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THE CRYSTAL STRUCTURE OF AMMONIA MONOHYDRATE

Ivar Olovsson and David H. Templeton
April 1959

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ABSTRACT

The crystal structure of ammonia monohydrate, $NH_3 \cdot H_2O$, has been determined from three-dimensional X-ray data. Exposures at -95° and -160°C indicate the same structure. The crystals are orthorhombic (space group $P2_12_12_1$) with four molecules in a unit cell of dimensions: a=4.51±0.01, b=5.587±0.003, c=9.700 ±0.005 Å at -160°C. The structure contains planar chains of water molecules connected by hydrogen bonds of 2.77 Å. The chains are crosslinked by the ammonia molecules into a three-dimensional network by short bonds (2.77 Å) of the type O-H---N and long bonds (3.21, 3.26, 3.29 Å) of the type O---H-N.

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INTRODUCTION

All earlier work on the system ammonia-water indicated two stable hydrates, $NH_3 \cdot 1/2\ H_2O$ and $NH_3 \cdot H_2O$, in the literature sometimes called ammonium oxide and ammonium hydroxide, respectively. In view of the structural and other properties, it seems that ammonia hemihydrate and ammonia monohydrate are somewhat more adequate names and these are used here. Recently a detailed study of the region around the eutectic between ice and ammonia monohydrate seemed to indicate a dihydrate, $NH_3 \cdot 2H_2O$, melting incongruently at -98°C (Rollet and Vuillard, 1956). The structures of these phases are of considerable interest because of the hydrogen bonding which occurs in them. The crystal structure of the hemihydrate has been determined by Siemons and Templeton (1954). The present work involves the determination of the structure of the monohydrate. X-ray photographs taken at -95° and -160°C indicate the same structure; the results below refer only to the data from -160°C.

The melting point of the monohydrate as determined in some earlier works is: -79.3°C (Rupert, 1910), -79.0° (Postma, 1920), -79.0° (Elliott, 1924), -79.01° (Hildenbrand and Giauque, 1953), -77.0° (Mironov, 1955).

Measurements of the eutectic heat of fission by Hildenbrand and Giauque (1953) show that the monohydrate must crystallize in very pure form (to within 0.05% at the eutectic region) and not as solid solution.

Preparation of the Samples

The crystals were grown from samples of solutions of ammonia and water sealed in glass capillaries. The ammonia and water were distilled twice in a vacuum system. The capillaries were made by drawing out one end of a thin walled glass tube (diameter about 2 mm) to a diameter of 0.1 to 0.2 mm and a wall thickness of 0.01 to 0.02 mm. They were connected to the vacuum

system by a short plastic tubing (polyvinyl chloride) of the same diameter as the wide end of the capillary. This made it possible to replace a capillary very easily and still get a sufficiently good vacuum. The capillary was evacuated; water and then ammonia were distilled into it, and the capillary was melted off. Weighing the capillary when empty, after filling with water and after melting off gave the composition of the sample. The desired composition was easily obtained by trial and error. The capillary used for the X-ray work had the ratio 0.97 moles ammonia per mole of water.

Apparatus

The X-ray photographs were taken in a modified Weissenberg camera. The setup resembles that described by Kreuger (1955) with some modifications to make it even simpler to handle. Single crystals were grown in the camera in the ordinary way by blowing a cool stream of gas parallel to the capillary (Abrahams, Collin, Lipscomb, and Reed, 1950) and following the growth with a polarizing microscope. The cooling gas was obtained by boiling nitrogen directly from a 100-liter Dewar. This amount of nitrogen is more than enough for the complete experiment and makes refilling of the Dewar unnecessary. The gas from the Dewar passed through a carefully insulated flexible copper tube to the glass Dewar tube inside the layer-line screen. This flexibility makes the shifting to higher layers simple. Covering the slit of the layer-line screen with thin Mylar film completely prevented icing on the capillary. Icing on the outside of the layer-line screen was overcome by heating the screen on the outside. The temperature was measured with a copper-constantan thermocouple inside the glass Dewar tube with the junction about 2 mm from the end of the capillary. The temperature was kept constant to within $\pm 2^{\circ}C$. While growing the crystal, it was apparent that the melting point was in reasonable agreement with earlier published data cited above.

