

group (Goodgame, Jeeves, Phillips & Skapski, 1975; see also Swaminathan & Sundaralingam, 1979).

Besides the crystal-packing similarities, the conformations of the ribonucleotides in these structures are remarkably similar with only small fluctuations in their preferred domains (Table 7). The glycosyl torsion angle χ is *anti*; the ribose pucker is C(2')-*endo*; the exocyclic C(4')-C(5') conformation ψ is *gauche*⁺ and the C(5')-O(5') conformation ϕ is *trans*. The crystal structure of the disodium salt of cytidine 5'-phosphate (Table 7) has not yet been solved, but the similarity between its cell constants and the related structures suggests that it, too, would be expected to be homologous with the others. The only exception to the above structures is barium adenosine 5'-monophosphate heptahydrate which is monoclinic, space group C2 ($Z = 4$) (Sternglanz, Subramanian, Lacey & Bugg, 1976). The main difference between this structure and the others (Table 7) is in the sugar pucker and the barium coordination which is exclusively by water molecules. The nucleotide sugar conformation is C(4')-*exo*, C(3')-*endo*, $P = 41(2)^\circ$, $\tau_m = 42(1)^\circ$; χ is *anti* [69(1)°], ψ is *gauche*⁺ [58(1)°] and ϕ is *trans* [217(1)°].

It might be mentioned that in contrast to ribonucleotides, deoxyribonucleotides generally tend to show greater conformational variability, stemming from the fact that the deoxyribofuranoid ring is inherently more flexible than the ribofuranoid ring (Sundaralingam, 1975, and references therein).

We gratefully thank Dr S. T. Rao for his assistance in the computations and the University of Wisconsin College of Agricultural and Life Sciences and the National Institutes of Health (Grant GM-17378) for supporting this research.

Acta Cryst. (1980). **B36**, 570–574

Neutron Profile Refinement of Potassium and Rubidium Oxalate Monoperhydrates

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(Received 13 September 1979; accepted 22 October 1979)

Abstract

Neutron powder data collected at 300 K with 1.9 Å radiation have been refined to give the D atom positions in the isotopic perhydrates $K_2[C_2O_4] \cdot D_2O_2$

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and $Rb_2[C_2O_4] \cdot D_2O_2$. The atomic parameters for the Rb compound have been improved considerably (except for Rb) over the previous single-crystal X-ray results, whereas the values for the K compound are comparable with the X-ray work. The dihedral angles

of the D_2O_2 molecules are towards the lower end of the range previously found at 102 (1) and 111 (1)° respectively. The hydrogen bonds have been shown to be reasonably linear at 172.5 (9) and 174.5 (7)°.

Introduction

Perhydrates contain H_2O_2 of crystallization in an analogous fashion to the water in hydrates. They are of considerable technological importance as non-polluting oxygen carriers. The structures of several perhydrates have been studied by X-ray methods, *e.g.* $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ (Adams & Pritchard, 1977; Carondo, Griffith, Jones & Skapski, 1977) and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ (Adams & Pritchard, 1978). In addition, the structure of $Na_2CO_3 \cdot 1\frac{1}{2}D_2O_2$ has been refined from neutron data (Adams, Pritchard & Hewat, 1979). The most interesting part of these structures is always the H_2O_2 conformation and environment, including hydrogen-bonding details, since these give insights into the stability of the perhydrates. It is apparent that neutron diffraction should give a clearer picture of these features, for the H (or D) atoms can be located readily. Neutron profile refinement (Rietveld, 1969) is especially appropriate since the basic structures of these compounds are known from the X-ray results and additionally the data-collection time is short (~12–24 h), which is advantageous with samples which decompose with time. The alkali-metal oxalate perhydrates are of especial interest since, although not all of these compounds form hydrates, they all form perhydrates. Indeed, they are the only chemical series of perhydrates known: the K and Rb samples are both relatively stable and are isomorphous (Pedersen, 1967). The location of the H atoms and therefore better hydrogen-bond definition for this series of perhydrates might enable calculation of crystal cohesive energy which could be correlated with variable chemical stability. Additionally, the determination of the dihedral angle (φ) of the peroxide molecule would be of interest since a wide range of values (90–180°) has been found. The φ values quoted by Pedersen were derived only from the O atom positions and therefore make the unjustified assumption of a linear H bond.

