

Refinement of the Crystal Structure of Potassium Oxalate Monohydrate, $K_2C_2O_4 \cdot H_2O$

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The crystal structure of potassium oxalate monohydrate has been refined from three-dimensional X-ray diffraction data. The compound crystallizes in the monoclinic system, space group $C2/c$ with four $K_2C_2O_4 \cdot H_2O$ groups in a unit cell of dimensions:

$$a = 9.21 \text{ \AA}, \quad b = 6.165 \text{ \AA}, \quad c = 10.66 \text{ \AA}, \quad \beta = 110.9^\circ$$

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 $2.746 \pm 0.011 \text{ \AA}$, and two potassium atoms at a distance of $2.904 \pm 0.008 \text{ \AA}$. The potassium ion displays distorted dodecahedral eight-coordination. The coordination group comprises seven oxalate oxygens and one water oxygen. The K-O distances range from $2.745 \pm 0.008 \text{ \AA}$ to $3.015 \pm 0.008 \text{ \AA}$. The oxalate ion is centrosymmetric and planar. The C-O distances are $1.238 \pm 0.011 \text{ \AA}$ and $1.247 \pm 0.011 \text{ \AA}$. The C-C distance is $1.585 \pm 0.015 \text{ \AA}$, and the angle O-C-O is $126.4 \pm 0.7^\circ$.

In a recent proton magnetic resonance investigation of $K_2C_2O_4 \cdot H_2O$ by Pedersen and Holcomb,¹ the water molecule was found to be differently oriented than proposed by Hendricks² in an X-ray diffraction study from 1935. If the orientation of the water molecule is changed in Hendricks' structure, however, to conform to the proton magnetic resonance result, the coordination around the water molecule becomes rather unusual. As the work by Hendricks is not particularly accurate, it was found worth while to try to refine the structure of $K_2C_2O_4 \cdot H_2O$ from three-dimensional X-ray diffraction data. The interatomic distances and angles in the oxalate ion, as given by Hendricks, deviate significantly from more recent values, and this suggests that the atomic positions found are, at best, rather inaccurately determined. The result of the refinement to be reported in this paper shows that the structure proposed by Hendricks is correct in coarse features only. The interatomic distances given by Hendricks deviate markedly from the ones to be given in this paper. The most striking parameter change is in the y -parameter of the water molecule, the difference between Hendricks' and our value being 0.6 \AA .

THE REFINEMENT

Our X-ray data were obtained from multiple film Weissenberg diagrams taken rotating about the b -axis and using $\text{CuK}\alpha$ radiation. The intensities of zero, first, second, third, and fourth layers were estimated visually and corrected in the usual way for Lorentz- and polarization effects, but not for absorption and extinction. The appearance of the spots on the higher level Weissenberg diagrams were allowed for using the method described by Philips.³ Analytical constants for the atomic scattering factors derived for $\text{CuK}\alpha$ radiation, given by Moore,⁴ were used throughout the calculations.

The found dimensions of the unit cell, containing four formula units, were:

$$a = 9.21 \text{ \AA}, b = 6.165 \text{ \AA}, c = 10.66 \text{ \AA}, \beta = 110.9^\circ.$$

These values are in accordance with Hendricks' values:

$$a = 9.32 \text{ \AA}, b = 6.17 \text{ \AA}, c = 10.65 \text{ \AA}, \beta = 110^\circ 58'.$$

As judged from systematic absences, two space groups are possible, $C2/c$ and Cc . Hendricks chose the space group with highest symmetry $C2/c$, and proposed a structure which gave fair agreement with the observed intensities. Unusual dimensions of the oxalate ion suggest low accuracy of the atomic positions of the lighter atoms. As the cations give the dominant contribution to the X-ray reflection intensities, the agreement between the observed and calculated intensities indicates that the cations are approximately arranged according to the space group $C2/c$. However, Jeffrey and Parry⁵ point out that there is no evidence that the configuration of oxalate ions and water molecules have the same symmetry, and the space group assignment must be regarded as inconclusive.

The difference between the two space groups is the set of two-fold axes parallel to the b -axis. In $C2/c$ the oxalate ion must have a centre of symmetry and the water molecules must be located on the twofold axes, whereas in Cc there are no symmetry restrictions.

Pedersen and Holcomb,¹ from their proton magnetic resonance data, find all intramolecular proton-proton vectors to be parallel and oriented normal to the b -axis, and hence conclude that the water molecules sit on two-fold axes. This supports Hendricks' choice of space group $C2/c$ as being correct. Therefore the refinement of the structure of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was started on this basis. As shown below, the structure refined satisfactorily assuming this space group.

