tact [N(3)–O(3) = 3·05 Å], but N(2) is not. Perhaps the shrinkage of the C–N ring along the N(3)$\cdots$N(3') direction as discussed above may be attributed in part to a probable strain due to the compact packing of molecules along approximately the same direction. All hydrogen atoms are also involved to the short O$\cdots$H intermolecular contact, where the O(2)$\cdots$H(4) distance is particularly short, 2·36 Å. It appears to form a weak intermolecular hydrogen bond of the type C–H$\cdots$O, in which the C$\cdots$O distance is 3·37 Å and the C–H–O angle is 153 degrees. A similar type of close intermolecular approach of hydrogen atoms and oxygen atoms of nitro groups has been observed in the structure of tetryl and other nitro-compounds, as discussed by Cady (1967).

The anisotropic thermal motion of each atom was examined by converting the thermal parameters in Table 2 into the three components of a root-mean-square displacement from the equilibrium position. The results are given in Table 5. The oxygen and hydrogen atoms which occupy the terminal position of the molecular bond chain exhibit clearly larger vibrations than those of the ring-atoms [e.g. N(2), N(3), C(1), C(2)], as we can expect. The direction of the largest r.m.s. component (R_3) of each atom in the two NO$_2$ groups is also presented in this Table as evidence of the rigid-body oscillations of the nitro group. Assuming that the N(2), N(1), O(1), O(2) atoms of the N(2)-nitro group are bound by rigid bonds and vibrate collectively about the N(2) atom, the largest vibration direction of an atom 'X' in the NO$_2$ group should be perpendicular to the direction from the N(2) atom to the 'X' atom if the effect of the anisotropic motion of the N(2) atom is negligible. Consequently the orientation of the largest vibration component is described by the angles from three orthogonal vectors, A_1, A_2, A_3, which are defined by N(2)–X, $A_1 \times$ [O(1)–O(2)], and $A_1 \times A_2$, respectively. The vibration directions of the atoms in the N(3)-nitro group are described in the same way. The vibration directions measured from the A_1 direction are essentially 90 degrees for all atoms of the two nitro groups. This supports the assumption of the rigid-body oscillation of the nitro group. The investigation of the deviations from the A_2 and A_3 directions suggest that the nitrogen atom of the NO$_2$ group oscillates predominantly in the nitro-group plane and the oxygen atoms exhibit a combination of the two predominant motions; in-plane oscillation about the base atom [N(2) or N(3)] and oscillation about the N–N axis.

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The Behaviour of the Sulphate Groups in the Alum Structures

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Each of the sulphate groups in any alum structure is situated with the sulphur atom and one oxygen atom on a threefold axis and with the other three oxygen atoms in general positions round this axis. The oxygen atoms, and in particular those on the threefold axes, are subject to anomalous behaviour which has been explained by Larson & Cromer in terms of disorder of the sulphate groups. It is shown, however, that the oxygen atoms are more probably subject to extreme thermal motion, the nature of which it is difficult to postulate without violation of the space-group symmetry requirements.

Introduction

Since the completion of the investigations of the alum structures by Lipson & Beevers (1935) and Lipson (1935), interest in the various properties of these double salts has continued and one of the features that has attracted attention has been the anomalous behaviour of the sulphate groups (Bacon & Gardner, 1958; Larson & Cromer, 1967; Ledsham & Steeple, 1968a,b, 1969). In order to conform to the space

group $Pa3$ to which the alums belong, each sulphate ion is oriented with the sulphur atom and one oxygen atom in special positions on a threefold axis with the remaining three oxygen atoms in general positions round this axis. In a two-dimensional neutron-diffraction study of potassium chromium alum, Bacon & Gardner (1958) found it necessary to allocate to the thermal parameters of the special and general oxygen atoms the abnormally high values of 8·0 and 6·9Å² respectively. During the course of a three-dimensional investigation, Larson & Cromer (1967) assigned values of 13 and 7Å² to the thermal parameters of these particular atoms in the structure of potassium aluminum alum, and rather lower values to these same two parameters in ammonium aluminum alum and rubidium aluminum alum. However, Larson & Cromer concluded that the features of the different Fourier syntheses obtained by them and the results obtained by Bacon & Gardner could be better explained by the assumption of some degree of disorder in the sulphate groups; this disorder was introduced by the inversion of a certain fraction of these groups along the threefold axis. They calculated that in the potassium aluminum alum structure about one-third of the the groups were reversed in this manner but their results for the ammonium and rubidium alums were less conclusive. In support of their disorder theory, Larson & Cromer suggest that the change in phase at 192·5°K in potassium chromium alum reported by Ray & Ray (1965) may be associated with the ordering of the sulphate groups at this temperature.

