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Hydrogen Bond Studies

26.* The Crystal Structure of Ammonium Acetate Monammine, $CH_3COONH_4 \cdot NH_3$ (at − 40 and − 190°C)

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The crystal structure of ammonium acetate monammine, $CH_3COONH_4 \cdot NH_3$, has been determined at −40 and −190°C from three-dimensional X-ray data. Four formula units crystallize in an orthorhombic unit cell with the dimensions $a = 6.169$, $b = 6.742$, $c = 13.311$ Å at −40°C and $a = 6.175$, $b = 6.740$, $c = 13.037$ Å at −190°C. The space group is $P2_12_12_1$. The structure is built up from CH_3COO^-, NH_4^+, and NH_3 groups closely linked by hydrogen bonds into puckered layers which are held together by strongly bent or bifurcated hydrogen bonds. A comparison of the packing at the two temperatures is made. A pronounced difference in the weak intermolecular bonds is observed.

The present work forms part of a series of structure studies of the hydrogen bonds in compounds formed between a simple carboxylic acid (acetic acid, formic acid) and ammonia or hydrazine. The structures of ammonium acetate [1] and ammonium formate [2] have been reported earlier.

A determination of the melting-point diagram for the system acetic acid — ammonia was made by Davidson and co-workers.[3] In addition to the familiar salt ammonium acetate, CH_3COONH_4, and the acidic compound, $CH_3COONH_4 \cdot CH_3COOH$, they reported the existence of three ammines of ammonium acetate, *viz.* $4CH_3COONH_4 \cdot NH_3$, $CH_3COONH_4 \cdot 1(\text{or } 1.5)NH_3$, and $CH_3COONH_4 \cdot 8NH_3$. Complementary investigations of the system ammonium acetate — ammonia (*e.g.* vapour pressure measurements) were recently made by Lindenberg,[4] who states that the only ammines formed in the system are the ammonium acetate monammine and the previously not reported diammine salt, $CH_3COONH_4 \cdot 2NH_3$.

* The preceding paper in this series: *Hydrogen Bond Studies 25. A Neutron Diffraction Study of Hydrazinium Hydrogen Oxalate*, $N_2H_5HC_2O_4$ by Å. Nilsson, R. Liminga and I. Olovsson appeared in *Acta Chem. Scand.* **22** (1968) 719.

The present study is concerned with the monammine salt, $CH_3COONH_4 \cdot NH_3$. Two sets of single-crystal X-ray diffraction data were obtained at −40 and −190°C, respectively. These were used in two independent refinements in order to study the thermal expansion in detail. As pointed out by Lonsdale and co-workers [5] it is very interesting to know how both positional and thermal parameters change with temperature and to interpret the results in terms of molecular reorientations, changes in lengths and directions of intermolecular bonds, and related effects.

EXPERIMENTAL

$CH_3COONH_4 \cdot NH_3$ was prepared from ammonium acetate and ammonia, dried over potassium hydroxide. The ammonium acetate was obtained as described earlier [1] by repeated crystallization from ethanol (99.5 %), and was finally dried over calcium sulfate (Drierite) in a desiccator.

As seen from the melting-point diagram [3] the monammine melts incongruently and it is obviously not possible to grow single crystals in the ordinary way from a liquid of equimolar composition of ammonium acetate and ammonia. According to the same diagram the liquid should contain more than 75 mole % NH_3, *i.e.* more than 2 moles NH_3 per mole CH_3COONH_4, to give the 1:1 compound as the first precipitated solid phase.

Samples were prepared by distilling ammonia under vacuum into weighed capillaries containing known amounts of ammonium acetate. The capillaries were finally sealed off and the amount of ammonia was determined by reweighing the capillaries. By trial and error a sample was obtained containing 76 mole % NH_3 and a single crystal was grown at about + 2°C in a low-temperature Weissenberg camera described earlier.[6] The part of the capillary exposed to the X-rays had a diameter of 0.22 mm and a wall thickness of approximately 0.015 mm.

Multiple-film (five) equi-inclination Weissenberg photographs were taken at −40 and −190°C using unfiltered CuK radiation. Seven layers, $k = 0$ to 6, were recorded at both temperatures. The total number of reflections recorded at −40°C was 665, corresponding to about 87 % of the reflections within the copper reflection sphere. Of these, 72 were too weak to be observed. The corresponding numbers for the data collected at −190°C were 658, 86 %, and 29. The relative intensities of the reflections were obtained by visual comparison with an intensity scale. The intensity range was 1 to 7500. The data were corrected for the Lorentz and polarization effects. No absorption correction was applied, since the linear absorption coefficient is 8.5 cm^{-1} for Cu$K\alpha$ radiation and the diameter of the crystal cylinder was relatively small. No corrections for extinction effects were made.

UNIT CELL AND SPACE GROUP

The diffraction symmetry was *mmm*, indicating an orthorhombic unit cell. The a and the c dimensions were based on zero-layer oscillation photographs and the b dimension on rotation photographs. Each of these photographs was calibrated with a quartz single crystal, and all patterns were 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), $\lambda(\text{Cu}K\alpha_1) = 1.54051$ Å, $\lambda(\text{Cu}K\alpha_2) = 1.54433$ Å, $\lambda(\text{Cu}K\beta) = 1.39217$ Å. The a and the c dimensions were determined by least-squares treatment of the θ values (>35°) using the program CELSIUS. They were based on 83 observations at −40°C and 94 at −190°C. The b dimensions were calculated from 11 and 14 observations, respectively. The unit cell dimensions with standard deviations are as follows:

(−40°C)	(−190°C)
$a = 6.169 \pm 0.001$ Å	$a = 6.175 \pm 0.002$ Å
$b = 6.742 \pm 0.005$	$b = 6.740 \pm 0.005$
$c = 13.311 \pm 0.003$	$c = 13.037 \pm 0.003$
$V = 553.6$ Å^3	$V = 542.6$ Å^3

With four formula units in the cell the calculated density of the solid is 1.129 g·cm^{-3} at −40°C and 1.152 g·cm^{-3} at −190°C. No experimental determination of the density has been made.

The following systematic absences were observed: $h00$ and $00l$ for h and $l = 2n + 1$, respectively. The $0k0$ reflections were not recorded. The space groups $P2_12\ 2_1$ and $P2_12_12_1$ are accordingly both possible. In the three-dimensional Patterson function $P(u,v,w)$ there was a larger concentration of peaks in the section $P(u,1/2,w)$ than in $P(u,0,w)$, which indicates a translation of 0.5 along the twofold axis parallel to [010]. The space group $P2_12_12_1$ was accordingly chosen as the most probable, and the subsequent successful determination of the structure confirmed this choice.

DETERMINATION OF THE CRYSTAL STRUCTURE

Location of the atoms. A Patterson function was calculated using the three-dimensional data recorded at −190°C and with the inter-layer scale factors based on the relative exposure times.

The intramolecular O—O vector in the acetate group was ascribed to a peak at (0, 0.34, 0). By examination of the three Harker sections the location of these oxygen atoms in the unit cell could be determined. In a similar way it was possible to determine the position of the methyl carbon after the intramolecular C—O vectors had been found. However, the location of the second carbon had to be calculated from known dimensions of the acetate group [1] as no appropriate vectors could be identified.

The three-dimensional electron density based on the preliminary atomic coordinates determined so far gave no clear indication of the positions of the two nitrogen atoms. As hydrogen bonds were expected to be present in the structure, loci of vectors with lengths 2.8—3.3 Å in the Patterson synthesis were examined. Several rather diffuse peaks were found, which gave rise to a great number of possible trial structures. However, some of these could be disregarded from a re-examination of the Harker sections. By comparison between the observed and calculated structure factors the positions of the nitrogen atoms giving the most satisfactory agreement could be determined.

Refinement. The intensities recorded at −40 and −190°C, showed considerable differences for some of the high angle reflections, which could not be explained by a difference in temperature factors. In order to study the thermal expansion of the structure in detail both data sets were used in independent series of refinements.

The preliminary atomic coordinates of all atoms except the hydrogen atoms were improved by three-dimensional electron density calculations. Further refinement of the atomic parameters was performed by the method of least squares. After some cycles, refining inter-layer scale factors, coordinates and isotropic temperature parameters, the resulting shifts were no longer

significant. At this stage values of the discrepancy index $R = \sum||F_o| - |F_c||/\sum|F_o|$ were 0.139 (−40°C) and 0.117 (−190°C).

The thermal parameters of all atoms were now subjected to anisotropic refinement in two cycles which reduced the R values to 0.094 (−40°C) and 0.107 (−190°C). The inter-layer scale factors were fixed to the values obtained from the final isotropic refinements and an overall scale factor was refined. The total number of parameters varied increased from 31 to 55.

Three-dimensional $(F_o - F_c)$ syntheses were calculated based on the parameters of the last cycles of anisotropic refinement. Only reflections with $\sin\theta/\lambda$ less than 0.5 Å^{-1} were used. In both sets of difference maps peaks appeared close to the locations expected for the ten hydrogen atoms in the structure. The remaining spurious peaks were less than half as high. The positional parameters of the hydrogen atoms were calculated as will be described below.

Further least-squares refinements were now performed including the hydrogen atoms with fixed parameters. The Debye-Waller factors, B, used for the hydrogen atoms were 4 Å^2 (−40°C) and 2 Å^2 (−190°C). The parameters varied were the same as before. The R values were reduced to 0.077 (−40°C) and 0.093 (−190°C), merely by including the hydrogen atoms, and dropped further to 0.073 and 0.088, respectively, after two cycles. At this stage seven and ten reflections, respectively, were excluded from the data sets. They were all low angle, high intensity reflections with values of F_o smaller than F_c, possibly due to secondary extinction effects or substantial error in the intensity measurement. The refinements were completed with another two cycles and gave the final R values 0.069 (−40°C) and 0.082 (−190°C). As seen from Tables 1 and 2, the calculated standard deviations for the atomic parameters are nearly the same at both temperatures.

The Fourier calculations were made using the program DRF. The least-squares refinements, using the full-matrix program LALS, were based on F values, minimizing the function $\sum w(|F_o| - |F_c|)$.[2] The weights were calculated according to the expression, $w = 1/(a + |F_o| + c|F_o|^2)$. Final values used for a and c were 2.0 and 0.03, respectively. A weight analysis indicated essentially correct weighting factors w. Reflections too weak to be measured were given

Table 1a. Atomic coordinates (× 10^4) at −40 and −190°C with standard deviations within parentheses. The differencies (in Å) between the two sets of parameters are calculated assuming the same origin for both unit cells, *e.g.* $\Delta X = [a{\cdot}x]_{-40°C} - [a{\cdot}x]_{-190°C}$

		O(1)	O(2)	C(1)	C(2)	N(1)	N(2)
	x	2208(8)	2212(8)	1294(8)	−1087(11)	9719(7)	5611(8)
−40°C	y	3159(8)	6413(8)	4777(10)	4740(14)	−0232(9)	−0158(10)
	z	1042(2)	1110(2)	1189(2)	1478(4)	0675(2)	1701(2)
	x	2210(8)	2206(7)	1290(9)	−1109(10)	9675(7)	5575(8)
−190°C	y	2908(8)	6181(8)	4502(10)	4432(12)	−0468(9)	−0335(9)
	z	1007(2)	1164(1)	1201(2)	1486(3)	0670(2)	1701(2)
	ΔX	−0.003	0.002	0.002	0.014	0.021	0.019
	ΔY	0.168	0.155	0.184	0.206	0.159	0.119
	ΔZ	0.074	−0.040	0.017	0.030	0.025	0.047

Table 1b. Atomic coordinates ($\times 10^3$) for the hydrogen atoms calculated as described in the text. No standard deviations have been estimated.

