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Neutron Profile Refinement of Rubidium Oxalate Perdeuterate, $Rb_2[C_2O_4].D_2O_2$, at 5 K

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Abstract

The structure of $Rb_2[C_2O_4].D_2O_2$ at 5 K is basically that observed at room temperature but with minor adjustments. The Rb—O coordination distances have decreased by 0·04 Å and the bond lengths in the D_2O_2 molecule have decreased slightly whereas the already long C—C distance in the oxalate anion has increased to 1·616 (4) Å, one of the largest values to date. The angle O—O—D has remained unaltered whereas the dihedral angle in the D_2O_2 molecule, which is very environmentally sensitive, has decreased by 6·5°. In addition the hydrogen bond has become almost linear [177·6 (4)° compared with 174·5 (7)° at room temperature].

Introduction

Recently, as part of a study of simple salt perhydrates (Adams & Pritchard, 1978; Adams, Pritchard & Hewat, 1979) we had occasion to re-examine the room-temperature crystal structures of $K_2[C_2O_4].D_2O_2$ and $Rb_2[C_2O_4].D_2O_2$ (Adams, Ramdas & Hewat, 1980) to find the D atoms accurately and hence define the molecular geometry of D_2O_2 in these compounds. It had been found that the dihedral angle of this molecule can vary between wide limits depending upon the hydrogen-bonding environment (Pedersen, 1967). The opportunity has also been taken to study the Rb compound at 5 K. There proved to be no phase transition down to this temperature and the neutron powder pattern was easily indexable on a cell refined slightly from the known room-temperature cell, *i.e.* space group $C2/c$, $a = 9{\cdot}1499$ (2), $b = 6{\cdot}7475$ (2), $c = 11{\cdot}0648$ (3) Å, $\beta = 107{\cdot}606$ (1)°, $Z = 4$. The e.s.d.'s of the cell parameters do not include a contribution from the uncertainty in the neutron wavelength. The unit-cell volume has decreased by 2·5% from that at 300 K.

In addition to determining the D-atom positions accurately we have improved the precision with which all of the atoms in the structure are known, except for Rb, as a consequence of the use of neutron, rather than X-ray, diffraction. The use of neutron profile refinement (Rietveld, 1969) was indicated since the structure was already known in outline and the number of parameters to be refined was below that considered to be a limit for this technique (~40). The short experimental time required with these relatively unstable compounds was useful, as was the fact that large crystals were not required.

Experimental

The sample was prepared by first reacting stoichiometric amounts of Rb_2CO_3 with oxalic acid dihydrate and recrystallizing the product (in a dry-box under N_2) from a solution of 87% (w/w) H_2O_2 in D_2O. There is rapid H/D exchange in H_2O_2/D_2O mixtures and the maximum isotopic purity of D in the D_2O_2 in the crystals was calculated as 92%. The structure refinement later gave an experimental value of 85 ± 2%. The data were collected on the high-resolution powder diffractometer D1A at the ILL, Grenoble (Hewat & Bailey, 1976). The sample was contained in a 16 mm diameter vanadium tube, which was maintained at 5 K in a cryostat. Data ranging in 2θ from 6 to 160° were collected in 22 h at a wavelength of 1·909 Å. The background was estimated by linear interpolation from regions where no Bragg peaks occurred. Small peaks due to $Rb_2[C_2O_4].D_2O$ were removed from the diffraction record. The refinement was performed by the Rietveld (1969) technique with the programs of Hewat (1973*a*,*b*) and isotropic thermal parameters. No improvement resulted from anisotropic refinement. The D atom was located from a difference synthesis. A final $R_{\text{nuclear}} = 9{\cdot}1\%$ (Hewat, 1973*a*), corresponding to $R = 6{\cdot}3\%$, was obtained. The scattering lengths were from *International Tables for X-ray Crystallography* (1974). The site occupancy of the D atoms was allowed to vary to obtain the isotopic H/D ratio. Final coordinates are

0567-7408/80/051096-03$01.00

Table 1. *Final atomic parameters (e.s.d.'s in parentheses)*

	x	*y*	*z*	*B* (Å^2)
Rb(1)	0·3596 (3)	0·3394 (4)	0·3631 (2)	0·5 (1)
O(1)	0·3049 (3)	0·4739 (5)	0·0883 (3)	0·4 (1)
O(2)	0·1175 (3)	0·2545 (5)	0·0856 (3)	0·4 (1)
C(1)	0·2284 (3)	0·3194 (4)	0·0516 (2)	0·6 (1)
O(3)	0·4571 (5)	−0·0096 (6)	0·1812 (3)	0·5 (2)
D(1)	0·5192 (6)	−0·0978 (7)	0·1475 (4)	1·3 (2)

given in Table 1 and a comparison of calculated and observed profiles is in Fig. 1.*

Results and discussion

The structure is basically that found at room temperature (Pedersen, 1967; Adams, Ramdas & Hewat, 1980) with small adjustments to the molecular and ionic geometry. It should be noted that in Pedersen's (1967) work the labelling of O(1) and O(2) has become transposed between the atom coordinate list and the molecular geometry tables. The atomic positions have been determined more accurately than in the room-temperature studies, but the thermal parameters derived from the profile refinement are very dependent upon the choice of background. It is only possible to refine atoms anisotropically when the structure is simple with easily interpolated background.

