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Ammonium Oxalate Monohydrate: Structure Refinement at 30 °K

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A full set of three-dimensional diffraction data obtained, with liquid hydrogen cooling, at 30 °K (−243 °C) and with Cu radiation, was used to refine the structure of ammonium oxalate monohydrate. The value obtained for R was 0.080 and the e.s.d. of coordinates was of the order 0.004 Å. The oxalate ion is found to be twisted (as at room temperature) by $26.6^\circ \pm 0.4^\circ$; strong hydrogen bonding is responsible for this and the hydrogen atoms themselves appear in the difference Fourier synthesis. The central carbon-carbon bond of the oxalate ion is abnormally long: 1.569 Å (e.s.d., 0.008 Å) — a peculiarity not yet understood but shared by some other oxalates and related molecules. The root mean square thermal vibration amplitudes of the C, N and O atoms are of the order of 0.09 Å.

Introduction

Ammonium oxalate monohydrate, whose structure was first found twenty-eight years ago by Hendricks & Jefferson (1936) and then refined two-dimensionally by Jeffrey & Parry (1952*a*), is interesting because of the unexpected shape of the oxalate ion. In oxalic acid, both anhydrous and hydrated, the molecule is accurately planar (Hendricks, 1935; Cox, Dougill & Jeffrey, 1952; Ahmed & Cruickshank, 1953; Pringle, 1954) and in oxalates generally, including the oxalato complex ions of chromium, the ion is planar (Hendricks, 1935; Hendricks & Jefferson, 1936; Griffith, 1943; Niekerk & Schoening, 1951, 1952; Jeffrey & Parry, 1954; Beagley & Small, 1964). Even the ester dimethyl oxalate is also planar (Dougill & Jeffrey, 1953). But in this particular oxalate the ion is twisted about the central carbon-carbon bond by nearly 30°. This is the more surprising in view of the possibility of resonance in the highly symmetrical ion.

The work now reported was done to investigate this interesting situation with some, at least, of the refinements that modern techniques can offer. It was also an exercise in the collection of diffraction data at liquid hydrogen temperatures.

Experimental

With copper radiation, complete three-dimensional data were collected at liquid hydrogen temperatures.

Copper radiation was used, mainly for the sake of its low background. Four different crystal specimens were employed. To reduce absorption errors, these were all ground to cylindrical shape with diameters of approximately 0.20 mm. (The linear absorption coefficient for copper radiation is 13 cm^{-1} and corrections for absorption were not applied). These specimens had the a , b , c and $[110]$ axes parallel to the cylinder axis, respectively. The shaping of these specimens was carried out on an Airbrasive unit which has been described by Pringle (1960). For the experimental work the specimens were enclosed within thin-walled capillary tubes of the type supplied by Pantak. These had a wall-thickness of $\sim 1 \mu$ and photographs showed almost no halo from scattering by the glass. Diffraction spectra were recorded on film by both Weissenberg and oscillation techniques. All the spectra within the limiting sphere were covered, giving 456 independent measurements; of these, 24 were effectively of zero magnitude and the least-squares refinement was therefore based on 432 structure factors.

All the experimental data were obtained with the crystal held at 30 °K by the use of liquid hydrogen cooling. Cooling was effected by the use of the usual principle of cold gas flow, the gas in this case being hydrogen derived from boiling liquid hydrogen. The apparatus for cooling the crystal was essentially as has been described elsewhere (Robertson, 1960). A gas flow cryostat with the stream of cold gas

flowing vertically downwards was mounted over a Leeds Weissenberg goniometer, set up vertically for the purpose. The rate of boiling of liquid hydrogen was controlled by adjustment of current in an electrical heater. The overall rate of consumption of liquid hydrogen, inclusive of wastage by heat leakage, *etc.* was about $550 \text{ cm}^3 \cdot \text{hr}^{-1}$.

The temperature at the site of the crystal was not measured directly, during diffraction, but was determined in a separate experiment. A very small thermocouple junction (of S.W.G. 45 copper and constantan wires, diameter 0.071 mm, hard soldered), comparable in size to the crystal ($\sim 0.3 \text{ mm}$), was placed inside a thin-walled capillary tube and mounted in exactly the same position as the crystal specimen had been. The leads of the thermocouple junction were coiled both within the capillary and outside it around its base, to minimize errors caused by heat conduction in the wires. The junction was then cooled by the gas flow cryostat under conditions identical with those used throughout the diffraction work. Calibration of the thermocouple system was carried out in a prior experiment, with liquid nitrogen ($77.4 \text{ }^\circ\text{K}$) for the 'hot' junction, *i.e.* the fine-wire junction held in the position of the specimen, and liquid hydrogen ($20.4 \text{ }^\circ\text{K}$) for the cold junction, also a copper-constantan couple.

There was no difficulty in reaching or maintaining the low temperature, but difficulty was constantly experienced in the avoidance of frost at the site of the specimen. In principle, frost would have been avoided completely by the use of a shielding stream of dry hydrogen gas, obtainable by boiling off hydrogen gas from the liquid, but this was felt to be too expensive. As a more economical though less satisfactory method, the space within the layer-line screens was closed at the sides and the top by thin cellophane around the layer-line slot and by a flexible rubber sleeve between the top of the upper layer-line screen and the delivery tube of the cryostat. The base of the lower-layer-line screen was left open. Hydrogen gas (originating from the cold jet) filled this enclosure and spilled out from the base, upwards. Atmospheric air was thus kept out and the growth of frost was almost completely checked.

