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The Crystal Structure of Ammonium Nickel Sulphate Hexahydrate (NH₄)₂Ni(SO₄)₂ · 6H₂O

BY N. W. GRIMES, H. F. KAY AND M. W. WEBB

H. H. Wills Physics Laboratory, University of Bristol, Bristol, England

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Crystals of ammonium nickel sulphate hexahydrate are monoclinic with space group $P2_1/a$. The unit cell of dimensions $a = 9.181$, $b = 12.459$, $c = 6.239$ Å, $\beta = 106^\circ 57'$ contains two formula units.

Projections of the structure on three crystallographic planes are given. The sulphate group and nickel-water complex have bond lengths and orientations somewhat different from those published for the isomorphous salt (NH₄)₂Mg(SO₄)₂ · 6H₂O.

A system of hydrogen bonding is suggested for the water molecules and the ammonium group. The former is in good agreement with recent proton resonance data and the latter has been used to explain the cleavage parallel to (010).

Introduction

During the past few years the technique of paramagnetic resonance has been extensively applied to investigate the lower energy levels of paramagnetic ions subjected to a crystal field such as occurs in hydrated salts. The interpretation of the resonance spectra depends upon a knowledge of the spatial structure of the magnetic ion complex and can be tested quantitatively only if this structure is known with precision. We were also interested in investigating probable hydrogen bonding in the structure.

The Tutton salts, of which isomorphous series ammonium nickel sulphate is a member, have been much investigated by the resonance technique, but the only published crystal structure is that of (NH₄)₂Mg(SO₄)₂ · 6H₂O (Hofmann, 1931). The structures of the other members of the series have been assumed to be similar.

Crystal data

Crystals of ammonium nickel sulphate are monoclinic and bluish green in colour. The unit-cell dimensions from oscillation photographs taken of carefully oriented and machine-turned cylindrical crystals are

$$a = 9.181 \pm 0.001, \quad b = 12.459 \pm 0.001, \\ c = 6.239 \pm 0.001 \text{ \AA}, \quad \beta = 106^\circ 57' \pm 2'.$$

These figures differ from those published by Mukherjee (1935) who gave

$$a = 8.98, \quad b = 12.22, \quad c = 6.10 \text{ \AA}, \quad \beta = 107^\circ 4'.$$

However, our calculated density is 1.922 ± 0.003 g.cm⁻³ in excellent agreement with Tutton's (1916) measured value of 1.923 g.cm⁻³ whereas Mukherjee's dimensions give a calculated density of 2.04 g.cm⁻³.

Systematic absences occur for $h0l$ with h odd and for $0k0$ with k odd. The space group is therefore $P2_1/a$. The number of formula units in the unit cell is two.

Determination of the structure

For evaluating the (100), (010) and (001) projections, the relevant intensities were recorded on zero-layer integrating-Weissenberg photographs by the multiple-film technique. Filtered Mo $K\alpha$ radiation was used. Roughly two-thirds of the intensities were measured photometrically with reference to a calibrated grey wedge. The very faint reflexions were estimated visually. The corrections for the Lorentz and polariza-

tion factors and for absorption in cylindrical crystals were made by using the *International Tables for X-ray Crystallography*, Vol. II.

Since the unit cell contains only two formula units it follows that the nickel atoms must lie on symmetry centres. Using the origin given in the *International Tables for X-ray Crystallography* for $P2_1/a$, the nickel positions were fixed as $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$.

The sulphur atom was assumed on average to be un-ionized, with each sulphate-oxygen atom having an extra half electron; the water oxygen atoms were assumed to be singly ionized (Pauling, 1940). The following scattering factors were therefore used:

- (i) Ni^{2+} Forsyth & Wells (1959) corrected for dispersion according to Dauben & Templeton (1955).
- (ii) S Viervoll & Øgrim (1949).
- (iii) $\text{O}^{\frac{1}{2}-}$ (From the sulphate group) Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); corrected at low $\sin \theta/\lambda$ for a charge of $-\frac{1}{2}$.

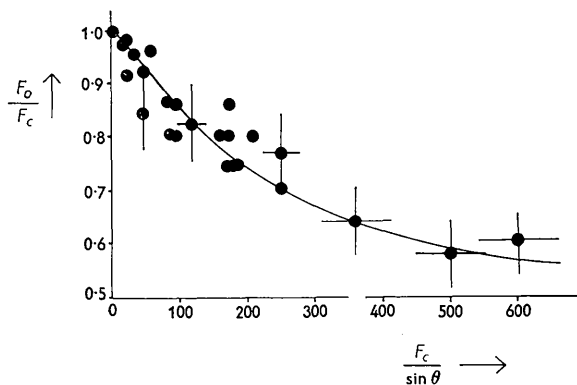


Fig. 1. The curve used for correction of extinction.

- (iv) NH_4^+ A scattering factor was calculated for this ion by regarding the hydrogen atoms as being smeared out over a sphere (Banyard & March, 1961).

