Single-crystal Raman Spectroscopy of the α Alums $CsM(SO_4)_2\cdot12H_2O$ (M = Co or Ir) between 275 and 1200 cm^{-1}

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Low-temperature polarised single-crystal Raman spectra of $CsM(SO_4)_2\cdot12H_2O$ (M = Co or Ir) have been recorded between 275 and 1200 cm^{-1}. A full assignment of the spectra has been completed, including all the Raman-active internal modes of the tervalent hexaaqua cation [$\nu_1(MO_6)$ 548 (Co) and 554 (Ir), $\nu_2(MO_6)$ 509 (Co) and 540 (Ir) and $\nu_5(MO_6)$ 332 av. (Co) and 314 av. cm^{-1} (Ir)]. The relationship between the wavenumber of the $\nu_1(MO_6)$ mode and the metal–oxygen bond length is significantly different for the tervalent cations of the second- and third-row transition metals than for those of first-row transition metals and Group 13 metals. Solution Raman spectra of $[Ir(OH_2)_6]^{3+}$ have enabled determination of $\nu_1(MO_6)_{aq}$ (536 cm^{-1}); the relationship between this value and that obtained at low temperature in the solid state closely follows that found previously for the chromium(III) and rhodium(III) aqua ions. The external modes of water co-ordinated to the tervalent cation are highly sensitive to the alum type, the metal–ligand bond length, and the stereochemistry of water co-ordination and provide additional insight into the metal–water interaction. This, in turn, casts light on the assignment of the external modes to particular molecular motions.

Recent low-temperature neutron diffraction studies of tervalent hexaaqua cations have revealed key aspects relating the stereochemistry of water co-ordination to the electronic structure of the tervalent cation.[1–4] Variations in the tilt and twist angles of the co-ordinated water molecule relative to the MO_6 framework may influence the electronic structure of the tervalent cation so that preferred orientations of water co-ordination depend on the electron count of the cation and that these preferred stereochemistries may persist even in strongly hydrogen-bonded environments.[3] A particularly striking example of these effects is provided by the α/β dimorphism of the caesium sulfate alums, $CsM^{III}(SO_4)_2\cdot12H_2O$, where M^{III} = Al, Ga, In, Ti, V, Cr, Mo, Mn, Fe, Ru, Co, Rh or Ir. For these salts the β modification is adopted by all the cations[5–8] except for Co, Rh and Ir which give α alums.[6,9] In these three cases the tervalent cation has a $(t_{2g})^6$ electron configuration with no valence d orbitals which can accept π-electron density from the ligand. Since the $(t_{2g})^5$ ion, Ru, gives a well defined caesium sulfate β alum[2] the relative stabilities of the structures must be finely balanced. A key difference between the α- and β-alum types is the stereochemistry of water co-ordination to the tervalent cation, where for the β modification trigonal-planar co-ordination is found whereas trigonal-pyramidal co-ordination pertains for the α modification. Therefore the study of the caesium sulfate α alums provides the opportunity to assess the impact of the different modes of water co-ordination to M^{III} on the spectroscopy of the aqua ion. In this paper we present single-crystal Raman spectra of the caesium sulfate alums of Co and Ir. These results are of importance since they allow us to evaluate the influence of the stereochemistry of water co-ordination on the internal modes of the tervalent hexaaqua cation and also on the external modes of co-ordinated water. Further, the changes to the metal(III)–ligand stretching frequency can be compared for all the elements of a triad (*i.e.* Co, Rh and Ir), this being unique for aqua ions and uncommon for other ligand systems.

Experimental

The caesium sulfate alums of cobalt(III) and iridium(III) were prepared using published procedures.[9,10] Large crystals suitable for single-crystal Raman spectroscopy were prepared by crystallisation from supersaturated solutions held at *ca.* 4 °C. For each alum the crystallographic axes could be deduced from the crystal morphology, this being predominantly octahedral. Scattering experiments of the type $X'(\alpha\beta)Y'$ were chosen since a complete data set could be obtained without reorientation of the crystal[11] (Porto notation is used to designate the scattering experiment where X,Y,Z are related to X',Y',Z by a rotation about Z by $\pi/4$ radians). The Raman activities of these scattering experiments are included in Figs. 1 and 2. Details of the Raman equipment have been given elsewhere.[12,13] The band intensities, wavenumbers and assignments are included in Tables 1 and 2. Spectra were recorded near liquid-nitrogen temperature, with the temperature of the sample being estimated from the intensity ratio of pairs of Stokes and anti-Stokes bands. Identification of the leakage of unwanted polarisations into the spectra has been aided by the use of computer subtractions, applied in the manner outlined in ref. 12. Solution spectra were run of samples contained in capillaries. No correction was made for polarisation scrambling due to the glass of the capillary.

