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The Crystal Structure of Methylammonium Chromium Alum

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It has generally been assumed that methylammonium chromium alum belongs to the β class of alums. The structure, however, is that of an α class alum with space group $Pa3$ and unit-cell edge 12·44 Å, and the result indicates that Lipson's classification in terms of the size of the monovalent ion should be modified to take account of the nature of the trivalent ion.

Introduction

It was shown by Lipson (1935) that the alums are polymorphous and that they could be classified as α, β, and γ alums according to their structure type. It appeared that the particular class of alum depended upon the size of the monovalent ion, and that if this ion were sufficiently large then the alum concerned would belong to the β class. However, Lipson (1935) demonstrated from morphological studies that the β class methylammonium aluminum alum could be induced to take up the α class structure, and the existence of this dimorphism was confirmed by a structure determination (Fletcher & Steeple, 1962) of a crystal of the alum which had been subjected to severe thermal cycling; in neither of these examples did the α structure occur naturally, so that Lipson's classification in effect remained inviolate. It is the purpose of this account to show that methylammonium chromium alum, which has always been considered to be a β alum, does, in fact, belong to the α class with crystal parameters similar to those of the dimorphic form of the corresponding aluminum alum; this inevitably suggests that, in addition to the size of the monovalent ion, the nature of the trivalent ion exercises some influence on the class to which a given alum belongs.

Experimental details

The unit cell was cubic with axial length, determined to an accuracy of $\pm\frac{1}{2}$%, of 12·44 Å. This, in conjunction with the measured density of 1·65 g.cm^{-3} corresponded to four molecules per unit cell. From the systematic absences from oscillation and zero-layer-line Weissenberg photographs, taken with Cu $K\alpha$ radiation, the space group was confirmed as $Pa3$.

Intensity data were collected by eye estimation of the reflexions on the $hk0$ Weissenberg photograph, and corrections were applied for absorption and for Lorentz and polarization effects. Initial scaling and temperature factors were obtained by Wilson's (1942) method.

Determination of the structure

The atomic parameters derived by Fletcher & Steeple (1962) for the α form of methylammonium aluminum alum were utilized as a trial structure and resulted in an agreement residual of 0·19 when the accidentally absent reflexions were omitted. In this initial calculation the empirical scattering-factor curve for the methylammonium group (Fletcher & Steeple, 1962) was used, but when it was replaced by the carbon, nitrogen and six hydrogen atoms of the group, all placed on the centres of symmetry at $(\frac{1}{2},0,0)$ *etc.*, the residual was still 0·19. Presumably the reason for this is that the eight atoms of the group are held by a covalent bond so that they share the electrons between them.

Refinement was continued by two-dimensional (F_o-F_c) syntheses with the Atlas computer and the scattering-factor data of Forsyth & Wells (1959) until the ultimate residual was 0·14; the calculation of this residual did not include those reflexions for which the calculated value of the intensity was less than the minimum observed value in the appropriate range of $\sin\theta$. No attempt was made to modify the thermal parameter B from its initial value of 1·5 Å^2, nor were the hydrogen atoms included in the refinement.

Final values of the observed and calculated structure factors are shown in Table 1; the electron-density distribution and the corresponding atomic positions are shown in projection in Fig. 1(*a*) and (*b*) respectively.

Table 1. *Comparison of observed and calculated structure factors*

$hk0$	$\lvert F_o\rvert$	F_c
020	17·0	−21·5
040	170·6	199·0
060	182·1	156·1
080	< 18·9	−6·8
0, 10, 0	73·5	82·6
0, 12, 0	36·5	31·4
0, 14, 0	28·8	27·0
210	81·8	81·7
220	151·5	170·9
230	32·8	−19·4
240	22·9	−12·8
250	20·9	20·6
260	149·6	171·1
270	35·6	41·3
280	100·6	101·3
290	43·8	−43·3
2, 10, 0	21·3	17·8
2, 11, 0	< 21·7	−2·5

Table 1 (*cont.*)