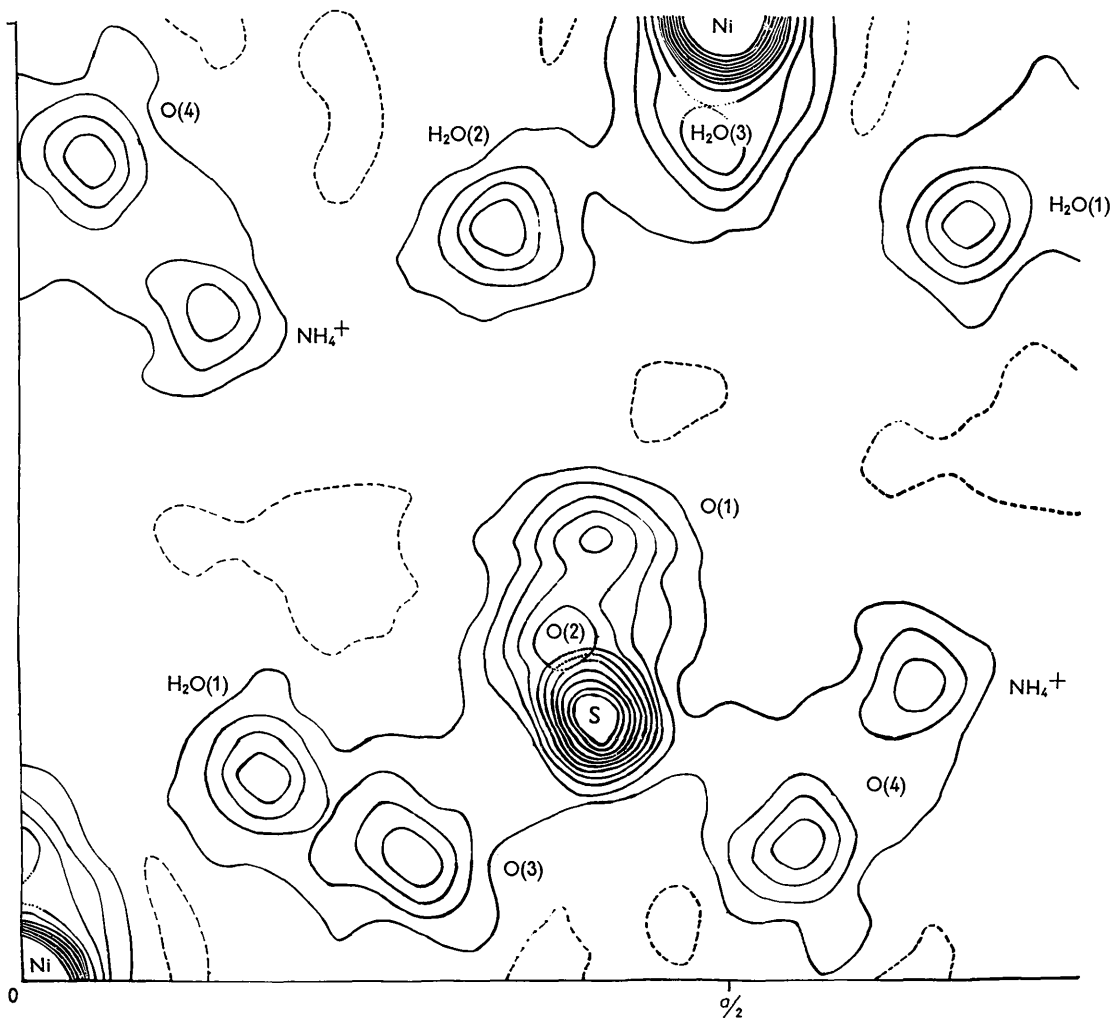


Fig. 2. Electron-density map of (001) projection (contours in equal arbitrary steps).

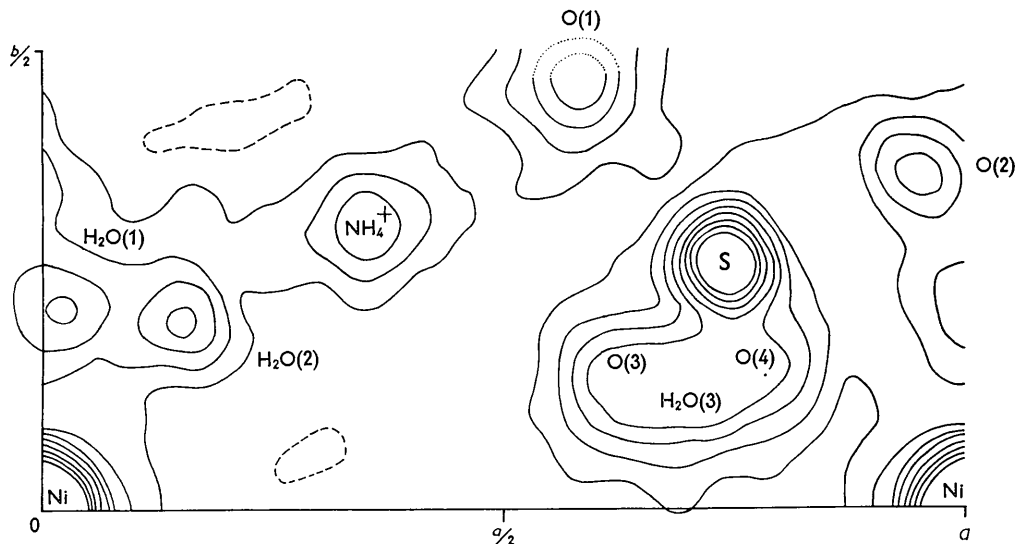


Fig. 3. Electron-density map of (100) projection (contours in equal arbitrary steps).

