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Hydrogen Bond Studies. XX.* The Crystal Structure of Ammonium Formate

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The crystal structure of ammonium formate has been determined at room temperature from three-dimensional single-crystal X-ray data. Two $HCOONH_4$ units crystallize in a monoclinic unit cell of space group *Pc* and dimensions $a=3·814$, $b=4·679$, $c=9·112$ Å, and $\beta=91·17°$. The structure was refined by the method of least squares with allowance for anisotropic thermal motion, and gave a final discrepancy index of 0·067. The ammonium ion forms four hydrogen bonds $N^+–H\cdots O^-$ of length 2·81–2·89 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 formate ion are: bond lengths, C–O = 1·237 and 1·246 Å; bond angle, O–C–O = 126·3°.

Introduction

Ammonia forms a great number of compounds with the simple organic acids HCOOH, CH_3COOH, and C_2H_5COOH. Systematic investigations of the crystal structures of the compounds $n NH_3.CH_3COOH$ ($n=\frac{1}{2}$, 1, 2, 3) are currently being made by the author to study the hydrogen bonds formed with carboxyl or carboxylate groups. As a complement to these studies investigations of the compounds formed between ammonia and formic acid have also been started which promise to provide interesting comparisons with the acetic acid compounds. The melting-point diagram of the system ammonia–formic acid shows the existence of the solid compounds $NH_3.4HCOOH$, $NH_3.2HCOOH$, $NH_3.HCOOH$, and $3NH_3.HCOOH$ (Becker & Davidson, 1963).

The present investigation concerns the 1:1 compound, ordinarily called ammonium formate, and is based on single-crystal X-ray data.

Experimental

Ammonium formate (*pro analysi*) was recrystallized several times from ethanol (99·5%) and dried over calcium sulphate (Drierite) in a desiccator. The crystals were very hygroscopic and the mounting had to be done in a dry-box.

The crystals had the shape of rectangular plates perpendicular to the *c* axis. Suitable crystals were chosen under a microscope and mounted in glass capillaries (0·2 mm in diameter) which were finally sealed.

Two crystals with dimensions less than 0·2 mm were used for the X-ray analysis, one mounted along the *a* axis and the other along the *b* axis. Multiple-film (five), equi-inclination Weissenberg photographs were taken using unfiltered Cu *K* radiation. Layers $0 \le h \le 3$ were recorded for the first crystal and layers $0 \le k \le 4$ for the second one. 81% or 297 of the unique reflexions within the Cu *K* sphere were recorded for crystal no. 1; of these, only 276 had measurable intensities. For crystal no. 2 the corresponding figures were 88% or 324 and 292 reflexions.

The relative intensities of the reflexions were obtained by visual comparison with a calibrated intensity scale. The intensity range was 1 to 8000. The data were corrected for Lorentz and polarization effects. No absorption correction was applied since the linear absorption coefficient is only 8·0 cm^{-1} and the crystals were relatively small.

Inter-layer scale factors were calculated with the program *INTERSCALE*. All observations were given the same weight. The number of common reflexions observed on both sets of films was 206.

Unit cell and space group

The diffraction symmetry $2/m$ indicated a monoclinic unit cell. Accurate cell dimensions were obtained from zero-layer oscillation photographs around the *a*, *b*, and *c* axes, calibrated with a quartz single crystal. The following numerical values were used: $a=4·913$ Å for α quartz (25°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 three photographs θ values were measured for a total of 151 reflexions. No θ value was less than 45°. A least-squares treatment of the observed θ values using the program *CELSIUS*, gave the following cell dimensions and standard deviations:

$$a=3·814\pm0·001,\ b=4·679\pm0·001,\ c=9·112\pm0·001\ \text{Å},\ \beta=91·17\pm0·01°\ .$$

Unit-cell volume = 162·6 Å³. With two $HCOONH_4$ units in the cell the calculated density of the solid is 1·288 $g.cm^{-3}$. A measured value for the density is 1·281 $g.cm^{-3}$ (Biltz & Balz, 1928, p. 338).

The absence of reflexions $h0l$ for $l=2n+1$ indicated the space group $P2/c$ or Pc. The structure could only

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* Part XIX: *Acta Cryst.* (1968), B**24**, 559.
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be solved in the space group *Pc* (no. 7, *International Tables for X-ray Crystallography*, 1952).

Determination of the crystal structure

Location of the oxygen, nitrogen and carbon atoms

A three-dimensional Patterson synthesis was calculated with the more complete data from the crystal rotating about the *b* axis. The same data were used in all further calculations.

