Fig. 2. Molecular dimensions (distances in Å, angles in °) for the DBTTF cation (a) and the $Cu_2Br_6^{2-}$ anion (b). Additional angles: Br(22)—Cu(10)—Br(20) 173·26 (3), Br(21)—Cu(10)—Br(20') 174·77 (4)°.

References

COHEN, M. J., COLEMAN, L. B., GARITO, A. F. & HEEGER, A. J. (1974). *Phys. Rev. B*, **10**, 1298–1307.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

EMGE, T. J., WIYGUL, F. M., CHAPPELL, J. S., BLOCH, A. N., FERRAIS, J. P., COWAN, D. O. & KISTENMACHER, T. J. (1982). *Mol. Cryst. Liq. Cryst.* **87**, 137–161.

FURUSAKI, A. (1979). *Acta Cryst.* A**35**, 220–224.

HONDA, M., KATAYAMA, C., TANAKA, J. & TANAKA, M. (1985). *Acta Cryst.* C**41**, 197–199.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

KATAYAMA, C., SAKABE, N. & SAKABE, K. (1972). *Acta Cryst.* A**28**, S207.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (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.

MOTHERWELL, S. (1976). *PLUTO78*. Program for drawing molecular and crystal structures. Univ. of Cambridge, England.

SHIBAEVA, R. P., ROZENBERG, L. P., ALDOSHINA, M. Z., LUBOVSKAYA, R. N. & KHIDEKEL, M. L. (1979). *Zh. Strukt. Khim.* **20**, 485–490.

SHIBAEVA, R. P., ROZENBERG, L. P. & LUBOVSKAYA, R. N. (1980). *Kristallografiya*, **25**, 507–513.

Structures of α- and β-Copper(II) Pipecolinate Dihydrate, Diaquabis-(2-piperidinecarboxylato)copper(II), [Cu(C6H10NO2)2(H2O)2]

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Abstract. $M_r = 356 \cdot 0$. α form: $P2_1/c$, $a = 11 \cdot 723$ (4), $b = 5 \cdot 749$ (3), $c = 11 \cdot 174$ (3) Å, $\beta = 104 \cdot 11$ (3)°, $V = 730 \cdot 4$ (5) Å^3, $Z = 2$, $D_x = 1 \cdot 62$, $D_m = 1 \cdot 60$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 15 \cdot 9$ cm^{-1}, $F(000) = 374$, $wR = 0 \cdot 032$ for 1413 observed $[I > 3\sigma(I)]$ reflections. β form: $P2_1/n$, $a = 5 \cdot 875$ (2), $b = 18 \cdot 618$ (5), $c = 7 \cdot 014$ (2) Å, $\beta = 106 \cdot 40$ (3)°, $V = 736 \cdot 0$ (4) Å^3, $Z = 2$, $D_x = 1 \cdot 61$, $D_m = 1 \cdot 60$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 15 \cdot 7$ cm^{-1}, $F(000) = 374$, $wR = 0 \cdot 031$ for 1370 observed reflections; for the standard space group $P2_1/c$: $a = 5 \cdot 875$ (2), $b = 18 \cdot 618$ (5), $c = 10 \cdot 342$ (3) Å, $\beta = 139 \cdot 42$ (3)°. The Cu atoms have distorted octahedral coordination, the pipecolinate radical acting as a bidentate ligand, bonded through the equatorial imino N and the carboxylate O, which are *cis* to each other. The two water molecules occupy the axial positions, at greater distance from the Cu. Distances and angles in the two forms are similar, but there are significant variances. The copper—water bond length is greater in the β form (2·611 *vs* 2·401 Å), and the torsion angles in the piperidine ring are larger in the α form. The difference in the structures lies in the tilt angles of the molecules relative to the symmetry elements of the space group.

