

## Hydrogen Bond Studies. XIV.\* The Crystal Structure of Ammonium Acetate

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The crystal structure of ammonium acetate has been determined at room temperature from three-dimensional single-crystal X-ray data. Four  $\text{CH}_3\text{COONH}_4$  units crystallize in a monoclinic unit cell of space group  $P2_1/c$  and dimensions  $a=4.787$ ,  $b=7.742$ ,  $c=12.015$  Å, and  $\beta=100.76^\circ$ . Two sets of data collected from two different crystals, rotating around the  $a$  and the  $b$  axes respectively, were used in least-squares refinements with allowance for anisotropic thermal motion. They gave final discrepancy indices,  $R$ , of 0.082 and 0.090 respectively and atomic coordinates which did not differ significantly from each other. The four hydrogen atoms of the ammonium ion form  $\text{N}^+-\text{H}\cdots\text{O}^-$  hydrogen bonds of length 2.80–2.83 Å, in an approximately tetrahedral arrangement. In the three-dimensional hydrogen-bonded network thus formed each oxygen atom accepts two hydrogen bonds. The dimensions of the acetate ion are: bond lengths, C–C 1.504, C–O 1.250 and 1.253 Å; bond angles, O–C–O  $123.4^\circ$ , O–C–C  $118.5$  and  $118.0^\circ$ .

### Introduction

The melting point diagram of the system ammonia–acetic acid shows the existence of the solid compounds  $\text{NH}_3 \cdot 2\text{CH}_3\text{COOH}$ ,  $\text{NH}_3 \cdot \text{CH}_3\text{COOH}$ ,  $5\text{NH}_3 \cdot 4\text{CH}_3\text{COOH}$ ,  $2\text{NH}_3 \cdot \text{CH}_3\text{COOH}$ , and  $9\text{NH}_3 \cdot \text{CH}_3\text{COOH}$  (Davidson, Sisler & Stoenner, 1944).

A comparison of the structures of these compounds should give a great deal of information concerning the nature of the hydrogen bond. The present investigation is the first in a series of crystal structure determinations of compounds formed in the system.

None of the crystal structures of these compounds have been reported before.

### Experimental

Ammonium acetate (*purum*) was recrystallized several times from ethanol (99.5%) and dried over calcium sulphate (Drierite) in a desiccator. The crystals were very hygroscopic and their mounting had to be performed in a dry-box filled with nitrogen which had been dried by passing through a liquid nitrogen trap.

The crystals had the shape of long, flat needles along the  $a$  axis. Suitable crystals were chosen under a microscope, carefully cut to size with a razor and mounted in glass capillaries which were finally sealed.

Two different crystals with approximate dimensions  $0.2 \times 0.3 \times 0.5$  mm were used for the X-ray analysis, one mounted along the  $a$  axis and the other along the  $b$  axis. Both of the crystals had the longest side parallel with the axis of the capillary. Multiple-film (five), equi-inclination Weissenberg photographs were taken with

Cu  $K$  radiation. Layers  $0 \leq h \leq 4$  were recorded for the first crystal rotating around the  $a$  axis and layers  $0 \leq k \leq 6$  for the second one rotating around the  $b$  axis. 78% or 780 of the non-extinguished reflexions within the Cu  $K\alpha$  sphere were recorded for crystal no. 1 and of these only 598 had measurable intensities. For crystal no. 2 the corresponding figures were 81%, 803 and 589 reflexions.

The relative intensities of the reflexions were obtained by visual comparison with a calibrated intensity scale. The intensity range was 1 to 4000. The data were corrected for the Lorentz and polarization effects. No absorption correction was applied, since the linear absorption coefficient is  $8.9 \text{ cm}^{-1}$  and both of the crystals were rotating around the longest side. No extinction correction was made.

Inter-layer scale factors were calculated, using a program designated INTERSCALE (see below). All observations were given the same weights. The number of reflexions common to both sets of films was 469.

### Unit cell and space group

The diffraction symmetry of  $2/m$  indicated a monoclinic unit cell. Accurate cell dimensions were obtained from zero-layer oscillation photographs around the  $a$  and the  $c$  axes, calibrated with a quartz single crystal. The following numerical values were used:

$a=4.913$  Å for  $\alpha$  quartz ( $25^\circ\text{C}$ ),  $\lambda(\text{Cu } K\alpha_1)=1.54051$  Å,  $\lambda(\text{Cu } K\alpha_2)=1.54433$  Å,  $\lambda(\text{Cu } K\beta)=1.39217$  Å.

On the two photographs  $\theta$  values were measured for 88 and 89 different reflexions respectively. No  $\theta$  value was less than  $30^\circ$ . A least-squares treatment of the observed  $\theta$  values using the program CELSIUS, gave the following cell dimensions and standard deviations:  $a=4.787 \pm 0.001$ ,  $b=7.742 \pm 0.001$ ,  $c=12.015 \pm 0.004$  Å,  $\beta=100.76 \pm 0.02^\circ$ . Unit-cell volume =  $437.5 \text{ Å}^3$ . With

\* The preceding paper in this series: *Hydrogen Bond Studies* 13. *The Crystal Structure of Hydrazinium Perchlorate Hemihydrate*,  $\text{N}_2\text{H}_5\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , by R. Liminga appeared in *Acta Chem. Scand.* (1967), 21, 1217.

four  $\text{NH}_3 \cdot \text{CH}_3\text{COOH}$  units in the cell the calculated density of the solid is  $1.169 \text{ g.cm}^{-3}$ . The measured value for the density is  $1.171 \text{ g.cm}^{-3}$  (Biltz & Balz, 1928).

Space group:  $P2_1/c$  (no. 14, *International Tables for X-ray Crystallography*, 1952).

### Determination of the crystal structure

#### *The orientation of the acetate group in the unit cell*

A three-dimensional Patterson synthesis was calculated with use of the data from the crystal rotating around the  $a$  axis.

