

ammonium alum crystals (β class) on rubidium alum (α class) and from the morphological features of the crystal so formed he concluded that the deposited methyl ammonium alum possessed the α structure.

Confirmation of this existence of dimorphism in methyl ammonium alum has now been obtained by causing both structures to be formed in the same single crystal and the present investigation was undertaken in order to determine the details of the α form of the crystal.

Experimental details

During the course of an investigation by X-ray diffraction of phase changes occurring in methyl ammonium alum at moderately low temperatures (Fletcher & Steeple, 1961) it was observed that single crystals from one particular batch showed weak traces of a structure other than that of the normal β alum and, after having been several times subjected to temperatures in the range 170 to 150 °K., that one of these crystals did not ultimately return to its initial room-temperature state. On subsequent Weissenberg photographs, taken at room temperature with Cu $K\alpha$ radiation and with the crystal oscillating about the original [001] direction, there appeared together two strong diffraction patterns both of which were characteristic of the space group $Pa\bar{3}$. Both space groups were confirmed as $Pa\bar{3}$ from rotation photographs and from further Weissenberg photographs obtained with the crystal oscillating about the other two cube axes. The linear dimensions of the respective unit cells, determined to an accuracy of the order of $\pm \frac{1}{2}\%$, were

$$a = 12.50 \text{ and } a = 12.17 \text{ \AA}.$$

Intensity data for the two structures were collected by eye estimation of the reflexions on the $hk0$ Weissenberg photograph; the Lorentz and polarization factors were applied but the crystal was sufficiently small for absorption corrections to be neglected. Scaling and temperature factors were obtained by Wilson's method (1942).

Determination of the structures

Utilization of the structural data published by Lipson (1935*b*) established that the structure having unit-cell edge of length 12.50 Å was that of the normal β form of methyl ammonium alum and from a Patterson projection along the [001] direction the sulphur atom of the second structure was located on a triad axis at (0.31, 0.31, 0.31). These are the eightfold fractional coordinates characteristic of the sulphur atom in the α -alum structure and since an α form of methyl ammonium alum had already been deposited on a crystal of rubidium alum (Lipson, 1935*a*) a trial structure was postulated for the former in which the atomic coordinates were those given by Lipson (1935*a*) for the latter; the atoms of the methyl ammonium group were all considered to be located on the centres of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) etc. Omitting all accidentally absent reflexions the agreement residual was 0.26 when calculated on the Mercury computer with scattering-factor data in the form published by Forsyth & Wells (1959).

Refinement was by two-dimensional ($F_o - F_c$) syntheses and in the closing stages it was possible to locate on a difference map six of the twelve non-equivalent hydrogen atoms of the water molecules, the remaining six being inserted by calculation after inspection of a model of the structure. The value of

