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## The Crystal Structure of Ammonium Hydrogen Oxalate Hemihydrate

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Crystals of  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  are orthorhombic (space group *Pnma*) with  $a = 11.228$ ,  $b = 12.329$ ,  $c = 6.898$  Å;  $\rho = 1.614$  g cm<sup>-3</sup>;  $Z = 8$ . The crystal structure was determined by direct methods. Full-matrix least-squares refinement with anisotropic temperature parameters for non-hydrogen atoms converged to an *R* index of 0.030. The  $\text{C}_2\text{O}_4$  group is found to be planar, the C–C distance being 1.548 Å. The crystal structure consists of infinite chains of hydrogen oxalate ions linked by hydrogen bonds (2.561 Å). These chains are connected transversely by weaker hydrogen bonds (2.780 Å) and by ionic bonds. Coordination and rotational stability of the  $\text{NH}_4^+$  ions are discussed. The relationship of the crystal structure to various physical properties is considered.

### Introduction

Single crystals of ammonium hydrogen oxalate hemihydrate exhibit an extremely large elastic anisotropy (Küppers, 1972*b*). This behaviour could possibly be explained in terms of special characteristics associated with interatomic bonds. Therefore, a structure analysis of  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  seemed desirable.

Structures of several oxalates have been previously investigated. In general these investigations reveal planar or nearly planar configurations of oxalate ions and an abnormally long C–C distance. It is a further purpose of this paper to present additional information concerning configurations of oxalate groups.

### Experimental

$\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  is orthorhombic. Large single crystals were prepared by evaporation from aqueous solution (Küppers, 1972*a*). The density of well-developed specimens (all dimensions approximately one cm) was measured by flotation and was found to be  $\rho = 1.613$  g cm<sup>-3</sup> at 20°C. Unit-cell parameters (designated ac-

cording to Groth, 1910) determined with a single-crystal diffractometer were:  $a = 11.228 \pm 0.003$ ,  $b = 12.329 \pm 0.003$ ,  $c = 6.898 \pm 0.002$  Å. Silicon ( $a = 5.43064$  Å) was used as a calibrating substance. From these measurements, and assuming  $Z = 8$ , a water content of  $\frac{1}{2}\text{H}_2\text{O}$  per formula unit is obtained. This is in contrast to data given by Groth (1910), who quotes the formula as  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The density calculated from X-ray measurements is  $\rho = 1.614$  g cm<sup>-3</sup>. This determination also shows that in the axial ratios cited by Groth (1910), 0.4524:1:0.5592, the first ratio should be doubled.

No measurable piezoelectric effect was observed. This result in addition to systematic absences indicated that the space group is *Pnma*. X-ray intensities were measured with a Siemens automatic diffractometer using Mo  $K\alpha$  radiation. The specimen for structure analysis was a crystal with a prismatic habit along [001]. Diameter and length were about 0.7 mm. 1392 independent intensities up to a maximum Bragg angle of  $2\theta = 58^\circ$  were determined. Each of these values is an average of four measurements of equivalent reflexions.

No absorption correction was considered necessary because the specimen had relatively equal dimensions and also because the linear absorption coefficient is only 1.7 cm<sup>-1</sup> for this compound.

\* This investigation was performed in collaboration with the Institut für Kristallographie of the Technische Hochschule Aachen.

Structure analysis

All calculations for solution of the structure were carried out by the program system X-RAY 70 (Stewart,

Kundell & Baldwin, 1970). Atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). After computing normalized structure factors |E|, phases were determined by direct

Table 1. Observed and calculated structure factors

Within each group columns contain the values of k, 10|F<sub>o</sub>| and 10F<sub>c</sub>. 'Less thans' are denoted by an asterisk.

Table with multiple columns containing numerical data for structure factors, organized into groups. Each group contains values for k, 10|F<sub>o</sub>|, and 10F<sub>c</sub>.

methods using the *SIGMA2* and *PHASE* procedures. An  $F_o$ -Fourier map computed with 116 reflexions (with  $|E| > 1.8$ ) revealed the positions of the C, N, and O atoms. The  $R$  value after 3 cycles of least-squares refinement with isotropic thermal parameters was 0.18. Reciprocals of standard deviations were used as weighting factors. One cycle with anisotropic temperature factors reduced  $R$  to 0.078. At this stage, it was possible to locate the hydrogens in a difference Fourier map. Inclusion of H parameters (with isotropic temperature factors) and exclusion of 'less-thans' ( $|F_o| < 2.0$ ) reduced  $R$  to 0.047 after two cycles of full-matrix least-squares refinement. Comparison of observed and calculated structure factors indicated appreciable extinction for reflexions with  $|F_o| > 35$ . A final  $R$  value of 0.030 was obtained when these reflexions were omitted from refinement.

Observed and calculated structure factors are listed in Table 1. Final fractional coordinates and thermal parameters are given in Table 2.

## Discussion

### Description of the crystal structure

Fig. 1 shows a stereoscopic view of a part of the unit cell. Atoms are represented by their thermal ellipsoids which are scaled to contain 50% probability of space occupancy. Planar  $C_2O_4$  groups lie approximately perpendicular to  $[001]$  which in this figure is the viewing direction.  $z$  coordinates of atoms constituting the oxalate group scatter around 0.25. Therefore the  $a$  glide, also located at 0.25, produces essentially a translation along  $[100]$ . As a consequence, the symmetry-equivalent oxalate groups have similar  $z$  values of about

Table 2. Fractional atomic coordinates, thermal parameters and standard deviations (in parentheses)

$\beta_{ij}$  are the coefficients in the expression:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

