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Hydrogen Bond Studies

32.* The Crystal Structure of Ammonium Acetate Diammine, $CH_3COONH_4 \cdot 2NH_3$

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The crystal structure of ammonium acetate diammine, $CH_3COONH_4 \cdot 2NH_3$, has been determined from three-dimensional single-crystal X-ray data obtained at −185°C. Four formula units crystallize in an orthorhombic unit cell with the dimensions: $a = 6.805$, $b = 12.493$, $c = 7.904$ Å. The space group is *Cmcm*. The structure is built up from CH_3COO^-, NH_4^+, and NH_3 groups linked into a three-dimensional network by normal hydrogen bonds ($N^+ - H \cdots N = 2.874$, $N^+ - H \cdots O^- = 2.832$, $N - H \cdots O^- = 3.163$ Å) and weak bifurcated hydrogen bonds. The methyl group is probably randomly oriented due to rotation or disorder.

The present structure determination of $CH_3COONH_4 \cdot 2NH_3$ belongs to a series of systematic studies of compounds formed between ammonia and simple carboxylic acids. Previously reported structures are those of $HCOONH_4$,[1] CH_3COONH_4,[2] and $CH_3COONH_4 \cdot NH_3$.[3]

According to the melting-point diagram of the system acetic acid-ammonia given by Davidson and coworkers [4] there exist three ammines of ammonium acetate, *viz.* $4CH_3COONH_4 \cdot NH_3$, $CH_3COONH_4 \cdot 1$(or 1.5)NH_3, and $CH_3COONH_4 \cdot 8NH_3$. The present investigation was started to study the structure of the proposed octammine salt as the large proportion of ammonia should give rise to an interesting hydrogen-bond system. However, a single crystal grown from a mixture with a composition of eight NH_3 to one CH_3COONH_4 turned out to be the diammine salt, $CH_3COONH_4 \cdot 2NH_3$. Recently published investigations (*e.g.* vapour pressure measurements) by Lindenberg [5] suggest that the only ammines formed in the system are $CH_3COONH_4 \cdot NH_3$ and $CH_3COONH_4 \cdot 2NH_3$.

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EXPERIMENTAL

In an attempt to prepare a sample of the octammine salt, $CH_3COONH_4 \cdot 8NH_3$, dry ammonia was distilled under vacuum into thin-walled capillaries containing known amounts of dry ammonium acetate. The capillaries were sealed off and the amount of ammonia determined by reweighing the capillaries. By trial and error a sample containing 90 mole % NH_3 was obtained. The starting materials were obtained as described earlier.[2,3] A cylindrical single crystal was grown at about −32°C in a Weissenberg camera modified for low temperature work.[6] The *c* axis was close to the cylinder axis.

Multiple-film (five), equi-inclination Weissenberg photographs were taken at −57 and −185±2°C using unfiltered Cu*K* radiation. Eight layers, $l=0$ to 7, were recorded at both temperatures. The two data sets showed only minor differences, which can be referred to changes in the temperature factors. Thus, only the data obtained at −185°C were used in the structure analysis. The total number of reflexions recorded at this temperature was 392, corresponding to about 87 % of the reflexions within the copper reflexion sphere. Of those recorded 29 were too weak to be measured. The relative intensities were estimated visually by comparison with an 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 only 7.9 cm^{-1} for Cu*K* radiation and the diameter of the crystal was 0.01 cm. No correction for extinction effects was made.

SPACE GROUP AND UNIT CELL

The diffraction symmetry *mmm* and systematic absences of *hkl* with $h+k$ odd and *h0l* with *l* odd indicate a choice between the orthorhombic space groups $Cmc2_1$ (No. 36), *C2cm* (No. 40, standard setting *Ama2*), and *Cmcm* (No. 63).[7] The subsequent refinements using all alternatives showed that the most probable space group is *Cmcm* but a structure with lower symmetry cannot be definitely excluded (*cf.* below).

The *a* and *b* axes were determined from zero-layer oscillation photographs and the *c* axis from rotation photographs. All patterns were calibrated with a quartz single crystal and recorded on the same film without removing the film from the cassette. The following constants were used: $a=4.913$ and $c=5.405$ Å for α quartz (25°C), $\lambda(\mathrm{Cu}K\alpha_1)=1.54051$ Å, $\lambda(\mathrm{Cu}K\alpha_2)=1.54433$ Å, $\lambda(\mathrm{Cu}K\beta)=1.39217$ Å. The *a* and *b* dimensions were fitted to the measured θ values (>32°) by the method of least squares using the program CELSIUS. They were based on 52 observations at −56°C and 56 at −185°C. The *c* dimensions were calculated from 54 and 56 observations, respectively. The unit-cell dimensions with standard deviations within parentheses are as follows:

	a	*b*	*c*	*V*
− 56°C	6.816(1) Å	12.493(1) Å	8.051(3) Å	685.6 Å^3
−185°C	6.805(1)	12.493(1)	7.904(3)	672.0

The density will be discussed in the following section.

