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Alkali-metal vanadium sulfate β alums, $MV(SO_4)_2 \cdot 12H_2O$ (M = K, Rb or Cs): structural anomalies related to unsymmetrical occupancy of the t_{2g} (O_h) orbitals

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Crystal structure determinations of the alums $MV(SO_4)_2 \cdot 12H_2O$ (M = K, Rb or Cs) showed that they all belong to the β structural class. This observation, while predicted earlier from the crystal morphology, is not expected from trends based on the sizes of the monovalent cations and results in formal 12-co-ordination for K^+ and Rb^+. The structures were determined at 120 (K) and 295 (Rb and Cs) K and refined to *R* values of 0.025, 0.040 and 0.022 for 877, 348 and 2008 independent 'observed' reflections, respectively. The crystals are cubic, space group $Pa\bar{3}$ with a = 12.253(5), 12.367(2) and 12.434(1) Å, respectively. Despite the relatively imprecise determination of the hydrogen-atom positions by X-ray diffraction, analysis of the available neutron structures indicates that the water co-ordination geometry may be deduced with good precision from the heavy-atom coordinates. On this basis the stereochemistry of water co-ordination to M^{III} is conserved in the three structures. The occurrence of the β structure for these salts is likely to be due to a preferred stereochemistry for water co-ordination to vanadium(III) which arises from lifting of the degeneracy of the $^3T_{2g}$ (O_h) ground term.

The alums, $M^IM^{III}(XO_4)_2 \cdot 12H_2O$ (X = S or Se), exhibit three structural modifications, namely α, β and γ,[1] which exhibit the same space- and site-group symmetry but have a different disposition of the ions within the lattice. Generally, the alum type depends on the identity of M^I and XO_4^{2-}, for example the structurally characterised potassium or rubidium sulfate alums adopt the α modification whilst the corresponding caesium salts conform to the β structure. Tervalent cations with ionic radii[2] ranging in size between Al^{3+} (0.675 Å) and In^{3+} (0.94 Å) may be incorporated into either lattice type.[3] The observation that the caesium sulfate alums of the Group 9 cations (Co, Rh and Ir) conform to the α modification[4,5] is surprising given that the tervalent ionic radii fall between those of Al^{3+} and In^{3+}, both of which give caesium sulfate β alums. This implies that the preference for a particular stereochemistry of water co-ordination to M^{III} may disturb the simple model for the prediction of the alum type based on the sizes of the constituent ions. The α structure of the caesium cobalt sulfate alum was earlier predicted by Haussühl[3] based on the observation that crystals of the β alums tend to grow with a conspicuous 210 face which is absent in those of α alums which display predominantly octahedral forms. On the basis of such observations of crystal morphology, Haussühl also classified the potassium and rubidium sulfate alums of vanadium as belonging to the β class. This prediction is counter to expectations based on the sizes of the ions, as described above. The dimorphism of the potassium and rubidium alums would imply a preferred orientation for water co-ordinated to vanadium(III), which is not apparent for chromium(III) or iron(III); it is hence important to confirm the assignment of the alum type by X-ray diffraction methods. In this paper crystal structures of the alums $MV(SO_4)_2 \cdot 12H_2O$ (M = K, Rb or Cs) are presented, the alum type is deduced and the reasons for their unusual structural chemistry are considered.

Experimental

The rubidium and caesium vanadium sulfate alums were prepared from VCl_3 using a method analogous to that described in the literature.[6] The salts were recrystallised from sulfuric acid (1 mol dm^{-3}) and stored under an atmosphere of nitrogen at *ca.* 5 °C.

Owing to the higher solubility and lower melting point of the potassium vanadium sulfate alum the salt was prepared by the comproportionation reaction of vanadium(II) and vanadium(IV). Potassium sulfate (9.3 g) was added to a solution of vanadyl sulfate (27 g) in sulfuric acid (46 cm^3, 2.2 mol dm^{-3}) which was then diluted to 60 cm^3 with water. The solution was divided into two parts: 28 and 32 cm^3. All subsequent operations were performed with solutions which had been deoxygenated and maintained under an atmosphere of argon. The 32 cm^3 portion of the solution was reduced with zinc amalgam (30 g) to produce the violet hexaaquavanadium(II) ion and this was decanted and added to the 28 cm^3 portion of the vanadyl solution to produce the blue-green hexaaquavanadium(III) ion. Storage under refrigeration gave violet crystals of $KV(SO_4)_2 \cdot 12H_2O$. These melt at temperatures appreciably above 25 °C and were stored at 4 °C under a nitrogen atmosphere.