Table 1. Final atomic parameters in fractions of unit cell lengths, and their standard deviations

	x	σ_x	y	σ_y	z	σ_z
S	0.0910	± 0.001	0.6360	± 0.0006	0.2586	± 0.0015
NH ₄	0.133	± 0.003	0.347	± 0.002	0.348	± 0.004
O(1)	0.089	± 0.004	0.729	± 0.002	0.419	± 0.004
O(2)	0.117	± 0.003	0.679	± 0.002	0.049	± 0.004
O(3)	0.220	± 0.004	0.570	± 0.002	0.377	± 0.004
O(4)	-0.051	± 0.003	0.573	± 0.002	0.220	± 0.006
H ₂ O(1)	-0.167	± 0.003	0.106	± 0.002	0.020	± 0.004
H ₂ O(2)	0.161	± 0.002	0.110	± 0.002	0.149	± 0.004
H ₂ O(3)	0.006	± 0.004	-0.065	± 0.002	0.300	± 0.003

(v) O⁻ (From the water molecules) Berghuis *et al.* (1955); corrected at low $\sin \theta/\lambda$ for the charge.

The (001) projection was examined first as it promised the clearest resolution. For this purpose the signs of the largest $F(hk0)$ values were calculated for Hofmann's structure for $(\text{NH}_4)_2\text{Mg}(\text{SO})_2 \cdot 6\text{H}_2\text{O}$. The electron-density map derived from these data gave the positions of most of the atoms in the structure. There were still, however, two possible positions for an oxygen of the sulphate group and two for a water molecule.

An R factor was calculated for each of the four possibilities, and that corresponding to the best value of R was selected as the most probable structure. A least-squares computer program using diagonal elements only was then used to refine the projection to an R of 13%.

At this stage it was noted that the temperature factor obtained by using all the intensities was $B=1 \text{ \AA}^2$ which is rather low for a structure of this type. On the other hand when the analysis was applied to medium intensities alone, B rose to 2 \AA^2 and the scale factor was also higher. However, using these latter values, F_c was consistently greater than F_o for the strong reflexions and it was therefore concluded that

extinction was occurring. It was also noted that if the reflexions were divided into $h+k$ even and $h+k$ odd (*i.e.* into reflexions in which Ni was either contributing or not contributing respectively) two different isotropic temperature factors could be recognized, one for Ni, $B=1.9 \text{ \AA}^2$ and another for the rest of the structure $B=2.3 \text{ \AA}^2$.

As the atomic positions were reasonably well known

Table 2. Bond lengths and angles

Water complex	
Ni-H ₂ O(1) = $2.05 \pm 0.025 \text{ \AA}$	H ₂ O(1)-H ₂ O(2) = $2.88 \pm 0.03 \text{ \AA}$
Ni-H ₂ O(2) = $2.03 \pm 0.035 \text{ \AA}$	H ₂ O(2)-H ₂ O(3) = $2.92 \pm 0.03 \text{ \AA}$
Ni-H ₂ O(3) = $2.03 \pm 0.025 \text{ \AA}$	H ₂ O(3)-H ₂ O(1) = $2.92 \pm 0.025 \text{ \AA}$
$\text{H}_2\text{O}(1)-\widehat{\text{Ni}}-\text{H}_2\text{O}(2) = 89^\circ 47' \pm 2^\circ$ $\text{H}_2\text{O}(2)-\widehat{\text{Ni}}-\text{H}_2\text{O}(3) = 92^\circ 7' \pm 2^\circ$ $\text{H}_2\text{O}(3)-\widehat{\text{Ni}}-\text{H}_2\text{O}(1) = 91^\circ 10' \pm 2^\circ$	
Sulphate group	
S-O(1) = $1.52 \pm 0.025 \text{ \AA}$	O(1)- $\widehat{\text{S}}$ -O(2) = $109^\circ 18' \pm 4^\circ$
S-O(2) = $1.50 \pm 0.025 \text{ \AA}$	O(2)- $\widehat{\text{S}}$ -O(3) = $109^\circ 18' \pm 4^\circ$
S-O(3) = $1.46 \pm 0.04 \text{ \AA}$	O(3)- $\widehat{\text{S}}$ -O(4) = $109^\circ 42' \pm 4^\circ$
S-O(4) = $1.49 \pm 0.025 \text{ \AA}$	O(4)- $\widehat{\text{S}}$ -O(1) = $109^\circ 24' \pm 4^\circ$
O(1)-O(2) = $2.48 \pm 0.05 \text{ \AA}$	O(1)-O(3) = $2.38 \pm 0.07 \text{ \AA}$
O(1)-O(4) = $2.46 \pm 0.05 \text{ \AA}$	O(2)-O(3) = $2.40 \pm 0.07 \text{ \AA}$
O(2)-O(4) = $2.50 \pm 0.05 \text{ \AA}$	O(3)-O(4) = $2.40 \pm 0.07 \text{ \AA}$

