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X-ray Evidence for a Single-Bonded Rotating Ammonium Ion in Struvite

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X-ray evidence is presented in favour of a single-bonded rotating ammonium ion in struvite at room temperature. The evidence consists of difference Fourier syntheses, bond lengths and the shape and orientation of the vibration ellipsoid.

Introduction

In the previous paper (Whitaker & Jeffery, 1970, subsequently referred to as WJ) the crystal structure determination of struvite is discussed. During the determination it was concluded that the ammonium ion

was singly bonded to an oxygen atom and the ion then rotated about this bond as axis. This paper presents the evidence for this. The atomic designation is the same as in Whitaker & Jeffery (1970).

Experimental

The structure was solved and refined using anisotropic temperature factors until the residual remained sta-

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tionary at 3.9%. A three-dimensional difference Fourier synthesis was calculated. It was found that the largest peaks on the difference map were not due to the individual hydrogen atoms connected with the water molecules, but were in a more or less continuous shell of electron density around the nitrogen atom (Fig. 1). The standard deviation of the electron density for this diagram is $0.17 \text{ e.}\text{\AA}^{-3}$ (Cruickshank, 1949, 1950).

Although examination of the bc plane through the nitrogen atom [Fig. 1(i)] indicates two peaks which, at first sight, may be thought to be due to hydrogen atoms, closer inspection indicates that the angle subtended by these peaks at the nitrogen atom is approximately $140\text{--}150^\circ$ and this would indicate a very distorted tetrahedron when compared with the normal tetrahedral angle of 109.4° . In addition it is not possible to find two other peaks tetrahedrally related to these two. Thus it would appear that in this structure the ammonium ion cannot be in the orientation of a stationary tetrahedron but apparently must be in a state of static or dynamic disorder.

Because of this disorder it was decided to try and correct for the ammonium group by assuming that it was in a state of statistically uniform disorder and a scattering factor for a rotating ammonium group was calculated (Davis & Whitaker, 1966) using the self-consistent wave functions of Bernal & Massey (1954).

Refinement including the ammonium group

The structure was again refined using the scattering factor for a rotating ammonium ion. In spite of there being no increase in the number of parameters in the refinement, the final residual fell to 3.7%, the standard deviation of electron density to $0.15 \text{ e.}\text{\AA}^{-3}$ and the

standard deviations of the individual parameters improved, on average, by about 10%. The differences in the parameters from the two refinements were not significant (only one parameter out of 69 shifted by more than twice the standard deviation).

A difference Fourier synthesis calculated at this stage showed that most of the electron density shell about the ammonium group position was no longer significant but two peaks remained (Fig. 2). The heights of these two remaining peaks in terms of the standard deviation of electron density, σ , are 2.7σ and 1.4σ .

Thus it would appear that, in struvite, the ammonium group is not only in a state of disorder, but the disorder is not completely random.

However, there is a second possible explanation. The larger peak can be explained by considering the environment of the ammonium group. The atomic configuration around it is a distorted trigonal prism and the interatomic distances at this stage of refinement are given in Fig. 3. It can be seen that the larger peak lies in the direction of the shortest interatomic bond, the nitrogen atom to the oxygen atom O(1), of bond length 2.805 \AA . (Subsequent refinement increased this bond length to $2.818 \pm 4 \text{ \AA}$ (WJ). This alteration of bond length does not alter the substance of the following discussion. Alterations of the other bond lengths are smaller than in this one.)

As Pimentel & McClellan (1960) give $2.88 \pm 0.13 \text{ \AA}$ as the average for nitrogen-oxygen bonds in ammonium compounds, it would appear that hydrogen bonding probably takes place in this bond. Further evidence for this bonding is the height of the peak. This corresponds to $0.36 \text{ e.}\text{\AA}^{-3}$ relative to the zero of the entire Fourier synthesis and may be compared with the values obtained for the hydrogen peaks of the water mole-