		N(1)				N(2)			C(2)		
		H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)
−40°C	x	825	1064	1064	949	494	585	461	−142	−150	−198
	y	−20	102	−146	−18	−158	−19	82	337	612	469
	z	104	81	83	−9	165	243	136	190	187	76
−190°C	x	821	1061	1060	935	482	581	470	−135	−163	−205
	y	−41	75	−170	−54	−162	−28	82	336	590	400
	z	104	79	85	−10	152	247	143	212	175	85

Table 2a. Thermal vibration tensor components ($Å^2 \times 10^4$) with standard deviations within parentheses. U_{ij} are coefficients in the expression $\exp[-2\pi^2(h^2a^{-2}U_{11} + \ldots + 2hka^{-1}b^{-1}U_{12} + \ldots)]$. For hydrogen the Debye-Waller factors $B = 4.0$ and 2.0 $Å^2$ were used at −40 and −190°C, respectively.

		O(1)	O(2)	C(1)	C(2)	N(1)	N(2)
−40°C	U_{11}	366(15)	389(15)	358(16)	464(21)	300(13)	351(15)
	U_{22}	457(18)	433(18)	449(24)	635(33)	535(20)	643(24)
	U_{33}	798(20)	618(16)	448(16)	967(32)	524(15)	548(17)
	U_{12}	17(12)	−42(12)	17(17)	47(23)	−7(14)	−1(16)
	U_{13}	−1(16)	−5(14)	−22(14)	−215(24)	−17(11)	22(12)
	U_{23}	46(14)	−10(12)	4(17)	−22(28)	−31(14)	16(16)
−190°C	U_{11}	184(15)	162(13)	184(18)	206(20)	119(14)	165(15)
	U_{22}	189(19)	143(17)	189(23)	287(27)	197(20)	263(22)
	U_{33}	317(15)	224(13)	177(16)	366(22)	240(14)	211(14)
	U_{12}	22(13)	−17(12)	−7(20)	−20(23)	−1(16)	−4(17)
	U_{13}	−6(13)	−21(12)	−11(14)	−86(18)	−14(12)	19(12)
	U_{23}	9(11)	3(10)	56(16)	5(19)	4(13)	5(14)

Table 2b. Root-mean-square components R_i (Å) of thermal vibration along principal axes of the ellipsoids of vibration. The standard deviations have been multiplied by 10^3.

		O(1)	O(2)	C(1)	C(2)	N(1)	N(2)
−40°C	R_1	0.191(5)	0.191(6)	0.187(6)	0.195(9)	0.173(4)	0.187(4)
	R_2	0.213(5)	0.214(6)	0.213(10)	0.252(8)	0.224(7)	0.234(4)
	R_3	0.284(4)	0.249(4)	0.213(9)	0.324(8)	0.237(7)	0.254(5)
−190°C	R_1	0.128(11)	0.118(12)	0.115(17)	0.126(13)	0.106(8)	0.124(9)
	R_2	0.145(10)	0.133(11)	0.125(9)	0.174(9)	0.143(8)	0.146(8)
	R_3	0.179(5)	0.150(7)	0.161(13)	0.202(10)	0.155(6)	0.167(8)

zero weight in all calculations, 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 *International Tables* (Vol. III, p. 202).[7]

Table 1 lists the final positional parameters for the structure at the two temperatures. The anisotropic thermal parameters β_{ij} were transformed into the vibration tensor components U_{ij} according to Scheringer [8] and these latter are shown in Table 2a. The root-mean-square components of thermal displace-

ment along the principal axes of the ellipsoids are given in Table 2b. The observed and final calculated structure factors are compared at both temperatures in Table 3a and b, respectively. Distances and angles with standard

