

The Crystal Structure of Rubidium Oxalate Monohydrate, $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$

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The crystal structure of rubidium oxalate monohydrate has been determined from three-dimensional X-ray diffraction data. The rubidium oxalate monohydrate is isomorphous with the corresponding potassium salt.

The compound crystallizes in the monoclinic system, space group $C2/c$, with four $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ groups in a unit cell of dimensions:

$$a = 9.662 \text{ \AA}, b = 6.350 \text{ \AA}, c = 11.088 \text{ \AA}, \beta = 109.4^\circ$$

The water molecule, situated on a two-fold axis, is found to have an approximately planar coordination of four nearest neighbors, two oxalate oxygens at a distance of $2.785 \pm 0.019 \text{ \AA}$, and two rubidium ions at a distance of $3.027 \pm 0.016 \text{ \AA}$, the angle $\text{O}_1\text{-O}_{\text{water}}\text{-O}_1'$ is $126.2 \pm 0.7^\circ$. The rubidium ion displays distorted dodecahedral eight-coordination. The coordination group comprises seven oxalate oxygens and one water oxygen. The Rb-O distances range from $2.946 \pm 0.016 \text{ \AA}$ to $3.215 \pm 0.016 \text{ \AA}$. The oxalate ion is centrosymmetric and planar. The C-O distances are $1.271 \pm 0.026 \text{ \AA}$ and $1.272 \pm 0.026 \text{ \AA}$. The C-C distance is $1.58 \pm 0.04 \text{ \AA}$, and the angle O-C-O is $125.2 \pm 1.5^\circ$.

As a part of an investigation of the hydrates of the alkalimetal oxalates with X-ray diffraction and proton magnetic resonance methods, we have determined the crystal structure of rubidium oxalate monohydrate. The rubidium oxalate monohydrate is isomorphous with the corresponding potassium salt,¹ as pointed out by Hendricks.²

EXPERIMENTAL

Rubidium oxalate monohydrate crystallizes from a water solution in the form of small diamond shaped plates. The intensity data consisted of multiple film zero-, first-, second-, third-, and fourth-layer equi-inclination Weissenberg-diagrams taken rotating about the b -axis (plate-diagonal), and using Ni-filtered $\text{CuK}\alpha$ radiation. The intensities were estimated visually, and corrected in the usual way for Lorentz and polarisation effects, but not for absorption and extinction. The appearance of the spots on the higher level Weissenberg-diagrams were allowed for using a method described by Philips.³ Analytical constants for the atomic scattering factors derived for $\text{CuK}\alpha$ radiation, given by Moore,⁴ are used throughout the calculation. The unit cell dimensions were

determined from oscillation- and Weissenberg-diagrams, and refined by Guinier powder patterns using $\text{CuK}\alpha_1$ radiation. The values are:

$$a = 9.662 \text{ \AA}, b = 6.350 \text{ \AA}, c = 11.088 \text{ \AA}, \beta = 109.4^\circ$$

The compound crystallizes in the monoclinic system, space group $C2/c$ with four $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in the unit cell.

STRUCTURE DETERMINATION

From the Weissenberg data the (010) Patterson projection was worked out, showing great resemblance to the corresponding Patterson map for potassium oxalate monohydrate. Because of the isomorphism with potassium oxalate monohydrate,¹ refinement in the $h0l$ -projection was started immediately. The parameters for the rubidium atom were determined from the Patterson map. For all the lighter atoms, however, parameters found in $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ were used as initial values. The parameters were refined by Fourier syntheses and by difference syntheses, where the contribution from the rubidium ions to the structure factors had been subtracted. Also a two-dimensional least squares refinement was undertaken, resulting in reliability index $R = 0.10$. Further three-dimensional full matrix least squares refinement¹¹ was carried out, introducing anisotropic thermal parameters for the different atoms. The resulting reliability index $R = 0.102$. The final parameter values and their standard deviations are given in Table 1. In Table 2 the anisotropic thermal parameters are listed with their standard deviations. Interatomic distances and angles calculated from the final parameter values are given in Table 3.*

Table 1. Final positional parameters and their standard deviations in parentheses, as fractions of the cell edges.

	<i>x</i>	<i>y</i>	<i>z</i>
Rb ⁺	0.1290 (0.0001)	0.8156 (0.0005)	0.1297 (0.0001)
O ₁	0.1335 (0.0011)	0.2748 (0.0037)	0.0933 (0.0013)
O ₂	0.3262 (0.0015)	0.4768 (0.0027)	0.0940 (0.0011)
O _w	0.0000	0.4733 (0.0040)	0.2500
C	0.2396 (0.0023)	0.3216 (0.0038)	0.0546 (0.0017)

* A complete set of observed and calculated structure factors may be obtained upon application to the author.