The refinement was started in the $h0l$ projection, using Hendricks' parameter values as initial values. The parameters for the different atoms were refined by Fourier syntheses and by difference syntheses where the contribution from the potassium atom to the structure factors had been subtracted. Further, a two dimensional least squares refinement was undertaken, resulting in a reliability index, $R = 0.13$. There are heavy overlap of the potassium atom and one of the oxalate oxygens in this projection, and therefore the parameter values for these atoms are not particularly accurate. The values were, however, used as starting point for the three-dimensional refinement. Initial values for the y -parameters for all atoms, except hydrogen,

were estimated from reasonable distances and Hendricks' parameter values. In the first cycles of three-dimensional least squares refinement all parameters, except the y -values, the thermal parameters, and the scale factors, were kept constant. In the next cycles the parameters of all atoms except hydrogen were refined, the reliability index at this stage being 0.128. Further refinement was performed introducing individual anisotropic thermal parameters, resulting in reliability index $R = 0.103$. At this stage of the structure determination the hydrogen atom was included in the calculation of structure factors. Trials

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

	x	y	z
K ⁺	0.1316 (0.0002)	0.8312 (0.0005)	0.1320 (0.0002)
O ₁	0.1272 (0.0009)	0.2713 (0.0015)	0.0915 (0.0007)
O ₂	0.3204 (0.0009)	0.4874 (0.0017)	0.0929 (0.0007)
O _w	0.0000	0.4951 (0.0025)	0.2500
C	0.2352 (0.0011)	0.3251 (0.0021)	0.0546 (0.0008)
H	0.035 (0.015)	0.398 (0.026)	0.180 (0.013)

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}
K ⁺	0.0074 (0.0003)	0.0107 (0.0012)	0.0021 (0.0002)	0.0000 (0.0007)	0.0018 (0.0004)	0.0005 (0.0005)
O ₁	0.0085 (0.0009)	0.0080 (0.0031)	0.0040 (0.0006)	-0.0041 (0.0026)	0.0085 (0.0011)	-0.0061 (0.0021)
O ₂	0.0099 (0.0010)	0.0153 (0.0037)	0.0032 (0.0006)	-0.0073 (0.0028)	0.0039 (0.0013)	-0.0046 (0.0021)
O _w	0.0186 (0.0022)	0.0107 (0.0053)	0.0064 (0.0012)		0.0137 (0.0026)	
C	0.0070 (0.0013)	0.0177 (0.0059)	0.0015 (0.0007)	-0.0005 (0.0034)	0.0012 (0.0015)	0.0031 (0.0026)

Final B value in the isotropic thermal parameter, $\exp-(B \sin^2\theta/\lambda^2)$, for the hydrogen atom is 0.2 Å².

to locate the hydrogen atom from a difference map failed. The assumed hydrogen atom position was therefore calculated from the water molecule arrangement deduced from proton magnetic resonance results. It was also decided to try to refine the hydrogen atom parameters. The effect on the R -value was small, however, it dropped to 0.101, but the standard deviation of the hydrogen atom parameters decreased during the refinement.

The final parameter values and their standard deviations as fractions of the cell edges are given in Table 1. In Table 2 the anisotropic thermal parameters

Table 3. Mean square vibrational displacements along the principal axes, and the components in Å of unit principal axes vectors (1 Å) along the direct cell edges.

	principal axes	m.s.d. $\langle \bar{u}^2 \rangle$	x	principal axis components	z
				y	
K ⁺	1	0.0298	1.0030	0	0.0085
	2	0.0204	0	1	0
	3	0.0106	0.3925	0	1.1100
O ₁	1	0.0369	0.9055	-0.3598	0.7166
	2	0.0164	-0.5602	-0.7022	0.2833
	3	0.0059	-0.1096	0.6147	0.7430
O ₂	1	0.0434	0.8911	-0.5463	0.2215
	2	0.0265	-0.4521	-0.7367	0.3664
	3	0.0130	0.3844	0.3985	0.9810
O _w	1	0.0679	1.0630	0	0.4960
	2	0.0236	-0.1110	0	0.9547
	3	0.0199	0	1	0
C	1	0.0329	0	1	0
	2	0.0318	-0.9459	0	0.1299
	3	0.0073	0.3776	0	0.8010

Table 4. Interatomic distances and valence angles \pm standard deviation.