Introduction. In a recent paper, Albanese & Haendler (1983) reported on the magnetic and electronic characterization of Cu complexes of a series of aminocarboxylic acids. Structures of only a few of these have been determined, and additional research is desirable in view of the potential pharmacological importance of Cu complexes (Sorenson, 1978). One of the complexes studied was copper(II) pipecolinate dihydrate, for which distorted octahedral configuration was predicted. This complex has been isolated in two polymorphic forms, differing in molecular packing, and arbitrarily designated as α and β.

Experimental. Single crystals of the α form were obtained by slow evaporation of a solution produced by addition of freshly prepared copper(II) hydroxide (Brauer, 1965) to a hot solution of a slight excess of pipecolinic acid, followed by quick filtration. The light-blue crystals were too small for data collection, but a satisfactory crystal was isolated from a mixture with the darker-blue β form, the result of evaporation of a 2:1 mixture of aqueous pipecolinic acid and copper(II) acetate monohydrate solutions. The X-ray powder diffraction patterns are different; analyses are consistent with those reported. Density of a bulk sample was determined pycnometrically in toluene.

The crystal of the α form was a light-blue rectangular parallelepiped, $0 \cdot 20 \times 0 \cdot 30 \times 0 \cdot 60$ mm; that of the β form was a dark-blue flat plate-like parallelepiped, $0 \cdot 42 \times 0 \cdot 35 \times 0 \cdot 08$ mm. Nicolet four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 15 reflections (to $\theta = 15°$ [10° for β form]) for measurement of lattice parameters at 293 (1) K. Empirical absorption correction, using ψ scan with 5 [4] reflections, range $= 11 \cdot 4° < 2\theta < 30 \cdot 4°$ [11·5, 28·3°], transmission factors $0 \cdot 75 - 1 \cdot 00$ [0·70, 1·00]. Max. $\sin\theta/\lambda = 0 \cdot 650$ [0·650] Å^{-1}. h 0 to 15 [0 to 7], k 0 to 7 [0 to 24], l −14 to 14 [−9 to 9]. 6 [6] check reflections, frequency 300 [200], no indication of deterioration or alignment changes. No extinction correction. 1684 [1692] unique reflections measured, 271 [322] unobserved with $I \leq 3\sigma(I)$. Structures solved by *DIRDIF* (Beurskens & Noordik, 1971; Gould, van den Hark & Beurskens, 1975; van den Hark, Prick & Beurskens, 1976) for the non-hydrogen atoms. Least-squares refinement on F, initially with block-diagonal approximation and isotropic to anisotropic thermal parameters. H atoms located on difference Fourier maps and by superposition of Dreiding models on scaled unit-cell projections and refined by block-diagonal method. Final full-matrix least-squares refinement, with all observed reflections, anomalous dispersion for Cu, and $B = 5 \cdot 0$ Å^2 for H atoms, converged at $R = 0 \cdot 048$ [0·54], $wR = 0 \cdot 032$ [0·031], $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0 \cdot 11$ [0·33], exclusive of H shifts. $S = 0 \cdot 97$ [0·97]. Final difference map showed max. and min. peaks of $0 \cdot 61$ and $-0 \cdot 52$ e Å^{-3} [0·64,

$-0 \cdot 41$ e Å^{-3}]. Error analyses showed no systematic errors as functions of $\sin^2\theta$ or F_o. No significant correlations. Atomic scattering factors for the non-hydrogen atoms were those of Hanson, Herman, Lee & Skillman (1964), and for H those of Stewart, Davidson & Simpson (1965). Correction terms for anomalous dispersion for Cu taken from *International Tables for X-ray Crystallography* (1974). National Research Council of Canada programs (Ahmed, 1973) were used for most computations. *ORXFLS3* (Busing, Martin & Levy, 1971) was used for the full-matrix least-squares calculation and *ORTEP*II (Johnson, 1976) for the thermal-ellipsoid plots.

