

The Crystal Structure of Ammonia Monohydrate*

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The crystal structure of ammonia monohydrate, $\text{NH}_3 \cdot \text{H}_2\text{O}$, 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: $a = 4.51 \pm 0.01$, $b = 5.587 \pm 0.003$, $c = 9.700 \pm 0.005$ Å at -160 °C. The structure contains planar chains of water molecules connected by hydrogen bonds of 2.76 Å. The chains are crosslinked by the ammonia molecules into a three-dimensional network by short bonds (2.78 Å) of the type $\text{O}-\text{H} \cdots \text{N}$ and long bonds (3.21 , 3.26 , 3.29 Å) of the type $\text{O} \cdots \text{H}-\text{N}$.

Introduction

All earlier work on the system ammonia–water indicated two stable hydrates, $\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$, 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, $\text{NH}_3 \cdot 2\text{H}_2\text{O}$, melting incongruently at -98 °C. (Rollet & 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 & 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 (Rupert, 1910), -79.0 (Postma, 1920), -79.0 (Elliott, 1924), -79.01 (Hildenbrand & Giauque, 1953), -77.0 °C. (Mironov, 1955).

Measurements of the eutectic heat of fusion by Hildenbrand & 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 & 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.

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The temperature was kept constant to within ± 2 °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 °C. by the use of Cu K -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 & 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:

$$a = 4.51 \pm 0.01, \quad b = 5.587 \pm 0.003, \quad c = 9.700 \pm 0.005 \text{ \AA} \\ (t = -160 \text{ °C.}; \text{ Cu } K\alpha_1 \lambda = 1.54051 \text{ \AA}, \\ \text{ Cu } K\alpha_2 \lambda = 1.54433 \text{ \AA}).$$

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 & Ugrinic (1954).

Siemons & 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 (Siemons & Templeton, 1954).

Hildenbrand & 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 & Templeton, 1954), and that of ammonia, 0.86 (calculated) at -196 °C. (Olovsson & 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 $P2_12_12_1$ and $P22_12_1$ 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 $P222$, $Pmm2$, $Pmmm$ or $P222_1$. It turns out that only $P2_12_12_1$ 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 of space group to be correct. The atoms are in the general positions:

$$(x, y, z); \quad (\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z); \\ (\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}); \quad (\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z).$$

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 deviations and R_3 essentially did not decrease further. The total number of cycles was about thirty. 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 times). The weight (w) was taken as a constant $\frac{1}{16} F_{\min}^2$, if the uncorrected intensity was less than 16 times the minimum observed value, and otherwise as $1/F_o^2$ (Hughes, 1941). For reflections 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 1. The 'unreliability factors' at this point were:

Table 1. Atomic parameters and standard deviations

(a) After refinements without hydrogen	(b) After final refinements with hydrogen
Oxygen:	Oxygen:
$x = 0.2412 \pm 0.0017$	$x = 0.2410 \pm 0.0015$
$y = 0.1102 \pm 0.0006$	$y = 0.1107 \pm 0.0006$
$z = 0.0166 \pm 0.0003$	$z = 0.0168 \pm 0.0003$
$B = 1.40 \text{ \AA}^2$	$B = 1.42 \text{ \AA}^2$
Nitrogen:	Nitrogen:
$x = 0.2639 \pm 0.0021$	$x = 0.2641 \pm 0.0019$
$y = 0.2725 \pm 0.0008$	$y = 0.2720 \pm 0.0007$
$z = 0.3348 \pm 0.0004$	$z = 0.3345 \pm 0.0004$
$B = 1.59 \text{ \AA}^2$	$B = 1.57 \text{ \AA}^2$