Experimental

Potassium and rubidium oxalate monohydrate crystals were prepared by slow crystallization of a solution formed by reaction of stoichiometric amounts of the carbonate and oxalic acid. The monohydrates were then recrystallized in a glove box under dry nitrogen from a solution made up of 87% (w/w) H_2O_2 diluted with D_2O . Exchange is rapid in this system and the maximum isotropic substitution possible of D in the

hydrogen peroxide of crystallization was 92%. On refinement of the structure the actual substitution was found to be 81% in both the K and Rb samples.

The powdered materials were placed in 16 mm vanadium cans and the diffraction record collected at 300 K on the high-resolution powder diffractometer D1A (Hewat & Bailey, 1976) at the Institut Laue-Langevin, Grenoble, with 1.909 Å neutrons from 6 to 110° (2θ) for 24 h for the K and from 6 to 160° (2θ) for 24 h for the Rb sample.

Refinement of the data was performed with the modified version (Hewat, 1973*a,b*) of the original neutron profile-refinement program of Rietveld (1969). The starting point in both cases was the X-ray structure of Pedersen (1967). The background was estimated by interpolation from regions where Bragg peaks did not occur. The D atom was located from a difference synthesis. The data refined with isotropic temperature factors to R_f^* of 12.0% (K) and 11.9% (Rb), *i.e.* conventional R factors of 9.1% (K) and 9.0% (Rb). No attempt was made to use anisotropic thermal parameters since the quality of the data did not justify it. There was contamination of the diffraction trace of the K compound with some peaks due to hydrate (which is the decomposition product). The

* R_f is defined as $100 \frac{\sum I_o - \frac{1}{c} I_c / \sum I_o}{\sum I_o}$, where I_o and I_c are observed and calculated separated intensities for each Bragg peak. The observed profile intensity is divided up among overlapping reflections according to the relative contributions of these reflections computed from the refined structure.

Table 1. *Crystal data*

(a) $K_2[C_2O_4] \cdot D_2O_2$: $C2/c$, $a = 8.9525$ (8), $b = 6.5139$ (6), $c = 10.942$ (1) Å, $\beta = 108.450$ (5)°, $Z = 4$
(b) $Rb_2[C_2O_4] \cdot D_2O_2$: $C2/c$, $a = 9.2580$ (3), $b = 6.7709$ (2), $c = 11.1699$ (4) Å, $\beta = 107.471$ (2)°, $Z = 4$

Table 2. *Final atomic parameters with e.s.d.'s in parentheses*

(a) $K_2[C_2O_4] \cdot D_2O_2$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
K(1)	0.3551 (17)	0.3421 (19)	0.3616 (11)	4.3 (3)
O(1)	0.3069 (7)	0.4755 (11)	0.0918 (7)	2.1 (2)
O(2)	0.1150 (10)	0.2458 (11)	0.0832 (7)	3.1 (2)
C(1)	0.2298 (7)	0.3189 (9)	0.0512 (5)	1.3 (1)
O(3)	0.4574 (9)	−0.0093 (12)	0.1866 (6)	2.4 (2)
D(1)	0.5113 (11)	−0.0917 (15)	0.1426 (8)	2.4 (4)
(b) $Rb_2[C_2O_4] \cdot D_2O_2$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Rb(1)	0.3612 (5)	0.3328 (6)	0.3641 (4)	2.6 (1)
O(1)	0.3034 (6)	0.4681 (8)	0.0857 (5)	3.3 (1)
O(2)	0.1188 (6)	0.2542 (7)	0.0855 (5)	2.6 (1)
C(1)	0.2300 (5)	0.3168 (6)	0.0512 (4)	2.5 (1)
O(3)	0.4586 (6)	−0.0123 (8)	0.1806 (5)	3.3 (1)
D(1)	0.5221 (7)	−0.1040 (8)	0.1496 (6)	2.4 (2)