From the geometry of the acetate group (e.g. Speakman & Mills, 1961) vectors with the approximate lengths 1.25, 1.50, 2.25 and 2.40 Å are expected to be found. Loci of vectors with these lengths were plotted in the Patterson maps. However, the loci of the very shortest vectors could give but little information because of the heavy overlap from the origin peak. One rather high peak was found at a distance of about 2.25 Å from the origin, defining a vector parallel to the (010) plane. As there were no other peaks at similar distances the one found was assumed to be the vector between the two oxygen atoms of the acetate group. On the sphere with radius 2.40 Å only two rather small peaks were found. They were assumed to be the vectors between the methyl carbon and the oxygen atoms of the carboxyl group, as their directions fitted well with the oxygen–oxygen vector already found.

#### *The location of the acetate group in the unit cell and the atomic coordinates of the nitrogen atom*

Neither Harker vectors nor general vectors between atoms of different acetate groups could be found because of heavy overlap of peaks. As the structure was supposed to contain hydrogen bonds, 2.8–3.1 Å long, loci of such vectors were plotted in the Patterson maps. Four well resolved peaks, 2.8 Å from the origin and with nearly equal height, were found. These were assumed to be vectors between nitrogen and different oxygen atoms, as none could be a vector between two oxygen atoms because of the crystal symmetry and the orientation of the acetate group.

After some other general vectors N—O had been found, it was possible to assume a trial structure. The coordinates of the carboxyl carbon were calculated assuming the acetate group to be planar and the C—C and C—O distances to be 1.50 and 1.25 Å respectively.

#### *Location of the hydrogen atoms and refinement of the atomic coordinates*

At first the preliminary atomic coordinates of all atoms except the hydrogen atoms were improved in a series of three-dimensional electron density calculations. The further refinement of the atomic parameters was performed by the method of least squares. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized. The weights,  $w$ , of the observations were calculated according to the expression suggested by Cruickshank,  $w = 1/(a + |F_o| +$

$c|F_o|^2)$ , with  $a = 2.0$  and  $c = 0.055$ . Reflexions too weak to be observed were given zero weight. In the first three cycles the parameters refined were the overall scale factor and individual isotropic temperature factors. In another ten cycles the atomic coordinates were also refined. The reflexions 020 and  $10\bar{2}$  were excluded in the last one as they were thought to suffer from secondary extinction errors. At this stage of the refinement the shifts of the atomic coordinates were less than one tenth of the estimated standard deviations and the discrepancy index  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  was 0.14. Unobserved reflexions were omitted in all calculations of  $R$  values.

Parallel with the calculations described above a series of least-squares refinements was made with the same starting values for the scale factors and atomic parameters. However, inter-layer scale factors as well as atomic coordinates and isotropic thermal parameters were allowed to vary. The result was compared with that derived when the experimentally found scale factors were kept fixed. The differences in atomic parameters and scale factors were less than 1 e.s.d.

A three-dimensional ( $F_o - F_c$ ) synthesis was now calculated to get information on the positions of the hydrogen atoms. As it was impossible to locate the hydrogen atoms with any accuracy in the resulting maps, another difference synthesis was calculated with the use only of the reflexions with  $\sin \theta / \lambda$  less than  $0.5 \text{ \AA}^{-1}$ . Seven rather diffuse peaks now appeared, four of which were approximately 1 Å away from the nitrogen atom and close to the straight lines connecting the nitrogen to its four neighbouring oxygen atoms. This is an indication that the compound contains ammonium ions. The other three peaks were at a distance of approximately 1 Å from the methyl carbon. Additional peaks appearing in the difference maps had a size of less than one third of those mentioned before and were disregarded.

A new series of least-squares refinements was performed. The hydrogen atoms were included with Debye-Waller factors  $7 \text{ \AA}^2$ . The corresponding values for the nitrogen and the methyl carbon were 3.7 and  $5.3 \text{ \AA}^2$ . The parameters varied were the atomic coordinates and individual isotropic thermal parameters for all atoms but the hydrogens, as well as the overall scale factor. After two cycles of refinement the  $R$  value had dropped to 0.12.

The difference syntheses, especially the first one based on all observed reflexions, indicated that the temperature vibrations of most of the atoms were appreciably anisotropic. The temperature factors of the oxygen, nitrogen and carbon atoms were therefore subjected to anisotropic refinement in two cycles, the other parameters varied being the same as before. At this stage of the refinement the  $R$  value was 0.082 and the shifts in the coordinates and thermal parameters were less than one tenth of the standard deviation.

A comparison of the interatomic distances before and after the introduction of anisotropic temperature factors showed that the differences were less than 2

e.s.d. and the improvement of the  $R$  value must be chiefly due to the changes in the thermal parameters.

In order to obtain better coordinates of the hydrogen atoms a new ( $F_o - F_c$ ) synthesis, with allowance for the anisotropic vibrations of the atoms, was calculated. All but the hydrogen atoms contributed to  $F_c$  and only reflexions with  $\sin \theta/\lambda$  less than  $0.5 \text{ \AA}^{-1}$  were used. The peaks for the four hydrogen atoms connected to nitrogen appeared more distinctly than before but the methyl hydrogen atoms were still difficult to locate accurately. New coordinates of the hydrogen atoms were calculated from the difference synthesis and used as starting values for another two cycles of least-squares refinement. The parameters varied were the same as before. The  $R$  value and the atomic parameters did not change significantly. The final positional parameters resulting from the data of crystal no.1 with  $a$  as rotation axis

are given in Table 1(a). The anisotropic temperature parameters  $\beta_{ij}$  were transformed into the vibration tensor components  $U_{ij}$  according to Scheringer (1966) and these latter are shown in Table 1(b).

In order to get a comparison between results derived from two different crystals of the same compound the data from crystal no.2 were used in a least-squares refinement starting with the atomic parameters of the very first cycle of least-squares refinement for data-set no.1. When the shifts of the parameters were about one tenth of the standard deviations, the discrepancy index  $R$  was 0.090. Table 1(a) and (c) show the positional parameters and vibration tensor components derived from data-set no.2.

The observed and final calculated structure factors of the two crystals, after the last cycle of refinement, are compared in Table 2(a) and Table 2(b) respectively.

Table 1. *The final atomic parameters*

(a) Atomic coordinates. Standard deviations (in parentheses) are given only for refined parameters.

