

similarity probably no conclusions can be made with regard to the angles of twist existing in solution.

The spectral change going from the planar biphenyl (253 $m\mu$) and non-planar *o*-diphenylbenzene (237 $m\mu$) (Dale, 1957) to C_6Ph_6 is rather surprising.

All the calculations were performed on an Elliott 803B computer using the programming system devised by Daly, Stephens & Wheatley (1967).

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The Crystal Structures of Sodium Chromium Alum and Caesium Chromium Alum

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Sodium chromium alum with $a = 12.40 \text{ \AA}$ and caesium chromium alum with $a = 12.50 \text{ \AA}$ both have space group $Pa\bar{3}$. Refinement of the structure of the sodium alum has resulted in a residual of 0.165 but no attempt has been made to refine the structure of the caesium alum. Sodium chromium alum, which has the α structure, does not fit into the classification scheme of Lipson, whereas caesium chromium alum, with the β structure does. In view of earlier work by Ledsham & Steeple it is concluded that the class of an alum structure is governed by the particular combination of monovalent and trivalent ions that is involved, and that there is no infallible rule for the pre-determination of a given structure.

Introduction

It has been shown by Lipson (1935) that the alums are polymorphous and can be classified as α , β and γ according to which of three different types of structure they belong to. Lipson suggested that the class was determined by the size of the monovalent ion, the γ class for small ions, the β class for large ions and the α class for those intermediate in size; with the exception of potassium chromium alum the investigations were confined to samples in which the trivalent ion was aluminum. The results are summarized in the fol-

lowing table, from which it can be seen that potassium chromium alum fitted into the classification scheme.

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

Ledsham & Steeple (1968) have found that methylammonium chromium alum has, unexpectedly, the α structure, and the object of the present work has been to determine also the structures of both sodium chro-

mium alum and caesium chromium alum. The former is of particular interest because its aluminum counterpart is the only known example of a γ alum.

Determination of the structures

The space group of both structures was confirmed as $Pa\bar{3}$; the axial length of sodium chromium alum was $12.40 \text{ \AA} \pm 0.05 \text{ \AA}$ and that of caesium chromium alum was $12.50 \text{ \AA} \pm 0.05 \text{ \AA}$. Comparison of the respective $hk0$ Weissenberg photographs with those of known α and β alums showed that sodium chromium alum had the α structure and that caesium chromium alum had the β structure. Further confirmation that the caesium alum belonged to the β class was forthcoming by comparison of the relative intensities of the $hk0$ reflexions from this alum with those of caesium aluminum alum, which have been estimated by Lipson (1935) as strong, weak, medium, and so on. Refinement of the structure was not undertaken.

The structure of sodium chromium alum was refined from intensity data collected by eye estimation of the $hk0$ reflexions on a zero-layer-line Weissenberg photograph. From a trial structure based on the coordinates of methylammonium chromium alum (Ledsham & Steeple, 1968), refinement was carried out by the minimum-residual method of Bhuiya & Stanley (1963) and with the scattering-factor data of Forsyth & Wells (1959). Calculation of the final agreement residual of 0.165 did not include either the accidentally absent reflexions or the contribution of the hydrogen atoms. It was not necessary to modify the overall thermal parameter, B , from its initial value of 1.5 \AA^2 .

Final values of the observed and calculated structure factors of sodium chromium alum are shown in Table 1; both the electron-density distribution and the corresponding atomic positions differ so little from those of methylammonium chromium alum (Ledsham & Steeple, 1968) that reproduction of the diagram would not serve any useful purpose.

