

The stereoview presented in Fig. 3 shows a central Cu ion, its coordination complex and the strong hydrogen bonds involving the atoms of the coordination complex.

Considering the hydrogen bonding from the viewpoint of the chlorate oxygen acceptors we observe that O(3) is involved in one strong and two weak bonds; O(4) is involved in two strong bonds; and O(5) is involved in one strong and one bifurcated bond. Thus, each of the inequivalent chlorate oxygens is involved in at least one strong hydrogen bond.

The present study is apparently the first which describes the structure of a tetraaquacopper(II) complex. In this case two additional oxygens from chlorate ions complete a coordination octahedron which is very similar in its dimensions, as shown above, to that formed by six water oxygens in the hexaaquacopper(II) perchlorate structure.

As the analyses above document, the 296 K structure differs but slightly from the 223 K structure and in a manner consistent with the difference in temperature.

In the present investigation the phase commonly crystallizing from aqueous solutions of copper(II) chlorate at room temperature was the tetrahydrate, not the hexahydrate.

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#### References

- BLACKBURN, A. C., GALLUCCI, J. C. & GERKIN, R. E. (1990). *Acta Cryst.* **B46**, 712–716.
- CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* **B38**, 2331–2341.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* **B28**, 3572–3583.
- GALLUCCI, J. C. & GERKIN, R. E. (1989). *Acta Cryst.* **C45**, 1279–1284.
- GALLUCCI, J. C. & GERKIN, R. E. (1990). *Acta Cryst.* **C46**, 350–354.
- HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- JEFFREY, G. A. (1987). *Patterson and Pattersons*, edited by J. P. GLUSKER, B. K. PATTERSON & M. ROSSI, pp. 193–221. Oxford Univ. Press.
- JEFFREY, G. A. & MALUSZYNSKA, H. (1986). *J. Mol. Struct.* **147**, 127–142.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*, Version 5.0. MSC, The Woodlands, Texas, USA.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
- TRUEBLOOD, K. N. (1986). *THMA11*. Univ. of California at Los Angeles, USA.

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## Structure of the $\alpha$ -D-Glucose–Sodium Chloride–Water Complex (2/1/1)

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#### Abstract

$2\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{NaCl} \cdot \text{H}_2\text{O}$ ,  $M_r = 436.8$ , trigonal,  $P3_1$  (No. 144),  $a = 16.836$  (3),  $c = 17.013$  (4) Å,  $V = 4176$  (2) Å<sup>3</sup>,  $Z = 9$ ,  $D_m = 1.56$  (by flotation in  $\text{CHCl}_3/\text{CCl}_4$ ),  $D_x = 1.563$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.9$  cm<sup>-1</sup>,  $F(000) = 2070$ ,  $T = 294$  K,  $R = 0.049$  ( $wR = 0.065$ ) for 3530 unique reflections with  $I > 3\sigma(I)$ . The asymmetric unit has six glucose molecules, three Na<sup>+</sup> ions, three Cl<sup>-</sup> and three water

molecules. The glucose molecules all have chair conformations with the C1–O1 groups axial and the remaining substituents equatorial; the mean C1–O1 bond length [1.388 (9) Å] is less than the mean of the other C–O bonds [1.425 (8) Å]. The Na<sup>+</sup> ions have distorted octahedral coordination [ $\text{Na} \cdots \text{O}$  2.341 (5) to 2.528 (4) Å]; the Cl<sup>-</sup> ions, water and glucose molecules are linked by an extensive network of hydrogen bonds which utilizes all O–H groups. The corresponding complexes of  $\alpha$ -D-glucose monohydrate with sodium bromide and with sodium

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iodide are isomorphous with the sodium chloride complex. A simple procedure is given for checking that automatic diffractometer cell-search routines have not missed a systematically weak set of reflections and produced an incorrect set of cell data.