Initially the space group was assumed to have a centre of symmetry. This implies that the nitrogen and the carbon atoms must occupy twofold special positions and the same is true for the hydrogen atom attached to the carbon. The space group *P*2/*c* has special positions with point symmetry 2 and $\bar{1}$ but only those of the first kind are possible for the carbon and hydrogen atoms because of the geometry of the formate group. Furthermore, the two oxygen atoms of the same molecule must be equivalent and related to each other by the twofold rotation axis through the carbon atom of the group. This means that one Harker vector $(2x,0,2z-\frac{1}{2})$ should be of approximate length 2·25 Å, according to the known shape of a formate group

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal vibration tensor components** (Å$^2\times 10^4$)

Standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	3996(12)	4290(8)	5656(5)	548(22)	435(22)	397(17)	44(13)	−52(14)	44(13)
O(2)	6056(15)	1417(8)	7387(6)	551(19)	474(23)	351(17)	86(16)	−42(12)	11(13)
C	4991(17)	3756(11)	6922(7)	461(21)	467(33)	370(23)	−15(18)	−13(16)	−51(18)
N	0	801(9)	0	389(19)	434(25)	371(20)	−24(14)	−54(15)	11(14)

Probable hydrogen coordinates ($\times 10^3$) (Standard deviations are not determined)

	x	y	z
H(1)	143	−73	−8
H(2)	128	236	21
H(3)	−127	99	−84
H(4)	−144	41	75
H(5)	493	520	758