The results summarized above have been obtained with the α alums. One outcome of the present series of investigations has been that the anomalous behaviour of the sulphate groups extends also to the β alums.

Experimental details

Two-dimensional structural data were collected at room temperature for the following alums

α class	β class
$CH_3NH_3Cr(SO_4)_2.12H_2O$	$CH_3NH_3Al(SO_4)_2.12H_2O$
$KCr(SO_4)_2.12H_2O$	$CH_3NH_3Cr(SO_4)_2.12H_2O$
$NaCr(SO_4)_2.12H_2O$	
$RbCr(SO_4)_2.12H_2O$	
$TlCr(SO_4)_2.12H_2O$	

The classification is that adopted by Lipson (1935).

After refinement of these structures using overall isotropic thermal parameters which ranged in value from 1·1 to 1·5Å² according to the alum concerned, there was present on each two-dimensional $(F_o - F_c)$ synthesis on area of negative electron density in the region of the point (0·25, 0·25); the depth of the hole was of the order of 7 e. Å⁻² for each alum. In the neighbourhood of the point (0·25, 0·25) two oxygen atoms in special positions on different threefold axes overlap in projection, and it was possible to eliminate the

electron-density trough by the allocation of a value of 12Å² to the isotropic thermal parameters of these atoms. There was in no case any evidence of a compensating peak on the opposite side of the sulphur atom such as would arise from the presence of disorder of the sulphate groups. This peak would be about 3·5 e.Å⁻² high and may conceivably have been masked by the lack of resolution inherent in a two-dimensional synthesis containing overlapping atoms.

At low temperatures, two-dimensional data were collected at 85°K for the α class potassium chromium alum and the β forms of both methylammonium aluminum and methylammonium chromium alum. Also available were the published structure-factor data obtained at 113°K by Fletcher & Steeple (1964) for the β form of methylammonium aluminum alum.

The results for potassium chromium alum were obtained from oscillation and Weissenberg photographs from which it was established that at 85°K the structure was still cubic with space group $Pa3$ and unit-cell dimensions of 12·17Å. This is at variance with the change of phase at 192·5°K reported by Ray & Ray (1965). The fractional atomic coordinates differed only marginally from those published by Lipson (1935) and the ultimate agreement residuals, excluding accidentally absent reflexions, were 0·17 at room temperature and 0·13 at 85°K; for the purposes of refinement of the low-temperature data the isotropic thermal parameter was assumed to be zero. At the low temperature the depth of the region of negative electron density at (0·25, 0·25) on the $(F_o - F_c)$ Fourier synthesis was reduced to 4·0 e.Å⁻². Thus there remains a deficiency of 2·0 e.Å⁻² in the contribution from each of the overlapping special oxygen atoms. This deficiency is relatively small when account is taken of the fact that at these low temperatures the projected electron density corresponding to an oxygen atom is about 14 e.Å⁻², a value that is approaching twice that at room temperature.

By virtue of the anomalous dielectric properties of methylammonium chromium alum observed at 160°K by Griffiths & Powell (1952) it is to be expected that at this temperature the crystal should undergo a phase change similar in nature to that determined by Fletcher & Steeple (1964) in methylammonium aluminum alum. The occurrence of such a phase change in methylammonium chromium alum was verified from measurements made on a series of oscillation photographs and first and second layer-line Weissenberg photographs obtained at 85°K. The low-temperature structure was orthorhombic with space group $Pca2_1$ and unit-cell dimensions all accidentally equal to 12·48Å.

In the change of phase from cubic to orthorhombic symmetry it should be a matter of chance as to which of three possible orientations the orthorhombic structure will assume. That is, it should be a matter of chance as to which of the three orthorhombic axes will be parallel to the original cubic axis about which

oscillation was taking place. However, possibly because of differential strains set up between the crystal and support when cooling occurs, the orthorhombic [100] direction was repeatedly the one to come out parallel to the axis of oscillation of the crystal. To determine the resulting y and z coordinates, transformation of the axes from those of space group $Pa3$ to those of space group $Pca2_1$ had first to be effected, and this involved a change from (x,y,z) to $(y,x,-z)$ accompanied by a transfer of the origin from (000) to $(0\frac{1}{4}\frac{1}{4})$. With the room-temperature structure as a starting point and assuming a value of zero for the overall thermal parameter the final agreement residual for the [100] projection of the low-temperature structure was 0·14; the accidentally absent reflexions were again omitted from the calculation of the residual. The negative region, now located near (0·25, 0·00) on the customary difference Fourier synthesis, was reduced in depth to a value of 3·0 e.Å^{-2}.

