

## Salt Hydrates. VIII. The Crystal Structures of Sodium Ammonium Orthochromate Dihydrate and Magnesium Diammonium Bis(Hydrogen Orthophosphate) Tetrahydrate and a Discussion of the Ammonium Ion

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The salt  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$  crystallizes in space group  $P2_12_12_1$ ,  $Z=4$ ,  $a=8.413$  (5),  $b=13.039$  (8), and  $c=6.219$  (4) Å and is isostructural with  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . The crystal structure was refined, using three-dimensional counter X-ray diffraction data, to  $R=0.132$  for 642  $F_{\text{obs}}$ . The Na ions are coordinated octahedrally by four water molecules and two chromate oxygen atoms. The octahedra share faces to form columns of composition  $[\text{Na}(\text{OH}_2)_2\text{OCrO}_3]^-$ . These columns are bonded to each other by hydrogen bonds donated by the water molecules and the ammonium groups. The salt should be formulated as  $[\text{Na}(\text{OH}_2)_2\text{OCrO}_3] [\text{NH}_4]$ . The compound  $\text{Mg}(\text{NH}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$  crystallizes in  $Pbca$ ,  $Z=8$ ,  $a=11.49$  (2),  $b=23.66$  (6), and  $c=8.62$  (1) Å. The structure was solved by the application of the direct method and refined to  $R=0.073$  for 307 three-dimensional counter X-ray diffractometer data. Its characteristic feature is the isolated group  $\text{Mg}(\text{OH}_2)_4(\text{OPO}_2\text{OH})_2$ , consisting of an Mg coordination octahedron and two tetrahedral  $\text{PO}_3\text{OH}$  groups in *trans* position to the Mg ion. The groups are hydrogen bonded to each other through bonds donated by the hydroxyl groups, the water molecules, and the ammonium ions. The compound can be formulated as  $[\text{Mg}(\text{OH}_2)_4(\text{OPO}_2\text{OH})_2] [\text{NH}_4]_2$ . The ammonium ions in both structures are five-coordinated. A survey of  $\text{NH}_4$  salts shows that the coordination number (C.N.) of the  $\text{NH}_4$  ion can vary from four to nine. When the C.N. is small (4 or 5) the hydrogen-bonding tendency of the  $\text{NH}_4$  ion is prevalent, when it is larger (7 to 9) its pseudo alkali character dominates. This double role may be responsible for the tendency of  $\text{NH}_4$  salts to exhibit transitions with a change in C.N. and hydrogen-bonding arrangements. The length of the N-H---O bonds can be predicted by the empirical relation:  $d(\text{N-H---O}) = (2.21 + 0.34p_{\text{O}})$  Å, where  $p_{\text{O}}$  is the electrostatic bond strength received by the acceptor oxygen atom. The effective radii of  $\text{NH}_4^+$  against oxygen atoms are 1.49 [4], 1.59 [5], 1.61 [6], 1.65 [7], 1.66 [8], and 1.69 [9] Å, where the C.N. is given in square brackets. The  $\text{NH}_4^+$  ion thus has an effective radius which is halfway between the radii of  $\text{Rb}^+$  and  $\text{Cs}^+$  ions, and is about 0.2 Å larger than for the  $\text{K}^+$  ion.

### Introduction

The ammonium ion,  $\text{NH}_4$ , forms a considerable number of oxy-salts which are isostructural with the corresponding potassium salts. It would be understandable if the coordination number of ammonium against oxygen in these compounds were as high as eight, because the potassium and ammonium ions are of comparable size. The ammonium ion also has a tendency in some of its compounds to be four-coordinated. This is understandable because of its facility to form four hydrogen bonds to suitable acceptor atoms. The two tendencies obviously are not easily reconcilable. To shed further light on the crystal chemistry of the  $\text{NH}_4$  group and of the N-H---O bonds formed by the ammonium ion, the crystal structures of  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  have been determined.

The chromate salt is isostructural with  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , the crystal structure of which has been determined by Corazza, Sabelli & Giuseppetti (1967). We had hoped to make a detailed comparison of N-H---O and O-H---O bond lengths in a chromate and a sulfate salt. This was not possible because unfortunately the quality of the crystals grown by us precluded a high-precision refinement.

$\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  has been synthesized and characterized by Frazier, Lehr & Smith (1963), who assumed that it is the synthetic equivalent of the mineral schertelite. Schertelite,  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , has been found by MacIvor (1907) in the bat guano of the Skipton Caves, near Ballarat, Victoria, Australia. According to Mrose (1972) it is associated with struvite ( $\text{MgNH}_4 \cdot 6\text{H}_2\text{O}$ ), newberyite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ), and dittmarite ( $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ).

Since MacIvor did not give any data on schertelite except its chemical composition, it is not certain that the  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  described by Frazier *et al.* (1963) really is the synthetic counterpart of schertelite or a different polymorph.

The previous paper in this series is by Tillmanns & Baur (1971).

### Experimental

Crystals of  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$  were prepared at room temperature by slow evaporation of a solution obtained by dissolving  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and  $\text{Na}_2\text{CO}_3$  in molar 1:1 ratio in water. The crystals were yellow and usually revealed a rough surface on microscopic examination. The diffraction peaks recorded on the diffractometer for several different crystals were broad

Table 1. *Crystal data and details of data collection*

	NaNH <sub>4</sub> CrO <sub>4</sub> ·2H <sub>2</sub> O	Mg(NH <sub>4</sub> ) <sub>2</sub> (PO <sub>3</sub> OH) <sub>2</sub> ·4H <sub>2</sub> O
<i>a</i>	8·413 (5) Å*	11·49 (2) Å
<i>b</i>	13·039 (8)	23·66 (6)
<i>c</i>	6·219 (4)	8·62 (1)
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>Pbca</i>
<i>V</i>	682 Å <sup>3</sup>	2342 Å <sup>3</sup>
F.W.	193·0	324·2
<i>Z</i>	4	8
<i>D<sub>x</sub></i>	1·879 g.cm <sup>-3</sup>	1·84 g.cm <sup>-3</sup>
<i>D<sub>m</sub></i>	1·842 g.cm <sup>-3</sup> †	1·82 g.cm <sup>-3</sup> ‡
Radiation, Ag <i>K</i> α	0·56083 Å	0·56083 Å
μ(Ag <i>K</i> α)	9·2 cm <sup>-1</sup>	2·6 cm <sup>-1</sup>
Diameter of crystal	0·04–0·06 cm	0·02 cm
μ <i>R</i>	0·180–0·195	0·026
Number of octants collected	7	8
Number of nonunique <i>I<sub>hkl</sub></i> measured	5915	3400
Number of unique <i>I<sub>hkl</sub></i>	782	451
Number of <i>I<sub>hkl</sub></i> = 0	140	144
Number of <i>I<sub>hkl</sub></i> used in refinement	642	307
2θ(max)	40·0	25·0
sin θ(max)/λ	0·610 Å <sup>-1</sup>	0·386 Å <sup>-1</sup>

\* Throughout this paper the number in parentheses indicates the estimated standard deviation in units of the least significant digit.

† Mellor (1948).

‡ Frazier *et al.* (1963).

and in a few cases showed peak-splitting. The crystal finally selected for intensity measurements did not show splitting of peaks. It was rod-like in shape with a length of 0·6 mm and a diameter of 0·4 mm. The data were collected on an automatic diffractometer using procedures as described in detail by Baur & Khan (1970); see also Table 1. Although the crystal was enclosed in a kerosine-filled glass capillary it still decomposed, and lost 5% of its scattering power during the time of data collection. The decomposition was monitored by the periodic measurement of three standard reflections. The intensities were corrected accordingly. The equivalent reflections and their standard deviations were averaged after applying the Lorentz-polarization corrections. The absorption effect was small, although slightly anisotropic due to the non-spherical shape of the crystal. Since the crystal was mounted with the longer dimension along the goniometer head axis, the effective range of μ*R* for the measured reflections was 0·180–0·195. This amounts to a maximum systematic error of ±1·2% in the intensities and therefore the absorption correction was neglected.

