Vibrational Spectroscopic Studies of Tervalent Hexa-aqua Cations: Oriented Single-crystal Raman Spectra between 275 and 1 200 cm^{-1} of the Caesium Rhodium Alums, $CsRh(SO_4)_2 \cdot 12H_2O$, $CsRh(SeO_4)_2 \cdot 12H_2O$, and $CsRh(SO_4)_2 \cdot 12D_2O$

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Oriented single-crystal Raman spectra of the caesium α-alums $CsRh(SO_4)_2 \cdot 12H_2O$, $CsRh(SeO_4)_2 \cdot 12H_2O$, and $CsRh(SO_4)_2 \cdot 12D_2O$ have been recorded at or below 80 K. The external modes of water co-ordinated to the mono- and ter-valent cations as well as the internal modes of $S(Se)O_4{}^{2-}$ and $[Rh\{OH(D)_2\}_6]^{3+}$ are found in the spectral region 275—1 200 cm^{-1}. A full assignment of the spectra in this region has been completed and the results are in close agreement with the predictions of factor group analysis. This work provides the first full vibrational characterisation of the Raman-active modes of the sulphate α-alum lattice. The site and factor group splitting of the $XO_4{}^{2-}$ vibrational modes is independent of the identity of X but highly dependent on the alum type, with the internal modes of $SO_4{}^{2-}$ in the caesium rhodium sulphate α-alums giving similar Raman band profiles to those of $SeO_4{}^{2-}$ in the caesium selenate α-alums. The internal modes of $[Rh(OH_2)_6]^{3+}$ are found at 548 [$\nu_1(RhO_6)$], 533 [$\nu_2(RhO_6)$], and 315 cm^{-1} [$\nu_5(RhO_6)$] in the low-temperature single-crystal spectra, while the $\nu_1(RhO_6)$ mode occurs at 529 cm^{-1} in solution (300 K, 1 mol dm^{-3} H_2SO_4). The relationship between the wavenumber of the $\nu_1(RhO_6)$ mode and the Rh–O bond length is significantly different compared with that obtained for the first-row transition-metal tervalent hexa-aqua ions.

Hexa-aqua cations are of undoubted importance to our understanding of the aqueous chemistry of metal ions. The study of crystal hydrates is an important means of determining the structure and bonding of aqua ions since the environment, co-ordination number, hydrolysis, and stereochemistry of the ion can be determined and maintained. The caesium alum lattice provides one of the few crystal systems well suited for the comparative study of tervalent hexa-aqua cations. The advantages follow from the diverse range of tervalent hexa-aqua cations able to be accommodated in the lattice, the availability of a broad body of *X*-ray [1–6] and neutron [2,7] structural data, the high crystal symmetry, and ease of crystallisation and stability of the resulting crystals. Structurally, the caesium alums are well behaved and do not suffer from the disorder of the sulphate anions which is prevalent among the α-alums of K^+, $NH_4{}^+$, and Rb^+.[8,9] Two caesium sulphate alum lattice modifications have been identified, the β-alum lattice which occurs with the majority of tervalent cations, and the α-alum lattice which occurs with Co^{III},[5] Rh^{III},[6] and Ir^{III}.[6] The differences between the caesium sulphate alum structures can be traced back to the stereochemistry of water co-ordination to the tervalent cation. For the α-alums trigonal pyramidal co-ordination geometry about the oxygen atom is adopted, whereas for β-alums the expected trigonal planar co-ordination geometry about oxygen prevails. Since the tervalent cation in each of the caesium sulphate α-alums so far identified has a $(t_{2g})^6$ electron configuration it is likely that interactions between the ligand and metal orbitals are sufficiently important so as to determine the stereochemistry of water co-ordination and thus to determine the alum type. Therefore the caesium alums provide an opportunity to study the influence of the *d* electrons on the stereochemistry of ligand co-ordination. In order to exploit this opportunity it is necessary to obtain an understanding of the two lattice types. Structural data for the caesium α-alums have been reported,[5,6] along with the single-crystal Raman spectra of the F_g components of the $\nu_3(SO_4{}^{2-})$ modes of the caesium sulphate alums of cobalt, rhodium, and iridium.[6] These spectra indicate that the caesium α- and β-alum types are spectroscopically distinct. No complete vibrational study of the caesium α-alum lattice has been published. Hence an important goal of this work is to provide a complete assignment of the Raman spectrum of the caesium α-alum lattice. To this end we have conducted single-crystal Raman studies of $CsRh(SO_4)_2 \cdot 12H_2O$, $CsRh(SeO_4)_2 \cdot 12H_2O$, and $CsRh(SO_4)_2 \cdot 12D_2O$. Similar single-crystal Raman studies on the corresponding series of caesium aluminium [10] and iron(III) [11] β-alums have demonstrated the utility of such a series in providing unambiguous assignments of the first-order phonon modes. Since the focus of this work is the internal modes of the tervalent hexa-aqua cation we limit this discussion to the spectral region 275—1 200 cm^{-1}. Finally, since the rhodium(III) hexa-aqua cation is extremely inert to substitution [12] ($t_{\frac{1}{2}} > 10^8$ s), we have been able to extend our results to the solution state. This enables an assessment to be made of the influence of the environment on the internal modes of the rhodium(III) hexa-aqua cation.

