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THE CRYSTAL STRUCTURE OF AMMONIUM OXIDE

W. J. Siemons and D. H. Templeton

January 19, 1953

Berkeley, California

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ABSTRACT

At low temperatures ammonia forms two stable hydrates $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, ammonium hydroxide and ammonium oxide respectively. The lattice constants of the hydroxide and the crystal structure of the oxide have been determined at -100°C. The structure of ammonium oxide contains planar chains of alternating ammonia and water molecules bonded by hydrogen bonds of the O-H--N and N-H--O type. The chains are cross linked into a three dimensional lattice by hydrogen bonds of the latter type. The open spaces in the lattice contain the remaining ammonia molecules each having a single hydrogen bond to the molecular lattice.

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INTRODUCTION

The system ammonia-water has been investigated by many workers, Rupert (1909), (1910), Smits and Postma (1911), Postma (1920), Elliott (1924), Giauque and Hildenbrand (1953). All results indicate that the system has two stable hydrates $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, which will be referred to as ammonium hydroxide and ammonium oxide respectively. The crystal structure of neither of the two hydrates has been reported. The values mentioned for the melting points vary for the different investigators. Giauque and Hildenbrand (1953) report 194.15°K for the hydroxide and 194.32°K for the oxide.

The crystal structure of the oxide and the lattice constants of the hydroxide have been determined by X-ray diffraction and the results are described below. Giauque and Hildenbrand (1953) have found that the oxide has a transition region at about 50-55°K. As our determination was made at about -100°C our results pertain to the high temperature form only.

Preparation of the samples.

The required amounts of ammonia and water vapor were measured out in a gas burette and condensed in a thin-walled Pyrex glass capillary with liquid nitrogen. Each capillary had a small bulb blown at the end to permit the use of a sizeable sample. In order

to have the liquid of the desired composition, an allowance was made for the fact that the vapor has a higher ammonia content than the liquid. After being filled, the capillary was sealed off and used as the X-ray diffraction sample.

The ammonia was prepared from ammonium chloride C.P. according to the method of Overstreet and Giauque (1937). The water was distilled twice.

Apparatus.

The following Roentgenphotographs were taken: Debye-Scherrer, oscillation, and equi-inclination Weissenberg. The sample was mounted vertically in the Debye-Scherrer and oscillation cameras and horizontally in the Weissenberg camera. It was cooled with a stream of cold nitrogen gas produced by electrical heating of liquid nitrogen in a small Dewar. This Dewar was equipped with an automatic refilling mechanism governed by a float. In this way, a picture series extending over several days was possible. The quantity of cooling gas and the size of the duct were so chosen that frosting over was not troublesome.

The diameter of the Debye-Scherrer camera was 180 mm, and those of the oscillation and Weissenberg cameras were 57.3 mm.

The preliminary investigations and the measurement of the lattice constants were made with the Debye-Scherrer camera.

The structure factors were determined with the oscillation and the Weissenberg photographs of single crystals.

The Weissenberg camera was modified for our purpose by using a film holder having only the lower half of the film, so that the

cooling was not interrupted between exposures. All photographs were taken with CuK α radiation (λ = 1.5418Å).

Preliminary investigations.

Samples were prepared with widely varying concentrations and powder photographs taken thereof. Starting with pure ammonia increasing amounts of water were added. Besides the lines of ammonia, another set appeared which was attributed to the ammonium oxide. This set could be indexed as tetragonal with lattice constants:

$$\underline{a} = \underline{b} = 8.41 \pm 0.03\text{Å} \quad \text{and}$$

$$\underline{c} = 5.33 \pm 0.02\text{Å} \text{ at } -95^\circ \pm 10^\circ\text{C}.$$

Increasing water concentration gave a third set attributed to the ammonium hydroxide. This set could be indexed as hexagonal with lattice constants:

$$\underline{a} = \underline{b} = 11.21 \pm 0.05\text{Å} \quad \text{and}$$

$$\underline{c} = 4.53 \pm 0.02\text{Å}, \text{ at } -95^\circ \pm 10^\circ\text{C}.$$

We were not able to get a picture of the conclusive cornerstone: ice and hydroxide together, as the liquid supercooled and could not be brought to crystallization.

The following table of compositions and sets of lines observed strongly supports our interpretation:

Table 1

Mole fraction of ammonia in sample	Sets of lines observed in powder picture
1.00	Ammonia
0.80	Ammonia, ammonium oxide
0.70	Ammonia, ammonium oxide
0.62	Ammonium oxide, ammonium hydroxide
0.59	Ammonium oxide, ammonium hydroxide
0.54	Ammonium oxide, ammonium hydroxide
0.52	Ammonium hydroxide

The ratios between the intensities of the lines in any one set stayed the same, when the concentration of ammonia was varied. In no case were lines observed not attributable to any of the three sets.