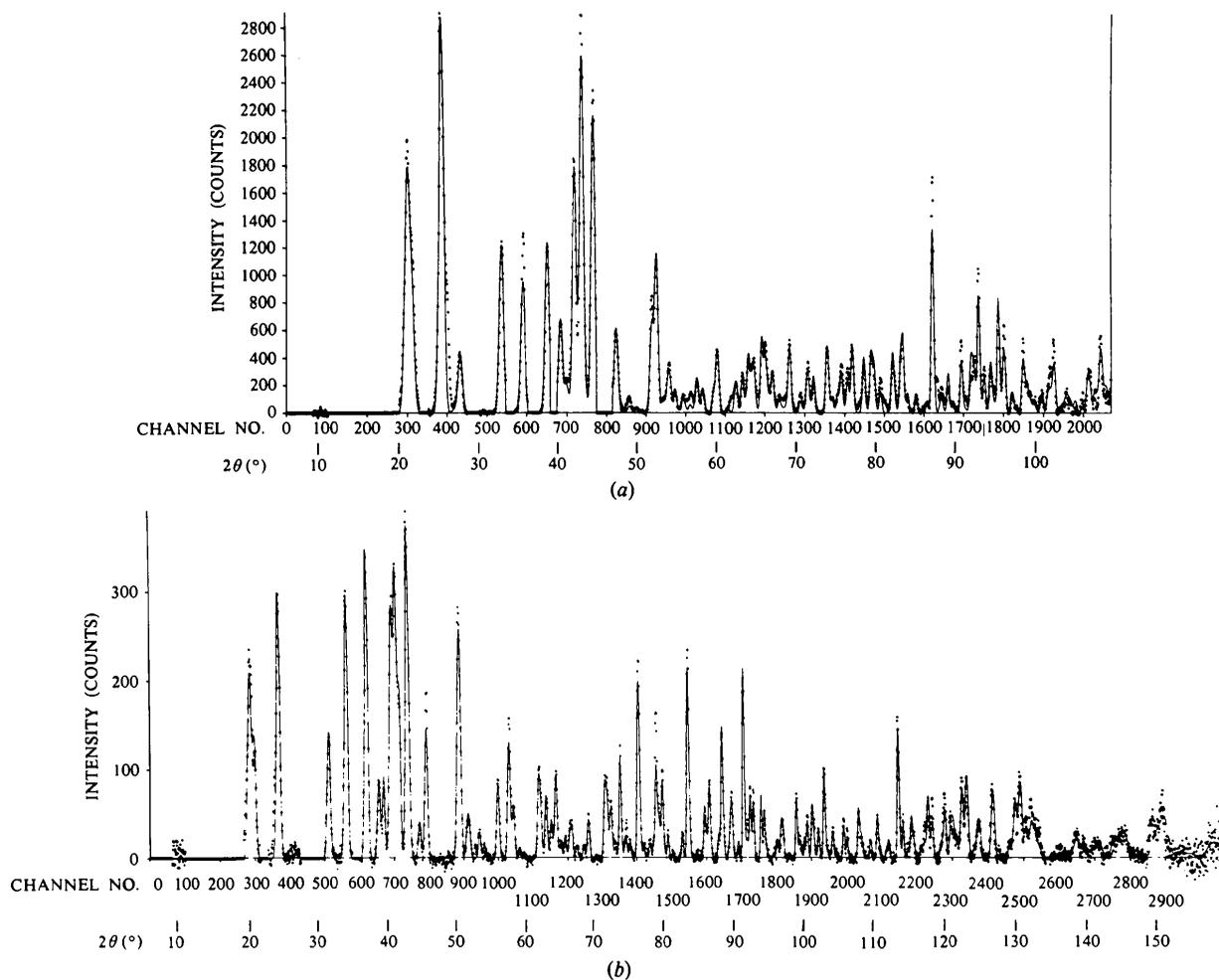


Fig. 1. Observed (· · ·) and calculated (—) diffraction profiles for (a) $K_2[C_2O_4] \cdot D_2O_2$ and (b) $Rb_2[C_2O_4] \cdot D_2O_2$ at 300 K.

stronger of these lines were deleted from the profile but some small contributions due to weaker hydrate reflections can be seen. The Rb data set had relatively poor counting statistics due to the small amount of sample available. Hydrate lines were again apparent in the diffraction record but were considerably weaker than in the K sample.