DETERMINATION OF THE CRYSTAL STRUCTURE

Chemical composition and atomic coordinates. At the initial stages of the analysis the composition of the compound was assumed to be $CH_3COONH_4 \cdot 8NH_3$. Each of the alternative space groups requires multiples of four of each chemically nonequivalent atom in the unit cell. Assuming

four formula units in the cell the calculated density for $CH_3COONH_4 \cdot 8NH_3$ will be 2.108 g·cm^{-3} at −185°C. This is notably higher than the density of the related compound $CH_3COONH_4 \cdot NH_3$ (1.129 g·cm^{-3} at −40°C and 1.152 g·cm^{-3} at −190°C).[3] The chemical composition was therefore suspected to be different from that initially assumed. The correct proportion of NH_3 to CH_3COONH_4 could be deduced in the subsequent analysis.

By assuming the centrosymmetrical space group *Cmcm* and four formula units in the cell, a preliminary structure was obtained from a three-dimensional Patterson synthesis in the following way. From geometrical considerations and peaks found on the lines $P(0,v,0)$ and $P(0,v,\frac{1}{2})$, and in the section $P(u,v,\frac{1}{2})$ it was possible to locate the heavy atoms of the CH_3COO^- and NH_4^+ ions. The carbon and nitrogen atoms then occupy fourfold special positions, Wyckoff notation *c*, with the point symmetry *mm*. The oxygen atoms lie in eightfold special positions, *g*, on the mirror planes at $z=1/4$ and 3/4. The z coordinate is thus equal to 1/4 for all of these atoms. The remaining peaks were situated on the lines $P(0,v,0)$ and $P(0,v,1/4)$, and in the section $P(u,v,1/4)$ in the Patterson maps. The nitrogen atoms belonging to the NH_3 molecules were thus expected to be close to the planes at $z=0$ and 1/2. Only one eightfold position, type *f*, could be found, which makes a total of only two ammonia molecules in the formula unit. All peaks in the Patterson synthesis could now be explained. A model showed a reasonable packing without any holes large enough to contain additional NH_3 molecules.

The calculated density assuming four $CH_3COONH_4 \cdot 2NH_3$ units per unit cell, 1.077 g·cm^{-3} at −56°C and 1.099 g·cm^{-3} at −185°C, compares well with the reported density of $CH_3COONH_4 \cdot NH_3$ (see above). Thus, it is evident that the crystal obtained was the diammine salt.

Refinement. In the proposed structure the acetate group (discounting the hydrogen atoms) lies in the mirror plane at $z=1/4$ (or 3/4). Furthermore, the oxygen atoms are related to each other by the mirror plane at $x=0$ (or 1/2) passing through the carbon atoms. As the geometry of the methyl group is not compatible with the symmetry *mm* three possible cases arise: 1) the space group *Cmcm* is correct, but the methyl group is randomly oriented with respect to the carboxylate group, either by rotation or by disorder according to Fig. 1*c* or *d*; 2) the mirror planes at $x=0$ and 1/2 are absent, *i.e.* the space group is *C2cm* and the molecular conformation of the acetate ion is that illustrated in Fig. 1*a* ($\varphi=0°$, φ is the dihedral angle defined by the two planes C—C—H and C—C—O); 3) the mirror planes at $z=1/4$ and 3/4 are absent, *i.e.* the space group is $Cmc2_1$, and the conformation is that shown in Fig. 1*b* ($\varphi=30°$).

From the X-ray data it cannot of course be concluded with certainty which space group is correct. However, in order to estimate the probability of the different space groups the subsequent refinement of the structure was performed using all three alternatives. The coordinates, individual isotropic thermal parameters and inter-layer scale factors were refined in a series of full-matrix least-squares calculations. In the noncentrosymmetrical cases the atoms showed a slight displacement from the previous mirror planes. In total, 20 parameters were varied in the centrosymmetrical case and 26 in the others. After several cycles the shifts of all parameters were about 0.1σ and the results were as follows. In *C2cm* all atoms were shifted back towards

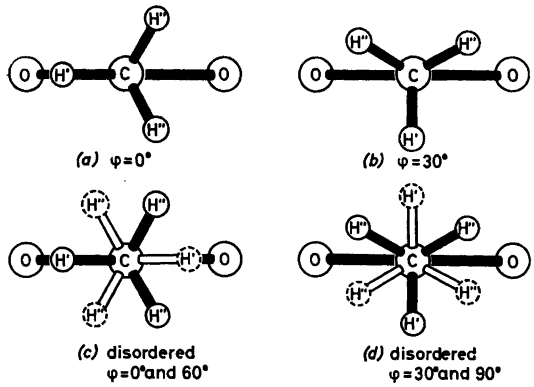

Fig. 1. Different models for the orientation of the methyl group with respect to the carboxylate group. The view is along the C—C axis. φ is the dihedral angle defined by the two planes C—C—H and C—C—O.

the previous mirror plane at $x=0$ and the situation was similar for $Cmc2_1$, except for the methyl carbon, which was moved away from the plane $z=1/4$. In all cases the Debye-Waller factors, B, for the corresponding atoms were about the same, except for the methyl carbon. When the symmetry was assumed to be *Cmcm* or *C2cm* a significantly higher B value was obtained for the methyl carbon, about 2.8 Å^2, as compared to 1.9 Å^2 in the case of $Cmc2_1$ (the mean value was 1.2 Å^2 for the rest of the atoms). As seen from Table 1 (column 1—2) the R values favour the space group $Cmc2_1$ at this stage of the refinement.