The growing of a single crystal of ammonium oxide in the capillary was extremely difficult when the mole fraction of ammonia in the liquid was incorrect by only 0.02. This is a strong indication that the oxide does not form solid solutions with either ammonia or ammonium hydroxide. A more accurate proof based on thermal measurements will be given by Giauque and Hildenbrand (1953) elsewhere.

Determination of structure factors.

The single crystal required for the oscillation and Weissenberg photographs was grown in a capillary mounted in the camera by slow lowering of the temperature. From a set of nuclei in the coldest end of the capillary, the one which has its c-axis parallel to the

axis of the capillary very soon grows ahead of the others. As the capillary is placed along the axis of the cylindrical film, a great number of reflections are excluded from observation. Lack of time, however, did not allow us to investigate the possibility of obtaining other orientations of the crystal, e.g., with bent capillaries and growing around the corner.

The intensities of the reflections were measured by visual comparison with known exposure scales. The intensities of the zero, first and second layer Weissenberg photographs were correlated with each other with the help of the oscillation photographs. The comparison with third and fourth layers was made with the help of calculated structure factors.

The measured intensities were corrected with the Lorentz and polarization factors. The values for the Lorentz factor for the higher order layers were those given by G. Tunnell (1939). The complete formula used was:

$$I_{corrected} = I_{obs.} \times \frac{\sin 2\theta}{1+\cos^2\theta} \times \frac{\sqrt{\cos^2\mu - \cos^2\theta}}{\sin\theta},$$

where μ is the angle between the reflecting crystal plane and the axis of rotation.

The choice of space group.

The volume of the unit cell is 377 Å^3. Rough measurements show that the density of liquid ammonium oxide around the melting point is a little over 0.8 g/cm^3 and that the solid has a higher value. If we assume four molecules of ammonium oxide per unit cell, the solid has a density of 0.916 g/cm^3. This is acceptable.

Langseth (1932) has observed in the Raman spectrum of aqueous solutions of ammonia the rotational bands of ammonia. It is also known that the degree of ionization of aqueous ammonia solutions is very small. It is thus very probable that the ammonia and water in ammonium oxide are present as such and not as ammonium ion and hydroxyl or even oxygen ion. This means that the unit cell of ammonium oxide contains four water molecules and eight ammonia molecules.

The observed structure factor magnitudes obeyed the following relations:

1) $F(hk\ell) = F(\bar{h}k\ell) = F(h\bar{k}\ell) = F(hk\bar{\ell})$

2) $F(hk\ell) \neq F(kh\ell)$ in general

3) $F(h0\ell) = 0$ for $h + \ell$ odd

4) $F(0k\ell) = 0$ for k odd

5) $F(00\ell) = 0$ for ℓ odd (from Debye-Scherrer pictures).

The crystal thus is not tetragonal as its powder indexing suggested, but orthorhombic with two axes equal within experimental error.

The space groups D_{2h}^{16} - Pbnm and C_{2v}^{9} - Pbn satisfy the relations between the structure factors mentioned above. The eightfold positions in Pbnm are:

d) x, y, z; $1/2 - x, 1/2 + y, z$; $\bar{x}, \bar{y}, \bar{z}$; $1/2 + x, 1/2 - y, \bar{z}$; $x, y, 1/2 - z$; $1/2 - x, 1/2 + y, 1/2 - z$; $\bar{x}, \bar{y}, 1/2 + z$; $1/2 + x, 1/2 - y, 1/2 + z$.

They require that two ammonia molecules be situated on top of each other in the direction of the c-axis = 5.33Å, while leaving

great open spaces elsewhere in the unit cell.

The special four fold positions,

a) 0, 0, 0; 0, 0, 1/2; 1/2, 1/2, 0; 1/2, 1/2, 1/2.

b) 1/2, 0, 0; 1/2, 0, 1/2; 0, 1/2, 0; 0, 1/2, 1/2.

are not possible for the same reason.

The general four fold positions,

c) $\underline{x}$, $\underline{y}$, 1/4; $\bar{\underline{x}}$, $\bar{\underline{y}}$, 3/4; 1/2 + $\underline{x}$, 1/2 - $\underline{y}$, 3/4;
1/2 - $\underline{x}$, 1/2 + $\underline{y}$, 1/4,

require that $F(hk\ell) = F(hk, \ell + 2)$, except for the dependence of θ on the atomic form factor.

Table 4 of observed intensities shows that this is very nearly the case, and for this reason Pbnm is chosen as the space group for the heavy atoms, oxygen and nitrogen. The reasons for choosing the symmetry of the hydrogens will be given later.

Determination of the nitrogen and oxygen positions.

Approximate $\underline{x}$ and $\underline{y}$ parameters for the heavy atoms were obtained from a Patterson vector diagram using the hk0-reflections. Further refinements were made by trial and error. For these and all following calculations of structure factors, molecular f-curves were used based on the atomic f-values from Internationale Tabellen (1935) and on the assumption that the molecules were rotating with spherical symmetry. This procedure is also used for Table 4, the final summary of observed and calculated structure factors.