### Introduction

One of the major uses of X-ray powder diffraction in the Metropolitan Police Forensic Science Laboratory is in drug analysis. Powder diffraction complements other analytical techniques and is used to identify the precise chemical form (salt, free base, acid) of restricted drugs and their excipients in a mixture. In one such recent case, a sample was shown to contain heroin, glucose and sodium chloride. Analysis by X-ray powder diffraction revealed sodium chloride and an unidentified substance as the major components; there was also some heroin hydrochloride, but no trace of glucose or glucose monohydrate. Evidence for compound formation between sucrose and sodium bromide or sodium chloride was established crystallographically many years ago (Beevers & Cochran, 1947) and this prompted us to consider that a similar reaction could have occurred between sodium chloride and glucose or glucose monohydrate. We have previously reported brief details of the  $\alpha$ -D-glucose-sodium chloride-water structure (Ferguson, Kaitner, Connett & Rendle, 1986), and have pointed out the pitfalls associated with less than careful diffractometer studies of this structure. Details of the powder diffraction pattern for the complex have also appeared (Rendle & Connett, 1988). Cho & Honzatko (1990) have recently published an account of this structure but have the wrong cell, Laue symmetry and space group. Full details of the correct structure for this compound are now reported here.

### Experimental

Dry mixtures of glucose monohydrate and sodium chloride in the ratios (1) 67:33, (2) 84:16, (3) 92:8 and (4) 96:4 (w/w) were made up and were found to react fairly readily, caking after a few hours. Powder diffraction photographs of the reaction products of each of these mixtures contained the same diffraction pattern as that of the unidentified substance mentioned above. The best diffractometer-quality crystals of what we eventually showed to be  $2C_6H_{12}O_6 \cdot NaCl \cdot H_2O$  were prepared by slow evaporation of the 84:16 glucose monohydrate/sodium chloride aqueous solution; those from other glucose monohydrate/sodium chloride mixtures were not of the same quality. The purity of the single crystals obtained from these crystallizations was checked by powder diffraction and the only pattern observed was that of the unknown substance.

In the absence of Weissenberg or precession camera facilities we use the following check process to ensure that our 'diffractometer-produced' cell data are correct and that systematically weak reflection sets (which might have been overlooked by automatic cell-search routines) are detected. We double the diffractometer-produced cell lengths and search low-order shells of data for the presence of reflections that could have been missed. For trigonal or hexagonal cells, the process will not necessarily detect a systematic error in the  $a$  (or  $b$ ) axes; one must rotate the diffractometer-produced lattice through  $30^\circ$  [e.g. by applying the transformation (2,1,0; -1,1,0; 0,0,1)] so that what was a diagonal of the diffractometer-produced trigonal cell becomes the new cell edge (and e.g. the 110 reflection of the diffractometer-produced cell becomes the 300 reflection of the larger cell), then search this lattice (which would have three times as many reflections). This was indeed the case with the present structure; the initial diffractometer-produced cell had  $a = b = 9.72 \text{ \AA}$ , but the above process revealed the presence of the true cell with  $a = b = 16.836 \text{ \AA}$ .

Accurate cell dimensions and crystal-orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range  $8 < \theta < 17^\circ$ . An initial survey of a complete sphere of reflections with  $2 < \theta < 10^\circ$  showed that while the weighted reciprocal lattice clearly had  $\bar{3}$  Laue symmetry it had approximate  $\bar{3}m$  symmetry; the  $00l$  reflections were present only if  $l = 3n$ , implying space groups  $P3_1$  or  $P3_2$ . For the data collection a fresh crystal was selected (crystal dimensions  $0.23 \times 0.25 \times 0.50 \text{ mm}$ ) and intensities of reflections with indices  $h - 21$  to  $0$ ,  $k 0$  to  $21$ ,  $l - 21$  to  $0$ , with  $2 < 2\theta < 54^\circ$  were measured;  $\omega$ - $2\theta$  scans,  $\omega$ -scan width  $(0.60 + 0.35 \tan \theta)^\circ$ ; graphite-monochromatized  $Mo K\alpha$  radiation; intensities of three reflections measured every 2 h showed some 20% loss of intensity towards the end of the data collection and a decay correction was applied (correction on  $I$  from 0.98 to 1.20). Data corrected for Lorentz and polarization effects; 6814 reflections were measured, 6274 unique ( $R_{int}$  0.022) and 3530 with  $I > 3\sigma(I)$  were labelled observed.