Unit-Cell and Space Group

Equi-inclination Weissenberg photographs were taken around the a axis, layers 0 to 3, at -95° and $-160^{\circ}C$ by the use of CuK-radiation. The relative intensities were estimated visually by the use of multiple-film

technique (4 films) and comparison with an intensity scale. The data were corrected for the Lorentz and polarization factors on the IBM-650 computer (Jones and Templeton, 1958). The data showed the diffraction symmetry mmm; the crystal is therefore orthorhombic. The unit-cell constants, determined from oscillation and quartz-calibrated zero-layer Weissenberg photographs are: a=4.51±0.01, b=5.587±0.003, c=9.700±0.005 Å (t=-160°C; $\lambda CuK\alpha_1$ = 1.54051 Å, $\lambda CuK\alpha$ = 1.54433 Å). The quartz crystal was provided by Dr. Adolph Pabst, Department of Geology, University of California, Berkeley. The cell dimension used for α quartz, a=4.913 Å at 25°C, is that given by Swanson, Fuyat, and Ugrinic (1954).

Siemons and Templeton (1954) indexed the powder and rotation photographs of this phase as hexagonal with a=11.21 and c=4.53 Å (at -95°C). The short orthorhombic axis is obviously equal to this hexagonal c axis. One notices moreover that the other two are in the ratio c/b=1.736, or nearly $\sqrt{3}$. With the ratio $\sqrt{3}$, the orthorhombic cell is metrically equal to a hexagonal lattice. A powder diagram of insufficient resolution or the rotation pattern for the short axis would therefore naturally be indexed as hexagonal, lacking other evidence. It is interesting that the ammonia hemihydrate which is also orthorhombic, is metrically tetragonal, to the accuracy of the measurements (Simeons and Templeton, 1954).

Hildenbrand and Giauque (1953) determined the approximate density of the liquid at -68°C to be 0.89 g cm^{-3}. With four molecules per unit cell, the calculated density of the solid at -160°C is 0.95. This may be compared with the density of ice, 0.92, that of ammonia hemihydrate, 0.92 (calculated) at -95°C (Siemons and Templeton, 1954), and that of ammonia, 0.86 (calculated) at -196°C (Olovsson and Templeton, 1959).

Systematic absences among the 270 independent reflexions were: (0k0) for k odd, (00ℓ) for ℓ odd (k=0 to 7, ℓ=0 to 12). The (h00) reflexions were not accessible, as the crystal was rotating around the a axis. These data give a choice between the space groups $P\ 2_1 2_1 2_1$ and $P\ 2\ 2_1 2_1$ if the absences are assumed to be space-group extinctions. Another possibility is that the absences are due to false symmetry; if so, the space group might be P 222, P mm2, P mmm, or $P\ 222_1$. It turns out that only $P\ 2_1 2_1 2_1$ gives a reasonable

trial structure in approximate agreement with the data. The subsequent refinement of the structure by the use of this space group gives good agreement with the data, which shows this choice to be correct. The atoms are in the general positions: (x,y,z); $(1/2-x,y,1/2+z)$; $(1/2+x,1/2-y,\bar{z})$; $(\bar{x},1/2+y,1/2-z)$.

Determination of the Atomic Coordinates

Simple considerations using a few reflexions led to a trial structure with the atomic coordinates: (0.25, 0.11, 0.00) and (0.25, 0.25, 0.33). Independent studies of the Patterson function gave the same result. After several cycles of least-squares refinements on the IBM-650, putting in both atoms as nitrogen, it appeared that the temperature factor for the first atom became much smaller than the second. This implies that the first atom should be oxygen. Also electron-density calculations trying both possibilities consistently gave a higher peak at the first atom. Apart from this, structural considerations based on these atomic positions definitely suggest the same choice.