Experimental

The caesium rhodium sulphate hydrate alum was prepared by the following method. A solution of sodium hydroxide (0.8 g) in water (10 cm^3) was added with stirring to a solution of rhodium trichloride (1 g) in water (10 cm^3). The mixture was centrifuged and the supernatant discarded. The pale yellow precipitate was washed by stirring it in water (50 cm^3), centrifuging, and discarding the supernatant. The procedure for rinsing was repeated three times. The precipitate was dissolved in 1 mol dm^{-3} sulphuric acid (20 cm^3) and a slight molar excess of caesium sulphate (20%, 0.9 g) added. The alum crystallised slowly over a number of days, producing large well-formed octahedra. The deuteriated analogue was prepared by an

Table 1. Vibrational frequencies and assignments for $CsRh(SO_4)_2 \cdot 12H_2O$ between 275 and 1 200 cm^{-1}

ν/cm^{-1}		$X'(ZZ)Y'$	$X'(ZX')Y'$	$X'(Y'X')Y'$	Assignment
307	F_g		80	15	$\nu_5(RhO_6)$
309	E_g	*ca.* 10		7	
316	F_g		60	12	
319	A_g	103			
325	F_g		*ca.* 10		
450	E_g	135		132	$\nu_2(SO_4^{2-})$
452	F_g		55		
459	F_g	*ca.* 5	120	*ca.* 20	
487	F_g		*ca.* 1		ρ_6
491	A_g	12			
512	E_g	*ca.* 20		*ca.* 20	
523	F_g		15		
533	E_g	1 204		1 303	$\nu_2(RhO_6)$
534	F_g		42		
548	A_g	2 436	18	*ca.* 50	$\nu_1(RhO_6)$
587	E_g	67		72	ρ_5
601	F_g		*ca.* 4		$\nu_4(SO_4^{2-})$
620	F_g	*ca.* 8	135	*ca.* 20	
636	E_g	157		163	
642	F_g		23		
690	E_g	33		34	ρ_4
694	F_g		*ca.* 4		
782	F_g		7		ρ_3
783	E_g	34		34	
790	F_g		4		
800	A_g	5			
917	F_g		11		ρ_2
938	E_g	58		58	
976	F_g		12		ρ_1
978	E_g	sh		23	
990	F_g		6		
978	A_g	28			$\nu_1(S^{16}O_3{}^{18}O^{2-})$
995	A_g	4 959	18	102	$\nu_1(SO_4^{2-})$
1 034	A_g	4			$[548(A_g) + 491(A_g)]$
1 088	F_g		*ca.* 3		$\nu_3(SO_4^{2-})$
1 102	E_g	92		85	
1 111	F_g		48		
1 136	F_g	12	170	26	

sh = shoulder.

analogous procedure. The caesium rhodium selenate alum was prepared by the dissolution of freshly prepared rhodium(III) hydroxide (0.58 g) in a minimum quantity of selenic acid followed by the addition of a stoicheiometric quantity of caesium carbonate (0.62 g). Crystallisation of the highly soluble alum is very slow and if an excess of the acid is used then the solution requires concentration or nucleation. The alum was recrystallised from selenic acid (2.4 mol dm^{-3}) to yield large crystals.

For each alum the crystallographic axes could be deduced from the crystal morphology which is predominantly octahedral. Scattering experiments of the type $X'(\alpha\beta)Y'$ or $X'(\alpha\beta)Z$ were chosen since a complete data set could be obtained without reorientation of the crystal[13] (standard Porto notation is used to designate the scattering experiments, with X,Y,Z being related to X',Y',Z by a rotation about Z by $\frac{\pi}{4}$ radians). The Raman activities of these scattering experiments have been given elsewhere.[10,11] Spectra were obtained using a Spex 1401 monochromator (fitted with a spatial filter) in conjunction with an RCA C31034 GaAs photomultiplier tube and a PAR discriminator and counter. Low temperature spectra were obtained using Oxford Instruments CF104 or CF1204 cryostats. The CF1204 cryostat was used to obtain spectra at liquid-helium temperature. In these experiments the crystal was in contact with an exchange gas (He) which thereby improved the efficiency of heat transfer from the sample. Spectra were recorded at or below liquid-nitrogen temperatures in order to reduce the possibility of thermal decomposition and because the narrower full widths at half height (f.w.h.h.) enable more precise determination of the band structures and positions. In each case the temperature of the crystal was estimated from the ratios of the Stokes and anti-Stokes bands. Raman spectra were obtained of solutions contained in capillaries (inside diameter 1 mm, Spex). No attempt was made to correct for polarisation scrambling due to the glass walls of the capillary.

Results and Discussion

The single-crystal Raman spectra of $CsRh(SO_4)_2 \cdot 12H_2O$, $CsRh(SeO_4)_2 \cdot 12H_2O$, and $CsRh(SO_4)_2 \cdot 12D_2O$ are given in Figures 1—3, while the band positions and assignments are given in Tables 1—3. Owing to imperfections in the scattering experiments the leakage of strong bands of one symmetry type into the other spectra is unavoidable. The extent of this leakage depends on the angle through which scattered light is collected, the quality of the crystal, and its alignment relative to the laboratory axes. Spectral subtraction techniques have been used to assist the assignment of bands to particular symmetry species. These procedures are particularly important in the identification of the bands of A_g symmetry since for this crystal system no scattering experiment yields only bands of A_g symmetry.

(*i*) *Factor Group Analysis* (*f.g.a.*).—The α- and β-alum modifications differ in their spatial relationship of the hydrogen bonding within the lattice. This leads to an overall difference in the efficiency of packing of the constituent ions, with the α-alums being more dense, *i.e.* they have a smaller unit-cell volume for a given size of tervalent hexa-aqua cation.[5,6] The crystal ($Pa3$, T_h^6) and site symmetries of the constituent atoms are the same in both cases. Therefore the f.g.a. appropriate for the β-alums is likewise appropriate for the α-alums and is given in Table 1 of ref. 14.