As noted above an unusual feature in the intensity distribution was noticed in the diffractometer work. One third of the reflections (those with  $h - k = 3n$  or  $h + 2k = 3n$ ) had for the most part very strong intensities, whereas the remainder (although 'observable') were generally weak. This implied that the structure would be largely determined by this special set of one-third the reflections that were strong, with very little of the structure contributing to the two-thirds of the reflections that were weak. From the unit-cell volume it was likely that the asymmetric unit contained six glucose molecules and at least three

sodium chloride and water moieties – a possibility of 81 non-H atoms to locate. To avoid this difficulty and in light of the intensity distribution noted above, we decided to work initially with only the subset of the one-third ‘strong’ reflections. If the ‘weak’ reflections are ignored, the unit cell can be transformed into a smaller one (with one-third the volume of the ‘true’ cell). The ‘small’ cell is obtained from the ‘true’ cell by the transformation  $(\frac{1}{3}, -\frac{1}{3}, 0; \frac{1}{3}, \frac{2}{3}, 0; 0, 0, 1)$  and has cell dimensions  $a = 9.720$  (3),  $c = 17.013$  (4) Å,  $V = 1392$  Å<sup>3</sup>. The  $c$  dimension does not change and the 00 $l$  reflections are still present only if  $l = 3n$ , implying space groups  $P3_1$  or  $P3_2$ .

We chose to work in  $P3_1$  initially. The structure was solved with the aid of *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982); this revealed two glucose molecules, and three other peaks which were initially assigned as sodium, chloride and oxygen (of a water molecule). Subsequent rounds of structure-factor and electron-density map calculations allowed us to distinguish the sodium ion clearly, but the two other sites had different peak heights, both greater than that expected for water, but less than that for chloride ion. Full-matrix refinement with the two water/chlorine sites being allowed for as partially occupied chlorine atoms, went smoothly and converged at  $R = 0.055$  (for 1783 ‘observed’ reflections) with the ‘chlorine’ occupancies 0.82 and 0.64. These values are consistent with the larger peak being  $[\frac{2}{3}(\text{Cl}^-) + \frac{1}{3}(\text{H}_2\text{O})]$  and the smaller peak being  $[\frac{1}{3}(\text{Cl}^-) + \frac{2}{3}(\text{H}_2\text{O})]$ , to give an overall composition in the asymmetric unit of the ‘small’ cell of  $2\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{NaCl} \cdot \text{H}_2\text{O}$ .

We pointed out previously (Ferguson *et al.*, 1986) that with the advantage of hindsight, we could have ‘solved’ this structure (to obtain a set of coordinates which could then be expanded to the correct cell) in an even simpler fashion. If we work in the ‘small’ cell and assume (wrongly) Laue  $3m$  symmetry (the  $R_{\text{int}}$  on averaging ‘equivalent’ reflections was 0.075 and there were several unacceptably bad ‘agreements’), the space group becomes  $P3_121$ . The asymmetric unit now only contains one glucose molecule, one half sodium ion on a special position  $(-x, -x, 0.5)$  and one other site which corresponds to  $0.5(\text{Cl} + \text{H}_2\text{O})$ . When we used *MULTAN82* with the ‘ $P3_121$ ’ data, it produced precisely this structure, which refined to an  $R$  value of 0.055. It was this cell, Laue symmetry and space group that Cho & Honzatko (1990) reported in their analysis.