The least-squares refinement of this structure (by the use of the program called LSII, Senko, 1957) minimizing R_3 (see below), was carried out further until the shifts in the atomic coordinates were less than about one tenth of the standard deviation and R_3 essentially did not decrease further. The total number of cycles was about twenty. The coordinates and individual isotropic temperature factors for oxygen and nitrogen and an over-all scale factor were refined (the interlayer scale factor was then based on the relative exposure time). The weight (w) was taken as a constant $1/16F_{min}^2$ if the uncorrected intensity was less than 16 times the minimum observed value, and otherwise as $1/F_o^2$ (Hughes, 1941). For reflextion too weak to be observed, the quantity F_o-F_c was set equal to zero in the sums for $F_c < F_{min}$ or equal to $-F_c$ for $F_c > F_{min}$. The coordinates, their standard deviations, and temperature factors are listed in Table I. The "unreliability factors" at this point were:

$$R_1 = \Sigma\|F_o| - |F_c\| \,/\, \Sigma|F_o| = 0.119$$

$$R_2 = [\,\Sigma(|F_o| - |F_c|)^2 \,/\, \Sigma|F_o|^2\,]^{1/2} = 0.135$$

$$R_3 = [\,\Sigma\underline{w}(|F_o| - |F_c|)^2/\Sigma\,\underline{w}|F_o|^2\,]^{1/2} = 0.143.$$

When we included the hydrogen atoms assigned to the hydrogen bonds as described below, and refined a couple of cycles more (keeping the hydrogen parameters fixed), the R factors decreased by 0.01: $R_1 = 0.108$, $R_2 = 0.125$, $R_3 = 0.133$. The hydrogen atoms were placed on the lines between hydrogen-bonded atoms at 1.01 Å from nitrogen and 0.96 Å from oxygen, respectively. In the last cycles, the scale factor for each layer was actually refined individually, but the deviation of the final scale factors from their mean value was quite small (less than 3%). The atomic parameters and the standard deviations after the final refinement are also listed in Table I; the observed and calculated structure factors are compared in Table II.

Discussion of the Structures

The structure is shown in Figs. 1 and 2. The bond distances and angles with their standard deviations, derived from the coordinates in Table I, Column b, are given in Table III. The correlations between symmetry-related atoms (Templeton, 1959) and the uncertainty of the unit-cell dimensions were considered in the calculations of these standard deviations.

The water molecules are hydrogen-bonded to each other into planar chains oriented along the a axis and approximately in the planes z = 0 or 1/2, respectively. The chains are cross-linked by the ammonia molecules into a three-dimensional network. It appears that the ammonia molecules are not bonded to each other; the neighbors to the nitrogen atom are one oxygen atom at 2.77 Å and three others at 3.21, 3.26, and 3.29 Å respectively. The oxygen atom has three close neighbors at 2.77 Å (one nitrogen and two oxygen atoms) and three others (nitrogen atoms) at 3.21, 3.26, and 3.29 Å. The centroid (C in Fig. 1 and Table III) of these three long bonds together with the three close neighbors forms an almost regular tetrahedron.

The chemical arguments about the locations of the hydrogen atoms are based on the generally accepted ideas that (a) the angles H-O-H and H-N-H are close to 109°, (b) the hydrogen atom is close to the axis of the bond, (c) only one hydrogen atom is present in each hydrogen bond, and (d) an electron pair is available reasonably close to each hydrogen bond. When these concepts are applied, it appears that the only reasonable assignment of hydrogen atoms

to the different atoms is that shown in Fig. 1. Notice however, that one of the hydrogen atoms of the water molecule is not shown in the picture. That is because at this stage it is impossible to decide to which one of the two oxygen neighbors the hydrogen atom should be pointed. Choice of one position fixes the hydrogen positions for the rest of the structure, which means that interchange between the two possible positions will not lead to extra entropy. As a matter of fact the electron-density sections show definite maxima corresponding to all the hydrogen atoms shown in Fig. 1. The second hydrogen atom in the water molecule does not stand out clearly, however, partly because of diffraction effects at just the locations possible for it. The electron density at x = 0.25 (based on the nitrogen and oxygen positions only) is illustrated in Fig. 3, where one hydrogen atom in water and ammonia respectively seems to be visible. (These peaks are also the only ones showing up in the corresponding (F_o-F_c) synthesis.)