Table 3a. Observed and calculated structure factors at −190°C. Reflections which were too weak to be measured are indicated with one asterisk. The $|F_o|$ values for these are given as $1/\sqrt{2}|F_{min}|$. Two asterisks indicate reflections which were excluded from the final refinements.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	2	8.5	8.2
0	0	4	65.8	87.9**
0	0	6	13.4	12.6
0	0	8	11.2	10.0
0	0	10	6.2	5.8
0	0	12	1.1	0.2 *
0	0	14	5.9	5.5
0	0	16	4.6	4.2
1	0	1	17.7	19.2
1	0	2	34.4	39.4**
1	0	3	43.2	49.4**
1	0	4	27.8	28.3
1	0	5	13.7	12.9
1	0	6	32.6	34.0
1	0	7	18.5	18.4
1	0	8	23.6	22.8
1	0	9	0.9	0.1 *
1	0	10	16.6	16.0
1	0	11	2.1	2.0
1	0	12	12.3	13.4
1	0	13	9.9	9.4
1	0	14	6.6	5.6
1	0	15	1.0	0.2 *
1	0	16	5.6	5.9
2	0	0	4.8	2.5
2	0	1	10.5	10.8
2	0	2	6.9	6.2
2	0	3	13.7	14.2
2	0	4	24.5	25.1
2	0	5	14.1	13.5
2	0	6	17.2	17.9
2	0	7	4.3	3.9
2	0	8	24.0	25.7
2	0	9	12.0	11.2
2	0	10	17.0	17.4
2	0	11	3.8	4.3
2	0	12	9.8	10.1
2	0	13	10.9	9.8
2	0	14	9.1	7.8
2	0	15	4.4	4.2
2	0	16	1.6	1.3
3	0	1	26.4	28.1
3	0	2	42.3	44.3
3	0	3	12.5	11.1
3	0	4	0.8	0.4 *
3	0	5	24.8	24.7
3	0	6	9.7	9.1
3	0	7	11.9	12.0
3	0	8	1.0	1.1 *
3	0	9	6.4	6.4
3	0	10	5.3	5.4
3	0	11	9.8	10.2
3	0	12	2.3	1.9
3	0	13	5.0	4.0
3	0	14	4.4	3.9
3	0	15	4.3	4.2
4	0	0	12.5	12.6
4	0	1	15.7	16.4
4	0	2	10.2	9.9
4	0	3	2.4	2.4
4	0	4	5.2	4.1
4	0	5	18.0	20.1
4	0	6	13.6	14.2
4	0	7	3.1	3.2
4	0	8	5.3	5.0
4	0	9	8.3	9.4
4	0	10	6.4	6.1
4	0	11	2.9	2.6
4	0	12	3.7	3.2
4	0	13	1.9	2.1
4	0	14	2.5	2.7
5	0	1	6.2	5.4
5	0	2	1.0	1.9 *
5	0	3	12.0	12.0
5	0	4	3.1	3.0
5	0	5	6.2	5.4
5	0	6	7.8	8.2
5	0	7	6.8	6.8
5	0	8	6.6	6.3
5	0	9	7.7	6.8
5	0	10	8.4	7.8
5	0	11	3.5	3.1
5	0	12	4.4	4.0
5	0	13	2.0	2.8
6	0	0	7.9	9.0
6	0	1	5.5	5.5
6	0	2	2.5	2.4
6	0	3	11.8	12.7
6	0	4	7.4	7.0
6	0	5	1.1	1.4 *
6	0	6	3.3	3.0
6	0	7	7.2	7.3
6	0	8	3.0	2.3
6	0	9	2.4	2.7
6	0	10	1.4	1.5
6	0	11	2.9	3.5
7	0	1	1.1	0.0 *
7	0	2	7.8	7.9
7	0	3	6.0	5.4
7	0	4	6.2	5.9
7	0	5	2.1	2.1
7	0	6	0.8	0.6 *
7	0	7	7.3	7.9
0	1	2	18.7	19.9
0	1	3	4.4	3.5
0	1	4	2.7	3.0
0	1	5	10.3	11.1
0	1	6	33.5	38.7**
0	1	7	2.9	2.3
0	1	8	7.9	7.9
0	1	9	5.8	5.9
0	1	10	23.1	25.3
0	1	11	3.9	3.5
0	1	12	6.7	6.7
0	1	14	7.0	6.4
0	1	15	4.2	3.1
0	1	16	0.5	0.7
1	1	0	31.1	37.3**
1	1	1	9.7	8.4
1	1	2	11.6	12.5
1	1	3	42.0	52.0**
1	1	4	~23.9	26.9**
1	1	5	10.9	11.3
1	1	6	11.4	10.8
1	1	7	22.8	24.5
1	1	8	11.3	10.7
1	1	9	8.4	8.0
1	1	10	8.5	8.2
1	1	11	1.2	0.1 *
1	1	12	5.4	5.2
1	1	13	6.5	6.0
1	1	14	7.2	6.7
1	1	15	7.2	6.1
1	1	16	4.5	4.7
2	1	1	15.6	15.3
2	1	2	38.6	46.7**
2	1	3	17.7	19.7
2	1	4	9.7	9.9
2	1	5	11.8	11.4
2	1	6	8.5	8.5
2	1	7	18.5	20.2
2	1	8	4.1	4.0
2	1	9	2.0	1.8
2	1	10	6.1	6.1
2	1	11	11.1	11.7
2	1	12	1.2	0.9 *
2	1	13	5.8	5.3
2	1	14	2.0	1.8
2	1	15	6.3	6.1
2	1	16	2.8	3.7
3	1	0	3.4	2.7
3	1	1	21.7	23.0
3	1	2	8.0	7.0
3	1	3	4.3	3.9
3	1	4	11.2	11.2
3	1	5	16.9	18.0
3	1	6	3.0	3.2
3	1	7	3.9	3.1
3	1	8	10.6	11.8
3	1	9	6.9	6.3
3	1	10	2.2	2.7
3	1	11	4.4	4.7
3	1	12	4.5	4.1
3	1	13	4.3	3.6
3	1	14	1.1	1.0 *
3	1	15	5.5	6.4
4	1	0	3.6	3.6
4	1	1	13.9	13.9
4	1	2	11.4	10.9
4	1	3	4.8	4.6
4	1	4	3.0	2.5
4	1	5	14.1	15.5
4	1	6	1.0	0.6 *
4	1	7	4.5	4.4
4	1	8	5.5	5.5
4	1	9	2.5	3.0
4	1	10	3.1	2.5
4	1	11	5.8	5.1
4	1	12	7.5	7.1
4	1	13	6.8	6.0
4	1	14	2.2	2.3
5	1	0	15.1	16.5
5	1	1	4.8	4.8
5	1	2	2.4	2.2
5	1	3	4.3	4.4
5	1	4	5.2	5.2
5	1	5	2.9	2.9
5	1	6	2.4	2.2
5	1	7	1.7	1.9
5	1	8	8.4	7.9
5	1	9	8.4	7.3
5	1	10	4.8	3.7
5	1	11	5.0	3.8
5	1	12	6.1	6.8
6	1	0	2.0	2.1
6	1	1	2.0	2.3
6	1	2	4.1	4.0
6	1	3	7.3	7.8
6	1	4	4.1	4.1
6	1	5	5.2	4.8
6	1	6	0.8	0.6 *
6	1	7	4.9	4.8
6	1	8	3.9	3.2
6	1	9	3.9	3.2
6	1	10	1.2	0.6 *
6	1	11	3.6	3.4
6	1	12	1.2	0.6 *
6	1	13	3.6	3.4
6	1	14	2.7	3.0
6	1	15	1.2	1.9
7	1	1	3.8	3.6
7	1	2	1.2	0.6 *
7	1	3	3.6	3.4
7	1	4	1.5	1.5
7	1	6	3.6	2.9
7	1	7	2.3	1.9
0	2	1	21.0	22.6
0	2	2	6.4	6.9
0	2	3	11.7	12.1
0	2	4	12.7	13.3
0	2	5	1.4	1.6
0	2	6	16.5	15.9
0	2	7	8.2	7.6
0	2	8	6.4	6.6
0	2	9	5.1	4.9
0	2	10	12.1	12.9
0	2	11	9.2	9.4
0	2	12	1.6	1.3
0	2	13	1.0	1.2 *
0	2	14	3.7	3.5
0	2	15	3.3	3.2
0	2	16	4.5	5.4
1	2	0	16.3	17.6
1	2	1	13.9	13.9
1	2	2	24.1	25.8
1	2	3	22.7	25.2
1	2	4	7.4	6.7
1	2	5	9.8	9.6
1	2	6	8.6	7.9
1	2	7	9.5	9.8
1	2	8	3.9	3.4
1	2	9	2.9	2.1
1	2	10	7.0	6.7
1	2	11	2.4	2.6
1	2	12	2.0	2.0
1	2	13	9.3	8.7
1	2	14	7.9	6.7
1	2	15	1.3	1.5
1	2	16	1.3	1.5
2	2	0	33.3	40.0**
2	2	1	15.9	16.7
2	2	2	7.8	7.3
2	2	3	12.6	12.3
2	2	4	13.1	13.6
2	2	5	7.9	7.2
2	2	6	6.5	6.7
2	2	7	4.5	3.8
2	2	8	7.5	7.5
2	2	9	3.4	2.8
2	2	10	1.0	0.9 *
2	2	11	1.3	0.6 *
2	2	12	7.9	7.8
2	2	13	6.8	5.4
2	2	14	1.3	1.1
2	2	15	4.3	3.9
3	2	0	0.7	1.1 *
3	2	1	5.8	5.6
3	2	2	6.4	5.9
3	2	3	7.9	8.0
3	2	4	11.3	11.6
3	2	5	15.4	16.5
3	2	6	9.4	10.1
3	2	7	4.6	4.1
3	2	8	12.0	12.3
3	2	9	12.0	12.8
3	2	10	7.9	8.8
3	2	11	4.5	3.9
3	2	12	7.8	8.5
3	2	13	8.3	7.6
3	2	14	3.0	2.8
3	2	15	1.7	2.1
4	2	0	11.2	11.3
4	2	1	8.3	7.9
4	2	2	3.9	4.2
4	2	3	9.9	10.1
4	2	4	13.0	13.8
4	2	5	10.8	10.9
4	2	6	4.8	4.8
4	2	7	6.6	6.5
4	2	8	9.4	10.0
4	2	9	7.1	7.2
4	2	10	5.7	4.8
4	2	11	8.5	7.9
4	2	12	5.4	4.2
4	2	13	2.0	2.7
5	2	0	6.4	6.6
5	2	1	8.9	9.2
5	2	2	13.0	14.3
5	2	3	6.4	6.6
5	2	4	7.6	8.0
5	2	5	6.4	6.9
5	2	6	3.2	3.3
5	2	7	6.1	6.4
5	2	8	8.7	8.0
5	2	9	2.9	2.6
5	2	10	5.2	4.5
5	2	11	4.6	3.7
5	2	12	4.3	4.5
6	2	0	1.0	0.1 *
6	2	1	7.0	7.0 *
6	2	2	6.0	5.8
6	2	3	5.2	4.7
6	2	4	6.5	5.8
6	2	5	11.2	10.7
6	2	6	7.9	7.0
6	2	7	7.8	6.8
6	2	8	4.6	3.9
6	2	9	6.3	5.9
6	2	10	4.3	4.5
7	2	0	6.9	6.8
7	2	1	8.1	7.8
7	2	2	3.2	3.7
7	2	3	6.9	6.2
7	2	4	6.4	6.2
7	2	5	3.7	3.9
7	2	6	2.3	2.3
0	3	1	22.5	24.6
0	3	2	29.6	29.5
0	3	3	4.4	1.7
0	3	4	10.0	9.5
0	3	5	13.5	13.1
0	3	6	1.7	1.2
0	3	7	11.6	11.3
0	3	8	7.9	7.5
0	3	9	1.5	2.0
0	3	10	6.6	6.3
0	3	11	8.2	8.0
0	3	12	4.5	4.1
0	3	13	1.7	1.6
0	3	14	2.2	2.2
0	3	15	2.5	2.6
1	3	0	14.5	14.5
1	3	1	15.2	13.5
1	3	2	8.9	6.7
1	3	3	23.9	24.1
1	3	4	23.5	23.1
1	3	5	9.9	10.0
1	3	6	11.3	10.4
1	3	7	16.0	16.9
1	3	8	11.2	10.8
1	3	9	2.0	2.3
1	3	10	6.1	6.3
1	3	11	5.1	5.0
1	3	12	2.7	2.2
1	3	13	3.0	2.0
1	3	14	3.1	3.0
1	3	15	3.7	3.4
2	3	0	8.8	9.5
2	3	1	11.6	10.0
2	3	2	11.5	10.5
2	3	3	10.0	9.4
2	3	4	8.9	9.3
2	3	5	17.1	16.4
2	3	6	15.4	15.9
2	3	7	7.8	7.2
2	3	8	8.4	9.0
2	3	9	13.3	14.5
2	3	10	8.7	9.3
2	3	11	2.8	2.1
2	3	12	8.2	7.4
2	3	13	7.9	7.6
2	3	14	1.0	1.1
2	3	15	2.7	3.2
3	3	0	24.1	25.7
3	3	1	15.2	15.7
3	3	2	3.0	2.6
3	3	3	19.1	19.3
3	3	4	14.1	14.2
3	3	5	1.2	1.3
3	3	6	6.3	6.1
3	3	7	9.7	10.3
3	3	8	3.3	3.0
3	3	9	5.2	5.4
3	3	10	5.5	5.1
3	3	11	7.8	6.8
3	3	12	6.8	5.7
3	3	13	3.5	3.2
3	3	14	4.6	5.2
4	3	0	8.1	7.9
4	3	1	17.0	19.0
4	3	2	17.4	20.1
4	3	3	14.3	15.4
4	3	4	6.5	7.1
4	3	5	13.9	15.0
4	3	6	13.6	14.4
4	3	7	9.2	9.7
4	3	8	4.1	4.1
4	3	9	5.9	5.3
4	3	10	6.0	5.0
4	3	11	4.7	4.4
4	3	12	3.7	3.0
4	3	13	3.2	3.7
5	3	0	0.8	0.8 *
5	3	1	10.3	11.3
5	3	2	15.7	17.7
5	3	3	8.0	8.1
5	3	4	4.7	5.2
5	3	5	8.1	8.7
5	3	6	10.2	9.7
5	3	7	11.2	10.3
5	3	8	10.0	8.7
5	3	9	3.8	3.3
5	3	10	6.7	5.9
5	3	11	8.6	9.3
6	3	0	7.9	7.1
6	3	1	7.1	6.8
6	3	2	4.0	4.0
6	3	3	4.9	4.3
6	3	4	9.1	8.2
6	3	5	7.5	7.0
6	3	6	3.2	2.6
6	3	7	5.5	5.0
6	3	8	6.8	7.4
6	3	9	3.3	3.7
7	3	0	6.8	6.7
7	3	1	6.7	6.7
7	3	2	6.8	7.5
7	3	3	4.3	4.7
7	3	4	4.3	4.5
7	3	5	5.4	7.7
0	4	1	10.8	13.0
0	4	2	2.0	1.2
0	4	3	4.4	4.6
0	4	4	2.7	1.0
0	4	5	7.3	6.0
0	4	6	3.2	3.0
0	4	7	10.8	9.8
0	4	8	8.8	8.8
0	4	9	4.6	4.6
0	4	10	3.7	3.1
0	4	11	7.5	8.6
0	4	12	4.5	4.5
0	4	13	5.1	4.9
0	4	14	1.3	1.0
1	4	0	13.1	12.4
1	4	1	15.8	15.8
1	4	2	13.9	11.6
1	4	3	10.3	8.5
1	4	4	8.2	6.6
1	4	5	10.3	9.4
1	4	6	8.7	7.5
1	4	7	4.5	3.4
1	4	8	3.3	2.5
1	4	9	0.7	0.1 *
1	4	10	4.7	3.8
1	4	11	3.7	3.7
1	4	12	4.1	3.4
1	4	13	4.6	4.5
1	4	14	4.9	4.9
2	4	0	15.7	14.1
2	4	1	16.5	14.6
2	4	2	3.2	2.6
2	4	3	16.4	15.7
2	4	4	9.2	9.4
2	4	5	3.6	3.0
2	4	6	2.0	2.2
2	4	7	2.7	2.1
2	4	8	1.1	1.4
2	4	9	4.9	5.4
2	4	10	3.3	3.2
2	4	11	3.3	3.3
2	4	12	4.9	4.8
2	4	13	2.2	2.2
2	4	14	2.0	3.0
3	4	0	2.6	1.3
3	4	1	0.8	0.8 *
3	4	2	6.5	6.5
3	4	3	5.0	3.6
3	4	4	6.5	3.6
3	4	5	10.8	10.8
3	4	6	9.2	10.7
3	4	7	1.5	2.3
3	4	8	6.7	6.5
3	4	9	11.4	13.2
3	4	10	7.6	8.4
3	4	11	0.7	1.3 *
3	4	12	3.8	2.6
3	4	13	3.3	3.5
4	4	0	4.2	2.9
4	4	1	7.7	8.9
4	4	2	3.5	3.6
4	4	3	10.1	9.8
4	4	4	2.1	1.9
4	4	5	9.7	10.5
4	4	6	4.2	3.7
4	4	7	8.6	9.7
4	4	8	5.9	6.2
4	4	9	5.2	4.6
4	4	10	1.4	0.9
4	4	11	6.1	6.2
4	4	12	4.7	6.8

Table 3a. Continued.