The unit cell of the ‘small’ cell is the asymmetric unit of the ‘true’ cell and by appropriate mathematical transformations a starting set of coordinates for the ‘true’ cell refinement was obtained. All that we did not know at this stage was which of the ‘chlorine–water’ peaks from the ‘small’ cell were

water and which were chlorine. For one water–chlorine pair we selected water and chlorine sites to crack the pseudo-symmetry problem and determined which of the other two sets of water–chlorine peaks were water and chlorine by appropriate occupancy-factor refinement. As an elegant confirmation of the correctness of our choices, difference maps computed at intermediate stages of the refinement showed maxima in positions consistent with those anticipated for all water and glucose-hydroxyl H atoms. Refinement was by full-matrix least-squares calculations on  $F$ , initially with isotropic and then with anisotropic thermal parameters for the non-H atoms. Before the final rounds of calculations the C–H hydrogen atoms were positioned on geometrical grounds (C–H 0.95 Å) and the hydroxyl hydrogens (both glucose and water) were placed on the line-of-centres between the hydroxyl O atom and the atom to which they were hydrogen bonded (with O–H 0.95 Å); the hydrogens were then included (as riding atoms) in the structure-factor calculations. The final cycle of refinement included 729 variable parameters,  $R = 0.049$ ,  $wR = 0.065$ , goodness-of-fit = 2.06,  $w = 1/(\sigma^2 F_o + 0.0004 F_o^2)$ . Maximum shift/e.s.d. = 0.07; density in final difference map =  $\pm 0.36$  e Å<sup>-3</sup>; there were no chemically significant features. Our choice of space group was by chance the correct one as it leads to the correct absolute configuration for the glucose molecules. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a PDP-11/73 computer using *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983). Atomic coordinates\* and details of molecular geometry are given in Tables 1–3. Fig. 1 shows the hydrogen-bonding environment around a chlorine–water pair and illustrates the numbering scheme. Fig. 2 shows a general view of the glucose coordination about one Na<sup>+</sup> ion. These diagrams were prepared with *ORTEPII* (Johnson, 1976) as implemented in the *NRCVAX* suite of programs (Gabe, Le Page, Charland, Lee & White, 1989).

## Discussion

### Glucose molecules

The six independent glucose molecules in the asymmetric unit all have identical chair conformations with the substituent groups equatorial except

\* A copy of the Wrocław ECM X meeting abstract, lists of structure factors, thermal parameters, calculated hydrogen coordinates, torsion angles and independent views of the six glucose molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53839 (76 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



the orientation of the O3 hydroxyl group, which has one orientation in glucose molecules 1 and 6 and another orientation in molecules 2 to 5 [torsion angles  $Cn2-Cn3-On3-H$   $150^\circ$  ( $n = 1$ ),  $147^\circ$  ( $n = 6$ ), and  $-76$  to  $-77^\circ$  ( $n = 2,3,4,5$ )].

#### Chloride ion and water hydrogen bonding

The three independent chloride and water molecules each take part in four hydrogen bonds. Each chloride ion is hydrogen bonded to two symmetry-related glucose molecules and a water molecule; each water molecule is in turn hydrogen bonded to a pair of symmetry-related glucose molecules and a