Discussion. The final positional parameters are given in Table 1,* and principal bond distances and angles in Table 2. The unit cells are shown in projection in Figs. 1 and 2, H atoms being omitted. The Cu atoms have distorted octahedral coordination, the pipecolinate radical acting as a bidentate ligand, bonded through the equatorial imino N and the carboxylate O, which are *cis* to each other. The two water molecules occupy the axial positions, at greater distance from the Cu. This coordination is in contrast to that observed in the anthranilates, where carbonyl O atoms from two different ligands occupy the axial positions (Lange & Haendler, 1975; Boudreau, Boudreau & Haendler, 1983). This combination leads to a polymeric sheet structure and low solubility. The pipecolinates are molecular, highly soluble, and there is some indication of hydrogen bonding. The C—O distances in the carboxylate groups are significantly different, and the ring angles are consistent with sp^2 bonding of O(1) and C(1). The O(1)—Cu—N(1) angles are less than the characteristic 90° associated with square-planar Cu, a consequence of the constraints imposed by the formation of a five-membered chelate ring. The remaining angles are close to tetrahedral.

The Cu atoms lie on centers of symmetry, and the attached ligands are enantiomorphous. The torsion angles of the heterocyclic rings are different, as shown in Table 3. The signs are arbitrary. The ring is flatter in the β form. A thermal-ellipsoid plot of the α form is shown in Fig. 3. That of the β form is similar.

The two modes of molecular packing should correspond to virtually equi-energetic minima and solution enthalpies (Dunitz, 1979). The packing is similar, but the molecules are oriented differently relative to the symmetry elements of the space group. The arrangement adheres to the criteria of Kitaigorodsky (1973) for close packing of centrosymmetric molecules. There is

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indication of hydrogen bonding in the α form between O(1) and O(3) of adjacent molecules, involving the water H atoms. The O(1)$\cdots$O(3) distances are in the range 2·7–2·9 Å and the O(1)–H–O(3) angles are within 12° of being linear. Such proximity is not seen in the β form. A similar hydrogen-bonding network has been observed in diaquabis(pyrazinecarboxylato)-copper(II) (Klein, Majeste, Trefonas & O'Connor, 1982).

Fig. 1. Unit-cell projection of α-copper pipecolinate dihydrate as viewed along [010].

Table 1. Final positional parameters and isotropic thermal parameters

B values are from the final cycle of isotropic refinement.

