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On the Crystal Structure of the Rubidium Salt of Hydroxymalonic Dialdehyde

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The crystal structure determination of the rubidium salt of hydroxymalonic dialdehyde (= rubidium "reductonate", $Rb(C_3H_3O_3)H_2O$) is reported. The lattice is monoclinic with $a = 8.3 \pm 0.1$ Å, $b = 18.3 \pm 0.2$ Å, $c = 4.0 \pm 0.1$ Å, $\beta = 93° \pm 1°$. The space group is $P2_1/a$ (No. 14 in the International Tables [1]). The x and y parameters for the atoms have been determined. The z parameters were not calculated since the main features of the structure appeared in its xy projection.

When trying to solve the crystal structure of hydroxymalonic dialdehyde ("reductone") we found that it is probably non-centrosymmetric (space group No. 33 $Pn2_1a$ [1])[2]. The problem of determining the structure should then be very much facilitated if we could get some information concerning its C—O skeleton by investigating some related compounds. The work was thus begun by studying the structures of bromomalonic dialdehyde and rubidium "reductonate" (the rubidium salt of hydroxymalonic dialdehyde). A report concerning the crystal structure of the first compound will be given in *Acta Chem. Scand.*[3] and the second one is dealt with here.

A crystalline preparation of rubidium "reductonate" was kindly supplied by Professor Hans von Euler and Mr H. Hasselquist. It had been prepared by mixing water solutions of rubidium carbonate and hydroxymalonic dialdehyde. By very slow addition of acetone, crystals of rubidium "reductonate" then separated as leaf-like, rather long, yellowish, deliquescent plates. By evidence from the X-ray data, the formula of the compound was later on found to be $Rb(C_3H_3O_3)H_2O$.

By rotation and Weissenberg photographs the symmetry of the crystals was found to be monoclinic with the following cell dimensions:

$$\begin{aligned} a &= 8.3 \pm 0.1 \text{ Å} \\ b &= 18.3 \pm 0.2 \text{ Å} \\ c &= 4.0 \pm 0.1 \text{ Å} \\ \beta &= 93° \pm 1° \\ V &= 607 \text{ Å}^3 \end{aligned}$$

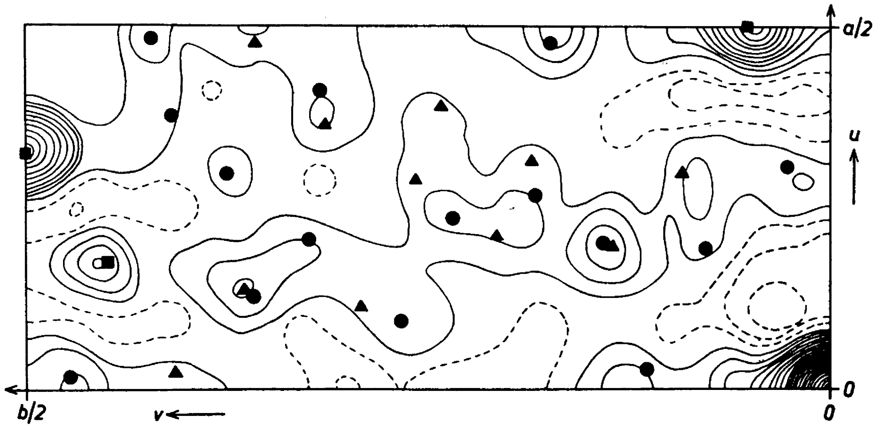

Fig. 1. The Patterson projection $P(uvp)$ for $Rb(C_3H_3O_3)H_2O$. In the figure the final vectors Rb—Rb (■), Rb—O (●), and Rb—C (▲) have been indicated. Dashed lines indicate negative values.

The following reflections were found to be systematically absent:

$$h0l \text{ with } h = \text{odd}$$
$$0k0 \text{ with } k = \text{odd.}$$

This is characteristic of the space group $P2_1/a$, which is another orientation of $P2_1/c$ (No. 14 in the International Tables of X-ray Crystallography [1]).

Because of the deliquescency of the crystals, their density could not be determined. However, by comparing the cell volume (607 Å^3) with that of hydroxymalonic dialdehyde (380 Å^3), we see that there should be 4 or 6 formula units in the unit cell.

