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The Structure of Potassium Dihydroxyacetate (I) and Rubidium Dihydroxyacetate (II)

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Abstract. (I) $K^+.C_2H_3O_4^-$, $M_r = 130.1$, monoclinic, Pc, $a = 5.791$ (4), $b = 7.727$ (6), $c = 11.445$ (6) Å, $\beta = 120.00$ (4)°, $V = 443.5$ Å³, $Z = 4$, $D_m = 1.92$, $D_x = 1.95$ Mg m⁻³, μ(Mo $K\alpha$, $\lambda = 0.71069$ Å) = 1.08 mm⁻¹, $F(000) = 264$, $T = 295$ (2) K, final $R = 0.036$ for 2203 data including both hkl and $\bar{h}k\bar{l}$ reflexions. (II) $Rb^+.C_2H_3O_4^-$, $M_r = 176.5$, monoclinic, $P2_1/c$, $a = 5.665$ (6), $b = 12.846$ (9), $c = 6.391$ (7) Å, $\beta = 96.03$ (7)°, $V = 462.5$ Å³, $Z = 4$, $D_m = 2.52$, $D_x = 2.53$ Mg m⁻³, μ(Mo $K\alpha$) = 11.2 mm⁻¹, $F(000) = 336$, $T = 300$ (1) K, final $R = 0.037$ for 1239 non-zero reflexions. The X-ray analysis showed that potassium and rubidium glyoxylate crystallized from aqueous solutions exist in the solid state as salts of dihydroxyacetic acid. In the dihydroxyacetate anions different conformations about the C—C bond are observed. All O-bonded H atoms are involved in hydrogen bonds.

Introduction. In the biochemical literature glyoxylic acid is presented mostly as the simplest aldehydoacid, CHO—COOH. However, X-ray analysis (Lis, 1983) has shown that glyoxylic acid crystallizes from water as dihydroxyacetic acid $CH(OH)_2COOH$. A similar result has been reported by Mattes & Uckelmann (1981) for the Na salt of this acid. Here are reported the crystal structures of potassium and rubidium salts of this acid.

Experimental. Potassium (rubidium) dihydroxyacetate was prepared by combining an equivalent quantity of glyoxylic acid monohydrate (Ferak Berlin) and

potassium (rubidium) carbonate in water. After slow evaporation of water many-faced, often twinned, crystals of (I) [rather irregular shaped crystals of (II)] appeared. D_m measured pycnometrically in 1,2-dibromoethane/CCl_4 for (I) and in 1,2-dibromoethane/$CHBr_3$ for (II). Systematic absences on Weissenberg photographs uniquely indicated the space group for (II). For (I) the possible groups were Pc and $P2/c$. Specimens $0.2 \times 0.25 \times 0.3$ mm for (I) and $0.4 \times 0.3 \times 0.4$ mm for (II) were cut from large crystals. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters [15 reflexions, $20 \le 2\theta \le 28°$ for (I) and $15 \le 2\theta \le 34°$ for (II)] and intensity measurements; 2θ–ω scan technique. 2484 unique intensities below $\theta = 30°$ for (I) ($h\ 0{\to}8$, $k\ {-}10{\to}10$, $l\ {-}15{\to}13$); 3051 reflexions below $\theta = 32.5°$ for (II) ($h\ 0{\to}8$, $k\ {-}19{\to}19$, $l\ {-}9{\to}9$). After each group of 50 reflexions two standards were measured, variation ±5%. Most calculations performed on a Nova 1200 computer with locally modified *XTL/XTLE* (Syntex, 1976) programs. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of anomalous dispersion included for all non-H atoms. Both structures solved by the heavy-atom method. The K (Rb) atoms were found from a Patterson map. In the case of (I) the noncentrosymmetric space group Pc was assumed. All other atoms were found from difference maps. In each structure, refinement based on F (K, Rb, O, C anisotropic, H isotropic) for reflexions with $I >$

Table 1. *The final atom coordinates and isotropic thermal parameters of potassium dihydroxyacetate*