Distances in the oxalate ion:



Hydrogen bond distance: O_w-O₁ = 2.746 \pm 0.011 Å

Distance in the water molecule:



Interionic distances:



are listed with their standard deviations. From the anisotropic thermal parameter values in Table 2 the mean square atomic displacements of the different atoms along their principal axes were calculated, using formulae developed by Busing and Levy.⁶ Also the directions of the principal axes relative to the crystallographic axes were calculated, and the results of these calculations are given in Table 3. The interatomic distances and angles calculated from the final parameters are given in Table 4.*

DISCUSSION

Inspection of the data presented in Table 3 reveals that some anisotropy of the motion of the different atoms is evident. However, great care should be exercised in the interpretation, as the present intensity data have been determined only from visual estimation of non-integrated films. For the oxalate ion, the data in Table 3 seem to indicate that the most pronounced rigid body oscillation is about the C—C bond, in accordance with the findings of Beagley and Small⁷ for the oxamate ion. This shows that the unexpectedly long C—C distance can not be explained as being due to anisotropic motion of the kind discussed by Cruickshank.⁸

The packing relations in $K_2C_2O_4 \cdot H_2O$ are displayed in Fig. 1. No direct evidence on the positions of the hydrogen atoms can be given from this work.

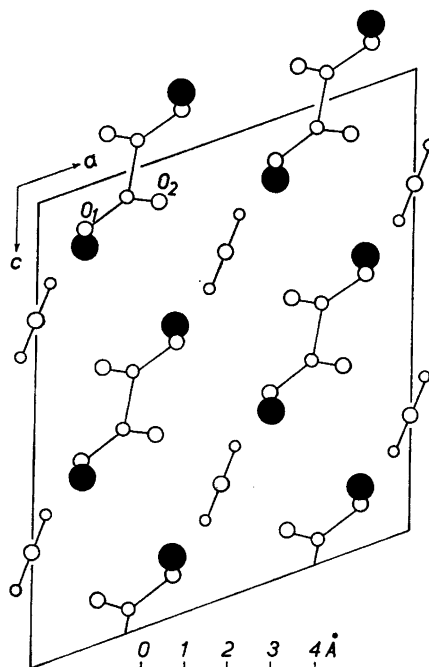


Fig. 1. Packing relations in $K_2C_2O_4 \cdot H_2O$ illustrated in projection upon (010).

* A complete set of amplitude data may be obtained upon application to the author.

The present work shows that the oxygen atoms situated closest to the water molecule, O_1 and O_1' , are at a distance of 2.746 Å from the water oxygen, which is a normal hydrogen bond distance. Further, the angle $O_1-O_{\text{water}}-O_1'$ is 119.7° showing that the water molecule can form two approximately linear hydrogen bonds to O_1 and O_1' . The angle between the $O_1-O_w-O_1'$ plane and the c -axis is 27° . Pedersen and Holcomb¹ found an angle of 22° between the proton-proton line and the c -axis. Hence, the proton magnetic resonance results support the conclusion that the water molecule forms two hydrogen bonds to O_1 and O_1' . It is not at present possible to decide if the water molecule really is twisted somewhat out of the $O_1-O_w-O_1'$ plane, as the results seem to indicate, as the uncertainty in the P.M.R. angle is not known.

Hendricks² claims that the water molecule is tetrahedrally surrounded by two potassium ions and the two oxalate oxygens O_2 and O_2' , all at a distance of 3.30 Å. The results of this investigation, however, show that the water molecules have an approximately planar coordination of four nearest neighbors, two potassium ions at a distance of 2.904 Å and the two oxalate oxygens O_1 and O_1' , at a distance of 2.746 Å. The O_2 oxygens are farther removed, the $O_{\text{water}}-O_2$ distance being 3.574 Å. The found coordination is somewhat surprising, as each water molecule in a hydrate structure usually is found to be coordinated to four nearest neighbors in a tetrahedral configuration, or more rarely to three nearest neighbors in a planar trigonal arrangement.⁹

The oxalate ion is found to be planar within the experimental uncertainty. From the data in Table 4 it is seen that the distances and angles observed are in good agreement with recent investigations on other oxalates.^{10,11} The same distortions from the expected regular ion are found: the C—C bond being long, 1.585 Å, and the angle O_1-C-O_2 being larger than 120° : 126.4° .

The potassium ion displays distorted dodecahedral eight-coordination.¹² The coordination group comprises seven oxalate-oxygens and one water-oxygen. The potassium-oxygen distances range from 2.745 Å to 3.015 Å, (mean value 2.875 Å), which compares well with earlier investigations, where the K—O distances are found to be within 2.66 Å — 3.10 Å.¹³ The potassium ions interconnect the oxalate ions to produce staggered chains running in the b -direction, and are further bonded to oxalate ions displaced $a/2$ in the x -direction and $c/2$ in the z -direction, thus giving rise to a tight interconnected three-dimensional network.

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