Anisotropic thermal parameters were subsequently refined for all the atoms together with the atomic coordinates and an overall scale factor. The number of parameters varied increased to 25 and 39, respectively, in the centrosymmetrical and noncentrosymmetrical cases. The relative inter-layer scale factors were taken as the values obtained in the last cycle of the corresponding isotropic refinement. In *Cmcm* the parameter shifts were less than 0.1σ after four cycles. In the acentric space groups the shifts for some of the parameters were still about 1σ after six cycles; the refinements were nevertheless interrupted at this stage as the R values did not change significantly

Table 1. Discrepancy indices $R'=\sum||F_o|-|F_c||/\sum|F_o|$ and $R''=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ at different stages of the refinements.

	Isotropic		Anisotropic		Isotropic+all hydrogen atoms		Anisotropic+all hydrogen atoms	
	R'	R''	R'	R''	R'	R''	R'	R''
Cmcm	0.145	0.175	0.115	0.138	0.122	0.148	0.094	0.111
C2cm	0.137	0.166	0.105	0.127				
$Cmc2_1$	0.126	0.151	0.106	0.127				

and the atoms gradually moved closer to positions compatible with *Cmcm*. In the case of $Cmc2_1$, it was particularly interesting to note that also the methyl carbon was subjected to relatively large shifts towards the previous mirror plane at $z=1/4$. A comparison of the final individual anisotropic thermal parameters revealed only small differences between the three space groups. This was true also for the thermal parameters of the methyl carbon, which indicated strong anisotropy in all three cases. The largest principal axis of the thermal ellipsoid was perpendicular to the plane of the acetate ion (*i.e.* to the plane $z=1/4$) and was about twice as large as for the rest of the atoms.

The comparably large anisotropy of the methyl carbon, C(2), may be due to a disorder between two equivalent positions related by the mirror plane at $z=1/4$. An attempt was made to refine the structure in *Cmcm* assuming two half carbon atoms moved out of the position on the mirror plane. A series of alternative models were used for varying $z_{C(2)} \neq 1/4$. In order to avoid ill-conditioned matrices of the normal equations the least-squares refinements were performed for fixed $z_{C(2)}$ in all cases. The R values remained nearly the same as $z_{C(2)}$ was varied in steps of 0.005 from 0.25 to 0.22, which means that the two half methyl carbons were allowed to move ≤ 0.24 Å from the position on the mirror plane. Only the thermal vibration perpendicular to the plane of the acetate molecule changed significantly as $z_{C(2)}$ was varied ($U_{33}=0.0190$ Å^2 for $z=0.22$ as compared to $U_{33}=0.0965$ Å^2 for $z=0.25$); the other parameters were virtually independent of the value of $z_{C(2)}$. Evidently, from the diffraction data it cannot be determined if the position of the methyl carbon is disordered. In the subsequent refinement and in the discussion below the position is assumed to be ordered, *i.e.* $z_{C(2)}=1/4$.

The corresponding R values after the anisotropic refinement were nearly equal in $Cmc2_1$ and *C2cm* (*cf.* Table 1). They are significantly lower as compared to those in *Cmcm* according to the significance test given by Hamilton [8] and a noncentrosymmetrical structure is accordingly suggested. However, other evidence favours *Cmcm*. Assuming *Cmcm* the geometry of the acetate ion is consistent with earlier results;[2,3] this is not the case when *C2cm* and $Cmc2_1$ are used. The standard deviations are unreasonably large in the acentric space groups (σ_x in *C2cm* and σ_z in $Cmc2_1$ are 5—7 times larger than in *Cmcm*).

By determination of the orientation of the methyl group it might be possible to exclude all but one space group according to the earlier discussion. In order to locate the hydrogen atoms separate three-dimensional difference syntheses were calculated using the three sets of parameters. However, all showed the same principal features. Near to the methyl carbon only four equivalent peaks were found. These were compatible with a disordered orientation of the methyl group (*cf.* Fig. 1*d*, $\varphi=30$ and 90°, position H″). The positions denoted H′ corresponded to negative electron density. The hydrogen atoms of ammonium and ammonia were clearly indicated at the expected positions. The only spurious peak of comparable size was observed in the middle of the C—C bond. As the refinements did not favour any particular acentric space group and the structure was most satisfactorily described in terms of the centrosymmetrical space group, *Cmcm* was considered to be the most appropriate choice.

Table 2. Atomic coordinates ($\times 10^4$) and thermal vibration tensor components ($\times 10^4$ Å^2) with standard deviations within parentheses. U_{ij} are coefficients in the expression $\exp[-2\pi^2(h^2a^{-2}U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}+\cdots)]$. The Debye-Waller factors $B=2$ Å^2 were used for the hydrogen atoms 1—4, and $B=3$ Å^2 for hydrogen atoms 5 and 6.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	1630(3)	−1128(2)	2500	184(14)	141(12)	186(18)	11(7)	0	0
N(1)	0	5201(3)	2500	191(18)	124(18)	158(28)	0	0	0
N(2)	0	3131(2)	4996(4)	369(18)	140(15)	97(22)	0	0	3(10)
C(1)	0	−659(3)	2500	207(20)	148(20)	32(27)	0	0	0
C(2)	0	572(4)	2500	260(25)	97(22)	914(58)	0	0	0

Atomic coordinates ($\times 10^3$) for the hydrogen atoms.

