References

Brun, G. & Dumail, M. (1971). *C. R. Acad. Sci. Sér. C*, **272**, 1866–1869.
Catti, M. (1979). *Acta Cryst.* **B35**, 1041–1046.
Durand, J., Loukili, M., Tijani, N., Rafiq, M. & Cot, L. (1988). *Eur. J. Solid State Inorg. Chem.* **25**, 297–303.
Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.
Loopstra, B. O. (1958). *JENER Rep.* No. 15.
Loub, J. & Kratochvil, B. (1987). *Chem. Listy*, **81**, 337–356.
Marcos, M. D., Gómez-Romero, P., Amorós, P., Sapiña, F., Beltrán-Porter, D., Navarro, R., Rillo, C. & Lera, F. (1990). *J. Appl. Phys.* **67**, 5998–6000.
Sapiña, F., Gómez-Romero, P., Marcos, M. D., Amorós, P., Ibáñez, R., Beltrán, D., Navarro, R., Rillo, C. & Lera, F. (1989). *Eur. J. Solid State Inorg. Chem.* **26**, 603–617.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Weakley, T. J. R. (1979). *Acta Cryst.* **B35**, 42–45.

Acta Cryst. (1991). C**47**, 1155–1158

Structure of Sodium 2-Keto-D-gluconate Monohydrate (Sodium D-*arabino*-2-Hexulosonate Monohydrate)

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(*Received* 8 *July* 1990; *accepted* 18 *September* 1990)

Abstract. $Na(C_6H_9O_7).H_2O$, $M_r = 234{\cdot}13$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}269\,(4)$, $b = 8{\cdot}692\,(1)$, $c = 14{\cdot}251\,(2)$ Å, $V = 900{\cdot}4\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}72$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}710730$ Å, $\mu = 1{\cdot}88$ cm^{-1}, $F(000) = 488$, $T = 293$ K, final $R = 0{\cdot}034$ for 2045 reflections [$I > 2\sigma(I)$]. The sugar adopts the β-pyranose form. The sodium ion is surrounded by six O atoms originating from two molecules of 2-keto-D-gluconic acid and a water molecule. The compound forms infinite chains along a twofold screw axis parallel to **a**. One of the hydroxyl groups bridges between two sodium ions. The pyranose ketogluconic acid acts on one side as a tridentate ligand *via* O(11), O(61) and O(51), and as a bidentate ligand on the other side *via* O(41) and O(51). All available OH hydrogens participate in hydrogen bonding, further stabilizing the crystal lattice.

Introduction. As a part of a research program to examine the metal-ion-promoted reactions of 5-keto-D-gluconic and 2-keto-D-gluconic acid, for which compound-selective chemo- and biocatalytic preparative methods have recently become available (Smits, Kuster, van der Wiele & van der Baan, 1986), several complexes with monovalent cations have been prepared.

Crystals of the sodium, potassium, caesium and silver salts of 2-keto-D-gluconic acid have been obtained.

The formation of chelate ring systems in calcium 2-keto-D-gluconate trihydrate has been established crystallographically by Mazid, Palmer & Balchin (1976). The different overall stoichiometry resulting from the use of monovalent cations justifies the determination of the crystal structure of the sodium salt.

Experimental. A sample of sodium 2-keto-D-gluconate was supplied by AKZO Research BV (Arnhem, The Netherlands). The potassium, caesium and silver complexes were obtained by removal of sodium from the original sample with the use of acidic Dowex ion-exchange resin, followed by addition of an equivalent amount of the appropriate metal bicarbonate or metal nitrate. Crystalline material was obtained by precipitation from aqueous solution at room temperature by addition of ethanol until the solution became turbid (10 mmol dissolved in 5 ml water, about 4·5 ml ethanol added). A colourless needle of sodium 2-keto-D-gluconate monohydrate, grown from water/ethanol at room temperature, had approximate dimensions 0·25 × 0·3 × 0·6 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell constants from setting angles of 24 reflections, $9 < \theta < 12°$. Corrections for Lorentz and polarization effects. Transmission coefficients 0·97 to 1·02; absorption correction was applied with *DIFABS*