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

Table 2. *Observed and calculated structure factors*

Data collected around the *b* axis. An asterisk indicates reflexions which were too weak to be measured. F_o values for these are given as $(1/\sqrt{2})F_{min}$ for the reflexions in question.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	8	2.5	2.6
0	0	6	9.1	9.0
0	0	4	17.5	17.6
0	0	2	17.7	18.6
1	0	10	4.3	3.8
1	0	8	3.8	3.8
1	0	6	9.6	9.7
1	0	4	7.6	6.7
1	0	2	16.5	16.3
1	0	0	15.9	15.8
1	0	-2	32.9	34.0
1	0	-4	8.1	7.2
1	0	-6	1.3	11.2
1	0	-8	6.5	6.7
1	0	-10	1.4	0.7 *
2	0	10	1.1	0.9 *
2	0	8	3.5	3.2
2	0	6	3.9	4.0
2	0	4	11.8	11.9
2	0	2	7.9	7.6
2	0	0	14.6	14.4
2	0	-2	13.4	13.6
2	0	-4	7.5	7.0
2	0	-6	3.3	3.3
2	0	-8	4.0	3.9
2	0	-10	3.4	3.0
3	0	8	3.3	3.0
3	0	6	1.5	0.5 *
3	0	4	1.4	0.1 *
3	0	2	4.5	4.5
3	0	0	2.5	2.5
3	0	-2	6.6	7.2
3	0	-4	5.8	6.7
3	0	-6	1.4	0.9 *
3	0	-8	3.1	2.9
4	0	6	2.9	3.2
4	0	4	2.0	1.8
4	0	2	1.8	2.0
4	0	0	1.5	0.5 *
4	0	-2	1.5	1.0 *
4	0	-4	2.4	2.0
4	0	-6	2.0	2.3
0	1	11	1.2	1.2
0	1	10	2.6	2.4
0	1	9	1.0	0.7 *
0	1	8	6.5	7.3
0	1	7	5.1	5.4
0	1	6	4.0	4.1
0	1	5	6.1	6.4
0	1	4	11.1	11.8
0	1	3	9.3	10.3
0	1	2	9.1	10.6
1	1	11	1.0	1.0
1	1	10	2.4	2.0
1	1	9	1.0	0.8 *
1	1	8	2.9	3.1
1	1	7	1.0	0.1 *
1	1	6	7.8	8.4
1	1	5	7.1	7.0
1	1	4	5.8	5.0
1	1	3	7.9	8.0
1	1	2	17.1	19.7
1	1	1	11.3	11.8
1	1	0	19.0	21.4
1	1	-1	18.4	20.9
1	1	-2	11.2	11.5
1	1	-3	6.4	5.9
1	1	-4	5.3	4.6
1	1	-5	7.1	6.6
1	1	-6	1.8	1.7
1	1	-7	3.3	3.2
1	1	-8	1.7	1.5
1	1	-9	2.5	2.2
1	1	-10	3.2	3.3
2	1	10	1.0	0.9
2	1	9	2.4	2.1
2	1	8	4.7	4.4
2	1	7	1.0	0.8 *
2	1	6	4.4	4.9
2	1	5	2.2	2.3
2	1	4	3.3	3.1
2	1	3	3.9	3.4
2	1	2	3.1	2.9
2	1	1	4.9	4.7
2	1	0	9.0	8.8
2	1	-1	6.4	6.2
2	1	-2	8.8	8.5
2	1	-3	10.1	9.6
2	1	-4	6.4	6.4
2	1	-5	1.6	1.6
2	1	-6	4.0	3.9
2	1	-7	3.7	3.8
2	1	-8	2.6	2.2
2	1	-9	2.1	1.8
2	1	-10	1.7	1.6
3	1	8	0.8	0.5 *
3	1	7	2.4	2.1
3	1	6	4.7	4.5
3	1	5	1.4	1.4
3	1	4	4.8	5.2
3	1	3	2.7	2.9
3	1	2	2.0	2.1
3	1	1	1.0	0.8 *
3	1	0	5.4	5.6
3	1	-1	3.0	3.0
3	1	-2	2.2	2.0
3	1	-3	2.3	2.5
3	1	-4	2.0	1.4
3	1	-5	2.9	3.0
3	1	-6	1.6	1.4
3	1	-7	1.0	1.0 *
3	1	-8	1.4	1.2
3	1	-9	1.5	1.6
4	1	6	1.0	0.9
4	1	5	1.1	0.9
4	1	4	2.2	2.0
4	1	3	1.0	0.7 *
4	1	2	2.6	2.5
4	1	1	1.6	1.3
4	1	0	1.6	1.4
4	1	-1	1.0	0.6 *
4	1	-2	3.4	3.4
4	1	-3	1.8	1.8
4	1	-4	1.7	1.4
4	1	-5	1.2	1.1
4	1	-6	1.0	0.8
0	2	11	1.6	2.2
0	2	10	1.1	1.2
0	2	9	3.5	3.6
0	2	8	0.9	0.8
0	2	7	4.7	5.0
0	2	6	0.9	0.9
0	2	5	3.0	3.0
0	2	4	4.3	4.0
0	2	3	11.5	10.7
0	2	2	9.2	9.1
0	2	1	12.5	14.3
1	2	10	1.2	1.2
1	2	9	3.7	3.8
1	2	8	2.5	2.7
1	2	7	6.3	7.3
1	2	6	2.5	2.7
1	2	5	2.3	2.3
1	2	4	2.8	2.7
1	2	3	9.1	8.7
1	2	2	2.9	2.8
1	2	1	6.9	6.4
1	2	0	3.9	3.4
1	2	-1	7.9	6.5