When three four fold sets of positions are chosen, there are three possibilities as to which will be assigned to oxygen. The final choice is based on the bond geometry and the arguments that

O-H--N bonds are shorter than N-H--O bonds and that both are more likely in the structure than N-H--N bonds.

For a given set of x and y parameters there are only four independent ways in which z-values can be assigned as either $z = 0.25$ or $z = 0.75$. Consideration of the $hk\ell$-reflections with ℓ odd showed only one way to be acceptable.

Using the observed structure factors, a Fourier refinement was made of the trial structure at $z = 0.25$. The resulting electron density map is shown in Figure 1. The calculated contributions of F(000) (=120) and $F(00\ell)$ (not observed) were included in the calculation of this map. The positions of the heavy atoms were found by graphical interpolation. The electron density is the highest at $x = 0.097$, $y = 0.261$, the position assigned to oxygen. The density there is 11% higher than at $x = 0.411$, $y = 0.131$ and 29% higher than at $x = 0.847$, $y = 0.039$.

A backshift correction was applied to the atomic coordinates calculated from the electron density section. The calculated structure factors used in this correction were multiplied by an empirical temperature factor of the form:

$$A \exp(-B \sin^2\theta/\lambda^2),$$

$$\text{where } B = 2.3 \times 10^{-16} \text{ cm}^2.$$

A comparison of F_{obs} with F_{calc} for the reflections at small θ shows the effect of absorption by the sample and the glass capillary, but no correction for this error was attempted.

Table 2 gives the values of the atomic coordinates. Table 3 and Figure 3 show the distances between the atoms and the angles between the lines connecting them. Table 4 gives the observed and

calculated structure factors. The latter ones are multiplied by the temperature factor given above.

The reliability factor,

$$R = \frac{\sum \left| |F_{obs}| - |F_{calc}| \right|}{\sum |F_{obs}|},$$

calculated from Table 4 for the different layers is: 0.19; 0.19; 0.19; 0.13 and 0.19 for the zero, first, second, third and fourth layer reflections respectively, using only the observed reflections.

Description of the structure.

Figure 2 gives the interpretation of the electron density map in Figure 1. The bulges in the level 1/2 e/Å^3 around the O and one of the two around the N_I atom are considered to be hydrogen atoms. We have no explanation for the second bulge. Thus we assume the water molecules to be completely situated in the mirror planes at $\underline{z}$ = 0.25 and $\underline{z}$ = 0.75 with their hydrogens close to the lines directed to the nearest N_I and N_{II} atoms in the same planes.

The distances given in Table 3 fall into two groups: smaller than 3.25Å and larger than 3.6Å. The former are considered to be bonded, the latter non-bonded. The bonded distances are between nitrogen and oxygen atoms. The nitrogen-nitrogen and oxygen-oxygen distances are all larger than 3.6Å. The only bond possible between nitrogen and oxygen, or more accurately ammonia and water, is a hydrogen bond of either the O-H--N or N-H--O type.

The four neighbors of a N_I atom, all oxygens, are nearly tetrahedrally situated around it as the table of bond angles shows. Two are at a distance of 3.22Å, one at 3.13Å and one at 2.84Å. The

latter has its hydrogen pointed towards the nitrogen and it is assumed that this bond is of the O-H--N type and that the other three are of the N-H--O type. Of the three hydrogens on the ammonia one is situated in the same mirror plane as the nitrogen atom, the others are presumed to be along symmetrical bonds directed to the next planes above and below. Thus the three N-H--O bonds are not equivalent and the one in the plane can be considered as stronger having the shorter distance.

The nearly tetrahedral arrangement in the ammonia molecule of the three hydrogens and the free electron pair (in our case thought to be along the O-H--N bond) is not much different from the situation in gaseous ammonia, Herzberg (1949).

The oxygen atoms have five neighbors, all nitrogens, two at a distance of 3.22Å, one at 3.13Å, one at 2.85Å and one at 2.84Å. The latter two are considered to be O-H--N bonds, the others N-H--O bonds. The angle between the O-H--N bonds is 116°, which is higher than the bond angle in water, but still acceptable. It is possible that this angle is smaller in the low temperature form, as the observations of Giauque and Hildenbrand (1953) indicate that the structure changes in passing the transition region.

The two free electron pairs of the water are supposedly shared by three N-H--O bonds. A similar arrangement has been observed in urea by Wyckoff and Corey (1934).

The ammonia molecules at the N_{II} positions have eleven neighbors, ten of which are at distances of 3.7Å or more, the eleventh, an O-atom at 2.85Å. As mentioned above, this bond is supposed to be of the O-H--N type.

The shape of the heat capacity curve observed by Giauque and Hildenbrand (1953) suggests that at the transition region rotation sets in. The ammonia molecules at the N_{II} form only one bond and thus do not form part of a molecular lattice like the ones at the N_I positions and like the water molecules. The most plausible inference is that the ammonia molecules at the N_{II} positions rotate. This agrees with the fact that the electron density at N_{II} is about 20% lower than at N_I.

