Structure of the alums. I. On the sulfate group disorder in the α-alums

Stanley C. Nyburg,^{a} Jon W. Steed,^{a} Slobotka Aleksovska^b and Vladimir M. Petruševski^{b*}

^{a}Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS, England, and ^{b}Institut za Hemija, PMF, Univerzitet Sv. Kiril i Metodij, Arhimedova 5, 91000 Skopje, Macedonia

Correspondence e-mail:
vladop@iunona.pmf.ukim.edu.mk

The crystal structures at room (296 K) and low (173 K) temperature of several α-alums have been refined by single-crystal X-ray structure analysis. Many α-alums of known structure are disordered, the sulfate anions occupying one of two possible sites. All those studied here exhibited such disorder and the relative occupancies of the two sites are in excellent agreement with those obtained by Raman spectroscopy, where the $\nu_1(SO_4)$ mode is seen as a doublet owing to the presence of two different types of sulfate ion. No phase transitions were noted on cooling but there is less disorder.

1. Introduction

The alums are a large class of double sulfates of the general formula $M^IM^{III}(SO_4)_2 \cdot 12H_2O$. M^I can be Na, K, Rb, Cs, Tl, NH_4, NH_3CH_3, NH_3OH, N_2H_5 etc.; M^{III} can be Al, Ga, V, In, Sc, Ti, Fe, Mn, Co, Ru, Rh, Ir and Mo. (Double salts are also known, iso-structural with the alums, in which the tetrahedral anion is selenate or tetrafluoroberyllate.) In this paper we refer to specific sulfate alums simply as M^IM^{III}.

All crystallize in the cubic space group $Pa\bar{3}$ with Z = four formula units per cell. The a cell parameter spans a relatively short range: *ca.* 12.14–12.69 Å. In all cases the M^{III} cations are in special equivalent positions and if these are allocated to $(0,0,0)$ *etc.*, the M^I cations are at $(\frac{1}{2},0,0)$ *etc.* Part of the unit-cell content for TlAl is shown in Figs. 1 and 2.[1] The tetrahedral sulfate ions lie on threefold axes of symmetry.

It was noted earlier that in some alums the sulfate group is anomalous. It was found (Bacon & Gardner, 1958) that the apparent B displacement factors of the sulfate O atoms were anomalously high. This was later found (Larson & Cromer, 1967) to be due to disorder, in which a more highly occupied sulfate group is accompanied by a less occupied group obtained, to within 0.5 Å or so, by reflection in a plane normal to the threefold axis through the S atom, Fig. 2. Such disorder has been shown to be present in a large number of alums, the disorder being more pronounced the smaller the radius of M^I: CsRh, CsIr (Armstrong *et al.*, 1983), no disorder; RbAl, very small disorder (Larson & Cromer, 1967); NH_3OHAl 3% (Abdeen, Will & Weiss, 1981); CH_3NH_3Al (Abdeen, Will Schäfer *et al.*, 1981), 4.2%; NH_4Al (Abdeen, Will, Schäfer *et al.*, 1981; Cromer & Kay, 1967) 12–17%; KAl (Larson & Cromer, 1967) 30% (confirmed in the present study, see below).

---

[1] All four M^I cations and three M^{III} cations per cell are shown.

Table 1
Experimental details.