The scattering lengths used were from *International Tables for X-ray Crystallography* (1974). The site occupancy of the D atoms was refined to allow for the effect of D/H substitution. The final coordinates are given in Table 2. Comparisons of the observed and calculated diffraction traces are given in Fig. 1.

Results and discussion

The cell parameters (Table 1) determined from profile analysis have very high accuracy (Hewat, 1973a)

although the e.s.d.'s quoted do not include the errors in the neutron wavelength. The geometry of the substructures is given in Tables 3 and 4. It appears that there is an error in Pedersen's (1967) labelling of O(1) and O(2): the labels have become transposed between the atomic-coordinate list and the table of bond distances and angles. Corrected values are given in Table 3. In those cases where the parameters can be directly compared there is good agreement between these results and those of Pedersen, although the values for the Rb compound are here of higher quality.

The oxalate ion has the usual distortions (Pedersen, 1967) and is planar. In the K sample the peroxide O—O distance is short at 1.355 (8) Å which is indicative of some partial random substitution of water for hydrogen peroxide (Pedersen, 1972). It did not prove possible, however, to locate the O or D peaks of such water. Consequent upon this low value for O—O, the O—O—D angle is slightly larger than that usually found at

107.9 (8)°. In the rubidium oxalate monoperhydrate the O—O length of 1.507 (7) Å is close to the theoretical O—O single-bond distance, implying little random substitution of peroxide by water. O—O—D is also closer to previous values at 100.8 (5)°. The dihedral angle found for H₂O₂ molecules has varied from 90.2° in solid H₂O₂ (Busing & Levy, 1965) to 180° in Na₂[C₂O₄].H₂O₂ (Pedersen & Pedersen, 1964) and indeed there is relatively free rotation about the central O—O bond (Hunt, Leacock, Peters & Hecht, 1965) with φ very dependent upon molecular environment. Pedersen's (1967) values of φ quoted for the title compounds were obtained by making the unjustified assumption of linear H bonds since the H positions could not be determined. Since the hydrogen bonds have been shown in this study to be relatively linear (Table 5, Fig. 2), the φ 's derived here [102 (1) and 111 (1)°] are reasonably close to those given by Pedersen (1967). This is not always the case for perhydrates. In Na₂CO₃·1½D₂O₂ (Adams, Pritchard & Hewat, 1979) the H bonds deviate 30° from linearity even though the H-bond lengths are as short as those found here.

Table 3. *Geometry of the oxalate and hydrogen peroxide groups*

(a) K ₂ [C ₂ O ₄].D ₂ O ₂		PED*	PED corrected
O(1)—C(1)	1.233 (9) Å	1.274 (9) Å	1.227 (9) Å
O(2)—C(1)	1.278 (12)	1.227 (9)	1.274 (9)
C(1)—C(1 ^h)	1.565 (9)	1.563 (13)	1.563 (13)
O(1)—C(1)—O(2)	128.1 (7)°	125.2 (6)°	125.2 (6)°
O(1)—C(1)—C(1 ^h)	120.2 (7)	114.7 (6)	120.1 (6)
O(2)—C(1)—C(1 ^h)	111.8 (5)	120.1 (6)	114.7 (6)
D(1)—O(3)	0.95 (1) Å	—	—
O(3)—O(3 ^h)	1.355 (8)	1.441 (9) Å	1.441 (9) Å
D(1)—O(3)—O(3 ^h)	107.9 (8)°	—	—

Note: (1) The oxalate anion is planar; (2) the dihedral angle for D₂O₂ is 102 (1)°.