(a) Heavy atoms. Atomic coordinates are  $\times 10^4$ , thermal parameters  $\times 10^5$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	4909 (1)	5111 (1)	2325 (1)	222 (6)	301 (6)	1233 (19)	21 (4)	-36 (9)	-42 (9)
C(2)	6182 (1)	4639 (1)	2498 (1)	238 (6)	271 (5)	1376 (20)	19 (5)	-46 (9)	9 (9)
O(1)	4786 (1)	6026 (1)	1621 (1)	328 (5)	298 (5)	1989 (19)	64 (4)	-38 (8)	119 (8)
O(2)	4101 (1)	4493 (1)	2937 (1)	233 (5)	398 (5)	2370 (21)	9 (4)	79 (8)	233 (9)
O(3)	7003 (1)	5301 (1)	1874 (1)	222 (5)	376 (5)	2916 (24)	4 (4)	38 (9)	330 (10)
O(4)	6360 (1)	3753 (1)	3164 (1)	342 (6)	367 (5)	2965 (24)	57 (4)	-25 (10)	394 (10)
O(5)	2086 (1)	2500	6482 (2)	362 (9)	379 (7)	2604 (35)	0	-130 (14)	0
N(1)	3331 (2)	2500	119 (3)	419 (11)	379 (9)	1694 (36)	0	115 (17)	0
N(2)	4453 (2)	2500	5028 (3)	592 (13)	383 (9)	1398 (31)	0	113 (18)	0

(b) Hydrogen atoms. Atomic coordinates are  $\times 10^4$ .

	$x$	$y$	$z$	$B$
H(1)	7797 (19)	4956 (15)	1986 (25)	2.81 (45)
H(2)	1617 (15)	1989 (12)	6379 (23)	2.40 (34)
H(3)	2925 (22)	2500	8998 (38)	2.69 (49)
H(4)	2850 (32)	2500	1032 (54)	7.98 (93)
H(5)	3808 (17)	3080 (17)	157 (27)	5.22 (51)
H(6)	3609 (18)	2500	5395 (29)	1.91 (39)
H(7)	4905 (24)	2500	6154 (46)	4.74 (64)
H(8)	4574 (15)	3071 (14)	4306 (27)	3.16 (39)

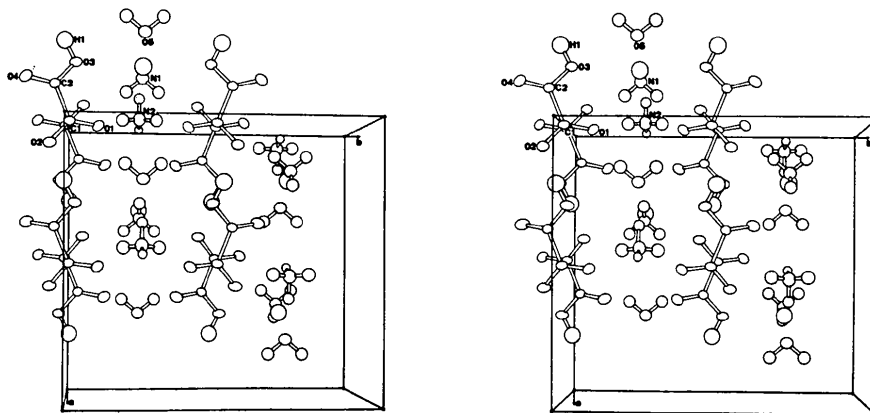


Fig. 1. Stereoscopic view of a part of the unit cell as seen down the  $c$  axis. Vertical direction is the  $a$  axis, horizontal direction is the  $b$  axis. (Drawn by *ORTEP*, Johnson, 1965).

0.25 or 0.75. The groups are linked together by hydrogen bonds (length = 2.561 Å) and form infinite chains extending along [100]. These chains are connected transversely by means of another hydrogen bond (2.780 Å) *via* the water molecules and also by ionic

interaction between ammonium ions and oxalate oxygens.

Oxygen O(5) of the water molecule occupies a special position and lies in the mirror plane *m*. The ammonium groups occupy two non-equivalent special

Table 3. Bond lengths (Å) and angles (°) with standard deviations for  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (present work),  $\text{LiHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (Thomas, 1972),  $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (Tellgren & Olovsson, 1971),  $\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  (Currie, Speakman & Curry, 1967),  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  (Haas, 1964), and  $\text{KHC}_2\text{O}_4$  (Einspahr, Marsh & Donohue, 1972)

	$\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{LiHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	$\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	$\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{KHC}_2\text{O}_4$
C(1)–C(2)	1.549 (2)	1.547 (1)	1.552 (2)	1.549 (3)	1.551 (9)	1.552
C(1)–O(1)	1.236 (2)	1.240 (1)	1.242 (2)	1.230 (4)	1.223 (6)	1.256
C(1)–O(2)	1.257 (2)	1.259 (1)	1.251 (2)	1.247 (4)	1.272 (6)	1.234
C(2)–O(3)	1.304 (2)	1.309 (1)	1.313 (2)	1.291 (4)	1.307 (6)	1.308
C(2)–O(4)	1.204 (2)	1.210 (1)	1.207 (2)	1.212 (4)	1.211 (6)	1.211
O(1)–C(1)–O(2)	127.17 (11)	127.10 (7)	127.5 (2)	127.5 (3)	127.3 (6)	127.72
C(2)–C(1)–O(1)	118.43 (11)	117.49 (6)	117.4 (2)	117.5 (2)	117.9 (4)	115.46
C(2)–C(1)–O(2)	114.40 (11)	115.40 (6)	115.2 (2)	115.0 (2)	114.5 (4)	116.82
O(3)–C(2)–O(4)	125.29 (11)	126.52 (8)	125.3 (2)	124.8 (3)	124.4 (6)	124.72
C(1)–C(2)–O(3)	113.10 (10)	110.87 (6)	113.1 (1)	113.3(2)	113.2 (5)	114.73
C(1)–C(2)–O(4)	121.61 (11)	122.61 (6)	121.6 (2)	121.8 (2)	122.1 (5)	120.55
H bond length	2.561 (2)	2.490 (1)	2.571 (2)	2.500 (4)	2.505 (5)	2.523 (2)

Table 4. C–C bond distances for various oxalates: (a) neutral oxalates, (b) hydrogen oxalates, and (c) crystals containing oxalic acid molecules

*R* is the reliability index for the respective structure determination.