A key factor in the assignment of the Raman spectra of the caesium alums is the E_g spectrum. All 17 bands of E_g symmetry which are expected to occur below 1 200 cm^{-1} are observed. These include a band arising from each of the external modes of water co-ordinated to both the mono- and ter-valent cation. The main simplifying feature of this observation lies in the clarification of the analysis of the external modes of co-ordinated water, since at least one of the components of each of these modes can be identified. This removes possible ambiguities concerning the assignment of the other modes which occur in the same spectral region. The f.g.a. for the modes expected between 275 and 1 200 cm^{-1} yields a total of 11 A_g + 11 E_g + 33 F_g Raman-active first-order phonon modes in the crystal. Good agreement between the expected and observed numbers of bands is found for $CsRh(SO_4)_2 \cdot 12H_2O$ (7 A_g + 11 E_g + 20 F_g) and $CsRh(SeO_4)_2 \cdot 12H_2O$ (7 A_g + 11 E_g + 22 F_g), but as a consequence of the poorer quality of spectra obtained for $CsRh(SO_4)_2 \cdot 12D_2O$ only 5 A_g + 9 E_g + 16 F_g bands are found. The assignment of these bands to first-order phonon modes is confirmed by their behaviour on selenate-for-sulphate substitution, isomorphous replacement of the metal, and deuteriation studies.

The analysis of the mid-wavenumber spectral region requires that the rotations and internal modes of $[Cs(OH_2)_6]^+$, the rotations of $[Rh(OH_2)_6]^{3+}$, and the translations and rotations of SO_4^{2-} occur between 0 and 275 cm^{-1}. For these modes a total of 6 A_g + 6 E_g + 18 F_g phonon modes are predicted by the f.g.a. Consistent with this, 3 A_g + 6 E_g + 14 F_g bands are observed for $CsRh(SO_4)_2 \cdot 12H_2O$, 4 A_g + 6 E_g + 12 F_g for

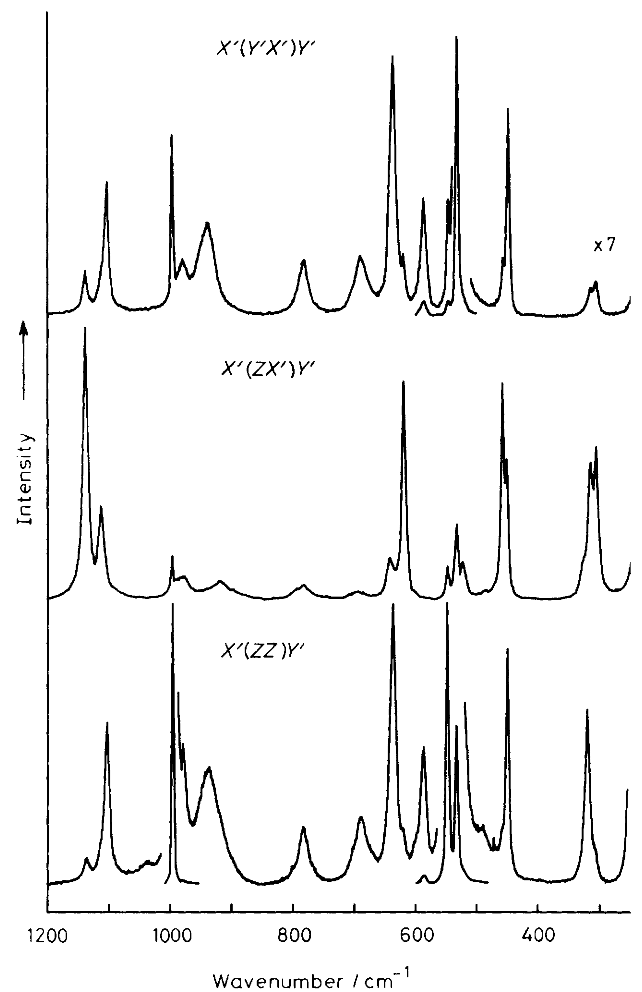

Figure 1. Single-crystal Raman spectra of $CsRh(SO_4)_2 \cdot 12H_2O$, between 275 and 1 200 cm^{-1} (85 K, spectral bandwidth 1.7 cm^{-1} at 600 cm^{-1}, step size 0.4 cm^{-1}, 70 mW, 514.53-nm radiation at the sample, count time 4 s)