0108-2701/91/061155-04$03.00

Table 1. *Atomic coordinates* [C(6) × 10^4, *others* × 10^5] *and equivalent isotropic thermal parameters* (Å^2, Na × 10^3, *others* × 10^2) *of the non*-H *atoms*

$B_{\rm eq} = (8\pi^2/3)\mathrm{trace}\mathbf{U}$.

	x	y	z	$B_{\rm iso}$
Na	99415 (14)	14487 (11)	50024 (7)	2330 (14)
C(1)	101730 (14)	2463 (11)	71612 (7)	144 (2)
C(2)	118921 (14)	−4550 (11)	66861 (7)	135 (2)
C(3)	133710 (14)	7696 (11)	65300 (7)	136 (3)
C(4)	149186 (14)	1390 (23)	59172 (7)	156 (3)
C(5)	141076 (28)	−4265 (23)	49976 (7)	167 (3)
C(6)	12627 (3)	−1601 (2)	5196 (1)	203 (3)
O(11)	93655 (14)	12808 (11)	66999 (7)	190 (2)
O(12)	97303 (14)	−2347 (11)	79457 (7)	242 (3)
O(21)	126578 (14)	−16588 (11)	71924 (7)	182 (2)
O(31)	140248 (14)	12987 (11)	74148 (7)	197 (2)
O(41)	162184 (14)	13146 (11)	57171 (7)	210 (2)
O(51)	133335 (14)	8710 (11)	45225 (7)	197 (2)
O(61)	112173 (14)	−9460 (11)	57869 (7)	173 (2)
O(W)	88417 (28)	5254 (23)	36025 (7)	338 (4)

Table 2. *Bond lengths* (Å), *bond angles* (°) *involving non*-H *atoms, torsion angles compared with those for calcium 2-keto*-D-*gluconate* (°), *and hydrogen-bond distances* (Å) *and angles* (°)

Na—O(11)	2·460 (1)	C(2)—O(21)	1·388 (2)
Na—O(51)	2·608 (1)	C(2)—O(61)	1·437 (2)
Na—O(61)	2·538 (1)	C(3)—C(4)	1·526 (2)
Na—O(W)	2·294 (1)	C(3)—O(31)	1·424 (2)
Na—O(41$^{\rm i}$)	2·386 (1)	C(4)—C(5)	1·519 (2)
Na—O(51$^{\rm i}$)	2·693 (1)	C(4)—O(41)	1·421 (2)
C(1)—C(2)	1·546 (2)	C(5)—C(6)	1·510 (2)
C(1)—O(11)	1·259 (2)	C(5)—O(51)	1·431 (2)
C(1)—O(12)	1·236 (2)	C(6)—O(61)	1·443 (2)
C(2)—C(3)	1·529 (2)		

O(11)—Na—O(51)	114·05 (4)	C(3)—C(2)—O(21)	108·6 (1)
O(11)—Na—O(61)	65·18 (4)	C(3)—C(2)—O(61)	108·5 (1)
O(11)—Na—O(W)	140·83 (6)	O(21)—C(2)—O(61)	112·1 (1)
O(11)—Na—O(41$^{\rm i}$)	122·50 (5)	C(2)—C(3)—C(4)	110·6 (1)
O(11)—Na—O(51$^{\rm i}$)	74·34 (4)	C(2)—C(3)—O(31)	109·3 (1)
O(51)—Na—O(61)	67·18 (4)	C(4)—C(3)—O(31)	112·1 (1)
O(51)—Na—O(W)	91·96 (5)	C(3)—C(4)—C(5)	108·9 (1)
O(51)—Na—O(41$^{\rm i}$)	71·12 (4)	C(3)—C(4)—O(41)	110·3 (1)
O(51)—Na—O(51$^{\rm i}$)	130·01 (4)	C(5)—C(4)—O(41)	108·5 (1)
O(61)—Na—O(W)	102·92 (6)	C(4)—C(5)—C(6)	109·5 (1)
O(61)—Na—O(41$^{\rm i}$)	135·67 (5)	C(4)—C(5)—O(51)	107·8 (1)
O(61)—Na—O(51$^{\rm i}$)	139·22 (4)	C(6)—C(5)—O(51)	109·9 (1)
O(W)—Na—O(41$^{\rm i}$)	92·69 (6)	C(5)—C(6)—O(61)	110·4 (1)
O(W)—Na—O(51$^{\rm i}$)	111·72 (5)	Na—O(11)—C(1)	118·47 (9)
O(41$^{\rm i}$)—Na—O(51$^{\rm i}$)	64·66 (4)	C(4)—O(41)—Na$^{\rm ii}$	114·43 (9)
C(2)—C(1)—O(11)	115·4 (1)	Na—O(51)—C(5)	113·55 (9)
C(2)—C(1)—O(12)	118·2 (1)	Na—O(51)—Na$^{\rm ii}$	100·25 (4)
O(11)—C(1)—O(12)	126·3 (1)	C(5)—O(51)—Na$^{\rm ii}$	113·09 (9)
C(1)—C(2)—C(3)	110·9 (1)	Na—O(61)—C(2)	105·90 (8)
C(1)—C(2)—O(21)	113·2 (1)	Na—O(61)—C(6)	109·01 (9)
C(1)—C(2)—O(61)	103·4 (1)	C(2)—O(61)—C(6)	113·3 (1)