Table 2. *Coordination around the cations and molecular geometry – comparison with room-temperature data*

Rb(1)–O(1)	3·066 (4) Å	Rb(1)–O(2^{v})	2·853 (4) Å
Rb(1)–O(1^{ii})	3·088 (4)	Rb(1)–O(2^{vi})	2·918 (3)
Rb(1)–O(1^{iii})	3·021 (4)	Rb(1)–O(3^{ii})	3·016 (5)
Rb(1)–O(1^{iv})	2·967 (4)	Rb(1)–O(3^{v})	2·969 (5)

The average value for Rb–O is 2·987 Å with average e.s.d. 0·004 (Å); *cf.* average values at 300 K of 3·027 Å with average e.s.d. of 0·007 Å (Adams, Ramdas & Hewat, 1980), and of 3·036 Å with average e.s.d. of 0·007 Å (Pedersen, 1967).

	5 K	300 K (Adams, Ramdas & Hewat, 1980)	300 K (Pedersen, 1967, corrected)
C(1)–O(1)	1·253 (4) Å	1·225 (7) Å	1·23 (1) Å
C(1)–O(2)	1·263 (4)	1·277 (8)	1·24 (1)
C(1)–C(1^{i})	1·616 (4)	1·584 (7)	1·57 (2)
O(1)–C(1)–O(2)	127·8 (3)°	127·1 (5)°	123·4 (7)°
O(1)–C(1)–C(1^{i})	118·6 (3)	118·6 (5)	120·2 (7)
O(2)–C(1)–C(1^{i})	113·6 (3)	114·2 (4)	116·4 (7)
D(1)–O(3)	0·972 (7) Å	0·99 (1) Å	–
O(3)–O(3^{ii})	1·487 (4)	1·509 (7)	1·44 (1) Å
D(1)–O(3)–O(3^{ii})	101·8 (4)°	100·8 (5)°	–
Dihedral angle for D$_2$O$_2$	104·5 (5)	111 (1)	–

In Table 2 we compare the geometry of the molecules and ions at 5 and 300 K. The Rb–O distances decrease at low temperature by ~0·04 Å. It is here that most of the unit-cell shrinkage is taken up. In addition the bond lengths in the D$_2$O$_2$ molecules contract slightly. On the other hand, while one of the C–O lengths also decreases slightly the other C–O and C–C distance increase as the temperature is reduced. This effect has been noted previously (de With, Harkema & van Hummel, 1976). It can be caused partly by the reduction in the librational amplitudes of the molecular groups at lower temperatures (B ~ 0·5 Å^2, *cf.* 3·0 Å^2 at 300 K), so giving an apparently longer bond; though if this were the whole reason then both the C–O bonds would be expected to increase at lower temperature. Nevertheless, it has been found (Bracher & Small, 1967) that even after making allowance for librational effects there can still be lengthening of bonds on cooling. The increase in the oxalate C–C distance is particularly noteworthy since the bond is often found to be longer than the single-bond length of 1·54 Å; for example, Pedersen (1964) found 1·585 Å in K$_2$[C$_2$O$_4$].H$_2$O at room temperature. The bond length found here is the longest so far reported at 1·616 (4) Å. There appears, however, to be no other study of the oxalate anion at such low temperatures.

The fact that the O–O bond in D$_2$O$_2$ obtained both here and in the 300 K neutron study (Adams, Ramdas & Hewat, 1980) is longer than that obtained by Pedersen (1967) is probably a consequence of a reduction in the amount of random substitution of D$_2$O$_2$ by D$_2$O relative to that of Pedersen's sample (there of H$_2$O$_2$ by H$_2$O). Such substitution often occurs in variable amounts in different batches of perhydrate crystals and can cause considerable apparent shortening in the peroxide O–O distances (Pedersen, 1972). In ammonium persulphate (Sivertsen & Sørum, 1969) where there is no such substitution to affect the peroxide bond, the O–O distance is 1·497 (8) Å. This substitutional effect is probably the reason for the extreme variability in the values of O–O distances derived for H$_2$O$_2$ or D$_2$O$_2$ over the years. The structure of H$_2$O$_2$ itself (Busing & Levy, 1965), studied by neutron diffraction, gave 1·453 (7) Å while the earlier X-ray work (Abrahams, Collin & Lipscomb, 1951) gave 1·49 (2) Å. A recent accurate X-ray and neutron determination of charge-density distribution in H$_2$O$_2$ at 110 K has been reported (Savariault & Lehmann, 1978)

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* Fig. 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35203 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Hydrogen-bonding parameters*

$O(3)–D(1)\cdots O(2^{vii})$	5 K	300 K (Adams, Ramdas & Hewat, 1980)	300 K (Pedersen, 1967, corrected)
$O(3)–D(1)$	0·972 (7) Å	0·99 (1) Å	–
$D(1)\cdots O(2^{vii})$	1·626 (6)	1·619 (9)	–
$O(3)\cdots O(2^{vii})$	2·597 (6)	2·603 (8)	2·74 (1) Å
$\angle O(3)–D(1)\cdots O(2^{vii})$	177·6 (4)°	174·5 (7)°	–

Symmetry code for tables

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

and bonding distances have been obtained from them. They gave O—O 1·461 (3) Å by X-rays and 1·458 (4) Å by neutron diffraction. It is difficult to assume in this case that the shorter bonds are caused by water substitution since their study showed no electron density maxima between the peroxide O atoms. The other parameters obtained in the neutron diffraction study were: O—H 0·988 (3) Å and O—O—H 101·9 (1)°, values very close to those found here.

The dihedral angle found for the D_2O_2 molecule in the title compound is 6·5° different from that at 300 K and demonstrates the ease with which the D_2O_2 molecule can cope with changes in hydrogen-bonding environment by rotation about the O—O bond. The hydrogen bond which joins chains of alternating hydrogen peroxide molecules and oxalate ions has become slightly shorter at 2·597 (6) Å and is almost linear (Table 3).

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