Results and Discussion

Description of the Structure.—For both the caesium sulfate α- and β-alum types the space group symmetry is $Pa\bar{3}$ (T_h^6) and the site symmetries of the constituent ions are the same. Whereas X-ray crystallographic data are sufficient to provide unambiguous assignment of the alum type,[6,14] the availability of neutron diffraction data is of key importance since this alone allows characterisation of the stereochemistry of $[M(OH_2)_6]^{3+}$. The importance of which follows from the observation that the size of the tervalent cation does not determine the type of caesium sulfate alum formed, rather it is the stereochemical preference for water co-ordination to M^{III}. Whereas a good range of neutron diffraction data is available for caesium sulfate β alums (Fe^{III},[1] Cr^{III}[3] and Ru^{III}[2]), the α modification has thus far only been characterised by a preliminary room-temperature neutron data set from $CsRh(SO_4)_2\cdot12H_2O$ the refinement of which is sufficient to define the stereochemistry of water

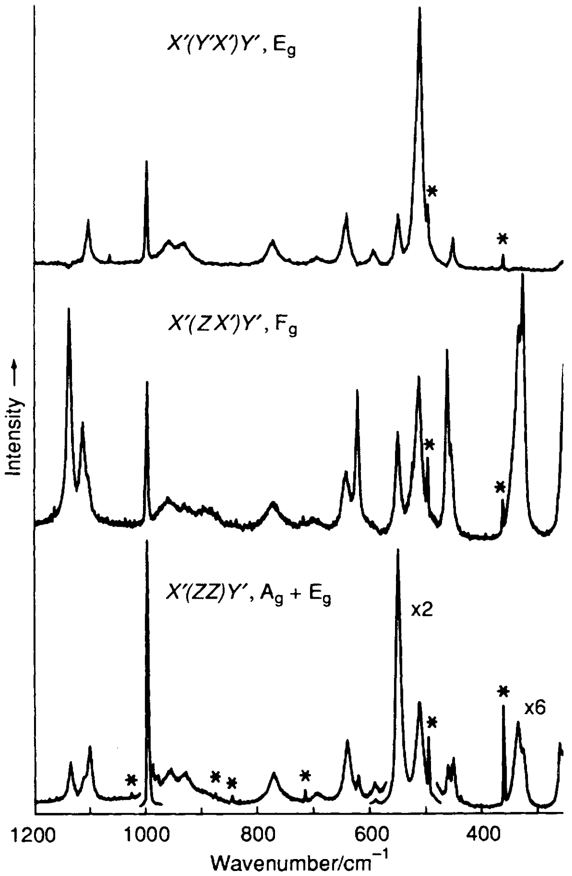

Fig. 1 Single-crystal Raman spectra of $CsCo(SO_4)_2{\cdot}12H_2O$, between 275 and 1200 cm^{-1} (90 K, spectral bandwidth 2.1 cm^{-1} at 600 cm^{-1}, step size 0.4 cm^{-1}, 30 mW, 476.5 nm radiation at the sample, count time 4 s, plasma emissions are designated by *)

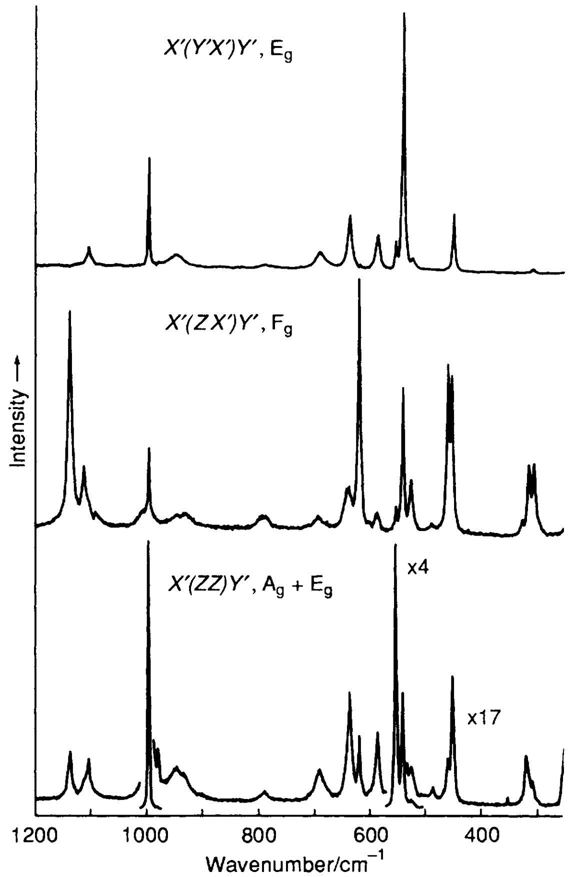

Fig. 2 Single-crystal Raman spectra of $CsIr(SO_4)_2{\cdot}12H_2O$, between 275 and 1200 cm^{-1} (80 K, spectral bandwidth 1.7 cm^{-1} at 600 cm^{-1}, step size 0.4 cm^{-1}, 100 mW, 514.5 nm radiation at the sample, count time 4 s)