Starting with the values of the coordinates reported by Corazza *et al.* (1967) for NaNH<sub>4</sub>SO<sub>4</sub>·2H<sub>2</sub>O, the parameters of the chromate salt were refined with isotropic temperature factors to an *R* of 13·2% (Table 2). A closer examination of the observed and calculated structure factors in Table 3 indicates clearly a need for a refinement with anisotropic temperature factors. Such a refinement had a marked effect on *R* which converged to 8·5%. However the anisotropic temperature factors *B*<sub>11</sub>, *B*<sub>22</sub>, and *B*<sub>33</sub> for all the atoms had values approximately in the ratio 11:4:1. This ratio cannot be explained by the neglected anisotropic absorption correction. It is also physically implausible that all

atoms are vibrating in the same crystallographic direction. It has to be assumed, therefore, that this effect is a result of inherent anisotropic mosaic defects of the specimen. Hence the results of the refinement with anisotropic temperature factors were considered unacceptable. The difference between the two refinements is small, because the positional parameters from the refinement with isotropic and with anisotropic temperature factors agree on the average within 1σ. In view of the overall poor accuracy of the structure determination, no attempt was made to locate the hydrogen atoms.

Table 2. NaNH<sub>4</sub>CrO<sub>4</sub>·2H<sub>2</sub>O, *positional parameters in fractions of the cell edges and thermal parameters with their standard deviations*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Cr	0·0970 (5)	0·1281 (3)	0·3832 (7)	1·9 (1) Å <sup>2</sup>
Na	0·261 (1)	0·490 (1)	0·900 (2)	2·5 (2)
O(1)	0·081 (2)	0·206 (1)	0·183 (3)	3·1 (4)
O(2)	0·082 (2)	0·189 (1)	0·607 (3)	3·6 (4)
O(3)	0·272 (2)	0·072 (1)	0·375 (3)	4·0 (4)
O(4)	0·039 (2)	0·539 (1)	0·134 (3)	2·9 (4)
O( <i>W</i> 5)	0·197 (2)	0·633 (1)	0·671 (3)	2·8 (3)
O( <i>W</i> 6)	0·090 (2)	0·404 (1)	0·654 (2)	2·4 (3)
N	0·156 (2)	0·856 (2)	0·376 (4)	2·6 (4)

Crystals of synthetic schertelite, Mg(NH<sub>4</sub>)<sub>2</sub>(PO<sub>3</sub>OH)<sub>2</sub>·4H<sub>2</sub>O, were supplied by Dr J. R. Lehr. Details of the intensity data collection and the crystal data are given in Table 1. The experimental procedure was the same as that for NaNH<sub>4</sub>CrO<sub>4</sub>·2H<sub>2</sub>O, but it was improved by using crystal-monochromatized radiation. The measured intensities were corrected for Lorentz-polarization effects and the absorption correc-

tions were neglected. The space group as determined by Frazier et al. (1963) was confirmed. The crystal structure was determined by direct methods and was refined using isotropic temperature factors (see Table 4). Of the 119 signs originally determined and used in the E map, 109 were found to be correct after the structure was refined. All the atoms lie on general eightfold positions. Because of the small number of observed data no attempt was made either to refine the structure with anisotropic temperature factors or to locate the hydrogen atoms. The final R is 7.3% for the structure factors reported in Table 5.

Table 3. NaNH4CrO4.2H2O, observed and calculated structure factors (x2) and sigma's (x10) used in the least-squares refinement

Table with columns for h, k, l, F\_o, F\_c, S.I.G., and F\_o/F\_c, S.I.G./F\_o. It lists observed and calculated structure factors and sigma values for various reflections.

Table 4. Synthetic schertelite, Mg(NH4)2(PO3OH)2.4H2O, positional and thermal parameters with their standard deviations

Table with columns for atom label (P(1), O(1), Mg, etc.), x, y, z coordinates, and B (thermal parameter) in Angstroms squared.

Table 5. Mg(NH4)2(PO3OH)2.4H2O, observed and calculated structure factors (x2) and sigma's (x10) used in the least-squares refinement

Table with columns for h, k, l, F\_o, F\_c, S.I.G., and F\_o/F\_c, S.I.G./F\_o. It lists observed and calculated structure factors and sigma values for various reflections.

The various programs used during this work are those listed by Baur & Khan (1970). In addition, a package of four programs (FAME, MAGIC, LINK & SYMPL) written by R. B. K. Dewar and Allen Stone for the application of the symbolic addition method of Karle & Hauptman was used to obtain an E map.

Description and discussion of the crystal structures

NaNH4CrO4.2H2O

Each Na atom is octahedrally coordinated by four water molecules and two oxygen atoms of the CrO4

group. The neighboring octahedra share faces to form columns extending parallel to the [001] direction (Fig. 1). The Na atoms are situated close to three of the six screw axes running parallel to the  $c$  axis in each unit cell. As a result, the sodium-oxygen columns illustrate clearly the  $2_1$  symmetry. These columns of composition  $[\text{Na}(\text{OH}_2)_2\text{O}]$  are the building blocks of the structure. Each chromate group is bonded directly to only one of these columns. The connection between the neighboring columns is provided by hydrogen bonds from the water molecules and from the  $\text{NH}_4$  groups to the chromate tetrahedra. Looking along the  $c$  axis (Fig. 2), the  $\text{Na}(\text{OH}_2)_2\text{O}$  columns display hexagonal packing, while the space between the columns is filled with the  $\text{CrO}_4$  and  $\text{NH}_4$  groups. The compound can therefore be formulated as  $[\text{Na}(\text{OH}_2)_2\text{OCrO}_3]^- [\text{NH}_4]^+$ , consisting of the columnar anions and of ammonium groups linked by hydrogen bonds.

Stephens & Cruickshank (1970) have recently refined the structure of  $(\text{NH}_4)_2\text{CrO}_4$ . The average Cr-O distances as determined by them before and after correct-

ing for librational thermal motion are, respectively, 1.645 and 1.658 Å. Within the experimental error the uncorrected value agrees with the average Cr-O length determined in  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$  [Table 6(a)]. The Na-O distances within the column  $\text{Na}(\text{OH}_2)_2\text{O}$  are equal for the chromate and the sulfate compound (Corazza *et al.*, 1967) within twice the combined standard deviations of the two determinations [Table 6(b)]. Therefore, the  $c$  cell constants of both compounds are nearly identical: 6.232 (8) Å in the sulfate, 6.219 (4) Å in the chromate. The hydrogen bonding proposed by us for the chromate [Table 6(c), Fig. 2] agrees with the one found in the sulfate compound. Both water molecules take part in hydrogen bonding and are coordinated tetrahedrally by the acceptor atoms and two sodium atoms. The average values of the four O-H...O bonds are identical within the limits of error in both compounds. Easwaran (1966) has determined the lengths and directions of the H-H vectors in  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  at room temperature from nuclear magnetic resonance (n.m.r.) studies. Because of the