	x	y	z		x	y	z		x	y	z
N(1) H(1)	0	567	345	N(2) H(3)	125	310	428	C(2) H(5)	132	87	184
N(1) H(2)	103	478	250	N(2) H(4)	0	247	562	C(2) H(6)	0	87	119

A new series of refinements analogous to that described above was now performed in *Cmcm*, including the hydrogen atoms with fixed parameters. The coordinates of the hydrogen atoms were derived from the difference synthesis except for those of the methyl group, which were calculated assuming the disordered model illustrated in Fig. 1*d* and a C—H distance of 1.10 Å. The six methyl hydrogens were introduced as half atoms. The Debye-Waller factors used were 2 Å^2 for the hydrogen atoms involved in hydrogen bonding and 3 Å^2 for the rest. In the last cycles 15 reflexions were excluded from the refinement. Five of these were at the edge of the films and ten were low angle, high intensity reflexions affected by errors in the intensity measurement and probably also by extinction effects. The final isotropic and anisotropic R values are given in Table 1. A refinement using the disordered model with $\varphi=0$ and 60° (*cf.* Fig. 1*c*) did not significantly change the parameters and the R values. An exclusion of the methyl hydrogens from the refinements increased R' to 0.102 and R'' to 0.130.

Table 2 lists the final atomic coordinates and vibration tensor components U_{ij}. The latter were obtained from the anisotropic thermal parameters β_{ij} according to Scheringer.[9] The r.m.s. components of thermal displacement along the principal axes of the ellipsoids are given in Table 3. The observed and calculated structure factors are compared in Table 4.

The Fourier calculations were made using the program DRF. In the least-squares refinements the full-matrix program LALS was used with minimization of $\sum w(|F_o|-|F_c|)$.[2] The weights were calculated according to the expres-

Table 3. Root-mean-square components R_i (Å) of thermal displacement along the principal axes of the ellipsoids.

	O	N(1)	N(2)	C(1)	C(2)
R_1	0.118	0.112	0.098	0.057	0.098
R_2	0.136	0.126	0.118	0.122	0.161
R_3	0.137	0.138	0.192	0.144	0.302