To minimize the fire and explosion hazard, the apparatus was surrounded by a large hood of aluminum sheet, open at the front and at the base. At the top, this hood led to an extraction system which removed air from the room at about $30 \text{ ft}^3 \cdot \text{min}^{-1}$. The rate of release of room-temperature hydrogen gas during normal operation of the cryostat was approximately $\frac{1}{4} \text{ ft}^3 \cdot \text{min}^{-1}$. The equilibrium concentration of hydrogen within the hood was therefore well below the explosion limit (about 10%). Locally, of course, the concentration was dangerous and every possible precaution was taken in regard to electrical contacts, *etc.* in this neighbourhood.

Variation of the temperature produced by the

cryostat was not attempted in this work. Operated under constant conditions, the apparatus maintained a constant temperature at the position of the crystal specimen. This temperature was found, by the procedure described above, to be $30 \text{ }^\circ\text{K}$, with an uncertainty of about $2 \text{ }^\circ\text{K}$. The unit-cell dimensions were also determined at this temperature; they were measured from selected spectra having good intensity and high Bragg angle. The positions of these reflexions on the film were measured from a fixed shadow-edge, calibrated by reference to the highest-angle powder lines from copper, silver and aluminum wires.

Basic data

Ammonium oxalate monohydrate;
(NH_4)₂(COO)₂·H₂O or C₂H₁₀N₂O₅; F.W. 142.1;
Orthorhombic; unit cell dimensions (Å):

Hendricks & Jefferson (1936)

<i>a</i>	<i>b</i>	<i>c</i>	
8.04	10.27	3.82	(room temp.)

This work

<i>a</i>	<i>b</i>	<i>c</i>	
8.035 ± 4	10.309 ± 4	3.795 ± 2	(room temp.)
8.017 ± 4	10.309 ± 4	3.735 ± 2	(30 °K)

Space group, $P2_12_12$ (D_2^3); No. 18;

Unit cell volume, 314.4 Å^3 (room temp.), 308.7 Å^3 (30 °K);

$D_m = 1.50$ (room temp.); $Z = 2$;

$D_x = 1.500$ (room temp.), 1.526 (30 °K); $F(000) = 152$.

It should be noted that the dimension of the *c* axis obtained by Hendricks & Jefferson was measured from layerline spacings only. This accounts for its comparatively large deviation ($\sim 1\%$) from the more accurate determination. Jeffrey & Parry did not redetermine the cell dimensions but utilized the values obtained by Hendricks & Jefferson.

Refinement

Refinement of the structure was carried out on the Ferranti Pegasus computer, with the least-squares program devised by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961).

To start off the refinement, the coordinates of Jeffrey & Parry (1952*a*) were used for the five heavy atoms. Good agreement was at once obtained with $R = 0.21$. For the five hydrogen atoms, coordinates for the structure factor calculations were derived from a model. In placing these hydrogen atoms, the assumption originally made by Jeffrey & Parry (1952*a*) that the ammonium group was rotating in the solid was abandoned. It was felt instead that the ammonium ion was likely to be making strong bonds with the