POSITIONS OF THE RUBIDIUM ATOMS

The positions of the rubidium atoms were determined from the Patterson projection $P(uvp)$ (Fig. 1) using the estimated intensities corrected for polarization and Lorentz effects. It shows two large maxima: one at $u = 0.324$, $v = \frac{1}{2}$ and one at $u = \frac{1}{2}$, $v = 0.050$, which should certainly correspond to Rb—Rb vectors. They could be explained only if four rubidium atoms are situated in the point position $4(e)$: $\pm(xyz)$; $\pm(\frac{1}{2} + x,\frac{1}{2}—y,z)$ with $x_{\mathrm{Rb}} = 0.088$ and $y_{\mathrm{Rb}} = 0.225$.

If there are six formula units per unit cell, we should have two additional rubidium atoms in one of the positions $2(a)$—$2(d)$. This would demand a Rb—Rb peak at $u = \frac{1}{2}$, $v = \frac{1}{2}$ in $P(uvp)$. Since there is a negative region at that point, we could safely say that the unit cell contains only four rubidium atoms and consequently only four organic anions.

Since the c axis is very short and only a limited number of reflections could be registered in $0kl$, we did not determine the z parameters of the atoms. However, this was not necessary since our intention of getting a rough picture of the C—O skeleton could be fulfilled even if the z parameters were not known.

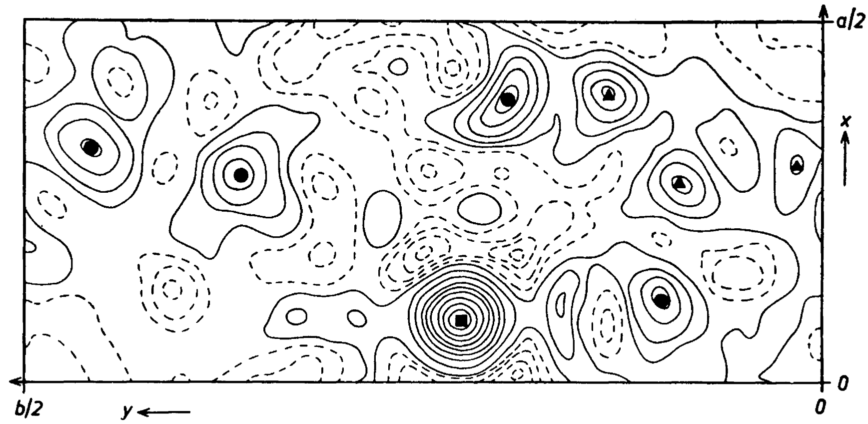

Fig. 2. The final electron density projection $\varrho(xyp)$ of $Rb(C_3H_3O_3)H_2O$. The positions of the Rb (■), C (▲) and O (●) atoms have been indicated. In the rubidium peak only every third contour has been marked. Dashed lines indicate negative values.

POSITIONS OF THE LIGHT ATOMS

To determine the positions of the light atoms the electron density projection $\varrho(xyp)$ was calculated. The signs of the F values were at first determined from the known rubidium contributions to the intensities. Later on, when the x and y parameters of the light atoms were approximately known, $\varrho(xyp)$ was corrected by considering the scattering of the light atoms also. However, only a few changes in the signs of the structure factors were necessary.

As is seen in Fig. 2, $\varrho(xyp)$ shows some low maxima which could be ascribed to oxygen and carbon atoms. Their parameters are:

4 A_1 in	4(e):	$\pm(xyz)$;	$\pm(\frac{1}{2}+x,\frac{1}{2}-y,z)$	with	$x = 0.11_6$,	$y = 0.10_1$
4 A_2 »		»	»	»	$x = 0.39_1$,	$y = 0.19_8$
4 A_3 »		»	»	»	$x = 0.32_1$,	$y = 0.45_8$
4 A_4 »		»	»	»	$x = 0.28_7$,	$y = 0.36_5$
4 A_5 »		»	»	»	$x = 0.27_5$,	$y = 0.09_0$
4 A_6 »		»	»	»	$x = 0.39_8$,	$y = 0.13_4$
4 A_7 »		»	»	»	$x = 0.29_9$,	$y = 0.01_7$

In addition there are some very weak maxima close to the large rubidium maximum. They are, however, certainly false peaks caused by diffraction effects from the heavy rubidium atom [4].

Space arguments were used to decide the nature of the atoms A_1 to A_7. It was assumed that oxygen atoms are situated at least 2.60 Å apart. The projection of an O—O distance on the xy plane is thus at least 1.67 Å since the two oxygen atoms could be at most $c/2 = 2.0$ Å apart in the z direction. Now, the xy projections of the shortest distances A_1—A_5, A_2—A_6, A_3—A_7, A_5—A_6, and A_5—A_7 are 1.2_8 Å, 1.1_8 Å, 1.4_7 Å, 1.3_0 Å, and 1.3_5 Å, *i.e.* they

Table 1. Calculated and observed structure factors *hk*0 for $Rb(C_3H_3O_3)H_2O$.