Table 2. *Observed and calculated structure factors*

All *F* values have been multiplied by 2.5

<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $
	$h=0$														
2	0	38	34	0	12	12	12	0	10	24	22	2	9	12	11
4	0	8	8	1	12	7	7	1	10	6	6	3	9	3	3
6	0	15	15					2	10	9	6	4	9	3	3
1	1	17	7		$h=1$			3	10	6	5	0	10	<2	<1
2	1	12	9	1	0	46	44	0	11	<2	1	1	10	8	7
3	1	43	46	2	0	5	3	1	11	3	1	2	10	6	6
4	1	12	10	3	0	5	4	2	11	5	5	3	10	<1	1
5	1	12	12	4	0	<2	<1	0	12	8	10	0	11	<2	1
6	1	9	8	5	0	21	26					1	11	<1	1
7	1	5	7	6	0	<3	<1					2	11	8	11
0	2	38	39	0	1	4	4		$h=2$						
1	2	22	22	1	1	49	57	1	0	2	3				
2	2	33	35	2	1	51	56	2	0	22	21		$h=3$		
3	2	20	17	3	1	19	19	3	0	5	6	1	0	25	21
4	2	33	33	4	1	3	3	4	0	3	5	2	0	3	5
5	2	3	4	5	1	11	9	5	0	<2	2	3	0	5	4
6	2	<3	3	6	1	8	7	6	0	13	13	4	0	<2	<1
7	2	5	5	0	2	36	40	0	1	7	8	5	0	16	19
1	3	70	83	1	2	45	49	1	1	12	11	6	0	<1	<1
2	3	13	9	2	2	34	30	2	1	3	2	0	1	3	4
3	3	5	5	3	2	22	20	3	1	33	35	1	1	22	21
4	3	4	3	4	2	18	19	4	1	8	8	2	1	25	26
5	3	4	5	5	2	12	12	5	1	11	10	3	1	12	11
6	3	<3	3	6	2	5	5	6	1	8	7	4	1	3	3
0	4	27	23	0	3	<1	<1	0	2	26	26	5	1	8	7
1	4	5	8	1	3	9	10	1	2	10	10	6	1	2	5
2	4	20	21	2	3	28	28	2	2	26	21	0	2	11	11
3	4	5	1	3	3	13	10	3	2	10	10	1	2	25	23
4	4	25	26	4	3	17	17	4	2	24	26	2	2	16	16
5	4	14	14	5	3	<3	1	5	2	2	3	3	2	11	12
6	4	<3	2	6	3	18	18	6	2	2	2	4	2	12	13
1	5	12	10	0	4	44	46	0	3	1	1	5	2	9	8
2	5	27	25	1	4	36	36	1	3	45	51	0	3	2	1
3	5	28	29	2	4	21	21	2	3	12	11	1	3	5	5
4	5	4	3	3	4	18	18	3	3	4	3	2	3	18	17
5	5	9	9	4	4	4	3	4	3	4	5	3	3	7	5
6	5	<2	1	5	4	9	9	5	3	4	4	4	3	10	11
0	6	48	53	6	4	10	8	6	3	2	3	5	3	<2	1
1	6	13	12	0	5	3	3	0	4	24	21	0	4	23	25
2	6	20	16	1	5	13	12	1	4	9	7	1	4	17	17
3	6	7	6	2	5	30	29	2	4	16	15	2	4	12	12
4	6	<3	1	3	5	24	26	3	4	<2	1	3	4	10	11
5	6	9	8	4	5	<3	2	4	4	21	21	4	4	3	3
6	6	9	10	5	5	10	10	5	4	13	11	5	4	7	7
1	7	<2	<1	6	5	4	5	6	4	<1	1	0	5	5	5
2	7	11	12	0	6	20	20	0	5	5	4	1	5	6	7
3	7	20	20	1	6	14	15	1	5	6	5	2	5	17	18
4	7	11	9	2	6	<2	1	2	5	17	17	3	5	15	17
5	7	8	7	3	6	<2	1	3	5	21	22	4	5	<2	1
0	8	10	7	4	6	10	9	4	5	2	3	5	5	5	8
1	8	15	14	5	6	17	17	5	5	9	7	0	6	11	11
2	8	7	8	6	6	3	3	0	6	37	40	1	6	10	9
3	8	11	11	0	7	<2	<1	1	6	11	11	2	6	2	3
4	8	14	13	1	7	24	26	2	6	13	13	3	6	3	1
5	8	<2	2	2	7	19	19	3	6	7	6	4	6	6	6
1	9	23	21	3	7	<3	<1	4	6	<2	1	0	7	<2	1
2	9	12	12	4	7	<3	<1	5	6	7	7	1	7	15	17
3	9	5	3	5	7	4	3	0	7	3	3	2	7	13	12
4	9	4	3	0	8	<2	<1	1	7	2	1	3	7	2	<1
0	10	<2	<1	1	8	12	11	2	7	10	9	4	7	<1	2
1	10	8	8	2	8	16	15	3	7	16	17	0	8	<2	<1
2	10	7	7	3	8	9	7	4	7	9	8	1	8	9	8
3	10	<2	<2	4	8	18	17	5	7	6	6	2	8	11	10
4	10	8	9	5	8	3	4	0	8	6	5	3	8	6	5
1	11	<3	1	0	9	<3	<1	1	8	11	11	0	9	2	1
2	11	13	12	1	9	10	10	2	8	7	7	1	9	6	7
3	11	6	7	2	9	5	5	3	8	10	9	2	9	3	4
				3	9	11	9	4	8	11	11	3	9	3	6
				4	9	6	7	1	9	16	17	0	10	13	16
												1	10	2	4

