclination intensities were collected for the $0kl-5kl$ and $h0l$ levels (for a crystal $0.6 \times 0.08 \times 0.06$ mm) and these film packs were subsequently scanned on an Optronics P1000 microdensitometer by the SRC Microdensitometer Service at the Atlas Computer Laboratory.

Table 1. *Crystal data*

Space group $P2_12_12_1$; $a=9.29$ (2), $b=17.01$ (2), $c=9.47$ (2) Å (Cu $K\alpha$, $\lambda=1.5418$ Å), $Z=4$; $d_o=1.54$, $d_c=1.57$ g cm $^{-3}$

Determination of the structure

The intensities were corrected for absorption [$\mu(\text{Cu } K\alpha) = 29.5 \text{ cm}^{-1}$], Lorentz and polarization effects. They were put on a common scale with the $h0l$ cross-level data to give 1037 unique reflexions. Spots too weak to be recorded by the microdensitometer were given intensities equal to half the smallest measured intensity on the appropriate film pack. A Wilson plot (including these 'unobserved' reflexions) gave an overall B of 1.8 \AA^2 and E values were obtained for all reflexions.

MULTAN (Germain, Main & Woolfson, 1970) was used to solve the structure with 160 planes with $E > 1.4$. An E map computed with the set of phases with the second highest figure of merit gave a chemically reasonable set of peaks for the pyrophosphate anions. Cycles of refinement of the atomic positions followed by difference syntheses revealed the remaining atoms. Anisotropic refinement (including the scaling factors between the different levels) with unit weights for all reflexions gave a final R of 0.053 for the observed reflexions. An attempt to locate the positions of the H atoms on a difference map was unsuccessful and, when H atoms were placed in positions calculated from the C, N framework of the guanidinium ions, R upon refinement increased slightly and the parameter shifts for the H atoms became very large.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations apart from the structure solution were performed with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Final atomic and thermal parameters are given in Tables 2 and 3.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31959 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates and their standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	0.3968 (3)	0.2722 (1)	0.2362 (2)
P(2)	0.6010 (3)	0.3764 (1)	0.0945 (2)
O(1)	0.5410 (7)	0.2912 (3)	0.1460 (6)
O(2)	0.7398 (7)	0.3549 (3)	0.0151 (6)
O(3)	0.4888 (9)	0.4133 (4)	0.0060 (7)
O(4)	0.6394 (7)	0.4216 (3)	0.2266 (6)
O(5)	0.2738 (7)	0.2656 (3)	0.1263 (6)
O(6)	0.4254 (8)	0.1946 (3)	0.3038 (5)
O(7)	0.3629 (9)	0.3406 (3)	0.3330 (6)
C(1)	0.9266 (12)	0.5533 (5)	0.1146 (8)
N(1)	0.8891 (11)	0.5139 (4)	-0.0017 (7)
N(2)	0.8766 (10)	0.5286 (4)	0.2388 (7)
N(3)	1.0061 (12)	0.6184 (4)	0.1043 (4)
C(2)	0.6857 (14)	0.0602 (4)	0.1823 (9)
N(4)	0.7249 (11)	0.1323 (4)	0.1323 (9)
N(5)	0.5751 (11)	0.0541 (4)	0.2699 (8)
N(6)	0.7625 (13)	-0.0019 (5)	0.1459 (10)
C(3)	-0.0406 (13)	0.3217 (5)	0.3476 (9)
N(7)	-0.0114 (11)	0.3283 (5)	0.2077 (7)
N(8)	0.0775 (11)	0.3119 (4)	0.4312 (8)
N(9)	-0.1710 (10)	0.3265 (5)	0.4005 (9)