The assignment of hydrogen atoms to the bonds as above implies that one electron pair of the water molecule is used for three weak hydrogen bonds (3.21, 3.26, and 3.29 Å). This is completely analogous to the interpretation of the structure of solid ammonia (Olovsson and Templeton, 1959). The free electron pair of each ammonia molecule is there used to form three hydrogen bonds (to three other ammonia molecules) of 3.38 Å (at -102°C). The bonds are expected to be a little shorter in the case of the monohydrate, because the bond is here between nitrogen and oxygen as compared to nitrogen-nitrogen in ammonia.

Comparison with the structure of the hemihydrate (Siemons and Templeton, 1954) shows that in both cases the ammonia molecules are not bonded to each other and that the free electron pair of nitrogen is used to form the short bond to oxygen (2.77 and 2.84 Å respectively), with the assignment of hydrogen atoms as given. The difference in the lengths of the long bonds in the two cases (3.21, 3.26, and 3.29 Å in the monohydrate as compared to 3.13, 3.22, and 3.22 Å for one of the ammonia molecules in the hemihydrate) may be explained by the fact that, roughly speaking, in the first case oxygen contributes 1/3 of an electron pair to each bond N-H----O, and in the other, 2/3 of an electron pair.

In the case of ammonia, rotation around the three-fold axis is probably quite restricted. The arguments given by Olovsson and Templeton (1959) apply also for the ammonia molecules in the case of the monohydrate. From heat-capacity measurements by Hildenbrand and Giauque (1953), it is concluded that the entropy approaches zero at low temperatures, and thus the structural details must be essentially ordered in the crystalline state at low temperatures. They also found no indications of any transition from these low temperatures to the melting point. The fairly large deviations from the tetrahedral value of the angles between the long bonds may indicate that the hydrogen atoms are somewhat off the lines connecting the nitrogen and oxygen atoms (the hydrogen atoms in Fig. 1 are placed on these lines just for simplicity).

The interpretation of the infrared spectrum of the solid by Waldron and Hornig (1953) is in complete agreement with the presented structure. They found that the spectrum resembles very much that of crystalline NH_3 and H_2O respectively. They also found that at least two hydrogen atoms of ammonia are either not bonded at all or very weakly bonded (our work shows that actually all three hydrogen atoms of ammonia are weakly bonded).

Table I

Atomic parameters and standard deviations	
a. After refinements without hydrogen	b. After final refinements with hydrogen
Oxygen: $x = 0.2414 \pm 0.0018$	Oxygen: $x = 0.2411 \pm 0.0017$
$y = 0.1102 \pm 0.0007$	$y = 0.1099 \pm 0.0007$
$z = 0.0165 \pm 0.0004$	$z = 0.0169 \pm 0.0004$
$B = 1.82$ Å^2	$B = 1.65$ Å^2
Nitrogen:	Nitrogen:
$x = 0.2635 \pm 0.0023$	$x = 0.2641 \pm 0.0022$
$y = 0.2730 \pm 0.0009$	$y = 0.2717 \pm 0.0008$
$z = 0.3350 \pm 0.0005$	$z = 0.3345 \pm 0.0004$
$B = 2.08$ Å^2	$B = 1.80$ Å^2

Table II

Observed and calculated structure factors. All F values have been multiplied by 2.5.