	Na	Ca*
O(61)—C(2)—C(3)—C(4)	−57·5	−55·6
C(2)—C(3)—C(4)—C(5)	+56·7	+48·6
C(3)—C(4)—C(5)—C(6)	−56·1	−46·3
C(4)—C(5)—C(6)—O(61)	+57·7	+52·1
C(5)—C(6)—O(61)—C(2)	−61·2	−61·3
C(6)—O(61)—C(2)—C(3)	+60·1	+62·0

D—H···A	Angle	D—H	D···A	H···A
O(21)—H(21)···O(12)	101 (2)	0·91 (2)	2·686 (2)	2·36 (2)
O(21)—H(21)···O(11$^{\rm iii}$)	156 (2)	0·91 (2)	2·804 (2)	1·95 (2)
O(31)—H(31)···O(21$^{\rm iv}$)	135 (2)	0·81 (2)	3·046 (2)	2·42 (2)
O(41)—H(41)···O(11$^{\rm v}$)	160 (2)	0·83 (2)	2·683 (2)	1·88 (2)
O(51)—H(51)···O(12$^{\rm vi}$)	164 (2)	0·83 (2)	2·709 (2)	1·90 (2)
O(W)—H(W1)···O(12$^{\rm vii}$)	172 (2)	0·90 (2)	2·772 (2)	1·87 (3)
O(W)—H(W2)···O(31$^{\rm vi}$)	172 (2)	0·87 (2)	2·790 (2)	1·92 (2)

Symmetry code: (i) $x - 0{\cdot}5$, $-y + 0{\cdot}5$, $-z$; (ii) $x + 0{\cdot}5$, $-y + 0{\cdot}5$, $1 - z$; (iii) $2{\cdot}0 - x$, $-0{\cdot}5 + y$, $1{\cdot}5 - z$; (iv) $3{\cdot}0 - x$, $0{\cdot}5 + y$, $1{\cdot}5 - z$; (v) $1{\cdot}0 + x$, y, z; (vi) $2{\cdot}5 - x$, $-y$, $-0{\cdot}5 + z$; (vii) $1{\cdot}5 - x$, $-y$, $-0{\cdot}5 + z$.

* Mazid, Palmer & Balchin (1976).