Table 3. Temperature factors, U_{ij} , and their standard deviations for the 'heavy' atoms ($\times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	13 (2)	22 (1)	22 (1)	1 (1)	0 (1)	-2 (1)
P(2)	16 (2)	26 (1)	22 (1)	0 (1)	0 (1)	-2 (1)
O(1)	28 (6)	26 (2)	35 (3)	-0 (3)	15 (3)	0 (2)
O(2)	13 (5)	47 (3)	47 (3)	-9 (3)	20 (3)	-19 (3)
O(3)	27 (5)	61 (4)	56 (4)	1 (4)	-21 (4)	24 (3)
O(4)	19 (6)	45 (3)	35 (3)	-11 (3)	2 (3)	-14 (2)
O(5)	13 (5)	35 (3)	38 (3)	4 (3)	-10 (3)	-1 (2)
O(6)	36 (6)	35 (3)	32 (2)	2 (3)	-5 (3)	6 (2)
O(7)	50 (7)	32 (3)	33 (3)	-4 (3)	35 (3)	-13 (2)
C(1)	28 (8)	39 (4)	30 (4)	3 (5)	2 (5)	5 (3)
N(1)	40 (7)	64 (4)	29 (3)	7 (6)	1 (5)	3 (3)
N(2)	33 (7)	49 (4)	29 (3)	11 (5)	11 (4)	4 (3)
N(3)	90 (9)	35 (4)	55 (5)	-17 (5)	16 (6)	2 (4)
C(2)	36 (9)	24 (4)	44 (5)	-4 (5)	8 (5)	4 (4)
N(4)	49 (8)	28 (3)	58 (5)	-7 (4)	9 (5)	14 (3)
N(5)	34 (8)	39 (4)	44 (4)	-12 (4)	15 (5)	1 (3)
N(6)	66 (8)	32 (3)	69 (6)	7 (4)	17 (6)	3 (4)
C(3)	9 (7)	33 (4)	40 (4)	4 (5)	-3 (4)	9 (4)
N(7)	42 (7)	62 (5)	29 (4)	6 (6)	12 (4)	3 (4)
N(8)	25 (7)	53 (4)	41 (4)	1 (5)	-3 (4)	3 (3)
N(9)	13 (6)	65 (5)	52 (5)	-17 (5)	15 (5)	-8 (5)

Description and discussion of the structure

Bond lengths and angles are given in Table 4, details of hydrogen bonding in Table 5 and least-squares planes through the guanidinium ions in Table 6. The guanidinium ions¹ are planar within experimental error and the C-N bonds, although varying somewhat, are all within 3σ of the usual 1.33 \AA found in other guanidinium salts (Adams & Small, 1976). The monohydrogen pyrophosphate anion has a wide range of P-O lengths, but if the P-O-P bridge [$1.621 (8), 1.626 (6) \text{ \AA}$] is omitted the range is much reduced. The largest two values remaining [$1.550 (7), 1.536 (8) \text{ \AA}$] involve the O atoms between which there is a short intermolecular hydrogen bond. The $\text{HP}_2\text{O}_7^{3-}$ anion is almost identical with that found in $\text{K}_3\text{HP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (Dumas, Galigné & Falgouettes, 1973), except that in the latter case,