	Derived from data around the $a$ axis			Derived from data around the $b$ axis		
	$10^4x$	$10^4y$	$10^4z$	$10^4x$	$10^4y$	$10^4z$
O(1)	1203 (6)	1863 (3)	3175 (2)	1200 (6)	1863 (4)	3179 (2)
O(2)	3809 (5)	2193 (4)	4880 (2)	3816 (6)	2195 (4)	4878 (2)
N	607 (6)	-1548 (4)	3931 (3)	611 (7)	-1549 (4)	3935 (2)
C(1)	3167 (7)	2575 (5)	3851 (3)	3180 (8)	2579 (5)	3851 (3)
C(2)	4884 (10)	3951 (6)	3405 (4)	4875 (11)	3954 (7)	3405 (4)

	Hydrogen attached to nitrogen			Hydrogen attached to methyl carbon		
	$10^3x$	$10^3y$	$10^3z$	$10^3x$	$10^3y$	$10^3z$
H(1)	78	-46	369	H(5)	625	343
H(2)	7	-206	325	H(6)	383	450
H(3)	-83	-176	431	H(7)	570	467
H(4)	236	-175	430			

(b) Thermal vibration tensor components calculated from  $\beta_{ij}$  derived from the set of data with  $a$  as rotation axis. (Units of  $10^{-4} \text{ \AA}^2$ )\*

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	546 (17)	555 (15)	497 (16)	-97 (12)	-32 (13)	88 (11)
O(2)	524 (18)	751 (19)	404 (17)	-29 (13)	48 (12)	73 (12)
N	461 (19)	522 (16)	413 (18)	-69 (12)	51 (13)	-20 (12)
C(1)	406 (21)	470 (18)	454 (20)	56 (14)	79 (15)	46 (14)
C(2)	669 (30)	725 (26)	662 (29)	-152 (23)	139 (23)	128 (21)

(c) Thermal vibration tensor components calculated from  $\beta_{ij}$  derived from the set of data with  $b$  as rotation axis. (Units of  $10^{-4} \text{ \AA}^2$ )\*

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	580 (19)	611 (25)	448 (16)	-95 (14)	-50 (13)	81 (12)
O(2)	535 (17)	834 (27)	350 (16)	-75 (14)	22 (12)	75 (13)
N	474 (18)	575 (27)	333 (16)	-82 (14)	34 (12)	-13 (13)
C(1)	417 (21)	495 (31)	434 (21)	33 (16)	89 (15)	33 (16)
C(2)	675 (30)	807 (41)	597 (30)	-204 (24)	100 (22)	94 (23)

(d) Root-mean-square components  $R_i$  of thermal vibration along principal axes  $i$  of the ellipsoids of vibration. The estimated standard deviations are equal to or less than  $0.01 \text{ \AA}$ .

	Calculated from the $U_{ij}$ values of (b)			Calculated from the $U_{ij}$ values of (c)		
	$R_1$	$R_2$	$R_3$	$R_1$	$R_2$	$R_3$
O(1)	0.17 $\text{ \AA}$	0.23 $\text{ \AA}$	0.28 $\text{ \AA}$	0.18 $\text{ \AA}$	0.20 $\text{ \AA}$	0.31 $\text{ \AA}$
O(2)	0.18	0.22	0.29	0.17	0.21	0.31
N	0.19	0.20	0.25	0.18	0.19	0.26
C(1)	0.17	0.19	0.25	0.17	0.20	0.24
C(2)	0.12	0.28	0.32	0.13	0.25	0.34

\* $U_{ij}$  are coefficients in the expression  $\exp [-2\pi^2(h^2a^{-2}U_{11} + \dots + 2hka^{-1}b^{-1}U_{12} + \dots)]$



Table (2b). Observed and calculated structure factors. Data collected around the b axis\*

The same notation is used as in Table 2(a).