	x	y	z	$B(\text{Å}^2)$
α Form				
Cu	0·0000	0·0000	0·0000	2·04 (2)
O(1)	−0·0724 (2)	−0·2194 (4)	−0·1347 (2)	2·7 (1)
O(2)	−0·2420 (2)	−0·3071 (5)	−0·2632 (3)	4·6 (2)
O(3)	−0·0105 (3)	0·3080 (6)	−0·1475 (3)	3·4 (1)
N(1)	−0·1693 (3)	0·0563 (5)	0·0039 (3)	2·4 (1)
C(1)	−0·1836 (4)	−0·1941 (7)	−0·1773 (3)	2·8 (2)
C(2)	−0·2387 (3)	0·0037 (10)	−0·1230 (3)	3·6 (2)
C(3)	−0·3698 (3)	−0·0116 (11)	−0·1310 (4)	3·6 (2)
C(4)	−0·4112 (4)	0·2130 (10)	−0·0845 (4)	5·7 (2)
C(5)	−0·3387 (4)	0·2776 (8)	0·0420 (4)	3·8 (2)
C(6)	−0·2076 (4)	0·2754 (8)	0·0495 (4)	3·0 (2)
H(1)	−0·190 (5)	−0·075 (9)	0·038 (5)	
H(2)	−0·230 (4)	0·191 (9)	−0·166 (4)	
H(7)	−0·033 (4)	0·449 (9)	−0·139 (4)	
H(8)	0·014 (6)	0·307 (12)	−0·187 (5)	
H(31)	−0·380 (4)	−0·159 (9)	−0·069 (4)	
H(32)	−0·410 (4)	−0·047 (9)	−0·214 (4)	
H(41)	−0·390 (5)	0·352 (9)	−0·123 (5)	
H(42)	−0·493 (4)	0·198 (9)	−0·080 (4)	
H(51)	−0·362 (5)	0·155 (8)	0·088 (5)	
H(52)	−0·359 (4)	0·430 (8)	0·058 (4)	
H(61)	−0·164 (4)	0·299 (9)	0·119 (4)	
H(62)	−0·190 (4)	0·418 (8)	−0·013 (4)	
β Form*				
Cu	0·5000	0·5000	0·5000	1·97 (3)
O(1)	0·7017 (4)	0·5162 (1)	0·3232 (3)	2·3 (1)
O(2)	0·8097 (5)	0·4667 (2)	0·0770 (4)	3·7 (2)
O(3)	0·1656 (6)	0·5845 (2)	0·2944 (5)	3·4 (2)
N(1)	0·3695 (6)	0·4186 (2)	0·3152 (5)	3·0 (2)
C(1)	0·6957 (7)	0·4656 (2)	0·1994 (5)	2·7 (2)
C(2)	0·5558 (8)	0·3992 (2)	0·2239 (6)	3·6 (3)
C(3)	0·4805 (9)	0·3476 (3)	0·0550 (6)	2·9 (2)
C(4)	0·3616 (10)	0·2832 (2)	0·1086 (7)	3·9 (3)
C(5)	0·1764 (9)	0·3011 (3)	0·2132 (8)	3·9 (3)
C(6)	0·2550 (9)	0·3570 (3)	0·3756 (7)	2·8 (2)
H(1)	0·269 (9)	0·437 (3)	0·188 (8)	
H(2)	0·702 (9)	0·361 (3)	0·352 (7)	
H(7)	0·050 (10)	0·575 (4)	0·273 (10)	
H(8)	0·172 (11)	0·586 (3)	0·181 (8)	
H(31)	0·618 (10)	0·334 (3)	0·008 (7)	
H(32)	0·344 (10)	0·370 (3)	−0·045 (7)	
H(41)	0·305 (10)	0·252 (3)	−0·009 (8)	
H(42)	0·492 (9)	0·252 (3)	0·223 (8)	
H(51)	0·046 (10)	0·312 (3)	0·108 (7)	
H(52)	0·115 (10)	0·263 (3)	0·260 (8)	
H(61)	0·156 (10)	0·372 (3)	0·424 (8)	
H(62)	0·373 (9)	0·331 (3)	0·489 (8)	

* In the non-standard space group $P2_1/n$ the unique equivalent points are x, y, z and $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.
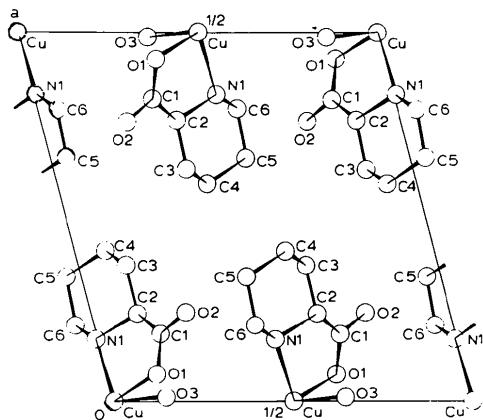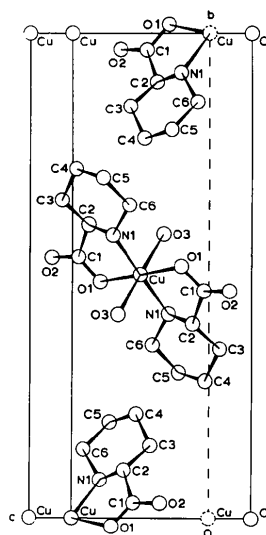

Fig. 2. Unit-cell projection of β-copper pipecolinate dihydrate as viewed in the $a\sin\beta$ direction.