Table 4. Bond lengths and angles

P(1)-O(1)	1.621 (8) \AA	P(1)-O(1)-P(2)	128.2 (4)°
P(1)-O(5)	1.550 (7)	O(1)-P(1)-O(5)	105.6 (3)
P(1)-O(6)	1.492 (6)	O(1)-P(1)-O(6)	104.8 (4)
P(1)-O(7)	1.514 (7)	O(1)-P(1)-O(7)	109.7 (4)
P(2)-O(1)	1.626 (6)	O(5)-P(1)-O(6)	110.8 (4)
P(2)-O(2)	1.536 (8)	O(5)-P(1)-O(7)	108.1 (4)
P(2)-O(3)	1.478 (8)	O(6)-P(1)-O(7)	117.2 (3)
P(2)-O(4)	1.512 (7)	O(1)-P(2)-O(2)	102.8 (3)
C(1)-N(1)	1.34 (1)	O(1)-P(2)-O(3)	107.9 (4)
C(1)-N(2)	1.33 (1)	O(1)-P(2)-O(4)	106.5 (3)
C(1)-N(3)	1.33 (1)	O(2)-P(2)-O(3)	114.5 (4)
C(2)-N(4)	1.36 (1)	O(2)-P(2)-O(4)	109.2 (4)
C(2)-N(5)	1.32 (1)	O(3)-P(2)-O(4)	114.8 (4)
C(2)-N(6)	1.32 (1)	N(1)-C(1)-N(2)	118.6 (9)
C(3)-N(7)	1.36 (1)	N(1)-C(1)-N(3)	120.0 (8)
C(3)-N(8)	1.36 (1)	N(2)-C(1)-N(3)	121.3 (8)
C(3)-N(9)	1.31 (1)	N(4)-C(2)-N(5)	119.7 (9)
		N(4)-C(2)-N(6)	118.9 (10)
		N(5)-C(2)-N(6)	121.3 (8)
		N(7)-C(3)-N(8)	114.7 (10)
		N(7)-C(3)-N(9)	123.4 (10)
		N(8)-C(3)-N(9)	121.8 (8)

where there is a similar short hydrogen bond (2.49 Å), the P–O distance to one of the O atoms is significantly longer than to the other [1.574 (3), 1.521 (3) Å] and the H atom was found to be attached to the O with the longer bond. For the title compound, the similarity in the two P–O distances would seem to indicate either that the bond is truly symmetrical or that the H atom is disordered between two positions either side of the hydrogen-bond centre (Speakman, 1972).

Table 5. *Hydrogen-bonding geometry* (Å)

Symmetry code

(i)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	(v)	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
(ii)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	(vi)	$\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$
(iii)	$1\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$	(vii)	$-1+x$	y	z
(iv)	$1\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$	(viii)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$

O(2)···O(5 ⁱ)	2.47 (1)	N(5)···O(6)	2.78 (1)
N(1)···O(2 ⁱⁱ)	3.04 (1)	N(6)···O(3 ⁱ)	2.96 (1)
N(1)···O(4 ⁱⁱⁱ)	2.81 (1)	N(6)···O(7 ^v)	2.93 (1)
N(2)···O(3 ^{iv})	2.99 (1)	N(7)···O(2 ^{vi})	2.98 (1)
N(2)···O(4 ^v)	2.86 (1)	N(7)···O(5)	2.96 (1)
N(3)···O(7 ^{vi})	2.93 (1)	N(8)···O(7)	2.85 (1)
N(4)···O(3 ⁱ)	2.89 (1)	N(8)···O(6 ⁱⁱ)	2.88 (1)
N(4)···O(5 ⁱ)	3.04 (1)	N(9)···O(4 ⁱⁱⁱ)	2.90 (1)
N(5)···O(4 ^v)	3.01 (1)	N(9)···O(6 ⁱⁱⁱ)	2.96 (1)

