

The Classification of the Chromium Alums

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It is shown that the structures of rubidium chromium alum and of thallium chromium alum belong to the α class of the alums. Crystals of methylammonium chromium alum grown in the absence of alcohol have the β structure and thus establish that this alum is dimorphous. The unit-cell dimensions of the three alums are: rubidium, 12.30 Å; thallium, 12.24 Å; methylammonium, 12.52 Å. Summaries are given of the classifications of the known alums from which it is concluded that the structural class is influenced to some extent by the nature of the trivalent ion.

Introduction

Lipson (1935) concluded that the structures of the alums could be classified as α , β or γ ; his results are tabulated below in order of increasing size of the monovalent ion.

Alum	Class
NaAl(SO ₄) ₂ 12H ₂ O	γ
NH ₄ Al(SO ₄) ₂ 12H ₂ O	α
KAl(SO ₄) ₂ 12H ₂ O	α
KCr(SO ₄) ₂ 12H ₂ O	α
RbAl(SO ₄) ₂ 12H ₂ O	α
CH ₃ NH ₃ Al(SO ₄) ₂ 12H ₂ O	β
CsAl(SO ₄) ₂ 12H ₂ O	β
TlAl(SO ₄) ₂ 12H ₂ O	α

The classification is expressed in terms of the size of the monovalent ion, and from the table it is apparent that thallium aluminum alum is the only one of those investigated which does not fit into the scheme; it may be significant that the exception is the only one of the monovalent ions which is not an alkali.

Klug (1940) later undertook an investigation of several alums in which the trivalent ion was chromium. His results, which are summarized in the table below, indicate that the chromium alums do not necessarily have the same structures as do their aluminum analogues. Thus the chromium alums of both rubidium and thallium would appear to belong to the β -class whereas the corresponding aluminum alums have the α -class structure.

Alum	Class
NH ₄ Cr(SO ₄) ₂ 12H ₂ O	α
RbCr(SO ₄) ₂ 12H ₂ O	β
CH ₃ NH ₃ Cr(SO ₄) ₂ 12H ₂ O	β
CsCr(SO ₄) ₂ 12H ₂ O	β
TlCr(SO ₄) ₂ 12H ₂ O	β

From further work, Ledsham & Steeple (1968*a*) reported that methylammonium chromium alum belonged to the α class; this alum was grown from an alcohol solution, but in the present investigations it has been established that when the crystals are grown

from a solution in water only, their structure is that of a β alum. Both methylammonium chromium alum and methylammonium aluminum alum (Fletcher & Steeple, 1962) are therefore dimorphous. The dimorphous forms of the aluminum alum were not, however, observed separately in different crystals by Fletcher & Steeple, neither has it been possible to achieve this in the present work. In view of the similarity in behaviour of the methylammonium chromium and the methylammonium aluminum alums it would seem unlikely that the corresponding alums containing rubidium as the monovalent ion would differ so much in their structures as to belong to different classes, as has been indicated by the independent investigations of Lipson and Klug. The fact that the rubidium ion is smaller than that of methylammonium suggests that it is the rubidium chromium alum that has been wrongly classified, and accordingly the structure of this alum has been redetermined. The structures of thallium chromium alum and of methylammonium chromium alum grown from a solution in water have also been examined.

Experimental details

Crystals of chromium alums having respectively rubidium, thallium and methylammonium as the monovalent ion were grown from solutions in water; in addition, crystals of rubidium chromium alum were grown from a solution which contained alcohol. Oscillation and Weissenberg photographs of a sample of each type of crystal were taken about the [001] direction with Cu $K\alpha$ radiation; intensity data were collected for the rubidium alum only, and these by eye estimation of the $hk0$ reflexions on a Weissenberg photograph. The Lorentz and polarization factors were applied to the intensities but absorption corrections were not made; scaling and temperature factors were determined by Wilson's (1942) method.