Table 3. Comparison of calculated and observed structure factors

h	k	l	F _c	F _o	h	k	l	F _c	F _o	h	k	l	F _c	F _o	h	k	l	F _c	F _o	h	k	l	F _c	F _o
2	0	0	+39.66	39.85	6	5	0	+2.56	3.43	0	6	0	+1.89	3.01	0	12	3	+7.24	7.30	10	0	8	+1.53	3.46
4	0	0	-5.97	5.93	6	2	0	+4.88	5.32	0	8	3	+15.02	15.06	0	12	5	+6.62	6.95	4	0	9	+1.37	3.01
4	0	0	+6.14	6.96	6	8	0	+4.88	5.32	0	10	5	+4.37	4.51	0	12	5	+6.38	6.12	6	0	9	+2.81	3.18
4	0	0	+10.00	9.53	6	10	0	+13.92	11.72	0	12	6	+6.82	6.49	0	12	6	+5.49	6.11	8	0	9	+1.61	3.11
10	0	0	+10.10	9.51	6	12	0	+7.56	8.10	0	14	0	+12.63	11.83	0	12	7	+0.59	2.86	2	0	10	+3.07	3.47
12	0	0	+8.13	8.51	6	14	0	+2.31	3.51	0	16	0	+8.00	8.43	0	13	4	+6.00	6.12	4	0	10	+3.44	3.53
14	0	0	+3.76	3.89	6	18	0	+5.03	7.43	0	18	0	+3.25	4.39	0	12	10	+1.70	3.20	6	0	10	+2.23	2.74
18	0	0	+1.38	1.18	6	20	0	+3.43	4.07	0	22	0	+1.97	3.41	0	13	1	-10.70	10.60	2	0	11	+2.53	3.46
1	3	0	+54.64	57.19	7	1	0	+26.79	24.72	0	1	2	-10.19	7.50	0	13	2	+3.09	2.55	4	0	11	+1.65	2.72
1	5	0	-6.32	5.49	7	3	0	+13.13	12.48	0	2	5	+10.01	7.94	0	13	4	+2.55	6.06	4	0	1	+1.56	2.49
1	5	0	+6.32	5.49	7	3	0	+7.10	7.24	0	1	4	+0.13	2.86	0	13	7	n.o.	n.o.	6	0	1	+14.28	12.61
1	6	0	-3.96	2.95	7	6	0	-0.41	3.37	0	1	5	+16.75	11.23	0	13	8	-1.21	3.08	8	0	1	-2.18	3.09
1	7	0	+6.78	5.04	7	7	0	+3.87	5.48	0	1	7	-4.19	5.07	0	14	2	-3.64	2.65	12	0	1	+7.42	8.87
1	8	0	+3.36	n.o.	7	8	0	+1.39	5.09	0	1	8	+2.12	3.14	0	14	3	+2.36	1.74	14	0	1	+3.90	7.01
1	9	0	+15.55	+14.17	7	9	0	+9.28	9.11	0	2	2	+3.90	4.99	0	14	4	+6.23	7.71	16	0	1	+1.27	3.42
1	10	0	-0.04	3.72	7	12	0	-4.12	4.43	0	2	3	+17.52	12.68	0	14	5	+3.50	n.o.	2	0	2	-18.38	17.81
1	11	0	+18.11	17.84	7	13	0	+6.04	5.40	0	2	4	+13.63	11.43	0	14	7	+1.42	3.67	4	0	2	+5.09	3.97
1	12	0	+2.89	4.59	7	15	0	+6.43	7.75	0	2	5	+10.01	7.94	0	14	8	+2.55	6.06	4	0	2	+14.28	13.95
1	13	0	+1.82	5.09	7	17	0	+3.96	5.93	0	2	6	+11.09	10.96	0	14	10	+1.20	3.21	8	0	2	+16.92	14.60
1	15	0	+2.06	2.54	8	1	0	-12.33	12.75	0	2	7	+4.95	4.96	0	14	11	+0.93	3.12	12	0	2	+4.86	2.86
1	17	0	+4.94	4.57	8	2	0	+8.23	6.95	0	2	8	+5.09	4.26	0	15	4	-3.14	n.o.	14	0	2	+3.78	3.28
1	18	0	-1.80	2.87	8	4	0	-0.02	5.73	0	2	9	+8.13	3.89	0	16	4	+5.25	6.54	16	0	2	+5.75	3.61
1	19	0	+6.57	7.56	8	4	0	+8.65	6.97	0	2	10	+3.51	4.06	0	16	7	+1.81	3.12	18	0	2	+1.65	2.97
2	1	0	+28.77	31.43	8	5	0	+3.07	3.60	0	2	11	+1.62	3.18	0	16	8	+1.58	3.18	2	0	3	+28.48	18.20
2	2	0	+19.67	21.29	8	6	0	+10.79	9.84	0	3	1	+25.01	17.41	0	17	3	-2.85	3.31	4	0	3	+11.04	8.73
2	3	0	-6.35	6.08	8	6	0	+2.52	4.25	0	3	2	+15.07	12.32	0	18	5	+3.77	6.35	4	0	3	+25.05	17.88
2	4	0	+24.23	24.32	8	9	0	+2.94	5.49	0	3	3	+24.27	17.75	0	18	2	+6.86	8.42	8	0	3	+21.95	19.65
2	5	0	-8.04	8.04	8	10	0	+3.58	3.59	0	3	4	+4.48	4.89	0	18	3	+3.30	3.35	10	0	3	+15.54	14.11
2	6	0	+16.20	14.87	8	11	0	+2.44	3.67	0	3	5	+4.48	3.47	0	18	5	+2.84	3.74	12	0	3	+2.99	n.o.
2	7	0	-2.58	3.36	8	12	0	+5.79	6.38	0	3	6	+1.45	2.79	0	18	6	+4.55	4.20	14	0	3	+2.45	n.o.
2	8	0	+10.64	10.16	8	13	0	+2.99	5.23	0	3	7	+4.11	3.97	0	20	4	+3.02	3.15	18	0	3	+1.47	3.66