h	k	l	$\|F_o\|$	$\|F_c\|$
5	4	0	8.5	7.7
5	4	1	11.5	11.6
5	4	2	7.7	7.3
5	4	3	5.0	5.1
5	4	4	7.8	8.7
5	4	5	6.2	6.9
5	4	6	2.1	1.7
5	4	7	4.8	4.1
5	4	8	7.1	7.4
5	4	9	3.5	3.5
5	4	10	2.0	1.9
6	4	0	0.7	0.3 *
6	4	1	3.3	2.7
6	4	2	7.2	6.4
6	4	3	4.8	4.3
6	4	4	9.4	10.3
6	4	5	6.4	5.8
6	4	6	3.6	2.8
6	4	7	3.9	4.5
7	4	1	3.6	4.8
7	4	2	1.5	2.3 *
0	5	1	4.2	4.5
0	5	2	4.7	5.3
0	5	3	10.7	9.4
0	5	4	7.1	6.4
0	5	5	12.4	12.7
0	5	6	2.1	1.9
0	5	7	12.1	11.8
0	5	8	3.8	5.3
0	5	9	13.7	14.1
0	5	10	1.1	1.4
0	5	11	4.8	5.0
0	5	12	1.3	1.1
0	5	13	4.8	6.6
1	5	0	5.5	3.8
1	5	1	10.7	9.8
1	5	2	11.2	9.0
1	5	3	12.6	10.9
1	5	4	13.4	12.0
1	5	5	3.2	3.0
1	5	6	10.7	9.7
1	5	7	7.2	7.4
1	5	8	5.1	6.1
1	5	9	2.3	2.2
1	5	10	3.0	3.9
1	5	11	5.8	5.9
1	5	12	5.0	5.7
1	5	13	0.8	1.0
2	5	0	5.5	4.4
2	5	1	13.8	13.0
2	5	2	8.7	7.1
2	5	3	4.6	4.6
2	5	4	3.8	3.1
2	5	5	6.8	6.3
2	5	6	10.1	10.5
2	5	7	3.7	3.4
2	5	8	5.1	4.3
2	5	9	1.6	1.3
2	5	10	6.6	7.4
2	5	11	2.2	1.7
2	5	12	5.3	5.7
3	5	0	4.2	3.7
3	5	1	2.9	2.0
3	5	2	11.8	11.6
3	5	3	2.9	3.1
3	5	4	6.9	7.9
3	5	5	3.1	3.0
3	5	6	7.4	7.3
3	5	7	5.9	5.0
3	5	8	2.3	3.0
3	5	9	3.5	3.1
3	5	10	4.4	4.3
3	5	11	3.0	3.0
3	5	12	1.7	2.5
4	5	0	6.4	6.4
4	5	1	6.4	6.4
4	5	2	6.4	5.4
4	5	3	4.3	3.5
4	5	4	7.0	6.4
4	5	5	1.6	2.2
4	5	6	5.1	6.0
4	5	7	2.5	2.3
4	5	8	3.9	3.8
4	5	9	4.1	3.9
4	5	10	1.8	2.1
5	5	0	2.4	2.7
5	5	1	5.5	5.1
5	5	2	5.3	4.3
5	5	3	5.1	4.0
5	5	4	1.8	1.1
5	5	5	1.2	0.9
5	5	6	0.5	0.5 *
5	5	7	4.5	4.0
5	5	8	4.3	4.7
6	5	0	4.4	4.1
6	5	1	3.1	2.9
6	5	2	3.9	4.1
6	5	3	1.4	1.1
6	5	4	2.4	2.2
6	5	5	3.2	4.5
0	6	1	16.2	22.9**
0	6	2	2.6	2.1
0	6	3	22.1	22.5
0	6	4	5.5	4.9
0	6	5	8.4	8.6
0	6	6	2.3	2.2
0	6	7	8.7	8.8
0	6	8	3.0	3.0
0	6	9	0.7	0.2 *
0	6	10	0.6	0.4 *
0	6	11	2.0	2.3
0	6	12	1.2	1.8
1	6	0	11.8	9.4
1	6	1	12.2	11.5
1	6	2	8.1	7.0
1	6	3	7.1	6.0
1	6	4	7.9	6.4
1	6	5	13.8	14.6
1	6	6	8.0	7.5
1	6	7	1.5	1.1
1	6	8	3.6	3.7
1	6	9	10.5	12.9
1	6	10	1.8	1.5
1	6	11	1.5	1.6
1	6	12	4.5	4.4
2	6	0	2.5	2.2
2	6	1	3.5	2.6
2	6	2	8.3	7.5
2	6	3	8.3	7.2
2	6	4	3.2	2.6
2	6	5	5.0	4.4
2	6	6	6.5	6.0
2	6	7	12.8	13.2
2	6	8	2.8	3.2
2	6	9	3.6	3.6
2	6	10	3.4	4.0
3	6	0	10.7	9.4
3	6	1	14.3	12.9
3	6	2	4.3	3.3
3	6	3	10.3	8.2
3	6	4	11.4	10.4
3	6	5	6.6	5.3
3	6	6	3.2	2.5
3	6	7	2.2	2.4
3	6	8	9.0	8.5
3	6	9	2.3	1.6
3	6	10	2.8	3.5
4	6	0	1.3	1.3
4	6	1	4.3	3.4
4	6	2	7.8	7.6
4	6	3	4.2	6.1
4	6	4	7.8	8.7
4	6	5	5.8	4.8
4	6	6	5.3	6.5
4	6	7	3.0	2.6
4	6	8	5.1	5.9
5	6	0	6.1	5.8
5	6	1	2.7	2.2
5	6	2	3.2	3.1
5	6	3	1.0	1.1
5	6	4	3.2	3.4
5	6	5	4.1	3.6

Table 3b. Observed and calculated structure factors at −40°C. Same notation is used as in Table 3a.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	4	47.2	84.9**
0	0	6	14.8	13.3
0	0	8	8.4	7.5
0	0	10	6.0	6.1
0	0	12	0.9	0.4 *
0	0	14	4.0	3.5
0	0	16	2.2	2.0
1	0	1	17.2	19.5**
1	0	2	34.3	38.2**
1	0	3	42.1	48.0**
1	0	4	26.6	29.1
1	0	5	13.9	13.0
1	0	6	28.0	28.9
1	0	7	16.5	15.8
1	0	8	19.7	18.7
1	0	9	1.1	1.9
1	0	10	10.7	10.5
1	0	11	1.8	1.8
1	0	12	7.7	7.8
1	0	13	4.5	4.7
1	0	14	2.6	2.3
1	0	15	0.9	0.7 *
1	0	16	2.5	2.4
2	0	0	3.7	1.7
2	0	1	12.1	11.7
2	0	2	6.2	5.2
2	0	3	14.2	13.3
2	0	4	23.7	21.6
2	0	5	12.0	11.8
2	0	6	16.2	15.4
2	0	7	3.1	2.9
2	0	8	20.8	19.5
2	0	9	7.6	7.5
2	0	10	11.9	12.4
2	0	11	2.1	2.5
2	0	12	6.0	5.6
2	0	13	4.9	4.7
2	0	14	4.9	4.3
2	0	15	1.9	2.1
2	0	16	1.0	0.9
3	0	1	23.8	23.9
3	0	2	36.3	40.3
3	0	3	12.1	10.9
3	0	4	0.7	0.6 *
3	0	5	20.2	20.3
3	0	6	7.4	7.1
3	0	7	11.2	10.6
3	0	8	1.4	1.4
3	0	9	4.4	4.1
3	0	10	3.8	4.0
3	0	11	7.1	7.2
3	0	12	1.9	1.6
3	0	13	3.0	2.4
3	0	14	2.3	2.0
3	0	15	2.2	2.1
4	0	0	10.2	10.5
4	0	1	12.7	13.4
4	0	2	8.8	9.0
4	0	3	1.9	2.0
4	0	4	3.4	3.4
4	0	5	14.6	15.3
4	0	6	10.6	10.6
4	0	7	2.6	2.7
4	0	8	4.4	3.7
4	0	9	6.0	5.9
4	0	10	2.6	2.6
4	0	11	1.0	0.8 *
4	0	12	2.2	2.1
4	0	13	4.8	5.1
5	0	0	0.9	1.3 *
5	0	1	4.8	5.1
5	0	2	0.9	1.3 *
5	0	3	9.3	9.1
5	0	4	2.7	2.8
5	0	5	4.5	4.2
5	0	6	5.5	5.2
5	0	7	3.8	3.7
5	0	8	4.6	4.0
5	0	9	5.0	4.4
5	0	10	5.2	4.1
5	0	11	0.9	0.6 *
5	0	12	2.1	1.8
5	0	13	1.0	1.4
6	0	0	5.1	5.8
6	0	1	3.5	3.5
6	0	2	2.6	2.6
6	0	3	7.0	7.3
6	0	4	4.1	4.2
6	0	5	1.0	1.2 *
6	0	6	3.0	2.8
6	0	7	3.7	3.5
6	0	8	1.5	1.2
6	0	9	1.6	1.5
6	0	10	0.7	0.7 *
6	0	11	1.7	1.7
7	0	1	0.9	0.5 *
7	0	2	4.9	4.6
7	0	3	2.3	2.3
7	0	4	3.7	3.5
7	0	5	0.8	0.8 *
7	0	6	0.7	0.1 *
7	0	7	3.7	3.7
7	0	8	1.9	1.9
0	1	2	19.3	22.0
0	1	3	2.2	2.7
0	1	4	0.8	0.7
0	1	5	4.0	3.3
0	1	6	32.4	34.2
0	1	7	0.6	0.5 *
0	1	8	9.0	9.1
0	1	9	1.3	1.2
0	1	10	16.8	17.5
0	1	11	0.8	0.8 *
0	1	12	5.9	6.2
0	1	13	0.8	0.3 *
0	1	14	2.2	3.0
0	1	15	0.8	0.3 *
0	1	16	1.3	1.1
1	1	0	33.8	38.5**
1	1	1	9.8	8.3
1	1	2	9.5	9.2
1	1	3	42.0	49.5**
1	1	4	22.5	23.6
1	1	5	9.0	8.7
1	1	6	10.7	10.4
1	1	7	19.9	19.9
1	1	8	8.0	7.7
1	1	9	3.1	3.0
1	1	10	6.7	6.3
1	1	11	0.8	0.8 *
1	1	12	2.0	2.0
1	1	13	3.3	2.9
1	1	14	3.7	3.4
1	1	15	3.9	3.1
1	1	16	1.5	1.3
2	1	0	0.8	0.4
2	1	1	11.7	10.9
2	1	2	38.6	44.3**
2	1	3	18.4	18.0
2	1	4	12.7	11.8
2	1	5	10.1	9.4
2	1	6	4.8	4.5
2	1	7	15.6	15.6
2	1	8	4.7	4.7
2	1	9	1.4	1.2
2	1	10	4.5	4.2
2	1	11	6.6	6.3
2	1	12	0.8	0.6 *
2	1	13	2.7	2.3 *
2	1	14	0.8	0.2 *
2	1	15	2.3	2.2
3	1	0	2.4	1.9
3	1	1	22.0	22.4
3	1	2	4.2	3.9
3	1	3	2.4	2.8
3	1	4	7.8	7.4
3	1	5	16.6	16.0
3	1	6	4.4	4.1
3	1	7	3.6	3.6
3	1	8	6.9	6.9
3	1	9	4.2	4.2
3	1	10	1.9	2.3
3	1	11	1.9	1.8
3	1	12	2.0	1.7
3	1	13	0.8	1.4 *
3	1	14	0.7	0.1 *
3	1	15	2.2	2.1
4	1	0	1.7	1.7
4	1	1	12.0	12.1
4	1	2	10.2	9.3
4	1	3	1.5	1.8
4	1	4	1.6	1.2
4	1	5	11.1	11.3
4	1	6	0.7	0.2 *
4	1	7	1.4	1.3
4	1	8	3.1	3.0
4	1	9	0.8	1.0 *
4	1	10	0.8	0.5 *
4	1	11	1.6	1.4
4	1	12	4.2	3.2
4	1	13	3.9	3.3
4	1	14	1.4	1.5
4	1	15	1.5	1.2
5	1	1	3.8	4.0
5	1	2	0.8	0.9 *
5	1	3	3.4	3.4
5	1	4	3.1	3.1
5	1	5	1.5	1.9
5	1	6	0.8	0.5 *
5	1	7	0.8	0.8 *
5	1	8	4.5	4.4
5	1	9	4.8	4.2
5	1	10	1.5	1.3
5	1	11	1.6	1.5
5	1	12	2.9	2.7
5	1	13	1.0	1.2
6	1	0	0.8	0.7 *
6	1	1	0.8	1.2 *
6	1	2	2.5	2.4
6	1	3	4.8	5.2
6	1	4	3.6	3.5
6	1	5	3.4	3.5
6	1	6	1.6	1.2
6	1	7	1.8	1.7
6	1	8	1.7	1.2
6	1	9	0.7	1.2 *
6	1	10	0.6	0.2 *
6	1	11	1.1	1.2
7	1	0	3.8	3.5
7	1	1	2.4	2.6
7	1	2	0.7	0.7 *
7	1	3	2.3	2.1
7	1	4	0.7	0.3 *
7	1	5	0.6	0.6 *
7	1	6	1.2	0.8
7	1	7	1.1	1.0
0	2	2	5.3	4.8
0	2	3	5.0	6.1
0	2	4	12.1	13.0
0	2	5	0.4	0.3 *
0	2	6	10.1	10.3
0	2	7	3.7	3.9
0	2	8	5.9	7.2
0	2	9	1.4	1.7
0	2	10	6.8	7.1
0	2	11	2.9	3.2
0	2	12	1.8	1.9
0	2	13	0.7	0.1 *
0	2	14	0.7	1.3 *
0	2	15	0.6	0.5 *
0	2	16	2.0	2.2
1	2	0	9.4	9.8
1	2	1	7.6	9.1
1	2	2	24.9	26.3
1	2	3	22.6	24.0
1	2	4	3.1	2.8
1	2	5	9.2	8.4
1	2	6	4.9	4.4
1	2	7	7.1	7.4
1	2	8	1.2	1.5
1	2	9	0.6	1.0 *
1	2	10	3.2	3.2
1	2	11	0.7	0.5 *
1	2	12	0.7	0.6 *
1	2	13	4.3	4.7
1	2	14	2.3	2.1
1	2	15	0.6	0.2 *
2	2	0	38.8	39.8
2	2	1	9.7	8.3
2	2	2	5.9	6.0
2	2	3	8.3	7.9
2	2	4	13.5	12.0
2	2	5	4.9	4.4
2	2	6	4.2	4.6
2	2	7	3.0	2.9
2	2	8	5.1	5.3
2	2	9	0.6	1.0 *
2	2	10	0.7	0.2 *
2	2	11	0.7	0.7 *
2	2	12	3.4	3.2
2	2	13	2.8	2.6
2	2	14	0.7	0.1 *
3	2	0	0.5	0.5 *
3	2	1	3.5	4.1
3	2	2	3.8	3.9
3	2	3	6.9	6.5
3	2	4	9.8	10.5
3	2	5	11.5	12.1
3	2	6	8.4	8.5
3	2	7	1.3	1.2
3	2	8	7.9	8.7
3	2	9	5.8	6.0
3	2	10	6.4	7.0
3	2	11	2.6	2.7
3	2	12	3.5	3.5
3	2	13	2.5	2.0
3	2	14	2.0	1.9
3	2	15	0.9	0.9
3	2	16	0.9	1.2
4	2	1	3.7	3.7
4	2	2	2.7	3.2
4	2	3	8.3	8.3
4	2	4	10.8	11.8
4	2	5	3.9	4.1
4	2	6	1.7	2.2
4	2	7	3.5	3.5
4	2	8	7.8	8.4
4	2	9	2.0	2.1
4	2	10	2.6	2.7
4	2	11	3.4	2.9
4	2	12	2.7	2.7
4	2	13	1.7	1.7
4	2	14	1.9	1.9
5	2	0	1.6	1.6
5	2	1	4.9	4.9
5	2	2	10.1	11.4
5	2	3	4.0	4.0
5	2	4	2.6	2.8
5	2	5	5.3	5.6
5	2	6	0.7	1.1 *
5	2	7	4.8	4.8
5	2	8	2.4	2.5
5	2	9	2.3	2.4
5	2	10	1.2	1.1
5	2	11	3.3	2.9
5	2	12	1.0	1.1 *
6	2	0	0.7	0.1 *
6	2	1	4.9	3.4
6	2	2	3.7	3.7
6	2	3	2.4	2.2
6	2	4	1.6	1.5
6	2	5	2.7	1.8
6	2	6	5.3	4.8
6	2	7	3.5	3.3
6	2	8	1.2	1.1
6	2	9	3.4	3.1
6	2	10	1.3	1.3
7	2	0	1.9	1.6
7	2	1	6.0	5.2
7	2	2	1.8	2.1
7	2	3	4.9	4.4
7	2	4	2.7	2.5