*hk*0	$\lvert F_o \rvert$	F_c
2, 12, 0	41·6	37·1
2, 13, 0	< 18·9	3·8
2, 14, 0	47·7	35·1
2, 15, 0	25·7	−22·4
410	97·6	−83·3
420	117·2	110·5
430	< 14·1	−19·6
440	64·8	61·7
450	16·3	−16·3
460	53·8	32·7
470	19·1	−6·5
480	70·6	71·4
490	36·6	22·6
4, 10, 0	< 19·4	−6·3
4, 11, 0	< 22·8	−1·9
4, 12, 0	48·5	52·7
4, 13, 0	17·9	23·0
4, 14, 0	32·6	29·9
4, 15, 0	25·2	19·2
610	95·2	96·8
620	81·4	103·1
630	20·8	−4·8
640	126·3	107·0
650	49·4	33·8
660	117·6	126·2
670	71·5	76·8
680	37·0	41·0
690	43·1	−55·7
6, 10, 0	57·1	53·8
6, 11, 0	20·5	19·0
6, 12, 0	31·9	28·6
6, 13, 0	< 15·4	7·5
6, 14, 0	20·6	21·2
810	40·3	−30·3
820	95·2	89·6
830	< 19·4	−21·8
840	49·6	50·0
850	20·9	−4·8
860	26·1	24·3
870	21·8	−18·5
880	78·0	73·1
890	21·0	25·7
8, 10, 0	19·7	18·8
8, 11, 0	17·9	−16·7
8, 12, 0	52·5	50·7
8, 13, 0	< 11·3	6·4
10, 1, 0	39·9	−55·1
10, 2, 0	26·4	26·4
10, 3, 0	53·2	63·6
10, 4, 0	48·2	57·6
10, 5, 0	< 21·7	0·0
10, 6, 0	57·1	49·7
10, 7, 0	< 20·8	−7·9
10, 8, 0	< 19·7	−13·4
10, 9, 0	25·7	27·5
10, 10, 0	33·8	34·4
10, 11, 0	16·6	−20·1
10, 12, 0	15·8	18·3
12, 1, 0	59·3	73·4
12, 2, 0	41·8	46·1
12, 3, 0	46·3	−36·6
12, 4, 0	45·5	53·8
12, 5, 0	< 19·3	0·8
12, 6, 0	45·4	43·4
12, 7, 0	37·6	37·7
12, 8, 0	33·2	37·8
12, 9, 0	< 12·5	1·6
12, 10, 0	29·4	35·7
14, 1, 0	20·1	−13·3
14, 2, 0	39·3	42·1
14, 3, 0	18·9	26·7
14, 4, 0	31·1	31·8
14, 5, 0	16·3	−24·8
14, 6, 0	25·7	23·5
14, 7, 0	10·3	−5·7