Discussion of the structure

Table 2 gives the fractional coordinates of all non-equivalent atoms, apart from those of the hydrogen atoms, in the structure of $\text{NaCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; those designated $\text{H}_2\text{O}(\text{Cr})$ refer to the water molecules which are associated with the chromium ion and those referred to as $\text{H}_2\text{O}(\text{Na})$ are the coordinates of those associated with the sodium ions. The electron-density projection along $[001]$ which resulted from the use of the coordinates in an $(F_o - F_c)$ synthesis had the large negative region around $(\frac{1}{4}, \frac{1}{4})$ which appears to be characteristic of the α -alum structure (Fletcher & Steeple, 1962; Larson & Cromer, 1967; Ledsham & Steeple, 1968).

Taken in conjunction with the results of Lipson (1935) and of Ledsham & Steeple (1968) the outcome of the present investigation demonstrates that the clas-

Table 1. Comparison of observed and calculated structure factors for $\text{NaCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}^*$

$h k l$	F_o	F_c
0 2 0	<8.9	2.2
0 4 0	169	231
0 6 0	163	185
0 8 0	<19.3	20.4
0 10 0	93.8	97.4
0 12 0	47.4	33.2
0 14 0	28.8	27.4
2 1 0	83.4	95.6
2 3 0	125	187
2 5 0	34.2	-25.0
2 7 0	27.4	-15.4
2 9 0	26.4	21.4
2 11 0	159	199
2 13 0	52.0	13.6
2 15 0	109	121
2 17 0	55.8	-49.2
2 19 0	21.2	27.6
2 21 0	<21.8	1.2
2 23 0	55.2	41.0
2 25 0	<19.1	1.8
2 27 0	57.2	49.6
2 29 0	29.6	-20.0
4 1 0	102	-97
4 2 0	124	120
4 3 0	<14.5	-25.2
4 4 0	79.2	78.0
4 5 0	16.8	-17.0
4 6 0	58.4	45.6
4 7 0	19.6	-9.8
4 8 0	104	99
4 9 0	42.8	29.6
4 10 0	<21.7	-0.8
4 11 0	<21.2	-8.4
4 12 0	62.8	65.0
4 13 0	17.8	24.0
4 14 0	43.6	30.8
4 15 0	30.4	18.2
6 1 0	116	118
6 2 0	92	134
6 3 0	30.2	-9.4
6 4 0	130	112
6 5 0	54.2	44.8
6 6 0	155	157
6 7 0	89.4	88.4
6 8 0	53.0	48.2
6 9 0	57.6	-58.4
6 10 0	81.6	65.8
6 11 0	<20.5	29.8
6 12 0	41.4	25.4
6 13 0	14.4	13.2
6 14 0	26.4	27.4
8 1 0	51.6	-47.4
8 2 0	100	102
8 3 0	<19.7	-28.6
8 4 0	65.2	65.6
8 5 0	21.2	-9.8
8 6 0	30.6	30.6
8 7 0	22.2	-19.6
8 8 0	97.8	96.0
8 9 0	21.0	27.8
8 10 0	19.8	12.4
8 11 0	<17.8	-24.2
8 12 0	60.2	62.4
8 13 0	11.2	12.4
10 1 0	53.0	-58.6
10 2 0	37.8	38.6
10 3 0	49.2	64.2
10 4 0	51.6	61.2
10 5 0	<21.8	7.6
10 6 0	72.2	62.8
10 7 0	<20.8	-12.6
10 8 0	<19.7	-14.8
10 9 0	36.4	30.2
10 10 0	50.0	45.8
10 11 0	13.4	-23.0
10 12 0	22.2	13.8
12 1 0	66.8	74.8
12 2 0	51.6	46.4
12 3 0	29.4	-37.6
12 4 0	54.2	64.4
12 5 0	<19.2	4.2
12 6 0	61.6	12.6
12 7 0	58.8	46.6
12 8 0	51.2	44.2
12 9 0	<12.4	2.4
12 10 0	30.2	32.0
14 1 0	23.2	-17.4
14 2 0	52.8	51.6
14 3 0	26.6	26.6
14 4 0	35.8	34.6
14 5 0	53.0	-24.6
14 6 0	36.2	25.8
14 7 0	8.4	-7.8

* F_o for the reflexion 040 should read 149 instead of 169.

