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The Crystal Structure of Ammonium Oxide

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At low temperatures ammonia forms two stable hydrates $NH_3.H_2O$ and $2NH_3.H_2O$, ammonium hydroxide and ammonium oxide respectively. The hydroxide is hexagonal with $a = 11{\cdot}21 \pm 0{\cdot}05$ Å and $c = 4{\cdot}53 \pm 0{\cdot}02$ Å at $-95 \pm 10°$ C. The oxide is orthorhombic (space group *Pbnm*) with $a = b = 8{\cdot}41 \pm 0{\cdot}03$ Å and $c = 5{\cdot}33 \pm 0{\cdot}02$ Å at $-95 \pm 10°$ 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.

Introduction

The system ammonia–water has been investigated by many workers (Rupert, 1909, 1910; Smits & Postma, 1911; Postma, 1920; Elliott, 1924; Hildenbrand & Giauque, 1953). All results indicate that the system has two stable hydrates $NH_3.H_2O$ and $2NH_3.H_2O$, 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. Hildenbrand & Giauque (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. Hildenbrand & Giauque (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 sizable 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 & 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. An automatic refilling mechanism governed by a float made possible a series of exposures on one crystal extending over several days. The quantity of cooling gas and the size of the duct were so chosen that frosting-over was not troublesome.

The preliminary investigations and the measurement of the lattice constants were made with the Debye–Scherrer camera of diameter 180 mm.

The structure factors were determined from the oscillation and the Weissenberg photographs of single crystals with film diameter 57·3 mm. 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 Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å).

Preliminary investigations

Samples were prepared with widely varying concentrations, and powder photographs were 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

$$a = 8{\cdot}41 \pm 0{\cdot}03,\; c = 5{\cdot}33 \pm 0{\cdot}02 \text{ Å at } -95 \pm 10^\circ \text{ C}.$$

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

$$a = 11{\cdot}21 \pm 0{\cdot}05,\; c = 4{\cdot}53 \pm 0{\cdot}02 \text{ Å at } -95 \pm 10^\circ \text{ C}.$$

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 assignment of the patterns to ammonium oxide and ammonium hydroxide respectively is strongly supported by the data of Table 1.

Table 1. *Sets of lines observed for various ammonia–water mixtures*

Mole fraction of ammonia in sample	Sets observed in powder pattern
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 has been given by Hildenbrand & Giauque (1953).

Determination of structure factors

The single crystal required for an oscillation or Weissenberg photograph was grown in a capillary mounted in the camera by slow cooling. From a set of nuclei in the colder 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, reflections with l greater than 4 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 by means 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 Tunnell (1939). The complete formula used was:

$$I_{\text{corr.}} = I_{\text{obs.}} \cdot \frac{\sin 2\theta}{1+\cos^2\theta} \cdot \frac{\sqrt{(\cos^2\mu - \cos^2\theta)}}{\sin\theta},$$

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. These data suggest that the ammonia and water in solid ammonium oxide are present as such, and not as ammonium ion and hydroxyl or even oxygen ion. This hypothesis is consistent with our final structure. Thus the unit cell of ammonium oxide contains four water molecules and eight ammonia molecules.

The observed structure-factor magnitudes obeyed the following relations:

(1) $|F|(hkl) = |F|(\bar{h}kl) = |F|(h\bar{k}l) = |F|(hk\bar{l})$,
(2) $|F|(hkl) \neq |F|(khl)$ in general,
(3) $F(h0l) = 0$ for $h+l$ odd,
(4) $F(0kl) = 0$ for k odd,
(5) $F(00l) = 0$ 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* require that two ammonia molecules be situated on top of each other in the direction of the c axis ($= 5{\cdot}33$ Å), while leaving great open spaces elsewhere in the unit cell. The special fourfold positions (a) and (b) (*Internationale Tabellen*, 1935) are not possible for the same reason. The more general fourfold positions:

$$(c) \pm(x, y, \tfrac{1}{4};\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{3}{4}),$$

require that $|F|(hkl) = |F|(h,k,l+2)$, except for the dependence on θ of the atomic form factors. The intensity data show 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 positions chosen for hydrogen, for reasons given below, also have the symmetry *Pbnm*.

Determination of the nitrogen and oxygen positions

Approximate x and y parameters for the heavy atoms were obtained from a Patterson vector diagram using the $hk0$ reflections. Refinements were made by trial and error and finally by calculation of the electron-density section through the mirror plane. For all calculations of structure factors, except some preliminary ones, molecular f-curves were used which were based on the atomic f-values from *Internationale Tabellen* (1935) and on the assumption that the molecules were rotating with spherical symmetry. It is assumed that this approximation does not affect the signs of the F's which are strong enough to be observed.