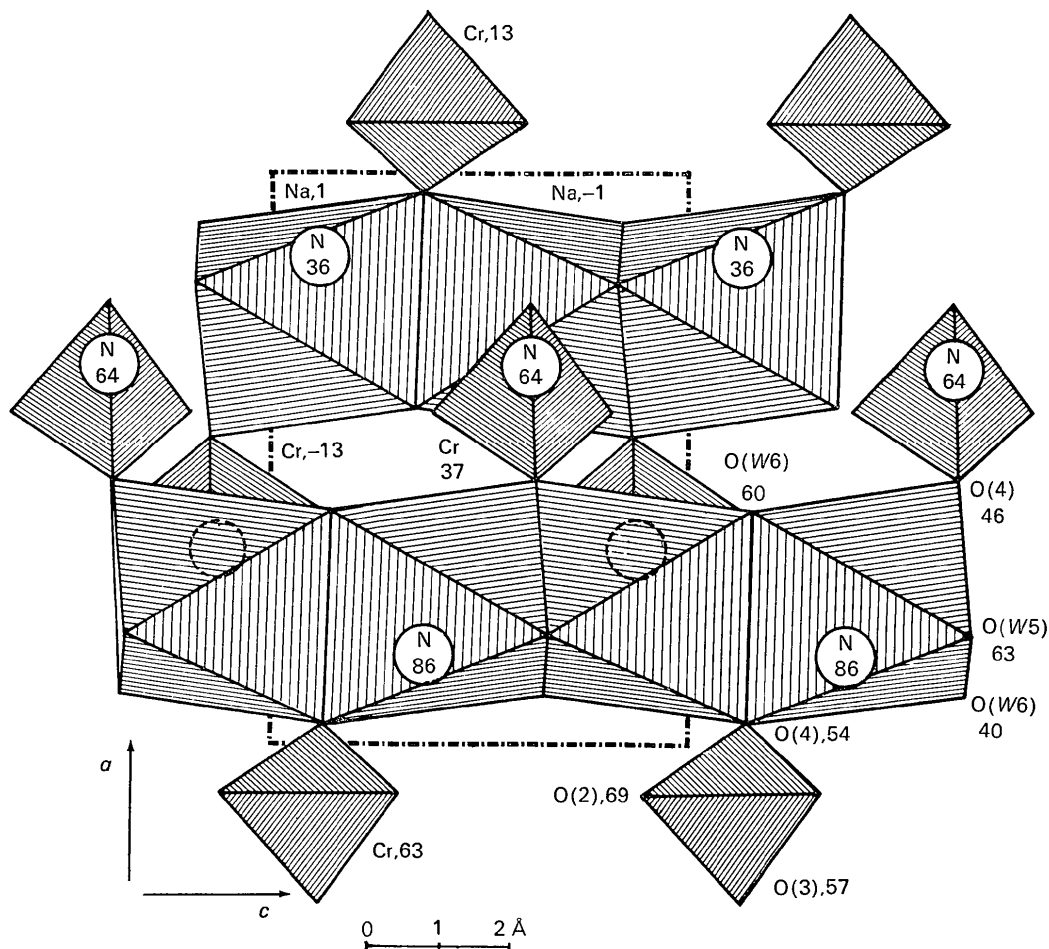


Fig. 1.  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ , view parallel [010]. Polyhedral representation, except for the nitrogen atoms of the ammonium ions, which are shown as circles. The heights of some of the central atoms of some of the polyhedra and of selected oxygen and nitrogen atoms are indicated in fractional coordinates  $\times 100$ .

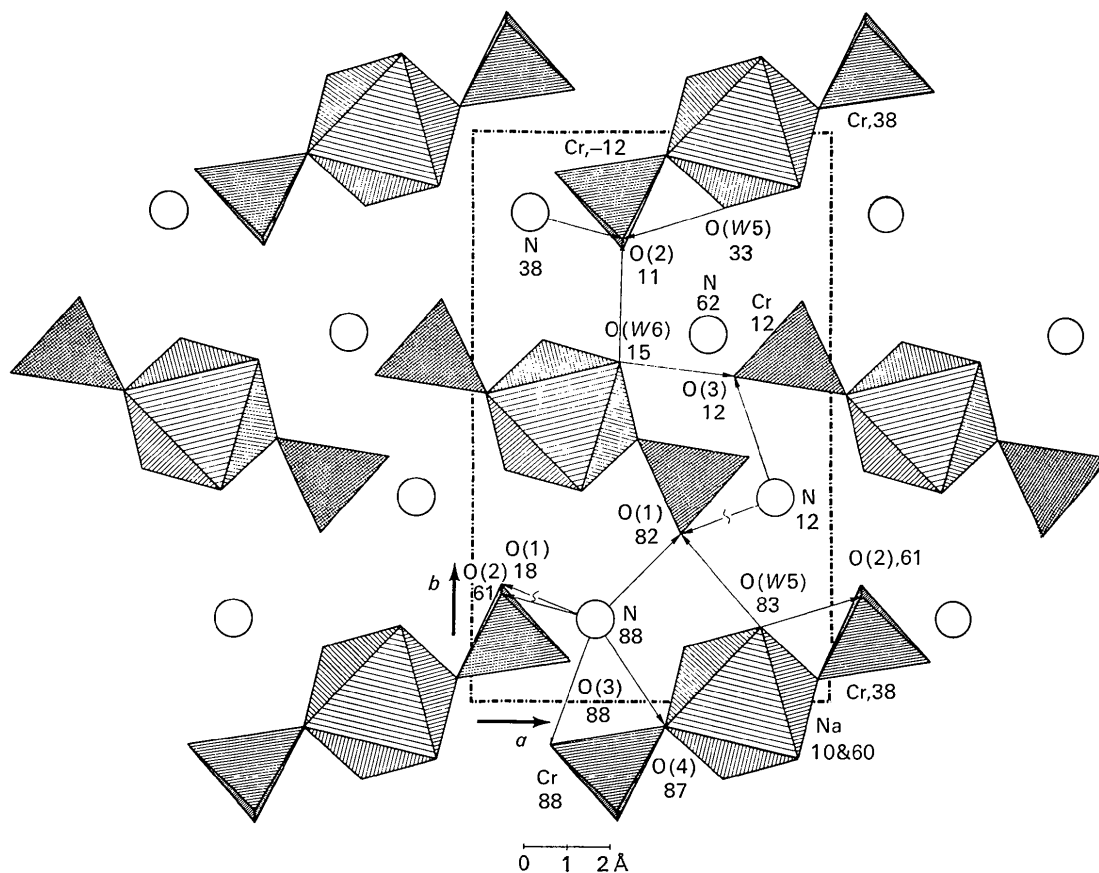


Fig. 2.  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ , view parallel [001]. The hydrogen bonds and the ammonium ion coordination are shown as arrows pointing toward the acceptor atoms. The complete hydrogen bonding coordination of every oxygen atom is displayed once.

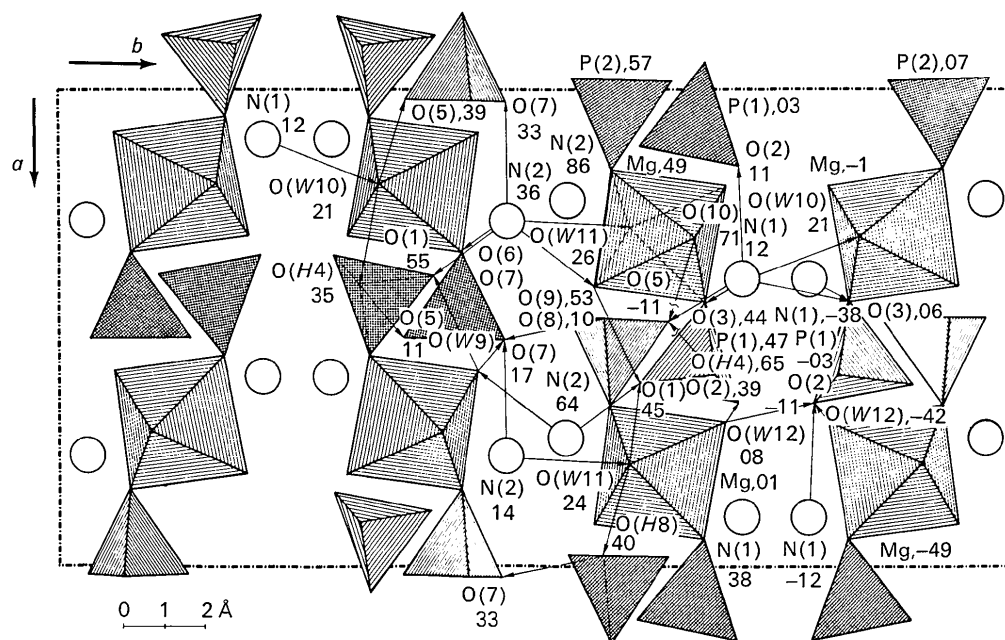


Fig. 3.  $\text{Mg}(\text{NH}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , view parallel [001].