Table 4. Observed and calculated structure factors. Reflexions, which were too weak to be measured are indicated with one asterisk, and these were assigned the intensity $\frac{1}{2} I_{min.}$ Two asterisks indicate reflexions, which were excluded from the final refinement.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	2	0	24.4	28.0 **
0	4	0	23.8	23.8
0	6	0	4.6	3.2
0	8	0	13.9	13.2
0	10	0	17.8	18.5
0	12	0	7.7	8.2
0	14	0	15.0	13.4
1	1	0	11.2	10.2
1	3	0	21.8	20.3
1	5	0	62.9	80.3 **
1	7	0	12.0	11.9
1	9	0	2.8	3.1
1	11	0	16.3	18.8
1	13	0	7.4	6.9
1	15	0	3.8	3.3
2	2	0	10.4	11.8
2	4	0	33.8	34.5
2	6	0	17.4	16.2
2	8	0	33.8	36.9
2	10	0	3.6	3.5
2	12	0	3.7	4.3
2	14	0	1.4	1.9 *
3	1	0	35.6	34.6
3	3	0	35.7	35.1
3	5	0	4.9	4.5
3	7	0	15.2	17.8
3	9	0	24.4	26.1
3	11	0	14.6	16.4
3	13	0	22.0	21.6
3	15	0	6.6	8.2
4	0	0	29.9	30.0
4	2	0	7.1	6.5
4	4	0	24.0	23.1
4	6	0	11.7	10.5
4	8	0	24.3	26.7
4	10	0	5.8	5.7
4	12	0	3.7	4.3
4	14	0	2.8	2.9
5	1	0	4.8	4.7
5	3	0	6.0	5.0
5	5	0	22.0	25.2
5	7	0	6.2	7.5
5	9	0	1.4	1.6 *
5	11	0	12.3	10.7
5	13	0	3.4	4.5
6	0	0	38.9	42.8
6	2	0	9.4	8.2
6	4	0	8.3	8.3
6	6	0	1.4	2.6 *
6	8	0	4.2	3.4
6	10	0	7.7	6.9
7	1	0	5.8	5.3
7	3	0	1.4	1.1 *
7	5	0	18.4	18.4
7	7	0	4.8	4.9
7	9	0	0.9	0.3 *
8	0	0	14.0	13.1
8	2	0	4.8	4.3
8	4	0	7.5	6.5
8	6	0	3.5	3.3
0	2	1	29.4	46.0 **
0	4	1	5.0	4.7
0	6	1	34.6	42.1 **
0	8	1	23.3	25.2
0	10	1	5.5	5.7
0	12	1	7.0	6.5
0	14	1	9.4	9.1
0	16	1	5.1	9.2 *
1	1	1	18.8	20.2
1	3	1	24.3	27.9
1	5	1	0.8	1.2 *
1	7	1	10.9	10.4
1	9	1	7.0	6.9
1	11	1	11.3	13.2
1	13	1	8.5	7.8
1	15	1	3.1	3.1
2	2	1	24.3	27.6
2	4	1	17.3	15.9
2	6	1	1.0	1.8 *
2	8	1	5.0	4.0
2	10	1	13.7	14.3
2	12	1	10.4	10.6
2	14	1	1.2	0.1 *
3	1	1	16.8	17.7
3	3	1	18.5	21.5
3	5	1	18.9	19.3
3	7	1	24.5	27.2
3	9	1	1.2	1.9 *
3	11	1	10.2	9.5
3	13	1	4.0	3.8
3	15	1	9.9	15.3 **
4	2	1	17.9	18.7
4	4	1	8.7	8.3
4	6	1	12.9	2.4
4	8	1	4.8	3.4
4	10	1	13.1	13.4
4	12	1	12.1	10.1
5	1	1	10.0	8.6
5	3	1	12.5	11.5
5	5	1	3.6	2.6
5	7	1	2.4	2.4
5	9	1	2.5	2.9
5	11	1	8.2	7.7
5	13	1	4.7	6.1
6	2	1	14.0	14.1
6	4	1	1.2	1.6 *
6	6	1	15.7	16.2
6	8	1	14.1	12.5
6	10	1	1.1	1.2 *
7	1	1	7.4	6.1
7	3	1	10.2	9.0
7	5	1	1.3	0.3 *
7	7	1	4.4	3.9
7	9	1	2.8	2.8
8	2	1	4.8	3.4
8	4	1	2.9	2.6
0	2	2	50.3	97.0 **
0	4	2	25.8	25.4
0	6	2	35.8	38.4
0	8	2	28.6	31.0
0	10	2	3.6	3.7
0	12	2	9.0	9.4
0	14	2	2.1	1.9
1	1	2	35.3	43.3 **
1	3	2	46.7	58.4 **
1	5	2	12.3	10.5
1	7	2	28.1	27.3
1	9	2	11.7	11.9
1	11	2	7.9	7.5
1	13	2	14.5	12.7
1	15	2	9.2	9.1
2	0	2	14.5	10.4 **
2	2	2	48.3	58.0 **
2	4	2	27.5	27.3
2	6	2	13.6	12.3
2	8	2	1.0	0.5 *
2	10	2	18.8	20.1
2	12	2	3.3	2.6
2	14	2	16.3	15.1
3	1	2	12.7	12.5
3	3	2	8.9	7.6
3	5	2	26.8	28.1
3	7	2	24.4	26.8
3	9	2	30.0	34.8
3	11	2	3.9	3.9
3	13	2	6.6	5.4
4	0	2	10.2	10.9
4	2	2	28.5	29.3
4	4	2	20.1	19.8
4	6	2	7.1	6.8
4	8	2	4.0	3.8
4	10	2	16.7	16.2
4	12	2	3.6	3.1
4	14	2	14.2	13.1 **
5	1	2	14.8	14.2
5	3	2	15.6	16.6
5	5	2	5.1	4.9
5	7	2	12.6	13.9
5	9	2	9.0	8.3
5	11	2	2.2	3.4
6	0	2	19.7	20.5
6	2	2	19.7	21.2
6	4	2	8.3	8.3
6	6	2	12.8	13.1
6	8	2	13.0	10.6
6	10	2	1.9	1.3
7	1	2	12.1	10.5
7	3	2	13.1	11.4
7	5	2	7.1	6.4
7	7	2	10.0	9.0
7	9	2	3.4	4.0
8	0	2	2.7	2.1
8	2	2	12.5	11.3
8	4	2	7.0	6.1
0	2	3	26.4	36.2 **
0	4	3	14.5	13.2
0	6	3	30.0	35.3
0	8	3	19.9	21.8
0	10	3	4.5	3.6
0	12	3	4.4	3.5
0	14	3	8.5	7.7
1	1	3	15.4	18.8
1	3	3	21.9	24.5
1	5	3	2.3	1.8
1	7	3	5.1	4.7
1	9	3	2.1	2.9
1	11	3	10.9	12.2
1	13	3	7.5	6.4
1	15	3	2.0	1.8
2	2	3	16.6	15.8
2	4	3	8.0	6.5
2	6	3	3.2	3.0
2	8	3	4.5	3.9
2	10	3	12.2	14.0
2	12	3	12.4	10.8
3	1	3	19.1	19.7
3	3	3	13.8	13.8
3	5	3	14.5	15.3
3	7	3	20.0	23.1
3	9	3	2.3	1.9
3	11	3	9.9	8.8
3	13	3	2.6	2.7
4	2	3	11.6	11.0
4	4	3	8.7	7.1
4	6	3	5.0	4.5
4	8	3	4.2	3.0
4	10	3	14.8	13.2
4	12	3	11.0	9.8
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5	5	3	3.6	2.2
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5	9	3	3.9	2.8
5	11	3	7.7	6.8
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6	4	3	2.1	2.5
6	6	3	14.2	13.9
6	8	3	12.9	11.2
6	10	3	0.9	0.7 *
7	1	3	6.7	5.7
7	3	3	10.3	8.6
7	5	3	0.9	0.3 *
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8	2	3	3.1	3.0
8	4	3	1.2	1.4
0	2	4	12.3	12.8
0	4	4	16.6	15.9
0	6	4	5.1	3.0
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0	10	4	14.3	14.7
0	12	4	8.6	6.8
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3	7	4	13.3	12.7
3	9	4	17.5	19.8
3	11	4	14.3	13.5
3	13	4	17.6	19.4
4	0	4	20.7	21.1
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4	4	4	15.5	15.6
4	6	4	10.9	10.8
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4	10	4	2.4	1.9
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5	3	4	6.0	4.9
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7	7	4	3.2	4.3
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8	2	4	2.0	3.5 **
0	2	5	25.3	30.2
0	4	5	8.3	6.5
0	6	5	18.0	19.7
0	8	5	16.6	17.0
0	10	5	2.0	2.3 *
0	12	5	2.6	2.0
0	14	5	5.1	8.3 **
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1	3	5	17.1	17.1
1	5	5	4.9	3.8
1	7	5	7.0	5.5
1	9	5	5.3	4.2
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1	13	5	5.1	4.6
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2	12	5	10.5	10.5
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4	6	5	4.1	3.9
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5	1	5	6.2	5.9
5	3	5	7.8	8.5
5	5	5	3.6	3.4
5	7	5	0.8	0.7 *
5	9	5	2.9	2.3
6	2	5	10.8	11.5
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6	6	5	10.4	10.4
6	8	5	7.7	9.5
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7	3	5	7.3	7.9
7	5	5	1.5	1.6
0	2	6	25.7	29.3
0	4	6	9.9	9.6
0	6	6	16.5	17.9
0	8	6	18.1	19.1
0	10	6	2.4	2.0
0	12	6	5.5	5.6
1	1	6	15.4	15.5
1	3	6	23.6	23.5
1	5	6	7.2	4.8
1	7	6	14.1	14.6
1	9	6	9.0	7.3
1	11	6	7.2	6.3
2	0	6	8.8	7.3
2	2	6	23.8	22.6
2	4	6	16.0	14.0
2	6	6	8.3	7.4
2	8	6	4.0	2.7
2	10	6	13.7	13.1
2	12	6	3.3	2.7
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3	3	6	8.2	7.1
3	5	6	14.3	16.4
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3	11	6	4.6	4.8
4	0	6	7.2	6.8
4	2	6	15.9	17.2
4	4	6	11.7	11.9
4	6	6	6.8	5.7
4	8	6	0.9	0.4 *
4	10	6	8.9	11.5
5	1	6	9.7	9.0
5	3	6	13.0	12.3
5	5	6	2.6	2.5
5	7	6	9.5	10.3
5	9	6	3.0	3.9
6	0	6	11.1	12.9
6	2	6	12.9	14.2
6	4	6	4.8	5.2
6	6	6	7.1	9.6
7	1	6	4.0	7.1 **
0	2	7	18.6	17.5
0	4	7	9.2	9.7
0	6	7	13.2	13.2
0	8	7	9.6	11.8
0	10	7	0.8	0.6 *
1	1	7	9.6	8.0
1	3	7	15.3	13.2
1	5	7	5.6	3.9
1	7	7	0.9	1.3 *
1	9	7	2.5	1.9
1	11	7	5.1	5.4
2	2	7	5.5	4.4
2	4	7	0.7	0.3 *
2	6	7	5.0	3.4
2	8	7	1.0	2.4
2	10	7	9.6	10.5
3	1	7	7.0	5.8
3	3	7	5.4	4.5
3	5	7	12.3	10.8
3	7	7	13.0	14.5
3	9	7	0.7	0.4 *
4	2	7	4.7	4.7
4	4	7	0.9	0.0 *
4	6	7	4.8	3.8
4	8	7	0.7	1.8 *
5	1	7	4.8	4.7
5	3	7	8.7	8.3
5	5	7	4.4	3.9
6	2	7	7.1	9.6