Table 3b. Continued.

h	k	l	$\|F_o\|$	$\|F_c\|$
7	2	5	2.4	2.1
7	2	6	1.1	1.1
7	2	7	1.5	1.7
0	3	1	12.6	11.2
0	3	2	29.1	29.1
0	3	3	1.5	0.4
0	3	4	13.3	13.1
0	3	5	6.0	5.4
0	3	6	1.4	0.5 *
0	3	7	4.2	4.9
0	3	8	7.8	8.2
0	3	9	0.6	0.5 *
0	3	10	5.9	6.1
0	3	11	2.2	2.3
0	3	12	2.3	2.6
0	3	13	0.7	0.0 *
0	3	14	1.3	1.6
1	3	0	20.8	20.4
1	3	1	7.2	6.7
1	3	2	6.8	6.2
1	3	3	19.9	19.8
1	3	4	17.3	18.9
1	3	5	8.3	8.3
1	3	6	9.6	9.7
1	3	7	12.2	11.6
1	3	8	7.1	7.4
1	3	9	0.6	0.6 *
1	3	10	4.6	4.9
1	3	11	1.4	1.5
1	3	12	0.7	1.2 *
1	3	13	1.7	1.6
1	3	14	1.3	1.3
1	3	15	1.7	1.9
2	3	0	3.6	3.7
2	3	1	11.2	11.1
2	3	2	13.0	11.7
2	3	3	4.6	4.4
2	3	4	5.5	5.1
2	3	5	9.9	10.0
2	3	6	15.9	15.2
2	3	7	4.3	3.9
2	3	8	7.5	7.3
2	3	9	4.7	4.8
2	3	10	6.7	7.2
2	3	11	2.1	2.0
2	3	12	4.7	4.9
2	3	13	2.8	2.7
2	3	14	0.6	0.3 *
2	3	15	0.8	1.3
3	3	0	26.6	27.8
3	3	1	6.6	6.8
3	3	2	4.2	3.8
3	3	3	8.8	8.7
3	3	4	14.8	14.8
3	3	5	0.6	0.5 *
3	3	6	6.4	6.6
3	3	7	3.9	4.0
3	3	8	2.5	2.4
3	3	9	2.5	2.9
3	3	10	4.3	4.6
3	3	11	3.0	3.1
3	3	12	0.7	1.4 *
3	3	13	0.6	1.1 *
3	3	14	2.0	2.8
4	3	0	2.9	3.0
4	3	1	6.8	7.8
4	3	2	18.6	19.9
4	3	3	10.8	11.4
4	3	4	6.5	6.6
4	3	5	7.7	7.7
4	3	6	9.1	9.2
4	3	7	7.7	8.2
4	3	8	3.6	3.7
4	3	9	2.6	2.4
4	3	10	2.7	2.5
4	3	11	2.5	2.5
4	3	12	1.0	1.0
4	3	13	1.1	1.4
5	3	0	1.1	0.5
5	3	1	11.4	11.8
5	3	2	6.9	6.5
5	3	3	6.9	7.3
5	3	4	4.3	4.5
5	3	5	7.5	7.4
5	3	6	4.2	4.3
5	3	7	3.4	3.1
5	3	8	6.7	6.0
5	3	9	1.7	1.8
5	3	10	3.3	3.7
5	3	11	1.8	2.1
6	3	0	2.2	2.3
6	3	1	5.2	5.0
6	3	2	2.7	2.9
6	3	3	3.6	3.6
6	3	4	3.1	2.6
6	3	5	4.6	4.5
6	3	6	2.3	2.2
6	3	7	4.1	4.1
6	3	8	2.0	2.0
6	3	9	0.9	1.1
7	3	0	4.8	4.6
7	3	1	3.4	3.3
7	3	2	1.8	1.8
7	3	3	1.5	1.7
7	3	4	1.9	2.0
7	3	5	4.6	5.5
0	4	1	5.2	5.4
0	4	2	2.1	1.4
0	4	3	1.9	2.0
0	4	4	1.9	1.7
0	4	5	2.6	2.9
0	4	6	5.5	4.8
0	4	7	3.5	3.5
0	4	8	5.5	5.4
0	4	9	1.4	1.8
0	4	10	4.1	4.6
0	4	11	1.9	1.8
0	4	12	2.1	2.0
0	4	13	1.1	1.3
0	4	14	1.0	1.3
1	4	0	6.7	6.5
1	4	1	8.0	7.0
1	4	2	14.4	13.8
1	4	3	10.7	10.0
1	4	4	3.4	2.9
1	4	5	5.0	4.9
1	4	6	5.1	4.9
1	4	7	3.7	3.7
1	4	8	1.1	1.2
1	4	9	0.5	0.9 *
1	4	10	1.1	1.3
1	4	11	1.4	1.5
1	4	12	1.3	1.3
1	4	13	2.8	3.0
1	4	14	1.8	1.2
2	4	0	19.2	19.3
2	4	1	7.5	6.6
2	4	2	2.8	2.6
2	4	3	8.4	7.6
2	4	4	9.2	8.7
2	4	5	3.1	3.0
2	4	6	2.5	2.6
2	4	7	1.8	1.4
2	4	8	0.5	1.1 *
2	4	9	1.9	2.1
2	4	10	1.2	1.4
2	4	11	1.2	1.3
2	4	12	1.5	1.5
2	4	13	1.6	1.5
2	4	14	0.8	1.0
3	4	0	1.5	1.3
3	4	1	0.9	0.8
3	4	2	2.8	2.6
3	4	3	3.8	3.3
3	4	4	4.8	5.1
3	4	5	6.4	6.7
3	4	6	6.5	6.8
3	4	7	0.5	0.6 *
3	4	8	4.8	3.3
3	4	9	4.9	4.6
3	4	10	6.0	5.4
3	4	11	1.1	1.2
3	4	12	2.7	2.8
3	4	13	1.5	1.5
4	4	0	7.5	7.5
4	4	1	3.9	3.8
4	4	2	1.9	1.7
4	4	3	5.7	5.9
4	4	4	8.2	8.2
4	4	5	4.0	3.7
4	4	6	1.3	1.2
4	4	7	4.3	4.0
4	4	8	6.6	6.3
4	4	9	1.3	1.5
4	4	10	2.0	1.8
4	4	11	2.2	2.0
4	4	12	2.1	2.5
5	4	0	3.2	2.5
5	4	1	5.1	5.0
5	4	2	8.1	8.1
5	4	3	3.3	3.0
5	4	4	3.3	2.9
5	4	5	4.3	4.2
5	4	6	1.7	1.6
5	4	7	4.1	3.5
5	4	8	2.5	2.2
5	4	9	2.0	1.9
5	4	10	1.0	1.0
6	4	0	0.5	0.9 *
6	4	1	3.8	3.6
6	4	2	3.6	3.2
6	4	3	1.9	1.8
6	4	4	3.5	3.1
6	4	5	5.2	4.9
6	4	6	3.4	3.2
6	4	7	2.0	2.0
7	4	0	2.6	2.8
7	4	1	2.9	3.8
0	5	1	2.6	2.8
0	5	2	4.3	3.8
0	5	3	6.2	5.3
0	5	4	1.9	2.0
0	5	5	5.8	5.9
0	5	6	5.6	5.8
0	5	7	5.1	4.9
0	5	8	2.6	2.7
0	5	9	5.2	5.4
0	5	10	4.6	4.8
0	5	11	1.5	1.3
0	5	12	1.6	1.7
0	5	13	1.9	2.2
1	5	0	9.8	8.5
1	5	1	5.7	4.5
1	5	2	5.2	4.4
1	5	3	9.7	9.1
1	5	4	7.5	6.5
1	5	5	1.6	1.4
1	5	6	5.4	5.1
1	5	7	5.7	5.8
1	5	8	1.5	1.5
1	5	9	0.8	0.9
1	5	10	2.4	2.6
1	5	11	1.9	2.1
1	5	12	1.3	1.4
1	5	13	0.9	1.1
2	5	0	2.7	2.3
2	5	1	6.0	5.4
2	5	2	7.5	8.1
2	5	3	5.3	4.8
2	5	4	3.4	3.3
2	5	5	4.1	3.7
2	5	6	4.2	3.7
2	5	7	4.4	4.7
2	5	8	2.1	2.1
2	5	9	0.5	0.6 *
2	5	10	3.0	2.8
2	5	11	2.0	2.3
2	5	12	1.3	1.6
2	5	13	0.7	0.9
3	5	0	2.9	2.6
3	5	1	6.6	6.7
3	5	2	6.5	5.1
3	5	3	0.4	0.5
3	5	4	3.1	3.2
3	5	5	4.6	5.4
3	5	6	2.6	2.5
3	5	7	1.7	1.5
3	5	8	1.7	1.7
3	5	9	1.6	1.8
3	5	10	1.0	1.1
3	5	11	0.8	0.9
3	5	12	0.3	0.3 *
4	5	0	2.5	2.1
4	5	1	4.4	4.5
4	5	2	4.0	4.1
4	5	3	1.2	1.0
4	5	4	2.7	2.2
4	5	5	3.9	3.6
4	5	6	2.8	2.4
4	5	7	0.5	0.5 *
4	5	8	1.4	1.3
4	5	9	0.6	0.7
4	5	10	0.5	0.7
5	5	0	3.7	3.3
5	5	1	2.6	1.9
5	5	2	2.3	2.0
5	5	3	2.3	1.9
5	5	4	0.4	0.5 *
5	5	5	0.4	0.7 *
5	5	6	0.4	0.3 *
5	5	7	1.3	1.0
5	5	8	2.5	2.5
6	5	0	1.4	1.2
6	5	1	0.9	0.9
6	5	2	1.3	1.1
6	5	3	2.0	1.8
6	5	4	1.3	1.4
6	5	5	1.6	1.9
0	6	1	8.3	10.7
0	6	2	2.0	1.4
0	6	3	12.3	11.2
0	6	4	11.2	10.0
0	6	5	3.6	3.4
0	6	6	2.7	2.3
0	6	7	4.5	4.4
0	6	8	2.1	2.0
0	6	9	0.4	0.1 *
0	6	10	1.5	1.4
0	6	11	1.0	1.1
0	6	12	0.3	0.1 *
1	6	0	3.8	5.6
1	6	1	5.2	5.3
1	6	2	6.4	6.5
1	6	3	5.7	5.5
1	6	4	5.1	4.5
1	6	5	6.3	6.4
1	6	6	5.5	5.3
1	6	7	3.1	2.9
1	6	8	4.1	3.6
1	6	9	4.5	4.5
1	6	10	2.7	2.4
1	6	11	0.3	0.8 *
2	6	0	1.9	2.0
2	6	1	2.8	3.0
2	6	2	3.2	2.9
2	6	3	3.9	4.3
2	6	4	3.5	3.6
2	6	5	4.3	3.7
2	6	6	4.9	6.1
2	6	7	4.5	4.0
2	6	8	1.9	1.8
2	6	9	1.9	1.8
2	6	10	3.0	2.9
2	6	11	2.5	3.1
3	6	0	3.4	3.8
3	6	1	5.7	6.3
3	6	2	6.2	6.1
3	6	3	3.8	3.8
3	6	4	4.2	4.3
3	6	5	4.2	4.2
3	6	6	1.1	1.3
3	6	7	2.3	2.4
3	6	8	2.3	3.2
3	6	9	2.6	2.1
3	6	10	0.7	1.8
4	6	0	1.8	1.9
4	6	1	2.9	2.7
4	6	2	3.6	3.7
4	6	3	2.2	2.2
4	6	4	2.9	2.7
4	6	5	4.0	4.1
4	6	6	2.6	2.5
4	6	7	1.2	1.1
4	6	8	1.6	1.9
5	6	0	1.8	2.0
5	6	1	1.1	1.5
5	6	2	1.4	1.4
5	6	3	1.6	2.2
5	6	4	0.8	1.0
5	6	5	1.2	1.2
5	6	6	1.6	2.2