	KAl (173 K)	KAl (RT)	TlAl (173 K)	TlAl (RT)	KCr (173 K)
Crystal data					
Chemical formula	$H_{24}AlKO_{20}S_2$	$H_{24}AlKO_{20}S_2$	$H_{24}AlO_{20}S_2Tl$	$H_{24}AlO_{20}S_2Tl$	$H_{24}CrKO_{20}S_2$
Chemical formula weight	474.39	474.39	639.66	639.66	499.41
Cell setting	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$
a (Å)	12.1350 (5)	12.1640 (5)	12.2070 (5)	12.2305 (5)	12.2133 (5)
b (Å)	12.1350 (5)	12.1640 (5)	12.2070 (5)	12.2305 (5)	12.2133 (5)
c (Å)	12.1350 (5)	12.1640 (5)	12.2070 (5)	12.2305 (5)	12.2133 (5)
V (Å³)	1786.98 (13)	1799.82 (13)	1818.98 (13)	1829.50 (13)	1821.79 (13)
Z	4	4	4	4	4
D_x (Mg m⁻³)	1.763	1.751	2.336	2.322	1.821
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71070	0.71070	0.71070	0.71070	0.71070
μ (mm⁻¹)	0.673	0.669	9.249	9.196	1.177
Temperature (K)	173 (2)	296 (2)	173 (2)	296 (2)	173 (2)
Crystal size (mm)	$0.6 \times 0.5 \times 0.5$	$0.6 \times 0.6 \times 0.5$	$0.2 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.2$	$0.8 \times 0.8 \times 0.8$
Data collection					
No. of measured reflections	1087	1101	1108	1115	1112
No. of independent reflections	584	592	596	599	597
No. of observed reflections	571	558	560	513	591
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0088	0.0091	0.0232	0.0262	0.0100
θ_{max} (°)	25.99	25.99	25.95	25.96	26.00
Range of h, k, l	$-10 \rightarrow h \rightarrow 10$	$-15 \rightarrow h \rightarrow 14$	$-15 \rightarrow h \rightarrow 14$	$-15 \rightarrow h \rightarrow 15$	$-15 \rightarrow h \rightarrow 15$
	$-14 \rightarrow k \rightarrow 14$	$-10 \rightarrow k \rightarrow 10$	$-10 \rightarrow k \rightarrow 10$	$-10 \rightarrow k \rightarrow 10$	$-10 \rightarrow k \rightarrow 10$
	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0222	0.0264	0.0231	0.0244	0.0443
$wR(F^2)$	0.0631	0.0728	0.0600	0.0692	0.1327
S	0.904	0.920	1.301	1.066	1.130
No. of reflections used in refinement	584	592	596	599	597
No. of parameters used	68	68	68	62	68
H-atom treatment	Mixed	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.6165P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 0.7284P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 2.1175P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.9092P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0922P)^2 + 1.5879P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.000	0.317	0.000	0.000
$\Delta\rho_{max}$ (e Å⁻³)	0.209	0.238	0.763	0.458	1.247
$\Delta\rho_{min}$ (e Å⁻³)	-0.328	-0.285	-0.612	-0.621	-1.895
Extinction method	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	0.069 (4)	0.064 (4)	0.0065 (5)	0.0330 (14)	0.015 (5)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs					
Structure solution	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)

Table 1 (continued)

	KCr (RT)	RbGa (RT)	TlGa (RT)
Crystal data			
Chemical formula	$H_{24}CrKO_{20}S_2$	$H_{24}GaO_{20}RbS_2$	$H_{24}GaO_{20}S_2Tl$
Chemical formula weight	499.41	563.5	682.4
Cell setting	Cubic	Cubic	Cubic
Space group	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$
a (Å)	12.2305 (5)	12.2679 (5)	12.2368 (5)
b (Å)	12.2305 (5)	12.2679 (5)	12.2368 (5)
c (Å)	12.2305 (5)	12.2679 (5)	12.2368 (5)
V (Å^3)	1829.50 (13)	1846.34 (13)	1832.33 (13)
Z	4	4	4
D_x (Mg m^{-3})	1.813	2.027	2.474
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71070	0.71070	0.71070
μ (mm^{-1})	1.172	4.426	10.572
Temperature (K)	296 (2)	296 (2)	296 (2)
Crystal size (mm)	$0.8 \times 0.8 \times 0.8$	$0.2 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.1$
Data collection			
No. of measured reflections	1114	1130	1118
No. of independent reflections	597	608	601
No. of observed reflections	574	505	498
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0144	0.0548	0.0207
θ_{max} ($°$)	25.96	26.00	25.95
Range of h, k, l	$-15 \rightarrow h \rightarrow 15$	$-10 \rightarrow h \rightarrow 10$	$-10 \rightarrow h \rightarrow 10$
	$-10 \rightarrow k \rightarrow 10$	$-15 \rightarrow k \rightarrow 15$	$-15 \rightarrow k \rightarrow 15$
	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0455	0.0423	0.0226
$wR(F^2)$	0.1353	0.1016	0.0639
S	1.110	1.101	1.058
No. of reflections used in refinement	597	608	601
No. of parameters used	68	68	68
H-atom treatment	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0961P)^2 + 1.0171P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 0.9565P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 1.5522P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.000	0.006
$\Delta\rho_{max}$ (e Å^{-3})	1.056	0.495	0.668
$\Delta\rho_{min}$ (e Å^{-3})	-1.526	-0.543	-0.412
Extinction method	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	0.021 (6)	0.0101 (14)	0.0130 (6)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Structure solution	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)