h		k		l		F <sub>o</sub>		F <sub>c</sub>	
h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	0	22.0	25.9	0	0	0	0.7	0.7
0	0	1	19.9	18.2	0	1	0	1.1	1.1
0	0	2	10.5	9.2	0	2	0	1.3	1.3
0	0	3	10.3	10.3	0	3	0	3.7	3.7
0	0	4	12.5	12.5	0	4	0	5.6	5.6
0	0	5	12.8	12.8	0	5	0	7.6	7.6
0	0	6	10.3	10.3	0	6	0	5.6	5.6
0	0	7	12.8	12.8	0	7	0	7.6	7.6
0	0	8	10.3	10.3	0	8	0	5.6	5.6
0	0	9	12.8	12.8	0	9	0	7.6	7.6
0	0	10	10.3	10.3	0	10	0	5.6	5.6
0	0	11	12.8	12.8	0	11	0	7.6	7.6
0	0	12	10.3	10.3	0	12	0	5.6	5.6
0	1	0	12.8	12.8	1	0	0	20.4	20.4
0	1	1	15.5	15.5	1	1	0	21.5	21.5
0	1	2	18.6	18.6	1	2	0	21.5	21.5
0	1	3	15.5	15.5	1	3	0	21.5	21.5
0	1	4	12.8	12.8	1	4	0	21.5	21.5
0	1	5	15.5	15.5	1	5	0	21.5	21.5
0	1	6	18.6	18.6	1	6	0	21.5	21.5
0	1	7	15.5	15.5	1	7	0	21.5	21.5
0	1	8	12.8	12.8	1	8	0	21.5	21.5
0	1	9	15.5	15.5	1	9	0	21.5	21.5
0	1	10	18.6	18.6	1	10	0	21.5	21.5
0	1	11	15.5	15.5	1	11	0	21.5	21.5
0	1	12	12.8	12.8	1	12	0	21.5	21.5
0	2	0	20.4	20.4	2	0	0	4.4	4.4
0	2	1	21.5	21.5	2	1	0	8.4	8.4
0	2	2	20.4	20.4	2	2	0	8.4	8.4
0	2	3	21.5	21.5	2	3	0	8.4	8.4
0	2	4	20.4	20.4	2	4	0	8.4	8.4
0	2	5	21.5	21.5	2	5	0	8.4	8.4
0	2	6	20.4	20.4	2	6	0	8.4	8.4
0	2	7	21.5	21.5	2	7	0	8.4	8.4
0	2	8	20.4	20.4	2	8	0	8.4	8.4
0	2	9	21.5	21.5	2	9	0	8.4	8.4
0	2	10	20.4	20.4	2	10	0	8.4	8.4
0	2	11	21.5	21.5	2	11	0	8.4	8.4
0	2	12	20.4	20.4	2	12	0	8.4	8.4
1	0	0	12.8	12.8	0	0	1	0.7	0.7
1	0	1	15.5	15.5	0	1	1	1.1	1.1
1	0	2	18.6	18.6	0	2	1	1.3	1.3
1	0	3	10.3	10.3	0	3	1	3.7	3.7
1	0	4	12.8	12.8	0	4	1	5.6	5.6
1	0	5	12.8	12.8	0	5	1	7.6	7.6
1	0	6	10.3	10.3	0	6	1	5.6	5.6
1	0	7	12.8	12.8	0	7	1	7.6	7.6
1	0	8	10.3	10.3	0	8	1	5.6	5.6
1	0	9	12.8	12.8	0	9	1	7.6	7.6
1	0	10	10.3	10.3	0	10	1	5.6	5.6
1	0	11	12.8	12.8	0	11	1	7.6	7.6
1	0	12	10.3	10.3	0	12	1	5.6	5.6
1	1	0	15.5	15.5	1	0	0	20.4	20.4
1	1	1	18.6	18.6	1	1	0	21.5	21.5
1	1	2	10.3	10.3	1	2	0	21.5	21.5
1	1	3	12.8	12.8	1	3	0	21.5	21.5
1	1	4	10.3	10.3	1	4	0	21.5	21.5
1	1	5	12.8	12.8	1	5	0	21.5	21.5
1	1	6	10.3	10.3	1	6	0	21.5	21.5
1	1	7	12.8	12.8	1	7	0	21.5	21.5
1	1	8	10.3	10.3	1	8	0	21.5	21.5
1	1	9	12.8	12.8	1	9	0	21.5	21.5
1	1	10	10.3	10.3	1	10	0	21.5	21.5
1	1	11	12.8	12.8	1	11	0	21.5	21.5
1	1	12	10.3	10.3	1	12	0	21.5	21.5
1	2	0	20.4	20.4	1	2	0	4.4	4.4
1	2	1	21.5	21.5	1	2	1	8.4	8.4
1	2	2	20.4	20.4	1	2	2	8.4	8.4
1	2	3	21.5	21.5	1	2	3	8.4	8.4
1	2	4	20.4	20.4	1	2	4	8.4	8.4
1	2	5	21.5	21.5	1	2	5	8.4	8.4
1	2	6	20.4	20.4	1	2	6	8.4	8.4
1	2	7	21.5	21.5	1	2	7	8.4	8.4
1	2	8	20.4	20.4	1	2	8	8.4	8.4
1	2	9	21.5	21.5	1	2	9	8.4	8.4
1	2	10	20.4	20.4	1	2	10	8.4	8.4
1	2	11	21.5	21.5	1	2	11	8.4	8.4
1	2	12	20.4	20.4	1	2	12	8.4	8.4
2	0	0	12.8	12.8	0	0	2	0.7	0.7
2	0	1	15.5	15.5	0	1	2	1.1	1.1
2	0	2	18.6	18.6	0	2	2	1.3	1.3
2	0	3	10.3	10.3	0	3	2	3.7	3.7
2	0	4	12.8	12.8	0	4	2	5.6	5.6
2	0	5	12.8	12.8	0	5	2	7.6	7.6
2	0	6	10.3	10.3	0	6	2	5.6	5.6
2	0	7	12.8	12.8	0	7	2	7.6	7.6
2	0	8	10.3	10.3	0	8	2	5.6	5.6
2	0	9	12.8	12.8	0	9	2	7.6	7.6
2	0	10	10.3	10.3	0	10	2	5.6	5.6
2	0	11	12.8	12.8	0	11	2	7.6	7.6
2	0	12	10.3	10.3	0	12	2	5.6	5.6
2	1	0	15.5	15.5	2	0	0	20.4	20.4
2	1	1	18.6	18.6	2	1	0	21.5	21.5
2	1	2	10.3	10.3	2	2	0	21.5	21.5
2	1	3	12.8	12.8	2	3	0	21.5	21.5
2	1	4	10.3	10.3	2	4	0	21.5	21.5
2	1	5	12.8	12.8	2	5	0	21.5	21.5
2	1	6	10.3	10.3	2	6	0	21.5	21.5
2	1	7	12.8	12.8	2	7	0	21.5	21.5
2	1	8	10.3	10.3	2	8	0	21.5	21.5
2	1	9	12.8	12.8	2	9	0	21.5	21.5
2	1	10	10.3	10.3	2	10	0	21.5	21.5
2	1	11	12.8	12.8	2	11	0	21.5	21.5
2	1	12	10.3	10.3	2	12	0	21.5	21.5
2	2	0	20.4	20.4	2	2	0	4.4	4.4
2	2	1	21.5	21.5	2	2	1	8.4	8.4
2	2	2	20.4	20.4	2	2	2	8.4	8.4
2	2	3	21.5	21.5	2	2	3	8.4	8.4
2	2	4	20.4	20.4	2	2	4	8.4	8.4
2	2	5	21.5	21.5	2	2	5	8.4	8.4
2	2	6	20.4	20.4	2	2	6	8.4	8.4
2	2	7	21.5	21.5	2	2	7	8.4	8.4
2	2	8	20.4	20.4	2	2	8	8.4	8.4
2	2	9	21.5	21.5	2	2	9	8.4	8.4
2	2	10	20.4	20.4	2	2	10	8.4	8.4
2	2	11	21.5	21.5	2	2	11	8.4	8.4
2	2	12	20.4	20.4	2	2	12	8.4	8.4

\* By mistake the reflexion 102, with F<sub>o</sub>=50.2 and F<sub>c</sub>=60.0, was not included in the refinement or in the Table.

The atomic scattering factors used are those for neutral O, N, C and H, given in *International Tables for X-ray Crystallography* (1962).