*hk*0	*F* calc	*F* obs	*hk*0	*F* calc	*F* obs	*hk*0	*F* calc	*F* obs
0 2 0	−52	(28)	3 1 0	−10	12	5 10 0	−10	0
0 4 0	34	25	3 2 0	−42	49	5 11 0	16	0
0 6 0	−36	30	3 3 0	1	6	5 12 0	10	0
0 8 0	22	28	3 4 0	44	50	5 13 0	−30	24
0 10 0	7	7	3 5 0	7	9	5 14 0	−10	0
0 12 0	−25	23	3 6 0	−35	30	5 15 0	26	27
0 14 0	19	28	3 7 0	3	0	5 16 0	7	0
0 16 0	−27	33	3 8 0	45	39	5 17 0	−10	0
0 18 0	16	14	3 9 0	0	0	5 18 0	0	0
0 20 0	−17	13	3 10 0	−48	38	5 19 0	0	0
			3 11 0	12	0			
1 1 0	14	14	3 12 0	35	32	6 0 0	−42	59
1 2 0	−23	21	3 13 0	− 3	0	6 1 0	11	0
1 3 0	−16	14	3 14 0	−16	17	6 2 0	42	52
1 4 0	23	15	3 15 0	6	0	6 3 0	7	0
1 5 0	21	18	3 16 0	15	17	6 4 0	−22	20
1 6 0	−26	22	3 17 0	2	0	6 5 0	8	0
1 7 0	−41	34	3 18 0	− 6	0	6 6 0	22	29
1 8 0	47	43	3 19 0	− 2	0	6 7 0	− 8	0
1 9 0	41	34				6 8 0	−11	0
1 10 0	−18	15	4 0 0	−44	53	6 9 0	5	0
1 11 0	−37	40	4 1 0	−48	63	6 10 0	− 7	0
1 12 0	6	0	4 2 0	34	50	6 11 0	3	0
1 13 0	28	35	4 3 0	18	33	6 12 0	7	0
1 14 0	−24	24	4 4 0	−24	26	6 13 0	4	0
1 15 0	−28	37	4 5 0	−33	37	6 14 0	−16	0
1 16 0	5	0	4 6 0	18	21	6 15 0	6	0
1 17 0	12	10	4 7 0	14	8	6 16 0	15	0
1 18 0	− 5	0	4 8 0	− 4	0	6 17 0	− 5	0
1 19 0	0	0	4 9 0	−16	12	6 18 0	−14	0
			4 10 0	− 7	0			
2 0 0	− 1	8	4 11 0	− 7	0	7 1 0	− 2	0
2 1 0	−39	38	4 12 0	10	0	7 2 0	19	22
2 2 0	−48	44	4 13 0	9	0	7 3 0	16	25
2 3 0	50	63	4 14 0	− 7	0	7 4 0	−11	0
2 4 0	26	24	4 15 0	−17	10	7 5 0	−16	20
2 5 0	−36	35	4 16 0	11	0	7 6 0	18	17
2 6 0	−16	20	4 17 0	18	17	7 7 0	15	22
2 7 0	40	38	4 18 0	−12	0	7 8 0	−21	22
2 8 0	0	0	4 19 0	− 4	8	7 9 0	−18	20
2 9 0	3	7				7 10 0	19	17
2 10 0	5	0	5 1 0	0	0	7 11 0	25	22
2 11 0	0	0	5 2 0	− 1	0			
2 12 0	− 3	0	5 3 0	7	8	8 0 0	− 6	0
2 13 0	3	0	5 4 0	9	0	8 1 0	20	28
2 14 0	8	0	5 5 0	−19	24	8 2 0	2	0
2 15 0	−20	14	5 6 0	−20	25	8 3 0	−25	28
2 16 0	− 8	0	5 7 0	35	37	8 4 0	− 8	0
2 17 0	28	28	5 8 0	11	0	8 5 0	22	22
2 18 0	14	17	5 9 0	−39	37			
2 19 0	−24	27						