deviations are given in Table 4. These were calculated from atomic parameters and standard deviations obtained from 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 programs used has been given in an earlier paper.[1]

ASSIGNMENT OF HYDROGEN

The bond distances to the nearest neighbours of the two non-equivalent nitrogen atoms are shown in Fig. 2; for standard deviations see Table 4.

The nitrogen atoms are joined by a relatively short bond (2.87 Å at both temperatures). A comparison with the hydrogen bond length in ammonia [9] (3.38 Å) definitely excludes the possibility of both nitrogen atoms being part of ammonia molecules, (*i.e.* the compound does not correspond to the formula $CH_3COOH{\cdot}2NH_3$). Instead the bond distance is close to the value expected for a hydrogen bond donated from an ammonium ion to the lone pair of an ammo-

nia molecule. The value agrees fairly well with those found by Olovsson in the ammine salts of the ammonium halides [10,11] (average distance: 2.94 Å in $NH_4Cl \cdot 3NH_3$, 2.89 Å in $NH_4Br \cdot 3NH_3$ and $NH_4I \cdot 3NH_3$, and 2.96 Å in $NH_4I \cdot 4NH_3$).

As seen from Fig. 2 N(1) is much closer to its oxygen ligands than N(2), (2.80—3.17 Å compared to 3.15—3.49 Å). From a comparison with the hydrogen bonds found by the present author in ammonium acetate [1] (2.80, 2.81, 2.82, and 2.83 Å) and ammonium formate [2] (2.81, 2.81, 2.86, and 2.88 Å) it is obvious that N(1) belongs to the ammonium ion. Furthermore, the distances from N(2) to neighbouring oxygen atoms do not deviate too much from the values found for the hydrogen bonds between ammonia and oxygen in $NH_3 \cdot H_2O$ [12] (3.25, 3.26, and 3.29 Å) and in $NH_3 \cdot \frac{1}{2}H_2O$ [13] (3.13, 3.22, and 3.22 Å). It is therefore assumed that N(2) belongs to an ammonia molecule. A more detailed description of the location of hydrogen is given below.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General. The packing situation is illustrated in Fig. 1. The structure can be described as built up from puckered layers (denoted as *A*, *B*, *C*, and *D*) consisting of CH_3COO^-, NH_4^+, and NH_3 groups closely linked by hydrogen bonds. The layers are approximately parallel to (001) and connected by strongly bent or bifurcated hydrogen bonds to double layers (*viz.* *B* to *C* and *D* to *A*), which are in turn held together by very weak bifurcated hydrogen bonds forming the three-dimensional structure.

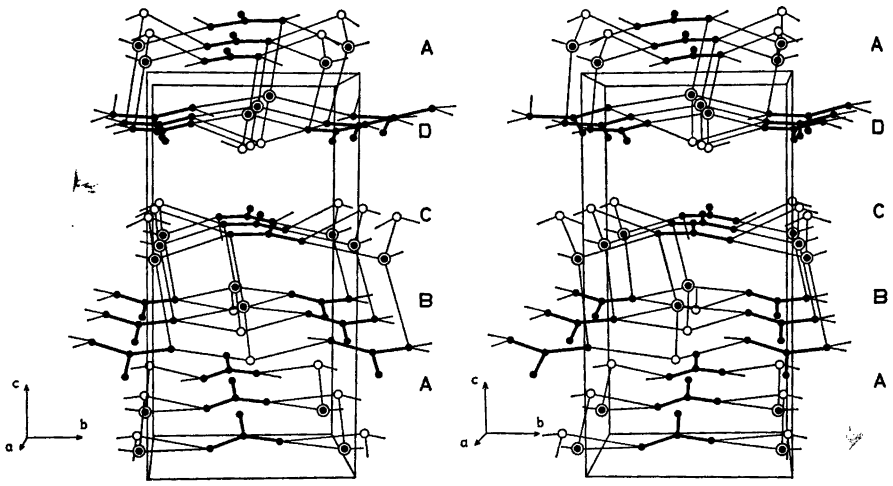

Fig. 1. A stereoscopic pair of drawings of the packing in ammonium acetate monammine at −190°C. The hydrogen atoms are omitted for the sake of clarity. Open circles are ammonia molecules and open circles with a dot are ammonium ions. Covalent bonds are shown as thick lines and assumed hydrogen bonds as thin lines. The very weak bifurcated bonds are omitted.

Table 4. Interatomic distances (Å) and bond angles (°). The standard deviations are given within parentheses (for the distances they are multiplied by 10^3).

The positions are denoted as follows:

[I]	x	y	z	[VII]	$-1+x$	$1+y$	z
[II]	$1+x$	y	z	[VIII]	$1-x$	$-1/2+y$	$1/2-z$
[III]	$-1+x$	y	z	[IX]	$1-x$	$1/2+y$	$1/2-z$
[IV]	x	$1+y$	z	[X]	$1/2+x$	$1/2-y$	$-z$
[V]	x	$-1+y$	z	[XI]	$-1/2+x$	$1/2-y$	$-z$
[VI]	$1+x$	$-1+y$	z				

Bond distances and angles within the acetate ion (*cf.* Figs. 2 and 4).

	−40°C	−190°C		−40°C	−190°C
C(1)−O(1)	1.243(5)	1.241(6)	O(1)−C(1)−O(2)	123.9(0.3)	124.2(0.4)
−O(2)	1.244(5)	1.266(6)	−C(2)	117.7(0.4)	117.8(0.4)
−C(2)	1.518(6)	1.528(6)	O(2)−C(1)−C(2)	118.4(0.4)	118.1(0.4)

Bond distances around the oxygen atoms (*cf.* Fig. 6).

O(1)···N(1)^{III}	2.797(5)	2.797(5)	O(2)···N(1)^{VII}	2.796(5)	2.822(5)
···N(1)^{XI}	3.094(5)	3.174(5)	···N(1)^{XI}	2.944(4)	2.876(4)
···N(2)^{I}	3.190(5)	3.150(5)	···N(2)^{IV}	3.219(5)	3.215(5)
···N(2)^{IX}	3.482(5)	3.493(5)	···N(2)^{IX}	3.379(5)	3.266(4)

Angles around the oxygen atoms (*cf.* Fig. 7).