Compound	<i>R</i> (%)	C–C distance	Reference
(a)			
$\text{Li}_2\text{C}_2\text{O}_4$	5.7	1.559 (4) (Å)	Beagley & Small (1964)
$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	6.6	1.570 (11)	Pedersen & Pedersen (1964)
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	3.9	1.574 (2)	Hodgson & Ibers (1969)
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	7.6	1.563 (13)	Pedersen (1967)
$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	8.2	1.572 (16)	Pedersen (1967)
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	8.0	1.569 (8)	Robertson (1965)
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	4.8	1.563 (2)	Pedersen (1972)
(b)			
$\text{KHC}_2\text{O}_4$	2.7	1.552 (2)	Einspahr <i>et al.</i> (1972)
$\text{LiHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	2.4	1.547(1)	Thomas (1972)
$\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	2.8	1.552 (2)	Tellgren & Olovsson (1971)
$\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	3.0	1.546 (2)	Present work
$\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	8.8	1.549 (3)	Currie <i>et al.</i> (1967)
$\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	5.0	1.551 (9)	Haas (1964)
(c)			
$\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	8.8	{ 1.549 (5) 1.544 (5) }	Currie <i>et al.</i> (1967)
$\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	5.0	{ 1.553 (9) 1.554 (9) }	Haas (1964)
$\alpha\text{-H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	2.8	1.538 (1)	Delaplane & Ibers (1969)

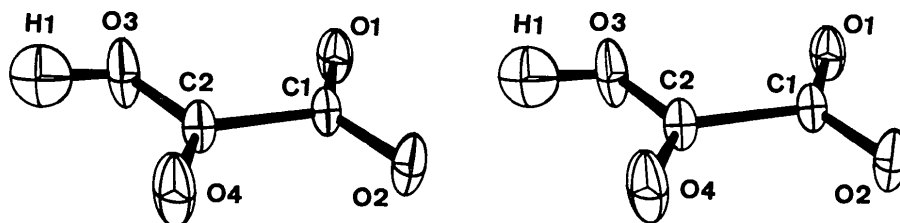


Fig. 2. Stereoscopic thermal ellipsoid plot of the hydrogen oxalate group (drawn by ORTEP, Johnson, 1965).

positions of multiplicity 0.5 in the mirror plane  $m$  instead of a general position.

#### The geometry of the oxalate group

Fig. 2 shows a stereoscopic view of the hydrogen oxalate ion. As frequently found in oxalates the carbon and oxygen atoms are in a planar arrangement, the least-squares equation (as related to a Cartesian  $\bar{A}$  coordinate system parallel to the orthorhombic axes) being:

$$0.0836 X + 0.3990 Y + 0.9131 Z = 4.439.$$

Displacements of individual atoms from this plane are (in  $\text{\AA}$ ): C(1) 0.0; C(2)  $-0.0033$ ; O(1)  $-0.0048$ ; O(2)  $+0.0054$ ; O(3)  $+0.0064$ ; O(4)  $-0.0037$ . Such deviations are within the range of experimental errors. The distance of H(1) from the plane is  $-0.0189$   $\text{\AA}$ . The mean oxalate plane is inclined at  $24^\circ$  to the  $c$  axis.

Bond distances and angles are listed in Table 3. C–O distances and angles around C(2) agree with those usually found in COOH groups. According to Hahn (1957) the measured bond angles yield a double-bond character of 23% for the C(2)–O(3) bond and 76% for the C(2)–O(4) bond. Values for the two angles C–C–O in the ionized C(2)–O(1)–O(2) group are appreciably different. This asymmetry, however, is observed in all acid oxalates. Table 3 contains, in addition to the data for  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , the corresponding bond lengths and angles of five other acid oxalates whose structures have been determined with high accuracy.

These six hydrogen oxalate groups exhibit remarkably similar geometries [if the values for O(1) and O(2) of  $\text{KHC}_2\text{O}_4$  (bold-faced in Table 3) are interchanged]. As shown by Pedersen (1968) the asymmetry of the COO group can be explained as a result of the way the hydrogen bonds are connected to the oxalate groups. In  $\text{KHC}_2\text{O}_4$  a hydrogen bond is formed between O(3) and O(1) (*i.e.* two oxygens adjacent in the oxalate residue), thus building a *cis* configuration, whereas in the five other hydrogen oxalates hydrogen bonds connect O(3) and O(2) (*i.e.* two oxygens located opposite each other in the oxalate residue), thus showing a *trans* configuration (see Fig. 3). In each case, bonds or angles related to the acceptor oxygen are comparable. This result is in accordance with the concept stated by Hahn (1957), that formation of a hydrogen bond  $\text{C}=\text{O} \cdots \text{H}$  weakens the  $\text{C}=\text{O}$  bond and correspondingly modifies bond angles.