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	y	z	B_{eq} or B_{iso}(Å^2)
K(1)	0·5267 (2)	0·7508 (1)	0·5*	2·47 (5)
K(2)	0·5*	0·7490 (1)	0·9329 (1)	2·38 (5)
O(1)	0·1280 (5)	−0·4746 (4)	0·3483 (3)	2·49 (16)
O(2)	−0·2753 (5)	−0·4550 (4)	0·1648 (3)	2·55 (16)
O(3)	0·3234 (6)	−0·5866 (4)	0·1902 (3)	3·56 (19)
O(4)	−0·0926 (5)	−0·5355 (4)	0·0054 (3)	3·31 (18)
O(5)	0·3597 (5)	0·0611 (4)	0·7730 (3)	2·65 (17)
O(6)	0·3244 (5)	0·0409 (4)	0·5703 (3)	2·54 (15)
O(7)	0·8419 (6)	−0·1050 (4)	0·8539 (3)	3·53 (20)
O(8)	0·8315 (6)	0·0149 (5)	0·6659 (3)	3·82 (20)
C(1)	−0·0282 (6)	−0·4694 (4)	0·2229 (3)	1·73 (18)
C(2)	0·1030 (7)	−0·4776 (4)	0·1340 (3)	1·99 (19)
C(3)	0·4546 (6)	0·0464 (4)	0·6960 (3)	1·65 (17)
C(4)	0·7596 (7)	0·0348 (5)	0·7664 (3)	1·93 (19)
H(1)	0·150 (7)	−0·365 (4)	0·120 (3)	1·4 (7)
H(2)	0·835 (8)	0·133 (6)	0·820 (4)	3·3 (9)
H(3)	0·489 (13)	−0·522 (7)	0·228 (7)	7·6 (16)
H(4)	0·007 (10)	−0·522 (6)	−0·048 (5)	4·5 (10)
H(7)	1·032 (11)	−0·060 (6)	0·936 (6)	6·7 (13)
H(8)	1·041 (11)	0·023 (6)	0·704 (6)	5·3 (11)

* Held fixed.

1·96σ(*I*); 281 reflexions considered unobserved for (I), 447 for (II). For both crystals an absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) applied on isotropically refined data; min. and max. absorption corrections 0·846 and 1·123 for (I) and 0·812 and 1·313 for (II). The symmetry-related reflexions for (II) were averaged after *DIFABS* to give 1686 unique reflexions; $R_{int}(wF^2) = 0·020$. Refinement of (II) gave final $R = 0·037$ and $wR = 0·032$; $w = 1/\sigma^2(F_o)$; maximum $\Delta/\sigma = 0·01$. For (I) the refinement based on hkl and $\overline{hkl}$ reflexions gave final $R = 0·036$ and $wR = 0·033$ (the refinement of the parameters for the inverted structure gave $R = 0·038$ and $wR = 0·036$); maximum $\Delta/\sigma = 0·13$. $(\Delta\rho)_{max}$ in final difference syntheses was 0·5 and 0·6 e Å^{-3} for (I) and (II) respectively. The final atomic parameters for (I) and (II) are given in Tables 1 and 2.*

Discussion. Crystals of (I) and (II) consist of dihydroxyacetate anions and potassium or rubidium cations respectively. The principal distances and bond and torsion angles are given in Table 3 for (I) and in Table 4 for (II). The crystal packing and the atom-numbering scheme are shown in Figs. 1 and 2.

In (I) there are two crystallographically independent dihydroxyacetate anions which differ in the conformation about the C—C bond. In the anions containing C(3) a tendency is observed for one [O(8)] of the two *gem*-hydroxylic O atoms to lie in the plane of the

Table 2. *The final atom coordinates and isotropic thermal parameters of rubidium dihydroxyacetate*

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	y	z	B_{eq} or B_{iso}(Å^2)
Rb	0·06800 (8)	0·14291 (3)	0·17229 (6)	2·01 (2)
O(1)	0·7373 (6)	0·3164 (3)	−0·0041 (5)	2·40 (23)
O(2)	0·9067 (5)	0·4247 (3)	0·2409 (5)	2·17 (22)
O(3)	0·4978 (6)	0·3649 (3)	0·4433 (5)	2·52 (23)
O(4)	0·3053 (6)	0·3572 (3)	0·1030 (5)	2·38 (22)
C(1)	0·7277 (7)	0·3784 (3)	0·1477 (6)	1·29 (25)
C(2)	0·4945 (8)	0·4019 (4)	0·2339 (6)	1·31 (25)
H(2)	0·472 (7)	0·480 (4)	0·249 (6)	1·3 (9)
H(3)	0·556 (9)	0·278 (4)	0·436 (8)	3·4 (11)
H(4)	0·150 (14)	0·369 (7)	0·136 (11)	11·5 (27)

Table 3. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and potassium coordination distances* (*average e.s.d.* 0·01 Å) *in compound* (I)