The data are inadequate to show the exact positions of the hydrogens in the mirror planes or approximately the positions of those outside these planes.

In the proposed structure the hydrogens of N_I are situated symmetrically with respect to the mirror planes and there is no argument against the same assumption for the average position of the hydrogens of N_{II}. The water molecules are completely in the planes at $\underline{z}$ = 0.25 or 0.75. The space group for the hydrogens is assumed to be the same as for the heavy atoms Pbnm.

The structure thus can be best described as consisting of planar chains of alternating hydrogen bonded ammonia and water molecules, cross linked into a three dimensional lattice by hydrogen bonds with rotating ammonia molecules in the open spaces of the lattice.

Accuracy of the results.

The limits of error in the lattice constants are estimated from the width of the observed lines in the Debye-Scherrer exposures. The $\underline{x}$ and $\underline{y}$ parameters of the heavy atoms were measured independently

from oscillation and from Weissenberg photographs. The final set of coordinates is the result of the Weissenberg series, since this series included over twice as many reflections. The accuracy in the x and y parameters is estimated from the differences between the two results. The highest correction required by the backshift was 0.003.

It is clear that the mathematical accuracy in the z-coordinates is less, as we have observed only four layers in the reciprocal lattice. We feel certain, however, that the heavy atoms are situated in the mirror planes for the following reasons: Fourier refinements of the z parameter by means of data from both the oscillation pictures and the Weissenberg pictures converge to $z \approx 0.25$ and 0.75; the final reliability factors are not bigger for the higher layers; the bond geometry makes it improbable that a heavy atom is outside a mirror plane. It is for these reasons that we have omitted the limits of error in the z-coordinates, and chosen Pbnm as the space group.

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Table 2

Coordinates of the heavy atoms from electron density map in Figure 1.

	x	y	z
N_I	0.411	0.131	0.25
N_{II}	0.847	0.039	0.25
O	0.097	0.261	0.25

Coordinates after application of backshift correction to x and y values, indicating estimated accuracy.

N_I	0.411 ± 0.005	0.131 ± 0.005	0.25
N_{II}	0.845 ± 0.005	0.037 ± 0.005	0.25
O	0.100 ± 0.005	0.261 ± 0.005	0.25

Table 3

Distances between heavy atoms.

The positions are indicated by the x, y and z coordinates between parentheses. The bonded distances are marked by the letters a to h. The following equalities are a result of the symmetry of the crystal: a = f, b = e, c = d, g = h.

	From	To	Distance in Å
a	N_I (0.411; 0.131; 0.250)	O (0.100; 0.261; 0.250)	2.84
b		O (0.400; -0.239; 0.250)	3.13
c		O (0.600; 0.239; 0.750)	3.22
d		O (0.600; 0.239; -0.250)	3.22
		N_I (0.589; -0.131; 0.750)	3.77
e	O (0.600; 0.239; 0.750)	N_I (0.589; -0.131; 0.750)	3.13
f		N_I (0.911; 0.369; 0.750)	2.84
g		N_{II} (0.345; 0.463; 0.750)	2.85
	N_{II}(0.655; 0.537; 0.250)	N_{II} (0.345; 0.463; 0.750)	3.78
		O (0.600; 0.239; 0.750)	3.69
		N_I (0.911; 0.369; 0.750)	3.71
		O (0.900; 0.739; 0.750)	3.77
		N_I (0.589; 0.869; 0.750)	3.90
h		O (0.400; 0.761; 0.250)	2.85

Table 3 (Cont'd)

Bond angles

Angle ab indicates the angle between the bonds a and b.

Compare Figure 3.

Angle	Value in °	
ab	111	tetrahedral arrangement around N_I
ac = ad	110	
bc = bd	107	
cd	112	
ce	73	
cf	125	
cg	80	
ef	114	
fg	116 ~ H-O-H bond angle.	

Table 4

Observed and calculated structure factors.

$hk\ell$	F_{obs}	F_{calc}	$hk\ell$	F_{obs}	F_{calc}
200	6.6	7.1	530	5.4	-4.2
020	4.3	-5.0	350	<2.2	-1.5
210	4.0	-3.2	600	7.5	-6.2
120	2.9	-1.1	060	5.5	-3.7
220	9.4	-9.5	610	<2.3	1.7
310	9.8	-10.2	160	7.0	7.4
130	12.0	15.2	620	8.3	8.3
320	9.5	-7.3	260	<2.4	-1.6
230	16.5	20.6	540	2.5	-3.3
400	16.1	-15.2	450	8.6	-8.5
040	6.1	7.1	630	5.3	-3.9
410	3.3	-3.5	360	6.6	6.5
140	5.6	4.6	710	5.0	5.0
330	7.9	-7.2	170	2.6	-1.1
420	4.0	3.1	550	<2.4	0.1
240	4.0	-1.1	640	<2.4	1.6
430	6.1	5.3	460	3.3	2.2
340	<2.0	0.1	720	3.3	2.6
510	7.0	5.1	270	5.4	5.1
150	3.4	1.7	730	<2.5	-0.1
520	5.0	-4.6	370	<2.5	0.3
250	7.1	-5.9	650	3.3	1.1
440	4.9	-3.8	560	3.3	3.4