co-ordination to M^{III}.[15] For the caesium sulfate β alums the angle between the plane of the co-ordinated water molecule and the M^{III}–O bond vector is 0.3(3)° (*i.e.* trigonal-planar co-ordination) and 35.5(10)° (*i.e.* trigonal-pyramidal co-ordination) for the α modification. The hydrogen bonds which extend from the water molecule co-ordinated to M^{III} are the strongest in the lattice [based on the r(O–H) and r(O···O) distances] and these direct the water and sulfate groups which comprise the co-ordination sphere of Cs^+. In both cases the MO_6 framework is only slightly distorted from octahedral and is aligned with the unit-cell axes. Thus the differences in the vibrational spectroscopy of $[M(OH_2)_6]^{3+}$ reflect differences in the co-ordination geometry and angular character of the hydrogen bonds extending from the cation rather than the orientation of the cation relative to the laboratory axes used in the scattering experiments.

The factor-group analysis (f.g.a.) of the caesium sulfate α alums has already been published[12,16] and requires only brief discussion. The internal modes of sulfate and the tervalent hexaaqua cation and the external (librational) modes of water co-ordinated to the mono- and ter-valent cations occupy the spectral region between 275 and 1200 cm^{-1}. Accordingly, for the first-order Raman spectrum $\Gamma_{275-1200}$ (calc.) = $11A_g + 11E_g + 33F_g$. For both $CsCo(SO_4)_2{\cdot}12H_2O$ ($6A_g + 10E_g + 21F_g$) and $CsIr(SO_4)_2{\cdot}12H_2O$ ($9A_g + 11E_g + 24F_g$) good agreement is found between the f.g.a. predictions and the observed spectra. In keeping with this analysis spectra recorded between 10 and 275 cm^{-1} yield similarly good agreement with the f.g.a. predictions. A key aspect to the assignment of the vibrational spectra of the caesium sulfate α and β alums has been the observation of all the bands attributable to first-order vibrational modes of E_g symmetry between 10 and 1200 cm^{-1}. For both $CsCo(SO_4)_2{\cdot}12H_2O$ and $CsIr(SO_4)_2{\cdot}12H_2O$ each of the modes of E_g symmetry can be accounted for, either by direct observation or strong inference (in the case of weak or accidentally coincident bands arising from E_g modes). The assignment of bands to first-order phonon modes follows from comparison of the spectra of $CsCo(SO_4)_2{\cdot}12H_2O$ and $CsIr(SO_4)_2{\cdot}12H_2O$ with those of $CsRh(SO_4)_2{\cdot}12H_2O$ where the assignment is based on the spectra of the corresponding deuteriate and selenate analogues.[16]

Assignment of the Spectra.—(*i*) *The internal modes of the tervalent hexaaqua cations.* For $CsRh(SO_4)_2{\cdot}12H_2O$ $\nu_1(RhO_6)$ gives rise to an extremely intense band at 548 cm^{-1} (A_g).[17] Similarly intense bands can readily be identified in the spectra of $CsCo(SO_4)_2{\cdot}12H_2O$ (Fig. 1) and $CsIr(SO_4)_2{\cdot}12H_2O$ (Fig. 2). Since no other modes can reasonably be expected to give rise to such intense bands in that spectral region, the band at 548 cm^{-1} (A_g) is assigned to $\nu_1(CoO_6)$ and that at 554 cm^{-1} (A_g) to $\nu_1(IrO_6)$. As is the case for each of the other alums so far studied, there is no indication of coupling between $\nu_1(MO_6)$ and other modes of similar wavenumber. This is best evidenced by noting that the intensities of the bands arising from these modes are insensitive to the identity of the metal, or more importantly to the intensity of the mode arising from $\nu_1(MO_6)$. Since in the cases of Co and Ir the intensities of this mode are extremely large, comparable to that of $\nu_1(SO_4)$, it can be inferred that $\nu_1(MO_6)$ is not strongly coupled to other vibrations of the lattice. According to the f.g.a. $\nu_1(MO_6)$ is expected to give rise to A_g and F_g components. In neither the single-crystal Raman spectra of the caesium rhodium sulfate or selenate alums[17] nor of the caesium sulfate β alums[12,13] does the F_g component occur with significant intensity; this too is the case for both $CsCo(SO_4)_2{\cdot}12H_2O$ and $CsIr(SO_4)_2{\cdot}12H_2O$.

