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Neutron diffraction study of ammonium oxalate monohydrate, $(NH_4)_2C_2O_4$, H_2O.

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Neutron diffraction intensities for 125 ($hk0$) and 45 ($0kl$) reflexions were measured to an estimated average accuracy of 4% on a single-crystal diffractometer at Canada India Reactor ($\lambda = 1{\cdot}029$ Å). The space group and unit cell as determined by X-rays and neutrons are $P2_12_12$, $Z=2$, $a=8{\cdot}04$, $b=10{\cdot}27$, $c=3{\cdot}82$ Å in agreement with previous X-ray results (Wyckoff, 1960).

Two cylindrical specimens of dimensions 7×2 mm and $5 \times 0{\cdot}8$ mm were used for collecting the data. The observed intensities, corrected for absorption, were reduced to absolute structure factors by comparing with the 400 reflexion from a standard sodium chloride crystal. Because of the good agreement between intensity measurements from two different sized crystals and also between the observed and calculated structure factors extinction was judged to be unimportant. The phases of most of the reflexions are reliably determined from the contributions of N, O and C.

Nuclear density projections were first drawn on (001) and (100) planes, based on neutron amplitudes and phases derived from the parameters of these atoms from X-ray study. The projections served to locate roughly the positions of hydrogen atoms. These positional parameters were refined by F_o, $(F_o - F_c)$ and one cycle of least-squares methods. Using neutron scattering lengths N, 0·94; C, 0·66; O, 0·58 and H, $-0{\cdot}38 \times 10^{-12}$ cm, and isotropic temperature factors 1·5 for nitrogen, 1·8 for carbon and oxygen and 3·0 Å^2 for hydrogen, structure factors were calculated. The final coordinates are given in Table 1. A projection of the neutron scattering density on (001) is shown in Fig. 1. The agreement ratio $R = (\Sigma w|F_o - F_c|/\Sigma w F_o^2)^{\frac{1}{2}}$ has the value 0·082. The weights of the observed structure factors were computed from the expression (Smith & Levy, 1962)

Table 1. *Atomic coordinates*

	x	y	z
C	0·092	0·027	0·068
O(1)	0·200	−0·056	0·140
O(2)	0·118	0·142	0·001
N	0·386	0·229	0·427
O(w)	0	0·500	0·198
H(w)	0·094	0·476	0·053
H(1)	0·482	0·268	0·287
H(2)	0·430	0·151	0·568
H(3)	0·288	0·194	0·291
H(4)	0·347	0·306	0·582

$$w = \frac{2C_N}{F_o \sqrt{[C_N + 2C_B + (0{\cdot}04C_N)^2]}}$$

where F_o is the observed structure factor, w its weight, C_N is the net count (total less background) and C_B is the background. (The numerical value 0·04 takes into account the variation in intensity). The average standard deviations of the atomic coordinates estimated by Cruickshank's (1949) method are 0·018 Å for hydrogen and 0·10 Å for other atoms. The mean standard deviations for bond lengths and angles are 0·023 Å and 1·9° respectively.

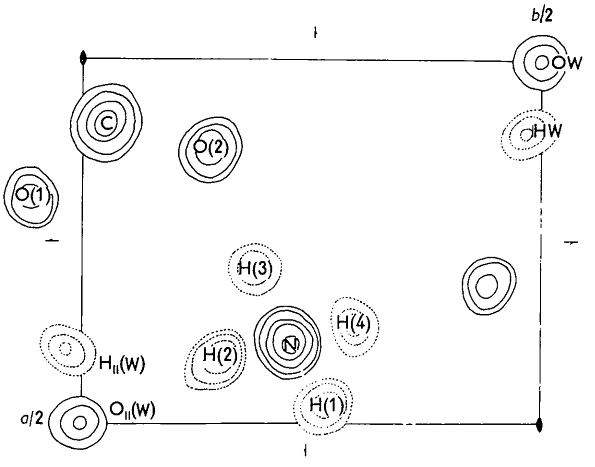

Fig. 1. A projection of the neutron scattering density on the (001) plane. Full lines are positive contours; broken lines are the negative contours of the hydrogen atoms. Contours drawn at arbitrary intervals.