h = 0				h = 1				h = 2				h = 3			
k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$
2	0	39	38	1	0	45	45	1	0	2	3	1	0	24	21
4	0	8	8	2	0	5	4	2	0	21	30	2	0	4	5
6	0	16	15	3	0	6	5	3	0	5	7	3	0	5	3
1	1	17	14	4	0	<3	<1	4	0	4	5	4	0	<2	<1
2	1	12	9	5	0	21	25	5	0	<2	2	5	0	16	18
3	1	44	45	6	0	<3	<1	6	0	13	12	6	0	<2	<1
4	1	12	10	0	1	4	4	0	1	7	9	0	1	3	5
5	1	12	12	1	1	48	57	1	1	12	10	1	1	21	21
6	1	10	8	2	1	50	57	2	1	3	2	2	1	24	26
7	1	6	7	3	1	19	19	3	1	32	35	3	1	12	11
0	2	38	47	4	1	4	4	4	1	8	8	4	1	3	4
1	2	23	23	5	1	11	9	5	1	11	10	5	1	8	7
2	2	33	32	6	1	9	7	6	1	8	7	6	1	3	5
3	2	20	18	0	2	36	40	0	2	26	24	0	2	11	11
4	2	33	32	1	2	44	50	1	2	10	10	1	2	24	23
5	2	3	4	2	2	33	31	2	2	26	22	2	2	16	16
6	2	<3	3	3	2	21	20	3	2	10	10	3	2	11	12
7	2	5	5	4	2	18	19	4	2	23	25	4	2	12	12
1	3	71	87	5	2	12	12	5	2	2	4	5	2	9	8
2	3	13	10	6	2	5	5	6	2	2	3	0	3	2	1
3	3	6	4	0	3	<2	<1	0	3	2	<1	1	3	5	6
4	3	4	4	1	3	9	11	1	3	43	50	2	3	17	16
5	3	5	5	2	3	28	28	2	3	12	11	3	3	7	6
6	3	<3	3	3	3	13	10	3	3	4	3	4	3	10	11
0	4	27	26	4	3	17	17	4	3	4	5	5	3	<2	<1
1	4	6	9	5	3	<3	2	5	3	4	5	0	4	22	24
2	4	21	20	6	3	18	17	6	3	2	3	1	4	17	17
3	4	5	<1	0	4	43	47	0	4	23	20	2	4	12	12
4	4	26	25	1	4	35	36	1	4	9	8	3	4	9	10
5	4	14	13	2	4	21	21	2	4	16	16	4	4	4	3
6	4	<3	2	3	4	18	18	3	4	<2	1	5	4	7	7

Table II (continued)

h = 0				h = 1				h = 2				h = 3			
k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$
1	5	13	12	4	4	4	3	4	4	20	21	0	5	6	5
2	5	27	25	5	4	10	9	5	4	13	11	1	5	6	7
3	5	28	28	6	4	10	8	6	4	<2	2	2	5	17	18
4	5	5	3	0	5	3	3	0	5	5	5	3	5	14	17
5	5	10	8	1	5	13	12	1	5	6	5	4	5	<2	2
6	5	<3	1	2	5	29	28	2	5	16	17	5	5	5	7
0	6	48	53	3	5	24	26	3	5	21	22	0	6	11	11
1	6	13	12	4	5	<3	2	4	5	2	3	1	6	10	9
2	6	21	17	5	5	11	10	5	5	9	7	2	6	3	3
3	6	8	6	6	5	4	5	0	6	36	38	3	6	3	2
4	6	<3	1	0	6	20	21	1	6	11	11	4	6	6	6
5	6	9	8	1	6	14	15	2	6	13	12	0	7	<2	<1
6	6	10	10	2	6	<3	2	3	6	7	6	1	7	15	17
1	7	<3	1	3	6	<3	2	4	6	<3	1	2	7	12	12
2	7	12	12	4	6	10	9	5	6	8	7	3	7	3	<1
3	7	20	19	5	6	17	16	0	7	4	3	4	7	<2	3
4	7	12	9	6	6	3	3	1	7	2	2	0	8	<2	<1
5	7	9	7	0	7	<3	<1	2	7	10	9	1	8	9	8
0	8	11	8	1	7	24	26	3	7	16	16	2	8	11	10
1	8	16	14	2	7	19	18	4	7	9	8	3	8	6	5
2	8	7	8	3	7	<3	<1	5	7	6	6	0	9	2	2
3	8	12	10	4	7	<3	1	0	8	6	5	1	9	6	7
4	8	14	12	5	7	4	4	1	8	11	11	2	9	3	4
5	8	<3	3	0	8	<3	<1	2	8	7	7	3	9	3	6
1	9	23	20	1	8	12	11	3	8	10	9	0	10	12	15
2	9	13	12	2	8	16	15	4	8	11	10	1	10	3	4
3	9	5	3	3	8	10	7	0	9	<2	1				
4	9	5	4	4	8	18	17	1	9	15	16				
0	10	<1	<1	5	8	4	4	2	9	12	11				
1	10	9	9	0	9	<2	<1	3	9	4	3				
2	10	8	7	1	9	11	10	4	9	3	4				
3	10	<3	2	2	9	5	5	0	10	<3	<1				
4	10	8	8	3	9	11	9	1	10	8	7				