Table 2. Anisotropic thermal parameters β_{ij} and their standard deviations in parentheses. The expression used is: $\exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb ⁺	0.0118 (0.0003)	0.0243 (0.0020)	0.0067 (0.0002)	0.0012 (0.0006)	0.0066 (0.0004)	0.0018 (0.0004)
O ₁	0.0114 (0.0014)	0.0146 (0.0071)	0.0111 (0.0013)	-0.0118 (0.0052)	0.0136 (0.0022)	-0.0094 (0.0052)
O ₂	0.0164 (0.0020)	0.0121 (0.0089)	0.0071 (0.0010)	0.0028 (0.0049)	0.0091 (0.0022)	-0.0048 (0.0036)
O _w	0.0300 (0.0043)	0.0000 (0.0116)	0.0122 (0.0023)		0.0243 (0.0056)	
C	0.0185 (0.0029)	0.0199 (0.0163)	0.0058 (0.0015)	0.0057 (0.0081)	0.0074 (0.0034)	-0.0048 (0.0050)

DISCUSSION OF THE STRUCTURE

The packing relation in Rb₂C₂O₄·H₂O is similar to the one found in K₂C₂O₄·H₂O. The two oxygen atoms situated closest to the water molecule, O₁ and O₁', are at a distance of 2.785 ± 0.019 Å from the water molecule. The corresponding distance found in K₂C₂O₄·H₂O is 2.746 ± 0.011 Å. This apparent difference between the two hydrogenbond lengths, 0.039 Å, is probably not significant, being only 1.8 times the e.s.d. according to the criteria given by Cruickshank.⁵

Table 3. Interatomic distances and valence angles \pm standard deviations.

Distances in the oxalate ion:

C—O ₁ = 1.271 ± 0.026 Å	< C—C—O ₁ = $116.6 \pm 1.7^\circ$
C—O ₂ = 1.272 ± 0.026 Å	< C—C—O ₂ = $118.2 \pm 1.7^\circ$
C—C = 1.58 ± 0.04 Å	< O ₁ —C—O ₂ = $125.2 \pm 1.5^\circ$

Hydrogen bond distance:

O _w —O ₁ = 2.785 ± 0.019 Å
< O ₁ —O _w —O ₁ ' = $126.2 \pm 0.7^\circ$

Interionic distances:

Rb—O ₁ = 2.946 ± 0.016 Å	Rb—O ₂ = 2.999 ± 0.016 Å
Rb—O ₁ = 2.950 ± 0.016 Å	Rb—O ₂ = 2.965 ± 0.016 Å
Rb—O ₁ = 3.215 ± 0.016 Å	Rb—O ₂ = 3.121 ± 0.016 Å
Rb—O ₂ = 2.986 ± 0.016 Å	Rb—O _w = 3.027 ± 0.016 Å

The angle O₁—O_{water}—O₁', however, is $126.2 \pm 0.7^\circ$ in rubidium oxalate monohydrate, whereas the corresponding angle for the potassium salt is $119.7 \pm 0.6^\circ$, showing that there is a significant change in this angle on going from potassium- to rubidium-oxalate monohydrate. This result supports the findings by Pedersen,⁶ that the H—H distance in the water molecule is significantly longer in rubidium oxalate monohydrate than in the potassium salt.

The angle between the $O_1-O_w-O_1'$ plane and the c -axis is determined to 29.5° . Pedersen⁶ has found an angle of 26° between the proton-proton line and the c -axis. Hence, the proton magnetic resonance results support the conclusion that the water molecule forms hydrogen bonds to O_1 and O_1' .

The same coordination around the water molecule is found in the two compounds, an approximately planar arrangement of four nearest neighbors, two oxalate oxygens, O_1 and O_1' , at a distance of 2.785 ± 0.019 Å, and two rubidium ions at a distance of 3.027 ± 0.016 Å.

The oxalate ion is found to be centro-symmetric and planar within the experimental uncertainty. The equation to the plane through O_1 , O_2 , and the centre of symmetry ($\frac{1}{2}$, $\frac{1}{2}$, 0) is: $x - 0.9499 y + 1.5016 z - 0.0125 = 0$, and the C atom is 0.02 Å out of this plane. From the data in Table 3 it is seen that the observed distances and angles in the oxalate ion are in good agreement with recent investigations on other oxalates.^{1,7,8} The same distortions from the regular ion is found: the C—C bond being long, 1.58 ± 0.04 Å, and the angle O_1-C-O_2 being larger than 120° , $125.2 \pm 1.5^\circ$.

The rubidium ion is surrounded by eight nearest neighbors, seven oxalate oxygens, and one water oxygen in a dodecahedral arrangement. The rubidium-oxygen distances range from 2.946 ± 0.016 Å to 3.215 ± 0.016 Å (mean value 3.026 Å), which compares well with earlier investigations where Rb—O distances from 2.90 Å—3.20 Å are observed.⁹ The mean value of the Rb—O distances is 0.15 Å longer than the corresponding K—O distance. This difference of 0.15 Å is just what one would predict from several sets of the atomic radii.¹⁰

The rubidium ions interconnect the oxalate ions to produce a relatively tight three-dimensional network.

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