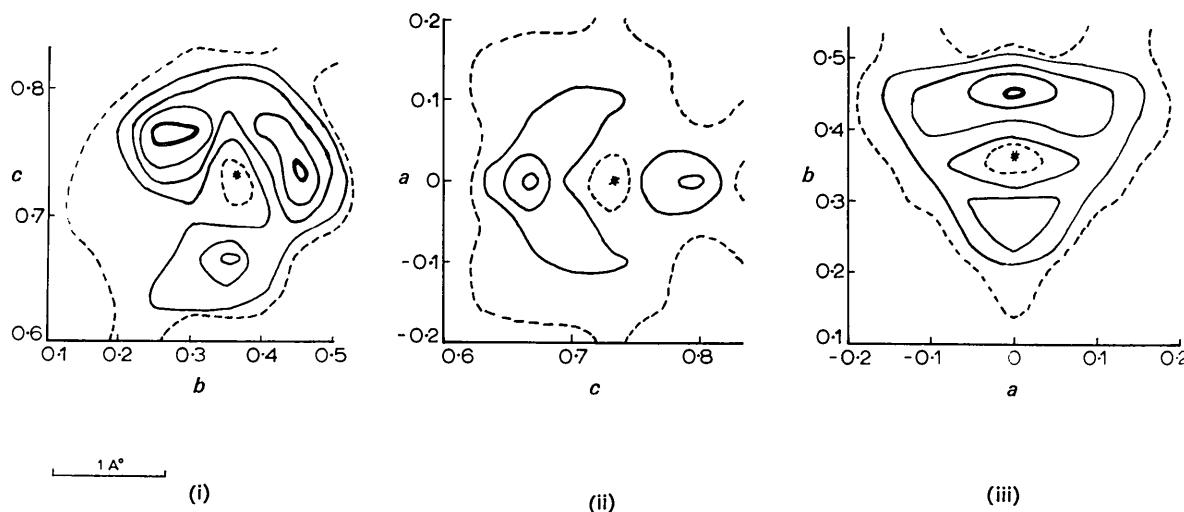


Fig. 1. Sections of a difference Fourier synthesis through the ammonium group when using a nitrogen scattering factor. The contours have been drawn relative to the centre of the nitrogen atom having zero electron density. The contouring is at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$, the $0.1 \text{ e.}\text{\AA}^{-3}$ contour being broken and $0.5 \text{ e.}\text{\AA}^{-3}$ contour heavy. (i) Perpendicular to a , (ii) perpendicular to b , (iii) perpendicular to c . The atomic centre is represented by *.

cules. The peak heights for the latter are in the range 0.32 to 0.36 $e.\text{\AA}^{-3}$ (see previous paper, WJ).

This suggests a second model for the ammonium group which might more nearly fit the results; namely one hydrogen bond between the nitrogen atom and oxygen atom O(1) and the remainder of the ammonium group rotating about this bond as axis. The other peak is not as significant, but may result from uneven rotation of the ammonium group due to the influence of the neighbouring atoms.

Thus it appears that the scattering would be best represented by the scattering of one hydrogen atom at its position along the bond, with the remaining three hydrogen atoms smeared out around an annulus at 109.4° to this bond. (Banyard & March (1961) have already pointed out that in the ammonium group it is the nitrogen atom that is electron deficient).

A scattering factor of this form would be very complicated to calculate and initially it was thought that the scattering factor for a randomly rotating ion would be a fairly good approximation. At a later stage in the investigation it was thought that a better approximation would be obtained by superimposing on the randomly rotating ion the effect of one hydrogen atom at its position on the bond. Both models were refined and compared. The differences between the effects of these models are generally small. As one would expect, the greatest effect is on the ammonium group, for which one position parameter differed by 4.3σ and one vibration parameter by 2.1σ . In addition, for one hydrogen atom [H(8)] a position parameter difference of 3.4σ was observed. All other parameter differences were less than 2σ .

When the refinement excluded this hydrogen atom, and employed a hydrogen temperature factor of 4.0, the residual, weighted residual, and standard deviation of electron density were 2.99%, 2.51% and $0.127 e.\text{\AA}^{-3}$

respectively. When the hydrogen atom was included these became 2.84%, 2.34% and $0.125 e.\text{\AA}^{-3}$, the same hydrogen temperature factor being used. There was thus a general improvement in the residual and weighted residual when the hydrogen atom H(1) was included, but this would be expected from the increase in the number of parameters used in the refinement.

Applying Hamilton's (1965) weighted residual test showed that the improvement in the weighted residual obtained by introducing hydrogen atom H(1) was significant at the $\frac{1}{2}\%$ level. But the same test was applied to compare the weighted residuals from the structures without H(1) but with constant hydrogen temperature factors and with independent refined temperature factors. Using independent refined temperature factors gave a significant improvement of the weighted residual at $\frac{1}{2}\%$ level, in spite of the absurd temperature factors obtained (WJ). Hence it would appear that the weighted residual test is unreliable in the present case. It is, however, interesting to note that introducing the hydrogen atom H(1) and keeping the hydrogen temperature factors constant gives a lower weighted residual than excluding the hydrogen atom and independently refining the hydrogen temperature factors, in spite of the greater number of parameters in the latter structure.

At a very late stage in the refinement, the vibration ellipsoids were calculated for the various atoms (and the rotating NH_4 group) (WJ). That for the ammonium group was, within experimental error, an oblate spheroid. The major axes were considerably greater (80%) than the unique axis and the latter was only 9° from the ammonium oxygen atom O(1) vector. This is what would be expected from a single-bonded ammonium group.