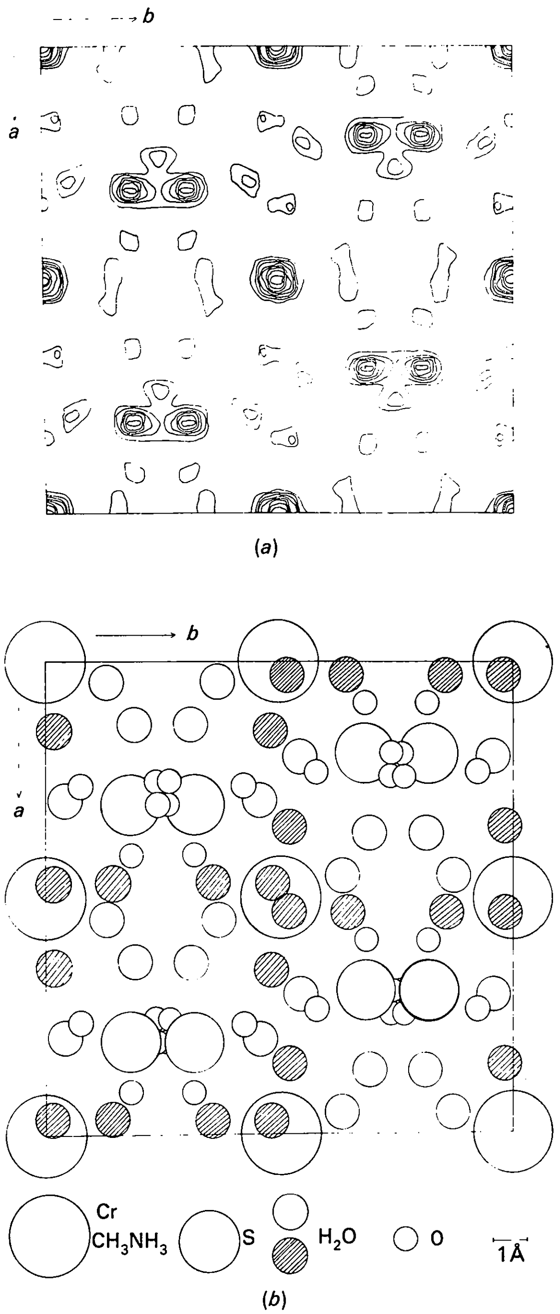

Fig. 1. (*a*) Projection of the electron-density distribution along [001]; contours are drawn at 10, 15, 20, 25, 30, 35, e.Å^{-2}. At ($\frac{1}{2}$, 0, 0) *etc.* the contours are drawn at 10, 20, 30, 40, 50, 60, 70, 80, e.Å^{-2}. (*b*) Corresponding projection of the atomic arrangement.

Table 2. *The fractional coordinates of non-equivalent atoms*

	x	y	z	Number of equivalent positions
C	0	0	0	4
CH_3NH_3	$\frac{1}{2}$	0	0	4
S	0·310	0·310	0·310	8
O	0·233	0·233	0·233	8
O	0·310	0·227	−0·080	24
$H_2O(Cr)$	0·161	0·021	−0·018	24
$H_2O(CH_3NH_3)$	0·047	0·136	0·302	24

Discussion of the structure

The fractional coordinates of all non-equivalent atoms, excluding those of the hydrogen atoms, are shown in Table 2. These differ so little from those of the atoms in the dimorphic form of methylammonium aluminum alum (Fletcher & Steeple, 1962) that contact distances and contact angles do not differ significantly from those given by Fletcher & Steeple. The water molecules associated with the chromium atom are designated $H_2O(Cr)$ and those associated with the methylammonium group are designated $H_2O(CH_3NH_3)$.

The electron-density projection which resulted from the final (F_o-F_c) synthesis showed a large negative region around $(\frac{1}{4},\frac{1}{4})$ which had a maximum value of 6·7 e.Å^{-2}. Such a large negative region was also observed in the α alum structures investigated by Fletcher & Steeple (1962) and by Larson & Cromer (1967), and it was suggested by the latter authors that the trough arose from disorder present in the SO_4 groups.

The different electronic configurations of the aluminum and the chromium atoms probably account for the difference in structure between methylammonium aluminum alum (in its usual form) and the corresponding chromium alum. Both atoms have three electrons in their respective outermost shells, which are the *M* shell for aluminum and the *N* shell for chromium, but whereas the *L* shell of the aluminum atom is full, the *M* shell of chromium is not. Thus electrons in the aluminum *L* shell cannot take part in the formation of molecular bonds but the electrons in the *M* shell of the chromium atom are not precluded from so doing. Since, too, the distance between the *L* and the *M* shells of the aluminum atom is very much greater than is that between the *M* and the *N* shells of the chromium atom it is reasonable to suppose that the nature of the trivalent ion does exercise some influence on the type of alum structure obtained. In this event it would be necessary to modify Lipson's classification of the alums to include the proviso 'for a given trivalent ion'.

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References

Fletcher, R. O. W. & Steeple, H. (1962). *Acta Cryst.* **15**, 960.

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.

Larson, A. C. & Cromer, D. T. (1967). *Acta Cryst.* **22**, 793.

Lipson, H. (1935). *Proc. Roy. Soc.* A**151**, 347.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.