Table 4 (Cont'd)

Observed and calculated structure factors

$hk\ell$	F_{obs}	F_{calc}	$hk\ell$	F_{obs}	F_{calc}
800	<2.5	0.1	490	<2.2	1.4
080	5.5	4.6	770	<2.1	3.1
810	<2.4	2.0	10,0,0	<2.1	2.2
180	<2.4	0.6	0,10,0	2.5	-3.8
740	2.4	1.7	860	<2.0	-0.4
470	<2.4	-1.1	680	2.8	-4.0
820	<2.4	-0.4	10,1,0	<1.9	-0.6
280	2.4	2.5	1,10,0	<1.9	0.7
660	3.0	2.0	10,2,0	2.3	-3.2
830	3.4	-2.6	2,10,0	<1.7	-0.3
380	2.4	-1.7	950	<1.6	-0.7
750	<2.4	0.3	590	1.7	1.6
570	<2.4	0.6			
840	<2.4	1.2	101	3.9	-4.7
480	4.0	-2.5	111	3.6	-6.2
910	<2.4	-2.4	021	13.4	-15.1
190	3.0	-2.4	211	16.0	16.9
920	<2.4	2.7	121	13.5	15.3
290	<2.4	1.6	221	3.3	-1.9
850	4.2	6.1	301	18.5	-16.9
580	<2.3	-2.4	311	6.2	3.8
930	<2.3	-0.4	131	10.6	9.3
390	<2.3	1.6	321	10.7	10.5
940	<2.2	1.2	231	<1.7	-1.7

Table 4 (Cont'd)

Observed and calculated structure factors.

hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}
041	5.3	-6.5	631	<2.6	-0.2
411	<1.9	-0.5	361	3.9	4.8
141	2.5	1.3	701	6.9	6.7
331	<1.9	1.5	711	<2.7	1.1
421	5.4	5.2	171	<2.7	-0.2
241	3.3	1.9	551	6.7	5.3
501	8.0	-6.9	641	3.1	-1.7
431	6.9	-6.0	461	<2.7	-0.8
341	2.7	-0.7	721	<2.7	-2.1
511	2.5	2.9	271	<2.7	0.3
151	9.7	-10.4	731	3.9	-4.2
521	3.8	-3.1	371	<2.7	-2.1
251	<2.3	1.3	651	<2.7	-0.7
441	4.2	3.4	561	<2.7	-0.4
531	8.1	-7.3	081	4.0	-4.6
351	5.3	4.8	811	<2.7	-0.6
061	3.1	1.9	181	4.0	-3.4
611	3.7	-2.0	741	<2.7	1.4
161	3.7	2.3	471	<2.7	1.0
621	2.9	1.3	821	<2.7	0.6
261	3.4	3.1	281	<2.7	0
541	<2.6	-0.8	661	3.9	-5.0
451	2.9	-1.1	831	3.9	3.7

Table 4 (Cont'd)

Observed and calculated structure factors.

hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}
381	5.2	-4.3	402	14.4	11.7
751	<2.6	0.5	042	4.8	-5.6
571	<2.6	-1.4	412	2.8	2.8
841	<2.5	-0.3	142	3.5	-3.4
481	<2.5	2.8	332	6.2	5.3
901	4.3	5.0	422	3.0	-2.3
911	<2.4	-0.7	242	3.0	0.8
191	<2.4	-0.9	432	4.5	-4.2
921	<2.3	-0.6	342	<2.5	-0.1
291	<2.3	0.9	512	5.7	-4.9
851	<2.2	0.9	152	3.3	-1.6
581	<2.2	-0.1	522	4.0	4.4
931	3.4	2.7	252	5.3	5.6
			442	3.6	3.6
202	4.3	-5.1	532	4.3	4.0
022	2.7	4.4	352	<2.8	1.2
212	3.0	3.0	602	5.1	5.9
122	2.0	0.5	062	3.9	3.5
222	6.1	7.0	612	<2.9	-1.5
312	6.0	6.8	162	5.1	-6.9
132	6.9	-10.1	622	6.9	-8.0
322	6.5	5.1	262	<2.9	1.3
232	13.5	-15.1	542	<2.9	2.8

Table 4 (Cont'd)

Observed and calculated structure factors.