Although structurally closely related, it has proved convenient to subdivide the alums into three groups, α, β and γ. In the α- and β-alums the sulfate group (if disordered, that most heavily occupied) has its O3 atom pointing directly towards M^{III} (see Fig. 1), whereas in the γ-alums it points to M^I (corresponding to the less occupied position of the sulfate ion in the α-alums, Fig. 2). The distinction between the α- and β-alums rests on a proposal (Beattie *et al.*, 1981) that in α-alums the water molecules lying closest to M^I form an almost flat, staggered ('crown'), six-membered ring (not shown in Figs. 1 and 2), whereas in the β-alums these water molecules lie on a strictly planar regular hexagon with M^I at its centre.

All water molecules are involved in O—H$\cdots$O hydrogen bonds, which are shown in Figs. 1 and 2 and discussed below. Spectroscopic evidence fully confirms the nature and extent of sulfate anion disorder (Eysel & Schumaker, 1977; Brooker & Eysel, 1990; Suresh *et al.*, 1996). More recently, Petruševski *et al.* (1998) have studied the Raman spectra of the KCr, RbCr and TlAl α-sulfate alums. RbAl, RbGa, KAl, TlAl, TlGa and NH$_4$Al are also currently being investigated (Petruševski *et al.*, 2000).

The doublet band due to the ν_1(SO$_4$) mode shows clearly that two types of sulfate anion are present in these structures. On the basis of the integrated intensities of the two peaks, it

could be concluded that sulfate disorder increases in the sequence Rb, Tl, K. No disorder was found in CsRh or CsIr. The crystallographic and spectroscopic results are thus seen to be in accordance with each other.

In an attempt to obtain more quantitative data, eight crystal structures were determined, those of TlAl, TlGa, RbGa, KAl and KCr at room temperature and of TlAl, KAl and KCr at
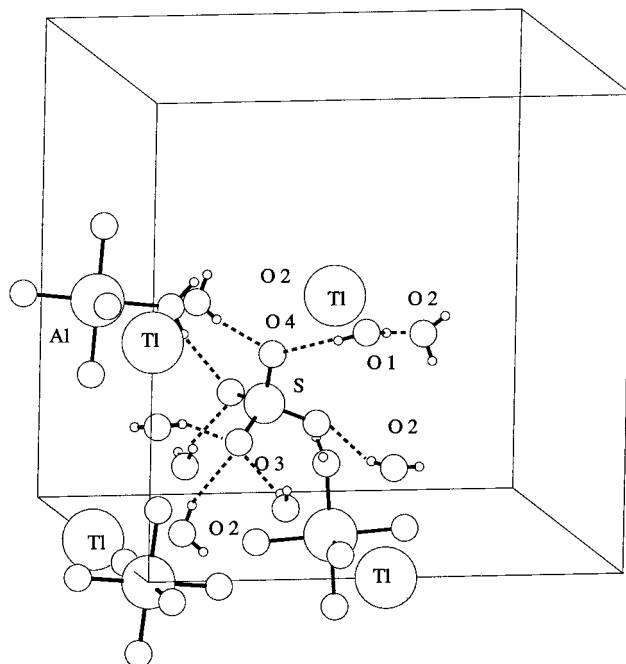