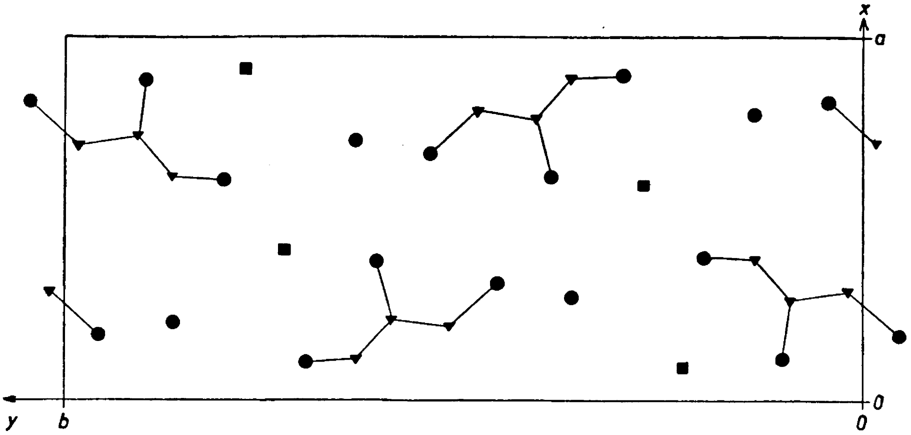

Fig. 3. Schematic picture of the atomic arrangement in the crystals of $Rb(C_3H_3O_3)H_2O$. The positions of the rubidium atoms have been marked with ■, the positions of the carbon atoms with ▲, and the positions of the oxygen atoms with ●.

are all shorter than 1.67 Å. Consequently there must be at least one carbon atom in each of these pairs. In addition to the chemical fact that the carbon atoms must form a chain, this leads to the conclusion that A_1, A_2, and A_3 are oxygen atoms and A_5, A_6, and A_7 carbon atoms. We have thus identified the atoms in the organic anion.

As for the remaining peak, A_4, it must correspond to a molecule of water of crystallization. The presence of such a molecule is also reflected in the relatively large difference in cell volume between the potassium and rubidium salts [2].

STRUCTURE PROPOSED FOR $Rb(C_3H_3O_3)H_2O$

The following x and y parameters are thus proposed for $Rb(C_3H_3O_3)H_2O$:
Space group: $P2_1/a$. 4 formula units per unit cell.

4 Rb in 4(*e*) with $x = 0.088$ and $y = 0.225$
4 C_1 » » » $x = 0.27_5$ » $y = 0.09_0$
4 C_2 » » » $x = 0.39_8$ » $y = 0.13_4$
4 C_3 » » » $x = 0.29_9$ » $y = 0.01_7$
4 O_1 » » » $x = 0.11_6$ » $y = 0.10_1$
4 O_2 » » » $x = 0.39_1$ » $y = 0.19_8$
4 O_3 » » » $x = 0.32_1$ » $y = 0.45_8$
4 O_4 (H_2O) » $x = 0.28_7$ » $y = 0.36_5$

$$4(e)\colon\ \pm(xyz);\ \pm(\tfrac{1}{2}+x,\tfrac{1}{2}-y,z)$$

With these parameters the intensities of the $hk0$ reflections were calculated. They were then corrected by an exponential factor of $10^{-0.34\sin^2\Theta}$ obtained with the ordinary procedure for the calculation of temperature factors. As is seen in Table 1, the agreement between observed and calculated data is satisfactory. The *R* value according to Booth [5] is 0.17 (absent reflections not included).

DISCUSSION OF THE STRUCTURE

Fig. 3 shows a schematic picture of the *xy* projection of the structure with the projected interatomic distances indicated. As is seen, the organic anion shows the same configuration as in bromomalonic dialdehyde [2], *i.e.* the oxygen atoms are situated on the same side of the C—C chain.

The coordination Rb—O is rather difficult to determine since the *z* parameters are not known. However, if we assume that the distances between rubidium and oxygen atoms in contact are about 3.0 Å, we see that the differences in the rubidium and oxygen *z* parameters should be in the vicinity of $c/2 = 2.0$ Å for Rb (0.088, 0.225)—O_1(0.11$_6$, 0.10$_1$), Rb(0.088, 0.225) —O_2 (0.39$_1$, 0.19$_8$), and Rb(0.088, 0.225)—O_2(−0.10$_9$, 0.30$_2$). Every other *z* difference gives some Rb—O distances less than 2.8 Å (= the sum of the ionic radii). The rubidium atom is thus in contact with at least 6 oxygen atoms forming a trigonal prism.

The *xy* projections of the distances between the water molecule O_4 and two rubidium atoms are 3 Å. Thus, if they all three have the same *z* parameter, the water molecule would be in contact with two rubidium atoms, which seems to be very plausible. We would then have a coordination Rb—8 O in the crystals.

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