close similarity between the two structures, Easwaran's results can be assumed to be also true for  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ . The n.m.r. study showed that the two crystallographically independent proton-proton vectors are both in the plane (001) at an angle of  $\pm 50^\circ$  from the **b** direction. The X-ray structure determinations show that the two water oxygen atoms are approximately in the same (001) plane. The vector  $\vec{O}_{\text{acc}} - \vec{O}_{\text{acc}}$  between the two oxygen atoms which serve as acceptor atoms to a water molecule, can be expected

Table 6. *Interatomic distances and bond angles in  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$*

The values for the sulfate compound are based on the work by Corazza *et al.* (1967).

(a)  $\text{CrO}_4$  group

	Chromate
Cr-O(1)	1.61 (2) Å
Cr-O(2)	1.61 (2)
Cr-O(3)	1.65 (2)
Cr-O(4)	1.63 (2)
Average of 4 Cr-O distances	1.625
O(1)-O(2)	2.65 (3)
O(1)-O(3)	2.66 (3)
O(1)-O(4)	2.65 (3)
O(2)-O(3)	2.64 (3)
O(2)-O(4)	2.67 (3)
O(3)-O(4)	2.65 (3)
O(1)-Cr-O(2)	110 (1)°
O(1)-Cr-O(3)	109 (1)
O(1)-Cr-O(4)	110 (1)
O(2)-Cr-O(3)	108 (1)
O(2)-Cr-O(4)	111 (1)
O(3)-Cr-O(4)	108 (1)
Average of 6 O-Cr-O angles	109.5

Table 6 (cont.)

(b) Na-coordination octahedron

	Chromate	Sulfate
Na-O(4)	2.39 (2) Å	2.382 (11) Å
O(4)	2.46 (2)	2.453 (10)
O(W5)	2.35 (2)	2.341 (9)
O(W5)	2.41 (2)	2.404 (8)
O(W6)	2.38 (2)	2.419 (9)
O(W6)	2.45 (2)	2.468 (9)
Average of 6 Na-O distances	2.407	2.41 <sub>1</sub> (10)
Range of O-Na-O angles		
close to 90°	81.0-106.3°	81.0-112.2°
Range of O-Na-O angles		
close to 180°	170.0-172.4	165.3-169.1
Closest approach of Na atoms	3.12 <sub>6</sub> Å	3.15 <sub>1</sub> Å
Range of O-O distances within the Na-coordination octahedron	3.12-3.79 Å	3.12-3.92 Å
	4.74-4.83	4.71-4.87

(c) Hydrogen bonding geometry

Water molecules

O(W5)→O(1)	2.81 (2) Å	2.783 (9) Å
O(W5)→O(2)	2.82 (2)	2.757 (14)
O(W6)→O(2)	2.82 (2)	2.816 (8)
O(W6)→O(3)	2.70 (2)	2.762 (10)
Average of 4 O(W)-H...O bonds	2.78 <sub>7</sub>	2.78 <sub>0</sub>
O(1)-O(W5)-O(2)	110.2 (7)°	110.0 (4)°
O(2)-O(W6)-O(3)	95.0 (7)	90.2 (3)

$\text{NH}_4$  group

N→O(1)	2.81 (3) Å	2.821 (10) Å
N→O(2)	2.83 (3)	2.908 (16)
N→O(4)	2.90 (3)	3.009 (9)
N→O(3)	2.98 (3)	2.973 (9)
N→O(1)	3.03 (3)	3.004 (16)
Range of angle O(3)-N-O	53-153°	47-146°
Range of angle [O(4)+O(3)]-N-O	75-127	81-123

Table 7. *Interatomic bond distances and bond angles in  $\text{Mg}(\text{NH}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$*

(a)  $\text{PO}_4$  groups

P(1)-O(1)	1.52 (3) Å		
P(1)-O(2)	1.52 (3)		
P(1)-O(3)	1.55 (3)		
P(1)-O(H4)	1.66 (3)		
Mean of 3 short bonds	1.52 <sub>7</sub>		
Mean of 4 bonds	1.56 <sub>0</sub>		
O(1)-O(2)	2.55 (3) Å	O(1)-P(1)-O(2)	114 (1)°
O(1)-O(3)	2.54 (3)	O(1)-P(1)-O(3)	112 (1)
O(1)-O(H4)	2.55 (3)	O(1)-P(1)-O(H4)	107 (1)
O(2)-O(3)	2.61 (3)	O(2)-P(1)-O(3)	117 (1)
O(2)-O(H4)	2.42 (3)	O(2)-P(1)-O(H4)	99 (1)
O(3)-O(H4)	2.55 (3)	O(3)-P(1)-O(H4)	106 (1)
P(2)-O(5)	1.51 (3) Å		
P(2)-O(6)	1.52 (3)		
P(2)-O(7)	1.53 (3)		
P(2)-O(H8)	1.63 (3)		
Mean of 3 short bonds	1.52 <sub>1</sub>		
Mean of 4 bonds	1.54 <sub>9</sub>		
O(5)-O(6)	2.55 (3) Å	O(5)-P(2)-O(6)	114 (1)°
O(5)-O(7)	2.52 (3)	O(5)-P(2)-O(7)	112 (1)
O(5)-O(H8)	2.47 (3)	O(5)-P(2)-O(H8)	103 (1)
O(6)-O(7)	2.52 (3)	O(6)-P(2)-O(7)	112 (1)
O(6)-O(H8)	2.58 (3)	O(6)-P(2)-O(H8)	110 (1)
O(7)-O(H8)	2.51 (3)	O(7)-P(2)-O(H8)	105 (1)

Table 7 (cont.)

(b) Mg-coordination octahedron	
Mg-O(3)	2.05 (3) Å
Mg-O(6)	2.09 (3)
Mg-O(9)	2.15 (3)
Mg-O(10)	2.11 (3)
Mg-O(11)	2.08 (3)
Mg-O(12)	2.05 (3)
Mean	2.08 <sub>8</sub>
Range of O-Mg-O angles close to 90°	86.0-98.8°
Range of O-Mg-O angles close to 180°	170.4-177.4
Range of O-O distances within the Mg-coordination octahedron	2.84-3.17 Å 4.12-4.19
(c) Hydrogen bonding geometry	
OH groups	
O(H4)→O(5)	2.67 (3) Å
O(H8)→O(7)	2.55 (3)
P(1)-O(H4)-O(5)	123 (1)°
P(2)-O(H8)-O(7)	107 (1)
H <sub>2</sub> O molecules	
O(W9)→O(1)	2.70 (3) Å
O(W9)→O(7)	2.72 (3)
O(W10)→O(5)	2.62 (3)
O(W10)→O(H4)	2.72 (3)
O(W11)→O(1)	2.70 (3)
O(W11)→O(H8)	2.71 (3)
O(W12)→O(2)	2.74 (3)
O(W12)→O(2)	2.76 (3)
O(1)-O(W9)-O(7)	95 (1)°
O(5)-O(W10)-O(H4)	119 (1)
O(1)-O(W11)-O(H8)	105 (1)
O(2)-O(W12)-O(2)	117 (1)
NH <sub>4</sub> groups	
N(1)→O(2)	2.78 (3) Å
N(1)→O(5)	2.88 (3)
N(1)→O(3)	2.95 (3)
N(1)↗O(3)	3.09 (3)
N(1)↘O(W10)	3.13 (3)
Range of angle O(W10)-N(1)-O	54-150°
Range of angle [O(W10)+O(3)]-N(1)-O	86-124
N(2)→O(1)	2.78 (3) Å
N(2)→O(6)	2.83 (3)
N(2)→O(7)	2.86 (3)
N(2)↗O(W9)	3.08 (3)
N(2)↘O(W11)	3.13 (3)
Range of angle O(W11)-N(2)-O	55-139°
Range of angle [O(W11)+O(9)]-N(2)-O	98-120