sion $w=1/(a+|F_o|+c|F_o|^2+d|F_o|^3)$. The final values used for a, c, and d were 1.6, 0.01, and 0.002. Reflexions too weak to be measured were given zero weight, and were also omitted in all calculations of R values. The atomic scattering factors used are those for neutral O, N, C, and H given in the *International Tables* (Vol. III, p. 202).[10] Distances and angles were calculated from the atomic coordinates and standard deviations obtained in the final least-squares calculation using the program DISTAN. The errors in the cell dimensions were also included. The illustrations were prepared by means of the plot program OR TEP. All calculations were performed on the CD 3600 computer in Uppsala. A more detailed description of the programs used has been given in an earlier paper.[2]

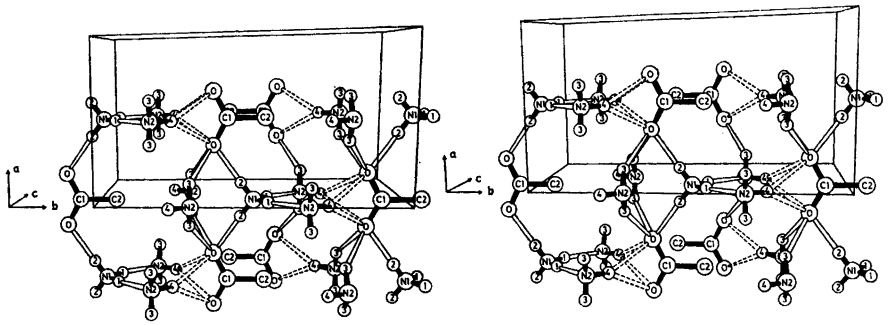

Fig. 2. A stereoscopic pair of drawings showing the hydrogen-bond pattern in ammonium acetate diammine. The methyl hydrogens are omitted as the orientation of the methyl group could not be determined with certainty in the analysis. The rest of the hydrogen atoms are denoted 1—4. Covalent bonds are filled. Full lines represent O···H distances less than 2.4 Å and broken lines represent O···H distances equal to 2.5 Å and assumed to be part of weak bifurcated hydrogen bonds.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General. A stereoscopic illustration of the structure is given in Fig. 2. The orientation of the methyl group could not be determined with certainty in the analysis and the methyl hydrogens are accordingly not included. Bond distances and angles involving the heavy atoms, are given in Figs. 3—5. The standard deviations are in the range 0.003—0.004 Å and 0.1—0.4° (except for C(1)—C(2): σ=0.006 Å). As the errors in the coordinates of the hydrogen atoms may be relatively large the bond distances and angles involving these atoms must be regarded as only approximate.