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.110$$

$$R_2 = \left[\frac{\sum (|F_o| - |F_c|)^2}{\sum |F_o|^2} \right]^{1/2} = 0.124$$

$$R_3 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} = 0.129.$$

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: $R_1 = 0.098$, $R_2 = 0.112$, $R_3 = 0.118$. 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 1; the observed and calculated structure factors are compared in Table 2. The atomic scattering factors used in these calculations were those of Berghuis *et al.* (1955) for neutral N and O, and those given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) for H.

Discussion of the structure

The structure is shown in Figs. 1 and 2. The bond distances and angles with their standard deviations, derived from the coordinates in Table 1, column (b), are given in Table 3. The correlations between symmetry-related atoms (Templeton, 1959) and the un-

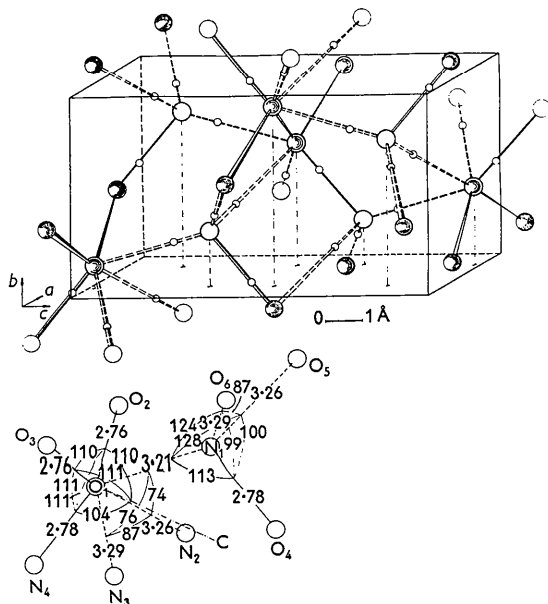


Fig. 1. The crystal structure of ammonia monohydrate. Shaded circles are oxygens; open circles are nitrogens. The short hydrogen bonds (2.76, 2.78 Å) are shown as solid lines, the long bonds (3.21, 3.26, 3.29 Å) are dotted. The centroid of these long bonds (C) is shown in the subfigure. The location of one of the hydrogen atoms in the water molecule is uncertain and not indicated.