to be approximately parallel to the H-H vector of the corresponding molecule. In the sulfate as well as in the chromate compound, the components of  $\overrightarrow{O_{acc}-O_{acc}}$  in the (001) plane are at an angle of about  $\pm 71^\circ$  with the *b* axis for O(W5) and of about  $\pm 41^\circ$  for O(W6), giving an average value of  $\pm 56^\circ$ . The approximate angles between  $\overrightarrow{O_{acc}-O_{acc}}$  and the (001) plane in the sulfate and chromate are, respectively,  $\pm 19$  and  $\pm 16^\circ$  for O(W5) and  $\pm 5$  and  $\pm 2^\circ$  for O(W6). Considering the limitations involved in a comparison of the results of

X-ray and n.m.r. studies, the agreement is satisfactory.

### Mg(NH<sub>4</sub>)<sub>2</sub>(PO<sub>3</sub>OH)<sub>2</sub>·4H<sub>2</sub>O

This crystal structure represents a new structure type, the main features of which are isolated groups consisting of a coordination octahedron around the Mg atom and two phosphate tetrahedra in *trans* position to the Mg atom (Fig. 3). These Mg(OH<sub>2</sub>)<sub>4</sub>(OPO<sub>2</sub>OH)<sub>2</sub> groups are arranged in layers parallel (010) at *y* values of approximately  $\frac{1}{8}$ ,  $\frac{3}{8}$ ,  $\frac{5}{8}$  and  $\frac{7}{8}$ . The bonding between the groups within the layers is accomplished by hydrogen bonds, mostly from the water molecules. The layers are also bonded to each other partly by hydrogen bonds coming from the ammonium groups, which are situated at *y* values of about 0,  $\frac{1}{4}$ ,  $\frac{1}{2}$  and  $\frac{3}{4}$ . The two ammonium groups, despite being crystallographically nonequivalent, are both very similarly coordinated [Fig. 3, Table 7(c)]. The compound can be formulated as [Mg(OH<sub>2</sub>)<sub>4</sub>(OPO<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub><sup>-</sup>[NH<sub>4</sub>]<sub>2</sub><sup>+</sup>, consisting of finite ions of two types joined by hydrogen bonds.

The Mg(OH<sub>2</sub>)<sub>4</sub>O<sub>2</sub> octahedron is more distorted [see Table 7(b)] than similar octahedra in other hydrated Mg salts. For comparison: in MgSO<sub>4</sub>·4H<sub>2</sub>O (Baur, 1962) the range of the Mg-O, O(W) distances is from 2.04 to 2.09 Å, the range of O-O distances is 2.85 to 3.08 Å, and the angles O-Mg-O vary from 86 to 95° in the Mg(OH<sub>2</sub>)<sub>4</sub>O<sub>2</sub> octahedron (there the two oxygen atoms from the sulfate group are in *cis* position). The irregular shape of the octahedral group may be only partly caused by the low accuracy of the structure determination. To a considerable degree, these distortions must be due to the fact that the different oxygen atoms are receiving widely different bond strengths [see Table 8(b)] from their surrounding cations (including the hydrogen atoms). The *mean* Mg-O bond length of 2.086 Å is almost identical to the average for 123 Mg-O distances of 2.085 Å reported by Baur (1970).

Both phosphate groups have one P-O bond length each [to O(H4) and to O(H8)] which is significantly longer than the average of the remaining three P-O bonds [Table 7(a)]. It can be safely assumed that the acidic hydrogen atoms are linked to these oxygen atoms (compare with the case of Na<sub>2</sub>PO<sub>3</sub>OH·7H<sub>2</sub>O, Baur & Khan, 1970). This, together with the fact that all water molecules are bonded to Mg atoms, means that the chemical formula has to be written as Mg(NH<sub>4</sub>)<sub>2</sub>(PO<sub>3</sub>OH)<sub>2</sub>·4H<sub>2</sub>O. Before the structure was determined formulations such as Mg(NH<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(H<sub>3</sub>O)<sub>2</sub>·2H<sub>2</sub>O or Mg(NH<sub>4</sub>)<sub>2</sub>[PO<sub>2</sub>(OH)<sub>2</sub>]<sub>2</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O could not be ruled out. The angular distortions in the two phosphate tetrahedra are of the same kind as discussed previously for a number of more accurately determined phosphate groups (Baur & Khan, 1970). The relationship between bond angle O-P-O ( $\alpha$ ) and mean bond length P-O in orthophosphates is:

$$\log [\sin (\alpha / 2)]=0.11-1.08 \log [d(\text{P}-\text{O})],$$

where the intercept and the slope of the equation have been empirically determined (rule 5, Baur, 1970). The value calculated from this equation for the average 'tetrahedral' angle involving the long P(1)–O(H4) and P(2)–O(H8) bond lengths is  $111^\circ$ , while the average angles between the short bonds (P–O) are calculated to be  $104.5^\circ$ . These calculated average values have to be compared with the corresponding averaged observed angles of  $113.5$  and  $105^\circ$  [Table 7(a)]: the agreement is satisfactory.

Table 8. *Electrostatic bond strengths* (Pauling, 1960; Baur, 1970)

H(W), H(H), and H(N) refer to hydrogen bonds involving the water molecules, the hydroxide groups, and the ammonium groups, respectively. Contributions to the hydrogen bond donor and to the acceptor are identified by *d* and *a*.

(a)  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$

	Na	Cr	H(W)	H(N)	P
O(1)		$\frac{1}{6}a$	$\frac{1}{6}a$	$2 \times \frac{1}{6}a$	2.00 v. u.
O(2)		$2 \times \frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	2.00
O(3)		$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{12}a$	1.75
O(4)	$2 \times \frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{12}a$	1.92
O(W5)	$2 \times \frac{1}{6}a$		$2 \times \frac{5}{6}d$		2.00
O(W6)	$2 \times \frac{1}{6}a$		$2 \times \frac{5}{6}d$		2.00
N				$4 \times \frac{5}{6}d$	3.33

(b)  $\text{Mg}(\text{NH}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$

	Mg	P	H(W)	H(H)	H(N)	P
O(1)		$\frac{1}{6}a$	$2 \times \frac{1}{6}a$		$\frac{1}{6}a$	1.75 v. u.
O(2)		$2 \times \frac{1}{6}a$	$\frac{1}{6}a$		$\frac{1}{6}a$	1.75
O(3)	$\frac{2}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$		$\frac{1}{6}a + \frac{1}{12}a$	1.83
O(H4)		$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{5}{6}d$		2.25
O(5)		$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	1.75
O(6)	$\frac{2}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	1.75
O(7)		$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{1}{6}a$	1.75
O(H8)		$\frac{1}{6}a$	$\frac{1}{6}a$	$\frac{5}{6}d$		2.25
O(W9)		$2 \times \frac{5}{6}d$	$\frac{1}{12}a$		$\frac{1}{12}a$	2.08
O(W10)		$2 \times \frac{5}{6}d$	$\frac{1}{12}a$		$\frac{1}{12}a$	2.08
O(W11)		$2 \times \frac{5}{6}d$	$\frac{1}{12}a$		$\frac{1}{12}a$	2.08
O(W12)		$2 \times \frac{5}{6}d$	$\frac{1}{12}a$		$\frac{1}{12}a$	2.00
N(1)					$4 \times \frac{5}{6}d$	3.33
N(2)					$4 \times \frac{5}{6}d$	3.33