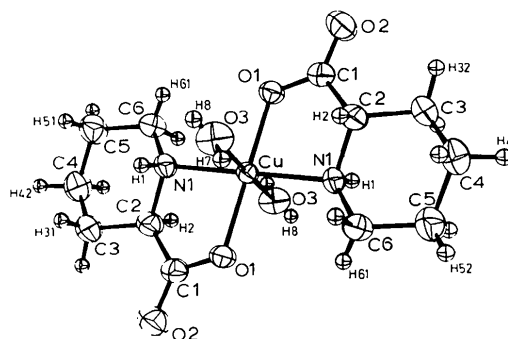
Fig. 3. Thermal-ellipsoid plot of α-copper pipecolinate dihydrate.

Table 2. *Bond distances* (Å) *and angles* (°)

	α	β		α	β
Cu—O(1)	1·989 (2)	1·966 (2)	C(3)—H(31)	1·12 (5)	0·99 (6)
Cu—N(1)	2·022 (3)	2·002 (3)	C(3)—H(32)	0·96 (4)	1·00 (5)
Cu—O(3)	2·401 (3)	2·611 (4)	C(4)—H(41)	0·97 (5)	0·99 (5)
C(1)—O(1)	1·281 (5)	1·275 (4)	C(4)—H(42)	0·97 (5)	1·10 (5)
C(1)—O(2)	1·221 (5)	1·229 (5)	C(5)—H(51)	0·95 (5)	0·92 (5)
C(1)—C(2)	1·507 (6)	1·520 (6)	C(5)—H(52)	0·94 (5)	0·90 (5)
C(2)—N(1)	1·484 (5)	1·460 (6)	C(6)—H(61)	0·83 (5)	0·80 (6)
C(2)—C(3)	1·520 (6)	1·492 (6)	C(6)—H(62)	1·13 (5)	1·02 (5)
C(3)—C(4)	1·516 (8)	1·488 (7)	O(3)—H(7)	0·87 (5)	0·68 (6)
C(4)—C(5)	1·507 (7)	1·511 (8)	O(1)···H(7)*	1·96 (5)	2·43 (6)
C(5)—C(6)	1·518 (7)	1·516 (7)	O(1)···O(3)	2·825 (4)	3·066 (5)
C(6)—N(1)	1·470 (5)	1·451 (6)	O(3)—H(8)	0·60 (5)	0·81 (5)
N(1)—H(1)	0·91 (5)	0·98 (5)	O(1)···H(8)	2·26 (5)	3·45 (6)
C(2)—H(2)	1·19 (5)	1·28 (5)	O(1)···O(3)′	2·837 (4)	—
O(1)—Cu—N(1)	83·1 (1)	84·1 (1)	N(1)—C(6)—C(5)	112·3 (4)	113·0 (4)
O(1)—Cu—O(3)	90·4 (1)	93·0 (1)	C(2)—N(1)—C(6)	111·3 (3)	113·6 (4)
N(1)—Cu—O(3)	90·6 (1)	90·5 (1)	H(7)—O(3)—H(8)	108 (7)	97 (7)
Cu—O(1)—C(1)	114·6 (2)	114·2 (2)	C(1)—C(2)—H(2)	116 (2)	105 (2)
Cu—N(1)—C(2)	105·0 (2)	105·8 (3)	C(6)—N(1)—H(1)	116 (3)	110 (3)
O(1)—C(1) C(2)	115·6 (3)	115·8 (3)	H(31)—C(3)—H(32)	110 (4)	116 (4)
O(2)—C(1)—C(2)	120·3 (4)	120·8 (4)	H(41)—C(4)—H(42)	117 (4)	107 (4)
N(1)—C(2)—C(1)	110·5 (3)	110·2 (4)	H(51)—C(5)—H(52)	118 (4)	98 (5)
N(1)—C(2)—C(3)	112·3 (4)	114·6 (4)	H(61)—C(6)—H(62)	108 (4)	104 (5)
C(2)—C(3)—C(4)	109·5 (4)	111·9 (4)	O(3)—H(7)···O(1)	172·8 (5)	157·1 (7)
C(3)—C(4)—C(5)	112·2 (4)	113·5 (4)	O(3)—H(8)···O(1)	168·1 (8)	—
C(4)—C(5)—C(6)	112·5 (4)	114·1 (4)			

* The dotted line represents a bond between atoms in different molecules.