Table 1. *Calculated and observed structure amplitudes*

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $					
2	0	0	7.0	7.3	6	8	0	2.2	2.2	2	4	1	4.8	4.5	2	0	2	4.5	3.1	2	8	2	3.6	3.1	2	6	3	7.9	6.9
4	0	0	24.3	24.3	7	8	0	3.6	3.8	3	4	1	13.2	13.5	3	0	2	11.2	10.7	3	8	2	9.0	8.7	3	6	3	8.7	7.9
6	0	0	5.9	6.1	8	8	0	11.7	12.5	4	4	1	20.3	20.2	4	0	2	27.1	26.8	4	8	2	11.4	9.5	4	6	3	9.7	7.8
8	0	0	11.2	10.5	1	9	0	11.6	11.6	5	4	1	5.9	5.8	5	0	2	3.7	3.1	5	8	2	8.7	7.5	5	6	3	12.1	10.5
10	0	0	20.2	19.8	2	9	0	14.0	15.4	6	4	1	9.0	9.4	6	0	2	12.3	12.5	6	8	2	5.6	4.3	6	6	3	3.4	4.0
1	1	0	17.0	17.7	3	9	0	5.6	5.9	7	4	1	6.4	5.6	7	0	2	7.3	5.7	7	8	2	7.3	7.2	0	7	3	6.1	4.4
2	1	0	10.6	10.3	4	9	0	3.5	2.7	8	4	1	8.6	8.8	8	0	2	8.6	7.9	0	9	2	15.8	13.4	1	7	3	12.0	9.8
3	1	0	34.7	34.2	5	9	0	5.9	5.8	9	4	1	2.7	2.0	9	0	2	11.3	11.1	1	9	2	4.3	3.8	2	7	3	4.7	4.4
4	1	0	5.4	4.8	6	9	0	5.3	5.8	0	5	1	3.2	3.2	0	1	2	16.0	15.5	2	9	2	10.7	10.5	3	7	3	5.8	5.7
5	1	0	7.3	7.9	7	9	0	2.7	0.8	1	5	1	8.6	8.0	1	1	2	20.6	19.3	3	9	2	3.9	3.6	4	7	3	3.4	2.6
6	1	0	6.9	7.1	0	10	0	9.4	8.9	2	5	1	8.6	8.0	2	1	2	15.7	15.7	4	9	2	3.9	3.6	5	7	3	3.6	3.3
7	1	0	12.6	12.8	1	10	0	15.1	15.0	3	5	1	11.7	12.0	3	1	2	2.3	2.8	5	9	2	6.8	6.3	6	7	3	2.3	2.9
8	1	0	4.2	3.4	2	10	0	9.0	8.5	4	5	1	15.3	15.1	4	1	2	3.8	3.7	6	9	2	6.8	6.9	0	8	3	8.1	7.5
9	1	0	5.9	5.6	3	10	0	10.7	10.6	5	5	1	11.5	11.1	5	1	2	7.0	7.1	0	10	2	7.4	6.7	1	8	3	6.7	5.8
10	1	0	1.4	0.9	4	10	0	6.8	7.0	6	5	1	7.6	7.6	6	1	2	5.3	6.1	1	10	2	6.5	6.4	2	8	3	11.9	12.0
0	2	0	22.2	19.8	5	10	0	3.2	2.5	7	5	1	7.6	6.7	7	1	2	6.4	5.1	2	10	2	10.9	10.5	3	8	3	5.1	5.8
1	2	0	9.0	8.9	6	10	0	2.9	2.3	8	5	1	2.5	1.0	8	1	2	8.3	7.4	3	10	2	9.8	11.0	4	8	3	7.3	6.9
3	2	0	28.8	34.0	1	11	0	5.8	5.6	9	5	1	2.8	3.3	9	1	2	6.5	6.8	0	11	2	1.6	1.5	0	9	3	5.0	4.5
4	2	0	21.6	20.6	2	11	0	5.8	5.6	0	6	1	16.7	16.3	0	2	2	10.9	10.7	1	11	2	7.2	6.9	1	9	3	6.4	6.8
5	2	0	8.9	8.5	3	11	0	1.8	1.3	1	6	1	19.0	18.2	1	2	2	17.1	16.7	2	11	2	1.3	1.2	2	9	3	8.0	8.4
6	2	0	5.6	4.8	4	11	0	2.0	1.9	2	6	1	12.8	12.7	2	2	2	2.4	2.4	0	12	2	4.3	4.6	0	10	3	3.3	3.1
7	2	0	14.5	15.0	5	11	0	5.4	5.6	3	6	1	9.5	9.7	3	2	2	12.9	13.3	1	12	2	2.3	4.7	1	10	3	0.9	0.9
8	2	0	7.1	6.4	0	12	0	2.7	2.6	4	6	1	15.0	14.8	4	2	2	9.3	8.6	0	0	3	3.0	3.0	0	0	4	2.7	2.5
9	2	0	6.1	5.7	1	12	0	1.6	1.6	5	6	1	8.1	7.7	5	2	2	12.7	12.6	1	0	3	2.3	0.1	1	0	4	5.2	5.1
10	2	0	7.6	7.4	2	12	0	3.3	3.2	6	6	1	6.3	6.5	6	2	2	9.4	9.2	2	0	3	4.0	3.6	2	0	4	5.5	5.2
1	3	0	8.0	7.1	3	12	0	7.6	7.7	7	6	1	7.6	7.5	7	2	2	10.8	9.4	3	0	3	3.4	3.0	3	0	4	5.6	5.4
2	3	0	21.1	23.1	4	12	0	5.4	6.2	8	6	1	8.8	9.1	8	2	2	5.9	5.4	4	0	3	14.7	14.8	4	0	4	6.5	6.8
3	3	0	10.2	10.5	1	13	0	4.1	4.3	9	6	1	2.3	3.9	9	2	2	2.3	2.5	5	0	3	3.3	2.9	5	0	4	13.6	15.3
4	3	0	21.1	21.1	2	13	0	3.2	4.1	0	7	1	16.6	15.7	0	3	2	11.7	11.7	6	0	3	7.7	6.8	0	1	4	6.7	6.0
5	3	0	2.8	2.4	0	0	1	36.3	41.1	1	7	1	4.7	4.6	1	3	2	6.2	6.1	7	0	3	7.9	7.3	1	1	4	3.2	2.4
6	3	0	21.2	22.1	1	0	1	16.0	15.3	2	7	1	2.7	2.1	2	3	2	2.7	2.1	8	0	3	4.9	5.8	2	1	4	10.4	10.6
7	3	0	13.9	15.4	2	0	1	4.0	4.0	3	7	1	3.3	3.6	3	3	2	18.9	19.0	0	1	3	14.5	14.8	3	1	4	4.3	5.1
8	3	0	2.9	1.9	3	0	1	2.3	1.7	4	7	1	7.4	7.3	4	3	2	9.3	9.2	1	1	3	10.0	9.6	4	1	4	1.6	1.2
9	3	0	2.7	2.7	4	0	1	4.3	5.1	5	7	1	10.4	11.5	5	3	2	3.9	4.0	2	1	3	10.7	11.3	5	1	4	6.6	7.3
10	3	0	2.9	3.7	5	0	1	16.4	16.3	6	7	1	4.8	4.5	6	3	2	9.7	10.1	3	1	3	9.2	10.7	0	2	4	6.0	5.8
0	4	0	21.8	21.7	6	0	1	3.5	1.5	7	7	1	5.0	4.2	7	3	2	10.6	8.9	4	1	3	2.8	2.4	1	2	4	9.9	9.4
1	4	0	30.1	29.5	7	0	1	3.9	3.7	8	7	1	1.8	1.7	8	3	2	5.6	5.9	5	1	3	9.0	8.7	2	2	4	5.5	5.4
2	4	0	14.0	14.6	8	0	1	2.9	1.5	0	8	1	4.0	3.4	0	4	2	8.1	7.9	6	1	3	5.9	5.8	3	2	4	2.3	1.7
3	4	0	4.3	4.5	9	0	1	5.1	4.0	1	8	1	11.8	11.9	1	4	2	15.7	15.8	7	1	3	11.0	10.9	4	2	4	1.5	1.3
4	4	0	7.2	6.9	10	0	1	7.2	7.7	2	8	1	9.5	9.5	2	4	2	10.1	9.5	8	1	3	4.0	3.6	5	2	4	4.7	5.2
5	4	0	4.0	3.3	0	1	1	16.5	16.1	3	8	1	15.7	18.4	3	4	2	6.6	5.7	0	2	3	10.3	10.4	0	3	4	9.9	9.5
6	4	0	2.1	1.2	1	1	1	22.7	24.7	4	8	1	6.6	7.1	4	4	2	11.8	10.9	1	2	3	16.7	16.3	1	3	4	8.8	8.9
9	4	0	3.3	3.0	2	1	1	36.6	42.3	5	8	1	6.4	4.7	5	4	2	5.3	5.5	2	2	3	2.8	2.7	2	3	4	8.1	8.2
1	5	0	15.3	14.9	3	1	1	24.4	25.2	6	8	1	5.1	3.9	6	4	2	9.2	8.7	3	2	3	8.2	8.7	3	3	4	8.8	8.1
2	5	0	26.0	27.7	4	1	1	13.7	12.9	7	8	1	14.9	13.6	7	4	2	5.8	3.9	4	2	3	7.4	7.6	4	3	4	5.2	5.6
3	5	0	3.2	1.9	5	1	1	10.6	10.2	8	8	1	5.3	7.1	8	4	2	5.5	6.9	5	2	3	11.5	10.5	5	3	4	3.1	3.7
4	5	0	11.5	11.7	6	1	1	19.2	18.5	0	9	1	6.4	7.2	0	5	2	10.1	9.7	6	2	3	6.5	6.5	0	4	4	8.1	8.4
5	5	0	5.9	6.1	7	1	1	7.0	8.1	1	9	1	3.7	3.7	1	5	2	13.4	12.4	7	2	3	5.3	6.1	1	4	4	5.5	5.9
6	5	0	4.3	3.3	8	1	1	10.1	8.7	2	9	1	15.1	15.9	2	5	2	10.3	10.1	0	3	3	6.1	5.8	2	4	4	1.8	1.3
7	5	0	5.4	5.5	9	1	1	8.0	7.8	3	9	1	2.6	2.0	3	5	2	7.4	8.0	1	3	3	6.9	7.4	3	4	4	7.0	7.8
8	5	0	5.4	5.7	10	1	1	6.7	7.4	4	9	1	10.5	9.2	4	5	2	8.9	3.8	2	3	3	8.4	8.3	4	4	4	6.8	6.5
9	5	0	6.4	7.1	0	2	1	40.7	48.9	5	9	1	12.2	10.7	5	5	2	6.9	5.4	3	3	3	11.5	11.5	0	5	4	3.6	3.7
0	6	0	7.0	7.3	1	2	1	27.6	28.2	6	9	1	9.7	9.5	6	5	2	12.2	11.2	4	3	3	5.3	5.6	1	5	4	1.2	1.6
1	6	0	10.7	10.6	2	2	1	8.8	8.9	7	9	1	2.9	2.3	7	5	2	2.9	2.3	5	3	3	6.9	5.8	2	5	4	3.9	4.0
2	6	0	16.0	16.8	3	2	1	17.5	18.1	0	10	1	8.7	8.2	8	5	2	3.2	2.8	6	3	3	4.3	3.6	3	5	4	1.2	1.3
3	6	0	9.5	9.5	4	2	1	12.6	11.3	1	10	1	6.0	5.9	0	6	2	5.3	4.2	7	3	3	2.6	2.3	4	5	4</		