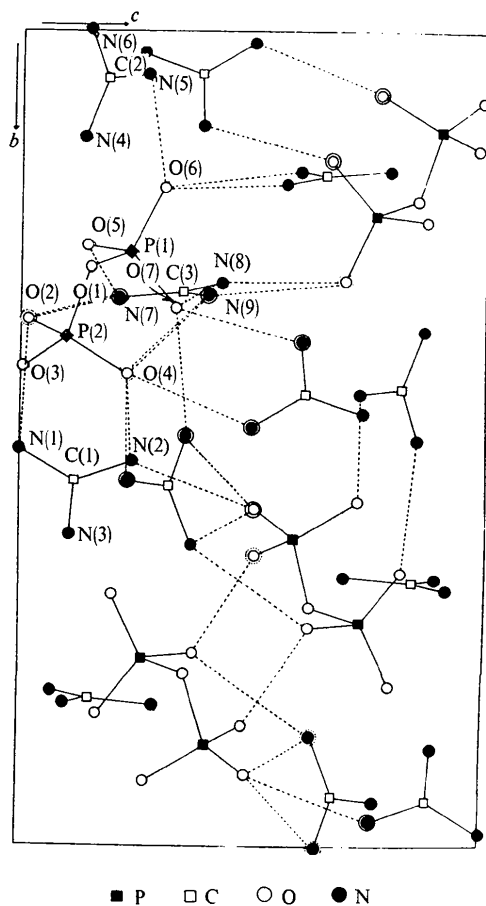


Fig. 1. Projection of the structure down *a*. A large circle represents an atom translated a above the cell shown. A large broken circle represents an a translation below the cell.

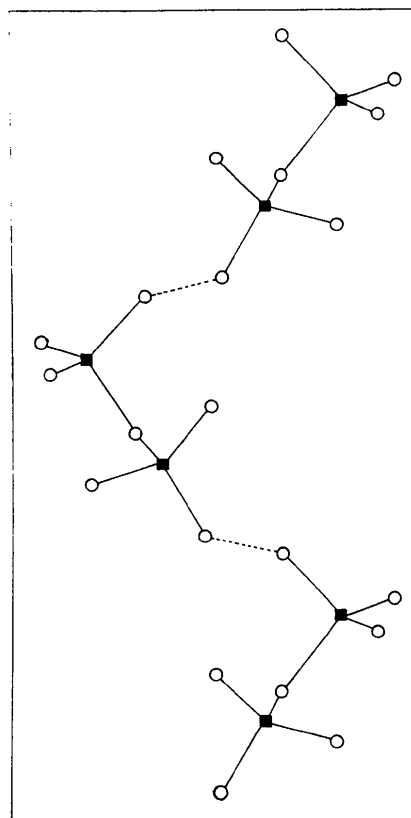


Fig. 2. Projection of the HP_2O_3^- groups onto (010) showing the short hydrogen bonds linking the anions into infinite chains.

Table 6. *Deviations of atoms from the least-squares planes* (Å)

(a) Plane through C(1), N(1), N(2), N(3)	
	$-7.62951x + 9.53762y - 0.97869z = -1.88607$
	C(1) -0.018 N(2) 0.006
	N(1) 0.006 N(3) 0.006
(b) Plane through C(2), N(4), N(5), N(6)	
	$5.61729x + 2.32467y + 7.43411z = 5.35872$
	C(2) -0.012 N(5) 0.004
	N(4) 0.004 N(6) 0.004
(c) Plane through C(3), N(7), N(8), N(9)	
	$0.87691x + 16.85815y + 0.88604z = 5.70506$
	C(3) -0.010 N(8) 0.003
	N(7) 0.003 N(9) 0.003

The structure (Fig. 1) consists of a three-dimensional hydrogen-bonded network in which 18 of the 19 H atoms are used. The pyrophosphate ions are linked into chains (Fig. 2) by the short O(2)···O(5ⁱ) hydrogen bonds, again in analogous fashion to $\text{K}_2\text{HP}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$. These chains are held together by the extensive hydrogen bonding of the guanidinium ions, it being the rule rather than the exception that each O atom accepts

three hydrogen bonds [indeed O(4) accepts four such bonds]. The bridging O(1) is anomalous in not accepting any hydrogen bonds.

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References

- ADAMS, J. M. & PRITCHARD, R. G. (1976). *Acta Cryst.* **B32**, 2438–2440.
ADAMS, J. M. & SMALL, R. W. H. (1976). *Acta Cryst.* **B32**, 832–835.