Table 3. *Torsion angles* (°) (*e.s.d.'s* ~0·4°)

	α	β
N(1)C(2)—C(3)C(4)	56·47	51·03
C(2)C(3)—C(4)C(5)	−52·85	−46·73
C(3)C(4)—C(5)C(6)	51·16	45·14
C(4)C(5)—C(6)N(1)	−51·65	−46·01
C(5)C(6)—N(1)C(2)	54·48	49·49
C(6)N(1)—C(2)C(3)	−57·91	−53·09

References

AHMED, F. R. (1973). *NRC Crystallographic Programs*. National Research Council of Canada, Ottawa.

ALBANESE, N. F. & HAENDLER, H. M. (1983). *Polyhedron*, **2**, 1131–1140.

BEURSKENS, P. T. & NOORDIK, J. H. (1971). *Acta Cryst*. A**27**, 187–188.

BOUDREAU, S. M., BOUDREAU, R. A. & HAENDLER, H. M. (1983). *J. Solid State Chem*. **49**, 379–384.

BRAUER, G. (1965). *Handbook of Preparative Inorganic Chemistry*. Vol. II, p. 1013. New York: Academic Press.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1971). *ORXFLS3*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, p. 321. Ithaca: Cornell Univ. Press.

GOULD, R. O., VAN DEN HARK, TH. E. M. & BEURSKENS, P. T. (1975). *Acta Cryst*. A**31**, 813–817.

HANSON, H. P., HERMAN, F., LEE, J. D. & SKILLMAN, S. (1964). *Acta Cryst*. **17**, 1040–1044.

HARK, TH. E. M. VAN DEN, PRICK, P. & BEURSKENS, P. T. (1976). *Acta Cryst*. A**32**, 816–821.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*, p. 23. New York: Academic Press.

KLEIN, C. L., MAJESTE, R. J., TREFONAS, L. M. & O'CONNOR, C. J. (1982). *Inorg. Chem*. **21**, 1891–1897.

LANGE, B. A. & HAENDLER, H. M. (1975). *J. Solid State Chem*. **15**, 325–332.

SORENSON, J. R. J. (1978). *Prog. Med. Chem*. **15**, 211–260.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys*. **42**, 3175–3187.

Calcium D-Glucarate Tetrahydrate, $Ca^{2+}.C_6H_8O_8^{2-}.4H_2O$: a Redetermination

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Abstract. $M_r = 320·3$, orthorhombic, $P2_12_12_1$, $a = 16·220$ (2), $b = 11·347$ (2), $c = 6·558$ (1) Å, $V = 1207·0$ Å^3, $Z = 4$, $D_x = 1·76$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1·5418$ Å, $\mu = 49·65$ cm^{-1}, $F(000) = 672$, $T = 293$ K, $R = 0·0514$ for 1012 observed reflections. The results have been compared with the original study of Taga & Osaki [*Bull. Chem. Soc. Jpn* (1976), **49**, 1517–1520], and show agreement with improved accuracy. The hydrogen positions have now been determined and a complete description of the hydrogen-bonding scheme is given.

Introduction. It is known that carbohydrates chelate Ca^{2+} ions both in aqueous solution and in the solid state, and interest in this has recently grown because of their important biological implications. The crystal structure of calcium D-glucarate has been reported previously by Taga & Osaki (1976) using film data with a final *R* value of 0·093. The aims of this analysis were to confirm the method of preparation, to refine the atomic parameters further and to determine the positions of the H atoms. Later this information will be used to compare the calcium coordination with that of