A striking feature common to all oxalates is the abnormally long distance between the two C atoms. Values observed for different oxalate compounds range between 1.54 and 1.58  $\text{\AA}$ . These are noticeably longer than usually observed for  $sp^2$ – $sp^2$  C–C single bonds which are found to scatter between 1.47 and 1.52  $\text{\AA}$  (Bastiansen & Traetteberg, 1962). A theoretical explanation for the lengthening of the central bond in the  $\text{C}_2\text{O}_4^{2-}$  ion has been given by Brown & Harcourt (1963). They have shown by MO calculations that this

phenomenon is caused by some delocalization of oxygen lone-pair electrons ( $2p$  electrons with atomic orbitals symmetric with respect to the COO plane) into an antibonding  $\sigma$  orbital between the C atoms.

Because in recent years many highly accurate structure analyses of oxalate compounds have been carried out, detailed discussion of measured C–C bond lengths is now possible. In Table 4, C–C distances of various oxalates ( $R$  values lower than 10%) are collected and classified into three groups. Group (*a*) contains neutral oxalates, group (*b*) hydrogen oxalates, and group (*c*) crystals which contain the oxalic acid molecule. The unit cells of the tetroxalates,  $\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , contain two (equivalent) hydrogen oxalate ions and two oxalic acid molecules. Therefore, these crystals are listed in group (*b*) and also in group (*c*) with their respective bond distances. As can be seen in Table 4 in general, crystals listed in group (*a*) have largest distances and those in group (*c*) smallest distances. If the C–C bond lengths of the different crystals are regarded as independent measurements with standard deviations as given in parentheses, an average, representative length for each group may be ob-

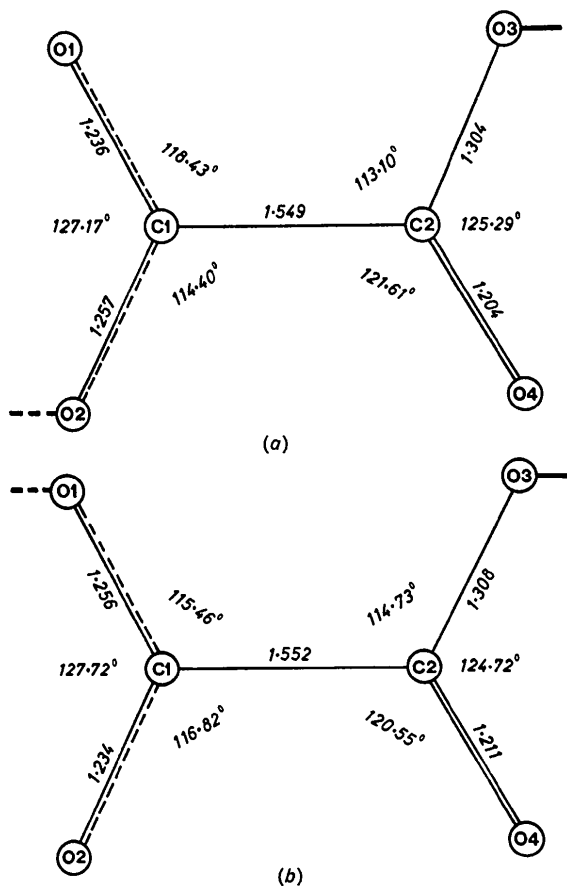


Fig. 3. Configuration of the oxalate group in (a)  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  and (b)  $\text{KHC}_2\text{O}_4$  (after Einspahr *et al.*, 1972).

tained by means of standard methods of error analysis. The weighted mean values and standard deviations are:

- (a)  $1.567_5 \pm 0.002_4$  Å
- (b)  $1.548_3 \pm 0.004_0$
- (c)  $1.538_4 \pm 0.002_8$ .

If we assume that the mean value as given for group (a) is the 'normal' bond length (due to the mechanism proposed by Brown & Harcourt, 1963), then the attachment of one [group (b)] or two [group (c)] H atoms to this ion apparently causes a shortening of the C–C bond length. This finding may be qualitatively explained within the framework of Brown & Harcourt's theory. On protonation of the  $C_2O_4^{2-}$  ion, the electron distribution around the appropriate oxygen, O(3), is changed. The orbital configuration of O(3) seems to be represented now predominantly by tetragonal  $sp^3$  hybridization [angle C(1)–O(3)–H(1) is found to be  $109.9^\circ$ ]. Electrons which were formerly lone-pair electrons are now involved in the O–H bond and no longer fulfill conditions attributed to them by Brown & Harcourt's model. Therefore, their contribution to the antibonding  $\sigma$  orbital is reduced.

It should be mentioned that these observations are not restricted only to oxalates. Terminating C–C distances of various other monobasic as well as dibasic

carboxylic acids are found, on the average, to be shorter than those of corresponding salts.

A final difference Fourier synthesis revealed a significant electron density maximum at the mid-point of the C–C bond (Fig. 4). This has also been observed by Beagley & Small (1963, 1964) for ammonium oxamate and lithium oxalate and also by Coppens, Sabine, Delaplane & Ibers (1969) for  $\alpha$ -oxalic acid dihydrate. The height of the peak is  $0.30 e \text{ \AA}^{-3}$ . Half width of the electron cloud as measured perpendicular to the oxalate plane is about  $0.86 \text{ \AA}$ , and when measured within the plane it is about  $0.70$  and  $0.53 \text{ \AA}$  (normal and parallel to the C–C bond, respectively). This anisotropy approximately corresponds to the anisotropy of the thermal translational motion of the oxalate residue (*cf.* later section).

#### Cation environment

Coordination of the  $NH_4^+$  ions is demonstrated in Fig. 5. This shows a section perpendicular to [010] at  $y=0.25$  (*i.e.* at the level of the mirror plane  $m$ ). Atoms lying in the mirror plane are represented by bold circles. Atoms situated outside the mirror plane (equal distances below and above) are indicated by dashed circles. Oxalate residues connecting oxygens O(1) with O(3) and O(2) with O(4) are indicated by dashed lines. Bond distances of nitrogens and of O(5) to surrounding oxygens are also given.