negatively charged oxygen atoms in its environment. The validity of this point of view, apparently accepted by Jeffrey & Parry in a later paper (1954), was proved by the subsequent course of the analysis. Around the ammonium group, there are eight oxygen atoms very roughly forming a cube. Four of these, in tetrahedral orientation, are at an average distance of 2.8 Å from the nitrogen, while the other four are at about 3.2 Å. This situation, which was noted by Hendricks & Jefferson, implied the existence of definite hydrogen bonds and made the placing of hydrogen atoms easy. Furthermore, around the water molecule there was also a tetrahedral distribution of close approaches. This was also noted by Hendricks & Jefferson, who refrained from postulating hydrogen bonds only because the separations were greater than the value of 2.55 Å which they believed to be necessary. Around this water molecule, two of the close approaches are negatively charged oxygen atoms; the other two are positively charged ammonium ions. The position of the hydrogen atoms was again easy to decide, therefore, and was in full accord with the assignment around the nitrogen, so that, while the ammonium ion directs a proton towards the water molecule, the water directs one of its lone pairs towards this ammonium ion.

Six cycles of least-squares refinement were carried out, of which the last five included the hydrogen atoms (with isotropic thermal parameters) and anisotropic thermal parameters for the heavy atoms. The value of R fell quickly to 0.10, then slowly to 0.080. Final values of the calculated structure amplitudes are listed, with the observed values, in Table 1; 24 terms for which the intensities were less than the minimum observable are omitted. The final values for the atomic coordinates are listed in Table 2, together with the thermal parameters and the associated standard deviations (e.s.d.). For C, N and O atoms,

the e.s.d. of coordinates is of the order of 0.004 Å, while for H atoms it is about 0.10 Å.