1	2	-2	4.2	3.4
1	2	-3	8.8	7.6
1	2	-4	5.9	5.4
1	2	-5	6.2	6.4
1	2	-6	2.8	3.0
1	2	-7	2.7	2.9
1	2	-8	1.6	1.8
1	2	-9	4.1	4.2
1	2	-10	0.9	1.1
2	2	9	1.8	1.7
2	2	8	0.6	0.6 *
2	2	7	4.0	4.2
2	2	6	2.3	2.7
2	2	5	7.0	8.0
2	2	4	3.6	3.5
2	2	3	0.6	0.3 *
2	2	2	4.2	4.5
2	2	1	10.8	10.9
2	2	0	5.7	5.3
2	2	-1	6.1	5.7
2	2	-2	1.8	1.5
2	2	-3	2.3	2.1
2	2	-4	1.1	1.1
2	2	-5	0.9	0.9
2	2	-6	1.4	1.4
2	2	-7	1.5	1.6
2	2	-8	0.9	0.9
2	2	-9	1.4	1.3
2	2	-10	0.7	0.9
3	2	8	0.7	0.7
3	2	7	2.9	2.9
3	2	6	0.6	0.9 *
3	2	5	2.8	2.7
3	2	4	0.6	0.7 *
3	2	3	4.1	4.4
3	2	2	1.0	1.1
3	2	1	1.1	1.1
3	2	0	2.0	2.0
3	2	-1	5.0	5.7
3	2	-2	2.5	2.7
3	2	-3	3.2	3.5
3	2	-4	1.6	1.5
3	2	-5	1.9	1.9
3	2	-6	1.5	1.4
3	2	-7	1.1	1.1
3	2	-8	0.4	0.3 *
4	2	5	2.4	2.9
4	2	4	1.2	1.3
4	2	3	1.8	1.9
4	2	2	0.9	0.7
4	2	1	1.9	1.9
4	2	0	0.6	0.6 *
4	2	-1	1.9	2.0
4	2	-2	0.6	0.3 *
4	2	-3	1.6	1.7
4	2	-4	0.5	0.7 *
4	2	-5	1.2	1.3
0	3	10	1.5	1.5
0	3	9	2.4	2.2
0	3	8	2.0	1.8
0	3	7	4.4	4.7
0	3	6	3.3	3.4
0	3	5	3.6	4.0
0	3	4	3.1	3.0
0	3	3	4.3	4.2
0	3	2	2.5	2.4
0	3	1	5.6	6.6
1	3	9	0.4	0.2 *
1	3	8	2.2	1.9
1	3	7	1.7	1.5
1	3	6	2.9	3.1
1	3	5	4.9	5.1
1	3	4	4.9	4.6
1	3	3	4.7	5.1
1	3	2	2.8	2.7
1	3	1	7.6	8.0
1	3	0	3.3	3.2
1	3	-1	10.9	10.8
1	3	-2	2.8	2.7
1	3	-3	2.3	2.0
1	3	-4	0.9	1.0
1	3	-5	2.7	2.5
1	3	-6	2.1	2.0
1	3	-7	1.4	1.4
1	3	-8	1.9	1.7
1	3	-9	1.9	1.8
2	3	8	1.8	1.6
2	3	7	2.4	2.1
2	3	6	2.4	2.3
2	3	5	1.7	1.8
2	3	4	3.1	3.5
2	3	3	1.1	1.2
2	3	2	3.4	3.3
2	3	1	1.5	1.3
2	3	0	2.0	2.0
2	3	-1	4.2	4.5
2	3	-2	2.2	2.2
2	3	-3	6.0	6.4
2	3	-4	0.9	1.0
2	3	-5	1.6	1.7
2	3	-6	0.8	0.7
2	3	-7	3.1	2.8
2	3	-8	0.8	0.9
2	3	-9	1.1	1.4
3	3	7	1.8	2.1
3	3	6	1.2	1.2
3	3	5	3.0	2.7
3	3	4	2.3	2.1
3	3	3	3.2	3.0
3	3	2	2.7	2.6
3	3	1	1.6	1.7
3	3	0	1.8	1.7
3	3	-1	2.7	2.5
3	3	-2	1.2	1.4
3	3	-3	1.2	1.3
3	3	-4	1.2	1.1
3	3	-5	2.1	2.0
3	3	-6	0.4	0.4 *
3	3	-7	0.3	0.3 *
4	3	3	1.1	1.2
4	3	2	1.3	1.4
4	3	1	1.7	1.6
4	3	0	1.3	1.4
4	3	-1	1.2	1.3
4	3	-2	0.8	0.8
4	3	-3	1.8	2.1
0	4	8	0.7	0.7
0	4	7	0.4	0.4 *
0	4	6	2.1	2.0
0	4	5	2.1	2.3
0	4	4	3.0	3.3
0	4	3	2.7	2.8
0	4	2	3.0	2.9
1	4	8	0.5	0.4
1	4	7	2.0	1.7
1	4	6	1.7	1.5
1	4	5	2.7	2.7
1	4	4	1.5	1.6
1	4	3	1.0	0.9
1	4	2	3.1	3.3
1	4	1	0.4	0.3
1	4	0	3.3	3.1
1	4	-1	2.5	2.7
1	4	-2	4.0	4.6
1	4	-3	3.3	3.5
1	4	-4	2.2	2.5
1	4	-5	2.2	2.3
1	4	-6	2.2	2.2
1	4	-7	2.5	2.5
1	4	-8	1.6	1.6
2	4	7	1.8	1.6
2	4	6	0.7	0.6
2	4	5	2.1	1.8
2	4	4	2.0	1.8
2	4	3	3.7	3.7
2	4	2	1.2	1.2
2	4	1	2.9	2.5
2	4	0	2.8	2.7
2	4	-1	2.8	2.7
2	4	-2	3.1	2.8
2	4	-3	1.6	1.3
2	4	-4	2.4	2.2
2	4	-5	0.6	0.6
2	4	-6	2.0	1.8
3	4	5	0.2	0.4 *
3	4	4	0.3	0.3 *
3	4	3	0.3	0.3 *
3	4	2	1.2	1.1
3	4	1	1.8	1.9
3	4	0	1.0	0.8
3	4	-1	1.6	1.5
3	4	-2	1.8	1.6
3	4	-3	2.0	2.1
3	4	-4	1.7	1.8
3	4	-5	1.2	1.4