The hydrogen bond geometry can be deduced without ambiguity from a consideration of the bond lengths and angles around the O(H) and O(W) oxygen atoms. In the asymmetric unit are ten oxygen–oxygen distances, which are not edges of coordination polyhedra and are shorter than  $2.8 \text{ \AA}$ . They correspond to the ten hydrogen atoms per formula unit which are covalently bonded to O(H) or O(W), and are therefore available for hydrogen bonding [Table 7(c)]. Since the corresponding angles P–O(H)–O<sub>acc</sub> and O<sub>acc</sub>–O(W)–O<sub>acc</sub> also have values falling within the acceptable limits for such angles, the hydrogen bonding assignment illustrated in Fig. 3 has a high probability of being correct. Of the 10 different hydrogen bonds, eight connect the  $\text{Mg}(\text{OH}_2)_4(\text{OPO}_2\text{OH})_2$  groups with each other within the layers, and only two, O(H8) → O(7) and O(W12) → O(2), provide links between the layers parallel (010).

### The coordination of ammonium ions and the N–H...O bond

The ammonium groups in  $\text{NaNH}_4\text{CrO}_4 \cdot 2\text{H}_2\text{O}$  and in  $\text{Mg}(\text{NH}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$  are five-coordinated [Tables 6(c), 7(c)]. The distances N–O vary from  $2.78$  to  $3.13 \text{ \AA}$ . The angles O–N–O deviate very far from the tetrahedral angle. If it is assumed that each of these groups forms three normal hydrogen bonds and one bifurcated bond, the range of the observed angles is reasonably close to the tetrahedral angle, provided the midpoint between the two acceptor atoms of the bifurcated hydrogen bond is chosen as the coordinating site for the calculation of the angles (as indicated by angle [O(N)+O(M)]–N–O in Tables 6 and 7, where O(N) and O(M) are the acceptor atoms of the bifurcated bond).

It has been shown (Baur, 1965) that water molecules in crystalline hydrates engage sometimes in bifurcated hydrogen bonds. But ammonium groups seem to form bifurcated, trifurcated and generally polyfurcated hydrogen bonds even more readily. Of the 30 ammonium salts listed in Table 9 only six contain  $\text{NH}_4^+$  ions which are approximately tetrahedrally four-coordinated and therefore can form more or less straight N–H...O bonds. In all the other compounds, the ammonium ions have coordination numbers (C.N.) ranging from five to nine. In these cases we must assume either that polyfurcated bonds are formed, or that the  $\text{NH}_4^+$  groups are in static or dynamic disorder, or even that no N–H...O bonding is present. The average N–O distance within a coordination polyhedron increases as a function of the C.N. of the ammonium group (Table 10). When we subtract the radius of the oxygen atom,  $1.37 \text{ \AA}$ , from these N–O distances we obtain a set of effective radii for the  $\text{NH}_4^+$  ion, which is directly comparable to the radii derived for  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  by Shannon & Prewitt (1969) for oxides and fluorides. Because the average C.N. of oxygen in these structures is 3.5, the value of the radius of the oxygen ion was

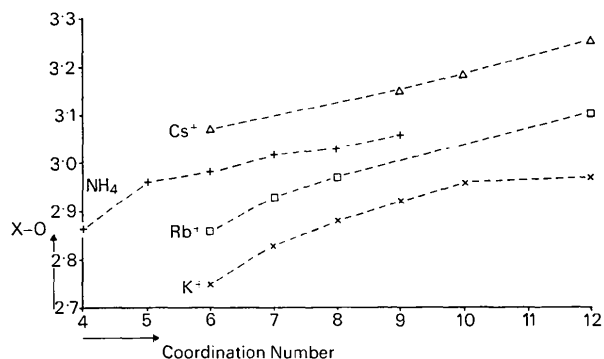


Fig. 4. X–O bond lengths where X =  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , vs. coordination numbers. Data for the ammonium ion are from the salts listed in Table 9, for the alkali ions from Shannon & Prewitt (1969).



Table 9. Coordination numbers (C.N.) and N–O distances in selected ammonium salts, and K–O bond lengths in a few isostructural K compounds

Only bond lengths up to 3.2 Å were accepted as coordination contacts.

	C.N.	Range of N–O, K–O distances	Reference
NH <sub>4</sub> LiSO <sub>4</sub>	4	2.85–3.14 Å	Dollase (1969)
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	4	2.91	Khan & Baur, unpublished
KH <sub>2</sub> PO <sub>4</sub>	8	2.83–2.89	Bacon & Pease (1953)
NH <sub>4</sub> H <sub>2</sub> AsO <sub>4</sub>	4	2.89	Khan & Baur, unpublished
KH <sub>2</sub> AsO <sub>4</sub>	8	2.80–2.91	Khan (1966)
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O	4	2.77–2.91	Mootz & Wunderlich (1970)
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O	4	2.78–2.80	Mootz & Wunderlich (1970)
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O	4	2.81–2.90	Mootz & Wunderlich (1970)
(NH <sub>4</sub> ) <sub>4</sub> P <sub>4</sub> O <sub>12</sub>	4	2.79–2.83	Koster & Wagner (1970)
(NH <sub>4</sub> ) <sub>4</sub> P <sub>4</sub> O <sub>12</sub>	6	2.89–3.14	Koster & Wagner (1970)
(NH <sub>4</sub> ) <sub>6</sub> [Zr(OH)(CO <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	4	2.78–2.90	Clearfield (1970)
(NH <sub>4</sub> ) <sub>6</sub> [Zr(OH)(CO <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	6	2.83–3.13	Clearfield (1970)
(NH <sub>4</sub> ) <sub>6</sub> [Zr(OH)(CO <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	6	2.85–3.15	Clearfield (1970)
Mg(NH <sub>4</sub> ) <sub>2</sub> (PO <sub>3</sub> OH) <sub>2</sub> ·4H <sub>2</sub> O	5	2.78–3.13	This work
Mg(NH <sub>4</sub> ) <sub>2</sub> (PO <sub>3</sub> OH) <sub>2</sub> ·4H <sub>2</sub> O	5	2.78–3.13	This work
NH <sub>4</sub> CrO <sub>4</sub> ·2H <sub>2</sub> O	5	2.81–3.03	This work
NH <sub>4</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	5	2.82–3.01	Corazza <i>et al.</i> (1967)
(NH <sub>4</sub> ) <sub>2</sub> As <sub>2</sub> O <sub>3</sub> OH	5	2.78–3.09	Khan, Straumanis & James (1970)
(NH <sub>4</sub> ) <sub>2</sub> As <sub>2</sub> O <sub>3</sub> OH	5	2.81–2.96	Khan <i>et al.</i> (1970)
MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	5	2.82–3.20	Whitaker & Jeffery (1970)
NH <sub>4</sub> IO <sub>3</sub>	5	2.86–3.15	Keve, Abrahams & Bernstein (1971)
Mg(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5	2.84–3.10	Margulis & Templeton (1962)
MgK <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	7	2.72–3.12	Kannan & Viswamitra (1965)
V(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5	2.90–3.15	Montgomery, Chastain, Natt, Witkowski & Lingafelter (1967)
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5	2.86–3.12	Montgomery <i>et al.</i> (1967)
Co(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	6	2.84–3.18	Montgomery <i>et al.</i> (1967)
Cd(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	6	2.86–3.15	Montgomery & Lingafelter (1966)
Mn(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	6	2.86–3.18	Montgomery, Chastain & Lingafelter (1966)
Ni(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	6	2.86–3.18	Grimes, Kay & Webb (1963)
Zn(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	6	2.89–3.18	Montgomery & Lingafelter (1964)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (ferroelectric)	6	2.86–3.17	Schlemper & Hamilton (1966)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (ferroelectric)	6	2.83–3.11	Schlemper & Hamilton (1966)
(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	6	2.80–3.01	Stephens & Cruickshank (1970)
(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	6	2.78–3.03	Stephens & Cruickshank (1970)
β-NH <sub>4</sub> B <sub>5</sub> O <sub>6</sub> (OH) <sub>4</sub> ·2H <sub>2</sub> O	6	2.94–3.02	Merlino (1969)
Cu(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	7	2.86–3.19	Brown & Chidambaram (1969)
NH <sub>4</sub> B <sub>5</sub> O <sub>7</sub> (OH) <sub>2</sub> ·H <sub>2</sub> O	7	2.86–3.05	Merlino & Sartori (1969)
(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	7	2.93–3.18	Beineke & Delgaudio (1968)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (paraelectric)	7	2.90–3.11	Schlemper & Hamilton (1966)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (paraelectric)	8	2.84–3.17	Schlemper & Hamilton (1966)
(NH <sub>4</sub> ) <sub>3</sub> B <sub>15</sub> O <sub>20</sub> (OH) <sub>8</sub> ·4H <sub>2</sub> O	7	2.93–3.10	Merlino & Sartori (1971)
(NH <sub>4</sub> ) <sub>3</sub> B <sub>15</sub> O <sub>20</sub> (OH) <sub>8</sub> ·4H <sub>2</sub> O	8	2.76–3.18	Merlino & Sartori (1971)
NH <sub>4</sub> ClO <sub>4</sub>	8	2.94–3.08	Smith & Levy (1962)
NH <sub>4</sub> HSO <sub>4</sub>	8	2.97–3.13	Nelmes (1971)
NH <sub>4</sub> HSO <sub>4</sub>	9	2.92–3.16	Nelmes (1971)