Table 2. *Atomic parameters*

Atomic coordinates (Å) and e.s.d. (Å × 10 ⁻³)						
Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C	0.749	0.234	0.259	5	4	5
N	3.124	2.326	1.601	4	4	4
O(1)	1.626	-0.623	0.522	3	3	4
O(2)	0.956	1.455	0.005	3	3	4
O(H ₂ O)	4.008	0.000	-0.687	—	—	6
H(1)	3.50	1.56	1.93	80	100	100
H(2)	3.83	2.81	1.24	90	90	100
H(3)	2.75	3.04	2.31	80	90	110
H(4)	2.41	2.03	1.16	90	90	110
H(5)	3.34	-0.12	-0.08	90	100	100

Thermal vibration tensor components, U_{ij} , (Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C	0.0071	0.0071	0.00046	0.0003	-0.0039	0.0002
N	0.0092	0.0125	0.0064	-0.0036	-0.0015	0.0000
O(1)	0.0062	0.0076	0.0077	-0.0021	0.0064	-0.0038
O(2)	0.0054	0.0066	0.0099	-0.0029	0.0014	0.0025
O(H ₂ O)	0.0070	0.0109	0.0035	0.0022	0.0000	0.0000

Estimated standard deviations of U_{ij} (Å² × 10⁻⁴)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C	19	20	20	34	33	36
N	17	18	19	31	34	36
O(1)	14	14	15	24	29	31
O(2)	13	13	16	24	30	32
O(H ₂ O)	20	19	24	37	—	—

Isotropic thermal vibration parameters: hydrogen atoms (Å²)

H(1)	0.0096	
H(2)	0.0372	
H(3)	0.0223	(e.s.d. ~ 0.0240)
H(4)	-0.0095	
H(5)	-0.0068	

A composite three-dimensional Fourier synthesis showing the oxalate ion and its environment viewed in the c direction is reproduced in Fig. 1.

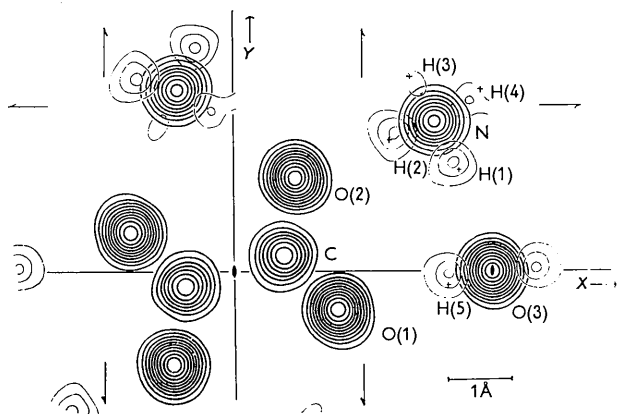


Fig. 1. Composite Fourier synthesis diagram. Contours for the heavy atoms C, N and O are at 2, 4, 6... (2)... 16, 18, 20 e.Å⁻³; contours for the hydrogen atoms are at 0.4, 0.6 and 0.8 e.Å⁻³ and are traced from the difference Fourier synthesis.

Discussion

(a) Molecular structure

Although the reduction in temperature produces anisotropic contraction of the crystal on cooling, there is no essential change of the crystal structure. The oxalate ion is twisted about the central C-C bond in just the same way as at room temperature. There is no substantial change in the angle of twist with the decrease of temperature. Both Hendricks & Jefferson, and Jeffrey & Parry obtained 28°. In this work, the equation of the plane of the carboxyl group is found to be,

$$-0.329x + 0.892y + 4.012z = 1.000$$

and the dihedral angle between the two COO⁻ planes is 26.6 ± 0.4°. A perspective view of the oxalate ion is given in Fig. 2, together with the dimensions of bonds and angles.

The carboxyl group itself has normal dimensions and is symmetrical, with the average C–O bond length, 1.258 Å. In a wide survey, Hahn (1957) concluded that a fully ionized carboxyl group should have equal C–O bonds of 1.260 Å enclosing an angle of 125° and making equal angles of 117.5° with the

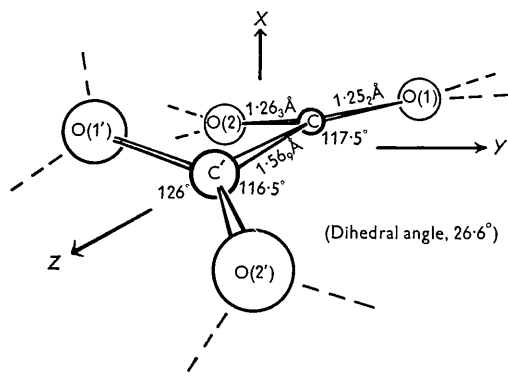


Fig. 2. Perspective drawing of the oxalate ion. Bond lengths are given in Å; e.s.d.: N ··· O = 0.006 Å, O ··· O = 0.005 Å.

C–C bond. The dimensions shown in Fig. 2 differ from Hahn's values by less than two standard deviations in all cases. The carbon–carbon bond, however, is certainly abnormal. Its measured length, 1.569 Å, with an e.s.d. of 0.008 Å, differs significantly from the normal simple single-bond distance of 1.541 Å (Sutton, 1958) and even more so from the bond distance to be expected between two trigonally hybridized carbon atoms. This distance, C_{sp^2} – C_{sp^2} , has been variously estimated as from 1.47 to 1.515 Å (Lide, 1962; Bastiansen & Traetteberg, 1962) and was recently chosen by Coulson & Skancke (1962), in a paper on *Some Abnormally Long Carbon–Carbon Bonds*, as high as 1.517 Å. Sundaralingam & Jeffrey (1962) have also proposed 1.52 Å. The C–C bond length found in this analysis exceeds Coulson's value by 0.052 Å. The unusual length of the C–C bond in ammonium oxalate was first found by Hendricks & Jefferson, who obtained 1.58 Å. Subsequently, Jeffrey & Parry obtained 1.56 Å and believed this to be insignificantly different from 1.54 Å, although we now see that it was the high value which was confirmed. The peculiar length of this bond may be ascribed in part to the twisted condition of the molecule which eliminates any resonance that might otherwise have shortened the central bond. But this cannot be the whole reason, as long C–C bonds in analogous molecules are also known and some have been confirmed with high precision. Thus, in lithium oxalate, Beagley & Small (1964) have found the central C–C bond distance to be 1.561 Å, with the e.s.d., 0.004 Å. The oxalate ion here is planar. Even more striking, because the analysis is still more precise, is the case of the oxamate ion in ammonium oxamate, $\text{NH}_2\cdot\text{CO}\cdot\text{COO}\cdot\text{NH}_4$, where the central bond length