(*Tables of Interatomic Distances*, 1958). However, no such vector could be found in the Patterson maps. The space group $P2/c$ was therefore discarded.

The lower symmetry of the space group Pc was then adopted in which all atoms occupy twofold general positions. The intramolecular oxygen–oxygen vector was found by drawing the loci of vectors, 2·25 Å long, in the Patterson maps. The two short carbon–oxygen vectors could not be found because of overlap from the origin peak. As hydrogen bonds were expected to be present in the structure, loci of vectors with lengths of 2·8–3·1 Å, were examined. Four vectors approximately 2·8–2·9 Å long were found. Hydrogen bonding was assumed to exist between the nitrogen atom and oxygen atoms of different formate groups in analogy with the structure of ammonium acetate (Nahringbauer, 1967). From the information obtained so far it was possible to calculate the coordinates of the nitrogen atom and the two oxygen atoms.

With the use of phase angles based on these trial coordinates, three-dimensional electron density maps were calculated in which the carbon atom also showed up clearly.

Location of the hydrogen atoms and refinement of the atomic coordinates

First the preliminary atomic coordinates of all atoms except hydrogen were improved in a series of three-dimensional electron density calculations. The Fourier syntheses, including the Patterson function, were computed with the program DRF.

The atomic parameters were further refined by the method of least squares. The function $\Sigma w(|F_o|-|F_c|)^2$ was minimized by the full-matrix program LALS. The weights of the observations were calculated with the formula $w=1/(a+|F_o|+c|F_o|^2+d|F_o|^3)$. The final values of the constants were $a=0{\cdot}8$, $c=0{\cdot}2$, and $d=0{\cdot}04$. Reflexions too weak to be observed were given zero weight. In the first three cycles only the overall scale factor and individual isotropic temperature factors were refined. In the following cycles the atomic coordinates were included in the refinement. When the shifts were less than one tenth of the estimated standard deviations the discrepancy index, $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ was 0·093. 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 the atomic parameters. In this case the inter-layer scale factors were also allowed to vary. The result was compared with that derived when the experimentally found scale factors were kept fixed. The differences in atomic coordinates, thermal parameters and scale factors were less than 1 e.s.d.

A three-dimensional (F_o-F_c) synthesis was now calculated in order to obtain information on the positions of the hydrogen atoms. Only the reflexions with $\sin\theta/\lambda$ less than 0·5 Å^{-1} were used. Five peaks could be interpreted as reasonable hydrogen positions. However, one of these was less well defined because of interference from the dumb-bell shaped residues of the withdrawn heavy atoms. These indications of anisotropic thermal motion were especially pronounced for the two oxygen atoms. Additional peaks appearing in the difference maps were disregarded as chemically unreasonable hydrogen positions (*cf.* the discussion).

A new series of least-squares refinements was now performed. The hydrogen atoms were included with coordinates calculated from the difference synthesis and isotropic temperature coefficients of 5 Å^2. The overall scale factor and atomic parameters for all atoms but the hydrogens were varied. The R value dropped to 0·090 after one cycle of refinement. The noticed indications of anisotropic thermal motion of the heavy atoms justified a change to anisotropic refinements, which increased the number of free parameters from 15 to 35. After two cycles of refinement the shifts in coordinates and thermal parameters were less than one tenth of the standard deviations. The final R value was 0·067.

A comparison of atomic coordinates before and after the introduction of anisotropic temperature factors showed that they differed by about 1 e.s.d. and

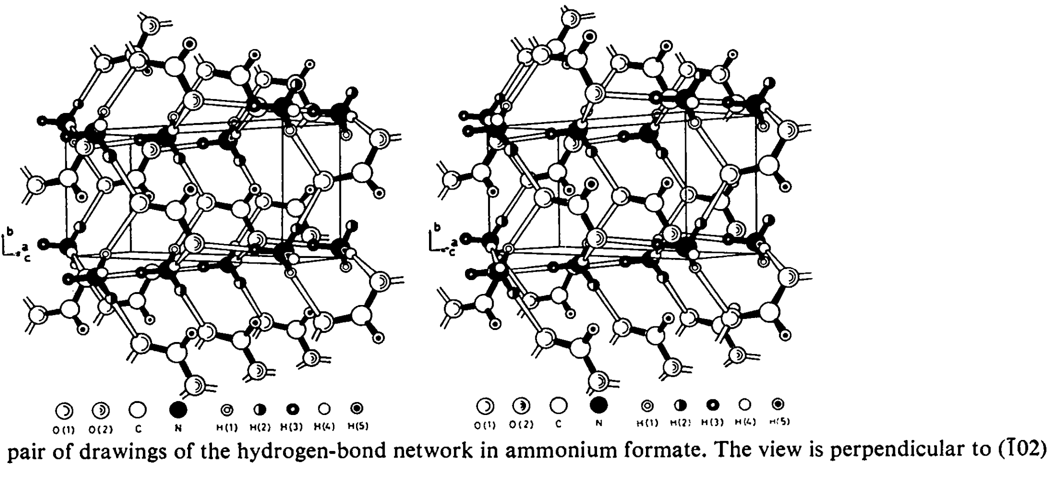

Fig. 1. A stereoscopic pair of drawings of the hydrogen-bond network in ammonium formate. The view is perpendicular to ($\bar{1}02$).

the improvement of the *R* value must be chiefly due to the changes in the thermal parameters. The final atomic coordinates and U_{ij} values with their standard deviations are given in Table 1. The anisotropic temperature parameters β_{ij} were transformed into the vibration tensor components U_{ij} according to Scheringer (1966).

Finally a new $(F_o - F_c)$ synthesis using all measured F_o was performed. The hydrogen atoms were not included. The new hydrogen positions did not differ significantly from those originally accepted.

In Table 2 the observed and the calculated structure factors are compared. The atomic scattering factors used are those for neutral O, N, C, and H, given in *International Tables for X-ray Crystallography* (1962).