$hk\ell$	F_{obs}	F_{calc}	$hk\ell$	F_{obs}	F_{calc}
452	6.6	7.3	832	<2.7	2.3
632	4.9	3.4	382	<2.7	1.4
362	5.1	-5.7	752	<2.7	-0.3
712	4.5	-4.6	572	<2.7	-0.6
172	<3.0	1.1	842	<2.5	-1.0
552	<3.0	0	482	3.2	2.6
642	<3.0	-1.5	912	<2.4	2.0
462	<3.0	-1.8	192	<2.4	2.0
722	3.8	-2.3	922	<2.4	-2.2
272	4.4	-4.3	292	<2.4	-1.3
732	<3.0	0.1	852	3.7	-5.1
372	<3.0	-0.3	582	<2.2	2.0
652	<3.0	-0.9	932	<2.1	0.4
562	<3.0	-3.1	392	<2.1	-1.5
802	<2.9	-0.1	942	<1.9	-1.0
082	4.3	-3.9	492	<1.9	-1.1
812	<2.9	-1.6	772	<1.9	-2.5
182	<2.9	-0.6	10,0,2	<1.8	-1.8
742	<2.9	-1.4	0,10,2	<1.8	3.1
472	<2.9	1.0	862	<1.8	0.4
822	<2.9	0.3	682	2.5	3.2
282	<2.9	-2.1			
662	<2.8	-1.8			

Table 4 (Cont'd)

Observed and calculated structure factors.

$hk\ell$	F_{obs}	F_{calc}	$hk\ell$	F_{obs}	F_{calc}
113	3.7	4.0	443	3.1	-2.3
023	7.6	7.6	533	6.2	5.6
213	8.8	-9.0	353	5.0	-3.8
123	7.3	-7.5	063	3.1	-1.5
223	<1.9	1.0	613	3.5	1.6
303	10.2	10.2	163	3.2	-1.7
313	2.5	-2.4	623	<2.8	-1.1
133	6.7	-6.0	263	<2.8	-2.4
323	6.9	-6.8	543	<2.8	0.4
233	<2.2	1.1	453	<2.8	0.7
043	4.1	4.1	633	<2.8	0.1
413	<2.3	0.3	363	3.2	-3.5
143	<2.3	-1.0	703	6.0	-4.9
333	<2.4	-1.0	713	<2.8	-0.7
423	4.5	-3.1	173	<2.8	0.4
243	<2.5	-0.9	553	5.0	-3.8
503	5.0	5.0	643	<2.8	1.4
433	4.2	4.3	463	<2.8	0.6
343	<2.6	0.3	723	<2.7	1.4
513	<2.6	-1.8	273	<2.7	-0.3
153	6.7	7.2	733	3.3	3.2
523	3.6	2.4	373	<2.7	1.5
253	<2.7	-0.9	653	<2.6	0.5

Table 4 (Cont'd)

Observed and calculated structure factors.

hk ℓ	F_{obs}	F_{calc}	hk ℓ	F_{obs}	F_{calc}
563	<2.6	0.3			
083	2.8	3.2			
813	<2.5	0.4	204	3.1	2.6
183	3.0	2.4	024	2.1	-2.5
743	<2.5	-1.0	214	<1.9	-1.7
473	<2.5	-0.7	124	2.2	-0.3
873	<2.4	-0.4	224	3.7	-3.6
283	<2.4	0	314	3.9	-3.8
663	3.3	3.6	134	5.0	5.6
833	2.5	-2.6	324	4.0	-3.0
383	3.1	3.0	234	8.4	8.5
753	<2.2	-0.4	404	9.1	-6.9
573	<2.2	1.0	044	3.0	3.2
843	<2.0	0.2	414	<2.4	-1.6
483	<2.0	-1.8	144	2.5	1.8
903	2.6	-3.2	334	5.1	-3.4
913	<1.9	0.4	424	<2.5	1.2
193	<1.9	0.5	244	<2.5	-0.7
923	<1.8	0.4	434	3.8	2.6
293	<1.8	-0.6	344	<2.6	0.1
853	<1.6	-0.6	514	4.6	2.7
583	<1.6	0.1	154	3.1	1.1
933	2.4	-1.8	524	3.1	-2.7

Table 4 (Cont'd)

Observed and calculated structure factors.

$hk\ell$	F_{obs}	F_{calc}	$hk\ell$	F_{obs}	F_{calc}
254	4.4	-2.9	654	<2.0	0.6
444	<2.6	-1.8	564	<2.0	1.8
534	3.7	-2.4	804	<1.9	0
354	<2.6	-0.9	084	3.0	2.5
604	3.7	-3.4			
064	3.1	-1.8			
614	<2.6	0.8			
164	4.5	4.4			
624	4.6	4.8			
264	<2.6	-0.8			
544	<2.6	-2.1			
454	4.6	-5.1			
634	<2.5	-2.5			
364	3.9	3.9			
714	3.1	3.1			
174	<2.4	-0.8			
554	<2.4	-0.1			
644	<2.3	1.1			
464	<2.3	1.1			
724	<2.3	1.6			
274	3.0	2.8			
734	<2.1	0			
374	<2.1	0.2			

