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Refinement of the Crystal and Molecular Structure of Potassium Oxalate Monohydrate

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The structure of potassium oxalate monohydrate, $(\text{COOK})_2 \cdot \text{H}_2\text{O}$, has been refined by least-squares techniques based on three-dimensional X-ray data obtained at room temperature with Mo $K\alpha$ radiation. The material crystallizes with four formula units in space group $C2/c$ of the monoclinic system in a cell with dimensions $a=9.222$ (3), $b=6.197$ (2), $c=10.690$ (5) Å, $\beta=110.70$ (3)°. The conventional R value on F is 0.039 and the estimated standard deviations of atomic coordinates are of the order 0.001 Å. There is a hydrogen bond, 2.760 (2) Å in length, between one of the oxalate oxygen atoms and the water molecule; the other oxygen atom does not participate in hydrogen bonding. The carboxyl groups are not symmetric, the bond between carbon and the hydrogen bonded oxygen atom being 1.260 (2) Å and the other C–O bond being 1.247 (2) Å. The central carbon–carbon bond is long – 1.574 (2) Å – and residual electron density of 0.26 e.Å⁻³ is found in the center of this bond.

Introduction

The structure of potassium oxalate monohydrate, $(\text{COOK})_2 \cdot \text{H}_2\text{O}$, has been previously investigated by

three-dimensional X-ray (Hendricks, 1935; Pedersen, 1964) and two-dimensional neutron diffraction (Chidambaram, Sequeira & Sikka, 1964), and also by proton magnetic resonance techniques (McGrath & Paine,

1964; Pedersen, 1966). A proton-proton distance of 1.5341 (15) Å, deduced from proton magnetic resonance studies (Pedersen, 1966), is consistent with the value of 1.557 (28) Å obtained from the neutron diffraction study of Chidambaram *et al.* (1964). One unusual feature of the hydrogen bonding scheme reported (Chidambaram *et al.* 1964) is that neither of the non-bonding electron pairs of the water oxygen atom nor their bisectors are directed towards the neighboring potassium cations. The crystal structure proposed involves infinite linear $\text{H}_2\text{O}-\text{C}_2\text{O}_4^{2-}-\text{H}_2\text{O}-\text{C}_2\text{O}_4^{2-}$ chains along $[10\bar{1}]$, which are linked at non-bonding distances with the potassium cations.

There are considerable differences in the bond lengths reported in various studies of the compound. The C-C bond length of 1.585 (15) Å in the oxalate fragment reported by Pedersen (1964) differs from the value of 1.555 (12) Å reported by Chidambaram *et al.* (1964). Moreover, there is doubt as to whether there is a significant difference between the two C-O bond lengths in the oxalate anion, and which, if either, is the longer. In order to resolve these differences and to reinvestigate the hydrogen bonding scheme, an accurate three-dimensional single crystal X-ray structural determination was undertaken; the results of this investigation are presented here.

Experimental

Potassium oxalate monohydrate (J. T. Baker, Reagent) was recrystallized from aqueous solution. A crystal specimen of the shape of a parallelepiped of dimensions 0.053 by 0.054 by 0.0091 cm was chosen, and mounted about the c^* axis. Preliminary examination on the precession camera confirmed the previous space group assignment of $C2/c$ or Cc . The space group $C2/c$ was assumed, and was confirmed by the structure analysis. Intensity data were collected on a Picker four-circle automatic diffractometer using Mo $K\alpha$ radiation. The mosaicity of the crystal specimen, as judged by the narrow-source, open-counter ω scan through several strong reflections, was acceptably low (Furnas, 1957).

Fifteen reflections were accurately centered using a very narrow vertical slit at a take-off angle of 0.55° ; these observations formed the basis for the least-squares refinement of cell parameters and orientation. The refinement was effected in our program *PICK* de-

scribed earlier (Corfield, Doedens & Ibers, 1967). The observations were made at 24°C with the wavelength assumed as $\lambda_{\text{Mo } K\alpha_1} = 0.7093 \text{ \AA}$. The cell parameters so derived, together with their associated standard deviations, are compared with the previously reported values in Table 1.

Intensity data were collected at a take-off angle of 1.0° ; at this angle, the peak intensity of a typical strong reflection was 75% of the maximum value as a function of take-off angle. The use of a small take-off angle, while decreasing the integrated count, ensures adequate resolution and allows a smaller scan range. The receiving aperture size selected to minimize extraneous background was 4.0 mm high by 4.0 mm wide; the aperture was positioned 21 cm from the crystal. The data were collected by the $\theta-2\theta$ scan technique at a scan rate of 1.0 degrees/minute. The scan range for relatively close-in reflections (those with 2θ less than 55°) was 1.3° in 2θ , from -0.50 to $+0.80^\circ$ from the calculated 2θ value; the scan range for relatively far-out reflections (those with 2θ greater than 55°) was 2.0° in 2θ , from -0.80 to $+1.20^\circ$ from the calculated 2θ value. Stationary counter background counts of 10 seconds were taken at each end of the scan. The Mo $K\alpha$ beam was filtered through 4.5 mil Zr foil after diffraction from the crystal; this thickness of Zr foil reduces the intensity of Mo $K\beta$ radiation by approximately 99.4% (Roberts & Parrish, 1962). Attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/second during the scan; the attenuators used were copper foils, their thickness being chosen to give attenuator factors of approximately 2.3. These attenuator factors were determined by recording the time taken for 10,000 counts to be observed with the various attenuators in the beam. The pulse height analyzer was set for approximately a 90% window, centered on the Mo $K\alpha$ peak.