C(1)—O(1)	1·258 (4)	C(3)—O(5)	1·257 (4)
C(1)—O(2)	1·245 (5)	C(3)—O(6)	1·247 (3)
C(2)—O(3)	1·389 (5)	C(4)—O(7)	1·385 (4)
C(2)—O(4)	1·408 (4)	C(4)—O(8)	1·414 (5)
C(1)—C(2)	1·546 (5)	C(3)—C(4)	1·534 (5)

O(1)—C(1)—O(2)	126·2 (4)	O(5)—C(3)—O(6)	126·0 (3)
O(1)—C(1)—C(2)	116·1 (3)	O(5)—C(3)—C(4)	115·4 (3)
O(2)—C(1)—C(2)	117·7 (3)	O(6)—C(3)—C(4)	118·5 (3)
O(3)—C(2)—O(4)	111·4 (3)	O(7)—C(4)—O(8)	111·6 (3)
O(3)—C(2)—C(1)	111·1 (3)	O(7)—C(4)—C(3)	108·4 (3)
O(4)—C(2)—C(1)	107·3 (3)	O(8)—C(4)—C(3)	108·0 (3)

O(1)—C(1)—C(2)—O(3)	36·2 (5)	O(5)—C(3)—C(4)—O(7)	57·6 (7)
O(1)—C(1)—C(2)—O(4)	158·1 (4)	O(5)—C(3)—C(4)—O(8)	178·7 (5)
O(2)—C(1)—C(2)—O(3)	−145·2 (5)	O(6)—C(3)—C(4)—O(7)	−122·5 (7)
O(2)—C(1)—C(2)—O(4)	−23·3 (5)	O(6)—C(3)—C(4)—O(8)	−1·5 (5)

K(1)	O(1^i)	2·72	K(2)	O(1^{iii})	2·83
	O(2^{ii})	2·82		O(2^v)	2·79
	O(3^{iii})	3·21		O(3^{iii})	2·74
	O(4^{ii})	2·74		O(4^v)	3·02
	O(5^{iv})	2·70		O(5^i)	2·89
	O(6^i)	2·83		O(6^{ii})	2·78
	O(8^i)	2·75		O(7^i)	2·79
				O(8^{vi})	3·00

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

Table 4. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and rubidium coordination distances* (*average e.s.d.* 0·01 Å) *in compound* (II)

C(1)—O(1)	1·261 (5)	C(2)—O(3)	1·418 (5)
C(1)—O(2)	1·269 (5)	C(2)—O(4)	1·410 (5)
C(1)—C(2)	1·514 (5)	C(2)—H(2)	1·02 (4)

O(1)—C(1)—O(2)	124·1 (4)	O(3)—C(2)—O(4)	110·9 (4)
O(1)—C(1)—C(2)	121·0 (4)	O(3)—C(2)—C(1)	110·6 (4)
O(2)—C(1)—C(2)	114·9 (4)	O(4)—C(2)—C(1)	109·9 (4)

O(1)—C(1)—C(2)—O(3)	114·8 (8)	O(2)—C(1)—C(2)—O(3)	−64·6 (8)
O(1)—C(1)—C(2)—O(4)	−8·0 (7)	O(2)—C(1)—C(2)—O(4)	172·6 (6)

Rb	O(1^i)	3·05	Rb	O(1^{iii})	2·98
	O(2^{iii})	2·86		O(2^{iv})	2·94
	O(3^{iv})	3·40		O(3^v)	2·97
	O(4)	3·11		O(4^{vi})	2·93

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

carboxyl group. A similar conformation occurs in the crystal of (II) and was earlier observed in crystalline dihydroxyacetic acid (Lis, 1983). The conformation of the anions containing C(1) is such that both hydroxylic O atoms are displaced from the carboxylate plane in the same direction. Thus the conformation of these anions is similar to the ideal conformation of the type observed in the Na salt (Mattes & Uckelmann, 1981), where the dihydroxyacetate anions are situated on a mirror plane. It should be noted that the third possible kind of conformation in which the hydroxyl O atoms are situated on opposite sides of the carboxylate plane is not observed in dihydroxyacetates.