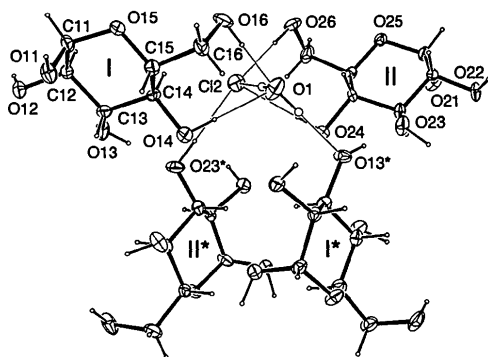


Fig. 1. The hydrogen-bonding environment of water molecule O1 and chloride ion Cl2. The glucose O atoms involved in this hydrogen bonding are numbered; also shown is the complete numbering scheme for glucose molecule 1 [the first digit in this numbering scheme is the molecule number (1 through 6)]. Roman numerals I and II refer to glucose molecules 1 and 2 in Table 1; I\* and II\* refer to molecules at equivalent positions  $y-x, -x, z-\frac{1}{2}$  and  $-y, x-y, z+\frac{1}{2}$  respectively. Ellipsoids for non-H atoms are at the 35% probability level. A pseudotwo-fold axis runs vertically between the water molecule and Cl<sup>-</sup> ion.

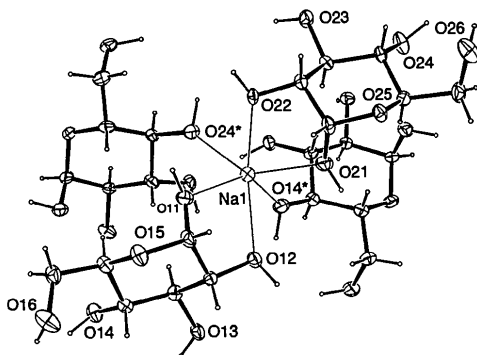


Fig. 2. A view showing the sodium ion coordination for NaI. Referring to the coordinates of Table 1, oxygen atoms O11 to O16 are as given, O21 to O26 are at equivalent position  $x, y, z+1$ , O14\* is at equivalent position  $-y, x-y, z+\frac{1}{2}$  and O24\* is at  $y-x, -x, z+\frac{1}{2}$ . Thermal ellipsoids are at the 35% level.

Table 3. Hydrogen-bond distances (Å)

O1—H1O1...Cl2	3.051 (7)	O33—HO33...Cl3 <sup>m</sup>	3.088 (5)
O1—H2O1...O13 <sup>r</sup>	2.732 (7)	O34—HO34...Cl3	3.162 (5)
O4—H1O4...Cl3	3.034 (4)	O36—HO36...Cl3	2.989 (6)
O4—H2O4...O43 <sup>m</sup>	2.773 (8)	O41—HO41...O66 <sup>m</sup>	2.678 (6)
O6—H1O6...Cl5	3.014 (7)	O42—HO42...O55 <sup>m</sup>	2.841 (6)
O6—H2O6...O63 <sup>m</sup>	2.736 (7)	O43—HO43...O33 <sup>m</sup>	2.730 (7)
O11—HO11...O36	2.614 (8)	O44—HO44...O4	2.921 (7)
O12—HO12...O45 <sup>r</sup>	2.809 (7)	O46—HO46...O4	2.734 (8)
O13—HO13...O23 <sup>m</sup>	2.757 (6)	O51—HO51...O16 <sup>r</sup>	2.681 (6)
O14—HO14...O1	2.901 (7)	O52—HO52...O25 <sup>r</sup>	2.857 (7)
O16—HO16...O1	2.697 (7)	O53—HO53...Cl5 <sup>m</sup>	3.088 (5)
O21—HO21...O46 <sup>r</sup>	2.706 (7)	O54—HO54...Cl5	3.151 (5)
O22—HO22...O35 <sup>m</sup>	2.861 (8)	O56—HO56...Cl5	2.996 (5)
O23—HO23...Cl2 <sup>r</sup>	3.104 (5)	O61—HO61...O26 <sup>m</sup>	2.650 (7)
O24—HO24...Cl2	3.152 (5)	O62—HO62...O15	2.819 (6)
O26—HO26...Cl2	2.992 (5)	O63—HO63...O53 <sup>m</sup>	2.766 (6)
O31—HO31...O56	2.676 (7)	O64—HO64...O6	2.869 (7)
O32—HO32...O65 <sup>r</sup>	2.840 (6)	O66—HO66...O6	2.737 (8)