As a check on electronic and crystal stability during the period of data collection, the intensities of four standard reflections were measured after every 200 reflections. No systematic change in these standards was observed. As a further check, two equivalent members, (hkl) and $(\bar{h}\bar{k}l)$, of the form $\{hkl\}$ of this centrosymmetric monoclinic crystal were measured. A total of 3031 intensities was measured within the sphere 2θ (Mo $K\alpha_1$) $\leq 75.00^\circ$. Past this point only a small fraction of the intensities was significantly above background.

Table 1. *Unit-cell dimensions* (Å)

<i>a</i>	<i>b</i>	<i>c</i>	β	Reference
9.32	6.17	10.65	110.97°	Hendricks, 1935
9.21	6.165	10.66	110.9	Pedersen, 1964
9.236	6.190	10.694	110.78	Chidambaram <i>et al.</i> 1964
9.222 (3) [†]	6.197 (2)	10.690 (5)	110.70 (3)	This work

Space group: $C2/c$, No. 15. Unit cell volume: 571.5 Å³.

Density calculated: 2.14 g.cm⁻³, $Z=4$. Density observed: 2.13 g.cm⁻³.

[†] Numbers in parentheses here and elsewhere in this paper are estimated standard deviations in the least significant digits.

All data processing was carried out as previously described (Corfield, Doedens & Ibers, 1967). The data were first corrected for background; the correction made is of the form

$$I = C - \frac{t_s}{2t_b} (B_H + B_L),$$

where C is the total integrated peak count obtained in a scan of time t_s , B_H and B_L are the background counts each obtained in time t_b , and I is the corrected integrated peak count. The corrected intensities were assigned standard deviations according to the formula

$$\sigma(I) = [C + 0.25 (t_s/t_b)^2 (B_H + B_L) + (pI)^2]^{1/2}.$$

The value of p was selected as 0.06; this term in the expression is used to prevent extremely high weight being given to very strong reflections (Busing & Levy, 1957). The values of I and $\sigma(I)$ were corrected for Lorentz-polarization and for absorption factors. The absorption coefficient μ of this compound for Mo $K\alpha$ radiation is 15.6 cm^{-1} , and for the sample chosen the transmission coefficients evaluated by numerical integration were found to range from 0.54 to 0.93. The values of F^2 of equivalent reflections were then averaged; the weighted R value on F^2 for the averaging was 0.060. The standard deviation of F^2 , $\sigma(F^2)$, was taken as either the average of the individual standard deviations of the equivalent members, or a value estimated from the range of the F^2 values of the equivalent members, whichever was the larger. The total number of independent reflections thus obtained was 1518, of which 237 had intensities less than their standard deviations.

Refinement

With four formula units in $C2/c$, the water molecule is constrained to lie on the twofold axis. The independent atoms are three oxygen atoms – O(1) and O(2) of the oxalate anion, O(3) of the water molecule – one carbon atom, one potassium atom, and one hydrogen atom.

Initial values for the atomic coordinates of the five non-hydrogen atoms were taken from Pedersen (1964). After two cycles of least-squares calculations, a difference-Fourier synthesis was computed; the hydrogen

atom was unambiguously located as the largest peak on the difference map. Least-squares refinements were carried out on F ; that is, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ is the observed structure amplitude, $|F_c|$ the calculated structure amplitude, and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c , the atomic scattering factors tabulated by Ibers (1962) were used for K, O and C, and those of Stewart, Davidson & Simpson (1965) for H. No correction was made for anomalous dispersion, since this is negligible for these atoms with Mo radiation.

The non-hydrogen atoms were assigned variable anisotropic thermal parameters and the hydrogen atom was assigned a variable isotropic thermal parameter; after two cycles of least-squares refinement of the 46 variables using only the 1044 independent reflections whose intensities were more than three times their standard deviations, the usual agreement factors, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and R_2 (or weighted R factor) = $(\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$, were 0.040 and 0.049 respectively. At this stage it was apparent that secondary extinction was significant, since for very strong low-order reflections $|F_o|$ was consistently smaller than $|F_c|$. An extinction correction of the form

$$F_o^{\text{corr}} = F_o [c\beta(\theta)I + (1 + c^2\beta^2(\theta)I^2)^{1/2}]^{1/2} = gF_o,$$

strictly valid only for a spherical crystal (Zachariasen, 1968), was applied; that is, the function $\sum w(|F_o| - |F_c|/g)^2$ was minimized, where c is the extinction coefficient, I the corrected intensity, and $\beta(\theta)$ is as described by Zachariasen (1963). Two further cycles of least-squares refinement reduced R_1 and R_2 to 0.037 and 0.048 respectively. A further cycle of least-squares refinement was carried out in which the hydrogen atom was also assigned variable anisotropic thermal parameters; this had little effect on R_1 but reduced R_2 to 0.047.

Examination of the agreement factors for different ranges of $|F_o|$ and $\lambda^{-1} \sin \theta$ showed no unexpected trends. There is no dependence of R_2 on $|F_o|$. That R_2 is relatively larger for small values of $\lambda^{-1} \sin \theta$ may result from errors in the model – for example, the neglect of bonding. A final refinement, using the 1154 independent reflections whose intensities were above twice their standard deviations, led to values of 0.039

Table 2. Positional and thermal parameters for $(\text{COOK})_2 \cdot \text{H}_2\text{O}$

	x	y	z	$\beta_{11}^{a,b}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.13179 (3)	0.83039 (5)	0.13194 (3)	701 (4)	1331 (8)	427 (3)	-10 (4)	181 (3)	106 (3)
O(1)	0.1258 (1)	0.2691 (2)	0.0913 (1)	810 (10)	1710 (30)	620 (10)	-190 (20)	470 (10)	-170 (10)
O(2)	0.3196 (1)	0.4869 (2)	0.0924 (1)	900 (10)	1310 (20)	580 (10)	-260 (10)	320 (10)	-230 (10)
O(3)	0	0.4974 (3)	$\frac{1}{2}$	1960 (40)	1270 (40)	940 (20)	0	980 (30)	0
C	0.2347 (1)	0.3257 (2)	0.0532 (1)	590 (10)	1080 (20)	336 (9)	30 (10)	192 (9)	10 (10)
H	0.022 (4)	0.420 (4)	0.199 (3)	2400 (600)	1300 (800)	1200 (400)	-1000 (600)	90 (40)	40 (50)

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

^b The values of β have been multiplied by 10^5 .