Preparation of hexaaquavanadium(III) ion as described above will lead to solutions containing significant quantities of hexaaquazinc(II). No evidence for contamination of the product by a zinc(II) species was apparent in the crystallography of the potassium vanadium alum. Further, preparation of the rubidium vanadium alum using the route involving the comproportionation reaction resulted in a product with vibrational spectra identical to those of the salt prepared from VCl_3.

Crystallography

Unique data sets were measured within the specified $2\theta_{max}$ limit using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers operating in conventional 2θ–θ scan mode, and fitted with monochromatic Mo-Kα radiation sources (λ = 0.710 73 Å). *N* Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction;[7] the coordinate setting follows that of the other caesium β alums we have studied.[4,5] Residuals at convergence are conventional R,R' on $|F|$, reflection weights being $[\sigma^2(F_o) + 0.000n(F_o)^2]^{-1}$. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained for $M^I = Rb$, and refined for $M^I = K$ and Cs. Neutral atom complex scattering factors were used (K^+, Rb^+ and Cs^+ excepted). The co-ordination geometry about the mono- and ter-valent cations is shown in Fig. 1. Data collection and analysis parameters are given in Table 1 and the positional and isotropic thermal parameters in Table 2. Pertinent geometrical parameters are given in Table 3.

Pertinent features/variations in procedure. For the caesium salt unusually well formed material devoid of twinning problems and diffracting to a high angle in 2θ was obtained. Data were measured with the intent (ultimately not realised) of taking advantage of the possibility of undertaking an electron-density distribution study and, accordingly, a full sphere was measured within the limit $2\theta_{max} = 110°$, yielding 72 998 reflections, merging, after appropriate corrections, to 3265 unique (merging R 0.048). Refinement of the structure proceeded according to that of the potassium salt, converging at $R = 0.022$ and $R' = 0.030$ for the 2008 'observed' reflections, extension of the description to encompass anharmonic terms in the vibrational model for the non-hydrogen atoms[9] resulted in a substantial reduction in the residuals, with the residual electron density ranging from −0.23 to 0.3 e Å^{-3}; their validity other than as an 'error sponge' may be questionable, however. Extinction effects in the potassium and rubidium salts were negligible; for the caesium salt (Becker-Coppens) g and ρ refined to $1.4(1) \times 10^{-4}$ and $4.4(2) \times 10^{-5}$. All values quoted in the text and deposition are for this case.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Crystallographic determination of the potassium and rubidium alum structures has been limited to the aluminium[10] and chromium[11,12] tervalent cations and in each case the structural parameters permit straightforward classification to the α modification.[4] In contrast, the structures of the potassium, rubidium and caesium sulfate alums of vanadium(III) are unequivocally of the β class. The criteria for classification of the alum structures based on single-crystal X-ray studies are outlined in ref. 4 and the relevant structural parameters are assembled in Table 4. Of these, the most reliable guide to the alum type is the co-ordination environment about the monovalent cation. The twelve oxygen atoms nearest to the monovalent cation define either an elongated icosahedron (α) or an elongated cuboctahedron (β), with the six oxygen atoms of two sulfate groups capping the relevant polyhedron along the axis of elongation. The six oxygen atoms of the water molecules about the monovalent cation are either arranged in the form of a puckered ring (α alums), with an $O(a)\text{–}M^I\text{–}O(a')$ angle in the range 64–67°, or define a plane (β alums) with an $O(a)\text{–}M^I\text{–}O(a')$ angle of 60°. For the potassium, rubidium and caesium vanadium sulfate alums the six water molecules about the monovalent cation define a plane [Fig. 1(*a*)] and the $O(a)\text{–}M^I\text{–}O(a')$ angle is found to be within 1 estimated standard deviation (e.s.d.) of 60°, indicating clearly the β modification. The other structural parameters which are sensitive to the alum type are also consistent with the classification of each of the vanadium sulfate alums as the β modification (Table 4). It is noteworthy that for neither the potassium nor the rubidium vanadium sulfate alums was there any sign of the disorder of the sulfate groups which is a feature of the structures of the aluminium and chromium potassium, rubidium and ammonium sulfate α alums.[10,13–15]