All calculations were performed on the CD 3600 computer in Uppsala, using the programs mentioned in the text. The illustrations are prepared by means of the plot program *ORTEP*. The programs used were described in an earlier paper (Nahringbauer, 1967).

Description and discussion of the structure

General

A stereoscopic illustration of the structure is given in Fig. 1. Bond distances and angles are listed together with their standard deviations in Table 3. The values within square brackets are bond distances corrected for thermal 'riding' and 'independent' motions respectively (Busing & Levy, 1964). In the discussion the former values are used although it is clear that these distances are not fully corrected. The molecular geometry is illustrated in Figs. 2 and 3.

The present compound $NH_3.HCOOH$ is assumed to contain NH_4^+ and $HCOO^-$ ions according to the discussion below. Four hydrogen bonds link the ammonium ions to the oxygen atoms of the carboxylate groups, thus forming a three-dimensional framework, in which each oxygen atom accepts two bonds. From Fig. 1, the hydrogen bonds designated $\mathrm{N{-}H(1)\cdots O(1)}$, $\mathrm{N{-}H(2)\cdots O(1)}$, and $\mathrm{N{-}H(3)\cdots O(2)}$, can be seen to link the ions in puckered layers roughly parallel to $(\bar{1}02)$, while the $\mathrm{N{-}H(4)\cdots O(2)}$ bonds connect these layers into a three-dimensional framework. A similar hydrogen bond system is found in ammonium acetate (Nahringbauer, 1967).

The formate ion

The two C–O distances are 1·237 ± 0·007 and 1·246 ± 0·007 Å, when corrections are made for thermal riding motion. The uncorrected values are 1·232 and 1·239 Å respectively. Corresponding distances in the

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

The values within square brackets are distances corrected for thermal (1) 'riding' and (2) 'independent' motion. The standard deviations of the distances are multiplied by 10^3.

The positions are denoted as follows:

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

(*a*) Within the formate ion (*cf.* Fig. 2).

	Distance (Å)		Angle (°)
C–O(1)	1·232 [1·237, 1·310] (7)	O(1)–C–O(2)	126·3 (0·6)
C–O(2)	1·239 [1·246, 1·311] (7)		

(*b*) Hydrogen bonds and angles around the oxygen atoms (*cf.* Fig. 2).

$\mathrm{O(1)\cdots N^{i}}$	2·884 [2·885, 2·913] (6)	$\mathrm{C{-\!-\!-}O(1)\cdots N^{i}}$	100·3 (0·4)
$\mathrm{O(1)\cdots N^{ii}}$	2·814 [2·818, 2·846] (6)	$\mathrm{C{-\!-\!-}O(1)\cdots N^{ii}}$	121·3 (0·4)
		$\mathrm{N^{i}\cdots O(1)\cdots N^{ii}}$	110·4 (0·2)
$\mathrm{O(2)\cdots N^{iii}}$	2·864 [2·867, 2·893] (6)	$\mathrm{C{-\!-\!-}O(2)\cdots N^{iii}}$	103·5 (0·5)
$\mathrm{O(2)\cdots N^{iv}}$	2·805 [2·808, 2·839] (6)	$\mathrm{C{-\!-\!-}O(2)\cdots N^{iv}}$	123·2 (0·4)
		$\mathrm{N^{iii}\cdots O(2)\cdots N^{iv}}$	109·1 (0·2)

(*c*) Hydrogen bonds and angles around nitrogen (*cf.* Fig. 3).

$\mathrm{N{-}H(1)\cdots O(1^{v})}$	2·884 [2·885, 2·913] (6)	$\mathrm{O(1^{v})\cdots N\cdots O(1^{vi})}$	110·4 (0·2)
$\mathrm{N{-}H(2)\cdots O(1^{vi})}$	2·814 [2·818, 2·846] (6)	$\mathrm{O(1^{v})\cdots N\cdots O(2^{vii})}$	122·2 (0·2)
$\mathrm{N{-}H(3)\cdots O(2^{vii})}$	2·805 [2·808, 2·839] (6)	$\mathrm{O(1^{v})\cdots N\cdots O(2^{viii})}$	80·0 (0·2)
$\mathrm{N{-}H(4)\cdots O(2^{viii})}$	2·864 [2·867, 2·893] (6)	$\mathrm{O(1^{vi})\cdots N\cdots O(2^{vii})}$	112·0 (0·2)
		$\mathrm{O(1^{vi})\cdots N\cdots O(2^{viii})}$	115·1 (0·2)
		$\mathrm{O(2^{vii})\cdots N\cdots O(2^{viii})}$	113·6 (0·2)

(*d*) Other distances less than 3·4 Å (*cf.* Fig. 5).

