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
$H_2O(Cr)$	0·151	0·011	−0·018	24
$H_2O(Rb)$	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
$NaCr(SO_4)_2 12H_2O$	α
$NH_4Cr(SO_4)_2 12H_2O$	α
$KCr(SO_4)_2 12H_2O$	α
$RbCr(SO_4)_2 12H_2O$	α
$CH_3NH_3Cr(SO_4)_2 12H_2O$	α or β
$CsCr(SO_4)_2 12H_2O$	β
$TlCr(SO_4)_2 12H_2O$	α

It can be seen by comparison of this summary with that given for the aluminum alums in the Introduction, 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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The Crystal Structure of K_3MoCl_6

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The Mo ions in K_3MoCl_6 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 K_3MoCl_6 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 & Gijsman, 1967). This could be explained if it is assumed that the Mo ions occupy non-equivalent lattice sites. 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 $K\alpha$ 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 $0·002 \times 0·020 \times 0·020$ cm^3, was selected

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from a batch of K_3MoCl_6 obtained from the S.W. Shattuch Chemical Company, Denver, Col., U.S.A. The mode of crystallization was shown to be with the c^* axis perpendicular to and the b axis in the plane of the plate.

Intensity data were collected on an integrating Weissenberg camera for all layers from $k=0$ to $k=5$ using Mo $K\alpha$ radiation. Microdensitometer readings of the films yielded 896 independent intensities out of a possible total of 1919. These were corrected for absorption by the method of Busing & Levy (1957), because of the large linear absorption coefficient ($\mu=36{\cdot}3$ cm^{-1}).

The space group was found to be $P2_1/a$ with $Z=4$.

Structure determination

An inspection of the diffraction data showed the reflexions with *hkl* all odd or all even to be generally

Table 1. *Final positional and temperature parameters*

In brackets, the standard deviation in units of the last decimal.

Atom	x	y	z	B
Mo(1)	0·0000	0·0000	0·0000	0·84 (5) Å^2
Mo(2)	0·5000	0·0000	0·5000	0·89 (5)
K(1)	0·1389 (4)	0·0318 (11)	0·4007 (4)	2·98 (11)
K(2)	0·3865 (4)	0·0656 (7)	0·1790 (4)	2·00 (10)
K(3)	0·2368 (4)	0·5679 (8)	0·1859 (4)	2·17 (10)
Cl(1)	0·1043 (4)	0·2063 (10)	0·1455 (4)	2·00 (9)
Cl(2)	0·4027 (4)	0·2699 (9)	0·4066 (4)	1·67 (9)
Cl(3)	0·3550 (4)	0·8171 (9)	0·3696 (4)	1·58 (9)
Cl(4)	0·1842 (4)	0·8629 (8)	0·0007 (4)	1·35 (8)
Cl(5)	0·9942 (4)	0·8008 (10)	0·1485 (4)	1·99 (9)
Cl(6)	0·1253 (3)	0·5066 (14)	0·3848 (3)	1·49 (7)

