Single-crystal Raman Study of Some Aquo-pentachloro-salts $[MCl_5(H_2O)]^{2-}$ (M = In or Fe)

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Raman single-crystal spectra are reported for eight hydrates and deuteriates $[MCl_5(H_2O)]^{2-}$ (M = In or Fe). Many fewer lattice modes were found than predicted, but for the anion internal modes factor-group predictions accord well with observation. A complete assignment in terms of anion C_{4v} symmetry is deduced. Deuteriation enabled identification of all skeletal modes associated with oxygen-atom motions. The most unusual feature of the assignments is that $\pi(MCl_4)$ modes come above $\delta(MCl_4)$ modes. Comparison with single-crystal assignments for $[InCl_5]^{2-}$ show that the largest change is in the A_1 $\pi(InCl_4)$ mode which is raised upon aquation of the complex.

In earlier work on the i.r. and Raman spectra of the series $[FeCl_5(H_2O)]^{2-}$ and $[InCl_5(H_2O)]^{2-}$ it was found that powder samples yielded spectra which had considerably fewer bands than predicted.[1] This was taken to mean that many closely spaced bands overlapped. It was difficult to suggest more than outline assignments based upon general appreciation of ranges in which particular vibrations occur. In this paper we report the results of several Raman single-crystal studies on compounds of this type. These results are a considerable improvement upon the powder work and allow an assignment to be made for all the internal modes of the anions.

The K^+ and NH_4^+ salts of $[FeCl_5(H_2O)]^{2-}$, and $(NH_4)_2[InCl_5(H_2O)]$ are isomorphous.[2] They have the symmetry *Pnma* (D_{2h}^{16}) with $z = 4$. Each metal atom is in approximately octahedral co-ordination; the octahedra are so arranged in the unit cell that the $M \leftarrow OH_2$ bonds are all in the *ac* plane (see Figure 1). All the compounds used in this study are believed to adopt the same structure.

EXPERIMENTAL

Crystals of the compounds $M^I_2[FeCl_5(H_2O)]$ were grown by slow evaporation of aqueous solutions of $FeCl_3,6H_2O$ and the appropriate salt, KCl, *etc.* $Cs_2[InCl_5(H_2O)]$ crystals were obtained by slow evaporation of aqueous solutions of CsCl and hydrated indium trichloride. We were unable to grow suitable crystals of the ammonium salt.

Corresponding deuteriates were obtained by evaporation of solutions of the appropriate anhydrous salts over dried silica gel. $(ND_4)_2[FeCl_5(D_2O)]$ was crystallised from a solution of NH_4Cl and $FeCl_3$ in a large excess of D_2O.

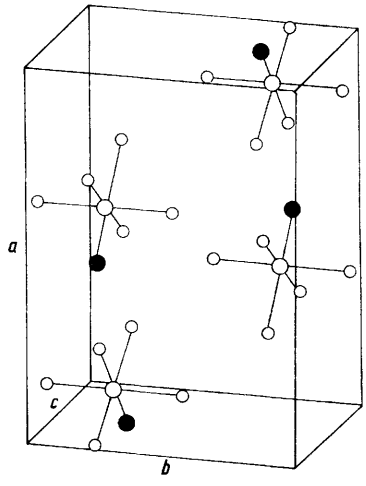


FIGURE 1 Anion positions in the unit cell of $K_2[FeCl_5(H_2O)]$

[1] D. M. Adams and P. J. Lock, *J. Chem. Soc.* (*A*), 1971, 2801.
[2] R. W. G. Wyckoff, 'Crystal Structures,' 2nd edn., vol. 3, Interscience, New York, 1965.

TABLE 1

Factor-group analysis for $K_2FeCl_5(H_2O)$ [a]

D_{2h}	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
N_T	16	11	16	11	11	16	11	16
T_A						1	1	1
T	5	4	5	4	4	4	3	4
R	1	2	1	2	2	1	2	1
N_i	10	5	10	5	5	10	5	10

Activities

	Raman					I.r.	
	xx yy zz	xy	zx	yz	z	y	x
Internal co-ordinates							
ν(Fe←OH_2)	1	0	1	0	0	1	0	1
ν(Fe–Cl)	4	1	4	1	1	4	1	4

[a] Hydrogen atoms are ignored. N_T = Total number of modes of unit cell; T_A = acoustic modes; T = translatory lattice modes; R = rotatory lattice modes; N_i = number of internal modes.