The assignment of $\nu_2(MO_6)$ is complicated by the presence

Table 1 Vibrational frequencies and assignments for $CsCo(SO_4)_2{\cdot}12H_2O$ between 275 and 1200 cm^{-1}

ν/cm^{-1}		$X'(ZZ)Y'$	$X'(ZX')Y'$	$X'(Y'X')Y'$	Assignment
324	F_g	*ca.* 15	140	14	$\nu_5(CoO_6)$
330	E_g(?)			*ca.* 1	
332	F_g		60	8	
333	A_g	45			
341	F_g		sh		
449	E_g	25		20	$\nu_2(SO_4)$
451	F_g		30		
459	F_g	14	115	5	
485	$A_g + F_g$	sh	2	sh	ρ_6
509	$E_g + F_g$	180	95	167	$\nu_2(CoO_6)$
548	$A_g + F_g$(?)	492	60	27	$\nu_1(CoO_6)$
590	$E_g + F_g$	8	3	9	ρ_5
602	F_g		3		
619	F_g	11	84		$\nu_4(SO_4)$
638	$E_g + F_g$	37	33	32	
692	E_g	5		4	ρ_4
699	F_g		5		
771	$E_g + F_g$	18	15	13	$\rho_3 = \omega_3$
886	F_g		6		$\rho_2 = \tau_3$
895	A_g	4	6		
930	$E_g + F_g$		8	11	
954	E_g	11		12	$\rho_1 = r_3$
956	F_g		12		
978	A_g	8			$\nu_1(S^{16}O_3{}^{18}O)$
995	A_g	1032	89	65	$\nu_1(SO_4)$
1100	E_g	31		27	$\nu_3(SO_4)$
1102	F_g		*ca.* 8		
1111	F_g	4	60		
1136	F_g	22	135		

sh = Shoulder.

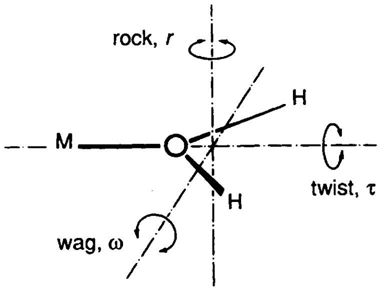

Fig. 3 The nomenclature for the external modes of co-ordinated water

of a close-lying external mode of co-ordinated water and the possibility of coupling with $\nu_2(SO_4)$. Strong bands are observed near to $\nu_1(MO_6)$ at 509 (E_g, Co) and 540 cm^{-1} (E_g, Ir). The intensities of these bands are markedly sensitive to the identity of the metal. The general patterns of these bands and their relative intensities are similar to those found for $CsRh(SO_4)_2{\cdot}12H_2O$ for which the assignment to $\nu_2(MO_6)$ is supported by deuteriation and selenate for sulfate substitution. The $\nu_2(SO_4)$ mode gives bands which are similar in each of the spectra of the caesium sulfate α alums despite the different wavenumbers of their respective $\nu_2(MO_6)$ modes. This suggests that there is little coupling between $\nu_2(MO_6)$ and $\nu_2(SO_4)$. An external mode of co-ordinated water also occurs in this spectral region and can potentially couple to the $\nu_2(MO_6)$ mode. Whereas the E_g components of $\nu_2(MO_6)$ are very intense and sensitive to the identity of the metal, the E_g components of the external mode are in both salts similarly weak and therefore E_g components of the two modes are not strongly coupled. The F_g components of $\nu_2(MO_6)$ are not so intense and therefore similar arguments concerning the coupling of the F_g components of the modes in question cannot be made and the possibility of such coupling cannot be ruled out.

The $\nu_5(MO_6)$ mode of a range of tervalent hexaaqua cations gives rise to bands in the spectral region 250–375 cm^{-1}. For the sulfate alums this region of the spectrum contains no other modes and thus the bands due to $\nu_5(MO_6)$ modes are easily identified and show little signs of coupling to other modes; this is evidenced by comparison between the spectra of hydrated and deuteriated crystals.[12,13,17] On this basis the cluster of bands found near 300 cm^{-1} are readily assigned to the $\nu_5(MO_6)$ modes of $[Co(OH_2)_6]^{3+}$ and $[Ir(OH_2)_6]^{3+}$. The positions and intensities of the bands resulting from these modes are sensitive to the identity of the metal whereas the band structure (the relative positions and intensities of the components of the mode) is highly dependent on the alum type. The band structures found for the caesium sulfate alums of cobalt and iridium are similar and are characteristic of that found for sulfate and selenate α alums.[12,13,17]