chosen to be 1.37 Å, in accordance with Shannon & Prewitt's tables. The comparison of the N–O distances with the corresponding K–O, Rb–O and Cs–O distances (Fig. 4) shows that the NH<sub>4</sub><sup>+</sup> ion is considerably larger than the K<sup>+</sup> ion: its size falls in between the sizes of the Rb<sup>+</sup> and Cs<sup>+</sup> ions. Nevertheless, NH<sub>4</sub><sup>+</sup> does occur in four and five coordination, while the large alkali ions always have a C.N. of six or higher. Numerous examples of pairs of isostructural K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> oxy-salts are known. However, in only three cases are the crystal structures of both members of such pairs accurately determined. In these cases (Table 9) the coordination number of the NH<sub>4</sub><sup>+</sup> ion is always smaller than the coordination number of K<sup>+</sup> in the corresponding potassium compound.

Table 10. Ammonium group, average N–O distances for different coordination numbers (C.N.) and effective radii, assuming that  $r_0^{2-} = 1.37$  ÅNo. refers to the number of NH<sub>4</sub><sup>+</sup> groups used in the averaging.

C.N.	Average N–O	$r_{\text{NH}_4^+}$	No.
4	2.86 Å	1.49 Å	8
5	2.96	1.59	11
6	2.98	1.61	13
7	3.02	1.65	5
8	3.03	1.66	4
9	3.06	1.69	1

Acceptor atoms which have a tendency for engaging in strong hydrogen bonds will favor the forming of a tetrahedral coordination around the NH<sub>4</sub><sup>+</sup> ion. This is

exemplified by  $\text{NH}_4\text{F}$  (Adrian & Feil, 1969), which crystallizes in the wurtzite structure with tetrahedral coordination around  $\text{NH}_4$ , and by the contrasting case of  $\text{NH}_4\text{Cl}$  (Levy & Peterson, 1952), which crystallizes in the  $\text{CsCl}$  structure with eight-coordination around  $\text{NH}_4^+$ . The fluoride ion is well known to be a stronger acceptor of hydrogen bonds than the chloride ion. Not only different kinds of anions can have varying abilities to engage in hydrogen bonding, but also the same kind of anion can, under different conditions, enter into hydrogen bonds of different strengths.

This has been discussed both in a general way and for the specific case of  $\text{O}-\text{H}\cdots\text{O}$  bonds by Baur (1970). The length and strength of hydrogen bonds depend on  $\Delta p$ , the difference of the bond strength values  $p_x$  (see Table 8) received by the donor and acceptor atoms of the hydrogen bond:

$$\Delta p = p_{\text{donor}} - p_{\text{acceptor}}$$

A predicted value for a hydrogen bond length can be obtained from an expression of the type

$$d(\text{O}-\text{H}\cdots\text{O}) = (a + b\Delta p) \text{ \AA}, \quad (1)$$

where  $a$  and  $b$  are empirically derived constants (rule 4, Baur, 1970). For the case of 392 hydrogen bonds, of the type  $\text{O}-\text{H}\cdots\text{O}$ , the correlation coefficient between bond length  $\text{O}-\text{H}\cdots\text{O}$  and  $\Delta p$  was found to be  $-0.68$ . For hydrogen bonds donated by an  $\text{NH}_4^+$  group, the  $p_{\text{N}}$  of the nitrogen atom is always constant; therefore, in this case we can modify expression (1) in such a way as to indicate that the bond length  $\text{N}-\text{H}\cdots\text{O}$  should depend only on the bond strength  $p_{\text{O}}$  received by the oxygen atom:

$$d(\text{N}-\text{H}\cdots\text{O}) = (a + bp_{\text{O}}) \text{ \AA}. \quad (2)$$

From the bonds occurring in the 30 ammonium compounds listed in Table 9, only those were included in the calculation, which could be identified with some degree of confidence as approximately straight hydrogen bonds. That means we excluded all cases where the geometry indicated that we might be dealing with a polyfurcated bond. The correlation coefficient between 86  $\text{N}-\text{H}\cdots\text{O}$  bond lengths and the corresponding  $p_{\text{O}}$  is  $0.67$ , which is similar to the correlation found for  $d(\text{O}-\text{H}\cdots\text{O})$  vs.  $\Delta p$  (Baur, 1970). For this sample size, the correlation is statistically highly significant. The intercept  $a$  equals  $2.21$  (8)  $\text{\AA}$ , the slope  $b$  equals  $0.34$  (4)  $\text{\AA}$  per valence unit (v.u.), the average difference between the observed bond length and the one predicted by the regression equation,

$$d(\text{N}-\text{H}\cdots\text{O}) = (2.21 + 0.34p_{\text{O}}) \text{ \AA}, \quad (3)$$

is  $0.054$   $\text{\AA}$  (see Fig. 5). A comparison of the ammonium group coordinations in the crystal structures listed in Table 9 indicates a tendency for salts with  $\text{NH}_4^+$  ions, which have small coordination numbers (4 or 5), to be bonded to slightly undersaturated oxygen anions (*i.e.*, to those with average  $p_{\text{O}}$  values around  $1.85$  v.u.). The ammonium groups, which have higher

C.N.'s, seem to be bonded generally to oxygen atoms that are more saturated ( $p_{\text{O}}$  values closer to  $2.00$  v.u.).