2	9	0	+8.37	8.13	8	14	0	+3.30	5.23	0	4	2	+36.95	26.85	0	2	0	+2.61	3.09	20	0	3	+1.40	2.57
2	10	0	+3.37	3.77	8	16	0	+2.96	3.60	0	4	3	+9.20	8.03	0	20	3	+2.44	3.01	2	0	4	+37.63	26.43
2	11	0	+6.99	6.66	8	17	0	-1.73	3.36	0	4	5	+9.88	10.67	0	20	6	+2.49	3.77	4	0	4	+15.90	13.96
2	13	0	-5.84	5.74	8	19	0	+5.66	5.93	0	4	7	+6.66	7.75	0	21	2	+2.33	3.24	6	0	4	-0.60	2.10
2	14	0	+10.77	11.13	9	2	0	+10.11	n.o.	0	4	7	+3.95	3.87	0	22	4	+2.49	3.77	8	0	4	+6.62	3.46
2	16	0	+6.19	6.80	9	3	0	+14.46	14.59	0	4	9	+3.44	6.08	0	2	2	+3.69	4.24	10	0	4	+13.59	14.64
2	17	0	+2.87	3.84	9	5	0	+8.41	8.93	0	4	10	+3.80	5.57	0	0	3	+39.26	28.94	12	0	4	+10.04	9.82
2	21	0	+2.94	3.19	9	9	0	+2.34	4.41	0	5	1	+15.72	14.04	0	4	4	+1.72	3.46	14	0	4	+7.44	7.74
2	22	0	+2.34	3.51	9	8	0	+1.07	3.52	0	5	2	-19.52	13.62	0	7	5	+18.05	12.95	20	0	4	+1.12	2.81
3	1	0	-21.47	22.38	9	9	0	+2.12	3.75	0	5	3	+13.81	11.60	0	0	6	+2.74	2.18	2	0	5	+11.98	7.59
3	2	0	-6.10	6.32	9	10	0	+3.91	4.86	0	5	4	-4.98	4.26	0	7	6	+9.29	9.03	4	0	5	+27.98	14.89
3	3	0	+17.20	16.83	9	11	0	+1.02	3.69	0	5	5	+11.02	10.85	0	0	8	+7.12	6.87	6	0	5	+1.07	3.56
3	4	0	+28.11	27.30	9	12	0	-4.10	5.87	0	5	6	+2.24	4.13	0	0	9	+1.89	1.85	12	0	5	+6.71	6.76
3	5	0	+30.93	32.61	9	13	0	+4.95	6.20	0	5	7	+3.19	3.33	0	0	11	+1.24	3.17	14	0	5	+5.22	4.28
3	6	0	+8.11	7.39	9	15	0	+3.85	3.50	0	5	9	+2.48	2.93	2	0	1	-27.49	21.92	16	0	5	+1.31	2.44
3	8	0	+12.81	12.87	9	17	0	+2.62	4.08	0	6	2	+22.16	13.93	4	0	1	+30.78	26.70	2	0	6	+2.08	2.16
3	8	0	+5.15	4.16	10	4	0	+4.76	4.24	0	6	2	+17.59	14.58	6	0	1	+30.78	26.70	4	0	6	+9.80	9.23
3	9	0	-2.33	3.60	10	5	0	+3.95	4.08	0	6	3	+17.70	14.05	8	0	1	+22.50	16.98	6	0	6	+2.55	17.16
3	10	0	-13.22	12.08	10	6	0	+7.52	8.60	0	6	4	+15.02	13.71	10	0	1	+6.22	5.45	8	0	6	+5.30	3.05
3	11	0	+5.79	3.83	10	8	0	+5.38	6.71	0	6	5	+2.82	3.61	12	0	1	+3.20	2.63	10	0	6	+3.38	3.30
3	12	0	1.88	4.58	10	9	0	-5.12	4.16	0	6	6	+4.23	4.21	14	0	1	-2.08	3.10	12	0	6	+2.91	2.41
3	13	0	+11.60	12.51	10	10	0	+4.13	6.36	0	6	7	+2.51	3.25	2	0	2	+10.06	8.89	14	0	6	+1.93	2.57
3	14	0	+1.55	2.96	10	16	0	+2.74	3.94	0	6	8	+4.12	4.46	4	0	2	+14.46	13.73	16	0	6	+3.35	3.83
3	15	0	+8.05	8.97	10	17	0	+3.34	4.41	0	6	9	+3.77	3.80	6	0	4	+5.25	6.19	18	0	6	+2.05	7.89
3	16	0	+3.22	3.93	11	3	0	+8.54	10.07	0	7	1	+11.57	10.63	8	0	2	+3.94	5.15	2	0	7	+2.95	1.61
3	20	0	+2.85	4.17	11	5	0	+2.62	4.08	0	7	3	+6.92	6.18	10	0	2	+2.80	2.53	4	0	7	+3.48	2.40
3	22	0	+1.89	3.09	11	7	0	-0.93	3.28	0	7	4	+4.38	4.63	14	0	2	+1.66	3.57	6	0	7	+6.60	4.21
4	1	0	+14.91	18.77	11	8	0	+3.21	4.08	0	7	6	+1.90	3.77	16	0	4	+5.38	6.46	8	0	7	+9.35	7.65
4	2	0	+40.28	43.48	11	13	0	+3.33	4.41	0	7	6	+1.05	2.38	2	0	3	+12.45	12.18	10	0	7	+8.81	10.76
4	3	0	-8.50	8.16	11	17	0	+1.71	3.26	0	7	7	+3.38	4.85	4	0	3	+11.99	10.95	12	0	7	+8.49	8.31
4	4	0	+32.98	32.61	11	19	0	+1.81	3.26	0	7	11	+0.45	3.22	6	0	3	+3.44	2.74	18	0	7	+1.62	3.44
4	5	0	-12.91	12.86	12	5	0	+3.30	4.25	0	8	1	+17.13	12.79	8	0	3	+1.32	2.70	13	0	8	+4.40	4.92
4	6	0	+1.55	2.68	12	6	0	+3.92	4.42</															