Table 3. Observed and calculated structure amplitudes ($\times 10$) in electrons

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
****	K =	0	****	****	K =	1	****	7	-10	50	50	0	-5	212	195	8	-6	134	137	3	-11	34	33	0	-4	328	295	8	-5	84	84	3	-10	184	187
U	-14	48	49	1	-17	50	48	7	-9	232	237	0	-4	328	295	8	-5	84	84	3	-10	184	187	0	-3	462	393	8	-4	211	213	3	-9	35	34
U	-2	179	165	1	-16	34	36	7	-7	92	92	0	-1	532	462	8	-3	196	195	3	-8	58	55	0	0	291	252	8	-2	118	120	3	-7	84	80
U	0	0	1846	1	-15	82	83	7	-6	164	166	0	0	291	252	8	-1	125	127	3	-6	320	326	0	2	183	159	8	0	197	201	3	-5	30	31
U	4	543	647	1	-13	77	77	7	-5	154	150	0	0	77	68	8	0	120	124	3	-4	224	229	0	11	32	24	8	1	38	38	3	-3	91	89
U	6	238	246	1	-12	84	85	7	-4	151	153	0	0	101	93	8	8	38	38	3	-3	91	89	0	12	101	93	8	8	38	38	3	-3	91	89
U	8	205	217	1	-10	145	150	7	-3	18	13	0	11	32	24	8	1	120	124	3	-3	91	89	0	12	101	93	8	8	38	38	3	-3	91	89
U	10	61	61	1	-9	107	108	7	-2	90	88	0	12	101	93	8	8	38	38	3	-3	91	89	0	12	101	93	8	8	38	38	3	-3	91	89
U	12	90	95	1	-9	89	90	7	-1	119	116	2	-15	64	65	8	9	77	78	3	-2	251	255	0	16	52	50	10	-17	17	19	3	-2	124	127
U	16	52	50	1	-8	161	163	7	0	87	88	2	-13	49	50	10	-17	17	19	3	-2	124	127	0	16	52	50	10	-17	17	19	3	-2	124	127
Z	-16	53	52	1	-7	317	330	7	1	121	121	2	-12	25	24	10	-15	43	43	3	0	44	46	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-14	107	111	1	-6	70	70	7	2	99	101	2	-11	156	158	10	-14	33	33	3	0	44	46	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-12	52	52	1	-5	238	243	7	3	156	160	2	-10	134	137	10	-13	61	61	3	2	140	146	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-10	187	186	1	-4	535	557	7	4	68	73	2	-9	77	78	10	-12	21	20	3	3	87	82	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-8	165	164	1	-3	373	379	7	5	68	79	2	-8	120	121	10	-11	83	84	3	4	188	190	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-6	331	318	1	-2	86	88	7	8	23	23	2	-7	223	227	10	-10	67	66	3	5	59	57	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-4	204	194	1	-1	231	229	7	9	53	53	2	-6	231	235	10	-9	64	65	3	6	60	58	0	14	107	111	1	-6	70	70	7	2	99	101
Z	-2	373	339	1	0	145	132	7	11	36	36	2	-5	135	135	10	-8	17	16	3	8	197	211	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	285	260	1	1	101	99	7	12	24	25	2	-4	42	42	10	-7	60	62	3	9	37	35	0	14	107	111	1	-6	70	70	7	2	99	101
Z	2	940	695	1	2	214	201	9	-17	33	28	2	-3	175	181	10	-6	32	30	3	10	17	19	0	14	107	111	1	-6	70	70	7	2	99	101
Z	4	179	176	1	3	253	251	9	-16	41	40	2	-2	688	701	10	-5	106	107	3	11	21	22	0	14	107	111	1	-6	70	70	7	2	99	101
Z	6	344	340	1	4	61	64	9	-15	79	80	2	-1	378	387	10	-4	43	45	3	12	142	140	0	14	107	111	1	-6	70	70	7	2	99	101
Z	8	25	25	1	5	247	254	9	-13	19	17	2	0	76	81	10	-3	37	36	3	14	23	24	0	14	107	111	1	-6	70	70	7	2	99	101
Z	10	134	140	1	6	152	154	9	-12	56	58	2	1	260	261	10	-2	79	81	5	-16	47	49	0	14	107	111	1	-6	70	70	7	2	99	101
Z	14	78	77	1	7	198	203	9	-11	140	143	2	2	432	437	10	-1	143	147	5	-15	29	28	0	14	107	111	1	-6	70	70	7	2	99	101
Z	16	48	47	1	8	36	37	9	-10	41	41	2	3	357	364	10	0	53	58	5	-14	55	55	0	14	107	111	1	-6	70	70	7	2	99	101
Z	18	53	53	1	9	221	228	9	-9	27	25	2	4	240	240	10	3	92	93	5	-12	155	157	0	14	107	111	1	-6	70	70	7	2	99	101
Z	16	22	24	1	10	82	84	9	-8	21	21	2	5	182	184	10	4	20	19	5	-11	40	42	0	14	107	111	1	-6	70	70	7	2	99	101
Z	14	23	22	1	11	62	64	9	-7	183	185	2	6	169	174	10	5	30	29	5	-10	109	110	0	14	107	111	1	-6	70	70	7	2	99	101
Z	12	146	147	1	13	91	93	9	-6	29	27	2	7	146	152	10	6	28	33	5	-9	33	37	0	14	107	111	1	-6	70	70	7	2	99	101
Z	10	110	114	1	14	58	57	9	-5	57	59	2	8	49	52	10	7	42	43	5	-8	117	119	0	14	107	111	1	-6	70	70	7	2	99	101
Z	8	368	379	1	15	46	45	9	-4	33	32	2	9	30	31	12	-15	18	20	5	-7	14	9	0	14	107	111	1	-6	70	70	7	2	99	101
Z	6	38	41	3	-18	36	37	9	-3	101	98	2	11	104	108	12	-14	35	36	5	-6	143	142	0	14	107	111	1	-6	70	70	7	2	99	101
Z	4	775	763	3	-17	89	87	9	-2	82	83	2	12	29	31	12	-13	30	30	5	-5	45	45	0	14	107	111	1	-6	70	70	7	2	99	101
Z	2	481	471	3	-15	61	59	9	-1	31	29	2	14	17	18	12	-11	69	68	5	-4	184	190	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	63	62	3	-14	52	51	9	0	26	25	2	15	84	81	12	-10	49	46	5	-3	35	37	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	365	373	3	-13	146	144	9	1	58	59	2	16	65	64	12	-9	63	63	5	-2	384	387	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	28	30	3	-12	32	30	9	2	93	94	2	17	23	25	12	-8	84	83	5	0	192	193	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	123	133	3	-11	118	119	9	3	95	108	2	18	27	25	12	-7	66	65	5	1	33	35	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	10	26	3	-10	59	60	9	4	92	91	2	19	73	74	12	-6	41	41	5	2	205	215	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	12	35	3	-9	184	184	9	6	83	81	2	20	101	101	12	-5	48	47	5	4	157	169	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	14	75	3	-8	119	118	9	7	63	64	2	21	167	168	12	-4	73	73	5	5	11	1	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	18	70	3	-7	98	99	9	8	18	19	2	22	118	121	12	-3	62	63	5	6	108	119	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	16	77	3	-6	53	51	9	9	56	56	2	23	195	195	12	-2	22	23	5	7	17	17	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	14	26	3	-5	326	327	9	10	30	28	2	24	141	140	12	0	66	66	5	10	96	95	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	12	55	3	-4	253	246	11	-16	40	38	2	25	288	286	12	1	81	82	7	-17	22	21	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	10	91	3	-3	84	80	11	-15	28	26	2	26	100	97	12	2	16	15	7	-16	38	40	0	14	107	111	1	-6	70	70	7	2	99	101
Z	0	8	185	3	-2	308	300	11	-14	33	34	2	27	207	206	12	4	41																	