is 1.564 Å, with the e.s.d., 0.002 Å (Beagley & Small, 1963b). This ion is also planar. Other molecules with neighbouring carbonyl groups, where the linking bond is long but not so accurately measured, are the pyruvate, oxobutyrate and 2-oxocaprylate ions (Tavale, Pant & Biswas, 1961, 1963, 1964). The bond in question has the lengths 1.579, 1.587 and 1.607 Å in these ions respectively, with standard deviations about 0.04 Å. The COO^- group in these ions is considerably rotated out of the plane defined by the neighbouring carbonyl group and the long C–C bond. None of these are overcrowded molecules. For the planar oxalate ion and oxalic acid molecule, it was argued, in order to account for their planarity, that there must be a significant electrostatic attraction between the carbonyl and the hydroxyl group (Jeffrey & Parry, 1952b). If this were so it would render the length of the bond in these molecules only the more remarkable. Clearly there must be some factor connected with the presence of two neighbouring carbonyl groups and perhaps also of ionic charge, which is responsible for the remarkable lengthening of the bond in all these cases. The phenomenon is not understood, and it is likely that further examples of abnormally long bonds will be established before a satisfactory theoretical explanation is forthcoming. At present it would seem that the most promising approach is the molecular orbital treatment of the A_2B_4 system as a whole, the theory then embracing also such molecules as N_2O_4 (which is isoelectronic with $\text{C}_2\text{O}_4^{2-}$ and whose central bond is highly abnormal), N_2F_4 , B_2Cl_4 and $\text{S}_2\text{O}_4^{2-}$. The most recent work of this kind, by Brown & Harcourt (1963) indicates that the C–C bond in oxalates should be slightly longer than in ethane, with a σ -bond order of 0.93.

In both lithium oxalate and ammonium oxamate, Beagley & Small found a low, but fully significant peak in the electron density difference map at the centre of the long C–C bond. Its height, 0.20 $\text{e}\cdot\text{\AA}^{-3}$, was about nine standard deviations of the electron density. This was associated by Beagley & Small (1963a) with the interatomic electrons involved in the bonding of the two carbon atoms and rendered visible by the unusual length of the bond. If this suggestion were correct, the effect should be seen in ammonium oxalate also. In ammonium oxalate, however, no such peak is found. Unfortunately, the accuracy of the present analysis (e.s.d. of $\rho(xyz) \approx 0.07 \text{ e}\cdot\text{\AA}^{-3}$) does not really allow one to expect it.

(b) Hydrogen bonding

There can be no doubt that it is the strong hydrogen bonding that is responsible for the twisted configuration of the oxalate ion. The existence of very favourable conditions for the formation of hydrogen bonds has already been referred to in connection with the placing of the hydrogen atoms prior to refinement.

All five hydrogen atoms are involved in bonding. That these atoms really do make these bonds is demonstrated by the difference Fourier synthesis (Fig. 1), where they are seen to have definite positions, each in a bonding orientation and not rotating as Jeffrey & Parry originally believed the NH_4^+ group to be. The distribution of these bonds around the oxalate ion is shown diagrammatically in Fig. 3, where the bond lengths also are given. As has been remarked earlier, both the ammonium ion and the water molecule are in tetrahedral environments. In addition, each carboxyl group oxygen is in a trigonal environment and makes (*i.e.* receives) two hydrogen bonds at approximately 120° to the C–O bond and approximately in one plane. The entire arrangement is favourable both for the protons, tetrahedrally attached to the nitrogen and to the water oxygen, and also for the lone pairs, tetrahedrally oriented on the water oxygen and trigonally oriented on the sp^2 -hybridized oxygens of the carboxyl group. The role of the lone pairs in hydrogen bonding may be usefully compared with that in the well-known dimers of carboxylic acids, which are so often nearly planar (Robertson, 1964).

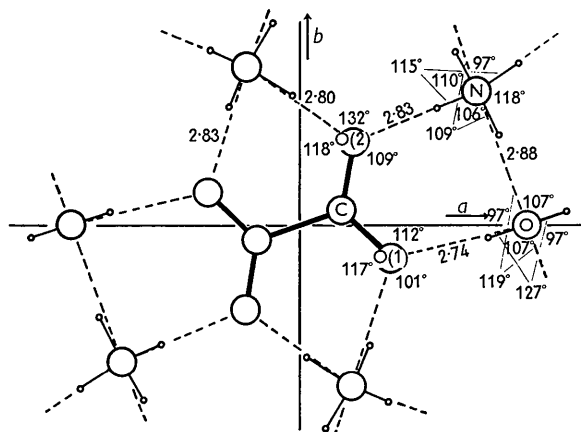


Fig. 3. Hydrogen bonding environment of the oxalate and ammonium ions and the water molecule. H-bonded distances are given in Å; e.s.d., C–C=0.008 Å; C–O=0.006 Å. The angles given are those between hydrogen-bonded contacts around the nitrogen and oxygen atoms; e.s.d., 0.5° .

