Determination of structure

The powder pattern consisted of a series of lines from a single cubic lattice, plus the few impurity lines. An extrapolation of *a versus* $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta,\theta)$ to 180° gave a lattice parameter of 3·610 Å. This, combined with the density, leads to one formula weight per unit cell. However, upon lengthy exposure, interspersed between these primary lines, was a set of barely discernible (invisible to a diffractometer) lines. These lines can be accounted for if the pattern is reindexed with the parameter doubled.

Table 1. *Observed and calculated structure factors*

hkl	*I**(obs.)	*F*(obs.)	*F*(calc.)
100	10,000	14·8	15·7
(110)	0	0	(0)
111	1,324	9·2	−5·9
200	3,689	22·2	28·5
210	2,853	11·6	12·0
211	133	2·7	2·1
220	1,354	16·7	20·5
(221)			
(300)	944	9·7	9·6
222	363	14·2	16·3
320	308	7·9	8·0
321	118	3·6	2·3
400	190	13·1	13·7
(322)			
(410)	659	8·5	7·1
(330)			
(411)	192	5·0	2·2
420	837	11·6	13·2
421	1,134	7·9	8·2

* Arbitrary scale.

The integrated intensities were measured with Cu *Kα* radiation by scanning with a Norelco diffractometer. The observed intensities are shown in Table 1. The indexing is on the basis of the 3·610 Å unit cell, the extremely weak secondary lines being ignored at this point. It will be observed that the 110 line is conspicuously absent.

On the basis of the lack of systematic absences and the one formula weight per unit cell, the space group can be assigned as *Pm*3*m* (O_h^1). From the usual structural considerations, one would anticipate that the Al^{3+} would be at the center of a cube, and the F^- ions at the face centers, and the water molecule distributed in some fashion within the cell. In order to find this distribution, it is necessary only to find the parameters that will cause the 110 line to vanish. If one tries various possibilities, it soon becomes clear that if (for convenience) the Al^{3+} is placed in 1(*a*) (0, 0, 0), the only combination that permits F_{110} to be zero, and gives reasonable intensity agreement of the strong lines, is to put the F^- in 3(*d*) ($\frac{1}{2}$, 0, 0; 0, $\frac{1}{2}$, 0; 0, 0, $\frac{1}{2}$) and to distribute randomly (*i.e.*, place $\frac{1}{3}$) of the water molecule in 3(*c*) (0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0). The F_{hkl}'s calculated on this basis are shown in Table 1. The F_{hkl}'s were calculated by assuming a temperature factor $B=2\cdot0$ for the Al^{3+} and F^-, and $B=4\cdot0$ for the O^{2-} ions. A scale factor was found by calculating $\langle F(\mathrm{cal})/F(\mathrm{obs})\rangle$. The final *R* index on the basis of all measured reflections is 16·4%.

Conclusions

$AlF_3.H_2O$ forms a cubic lattice, with the Al^{3+} at the body center of the cube and the fluoride ions at the face centers. The observed Al^{3+}–F^- distance (1·805 Å) is in good agreement with that reported by Naray-Szabo & Sasvari (1938) for the $[AlF_6]^{3-}$ anion (1·81 Å). The one water molecule is randomly distributed at the centers of the cube edges. There is apparently some correlation among the water molecules of the unit cells. This correlation is strong enough to appear to double the size of the unit cell, giving rise to weak superstructure lines. If the intensities of these faint lines were measured, the degree of order in the compound could be determined.

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The crystal structure of Tutton's salts. II. Magnesium ammonium sulfate hexahydrate and nickel ammonium sulfate hexahydrate.

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In the course of a series of investigations on Tutton salts (Montgomery & Lingafelter, 1964) the structures of magnesium ammonium and nickel ammonium sulfate hexahydrate $(NH_4)_2Mg(SO_4)_2.6H_2O$ and $(NH_4)_2Ni(SO_4)_2.6H_2O$ have been determined from three-dimensional X-ray diffraction data with Cu *Kα* radiation ($\lambda=1\cdot5418$) and refined by a least-squares procedure. The structures have already been reported elsewhere (Mg, Margulis & Templeton, 1962; Ni, Grimes, Kay & Webb, 1963), but a brief account of the present results is given since the previously published structure of the nickel salt was based on two-dimensional data.

Magnesium salt

Cell dimensions (calibrated with a_0 for NaCl = 5·6387 Å)

$$a=9\cdot383\pm0\cdot015,\quad b=12\cdot669\pm0\cdot02,\quad c=6\cdot220\pm0\cdot005\ \text{Å};$$
$$\beta=107^\circ\ 03'\pm6'.$$

R was 5·5 for 1132 reflections (*hk*0–*hk*4 inclusive) of which 97 were classified as unobserved. Our parameters do not differ significantly from those previously published and are not listed except for H atoms, which are being used in all subsequent investigations on the isomorphous series. The position of the H atoms was found from ΔF maps and the coordinates refined by a least-squares method (Busing & Levy, 1959). The results are listed in Table 1.