$\mathrm{N\cdots O(2^{v})}$	3·307 [3·308, 3·334] (6)
$\mathrm{N\cdots O(1^{ix})}$	3·307 [3·307, 3·332] (6)
$\mathrm{N\cdots O(1^{viii})}$	3·366 [3·368, 3·391] (5)
$\mathrm{N\cdots O(2^{x})}$	3·363 [3·365, 3·388] (6)
$\mathrm{N\cdots C^{v}}$	3·332 [3·333, 3·358] (7)
$\mathrm{N\cdots C^{viii}}$	3·376 [3·378, 3·400] (7)

formate ions of nickel formate dihydrate, determined with comparable accuracy but without thermal corrections, have been reported (Krogmann & Mattes, 1963). The values given for the two non-equivalent formate groups were 1·222, 1·256 Å, and 1·247, 1·278 Å, respectively. Comparison may also be made with the C–O distances, 1·264 ± 0·004 and 1·269 ± 0·004 Å (uncorrected 1·250 and 1·253 Å), found by the author in ammonium acetate. A slight shortening of the bonds is thus noticed in the ammonium formate, which is combined with an expected widening of the O–C–O bond angle. This is 126·3 ± 0·6 ° compared with 123·4 ± 0·3 ° for ammonium acetate.

The two formate oxygen atoms have very similar environments. Each oxygen atom accepts one shorter (O(1)···H–N=2·818, O(2)···H–N=2·808 Å), and one somewhat longer hydrogen bond (O(1)···H–N=2·886, O(2)···H–N=2·867 Å). The shorter O(1)···N contact makes an angle of 121·3° with the C–O(1) bond, the corresponding angle for O(2) is 123·2° (*cf.* Table 3(*b*) and Fig. 2). These hydrogen bonds deviate but little from the plane of the formate group; the angles between the planes defined by C, O(1), and O(2) and C, O(1), and N^{ii} or C, O(2), and N^{iv}, are 17 and 18°, respectively (Fig. 4). The longer hydrogen bonds deviate appreciably more from the plane of the formate group as seen from the same figure; the corresponding angles, defined similarly to those above, are 41 and 38°. The long O···N contacts make relatively small angles, (100·3 and 103·5°), with the C–O bonds (Fig. 2).

In ammonium acetate a nearly planar arrangement of the C–O bond and the two hydrogen bonds surrounding each carboxylate oxygen has been observed. However, for the present compound no such planarity is found. The distances of the carbon atom to the planes defined by an oxygen and its two hydrogen bonded nitrogen atoms are 0·94 and 0·89 Å, respectively.

Hydrogen bonding

Each nitrogen is approximately tetrahedrally surrounded by four oxygen atoms, which are equivalent in pairs and belong to four different formate groups. The O···N···O bond angles range from 80 to 122° [Table 3(*c*) and Fig. 3]. The N···O distances 2·808, 2·818, 2·867, and 2·886 Å (σ=0·006 Å) are all reasonable hydrogen bonds as expected from the presence of four hydrogen atoms available for hydrogen bonding. The bridging hydrogen atoms are assigned to the nitrogen atom forming an NH_4^+ ion. The N–H bond lengths are approximately 0·9 Å and the H–N–H bond angles range from 106 to 112°.

The possibility of a structure built from NH_3 and HCOOH molecules was not completely ruled out by the final difference synthesis. However, a molecular compound should imply the existence of *three* hydrogen bonds of the type N–H···O, and *one* of the type O–H···N. The N–H···O^- bond distances found in $CH_3COONH_4.NH_3$ (Nahringbauer, to be published), between NH_3 and a carboxylate oxygen atom, range

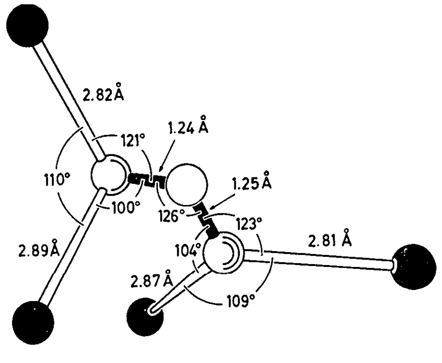

Fig. 2. Bond distances and angles involving the formate ion. The notation of the atoms is the same as in Fig. 1.

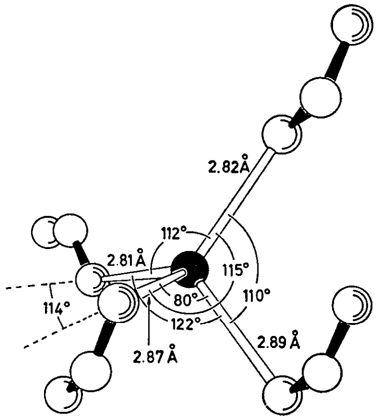

Fig. 3. Hydrogen bond distances and angles around the nitrogen atom. The notation of the atoms is the same as in Fig. 1.