Classification of the structures

Each of the alums belonged to the space group $Pa\bar{3}$ with lattice parameters of 12.30 Å for rubidium chro-

mium, 12.24 Å for thallium chromium and 12.52 Å for methylammonium chromium; the estimated errors were of the order of $\pm\frac{1}{2}\%$. From the zero-layer-line Weissenberg photographs it was evident that the thallium alum belonged to the α class and that methylammonium chromium alum had the β -class structure. Since the latter alum, when grown from a solution containing alcohol, was in the α class, it was thus established that the crystal was dimorphous. There was no evidence of dimorphism in rubidium chromium alum, and the crystal structure, which was that of the α class, was not affected by the method of growth of the crystal itself.

The density of the rubidium alum was 1.95 g.cm^{-3} , which corresponds to four formula units per unit cell. Refinement of the structure was begun from the atomic coordinates of the α -form of methylammonium chromium alum (Ledsham & Steeple, 1968*a*) and was continued with two-dimensional data by the minimum-residual method of Bhuiya & Stanley (1963), using the structure-factor data of Forsyth & Wells (1959), until the agreement residual reached 0.18; the value of the overall thermal parameter was 1.4 \AA^2 . Neither the accidentally absent reflexions nor the hydrogen atoms were included in the refinement process. Observed and calculated structure factors are listed in Table 1, and in Table 2 are shown the refined values of the fractional atomic coordinates; $\text{H}_2\text{O}(\text{Cr})$ and $\text{H}_2\text{O}(\text{Rb})$ refer to the water molecules associated with the chromium and the rubidium ions respectively.

Table 1. Comparison of observed and calculated structure factors for rubidium chromium alum

<i>h</i>	<i>k</i>	0	$ F_o $	F_c
0	2	0	95.8	96.2
0	4	0	224.6	308.2
0	6	0	251.4	275.4
0	8	0	63.0	74.0
0	10	0	118.0	132.4
0	12	0	100.4	102.0
0	14	0	40.8	57.6
2	1	0	78.8	97.6
2	2	0	151.0	253.0
2	3	0	20.4	-17.2
2	4	0	42.4	70.2
2	5	0	34.0	17.0
2	6	0	169.6	253.2
2	7	0	34.8	43.2
2	8	0	132.6	175.2
2	9	0	38.4	-42.6
2	10	0	57.0	72.2
2	11	0	<24.0	-4.0
2	12	0	77.4	87.6
2	13	0	26.6	10.8
2	14	0	91.4	88.2
2	15	0	43.2	-30.2
4	1	0	112.0	-86.2
4	2	0	184.0	206.6
4	3	0	<14.4	-18.6
4	4	0	141.6	148.2
4	5	0	<16.8	-12.6
4	6	0	116.8	110.4
4	7	0	<20.4	-13.6
4	8	0	148.4	149.0
4	9	0	32.6	20.0

Table 1 (cont.)

<i>h</i>	<i>k</i>	0	$ F_o $	F_c
4	10	0	53.2	44.0
4	11	0	<24.0	13.4
4	12	0	103.6	105.0
4	13	0	<20.4	13.0
4	14	0	72.4	68.6
6	1	0	116.8	95.8
6	2	0	178.0	182.6
6	3	0	<18.0	11.0
6	4	0	220.2	188.6
6	5	0	57.6	39.2
6	6	0	266.0	215.6
6	7	0	94.0	74.4
6	8	0	98.8	98.4
6	9	0	50.6	-48.6
6	10	0	147.2	115.0
6	11	0	23.0	27.6
6	12	0	89.2	62.8
6	13	0	25.6	14.4
6	14	0	52.8	58.4
8	1	0	34.8	-39.2
8	2	0	179.0	176.8
8	3	0	20.8	-30.8
8	4	0	145.6	122.2
8	5	0	<22.3	-2.4
8	6	0	80.4	73.0
8	7	0	24.0	32.2
8	8	0	169.4	148.2
8	9	0	33.4	29.4
8	10	0	71.0	61.0
8	11	0	<20.4	-15.2
8	12	0	88.6	86.0
8	13	0	<20.0	6.2
10	1	0	61.6	-61.2
10	2	0	93.8	100.8
10	3	0	64.8	65.8
10	4	0	104.0	104.8
10	5	0	<24.0	6.4
10	6	0	124.2	103.6
10	7	0	23.4	-17.8
10	8	0	50.2	38.8
10	9	0	46.6	24.2
10	10	0	79.0	79.0
10	11	0	<16.0	-9.2
12	1	0	70.8	82.0
12	2	0	78.0	78.0
12	3	0	23.2	-42.2
12	4	0	107.4	107.8
12	5	0	<21.6	4.0
12	6	0	103.6	83.6
12	7	0	61.6	47.8
12	8	0	88.8	70.0
12	9	0	<14.5	7.0
14	1	0	19.0	-18.8
14	2	0	81.8	95.8
14	3	0	25.6	29.8
14	4	0	59.6	70.0
14	5	0	15.8	-24.6
14	6	0	51.8	58.2