### Programs used

All calculations were performed on the CD 3600 computer in Uppsala, using the following programs:

*CELSIUS*, refinement of unit-cell dimensions, written by J. Tegenfeldt, Uppsala. A brief description has been given by Liminga (1965).

*INTERSCALE*, inter-layer scaling, written by W. C. Hamilton, Upton, New York. The method has been described by Hamilton, Rollett & Sparks (1965).

*DRF*, data reduction and Fourier calculations. Local modification of a program written by A. Zalkin, Berkeley, California.

*LALS*, full-matrix, least-squares calculations. Local modification of A. Zalkin's version of UCLALS1, originally written by P. K. Ganzel, R. A. Sparks and K. N. Trueblood, Los Angeles, California.

*DISTAN*, calculation of distances and angles, written by A. Zalkin.

*OR TEP*, a thermal-ellipsoid plot program for crystal structure illustrations, written by C. K. Johnson, Oak Ridge, Tennessee (Johnson, 1965).

### Description and discussion of the structure

#### General

The positional parameters obtained from the two different sets of data agree quite closely. A comparison of the values in Table 1(a) shows that the difference between corresponding atomic coordinates is mostly less than one standard deviation. An examination of

Table 3. *Interatomic distances and bond angles with standard deviations*

The values within square brackets are distances corrected for thermal 'riding' motion. The standard deviations of the distances are  $\times 10^3$ .

The positions are denoted as follows:

(i)	$-1+x$	$y$	$z$	(v)	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
(ii)	$-x$	$-y$	$1-z$	(vi)	$x$	$-1+y$	$z$
(iii)	$1-x$	$-y$	$1-z$	(vii)	$1-x$	$1-y$	$1-z$
(iv)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	(viii)	$1+x$	$y$	$z$

#### (a) Within the acetate ion (cf. Fig. 3)

Bond	Distance	Bonds	Angle
C(1)-O(1)	1.250 [1.264] (4) Å	O(1)-C(1)-O(2)	123.4 (0.3)°
C(1)-O(2)	1.253 [1.269] (4)	O(1)-C(1)-C(2)	118.5 (0.3)
C(1)-C(2)	1.504 [1.528] (4)	O(2)-C(1)-C(2)	118.0 (0.3)

#### (b) Hydrogen bonds and angles around the oxygen atoms (cf. Fig. 3)

O(1)···H(1) —N	2.824 [2.829] (4) Å	C(1) —O(1)···N	108.2 (0.2)°
O(1)···H(2 <sup>iv</sup> )-N <sup>iv</sup>	2.804 [2.806] (4)	C(1) —O(1)···N <sup>iv</sup>	117.5 (0.2)
O(2)···H(4 <sup>ii</sup> )-N <sup>ii</sup>	2.808 [2.812] (4)	N···O(1)···N <sup>iv</sup>	131.9 (0.1)
O(2)···H(3 <sup>iii</sup> )-N <sup>iii</sup>	2.830 [2.834] (4)	C(1) —O(2)···N <sup>ii</sup>	118.3 (0.2)
		C(1) —O(2)···N <sup>iii</sup>	125.1 (0.2)
		N <sup>ii</sup> ···O(2)···N <sup>iii</sup>	116.2 (0.1)

#### (c) Within the ammonium ion (cf. Fig. 2). Coordinates from Table 1(a) are used.

N-H(1)	0.90 Å	H(1)-N-H(2)	98°
N-H(2)	0.90	H(1)-N-H(3)	101
N-H(3)	0.89	H(1)-N-H(4)	117
N-H(4)	0.91	H(2)-N-H(3)	118
		H(2)-N-H(4)	105
		H(3)-N-H(4)	117

#### (d) Hydrogen bonds and angles around nitrogen (cf. Fig. 4)

N-H(1)···O(1)	2.824 [2.829] (4) Å	O(1)···N···O(1 <sup>v</sup> )	98.8 (0.1)°
N-H(2)···O(1 <sup>v</sup> )	2.804 [2.806] (4)	O(1)···N···O(2 <sup>ii</sup> )	117.4 (0.1)
N-H(3)···O(2 <sup>iii</sup> )	2.830 [2.834] (4)	O(1)···N···O(2 <sup>iii</sup> )	100.6 (0.1)
N-H(4)···O(2 <sup>ii</sup> )	2.808 [2.812] (4)	O(1 <sup>v</sup> )···N···O(2 <sup>ii</sup> )	104.2 (0.1)
		O(1 <sup>v</sup> )···N···O(2 <sup>iii</sup> )	118.8 (0.1)
		O(2 <sup>ii</sup> )···N···O(2 <sup>iii</sup> )	116.2 (0.1)

#### (e) Other distances less than 3.6 Å

O(2)···N	3.372 (4) Å
C(2)···O(1 <sup>viii</sup> )	3.474 (6)
C(2)···N <sup>iv</sup>	3.502 (6)
N···C(1)	3.427 (5)

the thermal vibration tensor components [*cf.* Table 1(*b*) and (*c*)] reveals that there are no appreciable differences in orientation and size of the ellipsoids of vibration. Table 1(*d*) shows a comparison between the root-mean-square displacements along the principal axes. All tables, with the exception of Tables 1 and 2, Figures and discussion are based on atomic parameters derived from crystal no. 1.

A stereoscopic illustration of the structure is given in Fig. 1. The hydrogen atoms have been assigned to the nitrogen and carbon atoms as illustrated in Fig. 2. Bond distances and angles are given together with standard deviations in Table 3. The values within square brackets are bond distances corrected for thermal 'riding' motion (Busing & Levy, 1964). In the discussion below the uncorrected values are used, as the bond distances taken from the literature for comparison were not corrected in the same way, with the exception of ammonium oxalate monohydrate (Robertson, 1965), where the correction was negligible. The molecular geometry is illustrated in Figs. 3 and 4.