The five hydrogen bonds fall naturally into three groups of differing type and systematically different bond lengths:

- (a) $\text{N}^+-\text{H} \cdots \text{O}(\text{H}_2\text{O})$: 2.879 Å,
- (b) $\text{N}^+-\text{H} \cdots \text{O}^-$: 2.803, 2.830, 2.833 Å,
- (c) $\text{O}-\text{H} \cdots \text{O}^-$: 2.743 Å.

The e.s.d. of these distances is about 0.006 Å. The bonds of group (b), between positive and negative ions, are noticeably short and are probably the strongest intermolecular bonds in the structure.

It is of interest to look for correlation of these hydrogen bonding distances with the infrared absorp-

tion of ammonium oxalate. If the curves of Nakamoto, Margoshes & Rundle (1955) are used (although their relationship for $\text{N}-\text{H} \cdots \text{O}$ is not strictly applicable to the case of NH_4^+), we obtain the predicted infrared absorption peaks, 3.17, 3.21, 3.22, 3.23, and 3.30 μ . The observed spectrum (in Nujol) shows strong absorption from about 3.0 μ to 3.35 μ .

The n.m.r. spectrum of crystalline ammonium oxalate has been discussed by Chidambaram (1962), especially in relation to the geometry of the water molecule. The orientation of the water protons was found to be almost exactly that of the hydrogen bonding contacts.

As for the hydrogen atoms themselves, it is at once apparent from Fig. 2 that the difference synthesis does not portray them in exactly the positions given by the least-squares refinement. To a large extent this result must be discounted, for the accuracy of the data is not very great, owing to the experimental difficulties of the low temperature work. Also there are indications (see Table 1) that some reflexions may suffer from extinction; if this were so, it would have affected the Fourier summation more than the least-squares refinement, where the weighting scheme reduces the importance of large structure amplitudes. In the Fourier synthesis, the e.s.d. of the electron density evaluated by the use of the simpler equation (strictly for centrosymmetric structures) of Cruickshank, (1949), was $0.073 \text{ e.}\text{\AA}^{-3}$. Thus the contours which outline the hydrogen atoms at intervals of $0.20 \text{ e.}\text{\AA}^{-3}$ in Fig. 2 do not have very exact positions. The e.s.d. of the coordinates of the atoms themselves is about 0.10 Å; therefore the discrepancies between the least-squares positions and the peak centres are in no case significant, although it is noticeable that the deviations are all in a similar sense: the Fourier synthesis tending to make the N–H and O–H distances shorter. The actual interatomic distances, determined from the coordinates of Table 2 are:

N–H(1): 0.92 Å	O(H ₂ O)–H(5): 0.92 Å
–H(2): 0.93	
–H(3): 1.07	(e.s.d. 0.10 Å)
–H(4): 0.89	

The mean value for the N–H distance, 0.95 Å, is much shorter than that given for NH_4^+ by Sutton (1958) or in *International Tables for X-ray Crystallography* (1962), *viz.* 1.034 and 1.033 Å respectively. It agrees, however, with that found in the very accurate study of NH_4HF_2 by McDonald (1960), 0.88 ± 0.03 Å, with the value obtained by Cruickshank, Jones & Walker (1964) in ammonium trifluoroacetate, 0.91 ± 0.06 Å, and with that of Beagley & Small (1963*b*) in ammonium oxamate, 0.95 ± 0.02 Å. The theoretical study of Banyard & Marsh (1960) indicated that the N–H distance should be even shorter than McDonald had found: 0.76 ± 0.06 Å was suggested. Thus the shorter distances indicated by the difference Fourier in this work, relatively inaccurate as it is, are not out of line with other results. Furthermore, libration of the

ammonium ion will tend to move the apparent electron density peak inwards.

(c) *Thermal motion*

The low temperature has the expected consequence that the mean square amplitudes of vibration, \bar{u}^2 , (see Table 2) are quite small: usually less than 0.01 \AA^2 , and averaging about 0.0075 \AA^2 , with e.s.d. 0.0002 \AA^2 for the C, N, and O atoms. This corresponds to $B=0.59 \text{ \AA}^2$ and to a root mean square vibration amplitude of about 0.09 \AA . At room temperature Jeffrey & Parry found $B=2.46 \text{ \AA}^2$, corresponding to $\bar{u}^2=0.031 \text{ \AA}^2$ and a root mean square amplitude of 0.175 \AA . Cruickshank (1956c) has shown that fairly simple assumptions for the vibrations of molecules in crystals predict an approximately linear increase of \bar{u}^2 with absolute temperature, except near or below the characteristic temperature, where quantum effects become important. In the case of ammonium oxalate, which is not strictly a molecular crystal because ionic forces are also present, we would expect higher characteristic temperatures and correspondingly less accurately linear increase of \bar{u}^2 with $^\circ\text{K}$. This does appear to be so. Taking \bar{u}^2 as 0.031 \AA^2 at $290 \text{ }^\circ\text{K}$, the linear relationship would give 0.0035 \AA^2 at $30 \text{ }^\circ\text{K}$, whereas in fact 0.0075 \AA^2 is found. This indicates comparatively high characteristic temperatures for the thermal motions in ammonium oxalate.

The thermal parameters of the hydrogen atoms have not been referred to above because the accuracy of the work was not sufficient to give very significant results of this fine detail (see Table 2).