- DUMAS, Y., GALIGNÉ, J. L. & FALGUEIRETTES, J. (1973). *Acta Cryst.* **B29**, 1623–1630.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
SPEAKMAN, J. C. (1972). In *Chemical Crystallography*, edited by J. M. ROBERTSON. London: Butterworth.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Update of April 1974. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Structure Cristalline de la Phase β -KYb₃F₁₀

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Potassium ytterbium fluoride β -KYb₃F₁₀ is hexagonal. The unit cell, with $a = 8.067$ (2), $c = 13.203$ (4) Å, contains four formula units and the space group is $P6_3mc$. The crystal structure has been solved from single-crystal diffractometer data by Patterson and Fourier syntheses and refined by a least-squares method with anisotropic temperature factors. The final R value is 0.032 for 789 independent observed reflexions ($R_w = 0.041$). The Yb atoms are surrounded by quadratic antiprisms of F atoms, and three antiprisms share two of their edges to form planar (Yb₃F₁₈)⁹⁻ groups. These groups are three-dimensionally linked, but they form four planes which stack, perpendicular to c , in the sequence $ABA'B'$. The two species of K atoms are surrounded by 15 and 16 F atoms respectively. Bindings between antiprisms and polyhedra are discussed as well as analogies between the structures of KY₃F₁₀, KYb₃F₁₀ and fluorite.

Introduction

Lors de l'établissement du diagramme d'équilibre du système KF–YbF₃, Labeau, Aléonard, Védrine, Boutonnet & Cousseins (1974) ont mis en évidence l'existence d'un composé KYb₃F₁₀, dont les variétés α et γ sont isotypes de KY₃F₁₀ étudié par Pierce & Hong (1973) [maille cubique de constante $a = 11,431$ (6) Å, groupe spatial $Fm\bar{3}m$, $Z = 8$], mais dont la variété β , formée à 796°C et stable jusqu'à 952°C, présente un type structural nouveau. Le composé β -KYb₃F₁₀ cristallise avec une maille hexagonale de constantes $a = 8,067$ (2), $c = 13,203$ (4) Å renfermant quatre unités formulaires. Les extinctions observées: $hh2hl$ n'existent qu'avec $l = 2n$, permettaient soit les trois groupes spatiaux hexagonaux $P6_3mc$, $P\bar{6}2c$ et $P6_3/mmc$, soit les deux groupes spatiaux trigonaux $P3|c$ et $P\bar{3}1c$.

L'étude structurale montrera que la structure de β -KYb₃F₁₀ se décrit dans le groupe hexagonal $P6_3mc$.

Conditions expérimentales

Le cristal choisi, de forme polyédrique, a été érodé jusqu'à l'obtention d'une sphère de 0,174 mm de diamètre.

Les intensités diffractées ont été mesurées à l'aide d'un diffractomètre automatique Philips PW 1100 utilisant la longueur d'onde de l'argent, avec monochromateur de graphite. Le domaine angulaire exploré s'étendait jusqu'à 30° (θ). Toutes les raies hkl de la sphère d'Ewald ont été mesurées en balayage ω -2 θ dans un domaine $\Delta\omega = 1,20 + 0,15 \text{ tg } \theta^\circ$, à la vitesse de 0,02° s⁻¹. Le temps de mesure du fond continu, de part et d'autre de ce domaine, a été adapté à l'intensité de la réflexion et n'ont été retenues que les intensités telles que $I_{\text{pic}} - 2\sqrt{I_{\text{pic}}} > I_{\text{fond continu}}$.

Ainsi ont été mesurées 14 597 réflexions. Après correction du fond continu et du facteur de Lorentz-polarisation, leur classement en fonction de θ croissant indiquait des intensités pratiquement identiques pour les raies hhl et hhl d'une part, hkl et hkl d'autre part. Ce qui permettait de trancher en faveur des groupes spatiaux hexagonaux. Après élimination des raies nulles, il restait 842 réflexions indépendantes: à chacune d'elles a été attribuée la moyenne des intensités des réflexions équivalentes.

La valeur du coefficient d'absorption linéaire de KYb₃F₁₀ est $\mu = 191,8 \text{ cm}^{-1}$ à la longueur d'onde $\lambda(\text{Ag K}\alpha)$. Le facteur de transmission pour un échantillon sphérique de $\mu R = 1,668$ variant de 23% de sa