The present compound  $\text{NH}_3 \cdot \text{CH}_3\text{COOH}$  contains  $\text{NH}_4^+$  and  $\text{CH}_3\text{COO}^-$  ions, as will be discussed below. Four hydrogen bonds of similar lengths [*cf.* Table 3(*b*)

and (*d*)] link the ammonium ions to the carboxylate oxygen atoms, thus forming a three-dimensional framework, in which each oxygen atom accepts two  $\text{N}^+\text{-H}\cdots\text{O}^-$  bonds. Each nitrogen atom is approximately tetrahedrally surrounded by four oxygen atoms, which are equivalent in pairs and belong to four different acetate groups. From Figs. 1 and 2 the hydrogen bonds designated  $\text{N-H}(2)\cdots\text{O}(1)$ ,  $\text{N-H}(3)\cdots\text{O}(2)$ , and  $\text{N-H}(4)\cdots\text{O}(2)$ , can be seen to link the ions in sheets roughly parallel to (010), while the  $\text{N-H}(1)\cdots\text{O}(1)$  bonds connect these sheets in the *b* direction.

In ammonium trifluoroacetate (Cruikshank, Jones & Walker, 1964) a very similar framework is found. The resemblance between the structures of ammonium acetate and ammonium trifluoroacetate can be understood in view of the similar possibilities for hydrogen bonding and the small difference between the van der Waals radii of fluorine and hydrogen.

The same kind of hydrogen bond system is also found in ammonium formate (Nahringbauer, to be published). In other respects, however, this latter structure is rather dissimilar because of the difference in size between the methyl group and the hydrogen atom.

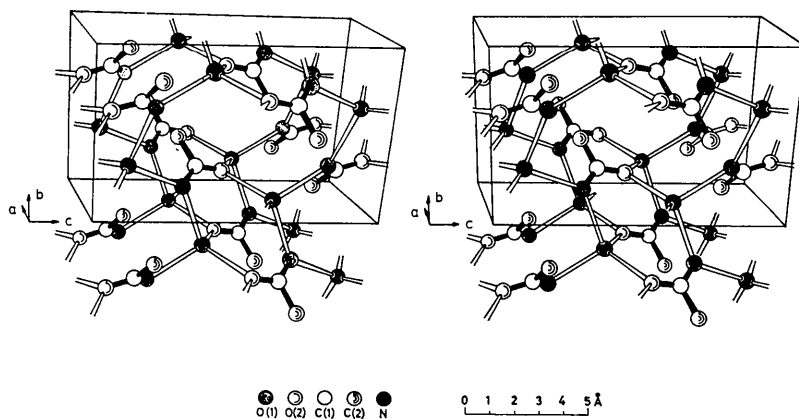


Fig. 1. A stereoscopic pair of drawings of the hydrogen-bond network in ammonium acetate. The hydrogen atoms are omitted for the sake of clarity. The view is nearly along the reciprocal  $a^*$  axis.

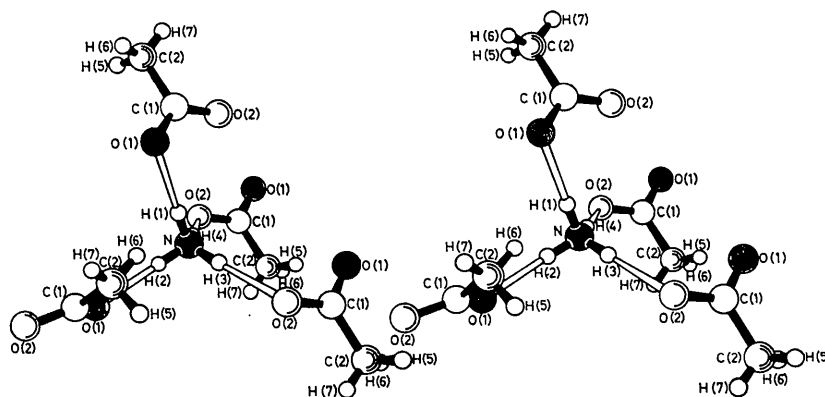


Fig. 2. A stereoscopic pair of drawings of the ammonium ion and the surrounding acetate ions. The positions of the hydrogen atoms are based on atomic coordinates in Table 1.

### The hydrogen bonds

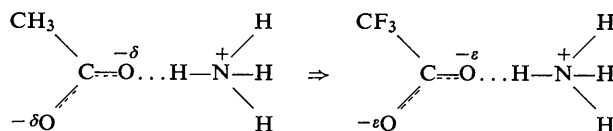
From chemical arguments ammonium acetate is expected to be composed of  $\text{NH}_4^+$  and  $\text{CH}_3\text{COO}^-$  ions. This is evidently true as seen from the positions of the hydrogen atoms, indicated in the difference maps, and it is finally proved by the hydrogen bond lengths found (2.804, 2.808, 2.824 and 2.830 Å):

(1) In an ionic compound the only possible hydrogen bonds are of type  $\text{N}^+\text{H}\cdots\text{O}^-$  and are expected to be of approximately the same length, 2.8–2.9 Å (Pimentel & McClellan, 1960), in agreement with the result.

(2) In a molecular compound, on the other hand, one would expect hydrogen bonds of type  $\text{O}\text{H}\cdots\text{N}$

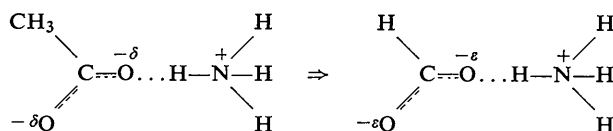
and  $\text{N}\text{H}\cdots\text{O}$ . A hydrogen bond of type  $\text{N}\text{H}\cdots\text{O}$  is expected to be longer than 3 Å, while the  $\text{O}\text{H}\cdots\text{N}$  hydrogen bond is thought to be significantly shorter (Olovsson, 1960; Pimentel *et al.*, 1960). Furthermore, contrary to the result, most of the hydrogen bonds should be of the longer type,  $\text{N}\text{H}\cdots\text{O}$ , and only one would be expected to be short.

The hydrogen bonds in ammonium acetate are significantly shorter than those found in ammonium trifluoroacetate (2.87, 2.89, 2.91 and 2.92 Å) by Cruickshank *et al.* (1964). This may be explained by the difference in effective electronegativity of the oxygen atoms in the two compounds. A substitution of the  $\text{CH}_3$  group by the more electronegative  $\text{CF}_3$  group



causes a decrease in negative charge on the oxygen atoms and should result in an increase in the hydrogen bond length.