Table 1. *Atomic coordinates for* H *atoms*

$[Mg(NH_4)_2(SO_4)_2 . 6H_2O]$

		x/a	*y/b*	*z/c*
N(10)	H(11)	0·058	0·337	0·225
	H(12)	0·208	0·305	0·394
	H(13)	0·095	0·344	0·487
	H(14)	0·174	0·421	0·346
O(7)	H(15)	0·200	0·091	0·317
	H(16)	0·227	0·134	0·116
O(8)	H(17)	−0·252	0·096	−0·059
	H(18)	−0·143	0·176	0·008
O(9)	H(19)	−0·097	−0·066	0·341
	H(20)	0·027	−0·135	0·325

Nickel salt

Cell dimensions (calibrated with a_0 for NaCl = 5·6387 Å)

$$a = 9{\cdot}241 \pm 0{\cdot}02,\ b = 12{\cdot}544 \pm 0{\cdot}015,\ c = 6{\cdot}243 \pm 0{\cdot}005\ \text{Å};$$
$$\beta = 106^\circ\ 58' \pm 6'.$$

The parameters were taken from the zinc and magnesium structures and were refined by least-squares to a final *R* of 0·070 for 1086 reflections of which 141 were classed as unobserved. Anisotropic temperature factors were used and absorption corrections applied. The hydrogen positions were verified from a three-dimensional ΔF summation and their positional parameters refined, but no great accuracy can be claimed for them. A list of atomic coordinates is given in Table 2. The main point of interest is the arrangement of water molecules about the nickel ion and bond lengths and angles are given in Table 3.

Table 2. *Final atomic coordinates*

		x/a	*y/b*	*z/c*
	Ni(1)	0·000	0·000	0·000
	S(2)	0·4074	0·1369	0·7390
	O(3)	0·4144	0·2272	0·5912
	O(4)	0·5485	0·0754	0·7883
	O(5)	0·2789	0·0671	0·6218
	O(6)	0·3839	0·1774	0·9478
	O(7)	0·1682	0·1071	0·1639
	O(8)	−0·1600	0·1100	0·0357
	O(9)	0·0019	−0·0661	0·2987
	N(10)	0·1354	0·3452	0·3543
N	H(11)	0·074	0·305	0·168
	H(12)	0·192	0·323	0·391
	H(13)	0·082	0·347	0·375
	H(14)	0·137	0·399	0·337
O(7)	H(15)	0·187	0·094	0·323
	H(16)	0·214	0·124	0·116
O(8)	H(17)	−0·245	0·089	−0·056
	H(18)	−0·146	0·184	0·023
O(9)	H(19)	−0·086	−0·058	0·352
	H(20)	0·004	−0·143	0·333

Table 3. *Bond length and angles*

Estimated standard deviation are given in parenthesis

Bond lengths (Å)		Bond angles (°)	
Ni–H_2O(07)	2·085 (0·012)	O(9)–Ni–O(7)	90·4 (0·4)
Ni–H_2O(08)	2·083 (0·012)	O(8)–Ni–O(7)	88·5 (0·4)
Ni–H_2O(09)	2·036 (0·012)	O(8)–Ni–O(9)	89·3 (0·4)
S–O(3)	1·475 (0·015)	O(3)–S–O(4)	109·6 (0·6)
S–O(4)	1·470	O(3)–S–O(5)	108·6
S–O(5)	1·486	O(3)–S–O(6)	109·5
S–O(6)	1·473	O(4)–S–O(5)	109·2
		O(4)–S–O(6)	110·3
		O(5)–S–O(6)	109·6

Table 4. *Intermolecular distances*

Bond	Relative position of second atom*			Bond length	
O(5)–O(7)	*x*	*y*	*z*	2·786	(0·026) Å
O(6)–O(7)	*x*	*y*	*z*+1	2·856	
O(4)–O(8)	*x*+1	*y*	*z*+1	2·725	
O(6)–O(8)	*x*+½	½−*y*	*z*+1	2·776	
O(3)–O(9′)	*x*+½	½−*y*	*z*+1	2·736	
O(5)–O(9′)	*x*	*y*	*z*+1	2·785	
O(9)–O(9′)	*x*	*y*	*z*+1	3·020	
O(3)–N(10)	*x*	*y*	*z*	2·970	

* This is the transformation relating each 'second atom' to the corresponding atom in the original asymmetric unit O(9′) is –O(9).

The length of the equatorial Ni–O bonds, 2·08 Å, is somewhat shorter than that predicted from ionic radii (2·12 Å, Pauling, 1960) but this does not appear significant. The axial bond (Ni–O(9)) is shorter by 0·048 Å, which repeats the pattern set by zinc and magnesium. The bond angles are very close to right angles. There are six hydrogen bonds, two for each water molecule, and these are listed in Table 4.

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