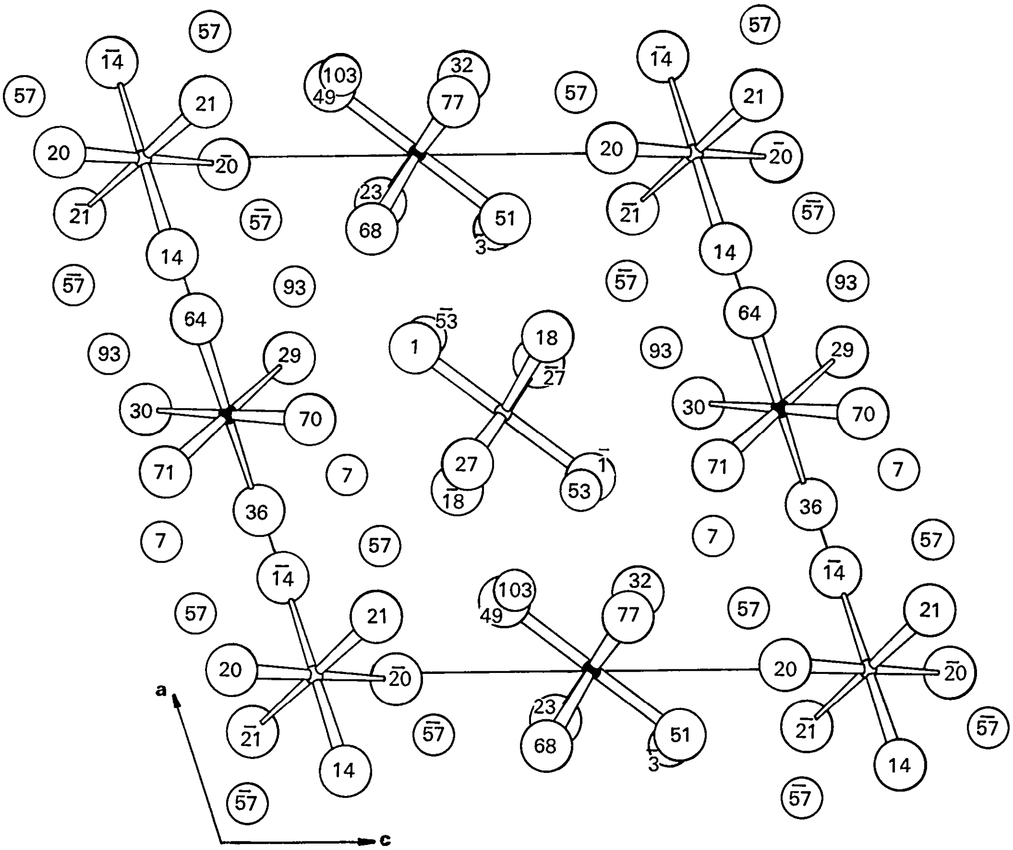

Fig. 1. Projection of the atomic positions on the (010) plane, showing the two different sets of octahedrally coordinated Mo ions. Large open circles: Cl. Medium open circles: K. Small black spheres: Mo at $y=\frac{1}{2}$. Small white spheres: Mo at $y=0$. Numbers in open circles show values of y in hundredths for K and Cl.

Table 2. *Bond lengths and angles in the* $MoCl_6^{3-}$ *ions*

In brackets, the standard deviation in units of the last decimal.

Bond lengths		Bond angles	
Mo(1)–Cl(4)	2·464 (5) Å	Cl(1)–Mo(1)–Cl(4)	90·75 (18)°
Mo(1)–Cl(1)	2·440 (6)	Cl(4)–Mo(1)–Cl(5)	90·52 (18)
Mo(1)–Cl(5)	2·432 (6)	Cl(1)–Mo(1)–Cl(5)	93·93 (21)
Mo(2)–Cl(2)	2·486 (6)	Cl(2)–Mo(2)–Cl(3)	90·40 (22)
Mo(2)–Cl(6)	2·430 (4)	Cl(2)–Mo(2)–Cl(3)	90·12 (24)
Mo(2)–Cl(3)	2·427 (5)	Cl(3)–Mo(2)–Cl(6)	91·95 (21)

stronger than the others. This indicated that the Mo ions occupy face-centred positions, *i.e.* 2(*a*) and 2(*d*) in space group $P2_1/a$. A Patterson synthesis yielded the approximate [4(*e*)] positions of the K and Cl ions.

Structure refinement

All 1919 reflexions, including the unobserved, were used in the least-squares refinement. The function to be minimized was $\Sigma w(cF_o^2-F_c^2)^2$ where the summation is over all reflexions; c is an appropriate layer scale factor and w the statistical weight of the observation. The weights were determined according to $w=F_o^2/F^{*2}$ for $F_o^2\le F^{*2}$ and $w=F^{*2}/F_o^2$ for $F_o^2>F^{*2}$, with F^{*2} having a value halfway along the intensity range.

In addition to the coordinates and layer scale factors, only atomic isotropic temperature parameters were refined. To speed up the calculations, the initial refinement cycles were performed with block-diagonal matrices only, leaving the full-matrix refinement to the last cycles.

The refinement was terminated when all calculated shifts were less than $0{\cdot}3\sigma$ and the difference synthesis showed no appreciable peaks. The final R index, defined as $R=\Sigma|F_o-F_c|/\Sigma F_o$, was 0·11.

A list of parameters appears in Table 1.

Discussion

The structure of K_3MoCl_6 can be regarded as a deformed substituted perovskite structure with the Mo(1), Mo(2), and K(3) ions in the centres of the Cl octahedra (Fig. 1).

The Mo ions occupy two different lattice sites, 2(*a*) and 2(*d*), which is in agreement with the assumptions based on the anomalous magnetic behaviour between 4° and 7°K, requiring two types of Mo ion corresponding to two different magnetic spin systems (van Dalen & Steenland, 1967; Herweijer & Gijsman, 1967).

Each Mo ion is surrounded by a slightly deformed Cl octahedron (Table 2) which, however, has been markedly rotated from its ideal position. These rotations seem to have reduced the difference in coordination between the K(3) ion and the other two K ions which exists in the ideal case, *i.e.* a sixfold coordination for the K(3) ion and a twelvefold coordination for the other K ions. This rearrangement results in the K(3) ion being coordinated by 8 Cl ions and the K(1) and K(2) ions by 10 to 11 Cl ions.

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