Table I. Comparison of observed and calculated structure factors

$hk0$	$ F_o $	F_c	$hk0$	$ F_o $	F_c	$hk0$	$ F_o $	F_c	$hk0$	$ F_o $	F_c
020	46.2	-37.6	420	89.4	79.4	6,11,0	26.6	32.4	10,7,0	<15.2	-12.6
040	138.0	187.2	430	13.4	-19.4	6,12,0	<16.8	4.6	10,8,0	22.4	-20.2
060	144.0	131.6	440	20.2	27.0	6,13,0	<14.4	9.4	10,9,0	25.2	27.2
080	16.0	-15.2	450	17.2	-7.2	6,14,0	<12.8	12.8	10,10,0	25.0	27.8
0,10,0	65.8	63.0	460	20.2	11.2				10,11,0	15.2	-19.4
0,12,0	<15.2	-4.6	470	14.8	-3.2	810	49.6	-44.2	10,12,0	<8.2	7.4
0,14,0	20.2	21.0	480	60.6	68.6	820	88.0	82.8			
			490	36.8	32.0	830	<13.8	-25.2	12,1,0	61.8	70.2
210	67.2	71.4	4,10,0	<15.2	-11.8	840	32.2	29.8	12,2,0	30.4	22.6
220	130.8	143.2	4,11,0	<15.2	-2.6	850	22.2	-6.0	12,3,0	23.2	-30.4
230	26.0	-21.2	4,12,0	34.0	38.2	860	<15.2	15.8	12,4,0	26.4	26.6
240	52.0	-65.0	4,13,0	16.2	23.4	870	27.0	-28.4	12,5,0	<17.6	8.4
250	<10.0	9.4	4,14,0	24.2	30.0	880	62.8	66.4	12,6,0	23.8	18.6
260	138.8	155.8	4,15,0	<9.0	17.4	890	26.2	32.4	12,7,0	37.8	37.4
270	37.4	30.4				8,10,0	<14.8	5.0	12,8,0	26.8	22.4
280	87.2	99.8	610	118.0	108.2	8,11,0	16.2	-17.6	12,9,0	18.8	11.2
290	47.4	-48.4	620	71.4	75.4	8,12,0	31.2	40.6	12,10,0	<8.2	17.0
2,10,0	<15.2	3.2	630	22.0	6.4	8,13,0	<10.2	6.2			
2,11,0	<15.6	-2.6	640	92.2	78.2				14,1,0	20.4	-15.8
2,12,0	29.6	25.6	650	51.2	44.4	10,1,0	46.4	-53.6	14,2,0	34.0	27.4
2,13,0	<14.2	-1.4	660	100.2	98.0	10,2,0	<15.2	-0.4	14,3,0	23.2	28.8
2,14,0	34.4	32.2	670	75.8	87.4	10,3,0	47.0	66.4	14,4,0	24.4	23.2
2,15,0	<11.4	-17.0	680	28.8	28.6	10,4,0	37.6	40.4	14,5,0	18.8	-22.4
			690	36.4	-44.6	10,5,0	<15.6	-1.4	14,6,0	18.6	15.6
410	102.2	-78.0	6,10,0	34.6	30.6	10,6,0	40.8	31.8	14,7,0	<8.0	-8.2