Table 3 (cont.)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	
11	4	81	80	6	4	59	64	3	-3	21	18	0	8	97	102	1	-2	50	53	2	4	18	22	
13	-12	88	85	6	5	23	22	3	-2	133	130	0	9	19	15	1	-1	44	48	2	6	49	49	
13	-11	24	23	6	7	115	113	3	-1	251	252	0	14	35	35	1	0	48	52	2	7	68	67	
13	-10	34	34	6	8	61	61	3	0	168	166	2	-14	84	84	1	1	103	114	4	-12	25	26	
13	-9	20	20	6	9	22	24	3	1	30	32	2	-12	52	47	1	4	37	39	4	-11	38	37	
13	-8	42	42	6	10	26	29	3	2	66	65	2	-10	125	124	1	5	101	110	4	-9	74	74	
13	-4	21	23	6	11	54	55	3	3	148	148	2	-8	134	138	1	6	33	36	4	-8	63	65	
13	-2	66	69	8	-14	41	40	3	4	73	75	2	-7	13	8	1	7	32	32	4	-7	40	38	
13	0	20	18	8	-13	75	75	3	5	36	34	2	-6	111	115	1	9	82	84	4	-5	93	95	
13	2	38	42	8	-12	54	56	3	6	50	52	2	-5	21	20	1	10	22	21	4	-4	24	21	
15	-8	33	37	8	-11	36	35	3	7	87	83	2	-4	22	24	3	-13	41	41	4	-3	27	26	
15	-4	41	43	8	-10	14	14	3	8	93	94	2	-3	19	22	3	-11	21	20	4	-1	41	44	
				8	-9	35	37	3	9	67	63	2	-2	54	52	3	-9	55	56	4	0	44	40	
				8	-8	23	25	3	11	67	63	2	0	44	65	3	-7	49	48	4	2	64	60	
				8	-7	122	123	3	12	43	41	2	1	18	17	3	-5	140	142	4	3	24	18	
				8	-5	47	47	3	13	37	33	2	2	188	185	3	-4	66	66	4	4	60	60	
				8	-4	84	86	5	-16	41	42	2	3	31	31	3	-3	41	41	4	5	65	64	
				8	-3	191	197	5	-15	40	41	2	4	103	104	3	-2	67	68	4	6	18	19	
				8	-2	37	38	5	-8	133	133	2	5	30	28	3	-1	192	195	4	8	53	56	
				8	-1	103	107	5	-7	116	116	2	6	123	131	3	0	105	104	6	-11	40	38	
				8	0	59	63	5	-6	17	16	2	8	54	51	3	2	55	56	6	-10	41	38	
				8	0	108	104	8	4	46	45	5	-5	67	64	2	10	84	84	3	3	119	124	
				8	0	29	27	8	5	75	75	5	-3	217	214	2	12	68	63	3	4	36	33	
				8	0	4	4	8	6	32	29	4	-2	26	23	4	-14	20	20	3	6	47	44	
				8	0	182	184	8	9	66	68	5	-1	70	71	4	-12	113	106	3	7	87	87	
				8	0	7	58	8	10	22	21	5	0	31	29	4	-11	36	35	3	8	25	22	
				8	0	142	136	10	-15	38	38	5	1	229	233	4	-8	189	175	3	9	35	34	
				8	0	10	95	10	-14	59	58	5	2	93	97	4	-7	53	51	3	11	64	64	
				8	0	14	42	10	-13	56	56	5	5	111	121	4	-6	101	97	5	-13	24	19	
				8	0	15	24	10	-12	52	53	5	6	58	69	4	-5	32	30	5	-12	29	28	
				8	0	15	44	10	-11	76	77	5	7	18	18	4	-4	207	197	5	-11	84	78	
				8	0	14	30	10	-10	74	77	5	9	49	45	4	-3	44	41	5	-9	37	35	
				8	0	13	63	10	-9	52	53	5	10	73	74	4	-2	34	36	5	-8	55	52	
				8	0	12	32	10	-8	54	57	5	11	44	39	4	-1	41	38	5	-7	75	71	
				8	0	11	125	10	-7	50	51	7	-15	19	28	4	0	91	83	5	-6	29	27	
				8	0	10	122	10	-6	82	83	7	-14	25	24	4	1	19	14	5	-5	30	26	
				8	0	9	105	10	-5	28	24	7	-13	55	89	4	2	31	32	5	-4	113	108	