The structure contains NH_4^+ and CH_3COO^- ions arranged in layers parallel to (001) at z=1/4 and 3/4. These are interleaved by NH_3 molecules located in z=0 and 1/2. The NH_4^+ and CH_3COO^- ions are linked by hydrogen bonds, N^+—H···O^-, into planar chains parallel to (001) and extending along the a axis. These chains are further connected to the adjacent NH_3 molecules by normal hydrogen bonds, N^+—H···N and O^-···H—N, and by very weak bifurcated bonds. The hydrogen-bond system thus gives rise to a three-dimensional network.

Each NH_4^+ ion donates four hydrogen bonds, which are accepted by two NH_3 molecules and two oxygen atoms belonging to different CH_3COO^- ions. The NH_3 molecules, which are all equivalent, are engaged in four hydrogen bonds: besides the bond accepted from the NH_4^+ ion the NH_3 molecule acts as a hydrogen donor for *two normal* bonds to oxygen atoms belonging to different CH_3COO^- ions and *one bifurcated* bond where the hydrogen atom is equally shared between two oxygen atoms of the same CH_3COO^- ion (*cf.* the broken lines in Fig. 2). The CH_3COO^- ion has the symmetry *mm* and the oxygen atoms are accordingly equivalent. Each oxygen atom is surrounded by one NH_4^+ and four NH_3 groups. However, two of these contacts are only components of bifurcated bonds (see above).

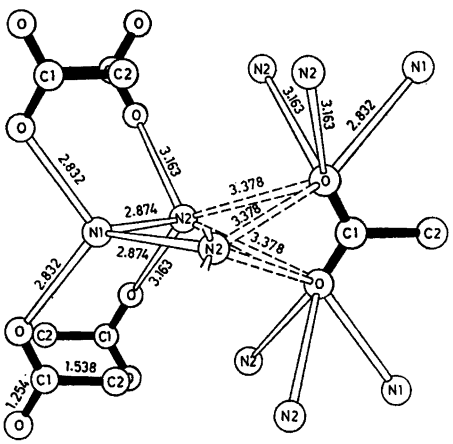

Fig. 3. Bond distances around the nitrogen and oxygen atoms and within the acetate ion. The standard deviations range from 0.003 to 0.004 Å except for the C—C distance, for which $\sigma=0.006$ Å. Covalent bonds are filled. Normal hydrogen bond distances are represented by full lines and distances between atoms engaged in bifurcated hydrogen bonds are drawn as broken lines. The orientation is the same as in Fig. 2.

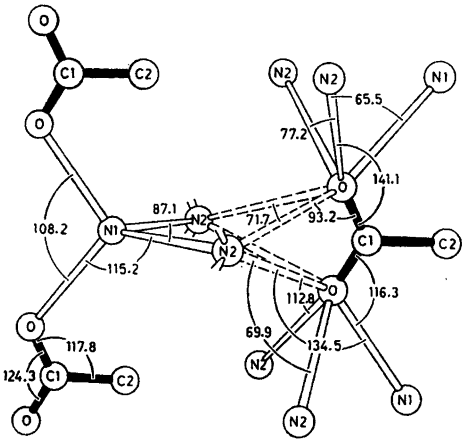

Fig. 4. Bond angles around N(1) and O and within the acetate ion. $\sigma=0.1-0.4°$. Notation as in Fig. 3.

Details of the structure and the hydrogen-bond system are discussed in the following sections.

The ammonium ion. The NH_4^+ ion has the symmetry *mm*. It is approximately tetrahedrally surrounded by two oxygen atoms and two nitrogen atoms, N(2). The N(1)···O and N(1)···N(2) distances, 2.832 and 2.874 Å,

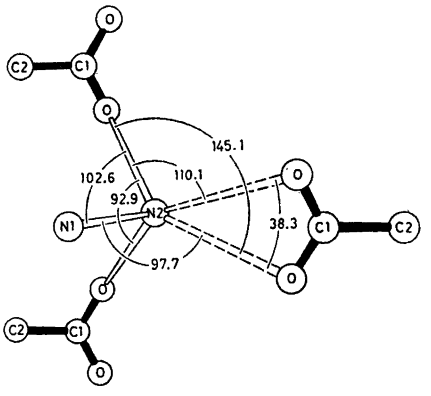

Fig. 5. Bond angles around N(2). $\sigma=0.1-0.4°$. Notation as in Fig. 3.

respectively, are comparable with the bonds in CH_3COONH_4 ($N^+—H\cdots O^-$ = =2.80—2.83 Å)[2] and $CH_3COONH_4 \cdot NH_3$ ($N^+—H\cdots O^-$=2.80—2.82 Å and $N^+—H\cdots N$=2.87 Å).[3]

The positions of the hydrogen atoms, H(1) and H(2), derived from the difference synthesis correspond to a nearly straight $N^+—H\cdots O^-$ bond but a somewhat bent $N^+—H\cdots N$ bond ($\angle$=167°). This seems reasonable as the bond angle O···N(1)···O=108.2° is nearly tetrahedral whereas the angle N(2)···N(1)···N(2) is only 87.1°. The corresponding H—N(1)—H angles are 106 and 104°, respectively. The N(1)—H(1) and N(1)—H(2) distances are 0.88 and 0.95 Å.