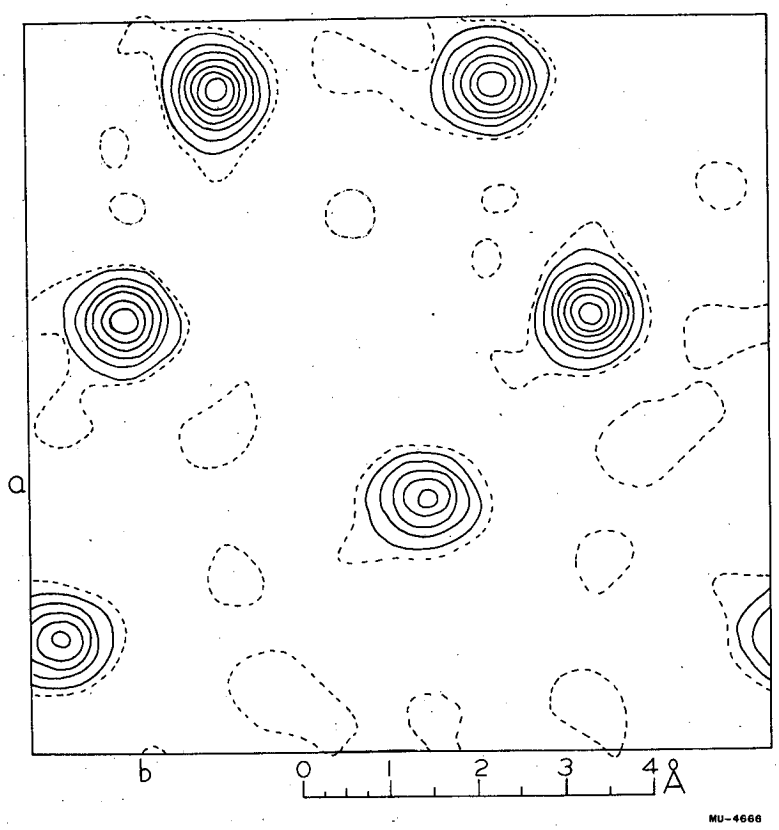

Fig. 1. Electron density map at z = 0.25. The solid intervals are at 1 e/Å^2. The dashed interval is at 1/2 e/Å^2.

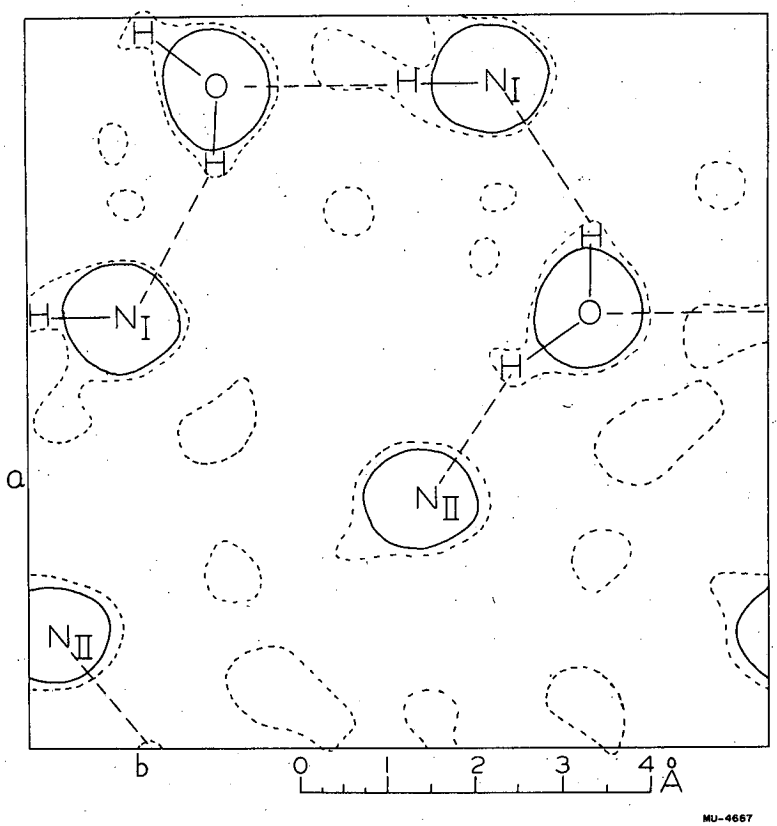

Fig. 2. Interpretation given to the electron density map in Figure 1. All contours higher than 1 e/Å^2 are omitted.