A replacement of  $\text{CH}_3$  by the slightly more electronegative hydrogen atom as in ammonium formate



should change the effective electronegativity of the oxygen atoms very little. The mean value of the hydrogen bond lengths, 2.84 Å (Nahringbauer, to be published), is about the same as that found in ammonium acetate.

### The acetate ion

The planes of the four symmetry-related acetate ions are either parallel or normal to each other (Fig. 1). The angles of tilt to (010) are approximately 45°. The carbon and oxygen atoms of the acetate ion deviate at most by 0.006 Å from the least-squares plane defined in Table 4 (pane 1).

There is a very small difference between the two C–C–O bond angles (118.0 and 118.5°) and the same is true for the two C–O bond distances (1.250 and 1.253 Å). This result is in agreement with conclusions drawn by Hahn (1957), that a fully ionized carboxyl group should have equal C–O bonds of 1.260 Å, making equal angles of 117.5° with the C–C bond. The O–C–O bond angle, proposed by Hahn to have a value of 126°, is 123.4° for ammonium acetate. An even higher value (128.0°) is found in ammonium trifluoroacetate by Cruickshank *et al.* (1964).

A comparison of bond distances and angles found in  $\text{RCOO}^-$  and  $\text{RCOOH}$  groups is made in Table 5(a) and (b) respectively. Only compounds related to ammonium acetate are represented.

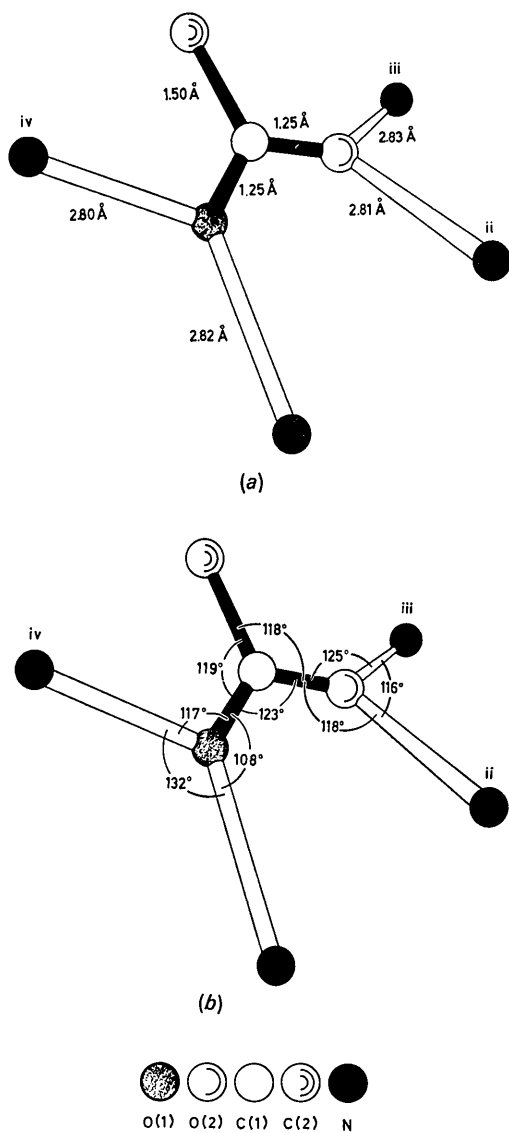


Fig. 3. (a) Bond distances and (b) angles involving the acetate ion.



Table 4. *Details of the planes of best fit*

Each plane is represented by  $lX+mY+nZ-p=0$  where  $l$ ,  $m$ , and  $n$  are direction cosines in a right handed orthogonal coordinate system such that  $X$  and  $Y$  are coincident with  $x$  and  $y$  of the crystallographic system.  $X$ ,  $Y$ , and  $Z$  are coordinates in Å. The calculations are made according to Blow (1960).

Plane	$l$	$m$	$n$	$p$
1	+0.6858	-0.6978	-0.2066	-1.8766
2	+0.8642	-0.3375	-0.3732	-1.8695
3	+0.0001	-0.9552	-0.2958	-3.2755

	Deviation from plane (Å)		
	1	2	3
O(1)	+0.002	-0.134	
O(2)	+0.002		-0.049
C(1)	-0.006	+0.064	+0.027
C(2)	+0.002		
N		+0.033	
N <sup>(iv)</sup>		+0.036	
N <sup>(ii)</sup>			+0.011
N <sup>(iii)</sup>			+0.012

The C-C contact is 1.504 Å, which agrees with the length 1.505 Å proposed by Brown (1959) for a single bond between  $sp^3$  and  $sp^2$  hybridized carbon atoms. A comparison with the corresponding bond in ammonium trifluoroacetate, 1.535 Å (not corrected for rotational oscillation), shows that the substitution of the methyl group with a trifluoromethyl group does not have a shortening effect in disagreement with the predictions of the hyperconjugation theory.

Each oxygen atom is surrounded by two nitrogen atoms and one carbon atom, which are approximately in the same plane as the central oxygen atom (*cf.* Figs. 1 and 3). The two least-squares planes defined by the two oxygens and the atoms surrounding them (planes 2 and 3, Table 4) make an angle of 64.4° with each

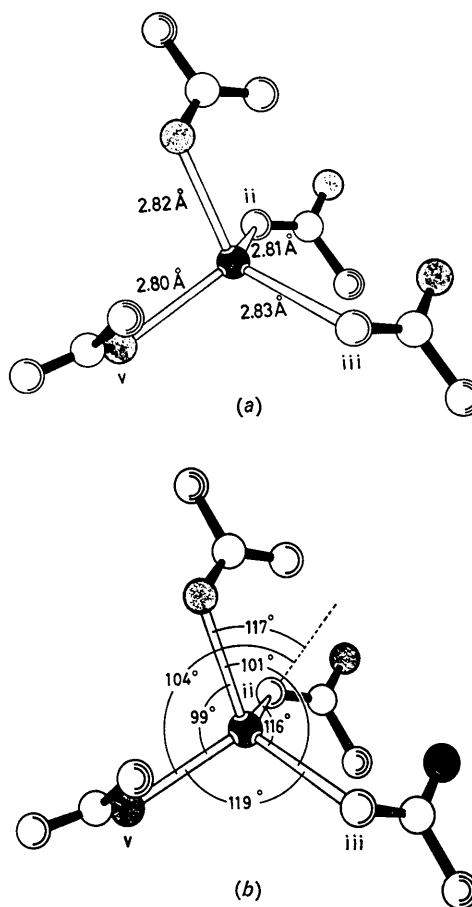


Fig. 4. (a) Bond distances and (b) angles around the nitrogen atom. The notation is the same as in Fig. 3.