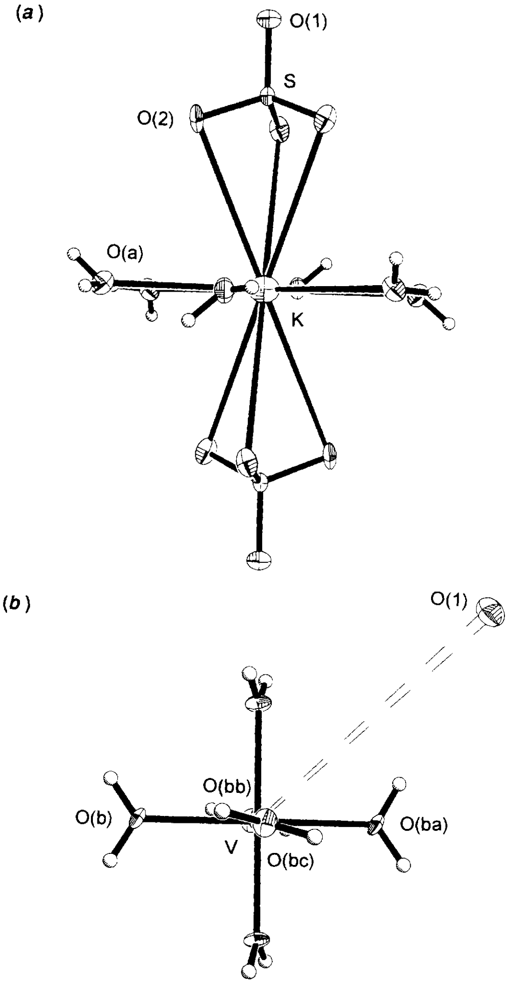

Fig. 1 Co-ordination geometry about the (*a*) monovalent and (*b*) tervalent cations in the β alum $KV(SO_4)_2{\cdot}12H_2O$ (120 K). Polarisability elipsoids are drawn at the 50% level. The O(1) atom included in (*b*) is not co-ordinated to the V^{III} but the $V^{III}\cdots O(1)$ vector is collinear with the crystallographic three-fold axis of $[V(OH_2)_6]^{3+}$

The vanadium alums thus provide the first examples of β alums of either potassium or rubidium for which a full structure determination has been performed. The morphology of the crystals of rubidium titanium sulfate alum also led to its classification as the β modification.[3] This classification is supported by single-crystal Raman spectra of the alum.[16] The remainder of the rubidium (M^{III} = Al, Ga, In, Cr or Fe) and potassium sulfate alums (M^{III} = Al, Ga, Cr or Fe) conform to the α modification.[3] The dimorphism of the potassium and rubidium sulfate alums is surprising given the unusually high-co-ordination geometry imposed on the relatively small monovalent cations. For example, the co-ordination sphere about the potassium cation comprises six oxygen atoms (water) at 3.136 Å and six oxygen atoms (sulfate) at 3.478 Å. This may be described as either 12-co-ordination (icosahedral) or 6 + 6-co-ordination, with the six closest oxygen atoms defining a regular hexagonal plane. Either geometry is unexpected for potassium and is therefore likely to be imposed by the hydrogen-bonding constraints of the lattice.