(Walker & Stuart, 1983). $2{\cdot}0 < \theta < 40°$; h 0 to 13, k 0 to 15, l 0 to 25. Standard reflections $0\bar{4}\bar{3}$, $\bar{2}3\bar{3}$, $\bar{3}2\bar{3}$, intensity variation 7·07%; 3169 measured reflections, 3166 independent, $R_{\rm int} = 0{\cdot}021$, 1121 reflections with $I < 2\sigma(I)$ were classified as unobserved. Direct methods. F used in LS refinement. All H atoms found in difference Fourier maps. Least-squares refinement of positional and non-H anisotropic thermal parameters; isotropic thermal factors of the H atoms coupled to one another, final value 3·1 Å^2. $S = 1{\cdot}696$, $w = 1/\sigma^2(F)$, $R = 0{\cdot}034$, $wR = 0{\cdot}037$; $(\Delta/\sigma)_{\rm max} < 0{\cdot}30$. Max., min. $\Delta\rho$ excursions in final difference synthesis 0·34, −0·26 e Å^{-3}. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Leiden University Computer (IBM 3083); *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1978) and programs written or modified by S. Gorter, R. A. G. de Graaff and E. W. Rutten-Keulemans.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.* Atomic distances and intramolecular bond angles for the non-H atoms are listed in Table 2. An extended and modified version of *ORTEP* (Johnson, 1965) was used for the projection of the asymmetric unit of sodium 2-keto-D-gluconate hydrate. This projection and the atomic labelling are given in Fig. 1.

The ketogluconate ion is in the β-pyranose form and is tridentate towards the sodium ion: the chelate is formed by a carboxylate oxygen O(11), the ring oxygen O(61) and a hydroxyl oxygen O(51). A fourth position is occupied by the coordinating water molecule. Six coordination is completed by two hydroxyl oxygens O(41) and O(51) of a neighbouring molecule, positioned along a twofold screw axis parallel to **a**. Fig. 2(a) shows a part of the resulting chain, with the hydrogen bridges which occur along it. The coordination geometry is distorted, with O—Na—O angles between 64·7 and 140·8°.

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* Lists of H-atom coordinates, atomic distances involving the H atoms, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53598 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An unusual feature of the helical chain is the bridging of a hydroxyl oxygen O(51) between two Na ions. To our knowledge, only one other structure with Na ions bridged by hydroxyl O atoms, orginating from methanol molecules, has been reported (Szeymies, Krebs & Henkel, 1984). The β-pyranose form of the 2-keto-D-gluconate ion is the major species in solution, as has been established with the aid of ^{13}C NMR (Crawford, Andrews, Faubl & Chmurny, 1980). Bond distances and angles are normal.

All available oxygen-bound H atoms are involved in hydrogen bonding (Table 2). An intramolecular bond connects the non-coordinating carboxylate oxygen O(12) and the non-coordinating hydroxy group O(21)—H(21) (see Fig. 2*a*). The torsion angle around C(1) and C(2) shows that O(21) and O(12) are in eclipsed positions [O(12)—C(1)—C(2)—O(21) = 4·8 (2)°]. One of the intermolecular hydrogen bonds occurs along the screw axis between the coordinating carboxylate oxygen O(11) and O(41) of a neighbouring molecule (Fig. 2*a*). Other intermolecular hydrogen bonds connect the different chains of molecules (Fig. 2*b*).

The torsion angles within the pyranose ring differ from those in calcium 2-keto-D-gluconate (Mazid, Palmer & Balchin, 1976), in accordance with the different modes of coordination in the two structures (Table 2). Values in the sodium compound are in the range calculated for a hypothetical ideal unstrained ring (55·8–61·7°; Kim & Jeffrey, 1967). The crystal packing and coordination of Na^+ can therefore be considered as extremely favourable.

The Guinier–de Wolff X-ray powder pattern of potassium 2-keto-D-gluconate is identical to that of the sodium salt, indicating X-ray isomorphism. Despite the larger cation [Na—O 2·4–2·7 Å, K—O generally 2·6–3·2 Å (Jeffrey & Fasiska, 1972)], the tridentate chelate apparently is large and flexible enough to incorporate a potassium ion. The caesium salt seemed to be similar to the sodium and potassium salts in its morphology and IR spectrum, but the X-ray powder pattern is inconclusive. Complete isomorphism of the caesium salt may not be possible because of the much larger atomic radius, Cs—O being about 3·0–3·7 Å (Templeton & Templeton, 1978).

The IR spectrum of the silver compound is identical to that of the potassium salt. The X-ray powder patterns of these are, however, completely different and probably reflect other requirements of the silver ion for its coordination environment.