(*ii*) *The internal modes of sulfate*. The band arising from $\nu_1(SO_4)$ occurs at 995 cm^{-1} (A_g) for both salts, this being coincident with that found for $CsRh(SO_4)_2{\cdot}12H_2O$.[16] This value is distinctly different from that found for the caesium sulfate β alums, 987 ± 1 cm^{-1}.[11,12] The form of the bands resulting from the $\nu_3(SO_4)$ and $\nu_2(SO_4)$ modes is similarly indicative of the alum type and the spectra of $CsCo(SO_4)_2{\cdot}12H_2O$ and $CsIr(SO_4)_2{\cdot}12H_2O$ conform to those expectations. The $\nu_4(SO_4)$ mode gives rise to bands which occur between 610 and 640 cm^{-1} which are close to external modes of co-ordinated water. The band profiles are characteristic of the alum type and are only weakly sensitive to the identity of the metal.

(*iii*) *The external modes of co-ordinated water*. The external or librational modes of co-ordinated water arise from rotations about its three principal axes, the form and nomenclature of these modes for a trigonal planar co-ordinated water molecule being shown in Fig. 3. Since there are two water molecules in the asymmetric unit, one associated with each cation, there are six external modes to be assigned. Examination of the X-ray and neutron diffraction structures of the alums shows that the hydrogen bonds extending out from the water co-ordinated to M^{III} are the strongest in the lattice, and therefore the external modes of water co-ordinated to the tervalent cation are

Table 2 Vibrational frequencies and assignments for $CsIr(SO_4)_2 \cdot 12H_2O$ between 275 and 1200 cm^{-1}

ν/cm^{-1}		$X'(ZZ)Y'$	$X'(ZX')Y'$	$X'(Y'X')Y'$	Assignment
305	E_g			*ca.* 3	$\nu_5(IrO_6)$
307	F_g	8	50	*ca.* 2	
315	F_g	*ca.* 3	48		
318	A_g	*ca.* 30			
326	F_g		8		
449	E_g	105		41	$\nu_2(SO_4)$
452	F_g		100		
459	F_g	25	110	*ca.* 6	
485	$A_g + F_g$	sh	4		ρ_6
525	E_g	10		7	
527	F_g		36		
540	$E_g + F_g$	366	102	169	$\nu_2(IrO_6)$
554	A_g	756	16	12	$\nu_1(IrO_6)$
586	$E_g + F_g$	45	12	23	ρ_5
600	$A_g + F_g$	2	4		
620	F_g	36	167	11	$\nu_4(SO_4)$
636	$E_g + F_g$	91	20	36	
641	F_g	sh	18		
680	$F_g + A_g$(?)	*ca.* 1	3		ρ_4
690	$E_g + F_g$	20	6	10	
700	F_g		2		
770	F_g		*ca.* 1		$\rho_3 = \omega_3$
786	E_g	5		2	
791	F_g		10		
926	F_g		5		$\rho_2 = \tau_3$
931	A_g	*ca.* 3			
944	$E_g + F_g$	10	6	6	
977	A_g	24			$\nu_1(S^{16}O_3{}^{18}O)$
995	A_g	2955	57	45	$\nu_1(SO_4)$
985	$E_g + F_g$		*ca.* 2	*ca.* 3	$\rho_1 = r_3$
1004	F_g		10		
1043	A_g	3			?[554(A_g) + 485(A_g)]
1089	F_g		4		$\nu_3(SO_4)$
1102	E_g	27		9	
1111	F_g	8	38	2	
1137	F_g	27	155	9	

expected to occur higher in wavenumber than those of the water co-ordinated to the univalent cation. This expectation must be treated with caution owing to the differing co-ordination numbers and geometry of the two unique water molecules. The f.g.a. indicates that each of the external modes gives rise to $A_g + E_g + 3F_g$ bands. The E_g bands are key to the assignment of the external modes since each is observed, or can be accounted for, and their lower density of states leads to fewer problems due to mixing of the vibrational coordinates. For $CsIr(SO_4)_2 \cdot 12H_2O$ there are six bands of E_g symmetry yet to be assigned and the six external modes are mapped onto these and are labelled ρ_1–ρ_6 in order of decreasing wavenumber. Close-lying bands of F_g or A_g symmetry are more or less ambiguously distributed among the various modes. The wavenumbers of these modes are in good agreement with those found for $CsRh(SO_4)_2 \cdot 12H_2O$, these having been assigned with the aid of deuteriation. For $CsCo(SO_4)_2 \cdot 12H_2O$ only five of the six bands of E_g symmetry are observed, with the sixth being either weak or accidentally coincident with other strong bands. Comparison of the wavenumbers of the external modes of co-ordinated water for the other α alums suggests that the sixth E_g component lies in the range 475–550 cm^{-1}. Consistent with this, A_g and F_g bands are observed at 485 cm^{-1} which are not readily assigned to any other mode and are therefore assigned to the external mode. This region of the E_g spectrum is dominated by the very strong E_g component of $\nu_2(MO_6)$ at 509 cm^{-1} and this is likely to have obscured the E_g component of the external mode.