For a series of salts related by the isomorphous substitution of the tervalent hexaaqua cation, differences in the structural chemistry may result from (*i*) the size of the tervalent cation or (*ii*) stereochemical preference for the orientation of the plane of the co-ordinated water molecule. Since V^{III} and Ti^{III} are intermediate in size between Al^{III} and In^{III}, the different

Table 1 Data collection and analysis parameters for $M^IV(SO_4)_2 \cdot 12H_2O$

	M^I = K	Rb	Cs
M	498.4	544.7	592.2
Sample temperature/K	*ca.* 120	295	295
Sample dimensions/mm	0.3	0.35	0.22 × 0.26 × 0.38
a/Å	12.253(5)	12.367(2)	12.434(1)
U/Å^3	1840(1)	1891.4(6)	1922.4(5)
D_m/g cm^{-3}	1.783_4[b]	1.915_4[b]	2.033_4[b]
D_c (Z = 4)/g cm^{-3}	1.80	1.91	2.05
μ_{Mo}/cm^{-1}	10.5	32.8	27.4
$\bar{T}_{min}$, $\bar{T}_{max}$	0.64, 0.66	(not recorded)	0.31, 0.40
F(000)	1032	1104	1176
$2\theta_{max}$/°	70	85	110
hkl Ranges	0–19	0–23	0–28
N	1363	1296	3265
N_o	877	348	2008
No. of variables	55	39	109
R	0.025	0.040	0.022
R'	0.036	0.059	0.030
n in weighting scheme	4	4	6

[a] Details in common: cubic, space group $Pa\bar{3}$; computation using the XTAL 3.2 program system.[7] [b] Ref. 8.

Table 2 Atomic coordinates for $M^IV(SO_4)_2 \cdot 12H_2O$

Atom	x	y	z	B_{iso}*/Å^2
M^I = K				
K	0.5	0.5	0.5	2.66(2)
V	0	0	0	0.600(8)
S	0.326 40(3)	(x)	(x)	0.805(8)
O(1)	0.257 0(1)	(x)	(x)	1.55(3)
O(2)	0.280 1(1)	0.331 5(1)	0.437 9(1)	1.49(4)
O(a)	0.051 9(1)	0.198 3(1)	0.346 6(1)	1.42(4)
H(a1)	0.018(2)	0.219(2)	0.301(3)	3.2(6)
H(a2)	0.117(2)	0.211(2)	0.324(2)	2.5(5)
O(b)	0.162 5(1)	−0.000 5(1)	−0.001 9(1)	1.11(3)
H(b1)	0.200(2)	−0.055(2)	0.011(2)	2.2(5)
H(b2)	0.197(2)	0.057(2)	−0.018(2)	3.0(6)
M^I = Rb				
Rb	0.5	0.5	0.5	3.60(4)
V	0	0	0	1.33(3)
S	0.328 1(1)	(x)	(x)	1.7(4)
O(1)	0.259 1(4)	(x)	(x)	3.4(2)
O(2)	0.282 2(4)	0.336 4(4)	0.437 4(4)	3.8(3)
O(a)	0.050 7(4)	0.204 3(4)	0.345 4(4)	2.7(3)
H(a1)	0.025(—)	0.210(—)	0.282(—)	4.1(—)
H(a2)	0.122(—)	0.200(—)	0.346(—)	4.1(—)
O(b)	0.161 4(3)	−0.000 5(3)	−0.001 8(5)	2.4(2)
H(b1)	0.205(—)	−0.054(—)	0.010(—)	3.6(—)
H(b2)	0.202(—)	0.057(—)	−0.013(—)	3.6(—)
M^I = Cs				
Cs	0.5	0.5	0.5	2.608(8)
V	0	0	0	1.393(8)
S	0.327 01(3)	(x)	(x)	1.612(9)
O(1)	0.259 5(1)	(x)	(x)	3.20(5)
O(2)	0.279 1(1)	0.336 95(9)	0.434 39(9)	2.70(3)
O(a)	0.051 71(5)	0.211 50(6)	0.341 99(5)	2.66(1)
H(a1)	0.009(1)	0.232(2)	0.278(2)	4.8(4)
H(a2)	0.118(2)	0.219(2)	0.315(1)	6.8(4)
O(b)	0.160 12(6)	−0.000 96(4)	−0.001 72(4)	2.37(1)
H(b1)	0.199(2)	−0.049(2)	0.007(1)	3.3(4)
H(b2)	0.196(1)	0.048(1)	−0.018(1)	2.9(3)

* For anisotropically refined atoms the B_{iso} value is the radius of the sphere of volume equal to that of the ellipsoid which it represents; for cubic crystals this is equal to $\frac{1}{3}(B_{11} + B_{22} + B_{33})$.