				8	0	8	27	10	-4	25	26	7	-12	89	89	4	3	41	43	5	-3	24	23	
				8	0	7	186	10	-3	32	25	7	-10	56	56	4	4	120	120	5	-2	43	41	
				8	0	6	96	10	-2	47	47	7	-9	109	105	4	6	70	65	5	0	30	31	
				8	0	5	161	10	-1	72	73	7	-8	56	56	4	7	29	28	5	1	138	134	
				8	0	4	117	10	0	37	36	7	-6	110	110	4	8	77	73	5	2	57	52	
				8	0	3	181	10	0	21	21	7	-5	103	104	4	10	40	38	5	5	71	67	
				8	0	2	193	10	0	7	34	35	7	-4	70	70	6	-14	49	47	5	6	31	30
				8	0	1	328	10	-1	43	44	7	-3	44	42	6	-12	57	55	5	7	32	28	
				8	0	0	229	10	-2	74	71	7	-2	31	32	6	-11	27	29	5	9	31	34	
				8	0	0	70	10	-3	45	47	7	-1	121	123	6	-10	82	82	7	-13	53	50	
				8	0	0	246	10	-4	66	66	7	0	64	63	6	-9	23	24	7	-11	24	19	
				8	0	0	35	10	-5	73	72	7	1	68	71	6	-7	33	32	7	-9	103	98	
				8	0	0	207	10	-6	17	17	7	2	47	48	6	-6	119	114	7	-8	32	31	
				8	0	0	75	10	-7	43	41	7	4	64	63	6	-5	49	49	7	-6	50	47	
				8	0	0	92	10	-8	33	32	7	5	36	34	6	-2	147	149	7	-5	99	95	
				8	0	0	50	10	-9	67	65	7	6	25	26	6	-1	40	39	7	-4	70	64	
				8	0	0	41	10	-10	20	19	7	7	61	63	6	0	46	41	7	-3	37	34	
				8	0	0	75	10	-11	74	75	7	8	21	22	6	1	14	14	7	-2	42	39	
				8	0	0	49	10	-12	22	20	7	9	29	27	6	2	85	85	7	-1	111	101	
				8	0	0	42	10	-13	54	56	9	-12	40	42	6	3	24	22	7	0	33	33	
				8	0	0	14	10	-14	21	23	9	-11	59	58	6	4	77	71	7	1	49	43	
				8	0	0	49	10	-15	54	53	9	-10	48	48	6	6	105	98	7	2	51	43	
				8	0	0	39	10	-16	24	23	9	-9	35	35	6	7	19	15	7	3	117	107	
				8	0	0	76	10	-17	34	33	9	-8	29	30	6	8	55	53	7	4	51	48	
				8	0	0	97	10	-18	111	111	9	-7	126	126	6	10	65	62	9	-11	41	38	
				8	0	0	85	10	-19	21	21	9	-6	21	23	8	-14	24	22	9	-9	24	27	
				8	0	0	147	10	-20	16	16	9	-5	19	16	8	-12	91	89	9	-7	82	78	
				8	0	0	47	10	-21	32	32	9	-4	32	32	8	-10	62	63	9	-6	66	63	
				8	0	0	170	10	-22	117	117	8	-8	101	99	9	-2	49	46	3	4	48	47	
				8	0	0	172	10	-23	46	45	8	-7	25	26	9	-1	33	31	5	-9	20	18	
				8	0	0	49	10	-24	83	83	8	-3	26	26	9	1	52	48	5	-8	20	22	
				8	0	0	157	10	-25	61	61	9	2	72	72	8	-1	26	25	9	2	39	36	
				8	0	0	116	10	-26	42	42	9	3	38	39	8	0	92	84	9	3	57	50	
				8	0	0	105	10	-27	86	85	9	5	69	64	8	2	29	27	9	4	20	12	
				8	0	0	50	10	-28	106	104	9	6	68	68	8	4	29	29	11	-9	39	41	
				8	0	0	234	10	-29	160	158	11	-13	20	18	8	6	67	61	11	-8	27	26	
				8	0	0	157	10	-30	52	53	11	-12	27	25	10	-11	20	16	11	-7	35	34	
				8	0	0	80	10	-31	25	24	11	-10	47	44	10	-10	80	77	11	-6	24	18	
				8	0	0	75	10	-32	235	242	11	-9	34	37	10	-7	18	16	11	-5	78	73	
				8	0	0	201	10	-33	244	252	11	-8	51	50	10	-6	79	77	11	-4	20	19	
				8	0	0	76	10	-34	23	23													