Figure 1
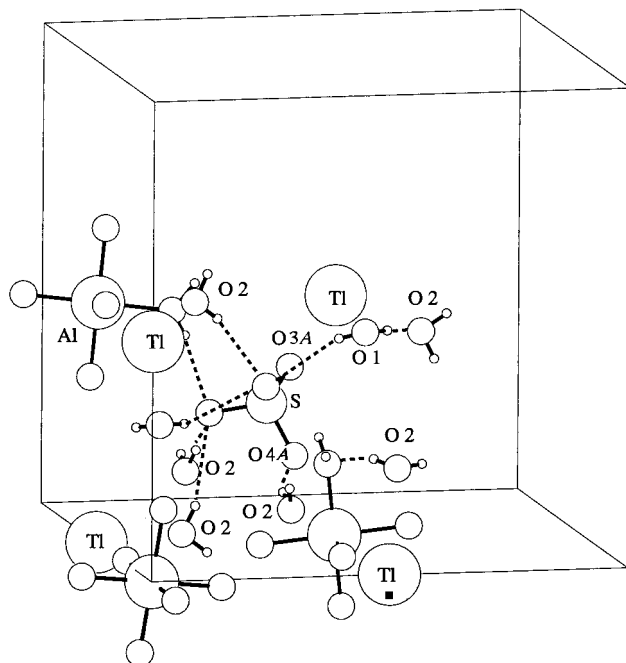Hydrogen bonding when the sulfate group nearest the origin is in its major position, with S—O3 pointing towards M^{III}.

Figure 2
Hydrogen bonding when the sulfate group nearest the origin is in its minor position, with S—O3A pointing away from M^{III}.

173 K. The structure analyses of TlAl, TlGa and RbGa are new, those of KAl and KCr refinements of an earlier determination.

2. Experimental

Well shaped octahedral crystals in the range 0.2–0.8 mm were grown by slow evaporation at room temperature of aqueous solutions containing the two required sulfate salts in stoichiometric ratio.

X-ray intensity data were collected on a Nonius Kappa-CCD diffractometer using monochromated Mo $K\alpha$ radiation with a specimen-to-image plate distance of 2.5 cm and 2θ limits 7.4–52° (maximum Müller index 15). Low-temperature data were collected at 173 K using an Oxford Cryostream low-temperature attachment. For each crystal, 90 frames were recorded, each being of 2° in φ and 30 s duration, except 20 s for KCr. The first ten frames were used for indexing reflections using the *DENZO* package and refined to obtain final cell parameters. A total of 16 000 reflections had their intensities integrated and scaled (Otwinowski & Minor, 1996), finally yielding 600 independent reflection intensities. The reduced data sets were corrected for absorption and decay (Otwinowski & Minor, 1996). Structure determination commenced with the known heavy-atom positions, the remaining non-H atoms being found and their positions and anisotropic displacement parameters refined using *SHELX*97 (Sheldrick, 1997) and *RES2INS* (Barbour, 1995). The occupancies of the S and O atoms of disordered sulfate ions were determined using the 'free variable' option of *SHELX*97. H atoms were allocated to sites found from final ΔF maps, except for TlAl at room temperature where a pair of positions on O2 were replaced by more acceptable theoretical positions. The former were refined for both position and isotropic displacement motion, the latter for displacement motion only. For all except the above TlAl case (62 parameters), there were 68 least-squares parameters. Refinement details common to each structure determination are given in Table 1.

3. Results and discussion

Fractional atomic coordinates have been deposited.[2] Bond lengths, interbond angles and other data are given in Tables 2 and 3.