Another consequence of the dependence of the  $\text{N}-\text{H}\cdots\text{O}$  bond length on the bond strength  $p_{\text{O}}$  received by the oxygen acceptor atom is reflected in the average length of the  $\text{N}-\text{H}\cdots\text{O}$  bonds received by oxygen atoms in different oxy-groups (Table 11). Since the  $p_{\text{O}}$  received by an oxygen atom in a phosphate group is  $1.25$  v.u., while in a perchlorate group it is  $1.75$  v.u., the chance for a phosphate oxygen atom to be undersaturated is larger than for an oxygen atom in the perchlorate group. Consequently, the  $\text{N}-\text{H}\cdots\text{O}$  bonds accepted by the oxygen atoms in the chemically different oxy-salts vary on the average as the bond strengths received by the oxygen atom from the central cation (P, S, Cl, *etc.*) vary.

Table 11. Bond strengths,  $p_{\text{O}}$ , received by the oxygen atoms from the central ion in different tetrahedral oxy-anions and the average lengths of the bonds  $\text{N}-\text{H}\cdots\text{O}$  accepted by these oxygen atoms

No. refers to the number of bond lengths used in the averaging. The data are from the compounds listed in Table 9.

	$p_{\text{O}}$	Bond length $\text{N}-\text{H}\cdots\text{O}$	No.
Phosphates	1.25 v.u.	2.83 $\text{\AA}$	21
Arsenates	1.25	2.85	8
Sulfates	1.50	2.97	80
Chromates	1.50	2.93	17
Perchlorates	1.75	3.02	8

Because of its large size, the  $\text{NH}_4^+$  ion should have coordination numbers similar to those of  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ , namely between 6 and 12, and should act like a pseudo alkali ion. However, the ammonium ion also has an appreciable tendency for forming hydrogen bonds and therefore it enters (despite its large size) in

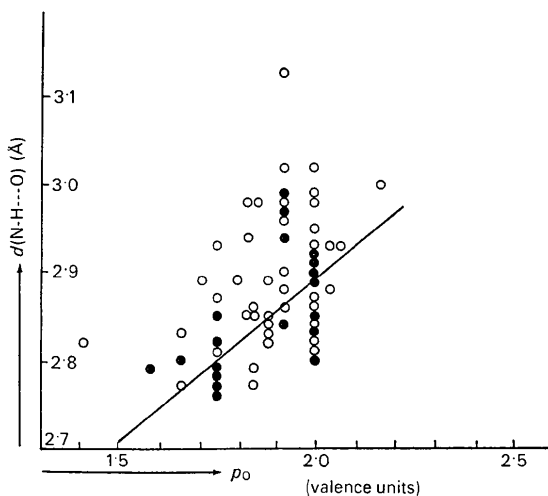


Fig. 5. Hydrogen bond length  $\text{N}-\text{H}\cdots\text{O}$  vs.  $p_{\text{O}}$ , the bond strength received by the acceptor oxygen atom, for 86 cases. Filled circles represent unresolved overlapping points. The regression line  $d(\text{N}-\text{H}\cdots\text{O}) = (2.21 + 0.34p_{\text{O}}) \text{ \AA}$  is shown.

some compounds, into four- and five-coordination against oxygen (Fig. 4). This double role that  $\text{NH}_4^+$  is playing in its salts may be responsible for the many interesting transitions exhibited by  $\text{NH}_4$  compounds in which coordination numbers and hydrogen bonding arrangements are changing. This is illustrated by  $(\text{NH}_4)_2\text{SO}_4$  (Schlemper & Hamilton, 1966), which is ferroelectric below  $223^\circ\text{K}$ , with six-coordination for both  $\text{NH}_4^+$  groups and short hydrogen bonds, while in its para-electric phase above  $223^\circ\text{K}$  the ammonium ions are seven- and eight-coordinated. It seems that the hydrogen-bonding tendency is more pronounced in the low-temperature phase, while the pseudo alkali ion character is exhibited in the high-temperature phase. This is also emphasized by the fact that para-electric  $(\text{NH}_4)_2\text{SO}_4$  is isostructural with  $\text{K}_2\text{SO}_4$  (arcanite).

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#### References

- ADRIAN, H. W. W. & FEIL, D. (1969). *Acta Cryst.* A25, 438.
- BACON, G. E. & PEASE, R. S. (1953). *Proc. Roy. Soc. A* 220, 397.
- BAUR, W. H. (1962). *Acta Cryst.* 15, 815.
- BAUR, W. H. (1965). *Acta Cryst.* 19, 909.
- BAUR, W. H. (1970). *Trans Amer. Cryst Assoc.* 6, 129.
- BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* B26, 1584.
- BEINEKE, T. A. & DELGAUDIO, J. (1968). *Inorg. Chem.* 7, 715.
- BROWN, G. M. & CHIDAMBARAM, R. (1969). *Acta Cryst.* B25, 676.
- CLEARFIELD, A. (1970). *Inorg. Chim. Acta*, 4, 166.
- CORAZZA, E., SABELLI, C. & GIUSEPPETTI, Y. (1967). *Acta Cryst.* 22, 683.
- DOLLASE, W. A. (1969). *Acta Cryst.* B25, 2298.
- EASWARAN, K. R. K. (1966). *J. Chem. Phys.* 45, 403.
- FRAZIER, A. W., LEHR, J. R. & SMITH, J. P. (1964). *Amer. Min.* 48, 635.
- GRIMES, N. W., KAY, H. F. & WEBB, M. W. (1963). *Acta Cryst.* 16, 823.
- KANNAN, K. K. & VISWAMITRA, M. A. (1965). *Z. Kristallogr.* 122, 161.
- KEVE, E. T., ABRAHAMS, S. C. & BERNSTEIN, J. L. (1971). *J. Chem. Phys.* 54, 2556.
- KHAN, A. A. (1966). *X-ray Studies on Some Crystals*. Ph.D. Thesis, Osmania Univ.
- KHAN, A. A., STRAUMANIS, M. E. & JAMES, W. J. (1970). *Acta Cryst.* B26, 1889.
- KOSTER, D. A. & WAGNER, J. J. (1970). *J. Chem. Soc. (A)*, p. 435.
- LEVY, H. A. & PETERSON, S. W. (1952). *Phys. Rev.* 86, 766.
- MACIVOR, R. W. E. (1907). *Z. Kryst. Min.* 42, 386.
- MARGULIS, T. N. & TEMPLETON, D. H. (1962). *Z. Kristallogr.* 117, 344.
- MELLOR, J. W. (1948). *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Vol. XI, p. 249. London: Longmans, Green and Co.
- MERLINO, S. (1969). *R.C. Accad. Lincei*, 47, 85.
- MERLINO, S. & SARTORI, F. (1969). *Acta Cryst.* B25, 2264.
- MERLINO, S. & SARTORI, F. (1971). *Science*, 171, 377.
- MONTGOMERY, H., CHASTAIN, R. V. & LINGAFELTER, E. C. (1966). *Acta Cryst.* 20, 731.
- MONTGOMERY, H., CHASTAIN, R. V., NATT, J. J., WITKOWSKI, A. M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* 22, 775.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1964). *Acta Cryst.* 17, 1295.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1966). *Acta Cryst.* 20, 728.
- MOOTZ, D. & WUNDERLICH, H. (1970). *Acta Cryst.* B26, 1826.
- MROSE, M. E. (1972). *U.S. Geol. Surv. Prof. Paper* 750A. In the press.
- NELMES, R. J. (1971). *Acta Cryst.* B27, 272.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd Ed., p. 547, Ithaca: Cornell Univ. Press.
- SCHLEMPER, E. O. & HAMILTON, W. C. (1966). *J. Chem. Phys.* 44, 4498.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B25, 925.
- SMITH, H. G. & LEVY, H. A. (1962). *Acta Cryst.* 15, 1201.
- STEPHENS, J. S. & CRUICKSHANK, D. W. J. (1970). *Acta Cryst.* B26, 437.
- TILLMANN, E. & BAUR, W. H. (1971). *Acta Cryst.* B27, 2124.
- WHITAKER, A. & JEFFERY, J. W. (1970). *Acta Cryst.* B26, 1429.