Symmetry code: (i)  $y-x, -x, z-\frac{1}{2}$ ; (ii)  $-y, x-y-1, z+\frac{1}{2}$ ; (iii)  $-y+1, x-y, z+\frac{1}{2}$ ; (iv)  $-y, x-y, z+\frac{1}{2}$ ; (v)  $-y, x-y, z-\frac{1}{2}$ ; (vi)  $x, y, z-1$ ; (vii)  $-y, x-y-1, z-\frac{1}{2}$ ; (viii)  $y-x+1, -x, z-\frac{1}{2}$ ; (ix)  $x, y, z+1$ ; (x)  $-y+1, x-y, z+\frac{1}{2}$ ; (xi)  $y-x+1, -x+1, z-\frac{1}{2}$ .

chloride ion as shown in Fig. 1 for O1 and Cl2. Every H atom was located in the crystal structure and all O—H hydrogens take part in an extensive hydrogen-bonded network; details are given in Table 3. Mean hydrogen-bond distances are Cl<sup>-</sup>...H—O(glucose) 3.080 (5), Cl<sup>-</sup>...H—O(water) 3.033 (6), and (water)O—H...O(glucose) 2.789 (7) Å.

#### Sodium coordination

The three independent sodium ions all have essentially identical coordination geometries; that for Na1 is shown in Fig. 2. Each sodium is coordinated by six O atoms from four glucose molecules (in symmetry-related pairs) in a distorted octahedral arrangement. The Na—O distances range from 2.341 (5) to 2.528 (4) Å and the O—Na—O angles are in the range 66.3 (2) to 140.5 (2)°.

The corresponding complexes of  $\alpha$ -D-glucose monohydrate with sodium bromide and with sodium iodide are isomorphous with the sodium chloride complex. The cell data [from powder diffraction studies (Rendle, Glazier, Ferguson & Jennings, 1989)] are:  $a = b = 16.4440$  (9),  $c = 17.633$  (1) Å (for the NaBr complex) and  $a = b = 16.5234$  (8),  $c = 17.878$  (1) Å (for the NaI complex).

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#### References

- B. A. FRENZ & ASSOCIATES, INC. (1983). *SDP-Plus Structure Determination Package*. College Station, Texas, USA.
- Beevers, C. A. & Cochran, W. (1947). *Proc. R. Soc. London Ser. A*, **190**, 257–272.
- BROWN, G. M. & LEVY, H. A. (1979). *Acta Cryst.* **B35**, 656–659.
- CHO, Y. & HONZATKO, R. B. (1990). *Acta Cryst.* **C46**, 587–590.
- CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* **B24**, 830–838.

- FERGUSON, G., KAITNER, B., CONNETT, B. E. & RENDLE, D. F. (1986). 10th Eur. Crystallogr. Meet. Collect. Abstr., Wrocław, Poland, Paper 2B-61, p. 204.
- GABE, E. J., LE PAGE, Y., CHARLAND, J.-P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384-387.
- HOUGH, E., NEIDLE, S., ROGERS, D. & TROUGHTON, P. G. H. (1973). *Acta Cryst.* **B29**, 365-367.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- RENDLE, D. F. & CONNETT, B. E. (1988). *J. Forensic Sci. Soc.* **28**, 295-297.
- RENDLE, D. F., GLAZIER, E. J., FERGUSON, G. & JENNINGS, M. C. (1989). Unpublished work.