Atoms O1 are those associated with M^{III} cations and O2 with M^{I} cations. Sulfate ion atoms O3 and O3A lie on three-fold axes when in major and minor sites, respectively. The other three sulfate ion atoms are O4 and O4A, respectively. Tables 2 and 3 also give the X-ray data residuals, R, for each structure and the site occupancies, s.o.f., of the major sulfate group. It is seen that the O—M^{I}—O angles subtended by adjacent O2 water molecules at M^{I} differ significantly from 60°

---

[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0101). Services for accessing these data are described at the back of the journal.

Table 2
Bond lengths (Å), interbond angles (°), residuals R, major sulfate occupancies, s.o.f. and spectroscopic intensity ratios (Raman) in the 296 K structures.

	KAl	KCr	TlAl	TlGa	RbGa
S—O3	1.447 (4)	1.442 (6)	1.439 (5)	1.435 (5)	1.439 (5)
S—O4	1.472 (2)	1.470 (3)	1.470 (2)	1.468 (3)	1.466 (3)
S—O3A	1.418 (3)	1.38 (2)	1.41 (3)	1.36 (3)	1.43 (6)
S—O4A	1.460 (4)	1.44 (1)	1.48 (1)	1.45 (2)	1.45 (2)
M^{I}—O2	2.954 (1)	3.010 (2)	3.065 (2)	3.081 (3)	3.081 (3)
M^{III}—O1	1.875 (1)	1.956 (2)	1.877 (3)	1.942 (3)	1.945 (3)
O3—S—O4	110.2 (1)	110.7 (2)	110.3 (2)	110.7 (2)	110.8 (2)
O4—S—O4′	108.7 (1)	108.2 (2)	108.6 (2)	108.2 (2)	108.1 (2)
O3A—S—O4A	109.4 (3)	107 (1)	109 (2)	107 (2)	109 (3)
O4A—S—O4A′	109.5 (3)	112 (1)	110 (2)	112 (2)	110 (3)
O2—M^{I}—O2′	66.61 (2)	65.84 (4)	66.07 (3)	65.77 (4)	65.79 (4)
O1—M^{III}—O1′	89.57 (5)	89.24 (9)	89.7 (1)	89.0 (1)	89.1 (1)
O1—H11	0.69 (2)	0.60 (4)	0.72 (4)	0.61 (4)	0.69 (5)
H11···O4	1.92 (2)	2.03 (4)	1.92 (4)	2.01 (4)	1.93 (6)
O1···O4	2.603 (2)	2.619 (4)	2.623 (4)	2.613 (4)	2.621 (4)
O1—H11···O4	169 (2)	171 (4)	167 (4)	168 (5)	170 (5)
O1···H12	0.89 (3)	0.85 (4)	0.81 (5)	0.72 (4)	0.94 (5)
H12···O2	1.74 (3)	1.77 (4)	1.82 (5)	1.89 (4)	1.68 (5)
O1···H12	2.626 (2)	2.611 (3)	2.620 (3)	2.611 (4)	2.612 (4)
O1···H12···O2	170 (2)	171 (4)	168 (4)	174 (4)	171 (4)
O2···H21	0.77 (3)	0.77 (8)	0.93	0.96 (8)	0.72 (8)
H21···O3	2.04 (3)	2.06 (8)	1.90	1.90 (7)	2.12 (7)
O2···O3	2.781 (2)	2.795 (4)	2.804 (4)	2.789 (4)	2.808 (5)
O2—H21···O3	161 (3)	160 (6)	165	154 (6)	160 (7)
O2—H22	0.78 (3)	0.78 (8)	0.81	0.63 (4)	0.75 (6)
H22···O4	1.98 (3)	2.09 (8)	1.97	2.13 (4)	2.01 (7)
O2···O4	2.756 (2)	2.750 (4)	2.740 (3)	2.749 (4)	2.763 (4)
O2—H22···O4	171 (3)	143 (7)	158	167 (4)	173 (6)
O1—H11	0.69 (2)	0.60 (4)	0.72 (4)	0.61 (4)	0.69 (5)
H11···O4A	2.19 (2)	2.27 (4)	2.18 (5)	2.25 (6)	2.23 (6)
O1···O4A	2.844 (5)	2.84 (2)	2.84 (3)	2.83 (3)	2.89 (5)
O1—H11···O4A	157 (2)	162 (4)	155 (4)	161 (5)	160 (5)
O2—H22	0.78 (3)	0.78 (8)	0.81	0.63 (4)	0.75 (6)
H22···O4A	2.15 (3)	2.16 (8)	2.06	2.23 (4)	2.15 (7)
O2···O4A	2.884 (5)	2.87 (1)	2.86 (2)	2.85 (2)	2.86 (3)
O2—H22···O4A	158 (2)	152 (7)	165	167 (3)	157 (6)
O2—H21	0.77 (3)	0.77 (8)	0.93	0.96 (8)	0.72 (8)
H21···O4A	2.40 (3)	2.50 (8)	2.40	2.3 (1)	2.6 (1)
O2···O4A	3.123 (6)	3.22 (2)	3.23 (3)	3.26 (4)	3.23 (5)
O2—H21···O4A	155 (3)	157 (6)	150	159 (5)	159 (7)
R	0.026	0.046	0.024	0.027	0.042
s.o.f.	0.697	0.766	0.843	0.830	0.892
Raman	0.692	0.750	0.850	0.821	0.886