The sensitivity of the external modes to alum type, sulfate/selenate exchange and changing metal–ligand interaction clarifies their assignment to individual librations of co-ordinated water. In Fig. 4 the wavenumber of the E_g component of each of the external modes of co-ordinated water is plotted against the metal(III)–water bond distance, this being related both to the volume of the alum lattice (for a given alum type)[6] and the metal–ligand interaction. Results are taken from low-temperature (80 K) single-crystal Raman spectra of caesium sulfate β alums,[12,13] α alums[17] and caesium selenate α alums.[12,13,17] Apart from $CsTi(SO_4)_2 \cdot 12H_2O$ (for which soft modes are observed at low temperature) and $CsRh(SeO_4)_2 \cdot 12H_2O$ [for which the bond-length dependence of the $\nu_1(MO_6)$ mode exhibits different characteristics compared to the other selenate alums] the E_g components of the external modes are easily related from one alum to another, an observation which suggests that coupling to other modes of the lattice is small. Considering first the caesium sulfate α and β alums. All six of the external modes of co-ordinated water are sensitive to the alum type. In particular the three highest-wavenumber external modes, ρ_1–ρ_3, exhibit a markedly different dependence on the size of the tervalent cation. For the β alums the wavenumbers of ρ_1 and ρ_2 decrease with increasing size of the tervalent cation whereas ρ_3 is insensitive to this parameter. This contrasts with what is observed for the caesium sulfate α alums where the wavenumbers of ρ_1–ρ_3 increase with increasing size of the tervalent cation. These trends can be traced back to the different dependence of $\nu_1(MO_6)$ on r(M–O) for the α alums, this being the opposite of that found for the β alums [increasing size of M^{III} gives decreasing $\nu_1(MO_6)$]. Hence for both α and β caesium sulfate alums ρ_1 and ρ_2 increase with increasing wavenumber of $\nu_1(MO_6)$ and are associated with the water molecules co-ordinated to M^{III}.

Two conflicting assignments of the external modes of water co-ordinated to M^{III} are discerned. One is to assign τ_3 on the basis of its expected low intensity in the infrared spectrum. On this basis,[18] ρ_2 is assigned to τ_3. Since the selenate α alums

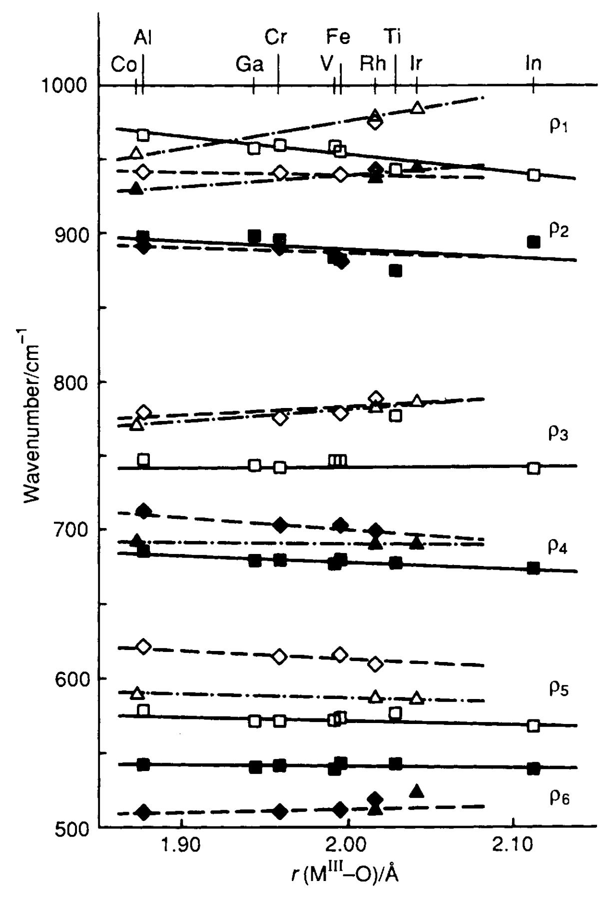

Fig. 4 Plots of the wavenumbers of the E_g components of the external modes of co-ordinated water against the metal(III)–water bond distance. Caesium sulfate α alums are designated by triangles, the corresponding β alums by squares, and caesium selenate α alums by diamonds; ρ_1, ρ_3 and ρ_5 are given as open symbols