Nitrogen N(2) is coordinated with seven oxygens. The only non-furcated hydrogen bond is formed by H(6), with O(5) acting as an acceptor. Distance N(2)–O(5) is the shortest bond ( $2.841 \text{ \AA}$ ) between N(2) and adjacent oxygens. H(7), which also lies in the mirror plane, forms a hydrogen bond bifurcated to O(1) and O(1'). H(8) and H(8') form bonds bifurcated to O(2) and O(4) or O(2') and O(4'), respectively.

In contrast, N(1) is coordinated by nine oxygen atoms. H(3) builds the only non-furcated hydrogen bond, once again to O(5). H(4) forms a bifurcated bond to O(4) and O(4') while H(5) and H(5') form trifurcated bonds to O(2), O(1) and O(3), or O(2'), O(1'), and O(3'), respectively.

As a result of the larger coordination number, bond distances around N(1) are generally longer, *i.e.* the cavity surrounding N(1) is larger than that surrounding N(2). Therefore, the  $N(1)H_4^+$  ion has a larger freedom of movement than the  $N(2)H_4^+$  ion. Movement of the three hydrogens H(4), H(5), and H(5') [probably oscillating around the axis N(1)–H(3)] was suggested by the following indications: (1) high isotropic temperature factors,  $B$ , for H(4) and H(5); (2) whereas other hydrogens could be associated with sharp maxima of a height between  $0.4$  and  $0.5 e \text{ \AA}^{-3}$  in the difference Fourier map, H(4) and H(5) were found to have smeared maxima of electron density with heights ranging from  $0.2$  to  $0.3 e \text{ \AA}^{-3}$ . In Fig. 6 the electron density within the plane which should contain H(4), H(5), and H(5') [normal to the axis N(1)–H(3)] is drawn as derived from a difference Fourier synthesis.

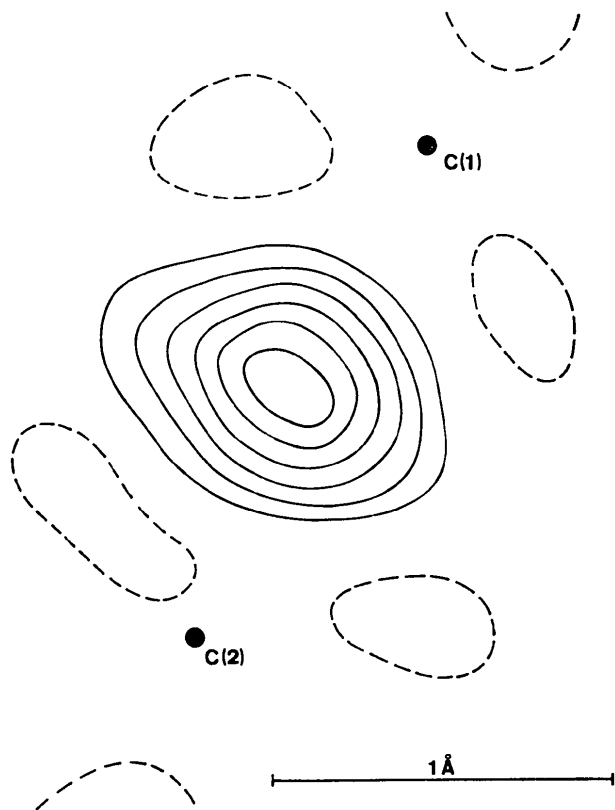


Fig. 4. Residual electron density between the C atoms, as revealed by a difference Fourier synthesis.

Electron density increases by  $0.04 \text{ e } \text{\AA}^{-3}$  from line to line. Because of the general problem of exactly locating hydrogen atoms with X-ray methods, this map does not precisely show the nearly threefold symmetry to be expected. However, it can be seen that the peaks, especially that of H(4), which lies in the mirror plane  $m$ , are smeared out tangentially. This may be the result of a thermally activated oscillation.

In order to compare the stability of the equilibrium positions of the hydrogens in the two ammonium ions, the electrostatic part of the lattice energy was calculated as a function of rotation angle  $\varphi$ . This angle describes rotation of the  $\text{NH}_4$  group around the non-furcated bond N(1)–O(5) or N(2)–O(5), respectively. Calculation was performed with a modification of the computer program *MANIOC* written by Baur (1965). The model used here assumes purely electrostatic interaction between positively charged hydrogens and the remaining ions of the lattice. In spite of neglect of other terms this model has been previously very successfully used for the determination of hydrogen positions in several crystals (Baur, 1965). For the present case an electric charge of  $+0.15e$  was attached to the hydrogens and a charge of  $+0.4e$  to the nitrogens.

The results of the computation are shown by Fig. 7. Lattice energy  $E$  is plotted versus rotation angle  $\varphi$  for both  $\text{N}(1)\text{H}_4$  and  $\text{N}(2)\text{H}_4$ .  $\varphi=0$  corresponds to the position where one hydrogen lies in the mirror plane at the

place found for H(3) and H(6).  $E$  is periodic with  $120^\circ$ . It may be seen that the potential barrier of the  $\text{N}(2)\text{H}_4$  group is appreciably higher than that of the  $\text{N}(1)\text{H}_4$  group. This finding generally explains the experimental results described above.

N–H and O–H distances obtained from the positions listed in Table 2 range between  $0.83$  and  $0.99 \text{ \AA}$ . Because, as frequently found in X-ray investigations, these distances are considerably lower than the 'real' distances as determined by neutron diffraction, their values are not reported.