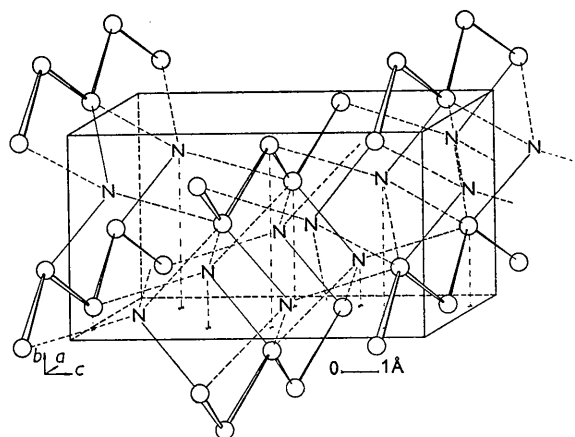


Fig. 2. The chains of water molecules and the way these are linked together by the ammonia molecules.

certainty 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 $\frac{1}{2}$, 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 2.78 Å and three others at 3.21, 3.26, and 3.29 Å respectively. The oxygen atom has three close neighbors at 2.78, 2.76, and 2.76 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 3) of these three long bonds together with the three close neighbors form an almost regular tetrahedron.

Table 3. Bond distances and angles with their standard deviations (compare Fig. 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		Around the nitrogen atom	
Bond	Distance (Å)	Bond	Distance (Å)
O_1-O_2	2.759 ± 0.005	N_1-O_4	2.775 ± 0.005
O_1-O_3	2.759 ± 0.005	N_1-O_1	3.212 ± 0.005
O_1-N_4	2.775 ± 0.005	N_1-O_5	3.263 ± 0.008
O_1-N_1	3.212 ± 0.005	N_1-O_6	3.294 ± 0.008
O_1-N_2	3.263 ± 0.008		
O_1-N_3	3.294 ± 0.008		
Bonds		Bonds	
Bonds	Angle (°)	Bonds	Angle (°)
$O_2-O_1-O_3$	109.6 ± 0.2	$O_4-N_1-O_1$	113.3 ± 0.1
$O_2-O_1-N_4$	111.4 ± 0.2	$O_4-N_1-O_5$	99.8 ± 0.2
$O_3-O_1-N_4$	110.7 ± 0.2	$O_4-N_1-O_6$	99.1 ± 0.2
$N_1-O_1-N_2$	73.5 ± 0.2	$O_1-N_1-O_5$	127.5 ± 0.2
$N_1-O_1-N_3$	76.3 ± 0.2	$O_1-N_1-O_6$	124.0 ± 0.2
$N_2-O_1-N_3$	86.9 ± 0.2	$O_5-N_1-O_6$	86.9 ± 0.1
$C-O_1-O_2$	109.7		
$C-O_1-O_3$	110.9		
$C-O_1-N_4$	104.2		

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 water molecules in the same chain. If the space-group symmetry stated here does not apply exactly to the hydrogen, or if there is disorder, the sense of the chains may be different in different parts of the crystal. Disorder of this sort would have a negligible effect on the entropy. 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.)

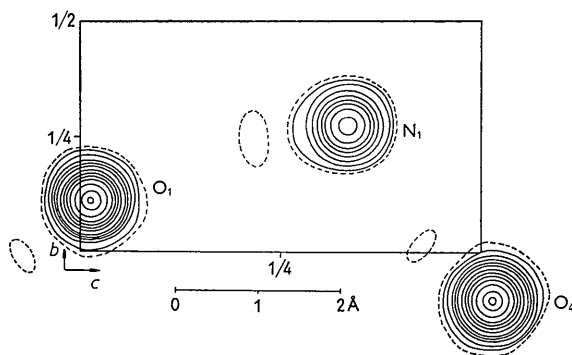


Fig. 3. Electron-density section at $x=0.25$. The solid contours are drawn at 1, 2, 3 ... $e.\text{\AA}^{-3}$. Dotted contours correspond to $\frac{1}{2} e.\text{\AA}^{-3}$.