and 0.049 for R_1 and R_2 respectively; no shifts of greater than one standard deviation from the values obtained in the previous least-squares refinement were observed. A value of R_2 on F^2 of 0.098 may be compared with that of 0.060 predicted from the agreement between equivalent reflections. This again suggests that there are residual errors in the model.

The positional and thermal parameters derived from this last cycle of least-squares refinement are presented in Table 2, along with the corresponding standard deviations in these parameters as estimated from the inverse matrix. The final values of $|F_o|$ (corrected for extinction effects) and $|F_c|$ (in electrons) are presented in Table 3; only the 1154 observations for which $F_o^2 > 2\sigma(F_o^2)$ were used in the refinement, and so only these reflections are listed in Table 3. Those reflections for which $F_o^2 \leq 2\sigma(F_o^2)$ all have $|F_o| < 2|F_c|$. The final extinction coefficient (in absolute units) is $1.45(22) \times 10^{-6}$. The estimated standard error in an observation of unit weight is 0.94.

Description of the structure

The overall structure is as found by Pedersen (1964) and by Chidambaram *et al.* (1964), but there are significant changes in the bond lengths of the oxalate fragment. The labelling scheme is shown in Fig. 1. A projection of the structure perpendicular to the b axis is shown in Fig. 2. The bond lengths and angles of the

oxalate fragment, together with their associated standard deviations, are compared with the previously reported values in Table 4. Also given in Table 4 are bond lengths and angles reported for other oxalate ions. The comparison of our results with the earlier data provides an excellent example of the relative ac-

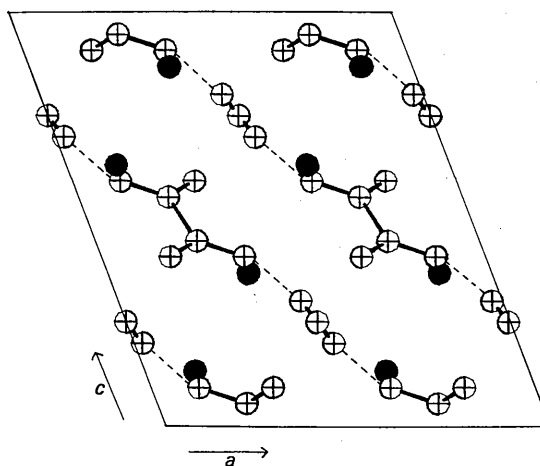


Fig. 2. Projection of one unit cell onto the (101) plane. K^+ ions are shown as solid circles. O(1)-H hydrogen bonds are represented by broken lines.

Table 4. Interatomic distances^a (Å) and angles^a (°) in the oxalate ion

Bond	This work	Pedersen ^b	Chidambaram ^c	(COONH ₄) ₂ ·H ₂ O ^d	(COOLi) ₂ ^e	(COOH) ₂ ·2H ₂ O ^f
C-C	1.5740 (24)	1.585 (15)	1.555 (12)	1.569 (8)	1.559 (4)	1.546 (2)
C-O(1)	1.2595 (16)	1.238 (11)	1.273 (13)	1.252 (6)	1.257 (3)	1.281 (2)
C-O(2)	1.2473 (17)	1.247 (11)	1.234 (17)	1.263 (6)	1.247 (3)	1.207 (2)
Angle						
O(1)-C-O(2)	126.27 (12)	126.4 (7)	125.1 (13)	126.0 (5)	127.1 (3)	127.1 (1) ^g
C-C-O(1)	115.76 (14)	116.4 (7)	116.1 (12)	117.5 (5)	116.4 (3)	111.9 (1) ^g
C-C-O(2)	117.96 (13)	117.1 (7)	118.8 (13)	116.5 (5)	116.5 (3)	121.0 (1) ^g

^a All distances and angles are uncorrected for the thermal motion.

^b Visually estimated X-ray data (Pedersen, 1964).

^c Two-dimensional neutron data (Chidambaram, Sequeira & Sikka, 1964).

^d Robertson (1965).

^e Beagley & Small (1964).

^f Delaplane & Ibers (1966).

^g Delaplane & Ibers (1969).

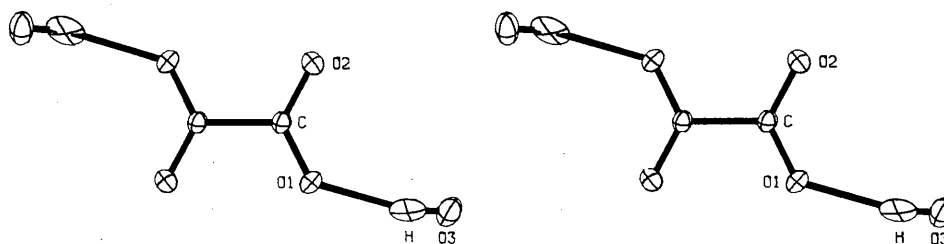


Fig. 1. Stereoscopic view of the oxalate fragment showing hydrogen bonding arrangement. There is a center of symmetry midway between the two carbon atoms. The view is normal to the C-O(1)-O(2) plane.

curacies of X-ray counter data, visually estimated X-ray data, and two-dimensional neutron data.