As there are no major discrepancies between the coordinates of C, O and N determined by this method and earlier by the X-ray method, the non-planarity of the oxalate radical shown by Hendricks & Jefferson (1936) is confirmed. The plane of one COO is turned through 28° with respect to the other. As suggested by Jeffrey & Parry (1952, 1954) the water molecules link the oxalate ions by means of O(w)–H · · · O hydrogen bonds into linear chains parallel to the x axis. The water–oxygen to carboxyl–oxygen distance is 2·80 Å and the angle O · · · O(w) · · · O is 125°, and the inclination of the O–O vectors to the x axis is 13·4°. The inter-hydrogen distance is 1·59 Å, the distance O(w)–H is 0·97 Å and the H–O(w)–H angle is 105·6°. These are in good agreement with the values obtained from a proton magnetic resonance study (Chidambaram, 1962). The O(w)–H···O angle is 168°, a departure from linearity of 12°, which

Table 2. *Interatomic distances and bond angles*

Bond lengths		Bond angles	
C–O(1)	1·25 Å	O(1)–C–O(2)	125·6°
C–O(2)	1·23	O(1)–C–C	114
C–C	1·58	O(2)–C–C	119·9
N–H(1)	1·02	H(1)–N–H(2)	108·9
N–H(2)	1·03	H(1)–N–H(3)	117·1
N–H(3)	1·01	H(1)–N–H(4)	104·3
N–H(4)	1·03	H(2)–N–H(3)	105·1
		H(2)–N–H(4)	111·4
		H(3)–N–H(4)	109·6
		N–H(1)–O$_{III}$(2)	169
		N–H(2)–O$_{II}$(w)	173·7
		N–H(3)–O(2)	170·3
		N–H(4)–O$_{II}$(1)	180

is not unusual in an H-bonded crystal. The H–H vector (water) makes an angle of 18° with the x axis indicating that the hydrogen atoms are not located exactly on the plane containing O(1), O(w) and $O_I(1)$ atoms. Listed in Table 2 are the dimensions of the oxalate and NH_4 groups.

The observed length of the N–H bond is good agreement with values from the compounds $NH_4H_2PO_4$ (N–H $1{\cdot}00 \pm 0{\cdot}02$ Å; Tenzer, Frazer & Pepinsky, 1958) and NH_3OHCl (N–H $1{\cdot}04 \pm 0{\cdot}01$ Å; Padmanabhan, Smith & Peterson, 1962). The H–N–H angles vary between 104 and 117°. Tenzer *et al.* have also reported distortion of the tetrahedral NH_4 group in $NH_4H_2PO_4$. The distortion observed may be due to hydrogen bonding resulting in a linear N–H $\cdots$ O bond. For further discussion on the distortion of the NH_4 tetrahedron, a more detailed study of thermal parameters of the hydrogen atoms with three-dimensional data is required.

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Interatomic distances in solid chlorine.

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Introduction

A tetragonal structure for solid chlorine was proposed by Keesom & Taconis (1936), based on powder data and limited single-crystal data; it was later shown to be incorrect by Collin (1952) on the basis of single-crystal data. The structure described by Collin is orthorhombic, and isotypic with those of solid bromine (Vonnegut & Warren, 1936) and iodine (Harris, Mack & Blake, 1928; Kitaigorodskii, Khotsyanova & Struchkov, 1953); the two positional parameters and one isotropic temperature factor were determined by trial and error. Because of our interest in interatomic distances and thermal vibrations in simple substances, we decided to carry out additional refinements on Collin's single-crystal data, including allowance for anisotropic thermal motion.