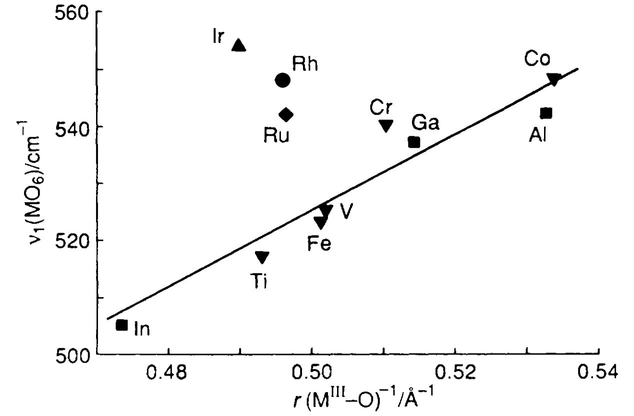

Fig. 5 The wavenumber of the $\nu_1(MO_6)$ mode plotted against the reciprocal of the metal(III)–water bond length for Group 13 (■), first- (▼), second- (◆) and third-row (▲) transition-metal cations. The straight line is drawn through the points for the Group 13 and first-row transition-metal cations

and sulfate α alums both have trigonal-pyramidal water co-ordination to M^{III}, the similarity of ρ_3 for these two sets of salts suggests an assignment to ω_3 as this motion involves a tilt of the water molecule (Fig. 3). This leaves ρ_1 to be assigned to r_3.

An alternative approach is to examine the sensitivity of the external modes to the M^{III}–O force constant [$\nu_1(MO_6)$]. Since τ_3 involves no disruption of the M^{III}–O bond length or σ bonding for trigonal-planar co-ordinated water molecules (Fig. 3), the insensitivity of ρ_3 to the identity of the metal for the sulfate β alums suggests its assignment to τ_3. The similar trends for ρ_3 for the sulfate and selenate α alums supports this assignment. The insensitivity of ρ_2 to the β to α structural change caused by selenate for sulfate substitution argues against its assignment to ω_3, leaving ρ_2 to be assigned to r_3 and ρ_1 to be assigned to ω_3.

Some insight into the assignment of these modes has been gained by the study of partially deuteriated salts[19] where the libration of the isotopomer either falls around the mean frequencies of the ω and τ librations or at the arithmetic mean of the r libration. We have recorded polarised single-crystal Raman spectra of $CsAl(SO_4)_2{\cdot}12(H/D)_2O$, with a H/D ratio of 0.3:1. Whereas the spectra are broadened relative to those of isotopically pure crystals there is a clearly defined shoulder on the low-wavenumber side of the band due to $\nu_4(SO_4)$, at *ca.* 607 cm^{-1}, which cannot be attributed either to isotopically pure librations or the arithmetic mean of a single libration. This wavenumber coincides with the arithmetic mean of the ρ_2 and ρ_3 modes of the deuteriated crystal, an observation which suggests that ρ_2 and ρ_3 are due to ω_3 and τ_3, although not necessarily in that order. This supports the initial approach to the assignments given above, *viz.* ρ_1 to r_3, ρ_2 to τ_3 and ρ_3 to ω_3.

The water co-ordinated to Cs^I is trigonal pyramidal; this together with involvement in three hydrogen bonds gives the oxygen atom a co-ordination number of four. The two hydrogen bonds for which the oxygen atom provides the hydrogens are to sulfate oxygen atoms and these are weak [$r(O \cdots O) \approx 1.8$ Å] compared to the remaining hydrogen bond which is between the two crystallographically distinct water molecules [$r(O \cdots O) \approx 1.6$ Å]. While the wavenumbers of the librations of this water molecule are sensitive to the alum type and selenate for sulfate substitution (Fig. 4), their assignment to particular motions is not straightforward. While it may be possible to model the potential about the water molecule and arrive at assignments of the ρ_4–ρ_6 modes we have not attempted such calculations at this stage. For our purposes it is sufficient to state that the behaviour of these modes is consistent with their assignment to librations of the water molecule co-ordinated to Cs^I.