C(1)−O(1)···N(1)^{III}	119.7(0.3)	118.7(0.3)	C(1)−O(2)···N(1)^{VII}	119.0(0.3)	118.5(0.3)
···N(1)^{XI}	87.0(0.2)	83.6(0.3)	···N(1)^{XI}	93.9(0.2)	96.8(0.2)
···N(2)^{I}	150.5(0.3)	147.6(0.3)	···N(2)^{IV}	155.9(0.3)	159.1(0.3)
···N(2)^{IX}	75.8(0.2)	73.2(0.2)	···N(2)^{IX}	80.2(0.2)	82.9(0.2)
N(1)^{III}···O(1)···N(1)^{XI}	121.0(0.1)	127.1(0.1)	N(1)^{VII}···O(2)···N(1)^{XI}	109.9(0.1)	103.7(0.1)
···N(2)^{I}	80.6(0.1)	81.3(0.1)	···N(2)^{IV}	80.1(0.1)	79.8(0.1)
···N(2)^{IX}	129.0(0.1)	129.0(0.1)	···N(2)^{IX}	130.6(0.1)	132.7(0.1)
N(1)^{XI}···O(1)···N(2)^{I}	101.0(0.1)	105.0(0.1)	N(1)^{XI}···O(2) ···N(2)^{IV}	92.8(0.1)	87.7(0.1)
···N(2)^{IX}	107.3(0.1)	102.5)0.1)	···N(2)^{IX}	113.7(0.1)	115.7(0.1)
N(2)^{I}···O(1)···N(2)^{IX}	74.7(0.1)	74,4(0.1)	N(2)^{IV}···O(2)···N(2)^{IX}	75.8(0.1)	76.8(0.1)

Table 4. Continued.

Bond distances around the nitrogen atoms (*cf.* Fig. 2).

N(1)···O(1)II	2.797(5)	2.797(5)	N(2)···O(1)I	3.190(5)	3.150(5)
···O(1)X	3.094(5)	3.174(5)	···O(1)VIII	3.482(5)	3.493(5)
···O(2)X	2.944(4)	2.876(5)	···O(2)VIII	3.379(5)	3.266(4)
···O(2)VI	2.796(5)	2.822(5)	···O(2)V	3.219(5)	3.215(5)
···N(2)	2.874(4)	2.868(5)	···N(1)	2.874(4)	2.868(5)

Angles around the nitrogen atoms (*cf.* Figs. 3 and 4).

O(1)II···N(1)···O(1)X	92.0(0.1)	86.2(0.1)	O(1)I···N(2)···O(1)VIII	136.1(0.1)	137.7(0.1)
···O(2)X	130.6(0.1)	124.3(0.2)	···O(2)VIII	106.2(0.1)	107.7(0.1)
···O(2)VI	108.9(0.1)	107.8(0.2)	···O(2)V	90.4(0.1)	91.0(0.1)
···N(2)	112.7(0.2)	113.3(0.2)	···N(1)	117.4(0.2)	118.0(0.2)
O(1)X···N(1)···O(2)X	42.6(0.1)	42.6(0.1)	O(1)VIII···N(2)···O(2)VIII	37.3(0.1)	38.1(0.1)
···O(2)VI	142.5(0.2)	149.1(0.2)	···O(2)V	103.2(0.1)	101.1(0.1)
···N(2)	84.4(0.1)	83.3(0.1)	···N(1)	93.7(0.1)	92.6(0.1)
O(2)X···N(1)···O(2)VI	103.7(0.1)	110.5(0.1)	O(2)VIII···N(2)···O(2)V	134.0(0.1)	133.3(0.1)
···N(2)	85.7(0.1)	85.8(0.1)	···N(1)	93.7(0.1)	92.2(0.1)
O(2)VI···N(1)···N(2)	113.6(0.2)	114.0(0.2)	O(2)V···N(2)···N(1)	116.4(0.2)	116.5(0.2)

The acetate ions are arranged with their O—O direction approximately parallel to the *b* axis. The planes of the groups are almost parallel to (001); the main deviation is a rotation of approximately +15 or −15° about the *b* axis. Each oxygen atom is coordinated by two ammonia groups and two ammonium ions (*cf.* Fig. 5). Of these eight N···O contacts only four are "normal" hydrogen bonds while the rest may be regarded as "abnormal", *i.e.* strongly bent or bifurcated. Two of the N···O contacts are components of a bifurcated bond which is very weak.

The nitrogen atom of the ammonium ion, N(1), is coordinated by five atoms: one N(2), two O(1), and two O(2). Two of the oxygen atoms belong to the same acetate group and interact with only one hydrogen atom; the atom O(2) seems to be the one which is most favourably arranged for hydrogen bonding. This is true especially at the lower temperature. With N(2) as well as with the other two neighbouring oxygen atoms three normal hydrogen bonds are formed.

For the ammonia, *i.e.* N(2), the environment is similar. In the same way as N(1) it is engaged in three normal hydrogen bonds: one accepted from N(1), and two donated to O(1) and O(2), respectively. These oxygen atoms

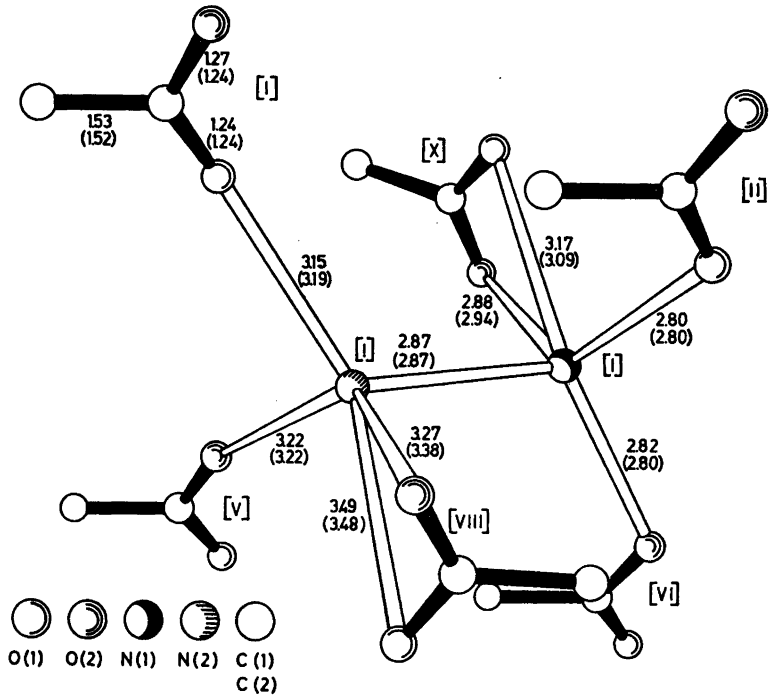

Fig. 2. Bond distances around the nitrogen atoms and within the acetate ion at −190°C. Corresponding values at −40°C are given in parentheses. Notation for the equivalent positions is given in square brackets. Covalent bonds are filled. The double lines represent other distances shorter than 3.9 Å.

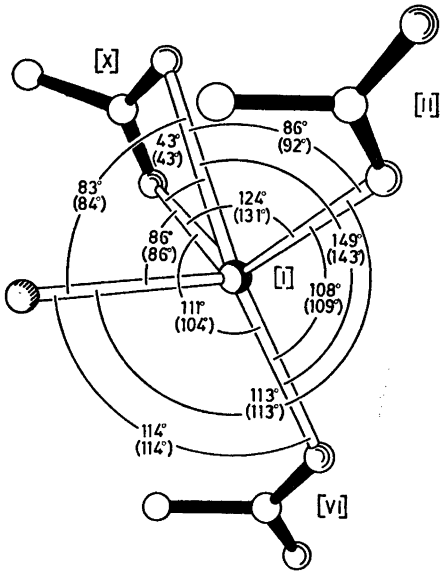

Fig. 3. Bond angles around N(1). The notation is the same as in Fig. 2.

belong to different acetate groups. The third hydrogen atom of ammonia is symmetrically situated with respect to the two oxygen atoms of the third neighbouring acetate ion. The interaction between these and the hydrogen atom is evidently very weak.

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

The ammonium ion. There are four hydrogen atoms in the ammonium ion but N(1) has five neighbours at possible hydrogen bond distances (*cf.* Fig. 2). The bond angles at N(1) defined by the three shortest distances (*viz.* N(1)···N(2), N(1)···O(1)^{II}, and N(1)···O(2)^{VI}) are approximately tetrahedral (*cf.* Fig. 3). The median of the two remaining connecting lines appproximately occupies the fourth tetrahedral direction. Three of the hydrogen atoms are thus expected to be close to the first three directions while the fourth hydrogen atom should be located between the remaining two N···O contacts. This assignment of hydrogen was verified experimentally in the difference syntheses. However, the hydrogen peaks were diffuse and H(1), H(2), and H(3) were therefore placed exactly on the straight lines connecting the hydrogen-bonded atoms. H(4) was placed in such a way that all H—N—H angles at N(1) became approximately tetrahedral. The N—H distance was assumed to be 1.03 Å.[14]

It is interesting to observe the significant changes in bond lengths for N(1)···O(1)^{X} and N(1)···O(2)^{X} with the decrease in temperature from −40 to −190°C. The former is elongated from 3.09 to 3.17 Å while the latter is shortened from 2.94 to 2.88 Å. Also most of the bond angles at N(1) which involve the atoms O(1)^{X} and O(2)^{X} differ significantly at the two temperatures (*cf.* Fig. 3). The O···H(4) distances (calculated from coordinates given in Table 1) are: O(1)^{X}···H(4) = 2.33 Å and O(2)^{X}···H(4) = 2.12 Å at −40°C

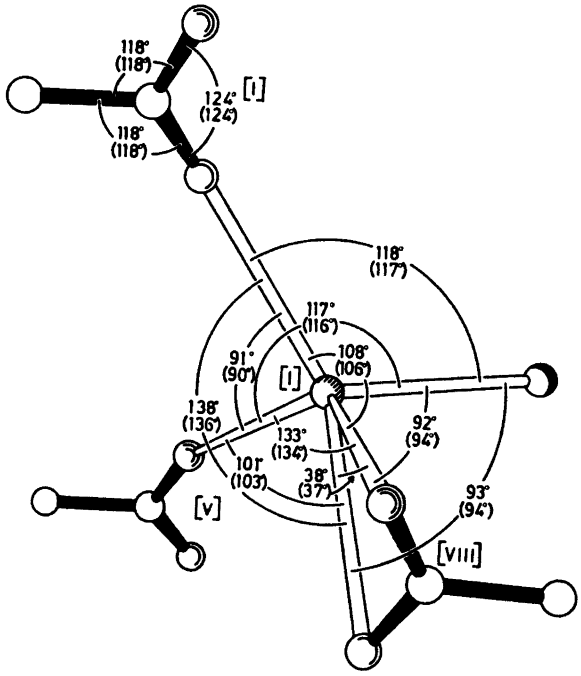

Fig. 4. Bond angles around N(2), and within the acetate ion. Notation as in Fig. 2.

while the corresponding distances at −190°C are 2.51 and 1.97 Å. The bond angles subtended at H(4) are: N(1)—H(4)···O(1)^{X} = 130° and N(1)—H(4)···O(2)^{X} = 135° at −40°C, and 122 and 146°, respectively, at −190°C.