Table 3 Interatomic distances (Å) and angles (°) of $M^IV(SO_4)_2 \cdot 12H_2O$*

	M^I = K	Rb	Cs
(*i*) The sulfate group			
S–O(1)	1.4736(8)	1.479(3)	1.453(2)
S–O(2)	1.480(1)	1.470(5)	1.467(2)
O(1)–S–O(2)	109.64(6)	110.4(2)	109.85(10)
O(2)–S–O(2^i)	109.31(7)	108.5(3)	109.09(9)
(*ii*) The vanadium			
V–O(b)	1.992(1)	1.996(3)	1.991(1)
O(b)–V–O(b^i)	90.84(5)	90.8(2)	90.95(5)
(*iii*) The univalent cation, M^I			
M^I–O(2)	3.478(2)	3.456(5)	3.510(2)
M^I–O(a^{ii})	3.136(2)	3.229(5)	3.345(1)
O(2)–M^I–O(2^i)	40.61(3)	40.4(1)	39.81(3)
O(a^{ii})–M^I–O(a^{iii})	60.03(3)	60.0(1)	60.00(2)
O(2)–M^I–O(a^{ii})	65.50(4)	66.4(1)	67.18(3)
O(2)–M^I–O(a^{iii})	80.12(4)	80.0(1)	80.38(3)
O(2)–M^I–O(a^{iv})	78.47(4)	77.3(1)	76.63(3)
(*iv*) The water molecules			
O(a)–H(a1)	0.74(3)	0.85(—)	0.99(2)
O(a)–H(a2)	0.86(3)	0.88(—)	0.89(2)
O(b)–H(b1)	0.82(3)	0.87(—)	0.77(2)
O(b)–H(b2)	0.84(3)	0.88(—)	0.78(2)
H(a1)–O(a)–H(a2)	103(3)	113(—)	99(2)
H(b1)–O(b)–H(b2)	116(3)	107(—)	106(2)

* Only independent values are given. Transformations of the asymmetric unit are: i (z, x, y), ii (z, $\frac{1}{2} - x$, y), iii ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$), iv ($\frac{1}{2} - y$, $1 - z$, $\frac{1}{2} + x$).

structural chemistry cannot be ascribed to size effects but *must* result from a preferred orientation of the water molecule co-ordinated to M^{III}. The orientation of this water molecule plays an important part in determining the alum type since this is linked to the co-ordination geometry of the monovalent cation by the strong hydrogen bonds O(b) ··· O(2) and O(b) ··· O(a).

The structural chemistry of the potassium and rubidium sulfate alums implies a difference in the preferred orientation of the water molecule co-ordinated to M^{III} for titanium and vanadium which is not apparent for chromium, iron or any of the Group 13 tervalent cations. Since of all the tervalent cations considered only Ti and V have asymmetric occupancy of the t_{2g} orbitals, giving octahedral complexes which have orbitally degenerate ground terms, differences in the structural chemistry may be due to electronic effects. Support for this proposition is based on low-temperature neutron-diffraction results from the caesium sulfate alums[17–20] for which differences in the orientation of the plane of the co-ordinated water molecule relative to the MO_6 axes may similarly be related to the occupancy of the t_{2g} (O_h) orbitals. This orientation is defined by the angle φ (defined in ref. 18), given by the angle between the plane of water molecule O(bd) and the plane defined by O(b), O(ba), O(bc) and O(bd) with the sign of the angle defined with respect to the molecular three-fold axis [Fig. 1(*b*)]. Preferred values of φ occur when there is unequal occupancy of the t_{2g} (O_h) orbitals and result from the dependence of the splitting of the energies of these orbitals on φ.[19,21,22] The lifting of the degeneracy of the t_{2g} (O_h) orbitals by a rotation about φ depends on the anisotropic character of the metal–water π interaction, this having recently been demonstrated by polarised neutron diffraction.[23]