An $(F_o - F_c)$ synthesis showed the deep negative region around $(\frac{1}{2}, \frac{1}{2})$ which appears to be characteristic of the α alums (Fletcher & Steeple, 1962; Larson & Cromer, 1967; Ledsham & Steeple, 1968*a, b*).

Conclusions

The respective classifications of rubidium chromium alum and thallium chromium alum do not agree with

Table 2. *Fractional atomic coordinates of non-equivalent atoms in rubidium chromium alum*

	x	y	z	Number of equivalent positions
Cr	0	0	0	4
Rb	$\frac{1}{2}$	0	0	4
S	0.312	0.312	0.312	8
O	0.237	0.237	0.237	8
O	0.313	0.227	-0.080	24
H ₂ O(Cr)	0.151	0.011	-0.018	24
H ₂ O(Rb)	0.043	0.146	0.302	24

those published by Klug (1940); this may be because Klug's deductions were made from consideration of only a few reflexions. By taking the present results in conjunction with those of Lipson (1935), Klug (1940) and Ledsham & Steeple (1968*a, b*) it is concluded that the chromium alums can now be classed as follows:

Alum	Class
NaCr(SO ₄) ₂ 12H ₂ O	α
NH ₄ Cr(SO ₄) ₂ 12H ₂ O	α
KCr(SO ₄) ₂ 12H ₂ O	α
RbCr(SO ₄) ₂ 12H ₂ O	α
CH ₃ NH ₃ Cr(SO ₄) ₂ 12H ₂ O	α or β
CsCr(SO ₄) ₂ 12H ₂ O	β
TlCr(SO ₄) ₂ 12H ₂ O	α

It can be seen by comparison of this summary with that given for the aluminum alums in the Introduction,

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The Crystal Structure of K₃MoCl₆

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The Mo ions in K₃MoCl₆ have been found to occupy two non-equivalent lattice sites in accordance with previous susceptibility and specific heat measurements.

Introduction

Previous measurements on the magnetic behaviour of K₃MoCl₆ have shown that magnetic spin ordering occurred at two different temperatures, *i.e.* at 4.7°K and 6.6°K (van Dalen & Steenland, 1967; Herweijer & Gijssman, 1967). This could be explained if it is assumed that the Mo ions occupy non-equivalent lattice sites.

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that only when sodium is the monovalent ion is there a clear-cut distinction between the structures of the aluminum and of the chromium alums. With methylammonium, the trivalent ion also affects the two alums differently in that the existence of dimorphism is much more readily demonstrated with the chromium alum than it is with the aluminum alum. Thus the type of structure possessed by a given alum is determined largely by the size of the monovalent ion (Lipson, 1935), and although the structure is influenced to some extent by the nature of the trivalent ion, this influence is not nearly so strong as was first presumed (Ledsham & Steeple, 1968*b*).

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In order to investigate the validity of this assumption, an X-ray diffraction study at room temperature was undertaken.

Experimental

The unit cell, determined from an X-ray powder diagram obtained with Cu K α radiation, was monoclinic with $a = 12.160$ (8), $b = 7.534$ (3), $c = 12.731$ (6) Å, and $\beta = 108.66$ (1)°.

A small crystal, in the shape of a thin plate with dimensions 0.002 × 0.020 × 0.020 cm³, was selected