The C—C bond lengths lie between 1·514 (5) and 1·546 (5) Å and the C—O(H) bond lengths are between 1·385 (4) and 1·418 (5) Å. All these values are comparable to those found earlier in dihydroxyacetic acid and its Na salt. There is no observed simple correlation between the kind of conformation about the C—C bond and the C—C or C—O bond lengths and C—C—O(H) bond angles. The differences in the (H)O—C—O(H) bond angles, which are between 110·9 (4) and 111·6 (3)°, do not exceed the limits of 3σ.
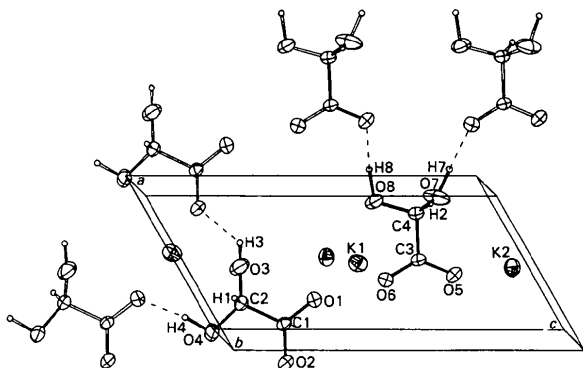

Fig. 1. View of the crystal structure of potassium dihydroxyacetate. Hydrogen bonds are denoted by dashed lines.
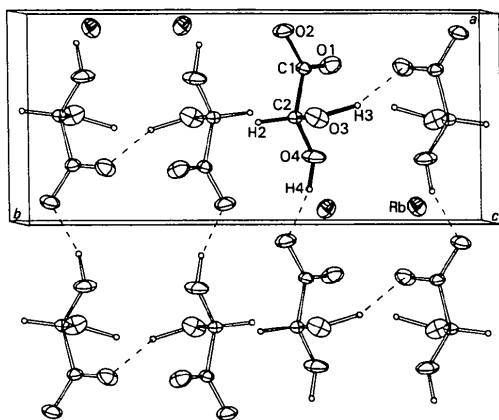

Fig. 2. View of the crystal structure of rubidium dihydroxyacetate. Hydrogen bonds are denoted by dotted lines.

Table 5. *Geometry of the hydrogen bonds for crystals (I) and (II)*

O—H···O	O···O	O—H	H···O	∠O—H···O
Compound (I)				
O(3)—H(3)···O(2ⁱ)	2·682 (4) Å	0·97 (8) Å	1·91 (8) Å	134 (6)°
O(4)—H(4)···O(1ⁱⁱ)	2·677 (4)	1·03 (6)	1·66 (6)	170 (5)
O(7)—H(7)···O(6ⁱⁱⁱ)	2·695 (4)	1·09 (7)	1·63 (7)	166 (6)
O(8)—H(8)···O(5ⁱ)	2·690 (4)	1·07 (7)	1·63 (7)	171 (6)

Symmetry code: (i) $x+1, y, z$; (ii) $x, -y-1, z-\frac{1}{2}$; (iii) $1+x, -y, \frac{1}{2}+z$.

Compound (II)				
O(3)—H(3)···O(1ⁱ)	2·698 (5)	1·17 (5)	1·61 (5)	152 (4)
O(4)—H(4)···O(2ⁱⁱ)	2·655 (4)	0·94 (9)	1·75 (9)	161 (8)

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x-1, y, z$.

In (I) there are two crystallographically different K⁺ ions. K(1) is coordinated by six O atoms at distances of 2·699 (3)–2·826 (3) Å, forming a strongly distorted octahedron; the seventh position at a distance 3·21 (1) Å is occupied by O(3). K(2) is surrounded by eight O atoms at distances of 2·739 (3)–3·022 (3) Å, which form a distorted square antiprism. The Rb⁺ ions in (II) are coordinated by eight O atoms at distances 2·86 (1)–3·40 (1) Å which form a rather irregular shape.

Both crystals are stabilized by intermolecular hydrogen bonds. The data on these bonds for both crystals are listed in Table 5. All the hydroxylic H atoms participate in hydrogen bonding; there is a single hydrogen bond to each of the carboxylate O atoms. In (II) the O(4) atoms as donors form infinite strings along **a** with the O(2) atoms, as shown in Fig. 2. These strings are connected by hydrogen bonds between O(3) (donor) and O(1) (acceptor) atoms giving two-dimensional nets. In (I) two crystallographically different anions form two independent two-dimensional hydrogen-bonded nets. The O(3) [O(8)] atoms are linked to the O(2) [O(5)] atoms by a cell translation along **a** forming infinite chains. These chains are connected by hydrogen bonds between O(4) [O(7)] (donor) and O(1) [O(6)] (acceptor) along **c**. These two kinds of layers are separated by $\frac{1}{2}$**b**.

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