While precise definition of the co-ordination geometry of hydrates requires high-quality neutron-diffraction results, some useful conclusions may be drawn from crystal structures. For the potassium and caesium vanadium alums the data sets were of sufficient quality to permit refinement of the hydrogen-atom coordinates; however, even in these cases the e.s.d.s are too large to permit meaningful discussion. Examination of the available neutron-diffraction results from alums reveals that the hydrogen bonds involving the water molecule co-ordinated to the tervalent cation are close to linear. Accordingly, the orientation of the co-ordinated water molecule can be estimated from the relevant oxygen-atom positions (Fig. 2). The applicability of this approach may be tested in cases where accurate H(D)-atom positions are available from neutron-diffraction experiments.[15,17–21,24] A selection of angles which define the stereochemistry about the oxygen atom and the orientation of the plane of the water molecule in relation to the MO_6 framework is given in Table 5. The oxygen-atom positions give a poorer estimate of the bond angles to hydrogen for the β than for the α alums; this is exemplified by the very low values of angle *B* [O(2′)–O(b)–O(a′)]. However, for both α and β alums the orientation of the plane of the water molecule relative to the MO_6 framework may be estimated from the oxygen-atom positions with reasonable accuracy (Table 5, φ *vs.* Φ and tilt *vs.* TILT). This approach is useful both because it permits a good estimate of the geometry of the hexaaqua cation based only on 'heavy-atom' positions and, in cases where accurate H(D) positions are available, strains (implied by non-linearity of the hydrogen bonds) within a structure can be assessed. For the caesium sulfate β alums there is close agreement between φ and Φ except in the case of $CsRu(SO_4)_2{\cdot}12H_2O$, where the angles are −22.0 and −19.9°, respectively. In the case of ruthenium(III) there is unequal occupancy of the t_{2g} (O_h) orbitals and this leads to the electronic stabilisation being maximised by a more negative value of φ. Comparison of the φ and Φ values suggests that the larger value of φ found for the ruthenium alum is not driven by the hydrogen-bonding considerations alone, but reflects the compromise between the hydrogen-bonding and electronic considerations, with the electronic factors operating in favour of a larger value of φ.

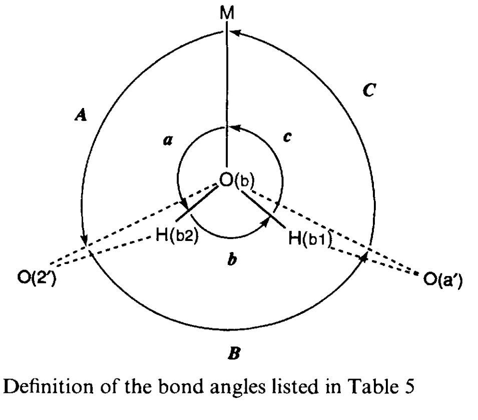

Fig. 2 Definition of the bond angles listed in Table 5

For the potassium, rubidium and caesium vanadium sulfate alums the co-ordination geometry of the water molecule co-ordinated to vanadium(III) is trigonal planar, with tilt angles ranging between 0 and 1°. The φ values range between −19.8 (Cs) and −19.3° (K). In the case of the caesium alum the φ value can be compared with the corresponding values for the similarly sized iron (−19.0) and ruthenium alums (−19.9°). The ruthenium(III) cation is low spin with a $(t_{2g})^5$ electronic configuration and like vanadium(III) gives octahedral complexes with orbitally degenerate ground terms. While the differences between the φ values are small, it is reassuring that the values obtained in cases where there is asymmetric occupancy of the metal (t_{2g}) orbitals are in excellent agreement. Since there are no potassium or rubidium β alums with cations which have orbitally non-degenerate ground terms, it is not possible to deduce whether the slight differences in the φ values of the different vanadium sulfate alums reflect any difference in the stereochemistry of the vanadium hexaaqua cation or an increase in the strain of the hydrogen bonds.