Table 5. *Comparison of bond lengths and angles in carboxylate and carboxyl groups*(a) Compounds with RCOO<sup>-</sup> groups

Compound	C-C	C-O(1)	C-O(2)	C-C-O(1)	C-C-O(2)	O(1)-C-O(2)	Reference
Present compound	1.50 Å	1.25 Å	1.25 Å	118.0°	118.5°	123.4°	
CH <sub>3</sub> COONH <sub>4</sub>							
Ammonium trifluoroacetate	1.54	1.26	1.27	115.3	116.4	128.3	Cruickshank, Jones & Walker, 1964.
CF <sub>3</sub> COONH <sub>4</sub>							
Bisglycino-copper(II) monohydrate	1.50	1.23	1.28	118.3	117.4	124.3	Freeman, Snow, Nitta & Tomita, 1964.
Cu(NH <sub>2</sub> CH <sub>2</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	1.49	1.24	1.29	119.7	117.5	122.8	
Aminoacetic acid (α-Glycine)	1.52	1.25	1.25	117.4	117.1	125.5	Marsh, 1958
NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> COO <sup>-</sup>							
Ammonium oxalate monohydrate (NH <sub>4</sub> ) <sub>2</sub> (COO) <sub>2</sub> ·H <sub>2</sub> O		1.25	1.26	117.5	116.5	126	Robertson, 1965.
Monopyridinecopper(II) acetate	1.47	1.25	1.25	115.0	118.1	127.3	Barclay & Kennard, 1961.
Cu <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> ·2C <sub>5</sub> H <sub>5</sub> N (mon.)	1.54	1.23	1.23			122.9	
Monopyridinecopper(II) acetate	1.55	1.25	1.24	115.7	116.4	127.8	Hanic, Štempelová & Hanicová, 1964.
Cu <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> ·2C <sub>5</sub> H <sub>5</sub> N (orth.)	1.53	1.25	1.25	117.2	118.9	123.3	

## (b) Compounds with RCOOH groups

Compound	C-C	C-O	C-OH	C-C-O	C-C-OH	O-C-OH	Reference
Sodium hydrogen diacetate	1.49 Å	1.24 Å	1.30 Å	122.3°	116.1°	121.7°	Speakman & Mills, 1961.
NaH(CH <sub>3</sub> COO) <sub>2</sub>							
Acetic acid	1.54	1.24	1.29	122	116	122	Jones & Templeton, 1958.
CH <sub>3</sub> COOH							
Oxalic acid		1.19	1.29	122.7	109.0	128.1	Cox, Dougill & Jeffrey, 1952.
(COOH) <sub>2</sub>							
Oxalic acid Dihydrate (COOH) <sub>2</sub> ·2H <sub>2</sub> O		1.19	1.29	122	113	126	Ahmed & Cruickshank, 1953.

Table 6. Bond angles in some compounds with related environment around their carboxylate oxygen atoms

Angle	CH <sub>3</sub> COONH <sub>4</sub>	CF <sub>3</sub> COONH <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> (COO) <sub>2</sub> ·H <sub>2</sub> O
C—O(1)···N <sup>iv</sup>	117·5°	119·5°	118°
C—O(1)···N	108·2	109·0	109
N—O(1)···N <sup>iv</sup>	131·9	130·3	132
C—O(2)···N <sup>iii</sup>	118·3	119·4	
C—O(2)···N <sup>iii</sup>	125·1	126·9	117
N <sup>iii</sup> ···O(2)···N <sup>iii</sup>	116·2	113·5	

other. Plane 2, fitted to O(1) and its ligands, is twisted 25·2° with respect to the plane of the acetate group (plane 1). The corresponding angle of twist for the least-squares plane fitted to O(2) and its ligands (plane 3) is 43·3°.

The same environment around the two oxygen atoms is found in ammonium trifluoroacetate (Cruikshank *et al.*, 1964) and ammonium oxalate monohydrate (Robertson, 1965). These great similarities are shown in Table 6, which gives the corresponding angles at the oxygen atoms of the three compounds. The values for ammonium trifluoroacetate are calculated from the coordinates reported by Cruikshank *et al.*

The C—O···HO angle in acetic acid and formic acid is 144° (Jones & Templeton, 1958) and 122° (Holtzberg, Post & Fankuchen, 1953), respectively. Jones & Templeton explained the remarkably large angle in acetic acid as a means of providing sufficient space for the methyl group, which otherwise would interfere with an oxygen atom of the neighbouring molecules. This problem does not exist in ammonium acetate, as here the carboxyl groups are linked by hydrogen bonds *via* the ammonium ion. The corresponding angles in this compound, C—O(1)···N<sup>iv</sup> and C—O(2)···N<sup>iii</sup>, are 117·5 and 125·1° [*cf.* Fig. 3(b)], and the closest contact between C(2) and neighbouring nitrogen atoms C(2)···N<sup>iv</sup> is 3·50 Å [*cf.* Fig. 3(a)].

The nearest C(2)···O distance between adjacent molecules is 3·47 Å, slightly larger than the sum, 3·4 Å, of the van der Waals radii for the methyl group and oxygen listed by Pauling (1960). The shortest methyl-methyl distance, C(2)···C(2<sup>vii</sup>), is 4·15 Å.

I wish to express my gratitude to the head of the Institute, Prof. G. Hägg, for all the facilities put at my disposal and to Dr I. Olovsson for his never failing interest in this investigation. Many thanks are also due to Mrs K. Svanberg for performing a part of the preliminary X-ray work and to Mrs V. Fredriks and Mrs M. Hillberg for skilful technical assistance.

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