The ammonia molecule. The coordination around the central atom of the ammonia molecule, *i.e.* N(2), is similar to that of N(1). As seen from Fig. 4, all bond angles subtended at N(2), show a marked deviation from the tetrahedral angle, which makes the location of the hydrogen atoms difficult. According to the preceding discussion the free electron pair of ammonia is used in a linear hydrogen bond from N(1) to N(2). The ammonia molecule is expected to be orientated with the threefold axis along N(1)···N(2) and with the hydrogen atoms suitably directed towards neighbouring acceptor atoms. The following positions of the hydrogen atoms were assumed to be the most reasonable: two hydrogen atoms are located near the straight lines connecting N(2) with O(1)^{I} and O(2)^{V}, respectively, and the third one occupies a symmetrical position with respect to O(1)^{VIII} and O(2)^{VIII}. These positions of the three hydrogen atoms (numbered 5, 6, and 7 in Fig. 5) were confirmed by the difference syntheses. The atomic coordinates were calculated from the indicated hydrogen peaks but modified a little to fit with tetrahedral H—N(2)—H and N(1)···N(2)—H angles and an N—H distance of 1.01 Å.[14]

The distance from H(6) to the neighbouring O(1) and O(2) atoms range from 2.4 to 2.6 Å, which implies a very weak interaction. A similar situation

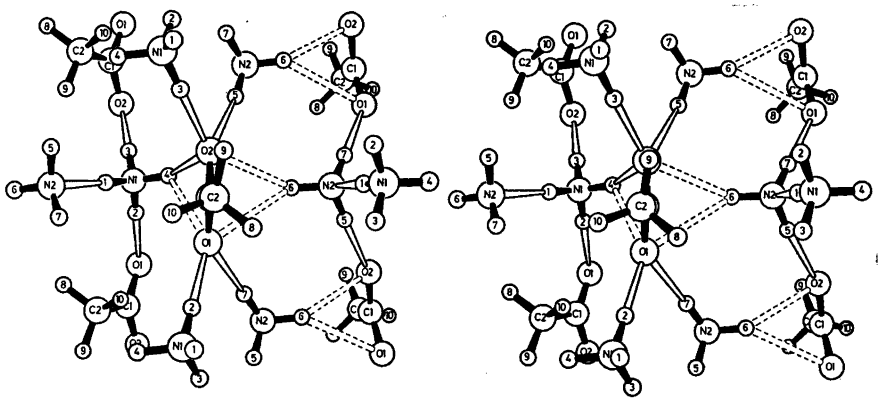

Fig. 5. A stereoscopic pair of drawings showing the locations of the hydrogen atoms at −190°C. The hydrogen atoms are numbered 1 to 10. O···H distances less than 2.4 Å are shown as solid double lines and longer ones (2.4−2.6 Å) are dotted. The view is along the C−C axis.

has recently been reported in the neutron diffraction study of $N_2H_5HC_2O_4$,[15] where one bifurcated and one trifurcated hydrogen bond is found. The O···H distances in the trifurcated bond are 2.38, 2.50, and 2.61 Å and the corresponding N−H···O angles are 119, 121, and 139°. For the bifurcated bond the O···H distances are not unusually long (1.93 and 2.24 Å). Compare also with the neutron diffraction study of $(NH_4)_2SO_4$[16] where several O···H contacts are found which in a similar way may be considered as parts of bifurcated or trifurcated hydrogen bonds. Some of the O···H distances are of about the same magnitude as in the present compound.

The acetate ion. The geometry and environment of the acetate group are shown i Figs. 2, 4, 6, and 7. The acetate ion is nearly planar at both temperatures. None of the atoms C(1), C(2), O(1), and O(2) deviate from the least-squares plane by more than 0.005 Å. The carbon-oxygen distances are of equal length at −40°C, C(1)−O(1) = 1.243 and C(1)−O(2) = 1.244 Å. However, at −190°C the C(1)−O(2) distance, 1.266 Å, is just significantly larger than C(1)−O(1), 1.241 Å (σ = 0.006 Å). Similar carbon-oxygen distances were found by the author in ammonium acetate [1] (1.250 and 1.253 Å, σ = 0.004 Å). The C(1)−C(2) bond length is 1.518 Å at −40°C and 1.528 Å at −190°C (σ = 0.006 Å), which is slightly longer than the corresponding distance in ammonium acetate, 1.504 Å. None of the bond distances mentioned have been corrected for thermal motion, but it may be noted that the thermal parameters for ammonium acetate are of about the same magnitude as those for the present compound at −40°C.

The angles within the acetate group are nearly the same at both temperatures, *viz.* C(2)−C(1)−O(1) = 117.7(117.8), C(2)−C(1)−O(2) = 118.4(118.1), and O(1)−C(1)−O(2) = 123.9(124.2)° (σ = 0.3−0.4°, *cf.* Table 4). The values at −190°C are given in parentheses. The corresponding bond angles in ammonium acetate agree fairly well with these values (C−C−O = 118.0 and 118.5°,

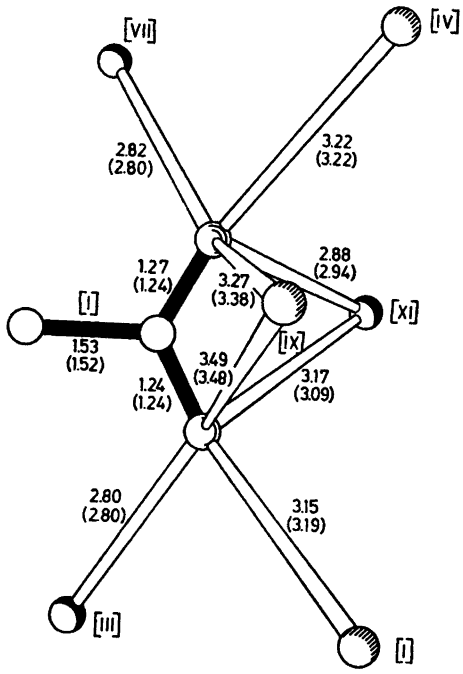

Fig. 6. Bond distances around the oxygen atoms. Notation as in Fig. 2.

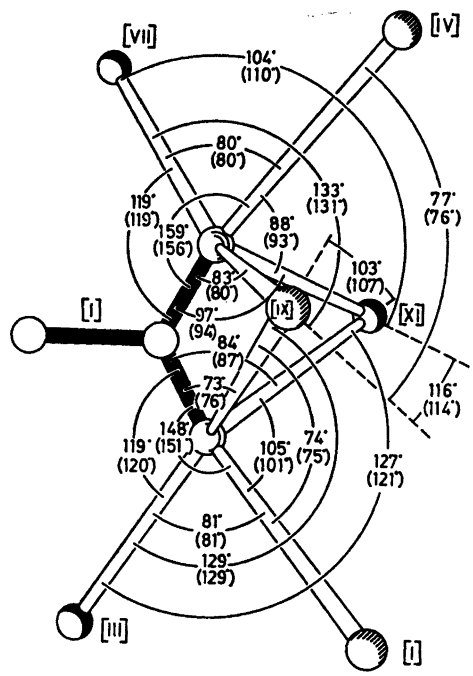

Fig. 7. Bond angles around the oxygen atoms. Notation as in Fig. 2.

and O—C—O = 123.4°, σ = 0.3°). The dimensions of the acetate ion found in some other compounds have previously been given by the author.[1]

The environment is very similar for O(1) and O(2). As seen from Fig. 5, both oxygen atoms accept two normal hydrogen bonds, one from an ammonia molecule and the other from an ammonium ion. Furthermore, they are similarly located with respect to H(4) and H(6) (these last O···H contacts may involve very weak interactions, bifurcated bonds). Most of the bond angles involving O(1) and O(2) are also nearly the same (*cf.* Fig. 7 and Table 4). These similarities are preserved as the temperature is changed.

However, a closer inspection reveals some significant differences. H(4) has about equal distances to O(1) and O(2) at −40°C, but at the lower temperature this hydrogen is much closer to O(2) which implies stronger H(4)···O(2) interaction. This difference in hydrogen bond acceptor power of O(1) and O(2) is in agreement with the observed difference of the C—O distances at the lower temperature (C(1)—O(1) has larger double bond character than C(1)—O(2)).

The hydrogen atoms of the methyl group could be clearly recognized in the difference syntheses. The coordinates used in the refinement (Table 1b) were calculated from the hydrogen peaks but modified to fit with a C—H distance of 1.10 Å[14] and tetrahedral bond angles at C(2). It is interesting to observe that at −40°C the dihedral angle defined by the two planes C—C—O and

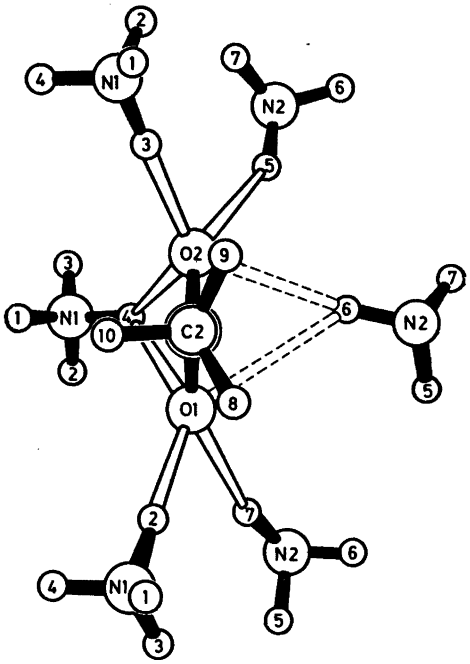

Fig. 8. The locations of the hydrogen atoms at −40°C. The notation of the bonds is the same as in Fig. 5.

C—C—H, is approximately 30° (*cf.* Fig. 8). When the temperature is lowered, however, the methyl group is rotated around the C—C bond and the dihedral angle decreases to approximately 0° (*cf.* Fig. 5). An analysis of the environment of the methyl group shows that at −190°C the C(2)—H(8) and C(2)—H(10) bonds point nearly directly towards two oxygen atoms. However, the calculated H···O distances are about 2.7 Å and can hardly imply any hydrogen bond interaction.

Additional comparison of the structure at the two temperatures. The changes in the structure with temperature are anisotropic as seen from the unit cell dimensions. Only the *c* axis is significantly altered. This is mainly due to a shortening of the distances between the layers *B* and *C*, and *D* and *A* (*cf.* Fig. 1). However, other essential changes in the structure are only revealed by comparison of the refined atomic parameters. The individual atomic translations range from 0.1—0.2 Å. As seen from Table 1, the changes in the *y* coordinates are significantly larger than the changes in the *x* and *z* coordinates. Together with the symmetry relations between the puckered layers this implies a translation of approximately 0.3 Å of *A* and *B* relative to *C* and *D* in the direction of the *b* axis. But *A* and *C* are moved only very little relative to *B* and *D*, respectively. The acetate group is rotated approximately 3° about the C—C axis.

The thermal motion changes nearly isotropically with temperature. A comparison of the U_{ij} values shows a reduction of 50—60 % at −190°C. As the thermal parameters may be slightly in error due to lack of experimental

scaling *etc.*, no detailed discussion will be made of the direction of the principal axes of the vibration ellipsoids or variations of these with temperature. For the same reason no thermal corrections were made in the calculation of the bond distances.

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