It is worthy of note that the carbon and nitrogen atoms of the CH_3NH_3 groups could each be located on the electron-density projection; the fractional coordinates of these and the other atoms, determined from this projection, are given in Table 1. The observed and calculated structure factors are given in Table 2.

Table 1. *Fractional atomic coordinates* (y and z) *of non-equivalent atoms in the orthorhombic phase of methylammonium chromium alum*

All atoms have four equivalent positions.

Atom	y	z
Cr	0·257	0·260
C	0·732	0·280
N	0·266	0·711
S	0·089	0·915
S	0·580	0·085
O	0·052	0·811
O	0·021	0·978
O	0·094	0·976
O	0·203	0·904
O	0·525	0·190
O	0·510	0·011
O	0·608	0·046
O	0·682	0·097
H_2O(Cr)	0·264	0·236
H_2O(Cr)	0·749	0·759
H_2O(Cr)	0·105	0·258
H_2O(Cr)	0·403	0·247
H_2O(Cr)	0·253	0·397
H_2O(Cr)	0·247	0·098
H_2O(M.A.)	0·299	0·591
H_2O(M.A.)	0·458	0·801
H_2O(M.A.)	0·807	0·425
H_2O(M.A.)	0·985	0·182
H_2O(M.A.)	0·086	0·521
H_2O(M.A.)	0·579	0·472

Table 2. *Comparison of observed and calculated structure factors for the* [100] *projection of the orthorhombic phase of methylammonium chromium alum*

0	k	l	$|F_o|$	$|F_c|$
0	1	0	<9·3	10·8
0	2	0	45·1	50·6

Table 2 (*cont.*)

0	k	l	$|F_o|$	$|F_c|$
0	3	0	<20·6	8·8
0	4	0	179	182
0	5	0	<24·7	34·2
0	6	0	214	240
0	7	0	<25·6	22·2
0	8	0	60·4	61·8
0	9	0	<30·3	3·2
0	10	0	61·2	34·6
0	11	0	<26·9	38·2
0	12	0	116	121
0	13	0	<24·9	35·2
0	14	0	55·2	67·0
0	15	0	<10·9	10·4
0	0	2	45·2	39·0
0	1	2	121	141
0	2	2	130	148
0	3	2	82·4	90·8
0	4	2	152	164
0	5	2	24·4	18·8
0	6	2	83·0	81·0
0	7	2	110	110
0	8	2	112	111
0	9	2	<29·6	32·0
0	10	2	101	122
0	11	2	84·8	62·2
0	12	2	<25·3	17·0
0	13	2	<22·4	18·4
0	14	2	51·8	70·2
0	15	2	<9·1	8·4
0	0	4	179	172
0	1	4	148	128
0	2	4	<23·0	23·0
0	3	4	99·2	55·6
0	4	4	118	89·4
0	5	4	<25·3	29·6
0	6	4	136	112
0	7	4	101	61·6
0	8	4	124	121
0	9	4	<33·0	40·2
0	10	4	71·0	62·4
0	11	4	84·8	82·2
0	12	4	57·4	48·8
0	13	4	21·8	24·8
0	14	4	35·8	32·2
0	15	4	<12·8	9·4
0	0	6	214	214
0	1	6	22·6	31·8
0	2	6	171	210
0	3	6	<27·2	15·0
0	4	6	49·6	32·4
0	5	6	<30·3	2·4
0	6	6	171	173
0	7	6	<30·6	37·0
0	8	6	29·8	29·6
0	9	6	<28·8	27·6
0	10	6	37·4	30·6
0	11	6	<25·6	18·8
0	12	6	32·0	62·4
0	13	6	18·4	34·8
0	14	6	32·0	45·2
0	0	8	60·4	46·4
0	1	8	23·0	45·0
0	2	8	98·4	101
0	3	8	83·2	68·2
0	4	8	86·8	69·4
0	5	8	63·2	47·2
0	6	8	111	86·6
0	7	8	113	102
0	8	8	108	96·6
0	9	8	<25·9	15·4

Table 2 (cont.)