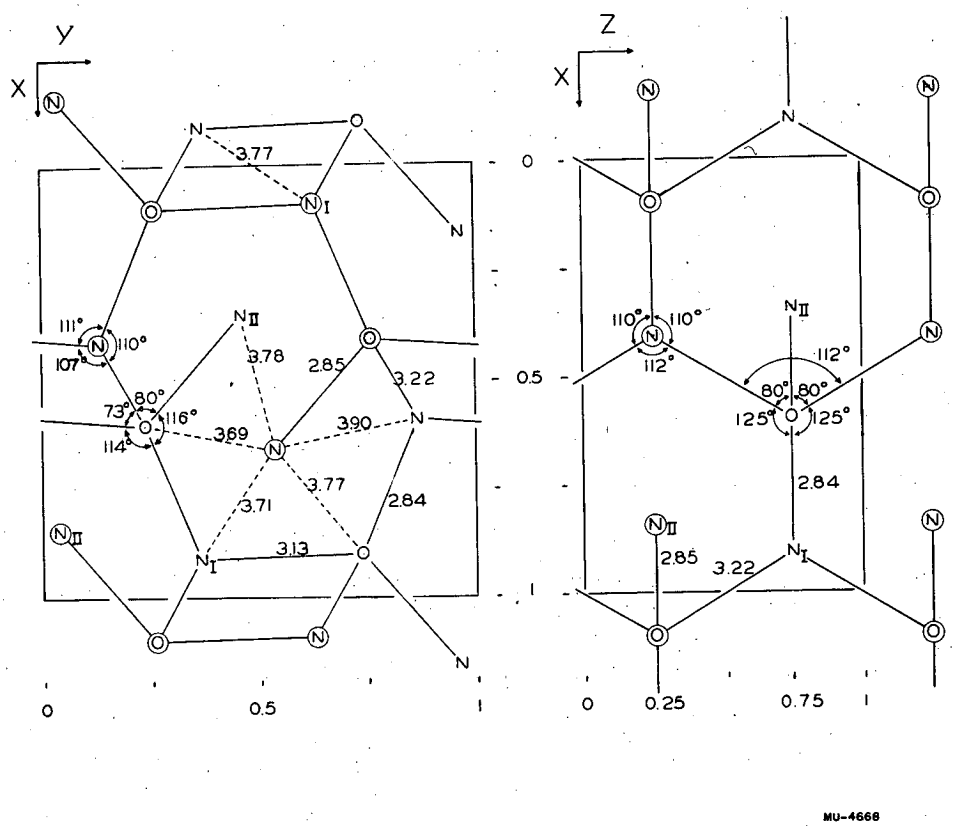

Fig. 3. Distances between heavy atoms and bond angles. The atoms in the plane z = 0.25 are circled. The solid lines are hydrogen bonds.

a. Projection on the plane 001.

b. Bounded projection of y = 0 to y = 0.5 on the plane 001.

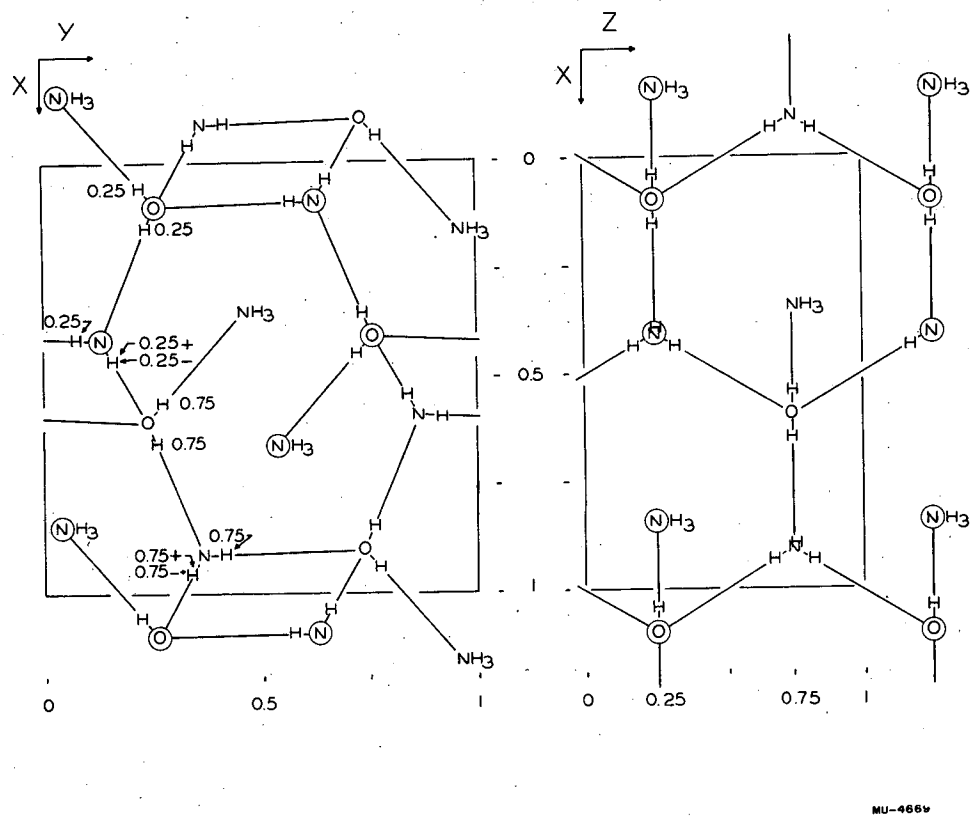

Fig. 4. Positions of the hydrogen atoms. The positions are not given on the same scale as those of the heavy atoms, but are only schematic. The heavy atoms in the plane z = 0.25 are circled.

a. Projection on the plane 001.

b. Bounded projection of y = 0 to y = 0.5 on the plane 010.