Table 1. *Comparison of single-crystal with powder data*

	Collin		Keesom & Taconis		
hkl	d_c†	$pF_o^2 \times 10^{-3}$	d_o	I_o	d_c‡
002	4·13	3	—	—	4·10
111	3·33	51	3·26	w	3·31
200	3·13	22	3·07	m	3·09
112	2·73	45	2·68$_5$	s	2·72
202	2·49	4	2·45$_5$	w	2·48
113	2·19	3	2·21	w	2·18
021	2·16	13	2·15	s	2·16
004	2·07	9	2·03	s*	2·06
114	1·80	6	1·82	m	1·79
023	1·74	16	1·75$_5$	w	1·74
204	1·73	16	1·70	s	1·71
400	1·56	8	1·54$_5$	w	1·54
223	1·52	22	1·50	w	1·52
115	1·51	12	1·49	s	1·50

* Intensity enhanced by silver sample holder.
† Calculated with $a = 6{\cdot}24$, $b = 4{\cdot}48$, $c = 8{\cdot}26$ Å (Collin, 1956).
‡ Calculated with $a = 6{\cdot}17$, $b = 4{\cdot}49$, $c = 8{\cdot}22$ Å.

Refinement

The 44 observed values of F tabulated by Collin were used to refine the parameters by least squares, with the full-matrix program ACA No. 217 of Gantzel, Sparks & Trueblood with the weighting scheme of Hughes (1941) and the form factors of Dawson (1960). In the first series the variables were the y and z parameters for the chlorine atom, a single temperature factor, and the scale factor. In addition, the effect on the results of varying the value of $4\,F_{\min}$ in the weighting scheme was studied. It was found that when $4\,F_{\min}$ was varied from 17·6 to 85·8 (on the same scale the smallest F_o, F_{337}, is 5·2, and the largest, F_{200}, is 85·8) the following parameters were obtained: $y = 0{\cdot}1155 \pm 0{\cdot}0034$ to $0{\cdot}1161 \pm 0{\cdot}0035$, $z = 0{\cdot}1014 \pm 0{\cdot}0008$, and $B = 3{\cdot}70 \pm 0{\cdot}24$ to $3{\cdot}43 \pm 0{\cdot}22$. In the second series anisotropy was allowed, and the same range of $4\,F_{\min}$ was used. The results in this case were $y = 0{\cdot}1166 \pm 0{\cdot}0038$ to $0{\cdot}1173 \pm 0{\cdot}0041$, $z = 0{\cdot}1016 \pm 0{\cdot}0008$ to $0{\cdot}1014 \pm 0{\cdot}0010$, $B_{11} = 3{\cdot}42 \pm 0{\cdot}47$ to $3{\cdot}27 \pm 0{\cdot}31$, $B_{22} = 4{\cdot}09 \pm 0{\cdot}40$ to $3{\cdot}85 \pm 0{\cdot}40$, $B_{33} = 3{\cdot}55 \pm 0{\cdot}27$ and $B_{23} = -2{\cdot}1 \pm 1{\cdot}2$ to $-1{\cdot}2 \pm 1{\cdot}6$. In each of the above refinements the shifts in the last cycle were less than 1×10^{-6}. The absence of any significant changes in the results as $4\,F_{\min}$ is varied would tend to indicate that there are no serious systematic errors in Collin's data. The values for the parameters for $4\,F_{\min} = 20{\cdot}8$ are: isotropic, $y = 0{\cdot}1161 \pm 0{\cdot}0035$, $z = 0{\cdot}1014 \pm 0{\cdot}0008$, $B = 3{\cdot}67 \pm 0{\cdot}23$, $R = 10{\cdot}4\,\%$; anisotropic, $y = 0{\cdot}1173 \pm 0{\cdot}0038$, $z = 0{\cdot}1016 \pm 0{\cdot}0009$, $B_{11} = 3{\cdot}43 \pm 0{\cdot}31$, $B_{22} = 4{\cdot}09 \pm 0{\cdot}40$,