Table 3
As for Table 2, but for crystals at 173 K.

Spectroscopic ratios (Raman) were not determined at this temperature.

	KAl	KCr	TlAl
S—O3	1.472 (2)	1.458 (5)	1.459 (5)
S—O4	1.475 (1)	1.472 (2)	1.471 (2)
S—O3A	1.440 (6)	1.46 (3)	1.39 (6)
S—O4A	1.484 (3)	1.47 (1)	1.55 (3)
M^{I}—O2	2.915 (9)	2.972 (2)	3.036 (2)
M^{III}—O1	1.874 (8)	1.961 (2)	1.880 (3)
O3—S—O4	109.63 (5)	109.9 (1)	109.7 (1)
O4—S—O4′	109.31 (5)	109.1 (1)	109.2 (1)
O3A—S—O4A	111.1 (2)	111.9 (9)	112 (1)
O4A—S—O4A′	107.8 (2)	107.0 (9)	107 (1)
O2—M^{I}—O2′	66.99 (2)	66.10 (3)	66.31 (4)
O1—M^{III}—O1′	89.35 (4)	88.83 (9)	89.6 (1)
O1—H11	0.73 (2)	0.65 (4)	0.74 (5)
H1···O4	1.89 (2)	1.97 (4)	1.90 (5)
O1···O4	2.607 (1)	2.614 (3)	2.625 (3)
O1—H11···O4	168 (2)	170 (4)	165 (5)
O1—H12	0.87 (2)	0.87 (4)	0.86 (5)
H12···O2	1.76 (2)	1.76 (4)	1.76 (5)
O···O2	2.618 (1)	2.603 (3)	2.608 (3)
O1—H12···O2	172 (2)	164 (3)	169 (5)
O2—H21	0.76 (3)	0.59 (4)	0.87 (5)
H21···O3	2.03 (3)	2.20 (4)	1.97 (5)
O2···O3	2.754 (2)	2.786 (4)	2.786 (4)
O2—H21···O3	159 (2)	177 (5)	157 (4)
O2—H22	0.85 (2)	0.74 (6)	0.75 (5)
H22···O4	1.92 (2)	2.03 (6)	2.03 (5)
O2···O4	2.753 (1)	2.757 (3)	2.743 (3)
O2—H22···O4	167 (2)	168 (5)	161 (5)
O1—H11	0.73 (2)	0.65 (4)	0.74 (5)
H11···O4A	2.19 (2)	2.33 (4)	2.21 (6)
O1···O4A	2.870 (4)	2.92 (2)	2.93 (3)
O1—H11···O4A	157 (2)	153 (3)	162 (5)
O2—H22	0.85 (2)	0.74 (6)	0.75 (5)
H22···O4A	2.08 (2)	2.21 (2)	2.08 (6)
O2···O4A	2.897 (4)	2.91 (2)	2.81 (3)
O2—H22···O4A	162 (2)	159 (5)	167 (5)
O2—H21	0.76 (3)	0.59 (4)	0.87 (5)
H21···O4A	2.33 (3)	2.62 (4)	2.29 (7)
O2···O4A	3.041 (4)	3.10 (2)	3.09 (3)
O2—H21···O4A	156 (2)	141 (4)	155 (4)
R	0.022	0.044	0.023
s.o.f.	0.787	0.913	0.940
Raman	–	–	–