0	k	l	$|F_o|$	$|F_c|$
0	10	8	76·4	52·4
0	11	8	31·6	52·0
0	12	8	41·6	56·6
0	13	8	30·6	45·8
0	0	10	61·2	76·6
0	1	10	87·2	35·8
0	2	10	98·4	68·2
0	3	10	30·2	32·6
0	4	10	28·8	41·0
0	5	10	60·0	50·0
0	6	10	89·6	62·2
0	7	10	88·0	80·0
0	8	10	80·6	70·2
0	9	10	21·8	34·8
0	10	10	39·0	35·6
0	11	10	31·6	34·4
0	12	10	21·4	31·4
0	0	12	116	120
0	1	12	< 26·6	19·0
0	2	12	84·0	66·6
0	3	12	< 26·4	5·6
0	4	12	54·6	44·0
0	5	12	23·2	36·2
0	6	12	93·0	75·6
0	7	12	< 20·2	9·6
0	8	12	20·0	30·2
0	9	12	< 14·8	3·6
0	10	12	9·8	25·2
0	0	14	55·2	68·8
0	1	14	58·6	57·2
0	2	14	48·2	36·8
0	3	14	18·1	30·8
0	4	14	44·2	36·6
0	5	14	< 15·8	7·0
0	6	14	29·2	42·4
0	7	14	29·6	37·6

The [001] projection of the orthorhombic phase of methylammonium aluminum alum was that obtained at 85°K. After the usual refinement procedure the agreement residual for this projection was 0·11 and the depth of the negative region of electron density on the $(F_o - F_c)$ synthesis was reduced to 3·0 e. Å^{-2}. Finally, on the difference electron-density map of the [001] projection of this alum, calculated from the data obtained at 113°K and published by Fletcher & Steeple (1964), the depth of the negative region was again 3·0 e. Å^{-2}.

Discussion of the anomaly

The present results indicate that the magnitude of the anomaly associated with the sulphate group is independent of the alum class and is roughly the same for all alums. Previous work has been confined to the α alums only and the results indicate that the magnitude of the anomaly varies from alum to alum of this class. Now if the sulphate groups are disordered, as proposed by Larson & Cromer, then the temperature at which ordering takes place will be well defined and will extend over only a narrow range. It is therefore conceivable that the results obtained by Larson & Cromer for three different α-alums were obtained

at three different temperatures in the neighbourhood of the transition temperature, thus accounting for different degrees of disorder in the three alums. On the other hand the results of the present work give no indication of an order–disorder transition at room temperature.

Normally an order–disorder transition is accompanied by a λ anomaly in the curve of specific heat against temperature, and in the specific-heat curve for the β form of methylammonium aluminum (Ashworth & Steeple, 1968) only one such anomaly was detected in the temperature range 14 to 300°K. This occurred at 176°K, the transition temperature between the cubic and orthorhombic phases, and the entropy change associated with this anomaly was 9·70 joule (mole)$^{-1}$°K^{-1}. Of this amount 9·14 joule (mole)$^{-1}$°K^{-1} is accounted for by the cessation of rotation of the CH_3NH_3 group, leaving an entropy excess of about 0·60 joule (mole)$^{-1}$°K^{-1}. This is less than one-tenth of the entropy change that would result from an order–disorder transition of the sulphate groups that would be of sufficient magnitude to account for the observed electron-density deficiency of 3·5 e. Å^{-2} for the oxygen atom on the threefold axis. Similar results have been observed in as yet unpublished work by Bunting & Steeple on the specific heat of the β form of methylammonium chromium alum in the temperature range 60 to 300°K.

There is thus no calorimetric evidence to support the theory of disorder of the sulphate groups. Further, if the electron-density anomaly were caused by disorder, then the disorder effect would persist unchanged as the temperature was lowered to that of the transition point, after which it would disappear completely. The X-ray diffraction results at 85 and 113°K show that although the anomaly is considerably reduced in size at these temperatures it does still persist and it points to the existence of some form of extreme thermal motion in the sulphate groups. The nature of this motion is, however, difficult to imagine. It must be such that it affects the oxygen atoms and especially so those on the threefold axes, but not the sulphur atoms; the motion must also conform with the requirements of the $Pa3$ space group. One explanation, albeit physically unrealistic, is that the sulphur group is in equally probable oscillation about any one of the three axes passing through the sulphur atom and each of the three oxygen atoms in general positions.