Solution spectra of $CsIr(SO_4)_2{\cdot}12H_2O$ in sulfuric acid (1 mol dm^{-3}) are similar in form to those of the corresponding rhodium and chromium salts which have already been reported. The slow rate of ligand exchange[20] and the pH of the solution requires that the tervalent cation be $[Ir(OH_2)_6]^{3+}$; this proposition is supported by the bands arising from totally symmetric sulfate vibrations which indicate the presence of $[SO_4]^{2-}$ and $[HSO_4]^-$ and give no evidence of sulfate co-ordinated to the tervalent cation. A strong polarised band is observed at 536 cm^{-1} which is not present in the spectra of the solvent and is assigned to $\nu_1(MO_6)$. This band occurs 18 cm^{-1} lower than in the crystal at 80 K. The difference between the room-temperature solution and the low-temperature crystal spectra is consistent with that found for the other kinetically inert tervalent cations, chromium (18 cm^{-1})[13] and rhodium (19 cm^{-1}).[17]

Discussion

The most striking feature to emerge from the single-crystal Raman spectra of the caesium sulfate alums of cobalt and iridium is the observation that $\nu_1(IrO_6)$ occurs at higher wavenumber than does $\nu_1(CoO_6)$, this despite the much smaller size of the cobalt(III) hexaaqua cation. In Fig. 5 our earlier plot of $\nu_1(MO_6)$ against $1/r(M^{III}-O)$ is extended to include the cobalt, rhodium, ruthenium and iridium alums. This shows that for all the first-row transition metals and the Group 13 metals there is a common relationship between the metal(III)–water bond length and $\nu_1(MO_6)$ and that this behaviour is not adopted by the second- and third-row transition metals rhodium and iridium. A room-temperature spectrum of a polycrystalline sample of $CsRu(SO_4)_2{\cdot}12H_2O$ has been reported[21] with $\nu_1(RuO_6)$ being assigned to a band at 532 cm^{-1}, an assignment confirmed by ^{18}O isotopic substitution. Since it is generally observed that $\nu_1(MO_6)$ increases by 10 cm^{-1} on cooling to 80 K an estimated value of 542 cm^{-1} is used in Fig. 5. It is clear from examination of this Figure that the second- and third-row transition metals give a markedly different dependence of $\nu_1(MO_6)$ on the metal–ligand bond length than pertains for the Group 13 and first-row transition metals. While the suggestion that it is the different tilt angles of the co-ordinated water molecules which are responsible for the trend of wavenumbers of $\nu_1(MO_6)$ for Co, Rh and Ir cannot be excluded given the limited data available for heavier transition metals, the data for $CsRu(SO_4)_2 \cdot 12H_2O$, which has trigonal-planar water co-ordination, disproves this interpretation. The intensities of the A_g components of $\nu_1(MO_6)$ are large and, using the A_g component of $\nu_1(SO_4)$ as an internal standard, decrease down the group Co(186) > Rh(117) > Ir(47). While the variation of the intensities of these modes is an important aspect of their spectroscopy it awaits a satisfactory description.

The well ordered behaviour of the external modes of co-ordinated water gives a clear indication of the highly regular character of the caesium sulfate/selenate alum lattice. The ability of the lattice to accommodate a wide range of sizes of tervalent cations with minimum disturbance to the hydrogen-bonding pattern may possibly be achieved by the ready deformability of the co-ordination sphere about caesium. A feature of the Raman spectroscopy of the alums is the observation and interpretation of the external modes of co-ordinated water, these being poorly defined in other crystals. Examination of the external modes of water co-ordinated to M^{III} shows that they can occur at surprisingly high wavenumber (*ca.* 1000 cm^{-1}) and depend both on the charge and identity of the tervalent cation. An understanding of these modes is important since it is the formation of strong hydrogen bonds between successive hydration spheres which underlies the enthalpies of hydration and mobilities of these ions in aqueous solution.

Conclusion

Low-temperature single-crystal Raman studies of $CsCo(SO_4)_2 \cdot 12H_2O$ and $CsIr(SO_4)_2 \cdot 12H_2O$ have enabled their complete assignment in the spectral region 275–1200 cm^{-1}, which includes the ν_1, ν_2 and ν_5 modes of the tervalent hexaaqua cations of Co and Ir. The $\nu_1(MO_6)$ modes for the second- and third-row transition metals have a different wavenumber dependence on the metal(III)–water bond length than do the first-row transition metals and the Group 13 metals. The intensities of the A_g components of $\nu_1(MO_6)$ decrease down the group Co > Rh > Ir, this being opposite to that found for the Group 13 cations where Al < Ga < In. Comparison of the wavenumbers of the E_g components of the external modes of co-ordinated water for a range of caesium sulfate and selenate alums has allowed an assignment of the external modes of water co-ordinated to the tervalent cation. These modes occur high in wavenumber and exhibit a dependence on the wavenumber of the $\nu_1(MO_6)$ mode and not the metal(III)–water bond length. In aqueous solution $\nu_1(IrO_6)$ occurs at 536 cm^{-1}, 18 cm^{-1} lower than in the crystal at 80 K. This value is in close agreement with predictions based on the solid-state and solution spectra of the hexaaqua cations of chromium(III) and rhodium(III) and suggests a similarity of the structures of the aqua ions in the solid state and in solution.

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