Table II (continued

h = 0				h = 1				h = 2				h = 3			
k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	k	ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$
1	11	<3	1	4	9	6	7	2	10	6	6				
2	11	13	12	0	10	24	21	3	10	<2	2				
3	11	7	6	1	10	6	6	0	11	<2	1				
0	12	13	11	2	10	9	6	1	11	<2	1				
1	12	7	7	3	10	6	5	2	11	8	10				
				0	11	<3	1								
				1	11	3	2								
				2	11	6	5								
				0	12	6	10								

Table III

Bond distances and angles with their standard deviations (compare Figure 1). The centroid to the bonds O_1-N_1, O_1-N_2, and O_1-N_3 is called C.

Around the oxygen atom: Bond	Distance (Å)	Around the nitrogen atom: Bond	Distance (Å)
O_1-O_2	2.765 ± 0.004	N_1-O_4	2.771 ± 0.006
O_1-O_3	2.765 ± 0.004	N_1-O_1	3.212 ± 0.006
O_1-N_4	2.771 ± 0.006	N_1-O_5	3.260 ± 0.010
O_1-N_1	3.212 ± 0.006	N_1-O_6	3.292 ± 0.010
O_1-N_2	3.260 ± 0.010		
O_1-N_3	3.292 ± 0.010		

Bonds	Angle (deg)	Bonds	Angle (deg)
O_2-O_1-O_3	109.30	O_4-N_1-O_1	113.30
O_2-O_1-N_4	111.52	O_4-N_1-O_5	99.77
O_3-O_1-N_4	110.67	O_4-N_1-O_6	98.98
N_1-O_1-N_2	73.56	O_1-N_1-O_5	127.52
N_1-O_1-N_3	76.35	O_1-N_1-O_6	123.98
N_2-O_1-N_3	87.00	O_5-N_1-O_6	87.00