and thus, using the criterion of Beattie *et al.* (1981), we can allocate all these alums to the α class.

3.1. The sulfate group

Some of the minor sulfate ions appear highly distorted, the S—O3A distances being very short (*e.g.* in TlGa and in KCr), which is comparable to SO_3. However, the positional standard uncertainties are large in these cases. The geometry is more acceptable for the KAl alum with smaller standard uncertainties, in contrast to data reported earlier for this alum (Larson & Cromer, 1967).

In the major sulfate groups at room temperature, the average S—O3 bond length is 1.448 (4) Å, the average S—O4 length being significantly longer, 1.465 (3) Å. Similarly, for the minor sulfate groups, the bond lengths are 1.44 (4) and 1.48 (4) Å, respectively.

At low temperature these differences in S—O bond lengths are less marked. We also observe, as have others (Larson & Cromer, 1967; Abdeen, Will, Schäfer *et al.*, 1981; Cromer & Kay, 1967) that the displacement factors for O3 and O3A in α-alums are always greater than those for O4 and O4A. It thus seems likely that the apparent more pronounced shortening of S—O3 and S—O3A relative to S—O4 and S—O4A is due to the well known effect of libration, which is clearly more pronounced at O3 and O3A than at O4 and O4A. Studies of sulfate-doped selenate atoms (Ivanovski *et al.*, 1999*a,b*), where a singlet peak (rather than a doublet) due to the $\nu_3(SO_4)$ mode

is often seen, indicate that the geometry of the SO_4 group is close to ideal.

Where there is sulfate group disorder, the Raman spectrum shows two close ν_1 peaks of differing intensity. The peak separation is due to the different crystal fields which the major and minor sulfate ions experience, and the differences in intensity directly due to the differences in site occupancy.

The results for the occupancies obtained here are given in Tables 2 and 3 and by spectroscopic methods in Table 2. The agreement is excellent and lends additional support to the theory that the extent of disorder is governed by the size of the M^I cation. The increased occupancy of the major sulfate group with decreasing temperature shows this to be the site of lower energy, confirming the spectroscopic results (Eysel & Schomaker, 1977). Studies at even lower temperatures would show whether disordered α-alums can perhaps be brought to the fully ordered state.

Fractional coordinates of the S atoms lie within the close range 0.306–0.313, which is typical of α-alums (Beattie *et al.*, 1981). In the β-alums the S atom is further from the M^{III} cation, with fractional coordinates between 0.326 and 0.332.