The least-squares program was then applied to the 120 medium and strong corrected intensities to give a final reliability index R for the (001) projection of 11%. Fig. 2 shows the electron-density map corresponding to this level of refinement.

A similar procedure was adopted for the (100) and (010) projections except that it was found that the above correction could not be applied satisfactorily, presumably because secondary extinction was comparable with primary extinction in the crystals used for these zones. The final R factors for the ($0kl$) and ($h0l$) reflexions were 12% (108 medium reflexions) and 14% (81 medium reflexions) respectively. The (100) electron-density map corresponding to this level of refinement is shown in Fig. 3.

For each zone of reflexions the atomic shifts recommended by the least-square calculations were all less than 0.6 times the standard deviation for the atom concerned, and the average recommended shift was 0.3 times the average standard deviation. Thus there was no further purpose in proceeding with the calculations.

The final parameters for the atoms, each co-ordinate being a mean from two least-squares refinements with equal weight given to all reflexions, are given in Table 1 together with the standard deviations for these values calculated according to Cruickshank (1959). Table 2 gives the bond lengths and angles corresponding to Table 1 and Table 3 gives a comparison between the observed (F_o) and calculated (F_c) structure factors.

Discussion of the structure

The structure of $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is best understood by reference to the projection on the (010) plane (Fig. 4) from which it can be seen that, as Hofmann pointed out, most of the atoms lie near to the $(\bar{2}01)$ planes. On the other hand the arrangement of the atoms within these planes (Fig. 5) is somewhat different from Hofmann's structure. In particular, the sulphate groups are differently oriented so that the close proximity of two oxygen atoms from different sulphate groups criticized by Wyckoff (1951), in his analysis of Hofmann's structure, has been eliminated in our structure.

The octahedron of water molecules around the divalent metal has also undergone a rotation from the Hofmann arrangement and the bond lengths have now become approximately equal at 2.03 Å, 2.03 Å and 2.05 Å, agreeing very well with the values quoted for the Ni-H₂O bond lengths in NiSO₄·6H₂O, *viz.* 2.02 Å, 2.02 Å, 2.04 Å (Beever & Lipson, 1932).