An estimate of the electronic stabilisation of the vanadium(III) cation in the β-alum lattice may be gained from the magnitude of the splitting of the energies of the t_{2g} (O_h) orbitals, δ. Electronic Raman spectra obtained from a range of vanadium sulfate alums[25] suggest a value of δ of 1940 cm^{-1}, this being largely insensitive to the identity of the monovalent cation. This implies a stabilisation of 2δ/3, or 1293 cm^{-1}, over that which applies when there is no splitting of the energies of the t_{2g} (O_h) orbitals (T_h symmetry). For the α alums the planes of the co-ordinated water molecules are aligned with the MO_6 framework (φ = 0°) but are tilted relative to the MO bond vector (unlike the β alums where φ = −19° and the tilt angle is 0°), giving an overall symmetry of S_6. The luminescence spectra of chromium(III) doped into α and β alums are consistent with the δ value for β alums being at least an order of magnitude greater

Table 4 Criteria for the classification of sulfate alums

Alum	S Fractional coordinate	Angle between M^{III}–O(b) and cell axes/°	$r[M^I\text{–}O(2)]/r[M^I\text{–}O(a)]$	O(a)–M^I– O(a)/°	Type
$KAl(SO_4)_2{\cdot}12H_2O$ [a]	0.307 5(4)	10.3(3)	1.271(5)	66.5(2)	α
$KCr(SO_4)_2{\cdot}12H_2O$ [b]	0.309(5)	8(3)	1.29(5)	66(2)	α
$KV(SO_4)_2{\cdot}12H_2O$	0.326 40(3)	0.69(4)	1.109(1)	60.03(3)	β
$RbAl(SO_4)_2{\cdot}12H_2O$ [a]	0.312 7(4)	8.3(4)	1.201(7)	65.9(2)	α
$RbCr(SO_4)_2{\cdot}12H_2O$ [c]	0.312	8.0	1.22	65	α
$RbV(SO_4)_2{\cdot}12H_2O$	0.328 1(1)	0.7(1)	1.070(2)	60.0(1)	β
$CsAl(SO_4)_2{\cdot}12H_2O$ [d]	0.328 41(9)	0.8(1)	1.032(2)	60.0(1)	β
$CsCr(SO_4)_2{\cdot}12H_2O$ [d]	0.328 13(8)	0.8(1)	1.038(2)	60.0(1)	β
$CsV(SO_4)_2{\cdot}12H_2O$	0.327 01(3)	0.70(4)	1.049(1)	60.00(2)	β

[a] Ref. 10. [b] Ref. 12. [c] Ref. 11, no e.s.d.s quoted for positional parameters. [d] Ref. 4.

Table 5 Stereochemistry of M^{III}–H_2O co-ordination as deduced from the coordinates of the hydrogen atoms (neutron) and from the hydrogen-bonding network (oxygen-atom positions)