The ammonia molecule. The central atom, N(2), of the ammonia molecule lies on the same mirror plane as N(1) and the carbon atoms C(1) and C(2). It is surrounded by six atoms at distances less than 3.4 Å, two N(1) and four O. However, one of the N(2)···N(1) contacts (3.253 Å) is without interest from the hydrogen-bond point of view.

The bonding situation of ammonia is very similar to that in $CH_3COONH_4 \cdot NH_3$.[3] Thus, the lone pair accepts a normal hydrogen bond from NH_4^+; the bond lengths were compared above. Two of the hydrogen atoms are involved in normal hydrogen bonds to oxygen atoms. The bond distances are quite similar: 3.163 Å in the diammine as compared to 3.15 and 3.22 Å in the monammine (−190°C). These hydrogen bonds are rather bent in the present compound ($\angle$=150°). The third hydrogen atom in the diammine, H(4), interacts equally with the two oxygen atoms of the same acetate ion; the H(4)···O distances are both 2.50 Å and the N(2)—H(4)···O angles are 152°. The N···O distances, 3.378 Å, may be compared with the components of the bifurcated bond in the monammine, 3.27 and 3.49 Å (−190°C). The arrangement of the neighbours around ammonia is also very similar to that in the monammine. The corresponding contact angles are about the same with values ranging from 38 to 145° in the diammine as compared to 38—138° in the monammine.

The ammonia molecule was found to have normal bond angles. The N(2)—H(3) and N(2)—H(4) distances are 1.02 and 0.96 Å, respectively.

The acetate ion. The acetate ion has the symmetry *mm* and is accordingly perfectly planar with the oxygen atoms structurally equivalent. The bond distances C—O=1.254 Å and bond angles C—C—O=117.8° and O—C—O=124.3° agree closely with the corresponding distances and angles in CH_3COONH_4[2] and $CH_3COONH_4 \cdot NH_3$.[3] Further references to the dimensions of the carboxylate group are given in the paper on CH_3COONH_4.

The C—C distance, 1.538 Å, in the present compound is longer than in CH_3COONH_4 (1.504 Å) and in the high-temperature form of $CH_3COONH_4 \cdot NH_3$ (1.518 Å). However, it does not differ significantly from the C—C bond length (1.528 Å) in the low-temperature form of the latter compound. The corresponding distances corrected for thermal "riding" motion[11] are in the same order as above: 1.569, 1.528, 1.537, and 1.532 Å. The standard deviations are of about the same magnitude in all compounds. In the present compound the strongly anisotropic motion indicated for the carbon atoms should be noticed (*cf.* Tables 2 and 3). As discussed above the largest principal axis of the ellipsoid

of C(2) is perpendicular to the plane of the acetate group and is unexpectedly large. It is not possible to determine from the diffraction data if this is due to a disorder of C(2) between two equivalent positions. The anisotropy of the carboxylate carbon C(1) is also remarkable as the thermal vibration is smallest perpendicular to the plane of the molecule.

Each oxygen atom of the carboxylate group accepts three normal hydrogen bonds from one NH_4^+ and two NH_3 groups. Furthermore, they interact with two hydrogen atoms H(4) of two other NH_3 groups but these O···H contacts are only parts of very weak bifurcated bonds. The $N^+—H\cdots O^-$ bond lies in the same plane as the acetate ion and approaches the oxygen atom from the side of the methyl group (*cf.* Figs. 3 and 4). The bond angle formed with the C(1)—O bond is 116.3°. A closely related situation is found in $CH_3COONH_4 \cdot NH_3$ (bond angles 118.7 and 118.5° at −190°C).[3] From the symmetry it follows that the centroid of the two O···H(3) and two O···H(4) contacts lies in the same plane as the acetate ion. It forms an angle of approximately 125° with the C(1)—O bond.

The orientation of the methyl group could not be determined from the present analysis. Attempts will be made to solve this problem by other methods. It is interesting to note that a rotation may be possible for the methyl group of an isolated acetate ion. Virtually the same conformation is obtained every 60° of internal rotation about the C—C bond as the two oxygen atoms of the carboxylate group are equivalent (*cf.* Fig. 1*c* or *d*). Thus, the barrier to rotation about this bond is expected to be sixfold, which usually results in a very small barrier height. This has been demonstrated in, *e.g.*, the related compounds CH_3NO_2 and CD_3NO_2[12] where the barrier heights are 0.005—0.006 kcal·mole^{-1}. In acetic acid[13] the two oxygen atoms of the carboxyl group are similar, but not completely identical, and the barrier, 0.483 kcal·mole^{-1}, lies somewhere between the typical value for a threefold and a sixfold barrier to rotation about the C—C bond.

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