3.2. The hydrated M^I and M^{III} cations

The M^{III} octahedron is almost regular at both room and lower temperatures, as in many other cases. The angle between the axes of this octahedron and the unit cell axes in the α-alums lies in the range 2.2–10.3° (here 5.9–10.7°), which is much larger than in the β-alums, 0.2–1.0° (Beattie *et al.*, 1981). Six water molecules surround M^I in an almost flat crown coordination. M^I—O2 distances range from 2.954 (1) Å in KAl to 3.081 (3) Å in TlGa and in RbGa, in accordance with the increase in effective radii in the sequence K, Tl, Rb (Shannon, 1976, gives cation radii: K 1.38, Tl 1.50, Rb 1.52 Å). For the minor sulfate ion, the variation in M^I—O3A is somewhat unexpected, having (at 296 K) the shortest distance in RbGa, 2.54 (6) Å, and the longest in KCr, 2.65 (2) Å. This odd behaviour in M^I—O3A distances may be the origin of the M^I cation-sensitive disorder, the minor sulfates being flipped into major sites more efficiently in the vicinity of larger cations such as Rb. However, the relatively large errors in the coordinates of S and O atoms in RbGa make this explanation somewhat speculative. Adjacent O2 atoms subtend angles at M^I in the range 65.8–67°. This is the basis of the α classification. In β-alums, as noted above, this angle is 60°.

3.3. Hydrogen bonds

Hydrogen-bond distances are given in Tables 2 and 3. Where the sulfate group is in its major site, the O3 atom, as illustrated in Fig. 1, acts as an acceptor for three O2 atoms of

water molecules associated with M^I cations at $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$ and $(0,0,\frac{1}{2})$. These O2 atoms are also acceptors for O1 water molecules associated with the M^{III} cation. (Only one such bond is shown in the figures.) O4 atoms of the sulfate in its major site form two hydrogen bonds each, both being acceptors for O1 and O2 water molecules. Where the sulfate ion is in its minor site, O3A is not hydrogen bonded at all. However, the O4A atoms are involved in no less than three hydrogen bonds each, two strong bonds to atoms O1 and O2 and a weaker one to a different O2 atom (see Tables 2 and 3, and Fig. 2). Presumably it is hydrogen bonding which contributes significantly to the total force field governing the particular orientations adopted by the sulfate ions in its two sites.

References

Abdeen, A. M., Will, G., Schäfer, W., Kirfel, A., Bargouth, M. O. & Recker, K. (1981). *Z. Kristallogr.* **157**, 147–166.

Abdeen, A. M., Will, G. & Weiss, A. (1981). *Z. Kristallogr.* **154**, 45–57.

Armstrong, R. S., Beattie, J. K., Best, S. P., Skelton, B. W. & White, A. H. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1973–1975.

Bacon, G. E. & Gardner, W. E. (1958). *Proc. R. Soc. Sect. A*, **246**, 78–90.

Barbour, L. J. (1995). *Res2INS.* University of Missouri, Columbia.

Beattie, J. K., Best, S. P., Skelton, B. W. & White, A. H. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2105–2111.

Brooker, M. H. & Eysel, H. H. (1990). *J. Phys. Chem.* **94**, 540–544.

Cromer, D. T. & Kay, M. I. (1967). *Acta Cryst.* **22**, 800–805.

Eysel, H. H. & Schumaker, G. (1977). *Chem. Phys. Lett.* **47**, 168–170.

Ivanovski, V., Petruševski, V. M. & Šoptrajanov, B. (1999a). *J. Mol. Struct.* pp. 480–487.

Ivanovski, V., Petruševski, V. M. & Šoptrajanov, B. (1999b). *J. Mol. Struct.* pp. 689–693.

Larson, A. C. & Cromer, D. T. (1967). *Acta Cryst.* **22**, 793–800.

Otwinowski, Z. & Minor, W. (1996). *Methods in Enzymology*, edited by C. W. Carter and R. M. Sweet, Vol. 276, pp. 307–326. New York: Academic Press.

Petruševski, V. M., Ivanovski, V., Šoptrajanov, B. & Žugić, M. (1998). *Proc. of the XVIth Intl Conf. on Raman Spectroscopy*, pp. 584–585. Cape Town, South Africa.

Petruševski, V. M., Ivanovski, V., Šoptrajanov, B. & Žugić, M. (2000). In preparation.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Suresh, G., Ratheesh, R., Jayasree, R. S., Nayar, V. U. & Keresztury, G. (1996). *J. Solid State Chem.* **122**, 333–337.