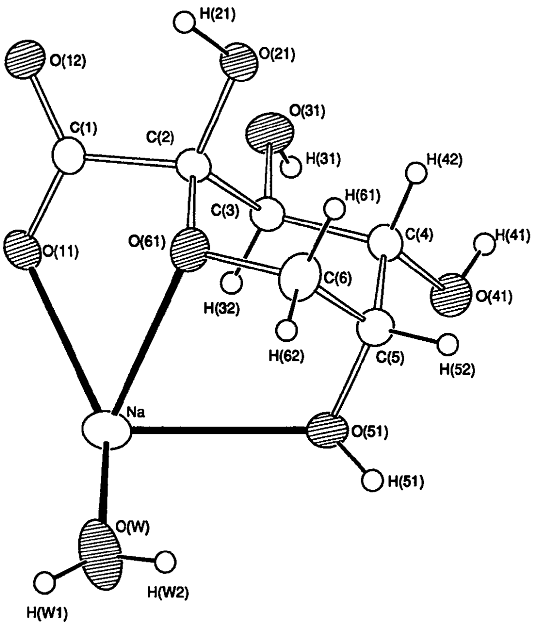

Fig. 1. *ORTEP* (Johnson, 1965) projection with 50% probability contours (non-H atoms) and atomic labelling of the asymmetric unit of sodium 2-ketogluconate monohydrate.

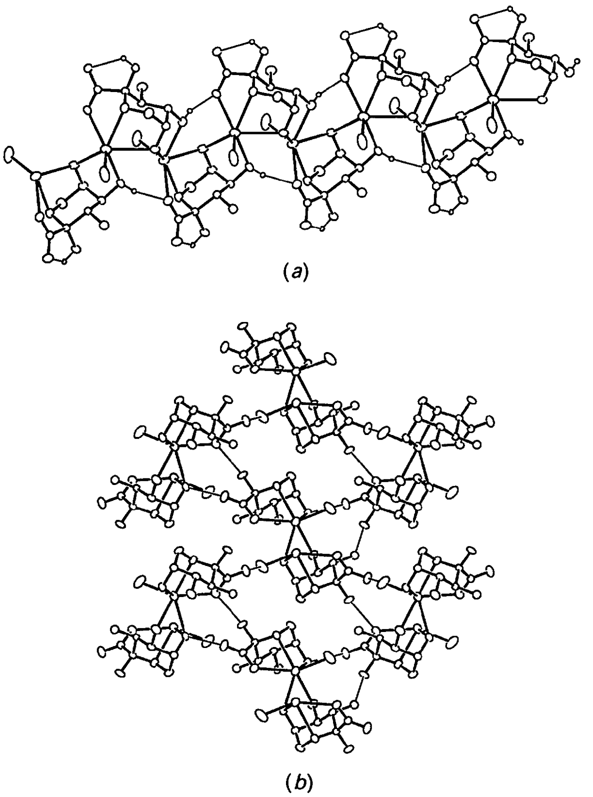

Fig. 2 (*a*) Molecules of sodium 2-ketogluconate monohydrate in a chain along the *a* axis. Two of the hydrogen bridges which occur along this axis are also shown, and the H atoms which are not involved in these hydrogen bridges are omitted for clarity. (*b*) A projection down the *a* axis showing the hydrogen bridges which connect adjacent chains. H atoms are omitted for clarity.

This investigation was carried out under the auspices of the Dutch National Carbohydrate Program (IOP-K). We thank AKZO for financial support.

References

Crawford, T. C., Andrews, G. C., Faubl, H. & Chmurny, G. N. (1980). *J. Am. Chem. Soc.* **102**, 2220–2225.

Jeffrey, G. A. & Fasiska, E. J. (1972). *Carbohydr. Res.* **21**, 187–199.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kim, S. H. & Jeffrey, G. A. (1967). *Acta Cryst.* **22**, 537–545.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mazid, M. A., Palmer, R. A. & Balchin, A. A. (1976). *Acta Cryst.* **B32**, 885–890.

Smits, P. C. C., Kuster, B. F. M., van der Wiele, K. & van der Baan, H. S. (1986). *Carbohydr. Res.* **153**, 227–235.

Szeymies, D., Krebs, B. & Henkel, G. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 804–805.