Chidambaram (1961) has determined the directions and lengths of the inter-proton vectors of the water molecules in the K₂Zn(SO₄)₂·6H₂O, Tutton salt, and found that large distortions in Hofmann's structure would have to be made for hydrogen bonding to occur. Our atomic positions suggest that each water molecule forms two hydrogen bonds to oxygen atoms from different sulphate groups (Fig. 4) and these suggested hydrogen bonds agree quite well with Chidambaram's inter-proton vectors. The vector between the sulphate

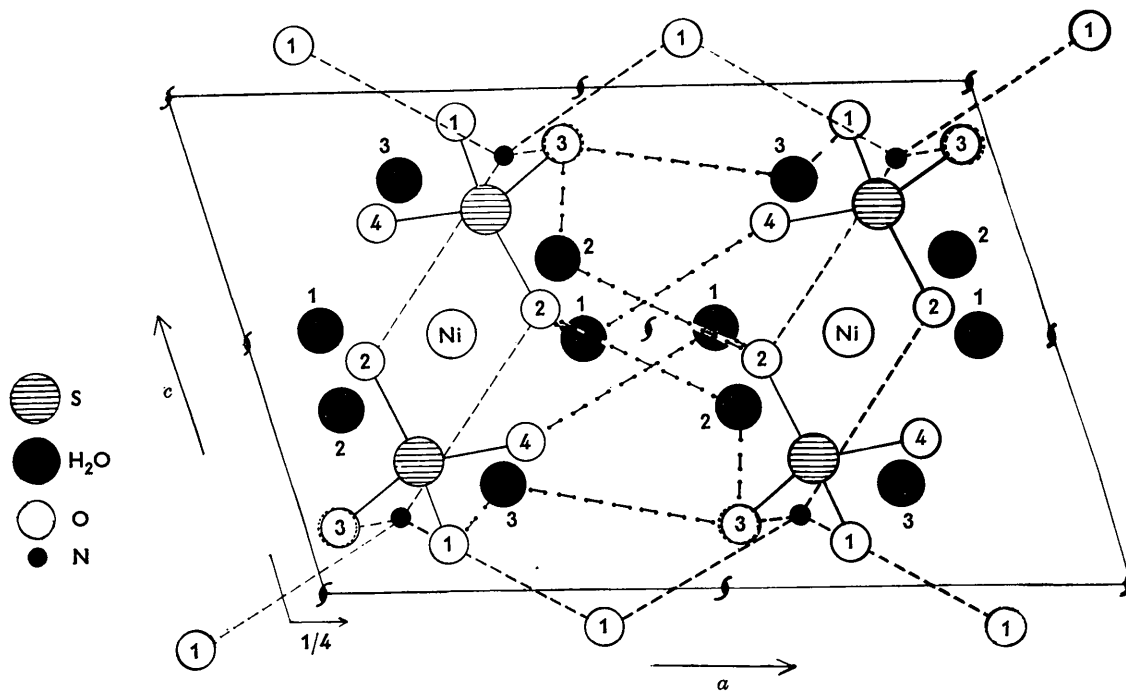
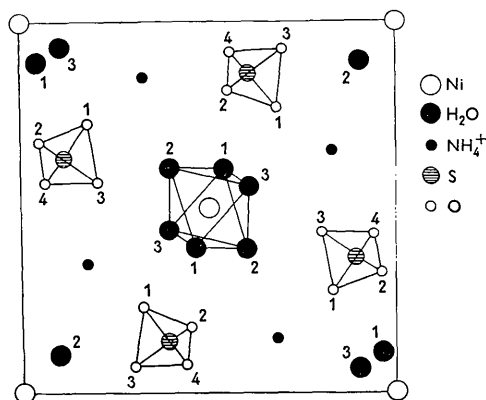


Fig. 4. (010) projection with origin shifted to $-\frac{1}{4}a, -\frac{1}{2}c$, showing the proposed hydrogen bonding as broken lines. The dotted O(3) is bound to the nitrogen atom and is either above or below the sulphate group shown (atoms numbered according to Table 1).

Table 4. Comparison of structure with proton resonance data

$O(1)-\hat{O}_{H_2O(3)}-O(3)$ 98°	$O(1)-O_{H_2O(3)}$ 2.71 Å	$O(3)-O_{H_2O(3)}$ 2.80 Å	φ_{Ni} $4.3 \pm 3^\circ$	φ_c $-8 \pm 5^\circ$	δ_{Ni} $37 \pm 3^\circ$	δ_c $40.5 \pm 2^\circ$
$O(2)-\hat{O}_{H_2O(2)}-O(3)$ 115°	$O(2)-O_{H_2O(2)}$ 2.81 Å	$O(3)-O_{H_2O(2)}$ 2.86 Å	$118.5 \pm 3^\circ$	$113 \pm 2^\circ$	$16.5 \pm 7^\circ$	$16.5 \pm 4^\circ$
$O(2)-\hat{O}_{H_2O(1)}-O(4)$ 104°	$O(2)-O_{H_2O(1)}$ 2.78 Å	$O(4)-O_{H_2O(1)}$ 2.62 Å	$20.2 \pm 2^\circ$	$20.5 \pm 5^\circ$	$42 \pm 4^\circ$	$46.5 \pm 2^\circ$

Fig. 5. Atomic arrangement within the $(\bar{2}01)$ planes (atoms numbered according to Table 1).

group oxygens bonded to a given water molecule should be approximately parallel to the inter-proton vector of this water molecule. In Table 4 the angles which the projection of the inter-proton vectors make with the a axis in the (010) plane, φ_c , and the angles δ_c which the inter-proton vectors make with the (010) plane are compared with the corresponding angles φ_{Ni} and δ_{Ni} made by the vectors between sulphate group oxygens bonded to the same water molecule. Table 4 shows that Chidambaram's results fit quite well with our oxygen and water-molecule positions. Also the distances between the hydrogen-bonded oxygen atoms and the angles they make at the water molecules are in the range for similar structures (2.68–2.06 Å and 84°–130°; Bacon & Curry, 1962).