When three fourfold sets of positions are found, there are three possibilities as to which will be assigned to oxygen. The final choice is based on the bond geometry and the argument that O–H···N bonds and N–H···O bonds are both more likely in the structure than N–H···N bonds. It corresponds to the highest peak in the electron-density section, even when signs are calculated for another choice.

For a given set of x and y parameters there are only four independent ways in which z-values can be assigned as either $z = 0{\cdot}25$ or $z = 0{\cdot}75$. Consideration of the hkl reflections with l odd showed only one way to be acceptable.

The final electron-density section is shown in Fig. 1. The calculated contributions of $F(000)$ and $F(00l)$ (not observed) were included in the calculation of this map. For backshift correction the calculated structure factors were multiplied by an empirical temperature factor of the form $A \exp(-B \sin^2\theta/\lambda^2)$, where $B = 2{\cdot}3\times10^{-16}$ cm^2. The largest backshift correction was 0·003 in the coordinates, and the average about 0·001. The corrected coordinates are listed in Table 2.

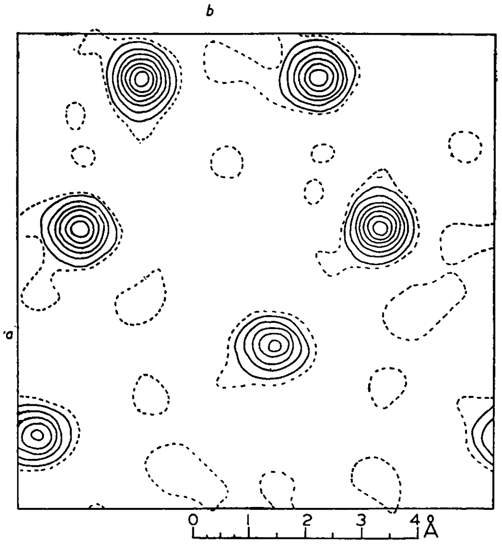

Fig. 1. Electron-density map at $z = 0{\cdot}25$. The solid intervals are at 1 e.Å^{-3}. The dashed interval is at ½ e.Å^{-3}.

Table 2. *Coordinates of the heavy atoms after backshift correction*

	x	y	z
N_I	$0{\cdot}411\pm0{\cdot}005$	$0{\cdot}131\pm0{\cdot}005$	0·25
N_{II}	$0{\cdot}845\pm0{\cdot}005$	$0{\cdot}037\pm0{\cdot}005$	0·25
O	$0{\cdot}100\pm0{\cdot}005$	$0{\cdot}261\pm0{\cdot}005$	0·25

A comparison of F_o with F_c 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 3* gives the observed and calculated structure factors of 347 reflections. The latter are multiplied by the temperature factor given above. The 'reliability factor',

$$R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|,$$

calculated from Table 3 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

Fig. 2 is a clinographic projection of the structure. The interatomic distances, given in Fig. 3, fall into two groups: smaller than 3·25 Å and larger than 3·6 Å. The former, indicated by lines joining atoms in Fig. 2,

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* Table 3, comprising 8 pages of typescript, has been deposited as Document No. 4077 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$ 1·25 for photoprints, or \$ 1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

are considered to indicate hydrogen bonds, the latter no bonds. The structure is seen to consist of a network in three dimensions of alternating nitrogen and oxygen atoms, connected by hydrogen bonds. Half of the ammonia molecules (designated N_{II}) are not part of this network, but are attached to it each by a single hydrogen bond. The shape of the heat-capacity curve observed by Hildenbrand & Giauque (1953) suggests that at the transition region rotation sets in. The most plausible inference is that the ammonia molecules at the N_{II} positions rotate, perhaps with the hydrogen bond as the axis. The electron density found at N_{II} is about 20% lower than at N_I, indicating more violent thermal motion for this nitrogen atom.

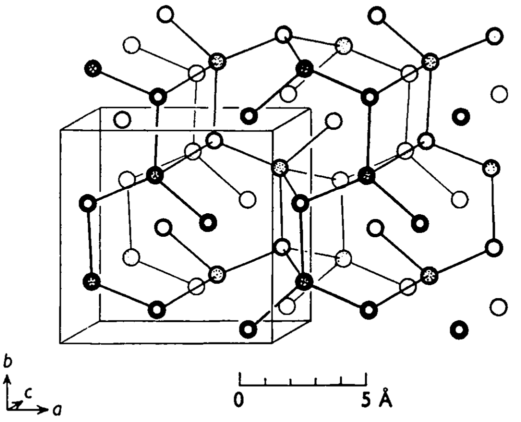

Fig. 2. Structure of ammonium oxide. The shaded atoms are oxygen, and lines joining atoms represent hydrogen bonds.