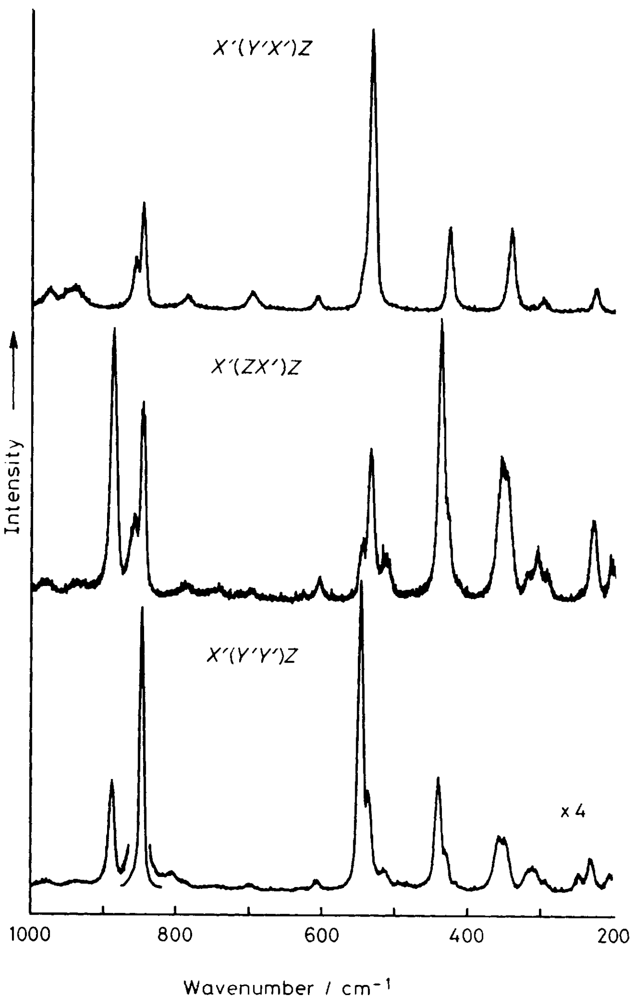

Figure 2. Single-crystal Raman spectra of $CsRh(SeO_4)_2 \cdot 12H_2O$, between 275 and 1 000 cm^{-1}; details as in Figure 1

$CsRh(SeO_4)_2 \cdot 12H_2O$ and $4A_g + 6E_g + 9F_g$ for $CsRh(SO_4)_2 \cdot 12D_2O$. For the caesium β-alums similarly good agreement with the f.g.a. predictions is observed both in mid- and low-wavenumber regions of the spectrum.[10,11] These observations are consistent with our partitioning of the spectrum into the mid- and low-wavenumber regions. Indeed, the good overall agreement between the spectra and the f.g.a. predictions enables the effective use of the f.g.a. of the individual modes as an aid to assignment.

(*ii*) *The Internal Modes of the Rhodium*(III) *Hexa-aqua Cation.*—The spectra between 275 and 1 200 cm^{-1} of $CsRh(SO_4)_2 \cdot 12H_2O$ are dominated by intense bands of A_g (995 and 548 cm^{-1}) and E_g (533 cm^{-1}) symmetry (Figure 1). For $CsRh(SeO_4)_2 \cdot 12H_2O$ correspondingly intense bands of A_g and E_g symmetry are readily identified (Figure 2). For $CsRh(SO_4)_2 \cdot 12D_2O$ an intense band of A_g symmetry is found at 525 cm^{-1}; however, no similar strong band of E_g symmetry is found (Figure 3). The assignment of the band at 548 cm^{-1} (A_g) to the $\nu_1(RhO_6)$ mode is indicated by its insensitivity to selenate-for-sulphate substitution and the shift on deuteriation (ν_D/ν_H expected $= \sqrt{18}/\sqrt{20} = 0.949$; found $= 0.955 \pm 0.008$). The f.g.a. indicates that a band of F_g symmetry is expected to accompany the A_g component. While bands of F_g symmetry are found close to 549 cm^{-1}, none of these is strong compared with the bands of F_g symmetry which are expected in the spectral region from an external mode of co-ordinated water. Since no corresponding band of F_g symmetry is found in the deuteriate, it is not reasonable to assign any of the F_g bands to the $\nu_1(RhO_6)$ mode. The F_g bands close to 548 cm^{-1} are adequately accounted for by leakage of the strong A_g band into the F_g spectrum to give the weak band at 549 cm^{-1}, and the assignment of the bands at 534 and 523 cm^{-1} to the F_g components of the $\nu_2(RhO_6)$ mode (see following discussion) and to an external mode of co-ordinated water respectively. The observation of a strong A_g component in the apparent absence of the expected F_g component is not unusual and is also found for the totally symmetric stretching modes of SO_4^{2-} and SeO_4^{2-} in this and other caesium alums,[10,11] as well as of the corresponding mode of the $[Fe(OH_2)_6]^{3+}$ ion in its caesium alums.[11]

The band arising from the $\nu_1(RhO_6)$ mode is remarkably intense, with an integrated intensity even greater than the band resulting from the $\nu_1(SO_4^{2-})$ mode. Indeed if the $\nu_1(SO_4^{2-})$ mode is used as an internal intensity standard the band arising from the $\nu_1(RhO_6)$ mode is more intense than the corresponding band in any of the caesium β-alums yet studied[10,11] (M^{III} = Al, Ga, In, Ti, V, Cr, or Fe). The extent of mixing of the $\nu_1(RhO_6)$ mode with other modes of similar energies can be estimated from the intensities of close-lying bands of A_g symmetry. Since no other bands with appreciable intensity are found close to the strong A_g component we conclude that the band at 548 cm^{-1} arises from a normal mode dominated by the

Table 2. Vibrational frequencies and assignments for $CsRh(SeO_4)_2 \cdot 12H_2O$ between 275 and 1 000 cm^{-1}