#### Thermal motion

The shape of the ellipsoids drawn in Fig. 2 suggests a rigid-body motion of the hydrogen oxalate residues. Where an oscillating group has a high symmetry usual procedures of determining the components of the libration tensor fail. Since, when H(1) is omitted, the oxalate ion has nearly symmetry  $mmm$ , an application of the program *TLS* of Schomaker & Trueblood (1968) yielded results which were physically meaningless (negative eigenvalues).

For this reason, analysis of thermal motion was made in accord with the method proposed by Beagley & Small (1963). The *S* tensor as introduced by Schomaker & Trueblood (1968) will be neglected in the following treatment. A molecular coordinate system was set up as follows: *L* axis parallel to the C–C bond,

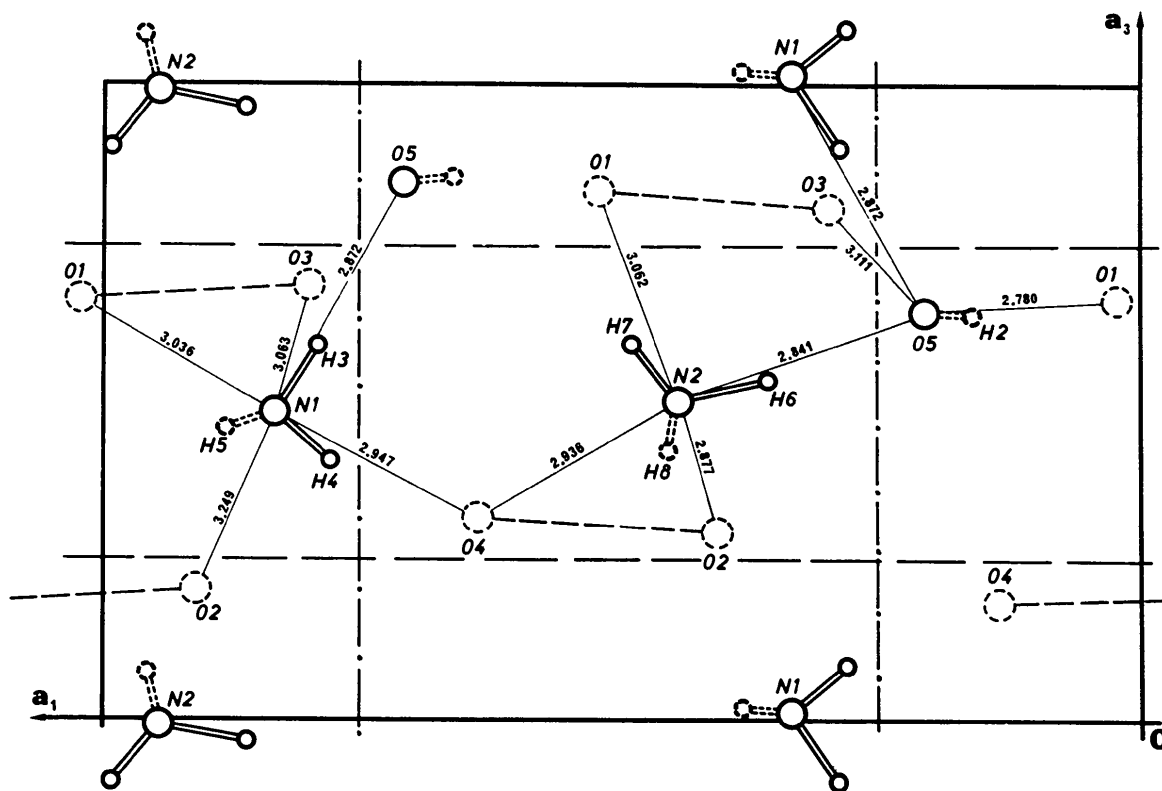


Fig. 5. Atomic arrangement in and near the mirror plane perpendicular to the  $b$  axis at  $y=0.25$ .

$N$  axis perpendicular to the oxalate plane, and  $M$  axis perpendicular to  $L$  as well as to  $N$ . This reference system is related to the orthorhombic system by the following direction cosines.

$L$	0.9236	-0.3755	0.0772
$M$	0.3737	0.8369	-0.3999
$N$	0.0836	0.3990	0.9131

The mean-square displacements  $U_{ii}$  together with the direction cosines of the principal axes of thermal ellipsoids with respect to the cell edges are listed in Table 5. In addition, Table 5 contains the mean-square displacements parallel to the axes  $L$ ,  $M$ , and  $N$ .

The displacements parallel to  $M$  are remarkably uniform. They may be attributed to translational motion

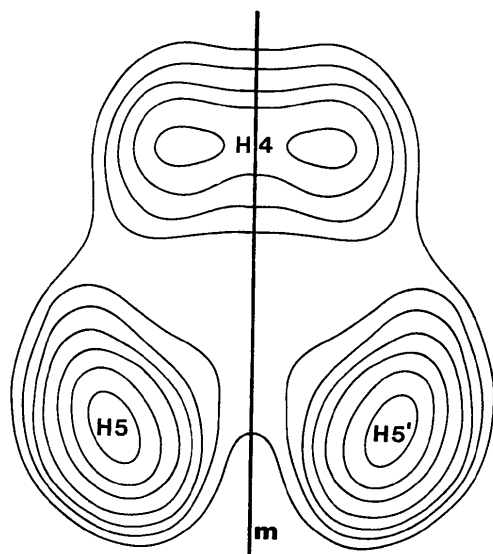


Fig. 6. Electron density in the plane built up by H(4), H(5) and H(5').  $m$  indicates the mirror plane.