Alum	Type	$a/°$	$b/°$	$c/°$	$a + b + c/°$	tilt[a]/°	φ[b]/°
$CsCr(SO_4)_2\cdot 12H_2O$[c]	β	122.9(2)	110.7(3)	126.3(2)	360(1)	0.9(4)	−19.0(4)
$CsFe(SO_4)_2\cdot 12H_2O$[d]	β	122.6(1)	110.4(3)	126.4(1)	359.4(8)	0.6(3)	−19.4(3)
$CsMo(SO_4)_2\cdot 12D_2O$[e]	β	122.7(1)	111.1(1)	126.2(1)	360.0(5)	1.8(1)	−19.7(1)
$CsRu(SO_4)_2\cdot 12H_2O$[f]	β	122.4(1)	112.6(2)	125.0(1)	360.0(8)	1.2(3)	−22.0(3)
$CsRh(SO_4)_2\cdot 12H_2O$[g]	α	116.6(2)	108.5(4)	120.2(2)	345(2)	35.5(6)	1.3(6)[h]
$CsFe(SeO_4)_2\cdot 12H_2O$[d]	α	122.3(1)	108.0(2)	125.2(1)	356(1)	18.6(3)	1.5(3)[h]
$NH_4Al(SO_4)_2\cdot 12H_2O$[i]	α	124.2(3)	107.4(4)	125.3(3)	357(2)	15.5(8)	0.8(8)[h]
$KV(SO_4)_2\cdot 12H_2O$	β						
$RbV(SO_4)_2\cdot 12H_2O$	β						
$CsV(SO_4)_2\cdot 12H_2O$	β						
		$A/°$	$B/°$	$C/°$	$A + B + C/°$	TILT[a]/°	Φ[b]/°
$CsCr(SO_4)_2\cdot 12H_2O$[c]		123.9(1)	107.2(1)	128.9(1)	360.0(6)	−0.5(3)	−19.0(3)
$CsFe(SO_4)_2\cdot 12H_2O$[d]		124.0(1)	108.3(1)	127.7(1)	360.0(6)	−0.9(2)	−19.0(2)
$CsMo(SO_4)_2\cdot 12D_2O$[e]		121.7(1)	110.8(1)	127.5(1)	360.0(6)	0.0(1)	−19.1(1)
$CsRu(SO_4)_2\cdot 12H_2O$[f]		123.3(1)	109.1(1)	127.6(1)	360.0(6)	−0.1(1)	−19.9(1)
$CsRh(SO_4)_2\cdot 12H_2O$[g]		122.6(2)	101.1(2)	125.5(2)	349(1)	28.3(6)	2.0(6)[h]
$CsFe(SeO_4)_2\cdot 12H_2O$[d]		126.0(1)	101.8(1)	128.1(1)	355.9(6)	17.2(2)	1.1(2)[h]
$NH_4Al(SO_4)_2\cdot 12H_2O$[i]		129.7(2)	100.4(2)	127.5(2)	358(1)	12.7(8)	0.1(8)[h]
$KV(SO_4)_2\cdot 12H_2O$		123.3(1)	106.1(1)	130.6(1)	360.0(6)	0.5(1)	−19.3(1)
$RbV(SO_4)_2\cdot 12H_2O$		124.7(1)	105.9(1)	129.5(1)	360.1(6)	0.3(2)	−19.5(2)
$CsV(SO_4)_2\cdot 12H_2O$		124.0(1)	108.2(1)	127.9(1)	360.1(6)	1.0(1)	−19.8(1)

[a] Angle between the vector M^{III}–O(b) and the plane defined by O(b), H(b1) and H(b2) (tilt) or O(b), O(a^i) and O(2^i) (TILT). [b] Angle between the MO_6 axes and O(b), H(b1) and H(b2) (φ) or O(b), O(a^i) and O(2^i) (Φ). [c] Ref. 19. [d] Ref. 17. [e] Ref. 20. [f] Ref. 18. [g] Ref. 23. [h] Owing to the large tilt of the plane of the co-ordinated water molecule, φ and Φ are defined as the angle between the vector H(b1)–H(b2) or O(a^i)–O(2^i) and the plane O(b), O(ba), O(bc) and O(bd). [i] Ref. 15.

than that found for the α alums (based on the splitting of the excited ^2E_g term).[26] This suggests that the electronic stabilisation of the vanadium(III) cation in the β-alum lattice is $2\delta/3$ or *ca.* 1230 cm^{-1}, or equivalently, 14.7 kJ mol^{-1}. This represents the upper limit on the energy difference between the α and β forms of the potassium or rubidium vanadium sulfate alums. A preferred stereochemistry of water co-ordination to vanadium(III) should be evident in a range of salts but, apart from the alums, the vanadium(III) hexaaqua cation has only been characterised structurally (X-ray and neutron) in the salt $[V(OH_2)_6][H_5O_2][CF_3SO_3]_4$.[21] In this case $[V(OH_2)_6]^{3+}$ exhibits approximate all-horizontal D_{3d} symmetry, consistent with predictions based on the electronic structure.

Conclusion

X-Ray analyses of the vanadium sulfate alums of potassium, rubidium and caesium have confirmed their adoption of the β modification. In the case of the potassium and rubidium salts the α modification is expected on the basis of the sizes of the constituent ions in the lattice. The structural chemistry is inferred to result from the electronic structure of the vanadium(III) cation which leads to a preferred geometry of the co-ordinated water molecule which is more closely realised for β than α alums. Accordingly, the hydrogen-bonded network is consistent with the adoption of a trigonal-planar mode of water co-ordination to vanadium(III) with a φ value similar to that found for ruthenium(III). Based on estimates of the electronic stabilisation of the co-ordination geometry of M^{III} for β over α alums (in the d^2 case) the energy difference between the potassium or rubidium α and β lattices is estimated to be less than 14.7 kJ mol^{-1}.

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