The oxalate anion is not completely planar, but consists of two parallel O(1)–C–O(2) planes separated by approximately 0.016 Å. The total bond angle around the carbon atom is 360.0 (2)°, but this angle is extremely insensitive to the separation noted, and should not be used as evidence for the planarity of the anion. From a wide survey of carbonyl structures, Hahn (1957) has deduced that a completely ionized carboxyl group has two equal C–O bonds of length 1.260 Å, an O–C–O bond angle of 125°, and two C–C–O bond angles of 117.5°. It is clear from the present work that the carboxyl groups in potassium oxalate monohydrate are not symmetric, the bond between carbon and the oxygen atom not involved in hydrogen bonding [C–O(2)] being significantly shorter than that between carbon and the hydrogen-bonded oxygen atom [C–O(1)]; the difference between these two bond lengths is 0.012 (2) Å. Moreover, the O(1)–C–C bond angle is significantly smaller than Hahn's value, while the O(2)–C–C bond angle is larger. These data clearly indicate that, as one would expect, the negative charge is preferentially associated with the hydrogen-bonded oxygen atom [O(1)]. This is in marked contrast to the structure of ammonium oxalate monohydrate (Robertson, 1965), where the carboxyl group was found to be symmetric. This difference is presumably due to the use, in the case of ammonium oxalate monohydrate, of protons in the cation to form strong hydrogen bonds to O(2).

As is found in both ammonium oxalate monohydrate (Robertson, 1965) and lithium oxalate (Beagley & Small, 1964), the C–C bond is abnormally long. This is possibly explained by the molecular orbital calculations of Brown & Harcourt (1963), which suggest that the C–C bond length in oxalates should be longer than that found in ethane (1.536 Å). Unfortunately, Brown & Harcourt's results also suggest that the bond in the non-planar oxalate ion of ammonium oxalate monohydrate should be longer than that found in planar oxalate anions; our value of 1.574 (2) Å for the very nearly planar oxalate anion in potassium oxalate monohydrate is insignificantly different from Robertson's value of 1.569 (8) Å for ammonium oxalate monohydrate.

Hydrogen bonding

The coordination of the water molecule in this structure is as found by Chidambaram *et al.* (1964). The bond lengths and angles associated with the water molecule, together with their estimated standard deviations, are compared with the previously reported values in Table 5. As is usual in X-ray studies, our value for the oxygen–hydrogen bond in the water molecule is much smaller than that found in the neutron study; it is, however, in good agreement with the value found in an X-ray study of oxalic acid dihydrate (Delaplane & Ibers, 1966). The length of the O(1)···O(3) hydrogen bond found here is consistent with the values reported by Pedersen (1964) and by Chidambaram *et al.* (1964). The H–O(3)–H bond angle is not significantly different from the value of 104.5° found in water vapor. The O(1)–H–O(3) angle of 165.9 (29)° is significantly different from 180°, as expected for a relatively weak hydrogen bond.

Thermal motions of the atoms

The root-mean-square amplitudes of vibration of the atoms are listed in Table 6. A stereoscopic view of the oxalate fragment, which also includes the hydrogen bonding arrangement, is shown in Fig. 1. The directions of vibration of the atoms are shown in the Figure. The anisotropy of thermal motion of the potassium ions is small.

Table 6. *Root-mean-square amplitudes of vibration (Å) along principal axes of thermal ellipsoids*

	Minimum	Intermediate	Maximum
K	0.1403 (5)	0.1616 (5)	0.1693 (5)
O(1)	0.1268 (14)	0.1699 (16)	0.2059 (16)
O(2)	0.1406 (16)	0.1639 (13)	0.1988 (16)
O(3)	0.1546 (23)	0.1572 (25)	0.2837 (28)
C	0.1258 (16)	0.1438 (17)	0.1511 (17)
H	0.05 (10)	0.25 (5)	0.32 (4)

The bond distances shown in Tables 4 and 5 can be 'corrected' for thermal motion using the 'riding' and 'independent' models (Busing & Levy, 1964). Some of the more important values are listed in Table 7. It is

Table 5. *Interatomic distances (Å) and angles^a (°) associated with the water molecule*

Bond	This work	Pedersen	Chidambaram	(COONH ₄) ₂ ·H ₂ O ^b
O(1)···O(3)	2.7602 (17)	2.746 (11)	2.744 (17)	2.743 (6)
O(1)—H	1.97 (3)	1.67 ^c	1.792 ^c	1.89 ^c
O(3)—H	0.80 (3)	1.1 (1)	0.963 (29)	0.92 (10)
Angle				
H—O(3)—H	106.9 (32)	113 (6)	107.9 (43)	127.0 (5)
O(1)—H—O(3)	165.9 (29)	167 ^c	169.1 (26)	154.3 ^c

^a All distances and angles are uncorrected for thermal motion.

^b Robertson (1965).

^c Values given with no associated errors are calculated from the parameters reported.

evident that the difference between the C—O(2) and C—O(1) bond lengths is approximately independent of the model used.

Table 7. Bond lengths corrected for thermal motion (Å)

Bond	Uncorrected	'Riding'	'In-dependent'
C—O(1)	1.2595 (16)	1.271	1.303
C—O(2)	1.2473 (17)	1.259	1.288
O(3)—H	0.80 (3)	0.81	0.93
C—C	1.5740 (24)	1.574	1.600

Residual electron density

A final difference-Fourier synthesis shows no peak higher than $0.33 \text{ e.}\text{\AA}^{-3}$; this highest peak is close to the potassium ion.* For ammonium oxamate (Beagley & Small, 1963), lithium oxalate (Beagley & Small, 1964) and oxalic acid dihydrate (Delaplane & Ibers, 1969), peaks were found in the center of the C—C bond in difference maps; a similar peak, of height $0.26 \text{ e.}\text{\AA}^{-3}$, is found in the present investigation. Areas of negative electron density are found in the vicinity of the oxalate oxygen atoms [O(1) and O(2)], which is again similar to the findings of Delaplane & Ibers (1969) in the case of oxalic acid dihydrate. These observations are in agreement with the predictions of Dawson (1965), which have been discussed in detail by O'Connell, Rae & Maslen (1966); the peak in the center of the C—C bond is believed to be due to the bonding electrons.