Thus the evidence in favour of a single-bonded ammonium group is the form of a difference Fourier synthesis (Fig. 2), the bond lengths (Fig. 3) and the shape

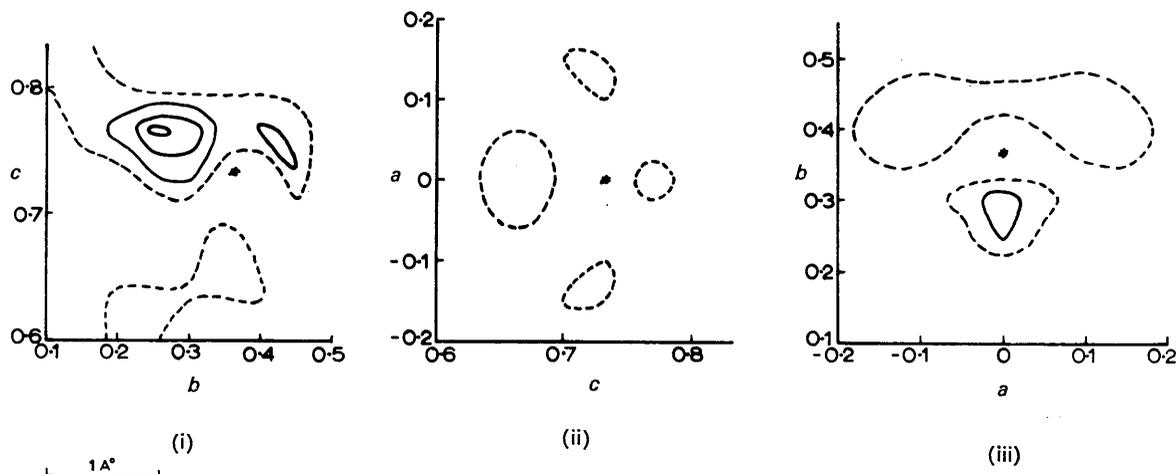


Fig. 2. Sections of a difference Fourier synthesis through the ammonium group when using a randomized ammonium scattering factor. The contouring is the same as in Fig. 1. (i) Perpendicular to a , (ii) perpendicular to b , (iii) perpendicular to c . The atomic centre is represented by *.

and orientation of the vibration ellipsoid, and this would appear to be fairly conclusive.

Discussion

No other X-ray diffraction evidence in the literature, in the form of electron density distributions, has been found concerning the possible bonding and orientation of the ammonium group. This is probably due to the necessity of making very accurate measurements of the diffracted beam intensities in order to detect the relatively small effects involved.

It would appear to be better to make neutron diffraction measurements because of the relatively large scattering factor of hydrogen compared with other

atoms and this is being done by one of us (A.W.). Evidence from neutron diffraction data from other compounds shows that the ammonium group may be either rotating about a fixed axis or about randomly oriented axes, or be fixed in the structure by at least two bonds. Similar evidence has been obtained from infrared spectra.

Probably the most exhaustive data have been obtained for the various phases of ammonium and deuterio-ammonium halides. For some of these phases both infrared and neutron diffraction data exist. The nomenclature, crystal type and transition temperatures of these various phases are given in Table I (after Levy & Peterson, 1953a). It is found that in some phases the ammonium group is tetrahedrally bonded, in others the ammonium group is in a state of disorder, while in others it is probably in a state of single-axis rotation.

Infrared data have shown that the ammonium group is tetrahedrally bonded in ammonium chloride phase III, deuterio-ammonium chloride phase III (Wagner & Hornig, 1950a), ammonium bromide phase III, deuterio-ammonium bromide phase III and phase IV (Wagner & Hornig, 1950b). The conclusions on deuterio-ammonium bromide phase III and phase IV have been confirmed by the neutron diffraction data of Levy & Peterson (1953a).

Evidence that a disordered ammonium group at random in two orientations exists in ammonium chloride phase II and deuterio-ammonium chloride phase II, has been obtained from both infrared data (Wagner & Hornig, 1950a) and neutron diffraction (Levy & Peterson, 1952). The conclusion regarding ammonium chloride phase II has been further confirmed by the electron diffraction studies of Stasova & Vainshtein (Vainshtein, 1964).

The same model fits the infrared data for ammonium bromide phase II and deuterio-ammonium bromide phase II (Wagner & Hornig, 1950b) together with the neutron diffraction data obtained for the latter compound (Levy & Peterson, 1953a).