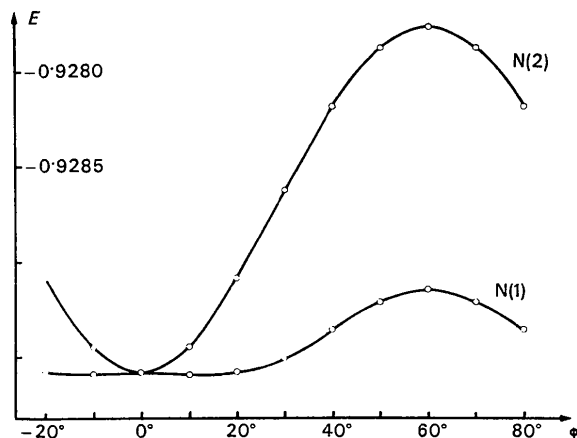


Fig. 7. Electrostatic part of the lattice energy,  $E$ , (units:  $e^2 \text{ \AA}^{-1}$  per formula unit) versus angle  $\phi$  which describes a rotation of  $\text{NH}_4^+$  groups around bonds N(1)-O(5) and N(2)-O(5).

of the whole ion parallel to  $M$ . The displacements are also relatively uniform along the  $l$  axis. The values of the C atoms are slightly lower, possibly indicating a small amplitude libration about  $N$ . This appeared to be negligible and was not considered here. Parallel to  $N$  the oxygens exhibit considerably larger displacements than the carbons. This indicates a libration around  $L$ . The average of the displacements of the carbons may be interpreted as a translation of the whole ion parallel to  $N$ . In addition, the difference between this value and the translational component of the oxygens should determine the rotation of the different oxygens around the  $L$  axis. The mean-square amplitudes of the translation of the whole oxalate group are then:

$$\begin{aligned} T_L^2 &= 0.0165 \pm 0.0015 \text{ \AA}^2 \\ T_M^2 &= 0.0244 \pm 0.0015 \\ T_N^2 &= 0.0289 \end{aligned}$$

Taking into account the distances of the oxygens from  $L$  the following mean-square libration amplitudes are obtained for the particular atoms

$$\begin{aligned} \text{O}(1) &= 0.0153 \text{ rad}^2 \\ \text{O}(2) &= 0.0236 \\ \text{O}(3) &= 0.0314 \\ \text{O}(4) &= 0.0452 \end{aligned}$$

Corresponding libration r.m.s. amplitudes are: 7.0, 8.8, 10.1, and 12.2°. These differing values indicate that the assumption of rigid-body motion is only approximately fulfilled. The rotation of the C(2)-O(3)-O(4) group around the C-C bond is apparently larger than that of the C(1)-O(1)-O(2) group.

Correcting the C-O bond distances for these librations corresponds to correction in accord with the riding model proposed by Busing & Levy (1964). The corrected values are:

$$\begin{aligned} \text{C}(1)\text{-O}(1) & 1.247 \text{ \AA} \\ \text{C}(1)\text{-O}(2) & 1.273 \\ \text{C}(2)\text{-O}(3) & 1.322 \\ \text{C}(2)\text{-O}(4) & 1.224 \end{aligned}$$

#### Relations to other properties

$\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  exhibits pronounced cleavage at (011). This behaviour may be explained in terms of the molecular arrangement in the crystal structure. The average height of the oxalate residues in the  $z$  direction is 0.25 and 0.75. The height of the  $\text{NH}_4$  ions is nearly 0.0 or 0.5. Thus, periodic bond chains are formed parallel to  $\langle 111 \rangle$  and  $\langle 011 \rangle$ . The strongest periodic bond chain of the structure is built up by the hydrogen-bonded oxalate residues along [100]. With this vector and the vectors mentioned above, planes of type  $\{011\}$  are established.

Refractive indices of  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  have been previously reported to be (for  $\lambda = 589 \text{ nm}$ ) (Küppers, 1972b):

$$\begin{aligned} n_a &= 1.5641 \\ n_b &= 1.5676 \\ n_c &= 1.4346 \end{aligned}$$



Table 5. Mean-square displacements,  $U_{ii}$  ( $\text{\AA}^2$ ), along the principal axes of the thermal ellipsoids; direction cosines,  $a_{ij}$ , relating the principal axes ( $i$ ) to the orthorhombic axes ( $j$ ); mean-square displacements,  $\bar{u}_L^2$ ,  $\bar{u}_M^2$ , and  $\bar{u}_N^2$  ( $\text{\AA}^2$ ) along molecular axes  $L$ ,  $M$ , and  $N$

Values are  $\times 10^4$

	$i$	$U_{ii}$	$a_{i1}$	$a_{i2}$	$a_{i3}$	$\bar{u}_L^2$	$\bar{u}_M^2$	$\bar{u}_N^2$
C(1)	1	304	1074	2623	-9509	148	257	268
	2	228	1174	9543	2749			
	3	139	9877	-1369	753			
C(2)	1	334	974	-207	-9950	152	228	309
	2	212	2176	9760	11			
	3	147	9716	2145	1001			
O(1)	1	489	-224	1866	9822	176	260	468
	2	262	-6669	-7345	1256			
	3	167	7450	-6518	1420			
O(2)	1	607	683	3181	9456	166	243	600
	2	273	307	-9483	3158			
	3	147	9974	-23	-716			
O(3)	1	748	258	2971	9545	162	225	742
	2	245	184	-9550	2961			
	3	141	9996	-160	-226			
O(4)	1	773	69	3273	9449	188	249	765
	2	262	-6829	-6889	2431			
	3	180	7305	-6470	2184			

(indices refer to orthorhombic axes). The crystal is quasi-uniaxial negative. This result is in agreement with the arrangement of the oxalate planes (approximately normal to the  $c$  axis), because the polarizability within the planes is larger than that normal to the planes (Hendricks & Deming, 1935; Küppers, 1972b).