(b) Rb ₂ [C ₂ O ₄].D ₂ O ₂		PED	PED corrected
O(1)—C(1)	1.225 (7) Å	1.24 (1) Å	1.23 (1) Å
O(2)—C(1)	1.275 (8)	1.23 (1)	1.24 (1)
C(1)—C(1 ^h)	1.587 (7)	1.57 (2)	1.57 (2)
O(1)—C(1)—O(2)	127.3 (5)°	123.4 (7)°	123.4 (7)°
O(1)—C(1)—C(1 ^h)	118.4 (5)	116.4 (7)	120.2 (7)
O(2)—C(1)—C(1 ^h)	114.3 (4)	120.2 (7)	116.4 (7)
D(1)—O(3)	0.99 (1) Å	—	—
O(3)—O(3 ^h)	1.509 (7)	1.44 (1) Å	1.44 (1) Å
D(1)—O(3)—O(3 ^h)	100.8 (5)°	—	—

Note: (1) The oxalate anion is planar; (2) the dihedral angle for D₂O₂ is 111 (1)°.

* PED indicates values quoted by Pedersen (1967) in her original X-ray studies of these materials.

Table 4. *Coordination around the cations*

(a) K ₂ [C ₂ O ₄].D ₂ O ₂			
K(1)—O(1)	2.97 (1) Å	K(1)—O(2 ^v)	2.69 (1) Å
K(1)—O(1 ^h)	3.03 (2)	K(1)—O(2 ^{vi})	2.84 (1)
K(1)—O(1 ^h)	2.92 (2)	K(1)—O(3 ^h)	2.98 (2)
K(1)—O(1 ^{iv})	2.94 (2)	K(1)—O(3 ^v)	2.85 (2)
(b) Rb ₂ [C ₂ O ₄].D ₂ O ₂			
Rb(1)—O(1)	3.130 (7) Å	Rb(1)—O(2 ^v)	2.903 (6) Å
Rb(1)—O(1 ^h)	3.123 (7)	Rb(1)—O(2 ^{vi})	2.934 (6)
Rb(1)—O(1 ^h)	3.041 (7)	Rb(1)—O(3 ^h)	2.999 (7)
Rb(1)—O(1 ^{iv})	3.004 (8)	Rb(1)—O(3 ^v)	3.038 (7)

Symmetry code for all tables and figures

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

Table 5. *Hydrogen-bonding geometry*
[bond O(3)—D(1)⋯O(2^{vi})]

(a) K ₂ [C ₂ O ₄].D ₂ O ₂		∠O(3)—D(1)⋯O(2 ^{vi})	172.5 (9)°
O(3)—D(1)	0.95 (1) Å		
D(1)⋯O(2 ^{vi})	1.67 (1)		
O(3)⋯O(2 ^{vi})	2.61 (1)		
(b) Rb ₂ [C ₂ O ₄].D ₂ O ₂		∠O(3)—D(1)⋯O(2 ^{vi})	174.5 (7)°
O(3)—D(1)	0.99 (1) Å		
D(1)⋯O(2 ^{vi})	1.619 (9)		
O(3)⋯O(2 ^{vi})	2.603 (8)		

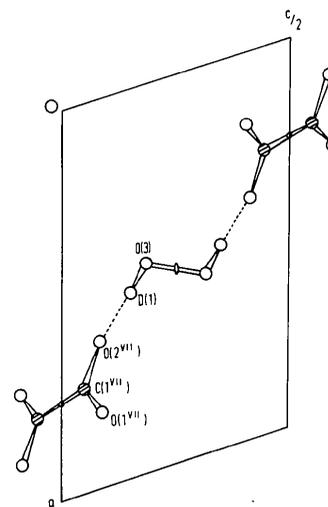


Fig. 2. Hydrogen-bonded chains of alternating C₂O₄²⁻ and D₂O₂ groups. These chains are held together by bonds to inter-chain cations.

We are grateful to Laporte Industries for the gift of the 87% hydrogen peroxide used and to Unilever Ltd for support.

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