* The estimated standard deviation, $\sigma(\Delta\rho)$, is $0.12 \text{ e.}\text{\AA}^{-3}$

A difference map through the approximate plane of the oxalate fragment is shown in Fig. 3.

In addition to local programs mentioned in the text, programs used in this work were local modifications of Johnson's *ORTEP* thermal ellipsoid plotting program, Busing & Levy's *ORFLS* least-squares and *ORFFE* function and error programs, Hamilton's *GONO9* absorption correction program, and Zalkin's *FORDAP* Fourier program.

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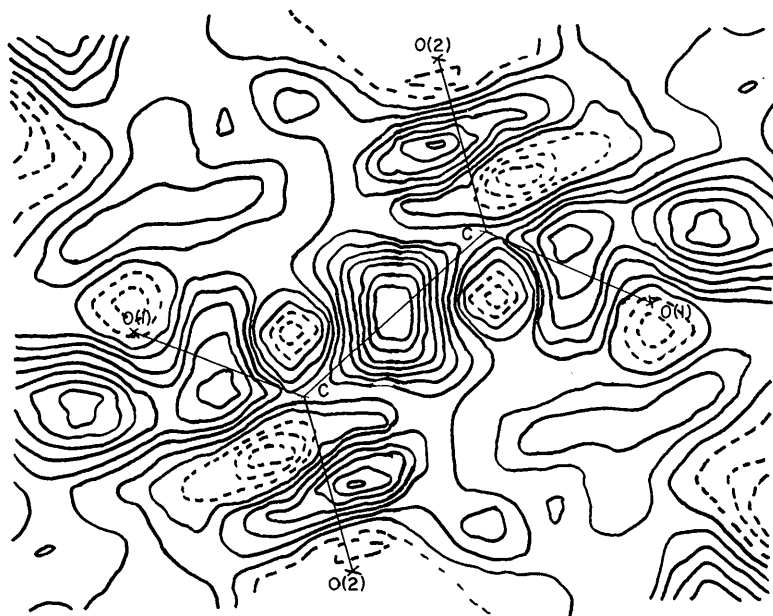


Fig. 3. Final difference-Fourier synthesis through the plane parallel to the C—O(1)—O(2) planes and passing through the center of the C—C bond. Contours are at intervals of $0.025 \text{ e.}\text{\AA}^{-3}$; negative contours are shown as broken lines.

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A Review of the Structure of Silicon Carbide

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The structure of silicon carbide and its polytypism are reviewed together with a brief discussion of the proposed mechanisms of crystal growth. The unit-cell parameters and stacking sequences are tabulated for 74 polytypes and the atomic positions listed for seven of the most common polytypes. A complete bibliography of the literature pertaining to the structure of silicon carbide is presented.

Introduction

The long-range structure of silicon carbide is extremely complex as a result of the one-dimensional disorder or polytypism. The short-range structure is simple, a four-coordinate, diamond-like arrangement of alternate silicon and carbon atoms. Since approximately 75 structures have been identified, and many completely determined, it seemed desirable to bring these data together for reference. While many are in the literature available to most researchers, a number of others are reported in Soviet and Chinese literature, and as such are less readily available.

Since no mechanism of crystal growth has been completely accepted, or has fully explained the formation of crystal structures having unit cells of the order of one thousand layers long, brief descriptions of several theories will be presented, without attempting to make a choice, merely to point out obvious failings and strong points of each.

The system of nomenclature used in this description of the various polytypes (Baumhauer, 1915) will, unless otherwise stated, be that of Ramsdell (1947). This convention is to assign a number corresponding to the number of layers in the hexagonal unit cell and a letter suffix designating the crystal symmetry: *C*, cubic; *H*, hexagonal; *R*, rhombohedral.

Description of the basic structure

Early work on the crystallography of SiC was devoted to goniometric studies of interfacial angles (Acheson,

1893; Baumhauer, 1912; Becke, 1895; Negri, 1906; Peacock & Schroeder, 1934; Peacock, 1934; Cortellezzi & Schroeder, 1934), which in the earliest studies showed at least two polytypes present in the first samples (Acheson, 1893). Morphological studies also showed the intergrowth of two or more polytypes within a single crystal (Baumhauer, 1915).

Early etching studies (Becke, 1895*a,b*) showed the different chemical behavior of the opposite basal planes (Figs. 1 and 2).

The first true structural studies were based on the work of Hull (1919, 1920), Ott (1925*a,b,c,d,e*, 1926, 1928) and others (Braekken, 1930; Espig, 1921; Hauer & Koller, 1916).

The structure of SiC can be described in several ways. For example the spatial location of each atom may be given. This is completely unambiguous, but for most purposes over complicated. The symmetry of a plane of atoms, resulting from the relative positions of the two adjacent layers can be designated; using this system the relation between layers of wider separation is not readily shown. Still other descriptions are based on the relative position of the various layers. One of the simplest is based on the relative orientation of layers of tetrahedra.

All silicon carbide structures are made up of a single basic unit, a plane of tetrahedra, arbitrarily either SiC₄ or CSi₄, shown in Fig. 3. Successive layers can arrange themselves in one of two ways: parallel or anti-parallel, as shown in Fig. 4(*a*) and (*b*).

Arbitrarily designating one orientation 'a', the other 'b', the parallel stacking of layers leads to an 'aa' se-