ν/cm^{-1}		$X'(Y'Y')Z$	$X'(ZX')Z$	$X'(Y'X')Z$	Assignment
294	F_g	17	16		$\nu_5(RhO_6)$
301	E_g			13	
307	F_g		31		
312	A_g	41			
319	F_g	sh	18		
345	E_g			75	$\nu_2(SeO_4^{2-})$
350	F_g	82	73		
357	F_g	87	80		
417	$F_g + A_g$(?)	14	sh		$\nu_4(SeO_4^{2-})$
429	E_g			76	
432	F_g	67	52	20	
440	F_g	178	157		
494	A_g	14			ρ_6
515	$F_g + E_g$(?)	34	25	sh	
536	E_g	158		243	$\nu_2(RhO_6)$
537	F_g		85		
548	A_g	489	34	43	$\nu_1(RhO_6)$
606	F_g	16	12		ρ_5
609	E_g			14	
626	F_g	4	4		
698	E_g			17	ρ_4
699	F_g	9	6		
715	F_g	sh	4		
742	F_g	7	7		
750	F_g	sh	6		ρ_3
788	$E_g + F_g$	14	9	13	
805	A_g	28			
847	A_g	1 780	110	92	$\nu_1(SeO_4^{2-})$
856	E_g	sh		45	$\nu_3(SeO_4^{2-})$
858	F_g	sh	45		
888	F_g	168	150	14	
934	F_g	sh	11		ρ_2
937	A_g	16	sh		
942	E_g			21	
976	E_g			18	ρ_1
978	F_g	10	11		
986	F_g	11	11		

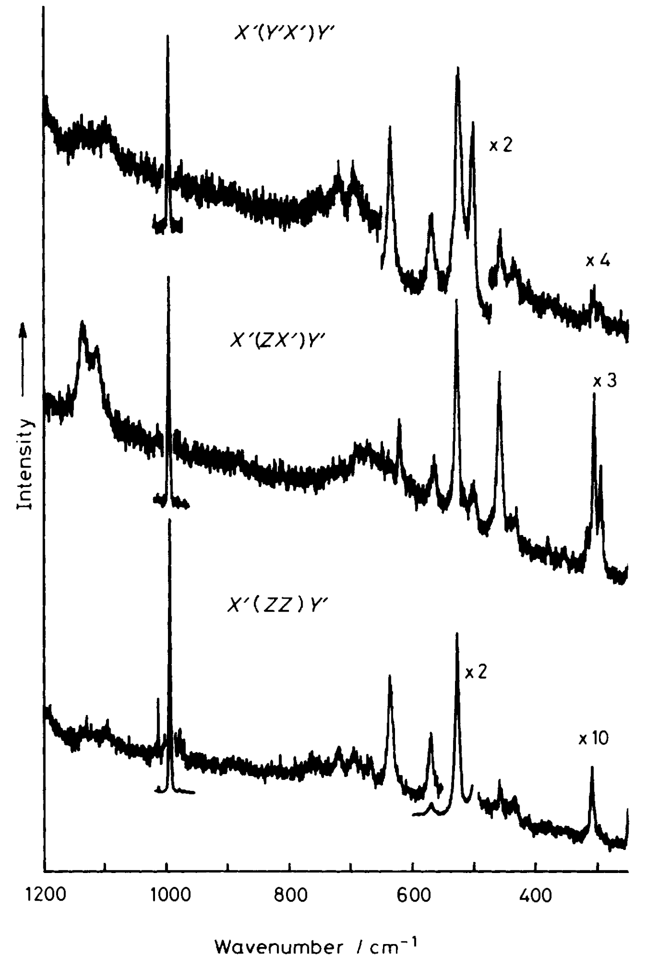

Figure 3. Single-crystal Raman spectra of $CsRh(SO_4)_2 \cdot 12D_2O$, between 275 and 1 200 cm^{-1} (40 K, spectral bandwidth 2.2 cm^{-1} at 600 cm^{-1}, step size 0.5 cm^{-1}, 70 mW, 487.98-nm radiation at the sample, count time 2 s)

$\nu_1(RhO_6)$ local mode. This interpretation is supported by the excellent agreement between the observed and calculated shifts on deuteriation.

The assignment of the $\nu_1(RhO_6)$ mode places an upper limit of 548 cm^{-1} on the wavenumber of the $\nu_2(RhO_6)$ mode. The f.g.a. indicates that one band of E_g symmetry and two of F_g symmetry are expected. The intense bands of E_g symmetry found at 533 cm^{-1} in the spectrum of $CsRh(SO_4)_2 \cdot 12H_2O$ and 536 cm^{-1} for $CsRh(SeO_4)_2 \cdot 12H_2O$ are assigned to the $\nu_2(RhO_6)$ mode based on (*a*) the insensitivity of the intensity [compared with the $\nu_1(RhO_6)$ mode] and wavenumber of the band to selenate-for-sulphate substitution, (*b*) the observation of a band of medium intensity at 502 cm^{-1} for $CsRh(SO_4)_2 \cdot 12D_2O$, *i.e.* with $\nu_D/\nu_H = 0.942 \pm 0.008$ in close agreement with that required for the $\nu_2(RhO_6)$ mode (0.949), and (*c*) the ready elimination of the only alternative assignment, *i.e.* to an external mode of co-ordinated water, by the absence of any bands with the required ν_D/ν_H of 0.723 (385 cm^{-1}) in the deuteriate. The identification of the two F_g components of the $\nu_2(RhO_6)$ mode is complicated by the presence of a close-lying mode of co-ordinated water. Unlike the E_g component of the $\nu_2(RhO_6)$ mode, which is *ca.* 50 times more intense than any of the close-lying bands of the same symmetry and is therefore not strongly coupled, the F_g bands near 534 cm^{-1} are of comparable intensity. Therefore the likelihood of significant coupling between the F_g components of these modes cannot be ruled out. The spectra of $CsRh(SO_4)_2 \cdot 12D_2O$ are of insufficient quality to resolve this problem. Based on its position, the sharp band at 534 cm^{-1} is tentatively assigned to the $\nu_2(RhO_6)$ mode. A similar interpretation is applied to the spectra of $CsRh(SeO_4)_2 \cdot 12H_2O$.