Only one arrangement of hydrogen atoms in the hydrogen bonds is consistent with the following assumptions: (1) The H-O-H and H-N-H angles in the water and ammonia molecules are close to 109°. (2) The hydrogen atom utilized in each hydrogen bond lies near the axis of the bond. (3) Only one hydrogen atom is present in each hydrogen bond. (4) An electron pair is available reasonably near to each hydrogen bond.

This arrangement of the hydrogen atoms in the bonds is shown in Fig. 4. The three hydrogens of the ammonia molecule at position N_{II} are not determined by hydrogen bonds, and consequently this molecule should be free to rotate, as mentioned above. All the other hydrogen atoms and all unshared valence electrons are involved in hydrogen bonds. The free electron pair of each nitrogen is used to form a single

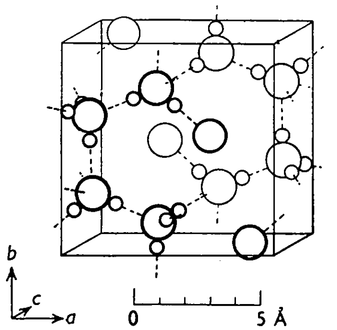

Fig. 4. Assignment of hydrogen atoms to the hydrogen bonds. The hydrogen atoms of the ammonia molecules N_{II}, which are assumed to rotate, are not shown.

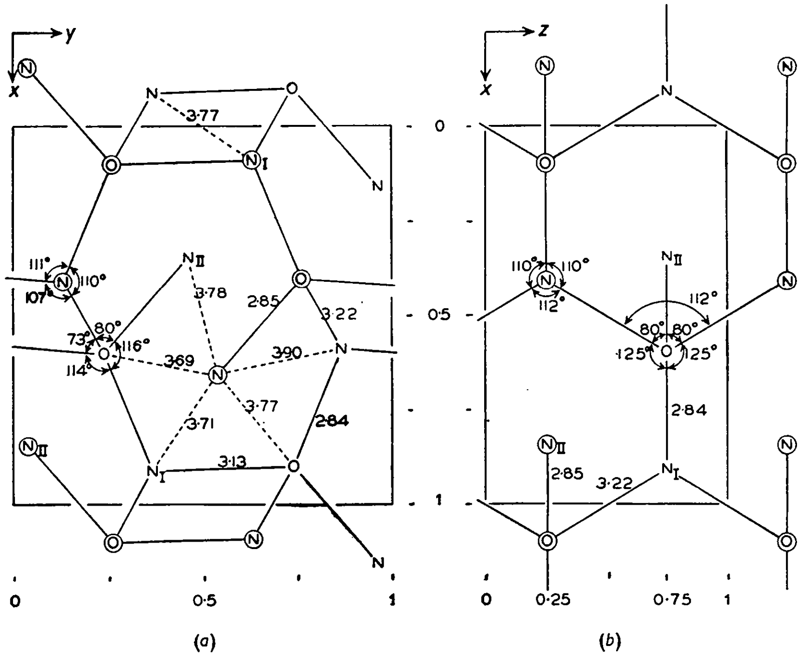

Fig. 3. Distances between heavy atoms and bond angles. The atoms in the plane $z = 0{\cdot}25$ are circled. The solid lines are hydrogen bonds. (a) Projection on the plane 001. (b) Projection on the plane 010 of the cell contents between $y = 0$ and $y = 0{\cdot}5$.

hydrogen bond, with distance 2·84 Å for N_I and 2·85 Å for N_{II}. The two electron pairs of each oxygen atom are utilized to form three bonds with distances 3·13, 3·22 and 3·22 Å. A similar arrangement has been observed in urea by Wyckoff & Corey (1934); in this case each oxygen forms four hydrogen bonds. The fact that the longer hydrogen bonds are those each having only two-thirds of an electron pair lends support to our assignment of hydrogen positions. A disordered arrangement of hydrogens, like that in ice, would be expected to give more nearly equivalent bonds of more nearly equal distance. An ionic structure, with all hydrogen atoms on nitrogen, would also be expected to have more nearly equal hydrogen bond lengths.

The nearly tetrahedral arrangement of the bonds at N_I, with angles from 107° to 112°, is not much different from the situation in gaseous ammonia (Herzberg, 1949). The angle between the $O\text{–}H\cdots N$ bonds at the water molecule 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 Hildenbrand & Giauque (1953) indicate a change in volume, and therefore in structure, when the transition region is passed.

The electron-density section (Fig. 1) shows bulges at the locations of the three hydrogens which lie in the mirror plane, two on oxygen and one on N_I. But an equally large spurious bulge appears on N_I, and these bulges may not be significant.

The location of the hydrogen atoms in the bonds has the symmetry *Pbnm*, and there is no argument against assuming the same symmetry for the average position of the hydrogens of N_{II}.

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 x and 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.

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 confident, 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 $z = 0{\cdot}25$ 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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