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## Absolute Optical Chirality of Dirubidium (+)-Tartrate and Dicaesium (+)-Tartrate Crystals

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### Abstract

The crystal structures and absolute optical chiralities of  $\text{Rb}_2[(2R,3R)\text{-C}_4\text{H}_4\text{O}_6]$ , RBT ( $M_r = 319.01$ ) and  $\text{Cs}_2[(2R,3R)\text{-C}_4\text{H}_4\text{O}_6]$ , CST ( $M_r = 413.88$ ) have been determined. For crystals grown from aqueous solutions containing (+)-tartrate ions the specific rotation was observed to be laevo over the visible-wavelength range along the optic axis and the space group was found to be  $P3_221 (D_3^2)$  in both cases. Crystal data at 298 K,  $\text{Cu K}\alpha$ ,  $\lambda = 1.54178 \text{ \AA}$ ; for RBT:  $a = 7.168 (1)$ ,  $c = 13.097 (1) \text{ \AA}$ ,  $V = 582.8 (2) \text{ \AA}^3$ ,  $Z = 3$ ,  $D_x = 2.726$ ,  $D_m = 2.727 (3) \text{ Mg m}^{-3}$ ,  $\mu = 16.61 \text{ mm}^{-1}$ ,  $F(000) = 450$ , final  $R = 0.0281$  and  $wR = 0.0572$  for 804 unique observed reflections; for CST:  $a = 7.432 (2)$ ,  $c = 13.526 (3) \text{ \AA}$ ,  $V = 647.0 (5) \text{ \AA}^3$ ,  $Z = 3$ ,  $D_x = 3.187 \text{ Mg m}^{-3}$ ,  $\mu = 67.56 \text{ mm}^{-1}$ ,  $F(000) = 558$ , final  $R = 0.0348$  and  $wR = 0.0521$  for 837 unique observed reflections. The relationship between optical rotation and structural chirality has been traced by following the rules established earlier for inorganic ionic crystals. It is shown that in the reported structures the intermolecular helical atomic arrangement of highly polarizable atoms (mainly oxygens and cations) rather than the contribution from the individual optically active organic molecules is responsible for optical rotation of the crystals. Special attention is paid to possible hydrogen bonds, both inter- and intramolecular, as they significantly influence the shape of the helices. The refractive indices and rotatory power, calculated from the structural data using a point-dipole polarizability theory, agree with the experimental results and support this point of view. Evidence is found that in concentrated solution RBT molecules also form helical arrangements.

### Introduction

As was shown by Glazer & Stadnicka (1986) the sense and even the magnitude of optical rotatory power can be explained for almost all the inorganic crystals with known absolute structure, as determined by anomalous X-ray scattering and measurements of the optical rotatory dispersion (ORD) carried out on the same crystal. This was demonstrated for low- and high-quartz, berlinite ( $\alpha\text{-AlPO}_4$ ), cinnabar ( $\alpha\text{-HgS}$ ), dicalcium strontium and dicalcium lead propionates,  $\text{Bi}_{12}\text{SiO}_{20}$  and  $\text{Bi}_{12}\text{GeO}_{20}$ , and  $\text{NaClO}_3$  and  $\text{NaBrO}_3$  as well as  $\alpha\text{-LiIO}_3$  (see also Stadnicka, Glazer & Moxon, 1985). An effort was made to explain the 'structural part' of the optical rotatory dispersion for  $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ , which is well known for the anomalous behaviour of its ORD (Stadnicka, Glazer & Koralewski, 1987), and also for  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$  (Stadnicka, Glazer & Koralewski, 1988), which is isostructural to the former and yet shows no  $d-d$  transitions in the cation. This approach also proved successful for  $\text{Bi}_{12}\text{TiO}_{20}$  (Swindells & Leal Gonzalez, 1988), for paratellurite ( $\alpha\text{-TeO}_2$ , Thomas, 1988) and for  $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  (Thomas & Gomes, 1989). In each of these materials (isotropic or uniaxial crystals) the sign of optical rotation was found to be correlated with particular helical features in the structure. Recently the approach has been extended to biaxial inorganic crystals ( $\alpha\text{-HfO}_3$ , Stadnicka & Koralewski, 1991).

The results presented here concern uniaxial crystals of dirubidium (+)-tartrate and dicaesium (+)-tartrate containing chiral optically active organic molecules. These crystals were selected first because they display optical activity along the optic axis with the opposite sign to that observed for their aqueous