We turn our attention to the deuteriate where the intensity of the E_g component of the $\nu_2(RhO_6)$ mode is about 5 times weaker, relative to the A_g component of the $\nu_1(RhO_6)$ mode, than in the hydrate. Even in the absence of complications caused by coupling with other modes, the absolute intensities of the set of internal modes of a hexa-aqua cation may change by as much as 50% on deuteriation[11] [*cf.* $CsFe(SO_4)_2 \cdot 12H_2O$]. However, the relative intensities of the internal modes are expected to be largely unaltered by deuteriation. Therefore the weakness of the E_g band resulting from the $\nu_2(RhO_6)$ mode in $CsRh(SO_4)_2 \cdot 12D_2O$ relative to the bands arising from the other internal modes of $[Rh(OD_2)_6]^{3+}$ is indicative of coupling involving the $\nu_2(RhO_6)$ mode in the deuteriate. This interpretation is supported by the observation of a greater than expected shift of the $\nu_2(RhO_6)$ mode on deuteriation and by the similarities of the relative intensities of the internal modes of $[Rh(OH_2)_6]^{3+}$ in the sulphate and selenate alums. In the spectra of $CsRh(SO_4)_2 \cdot 12H_2O$ a band of E_g symmetry is found at 690 cm^{-1} and is assigned to an external mode of co-ordinated water. A corresponding band is expected at 500 cm^{-1} for the deuteriate, close to that expected for the $\nu_2(RhO_6)$ mode (506 cm^{-1}). The spectra are interpreted by the presence of coupling between the E_g component of the $\nu_2(RhO_6)$ mode and that of an external mode of co-ordinated water, which gives rise to the

Table 3. Vibrational frequencies and assignments for $CsRh(SO_4)_2\cdot12D_2O$ between 275 and 1 200 cm^{-1}

ν/cm^{-1}		$X'(ZZ)Y'$	$X'(ZX')Y'$	$X'(Y'X')Y'$	Assignment
294	$F_g + E_g$	3	22	4	$\nu_5(RhO_6)$
305	F_g		31		
306	A_g	25		4	
315	F_g		6		
432	$E_g + F_g$	5	5	5	ρ_5
450	F_g		sh		$\nu_2(SO_4^{2-})$
457	E_g	7		7	
459	F_g		27		
502	$E_g + F_g$	40	7	35	$\nu_2(RhO_6) + \rho_4$
525	A_g	263	23	43	$\nu_1(RhO_6)$
564	F_g		6		ρ_3
568	E_g			14	
575	F_g		3		
618	F_g		8		
634	E_g	32		25	$\nu_4(SO_4^{2-})$
649	F_g		3		
688	F_g		4		ρ_2
695	E_g	4		5	
719	$E_g + A_g$(?)	5		4	ρ_1
723	F_g		4		
976	A_g	12			$\nu_1(S^{16}O_3{}^{18}O^{2-})$
994	A_g	790	78	87	$\nu_1(SO_4^{2-})$
1 095	$E_g + F_g$(?)	3	3	5	$\nu_3(SO_4^{2-})$
1 114	F_g	1	14	3	
1 134	F_g	2	17	3	

observed bands at 502 and *ca.* 520 cm^{-1} (both E_g). The wavenumber and relative intensity of the band at 520 cm^{-1} are difficult to determine as a result of the leakage of an intense A_g band (526 cm^{-1}) into the E_g spectrum.

The assignment of the remaining Raman-active internal mode of the $[Rh(OH_2)_6]^{3+}$ cation, the $\nu_5(RhO_6)$ mode, is straightforward. The f.g.a. predicts a total of 1 A_g + 1 E_g + 3 F_g bands. In the spectra of $CsRh(SO_4)_2\cdot12H_2O$ a cluster of bands is found at 319 (A_g), 309 (E_g), and 307, 316, and 325 cm^{-1} (F_g). Each of these bands can be readily identified in the spectrum of the deuteriate, 306 (A_g), 294 (E_g), and 294, 305, and 315 cm^{-1} (F_g), with a shift of 0.96 ± 0.01, in good agreement with the expected ratio of 0.949. The band profiles in the hydrate and deuteriate are very similar and this reflects the absence of coupling between the $\nu_5(RhO_6)$ mode and other modes in either $CsRh(SO_4)_2\cdot12H_2O$ or its deuteriated analogue. In $CsRh(SeO_4)_2\cdot12H_2O$ the $\nu_5(RhO_6)$ mode is similarly well separated from close-lying modes and occurs with a profile band similar to that of the corresponding modes in the sulphate analogues, although shifted by *ca.* 3–4 cm^{-1} to lower wavenumber.

The band profile for the $\nu_5(RhO_6)$ mode in the caesium rhodium sulphate alum is markedly different from the corresponding $\nu_5(MO_6)$ band profiles of the caesium sulphate β-alums which among themselves are quite similar.[10,11] This difference may result from the different alum type which is in turn related to the different stereochemistry of water co-ordination to M^{III}. The similarity of the band profiles of the $\nu_5(RhO_6)$ modes in the caesium sulphate and selenate alums, which are both of the α-alum type, contrasts with the changes of the corresponding bands in the caesium sulphate alums of aluminium, iron, and chromium when sulphate is substituted by selenate.[10,11] Further, the spectra of $CsRh[S(Se)O_4]_2\cdot12H_2O$ reveal that the factor group and site splitting of the $\nu_5(RhO_6)$ mode in $CsRh(SeO_4)_2\cdot12H_2O$ closely follows that found in the caesium selenate α-alums of aluminium, iron, and chromium. For the caesium selenate alums the plane of the water molecule co-ordinated to M^{III} is tilted, with recent neutron-diffraction results[7] on the $CsFe(SeO_4)_2\cdot12H_2O$ giving an angle of 18.6° between the Fe–O bond vector and the plane of the co-ordinated water molecule.