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 & 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 & 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 (2.78 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 $\frac{1}{3}$ of an electron pair to each bond N–H...O, and in the other, $\frac{2}{3}$ of an electron pair.

In the case of ammonia, rotation around the three-fold axis is probably quite restricted. The arguments given by Olovsson & Templeton (1959) apply also for the ammonia molecules in the case of the monohydrate. From heat-capacity measurements by Hildenbrand & Giaque (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 & 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).

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X-ray Study of Solid Ammonia*

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Ammonia and deuterio-ammonia have been studied by single-crystal and powder X-ray methods. There are four molecules in the cubic unit cell, and the space group is confirmed to be $P2_13$. The nitrogen parameter obtained by least-squares refinement is equal to 0.0401 for NH_3 at -102°C . and the same for ND_3 at -160°C . Cell dimensions, determined by powder methods, are: $a = 5.084 \text{ \AA}$ for NH_3 at -196°C ., 5.073 \AA for ND_3 at -196°C ., 5.091 \AA for ND_3 at -160°C ., and 5.138 \AA for NH_3 at -102°C . Each ammonia molecule is involved in six hydrogen bonds of approximate length 3.4 \AA . A possible assignment of the hydrogen atoms to these bonds is given. Electron-density maps give evidence of hydrogen positions with coordinates (0.85, 0.14, 0.99), in agreement with this assignment, but with hydrogen off the bond axis, making the H-N-H angles more nearly tetrahedral.

Introduction

Earlier X-ray work on solid ammonia was done by powder methods. Reported values of the unit-cell dimension vary considerably, and new determinations by powder methods have been done on ordinary ammonia at -102 and -196°C . and on deuterio-ammonia at -160 and -196°C . A single-crystal study has been undertaken to improve our knowledge of the atomic positions. The single-crystal work has been done on ordinary ammonia at -102°C . and on deuterio-ammonia at -160°C . All the present work is concerned with the cubic form, as the new low-symmetric modification (Mauer & McMurdie, 1958) does not form under the conditions of these experiments.

Experimental

The ammonia and deuterio-ammonia were distilled twice in a vacuum system and sealed in glass capillaries (diameter 0.1 to 0.2 mm.). The deuterio-ammonia had, according to the specifications accompanying the cylinder, been made from magnesium nitride and 99.5% D_2O . The vacuum system was filled with deuterio-ammonia and evacuated many times to eliminate most of the impurities containing hydrogen which would otherwise exchange with the heavy ammonia. In the mass-spectrometric analysis of samples from

the original cylinder the mole percentage of ND_2H decreased gradually to below 9% after about 30 repeated fillings and evacuations of the spectrometer. This can be considered to correspond to a content of hydrogen of less than 3%. Samples from the X-ray capillaries gave less than 4% hydrogen. The effect on the unit-cell dimension due to this impurity is well within the limits of accuracy stated in this work.

The single crystals were grown in the ordinary way in a modified Weissenberg camera (Olovsson & Templeton, 1959). Equi-inclination Weissenberg photographs, layers 0 to 5, were taken with rotation about $[110]$ at $-102 \pm 2^\circ\text{C}$. of ordinary ammonia and at $-160 \pm 2^\circ\text{C}$. of deuterio-ammonia. The relative intensities were estimated visually by using multiple-film technique (four films) and comparing with an intensity scale. The data were corrected for the Lorentz and polarization effects. Because of the symmetry, equivalent reflections occur in several layers and permit good interlayer scaling.

The powder photographs (Debye-Scherrer type) were taken with the Weissenberg camera setup with some modifications of the film holder to get reflections of as high order as possible. By moving the film holder between each exposure it was possible to take a great number of photographs on the same film with a minimum disturbance of the film setting. Each powder picture was about 5 mm. wide, and the different pictures were immediately adjacent to one another. Exposures were located on the film in the following order: 1, quartz; 2, NH_3 ; 3 and 4, NH_3 and ND_3 on top of each other; 5, ND_3 ; 6, quartz; 7 and 8, NH_3

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