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The Crystal and Molecular Structure of Dichloro-π-methylallyl-bis-(triphenylarsine)rhodium(III)

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A crystal structure analysis of dichloro-π-methylallyl-bis(triphenylarsine)rhodium confirms that the two group V donor ligands are *trans* to the allyl ligand and reveals symmetrical rhodium–allyl bonding. The dihedral angle between the allyl plane and the As(1)–Rh–As(2) plane is 126·6° and the methyl group is displaced from the allyl plane 0·2 Å towards the Rh^{III} ion. The rhodium(III) ion is in only slightly distorted octahedral coordination and the rhodium–carbon distances show a lengthening due to the *trans* influence of the two arsine ligands.

Introduction

Nuclear magnetic resonance, infrared and dipole moment studies of the series of compounds $L_2Rh(\pi-C_3H_4R)Cl_2$, where $L = Ph_3As$, Ph_3Sb, Ph_3P, $[p-(CH_3)_2NC_6H_4]_3As$, $[p-(CH_3)_2NC_6H_4]_3Sb$ and $(Ph_2CH_3)As$ and $R = H$, CH_3, have suggested that the group V donor ligands are *trans* to the allyl ligand (Volger & Vrieze, 1967). It has further been suggested that an increase in the total electron donor capacity decreases the activation energy in the intramolecular rearrangement of the allyl ligand and that this may therefore be a function of the 'trans effect' of the group V ligand (Vrieze & Volger, 1967). The influence of *trans*-coordinated ligands has previously been invoked to explain the asymmetry of the bonding in such compounds as bis-π-allylrhodium chloride and triphenyl-phosphinemethylallylpalladium chloride (Mason & Russel, 1966; Smith, 1968). The crystal structure analysis of one of the compounds in the above series, $(Ph_3As)_2Cl_2Rh(\pi-C_4H_7)$, now confirms that the two arsine ligands are *trans* to the allyl group and revealed that the latter is symmetrically bonded. Furthermore the Rh–C and allyl C–C bond lengths indicate a considerable 'trans effect' of the triphenylarsine group. Preliminary results of this analysis have been published previously (Hewitt & de Boer, 1968).

Experimental

$(Ph_3As)_2Cl_2Rh(\pi-C_4H_7)$ crystallizes from acetone in the form of red-brown rhombohedra. A suitable crystal of approximate dimensions, $0.25 \times 0.15 \times 0.075$ mm, was selected and sealed in a 0·2 mm diameter glass capillary.

The estimated value of the linear absorption coefficient equals 26.1 cm^{-1}, which is sufficiently low for absorption corrections to be neglected. A preliminary study was carried out on the precession camera, which revealed that the complex crystallized in a triclinic space group and indicated that the crystal quality was good. The rough cell parameters obtained from the precession study were refined by least-squares calculations (Anzenhofer, de Boer & Hewitt, 1970) using values of $\sin \theta$ and $\sin (-\theta)$ measured on the diffractometer as observed data. The following refined cell parameters* were obtained:

$a = 21.7816 \pm 5$, $b = 10.178 \pm 2$,

$c = 10.233 \pm 3$ Å,

$\alpha = 112.77 \pm 3$, $\beta = 111.48 \pm 3$,

$\gamma = 102.60 \pm 5°$,

$U = 1707.0$ Å^3, $D_x = 1.592$ g.cm^{-3} for $Z = 2$,

$M = 847.4$.

No attempt was made to obtain a value for the measured density, the calculated value being of the order expected for this kind of compound.

The necessary arc orientation instructions for the Nonius three-circle automatic single-crystal diffractometer were calculated (Anzenhofer, de Boer & Hewitt, 1970) and complete three-dimensional data to $\sin \theta = 0.42$ were collected using Zr-filtered Mo $K\alpha$ radiation

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* The program refines six parameters, A, B, C, D, E, F where $A = a^{*2}$, $B = b^{*2}$, $C = c^{*2}$, $D = 2a^*b^* \cos \gamma^*$, $E = 2b^*c^* \cos \alpha^*$, $F = 2c^*a^* \cos \beta^*$. Maximum and minimum values for the cell constants are calculated using standard deviations of the above parameters. The error estimates given above are five times this spread.