As regards the correlation of our results with the paramagnetic resonance data for ammonium nickel sulphate hexahydrate (Griffiths & Owen, 1952) it should be noted that the oxygen atoms belonging to the water molecules form an approximately regular octahedron about the nickel ion, whereas Griffiths & Owen observed a strong rhombic component to the cubic crystal field indicating orthorhombic or lower symmetry of the water complex. We believe that a three-dimensional refinement with further thermal vibration parameters will be necessary to show that the symmetry of the water molecule oxygen atoms has this rhombic component. However, we should like to propose an alternative explanation to the observations of Griffiths & Owen.

The detailed electron distribution in a water molecule is such that there are maxima of electron

density in approximately regular tetrahedral directions from the oxygen nucleus *i.e.* in the directions of the hydrogen nuclei and also in the plane of symmetry at right angles to the H–O–H plane. This means there are two distinct ways in which a water molecule may arrange itself relative to the positive metal ion namely (a) where all the atoms are coplanar and (b) where the nickel ion and the two hydrogen atoms occupy three vertices of a tetrahedron about the oxygen atom (Griffith, 1961). Using our suggested hydrogen bonds to determine roughly the positions of the hydrogen atoms (one third of the way along the $O_{H_2O} \cdots O_{SO_4}$ bond) we find that the aspects of $H_2O(1)$ and $H_2O(3)$ are of type (b) and that the aspect of $H_2O(2)$ is nearer to (b) than to (a). The crystal field exerted by the water molecules on the nickel ion would therefore have a component of less than orthorhombic symmetry even if the oxygens of the water molecules formed a regular octahedron.

Table 5. The positions of the sulphate oxygen atoms surrounding the ammonium ion, and their corresponding hydrogen-bond lengths and angles

Atom	x	y	z	Distance O–N (Å)
N	0.133	0.347	0.348	—
O(2)	–0.117	0.321	–0.05	2.87
O(3)	0.220	0.570	0.377	2.76
O(1)	0.411	0.229	0.581	2.92
O'(1)	–0.089	0.271	0.581	3.04
$O(1)-\hat{N}-O(1)=101^\circ$		$O(3)-\hat{N}-O(1)=121^\circ$		
$O(2)-\hat{N}-O(1)=139^\circ$		$O(3)-\hat{N}-O(1)=108^\circ$		
$O(2)-\hat{N}-O(1)=83^\circ$		$O(3)-\hat{N}-O(2)=112^\circ$		

We also propose a system of hydrogen bonding for the ammonium group in which the nitrogen atom is bonded to four sulphate-group oxygen atoms which are approximately at the vertices of a tetrahedron about the nitrogen atom. Table 5 and Fig. 4 show the positions of these oxygen atoms together with the relevant bond lengths and angles. The tetrahedral angles are rather large for two of these angles and this suggests that the hydrogen atoms lie some distance away from the line joining the nitrogen and oxygen atom. This system of hydrogen bonding avoids the close proximity of hydrogen atoms belonging to the ammonium groups and belonging to the water

molecules. Each ammonium group is bonded to three sulphate groups and each sulphate group is bonded to three ammonium groups. In this way, every hydrogen atom takes part in a bond to a sulphate oxygen atom so that three of the oxygen atoms from each sulphate group are involved in three hydrogen bonds and one, O(4), is involved in only one. This behaviour is also found to occur in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, where oxygen atoms take part in from 1 to 4 hydrogen bonds (Bacon & Curry, 1962).

An interesting feature of this suggested bonding system is that three of the hydrogen bonds from the ammonium group lie approximately parallel to the glide plane, whereas the fourth lies nearly perpendicular to it. Thus a framework of $\text{NH}_4\text{-SO}_4$ groups lies in layers parallel to (010) throughout the crystal. Such an arrangement is particularly interesting because it has been pointed out by Tutton (1916) that although all the salts of this isomorphous series show a good cleavage parallel to $(\bar{2}01)$, certain of the ammonium salts (the double sulphates and selenates of Mg, Ni, Mn and Cu) also show a good cleavage parallel to (010) which, with one doubtful exception, is never observed in the absence of the ammonium ion. We therefore suggest that this extra cleavage arises because of the layered structure of hydrogen bonds described above.

Finally, we would add that an investigation of the structure of ammonium copper double sulphate is to be published shortly and that, apart from the water complex, this structure is essentially the same as that of the salt described in this paper.

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