Table 2. *The fractional coordinates of non-equivalent atoms in NaCr(SO₄)₂·12H₂O*

	x	y	z	Number of equivalent positions
Cr	0	0	0	4
Na	$\frac{1}{2}$	0	0	4
S	0·310	0·310	0·310	8
O	0·239	0·239	0·239	8
O	0·307	0·224	-0·080	24
H ₂ O(Cr)	0·158	0·014	0·018	24
H ₂ O(Na)	0·042	0·136	0·302	24

sification of an alum structure depends upon the particular combination of monovalent and trivalent ions present. There does not appear to be any infallible criterion and therefore, should the details of an unknown structure be required, it would be advisable to

make an independent determination of the structure rather than to rely on any general scheme of classification of the alums.

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Molecular Nitrogen as a Ligand: The Crystal Structure of Nitrogenpentammineruthenium(II) Dichloride and Related Salts

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The X-ray crystal structure analysis of the chloride of nitrogenpentammineruthenium(II) has been carried out with diffractometer data. The salt crystallizes in the cubic system, $a=10\cdot141$ Å, space group $Fm\bar{3}m$, $F432$ or $F\bar{4}3m$; these are indistinguishable because all non-hydrogen atoms are in special positions. The structure is disordered, the nitrogen molecule randomly occupying one of the six octahedral positions around the ruthenium ion. Within the limits of accuracy imposed by the disorder, the Ru-N-N moiety is linear. An investigation has been made of the isomorphous bromide ($a=10\cdot41$ Å), iodide ($a=10\cdot94$ Å), tetrafluoroborate ($a=11\cdot166$ Å) and hexafluorophosphate ($a=11\cdot79$ Å).

Introduction

It has been known for some years that transition metals, in the form of complexes or in the metallic form, are necessary for the fixation of molecular nitrogen. Until recently no complexes containing molecular nitrogen as a ligand had been isolated. The preparation of nitrogenpentammineruthenium(II) salts, $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$, $\text{X}=\text{Cl}^-$, Br^- , I^- , BF_4^- , PF_6^- in these laboratories (Allen & Senoff, 1965; Allen, Bottomley, Harris, Reinsalu & Senoff, 1967) therefore raised questions as to the nature of nitrogen-metal bonding involved. A preliminary report of the X-ray structure analysis has appeared elsewhere (Bottomley & Nyburg, 1966).

Experimental

The iodide and bromide were prepared by method 1, the chloride, tetrafluoroborate and hexafluorophosphate by method 3 of Allen *et al.* (1967). The iodide formed pale yellow leaf-shaped crystals elongated along

[011]. The other salts were yellow octahedra. The crystals were mounted in thin-walled glass capillaries and were all less than 0·1 mm maximum dimension. Under these conditions μR is approximately 0·295 for $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{I}_2$ and 0·097 for $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$, where μ is the linear absorption coefficient (cm^{-1}) and R is the maximum radius of the crystal treated as a sphere. Lattice parameters for the iodide, bromide, tetrafluoroborate and hexafluorophosphate were determined from rotation and zero-layer Weissenberg photographs with Mo $K\alpha$ radiation. For the chloride, lattice parameters were obtained from a zero-layer Weissenberg photograph calibrated with aluminum using 22 Cu $K\alpha$ and Cu $K\beta$ reflexions with Bragg 2θ greater than 114° at 25°C . The data were treated by the method of least squares. These and other crystallographic data are summarized below:

$[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$	$M=285\cdot2$	$a=10\cdot141\pm 0\cdot001$ Å
	$V=1042\cdot90$ Å ³	$Z=4$
	$D_m=1\cdot83$ g.cm ⁻³ (flotation in $\text{CHCl}_3/\text{CHBr}_3$)	$D_c=1\cdot82$ g.cm ⁻³
		$F(000)=568$