The arrangement of the oxalate residues also explains the high elastic anisotropy observed in  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (Küppers, 1972b). The hydrogen bonds between the oxalate groups cause a high elastic stiffness along [100] ( $c_{11} = 6.71$  dyne  $\text{cm}^{-2}$ ), whereas weak bonds normal to the oxalate planes produce a low stiffness along [001] ( $c_{33} = 1.475$  dyne  $\text{cm}^{-2}$ ).

The position of the  $\text{NH}_4$  ions in the mirror plane looks like the position of the  $\text{NH}_4$  ions in the crystal structure of  $(\text{NH}_4)_2\text{SO}_4$  (Schlemper & Hamilton, 1966). In this crystal, by a flipping motion of the  $\text{NH}_4$  group out of the mirror plane, a ferroelectric phase transition takes place from space group  $Pnma$  to  $Pn2_1a$ . A similar mechanism might also be possible in  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , especially when the instability of the ammonium group  $\text{N}(1)\text{H}_4$  is considered. But no ferroelectric hysteresis under application of a voltage of  $2$  kV  $\text{cm}^{-1}$  was detectable in the temperature range between room temperature and  $-195^\circ\text{C}$ .

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## The Crystal Structure of Bis(pyrazine-2-carboxamide)copper(II) Perchlorate

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The crystal structure of bis(pyrazine-2-carboxamide)copper(II) perchlorate,  $\text{Cu}(\text{pyaH})_2(\text{ClO}_4)_2$ , has been determined from three-dimensional X-ray photographic data and refined by block-diagonal least-squares methods to give  $R=0.08$  for the 876 observed reflexions. The crystals are monoclinic with space group  $P2_1/a$ . There are two formula units in a unit cell of dimensions:  $a=10.36$ ,  $b=9.89$ ,  $c=8.77$  Å and  $\beta=110.7^\circ$ . The complex is centrosymmetric with two ligand molecules chelating to the central copper atom in *trans* positions through the amide oxygen atoms and the *ortho* nitrogen atoms of the rings. This part has a square-planar structure and the *meta* nitrogen atoms of the pyrazine ring of two neighbouring complex ions coordinate weakly to the central copper atom from the top and bottom of the coordination plane, thus completing octahedral coordination. Perchlorate ions do not coordinate to the copper atom but are bonded to the amide nitrogen atom of the ligand molecule by weak hydrogen bonds.

### Introduction

In the course of studies on the bivalent metal complexes of acid amides, X-ray crystal analyses of  $[\text{Ni}(\text{pia})_2]2\text{H}_2\text{O}$  (Nawata, Iwasaki & Saito, 1967),  $[\text{Ni}(\text{H}_2\text{O})_2(\text{piaH})_2]\text{Cl}_2$  (Masuko, Nomura & Saito, 1967),  $[\text{Cu}(\text{H}_2\text{O})_2(\text{piaH})_2]\text{Cl}_2$  (Brown, MacSween, Mercer & Sharp, 1971) and  $[\text{Cu}(\text{ClO}_4)_2(\text{paaH})_2]$  (Sekizaki, Marumo, Yamasaki & Saito, 1971) have revealed that the first complex has a structure with square-planar coordination through the amide nitrogen and ring nitrogen atoms of the ligand, while the remaining three have a structure with octahedral or distorted octahedral coordination through the amide oxygen and ring nitrogen atoms where *piaH* and *paaH* denote pyridine-2-carboxamide and pyridine-2-acetamide respectively.

On the basis of these structure determinations and of spectral and magnetic studies (Sekizaki, Tanase & Yamasaki, 1969; Sekizaki & Yamasaki, 1969*a*; Sekizaki & Yamasaki, 1970) it has been proposed that bis(pyrazine-2-carboxamide)copper(II) perchlorate,  $\text{Cu}(\text{pyaH})_2(\text{ClO}_4)_2$ , has a chelate structure with coordination through the amide oxygen and ring nitrogen atoms (Sekizaki & Yamasaki, 1969*b*). It was, however, very difficult to prove whether this complex has a square-planar structure by the coordination of pyrazine-2-carboxamide alone or a distorted octahedral

structure by the coordination of some other groups in addition to the two ligand molecules. This complex was subjected to X-ray crystal analysis in order to establish the stereochemical structure and to compare it with that of  $[\text{Cu}(\text{ClO}_4)_2(\text{paaH})_2]$ .

In the present paper the nitrogen atom of the pyrazine ring at the *ortho* position with respect to the carbon atom bonded to an amide group will be called the *ortho* nitrogen, and the other nitrogen atom at the *meta* position the *meta* nitrogen.

### Experimental

The complex,  $\text{Cu}(\text{pyaH})_2(\text{ClO}_4)_2$ , is obtained as blue crystals on letting a mixture of aqueous solutions of one mole of copper perchlorate and two moles of pyrazine-2-carboxamide stand overnight (Sekizaki & Yamasaki, 1969*b*). The unit-cell dimensions were determined from higher-order reflexions on Weissenberg photographs ( $\text{Cu } K\alpha_1$ ,  $\lambda=1.5405$  Å). The systematic absences are  $h0l$  with  $h$  odd and  $0k0$  with  $k$  odd. Hence the space group is  $P2_1/a$ . Equi-inclination integrated Weissenberg photographs were taken about the  $a$  and  $b$  axes up to the 3rd and 7th layers respectively.  $\text{Cu } K\alpha$  radiation ( $\lambda=1.5418$  Å) was used. The intensities were estimated visually and were converted to  $|F|$  by applying the Lorentz and polarization corrections. Absorption and extinction corrections were not made. A total of 876 independent non-zero reflexions were collected. The crystal data are:  $\text{Cu}(\text{C}_4\text{H}_3\text{N}_2\text{CONH}_2)_2(\text{ClO}_4)_2$ ,

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