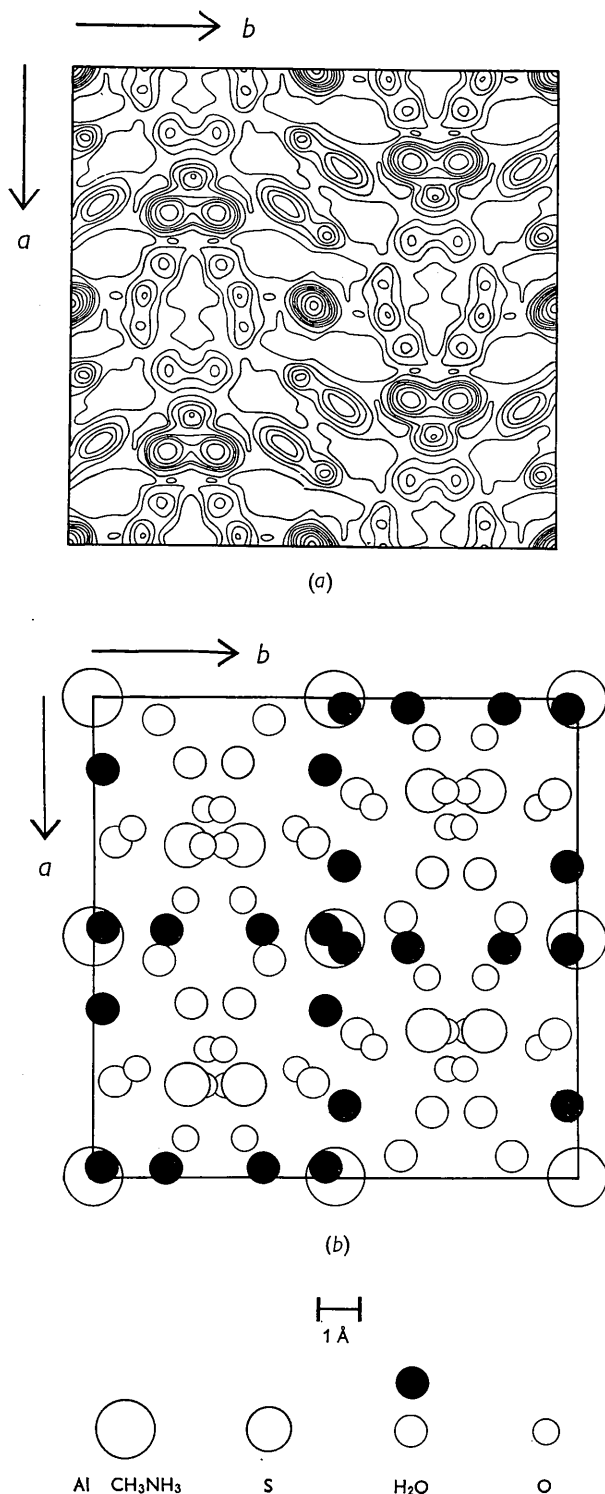


Fig. 1. (a) Projection of the electron-density distribution along [100]; contours are drawn at 3, 6, 9, 12, 15, 20, 30, 40 and 50 e.Å⁻². (b) Corresponding projection of the atomic arrangement.

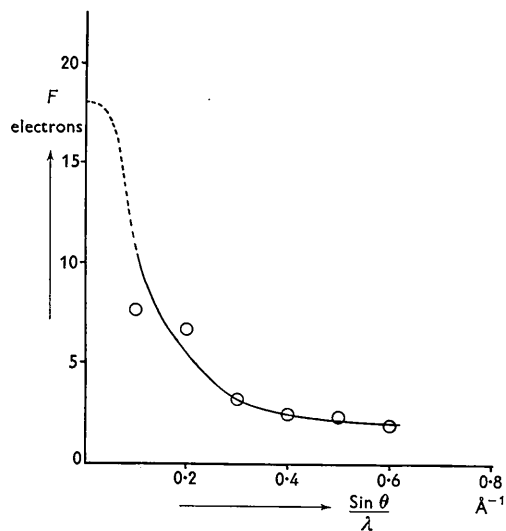


Fig. 2. Scattering-factor curve for methyl ammonium ion.

B in the expression $\exp(-B \sin^2 \theta / \lambda^2)$ was 2.2 Å² for each of the water hydrogen atoms and 1.9 Å² for all other atoms. Excluding those reflexions for which the calculated value of the intensity was less than the minimum observed value in the appropriate range of $\sin \theta$, the agreement residual obtained from the final list of observed and calculated structure factors shown in Table 1 was 0.17; the electron-density distribution and the corresponding atomic positions are shown in projection in Figs. 1(a) and 1(b) respectively.

During the course of refinement it was necessary to construct an experimental scattering-factor curve for the spherically-symmetrical methyl ammonium ion and for this purpose the $hk0$ reflexions with k even were divided into groups covering successive ranges of 0.1 Å⁻¹ in $\sin \theta / \lambda$, the value of the scattering factor at the centre of each range being taken to be the mean of the contributions of the methyl ammonium ion to the relevant structure factors in that range. These data are shown in Table 2 and are plotted in Fig. 2; the value of the scattering factor falls sharply as $\sin \theta / \lambda$ increases as might be expected from the diffuse distribution of electron density which would result from a spherically-symmetrical group.

Table 2. Scattering-factor data for methyl ammonium ion

Centre of range of $\sin \theta / \lambda$ in Å ⁻¹	0.1	0.2	0.3	0.4	0.5	0.6
Mean value of F for CH ₃ NH ₃ in electrons	7.6	6.7	3.1	2.4	2.3	1.9

Discussion of the structure

The fractional coordinates of all non-equivalent atoms and the values of the more important contact dis-

tances and contact angles are shown respectively in Table 3 and Table 4; the water molecules associated with the aluminium atom are designated $H_2O(Al)$ and those associated with the methyl ammonium group are designated $H_2O(CH_3NH_3)$. Because of the overlap present in projection it was not possible to calculate the errors in the bond and contact lengths by any of the standard methods, but from consideration of the effect on the value of the agreement residual of small changes in the values of the atomic coordinates it is estimated that the lengths quoted are not in error by more than 0.04 Å.