(*iii*) *The Internal Modes of Sulphate and Selenate.*—The internal modes of sulphate in the caesium rhodium sulphate alums are assigned by analogy to the published spectra of alkaline-earth-metal sulphates[15] and of caesium sulphate alums.[10,11] Differences in alum type have already been demonstrated to perturb the observed spectra. The $\nu_1(SO_4^{2-})$ mode in $CsRh(SO_4)_2\cdot12H(D)_2O$ occurs at 995 cm^{-1}, well outside the range found for caesium sulphate β-alums (987 ± 1 cm^{-1}). The $\nu_3(SO_4^{2-})$ mode, which is well separated from other bands in the spectrum, also exhibits a band profile markedly different from that observed for any of the caesium sulphate β-alums. The ν_2 and $\nu_4(SO_4^{2-})$ modes both occur in the spectral region characteristic of their local modes, but with distinctly different profiles compared with the caesium β-alums. In neither of these cases does the presence of coupling with other modes appear to be sufficiently strong so as to perturb significantly the resulting band profiles.

For the caesium rhodium selenate alum the internal selenate modes occur close in wavenumber to and with similar band profiles to those observed for the caesium selenate alums of aluminium,[10] chromium,[11] and iron.[11] The close agreement between the wavenumber and band profiles of the internal modes of selenate in all of the caesium selenate alums is consistent with there being a common structure for all of the caesium selenate alums.

Since the internal modes of selenate in $CsRh(SeO_4)_2\cdot12H_2O$ exhibit the usual characteristics observed in the caesium selenate alums, then the rhodium hexa-aqua cation does not have an unusual interaction with the anion. Thus perturbations to the internal modes of sulphate in $CsRh(SO_4)_2\cdot12H_2O$ are likely to be a result of the alum type. Comparison of the spectra of the caesium rhodium sulphate and selenate alums is consistent with this interpretation. The $\nu_3(SO_4^{2-})$ mode has a band profile similar to that of the $\nu_3(SeO_4^{2-})$ mode. In both cases the E_g component is strong and occurs at a lower wavenumber than that of the predominant F_g component. The separation of the E_g and F_g components is 34 cm^{-1} for the sulphate and 31 cm^{-1} for the selenate. The band profiles result from site splitting and factor group coupling of the individual modes. The similarity of the band profiles indicates that the site splitting and factor group coupling of the anions in the caesium rhodium sulphate and selenate alums is similar and is characteristic of the α-alum type. Close inspection of the ν_2 and ν_4 modes of sulphate and selenate reveals corresondingly consistent behaviour. These results reveal the remarkably regular form of the vibrational spectra of the caesium alum lattice types. Therefore comparison among the caesium sulphate α-alums and the caesium selenate alums provides a means of distinguishing the spectral changes which result from the change of alum type.

(*iv*) *The External Modes of Co-ordinated Water.*—The external modes of co-ordinated water, the rocks, wags, and twists, occur for both the mono- and ter-valent hexa-aqua cations. The relative ordering of these modes depends on the nature of the water co-ordination and the strength and directional nature of the hydrogen bonding. Since there is insufficient information to allow the unambiguous assignment of the observed bands to particular vibrational modes we adopt the previously established practice[10] of labelling the external modes of co-ordinated water ρ_1—ρ_6 in order of decreasing wavenumber.

Because each of the external modes of co-ordinated water has one component of E_g symmetry and there are six bands of E_g symmetry yet to be accounted for in the spectrum of $CsRh(SO_4)_2\cdot12H_2O$, the assignment is simply one to one. The

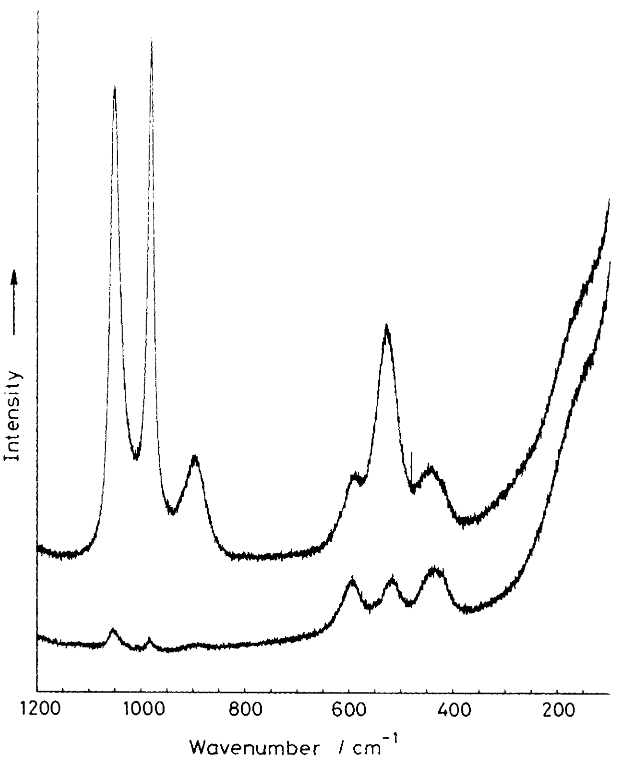

Figure 4. Polarised spectra of a saturated solution of $CsRh(SO_4)_2·12H_2O$ in sulphuric acid (1 mol dm^{-3}, spinning solution, 300 mW, 514.53-nm radiation at the sample, spectral bandpass 2.3 cm^{-1} at 600 cm^{-1}, step size 0.4 cm^{-1})