Templeton, L. K. & Templeton, D. H. (1978). *Acta Cryst.* **A34**, 368–371.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1991). C**47**, 1158–1160

Hydrolyse Lente du Cycle Oxadiazole: Structure d'un Complexe Binucléaire du $\mathrm{Cu^{II}}$ avec le Pyridoyl-2′ Pyridinecarbohydrazide

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(*Reçu le* 1 *décembre* 1989, *accepté le* 15 *octobre* 1990)

Abstract. Triaqua-[μ-(2-pyridoyl)pyridinecarbohydrazido-N,O,N',O',N'']-dicopper(II) dinitrate dihydrate, $[\mathrm{Cu_2(C_{12}H_8N_4O_2)(H_2O)_3](NO_3)_2.2H_2O}$, $M_r = 581$, monoclinic, $P2_1/c$, $a = 7{\cdot}977\,(5)$, $b = 15{\cdot}044\,(6)$, $c = 16{\cdot}629\,(5)$ Å, $\beta = 97{\cdot}98\,(8)^\circ$, $V = 1976{\cdot}26$ Å^3, $Z = 4$, $D_x = 1{\cdot}95\ \mathrm{g\ cm^{-3}}$, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 22{\cdot}02\ \mathrm{cm^{-1}}$, $F(000) = 1148$, $R = 0{\cdot}042$ for 2763 unique reflexions. The structure characterizes a binuclear complex of the (2′-pyridoyl)pyridinecarbohydrazide ligand obtained by opening the oxadiazole ring in 2,5-bis(2-pyridyl)-1,3,4-oxadiazole.

Introduction. Au cours de nos investigations relatives aux couplages magnétiques dans les complexes polynucléaires bâtis à partir de ligands polyazotés (Abraham, Capon, Nowogrocki, Sueur & Brémard, 1985; Abraham, Brémard, Lagrenée, Mernari & Sueur, 1986) nous avons mis en évidence le comportement versatile du bis(pyridyl-2)-2,5 oxadiazole-1,3,4 (bpo) dont la complexation conduit à la fois à des espèces mononucléaires (Wignacourt, Sueur & Lagrenée, 1990) ou polynucléaires (Lagrenée, Sueur & Wignacourt, 1988) suivant les conditions imposées.

Dans tous les cas, l'augmentation des temps de contact conduit à l'apparition d'une nouvelle espèce cristalline. Le présent travail est consacré à la caractérisation structurale de cette espèce et permet d'envisager le mécanisme de sa formation.

Partie expérimentale. Le ligand bpo est synthétisé suivant un mode opératoire décrit dans la littérature (Sharma & Tandon, 1984). 0,18 g (8×10^{-4} mol) de bpo dissout dans 10 ml de méthanol est additionné à 40 ml d'une solution aqueuse contenant 0,72 g ($3{,}2 \times 10^{-3}$ mol) de $\mathrm{Cu(NO_3)_2.2{,}5H_2O}$. La moisson cristalline apparue après quelques heures de contact est séparée par filtration. Le filtrat, abandonné une semaine à température ambiante laisse déposer une faible quantité de cristaux d'aspect différent de ceux isolés dans la moisson principale. Les cristaux sont collectés, ils se présentent sous forme d'aiguilles vertes utilisables pour l'étude radiocristallographique.

Le cristal retenu a pour dimensions 0,048 × 0,0115 × 0,008 mm, limité respectivement par des faces du type (100), (010) et (001). Paramètres de maille cristalline à partir de 25 réflexions ($5 < \theta < 20^\circ$). 3138 réflexions [$I > 3\sigma(I)$], collectées sur un diffractomètre à 4 cercles Phillips PW1100, balayage ω–2θ, ont été corrigées des effets de Lorentz–polarisation et de l'absorption, les facteurs de correction varient de 0,7644 à 0,9218. $(\sin\theta)/\lambda \le 0{,}5946$ Å^{-1}. 3 réflexions de référence mesurées toutes les 80 réflexions sans variation d'intensité. 2763 réflexions indépendantes ($0 \le h \le 9$; $0 \le k \le 17$; $-19 \le l \le 19$) sont traitées

0108-2701/91/061158-03\$03.00