C-O_1-O_2	109.89		
C-O_1-O_3	111.10		
C-O_1-N_4	104.32		

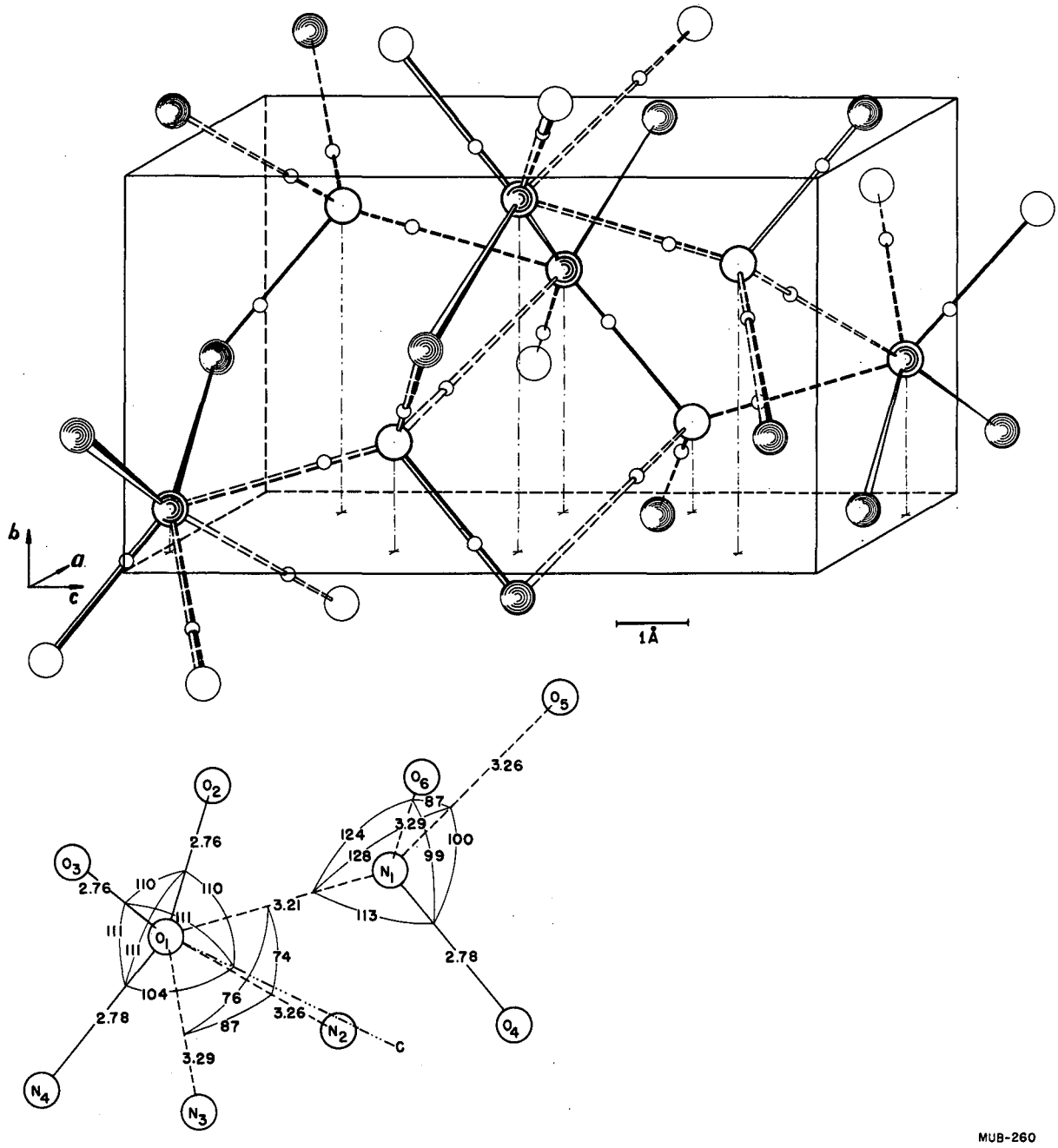
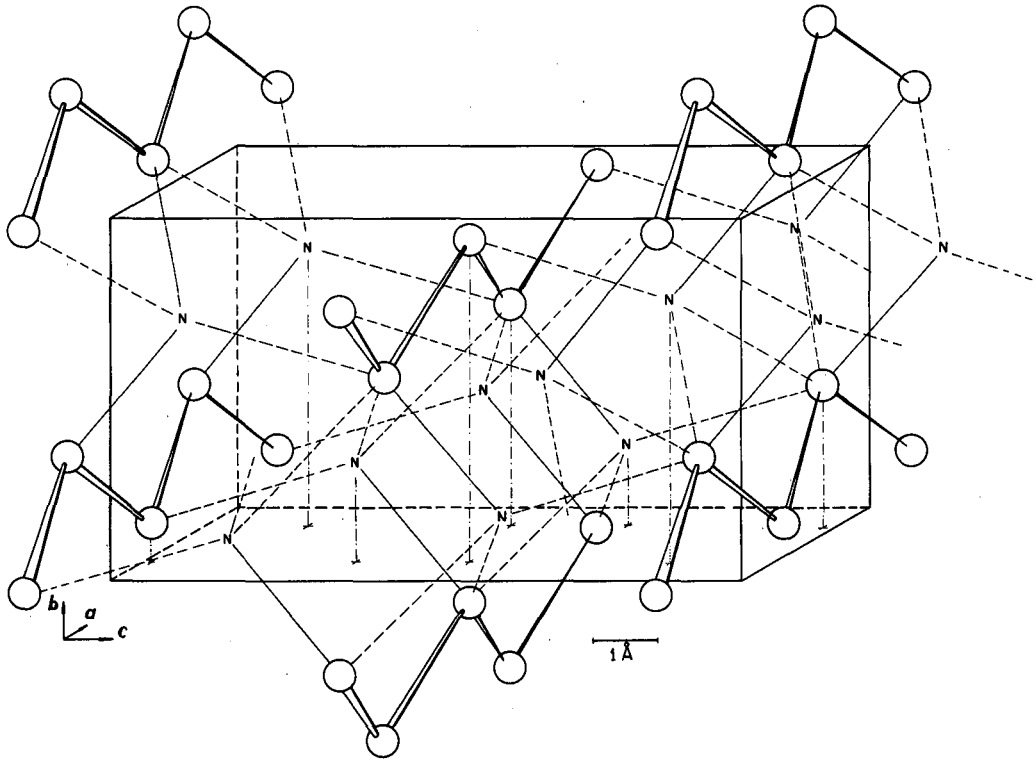
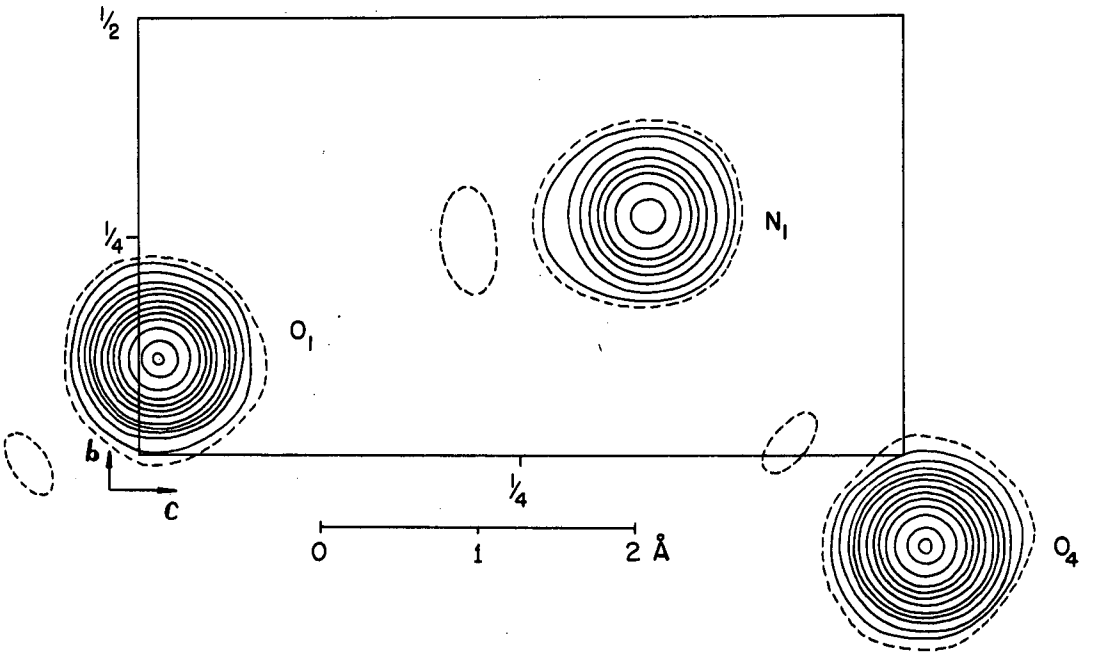


Fig. 1. The crystal structure of ammonia monohydrate. The short hydrogen bonds (2.77 Å) are shown as solid lines, the long bonds (3.21, 3.26, 3.29 Å) are dotted. The centroid of these long bonds (C) is shown in the subfigure. The location of one of the hydrogen atoms in the water molecule is uncertain and not indicated.



MU-16902

Fig. 2. The chains of water molecules and the way these are linked together by the ammonia molecules.



MU-16903

Fig. 3. Electron density at x = 0.25. The solid contours are drawn at 1, 2, 3 ··· e·Å^{-3}. Dotted contours correspond to 1/2 e·Å^{-3}.

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