A_g and F_g components found near the respective E_g components are assigned accordingly. Owing to the density of states of F_g symmetry the likelihood of coupling between the F_g components of the external modes of co-ordinated water and other modes is correspondingly higher. The assignments which result are in agreement with the spectra of the deuteriate. Instances of coupling between the external modes of co-ordinated water and other modes have already been discussed in the text. The assignment of the external modes of co-ordinated water in $CsRh(SeO_4)_2·12H_2O$ is similarly straightforward, although the E_g component of the ρ_6 mode is obscured by the intense E_g band of the $\nu_2(SeO_4{}^{2-})$ mode. While we note that the external modes of co-ordinated water occur at unusually high wavenumber, a detailed discussion of these modes is deferred until we present spectra of a wider range of caesium sulphate α-alums.

(*v*) *Solution Raman Spectra of* $[Rh(OH_2)_6]^{3+}$.—Polarised solution Raman spectra of saturated solutions of $CsRh(SO_4)_2·12H_2O$ in sulphuric acid (1 mol dm^{-3}) are given in Figure 4. The spectra are dominated by broad polarised bands at 1 050, 980, and 529 cm^{-1}, and depolarised bands at 600, 520, and 440 cm^{-1}. All but the bands of 529p and 520 cm^{-1} can be readily assigned to the internal modes of sulphate (451, 613, 981p, and 1 104 cm^{-1}) or hydrogen sulphate (417, 593, 885p, 1 050p, 1 230, and 1 340 cm^{-1}).[16] The band at 529 cm^{-1} is assigned to the $\nu_1[Rh(OH_2)_6]^{3+}$ mode, and that at 520 cm^{-1} to the $\nu_2[Rh(OH_2)_6]^{3+}$ mode on the basis of their polarisation properties. As expected the solution bands are significantly broader than the corresponding bands found in low-temperature single-crystal spectra.

The $\nu_1(RhO_6)$ mode of rhodium(III) hexa-aqua cation occurs at 548 cm^{-1} in the caesium sulphate alum at 80 K, 19 cm^{-1} higher in wavenumber than the polarised band assigned to the same mode in the solution spectrum. Solution Raman spectra of the chromium(III) hexa-aqua cation yield a polarised band at 522 cm^{-1}, 18 cm^{-1} lower in wavenumber than the $\nu_1(CrO_6)$ mode in $CsCr(SO_4)_2·12H_2O$.[11] Since the wavenumber difference between the solution and low-temperature single-crystal determinations of the wavenumber of the $\nu_1(MO)_6$ mode are the same for rhodium(III) and chromium(III) it likely that the pyramidal stereochemistry of water co-ordination to rhodium(III) which occurs in the solid is retained in solution.

Conclusions

The caesium alums provide a remarkably well behaved lattice for the study of tervalent hexa-aqua cations. The lattice is able to accommodate a wide range of tervalent cations spanning metal(III)–water bond lengths from 1.887 (Al) to 2.112 Å (In) without significantly altering the site splitting and factor group coupling of the vibrations of the constituent ions. Indeed, the site splitting and factor group coupling characteristic of the caesium α-alum lattice are not significantly perturbed even by substitution of sulphate for selenate. This provides an enormous advantage in the interpretation of the vibrational spectra. Deviations from the expected relative intensities and band profiles can be interpreted in terms of an observed normal mode comprising significant contributions from at least two local modes. The alternative means of establishing the extent of mixing of the local modes is a normal co-ordinate analysis. Calculations of this sort on so large a lattice are not trivial and represent a major undertaking in themselves.

Finally we turn to the internal modes of the rhodium(III) hexa-aqua cation. The $\nu_1(RhO_6)$ mode is found 23 cm^{-1} to higher wavenumber than the $\nu_1(VO_6)$ mode in $CsV(SO_4)_2·12H_2O$, in spite of the similar size of tervalent cations. Indeed, the $\nu_1(RhO_6)$ mode occurs to higher wavenumber than any of the $\nu_1(MO_6)$ modes in the caesium sulphate β-alums. Consequently the relationship previously found between the bond length and the stretching frequency[11] does not obtain for the rhodium(III) hexa-aqua cation. An explanation for this behaviour could be related to the different mode of water co-ordination or to stronger bonding of the 4*d* orbitals of the rhodium ion. An alternative explanation, that it results from the differences in the alum type, can be ruled out by the insensitivity of the wavenumber of the $\nu_1(MO_6)$ mode to selenate-for-sulphate substitution among the caesium sulphate β-alums (since an α/β change accompanies the substitution) and by the solution spectra which show that the relative energies of the $\nu_1(CrO_6)$ and $\nu_1(RhO_6)$ modes are the same as that observed in the respective crystals.

The full assignment of the caesium sulphate α-alum lattice enables the extension of these studies to the caesium sulphate alums of cobalt and iridium. A more detailed discussion of the internal modes of the rhodium(III) hexa-aqua cation will be reported with those results.

Acknowledgements

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