Since the oxalate ion can be regarded as a rigid body, its thermal motion as a whole can be analysed by the method of Cruickshank (1956a). With the origin at the centre of symmetry, molecular axes X, Y, Z were chosen as shown in Fig. 2. The moments of inertia about these axes are respectively $345.9, 226.8$ and $133.3 \times 10^{-40} \text{ g.cm}^2$. The components of the tensors T , describing the translational motions, and ω , describing the librational (or torsional) motions, are shown in Table 3. Taking the square roots of the diagonal terms, we find that the root mean square amplitudes of translational vibration of the molecule as a whole in the direction of the molecular axes, and of angular oscillations about them are,

$$\begin{aligned} \text{along } X: & 0.077 \text{ \AA}; & \text{about } X: & 3.3^\circ; \\ \text{along } Y: & 0.063 \text{ \AA}; & \text{about } Y: & 1.1^\circ; \\ \text{along } Z: & 0.089 \text{ \AA}; & \text{about } Z: & 1.4^\circ. \end{aligned}$$

Table 3. Values of T_{ij} and ω_{ij} , and their e.s.d. (in $\text{\AA}^2 \times 10^{-2}$ and deg^2 , respectively)

$$\begin{aligned} T &= \begin{bmatrix} 0.59 & 0.00 & -0.04 \\ & 0.40 & 0.00 \\ & & 0.80 \end{bmatrix} & \sigma(T) &= \begin{bmatrix} 0.00 & 0.00 & 0.00 \\ & 0.01 & 0.00 \\ & & 0.00 \end{bmatrix} \\ \omega &= \begin{bmatrix} 10.60 & 0.00 & -1.14 \\ & 1.18 & 0.00 \\ & & 1.92 \end{bmatrix} & \sigma(\omega) &= \begin{bmatrix} 0.30 & 0.07 & 0.02 \\ & 0.07 & 0.06 \\ & & 0.28 \end{bmatrix} \end{aligned}$$

The translational motions are not markedly anisotropic but the librations are rather markedly so, with the greatest oscillations taking place about the molecular X axis, *i.e.*, about the crystallographic c axis. This is consistent with the anisotropy of expansion of the crystal. While periodicity in the b direction is unaffected by rise of temperature and that in the a direction increases slightly, the periodicity along c increases very considerably. Between $30 \text{ }^\circ\text{K}$ and room temperature (about $25 \text{ }^\circ\text{C}$) the change in a is 0.2% ; in c it is 1.6% of the length at the lower temperature.

On the basis of the rigid body librations of the oxalate ion, corrections to the atomic coordinates of carbon and oxygen were computed, following Cruickshank (1956b). As the motions are relatively small, the greatest correction was only 0.0021 \AA ; however, these corrections have been incorporated in the atomic coordinates of Table 2.

The striking height of the electron density peaks is of course the direct consequence of the low temperature and the small thermal motions. The peak heights found (Fig. 1) are,

$$\begin{aligned} \text{O: } & 21.7 \text{ e.\AA}^{-3} \\ \text{N: } & 17.0 \\ \text{C: } & 15.7 \end{aligned}$$

The peak heights for hydrogen atoms vary from 0.4 to 0.8 e.\AA^{-3} , these being very much affected by the errors in the data.

It is a pleasure to make a number of acknowledgements: to Sir Gordon Cox, to whom I owe the suggestion of the extension of low temperature techniques to the liquid hydrogen range; to the Director and staff of the Leeds University Computing Laboratory; to Prof. Cruickshank, and Miss Pilling, Dr Truter and Dr Bujosa for their invaluable guidance in the computations as well as for the use of their programs; to Dr Hoare and the Leeds University Physics Department for the use of their hydrogen liquefier; to Mr Holey, who shaped the crystal specimens; and to the late Dr Hudson, Mr Sheldrick and other colleagues for advice.

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Enantiomorphism of the Oxalate Ion in Ammonium Oxalate Monohydrate

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There must be enantiomorphic forms of ammonium oxalate monohydrate because, in this structure, where the oxalate ion is twisted about its central bond, there is neither m nor $\bar{1}$ symmetry. It is intrinsically possible that these may exhibit enantiomorphous morphology. In fact, this can readily be observed and has been reported several times in the literature of classical crystallography.

The twisted oxalate ion is optically active and it is predicted that the crystal of ammonium oxalate monohydrate will rotate the plane of polarized light passing along its optic axes.

The ion $-\text{OOC}\cdot\text{COO}-$ is one that is so simple and so symmetrical that superficially one would not suspect it of even the possibility of enantiomorphism. It contains only two kinds of atom and only two different bond lengths. It has no asymmetric carbon atom. Its carbon atoms are not tetrahedral and there are no bulky substituents to hinder grossly the rotation about the central bond. In crystalline oxalates, it is almost invariably planar, with mmm symmetry. In solution, when the flexibility of the molecule gives it in effect its highest possible symmetry, no enantiomorphism is possible. In the solid state, however, where the molecule has a fixed configuration, it

requires only a simple twist of the central bond to render the molecule enantiomorphic. This is exactly the case in ammonium oxalate monohydrate, where the oxalate ion is twisted by about 27° .

To be enantiomorphic, it is necessary only that a molecule or structure be not superposable on its mirror image. The absence of mirror planes and of symmetry centres is essential. The presence of rotation axes is irrelevant. Ammonium oxalate monohydrate is orthorhombic and in the class 222; the space group is $P2_12_12$ and contains no centre of symmetry. The structure is well known; a refinement of it is reported in the preceding article (Robertson, 1965). The oxalate