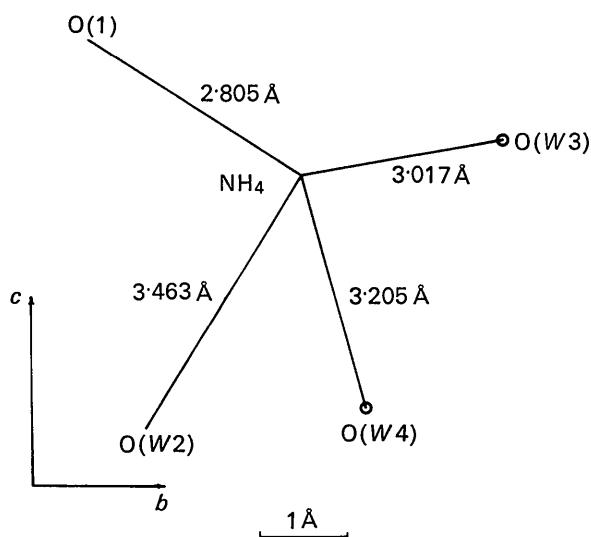


Fig. 3. The neighbouring atoms of the ammonium group in struvite projected on to the mirror plane. Atoms O(1) and O(W2) lie on this plane while the others O(W3) and O(W4) lie in pairs above and below it. The latter have been denoted by small open circles.

Table I. *Nomenclature, crystal type and transition temperatures of the phases of the ammonium and deuterio-ammonium halides*

		184.3°	
NH ₄ Cl:	phase I (NaCl)	←→	phase II (CsCl)
	phase II (CsCl)	←→	phase III (CsCl)
		175°	
ND ₄ Cl:	phase I (NaCl)	←→	phase II (CsCl)
	phase II (CsCl)	←→	phase III (CsCl)
		137.8°	
NH ₄ Br:	phase I (NaCl)	←→	phase II (CsCl)
	phase II (CsCl)	←→	phase III (tetragonal)
		~125°	
ND ₄ Br:	phase I (NaCl)	←→	phase II (CsCl)
	phase II (CsCl)	←→	phase III (tetragonal)
	phase III (tetragonal)	←→	phase IV (CsCl)
		-17.6°	
NH ₄ I:	phase I (NaCl)	←→	phase II (CsCl)
	phase II (CsCl)	←→	phase III (tetragonal)
		-41.6°	

Infrared evidence indicates that in the case of ammonium iodide phase I (Plumb & Hornig, 1953) the ammonium group is in a state of single-axis rotation. There is some measure of support for this idea from neutron diffraction data of deuterio-ammonium bromide phase I and deuterio-ammonium iodide phase I (Levy & Peterson, 1953b), the data being in agreement with any of three models, two static and the other the single-axis rotation model.

Generalizing from these results it would appear that single-axis rotation of the ammonium group exists in the high temperature forms of the ammonium halides but not in the low temperature structures. This is feasible because in the low temperature forms there may not be sufficient energy to break the hydrogen bonding. An alternative point of view is that single-axis rotation of the ammonium group only occurs in the crystallographically less stable phase, since in the high temperature forms the lattice is about to break up on melting. Struvite fits into with this generality as it is unstable at room temperature (Lonsdale & Sutor, 1966; Whitaker, 1968).

However, it is not correct to conclude that in all unstable compounds the ammonium group is partially or wholly rotating. From infrared data, Waddington (1958) concluded that the ammonium group was locked in position in both ammonium azide (NH_4N_3) and ammonium nitrite (NH_4NO_2), and neither of these are stable at room temperature. Waddington (1958) came to the same conclusion for ammonium hydrogen difluoride (NH_4HF_2), ammonium cyanate (NH_4NCO), ammonium thiocyanate (NH_4NCS) and ammonium nitrate (NH_4NO_3), while in the cases of ammonium perchlorate (NH_4ClO_4), ammonium borofluoride (NH_4BF_4), ammonium tetraphenylborate [$\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4$] and ammonium hexafluorophosphate (NH_4PF_6), the ammonium group is rotating. He also concluded that for ammonium fluorosulphate ($\text{NH}_4\text{SO}_3\text{F}$) and ammonium methanesulphonate ($\text{NH}_4\text{SO}_3\cdot\text{CH}_3$) the ammonium group 'is not completely locked in the lattice', although he does not state what he means by this phrase. His conclusion regarding ammonium perchlorate has since been confirmed by the neutron diffraction results of Smith & Levy (1962).

An electron diffraction study of the high temperature phase of cryptohalite [$(\text{NH}_4)_2\text{SiF}_6$] (Vainshtein, 1964)

indicated that in this phase there are six equally probable orientations of the ammonium group.

Thus it would appear that the ammonium group may in general either be stationary, or be rotating with random axial direction or have single-axis rotation, or be in a state of static disorder. The present results appear to be the only X-ray diffraction evidence in favour of the ammonium group having rotation about a single axis. It would appear that in the present, admittedly favourable, case, it is possible for X-ray diffraction techniques to give information about the ammonium group which, in the past, has only been obtained by other methods.

Acknowledgements appear in the previous paper.

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