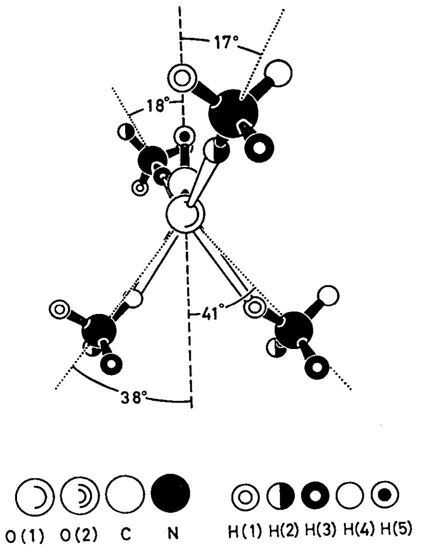

Fig. 4. View down the O···O direction of a formate ion showing the angles between planes defined by the carboxylate group and C–O···N, respectively.

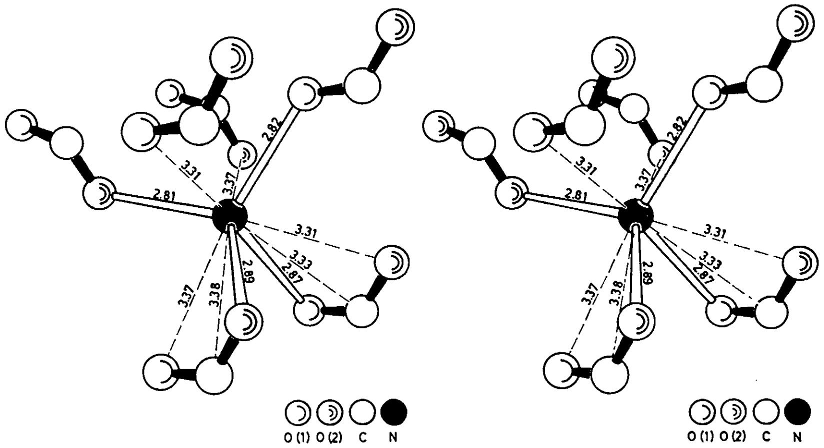

Fig. 5. A stereoscopic pair of drawings showing the packing arrangement around the ammonium ion. Hydrogen atoms are omitted.

from 3·15 to 3·22 Å; a hydrogen bond between NH_3 and an uncharged carboxyl oxygen would be expected to be still longer. Only the hydrogen bond O–H···N should be short; a mean value of 2·80 Å has been obtained from the bond lengths found in a number of different compounds (Pimentel & McClellan, 1960). From the observed hydrogen bond lengths and the discussion above it is evident that the only reasonable composition is the ionic one.

As mentioned in the preceding section, two of the hydrogen bonds are significantly longer than the other two, in contrast to ammonium acetate, where the hydrogen bond lengths are all nearly the same, *viz* 2·81, 2·81, 2·83, and 2·83 Å (σ=0·004 Å). These differences might be explained by the more close packing in the formate; Fig. 5 shows that the formate ions connected to nitrogen by the two longer hydrogen bonds are on the whole rather close to the nitrogen; the C···N and O···N contacts are all equal to or less than van der Waals distances. In order to attain this close packing the two formate ions have to be twisted, which results in relatively small angles (100·3 and 103·5°) between the hydrogen bonds and the C–O bonds. As these angles are less favourable for hydrogen bonding this might be one reason for the different hydrogen bond lengths in ammonium formate.

Remarks on packing and physical properties

Compared with ammonium acetate, ammonium formate has a closer packing. Fig. 5 shows that the nitrogen atom in ammonium formate is surrounded by another four oxygen atoms besides those bonded by hydrogen bridges. Together with the two short C···N van der Waals contacts mentioned before, these add up to 6 contacts in excess of the four hydrogen bonds, compared with only one such contact of comparable length in ammonium acetate.

The more favourable packing arrangement in ammonium formate is born out by a higher value of the density (1·29 compared with 1·17 g.cm^{-3} for ammonium acetate) and in equal melting points of the two substances (117 °C), although the hydrogen bonds are somewhat shorter in ammonium acetate than in ammonium formate.

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.

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References

Becker, B. & Davidson, A. W. (1963). *J. Amer. Chem. Soc.* **85**, 157.

Biltz, W. & Balz, G. (1928). *Z. anorg. allg. Chem.* **170**, 327.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1958). Special Publication no. 11, p. M107. London: The Chemical Society.

International Tables for X-ray Crystallography (1952). Vol. I, p. 85. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Krogmann, K. & Mattes, R. (1963). *Z. Kristallogr.* **118**, 291.

Nahringbauer, I. (1967). *Acta Cryst.* **23**, 956.

Pimentel, G. C. & McClellan, A. L. (1960). *The Hydrogen Bond*, p. 289. San Francisco and London: Freeman and Co.

Scheringer, C. (1966). *Acta Cryst.* **20**, 316.