Table 3. *The fractional coordinates of non-equivalent atoms*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	No. of equivalent positions
Al	0	0	0	4
CH_3NH_3	$\frac{1}{2}$	0	0	4
S	0.308	0.308	0.308	8
O	0.233	0.233	0.233	8
O	0.309	0.227	-0.080	24
$H_2O(Al)$	0.150	0.021	-0.018	24
$H_2O(CH_3NH_3)$	0.045	0.136	0.302	24
H	0.121	0.175	0.274	24
H	0.008	0.189	0.279	24
H	0.190	0.040	-0.075	24
H	0.207	0.030	0.040	24

Table 4. *Values of bond lengths and bond angles*

Bond length		
$H_2O(Al)-H_2O(Al)$		2.62 Å
$H_2O(Al)-Al$		1.85
S-O(special)		1.59
S-O(general)		1.43
O(special)-O(general)		2.51
O(general)-O(general)		2.29
$CH_3NH_3-H_2O(CH_3NH_3)$		2.98
$H_2O(Al)-H_2O(CH_3NH_3)$		2.65
$H_2O(Al)-O(general)$		2.68
$H_2O(CH_3NH_3)-O(general)$		2.75
$H_2O(CH_3NH_3)-O(special)$		2.70
Angle		
$H_2O(Al)-Al-H_2O(Al)$		90°
O(general)-S-O(general)		106
O(general)-S-O(special)		113
O(general)-O(general)-O(general)		60
O(general)-O(general)-O(special)		63
O(general)-O(special)-O(general)		54

Although the projection possesses only orthorhombic symmetry (the plane group is *pgm*) the requirements of the cubic symmetry of the structure were satisfied throughout the refinement by preserving the relationship *xy*, *yz*, *zx* between the coordinates of atoms related by the operation of the triad axis. The degree of

agreement between these coordinates and those of the corresponding peaks in the electron-density projection should provide a measure of the accuracy of the structure, but comparison was limited by the overlapping, to a greater or less degree, of every atom and it was possible to estimate only the values of the coordinates of one general oxygen atom peak and of two each of the aluminium and methyl ammonium waters. From the electron-density projection the positions of the peaks of the aluminium waters are at (0.150, 0.028); (0.480, 0.150) compared with atomic coordinates (0.150, 0.021); (0.482, 0.150). For the methyl ammonium waters the map coordinates are (0.045, 0.143); (0.138, 0.200) compared with atomic coordinates (0.045, 0.136); (0.136, 0.198).

The structure itself is that characteristic of an α alum (Lipson & Beever, 1935). As shown shaded in Fig. 1(b) a set of six water molecules is grouped octahedrally around each aluminium atom and a second (unshaded) set of six waters forms a more open group around each molecule of methyl ammonium. Contact between these two groups is made by hydrogen bonds between, on the one hand, each general oxygen atom of the sulphate group and one each of the aluminium and methyl ammonium waters, and, on the other hand, between each special oxygen atom and three of the methyl ammonium water molecules. The lengths of the hydrogen bonds vary from 2.65 Å to 2.75 Å.

The distances between nearest neighbours in the group of six water molecules arranged around the aluminium atom is 2.62 Å and that between the aluminium atom and the water molecules is 1.85 Å, the octahedral grouping being, of necessity, regular. In the sulphate group the special oxygen-general oxygen and the general oxygen-general oxygen distances are 2.51 Å and 2.29 Å respectively, and as no further shifts of the sulphate atoms were indicated by the ($F_o - F_c$) map it must be assumed that the tetrahedron formed by these atoms is not regular.

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