TABLE 2

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $Cs_2[InCl_5(H_2O)]$ at ambient temperature

Δ/cm^{-1}	$z(xx)y$	$x(yy)z$	$x(zz)y$	$x(zy)z$	$x(zx)z$	$x(yx)z$	D_{2h}
44						10	B_{1g}
48				11			B_{3g}
52			11				A_g
66	30	22	13				A_g
76				16			B_{3g}
90	21		4				A_g
124				7		27	B_{1g}
149		20		10			$A_g + B_{3g}$
162	185	15	55	40	7	142	$A_g + B_{1g} + B_{2g}$
174				26			B_{3g}
178						77	B_{1g}
184	26	25					A_g
190					6		B_{2g}
215		6	6				A_g
256						8	B_{1g}
271	250	106	46				A_g
280	60	98	49				A_g
310	60	167	23		6		A_g

The absence of O–H was checked by examination of the stretching region. Composition was checked by halogen analysis.

The crystals grown all had similar morphology, showing principally the faces of a distorted octahedron. The position of the axes was established from Weissenberg

TABLE 3

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $Cs_2[InCl_5(D_2O)]$ at ambient temperature

Δ/cm^{-1}	$x(yy)z$	$x(zy)z$	$y(zz)x$	$y(zy)x$	$y(xz)x$	$y(xy)x$	D_{2h}
36	14	7		15			$A_g + B_{3g}$
50	11	23	11	58			$A_g + B_{3g}$
66	14	4	36				A_g
90			16			5	A_g
126		17		35		18	$B_{1g} + B_{3g}$
148	19	32		64			$A_g + B_{3g}$
160			160		11	130	$A_g + B_{1g}$
168	19	100		193			B_{3g}
174						56	B_{1g}
186	24						A_g
191					8		B_{2g}
213			11				A_g
270	64		110	9		11	A_g
282	10		113	12			A_g
300	176		211	10		9	A_g

X-ray diffraction photographs of a small crystal of $(NH_4)_2[FeCl_5(H_2O)]$. In addition to octahedral faces the crystals exhibited (100) faces which were set normal to the propagation of the light in many experiments. For other runs faces were ground and polished normal to the *b* and *c* axes.

Raman spectra were obtained with a Coderg PH1 spectrometer with 632·8 nm excitation (*ca.* 35 mW at the sample). Cooling the crystals to *ca.* 120 K revealed no feature not present at room temperature.

RESULTS AND ASSIGNMENT

The results from the eight single crystals used are in Tables 2—9. They show a high degree of consistency. Taken together (Table 10) it is seen that some spectra show more bands than others owing to individual variations

TABLE 4

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $K_2[FeCl_5(H_2O)]$ at ambient temperature

Δ/cm^{-1}	$z(xx)y$	$z(xy)y$	$x(yy)z$	$x(zy)z$	$x(zx)y$	$x(yx)y$	$x(zz)y$	$x(yz)y$	D_{2h}
38		6				4	32		A_g
47	240	14			39	9	25		$A_g + B_{2g}$
70							50	6	A_g
77	43				16	39			$B_{1g} + B_{2g}$
85	18						16	6	A_g
89					58				B_{3g}
124	32						19		A_g
129		76				69			B_{1g}
132				43	6			44	B_{3g}
174				66				66	B_{3g}
177		130				114			B_{1g}
180				48					B_{3g}
183	168						75		A_g
190	139						89		A_g
222		67		48		56		48	$B_{1g} + B_{3g}$
226	52		38		23		89		$A_g + B_{2g}$
276		5	6			6	4		$A_g + B_{1g}$
300	252	74	250	14	14	59	240	23	A_g
384	52	7	51			6	35	2	A_g

TABLE 5

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $K_2[FeCl_5(D_2O)]$ at ambient temperature

Δ/cm^{-1}	$x(yy)z$	$x(zy)z$	$x(zx)z$	$x(yx)z$	$x(zz)y$	$x(yz)y$	D_{2h}
48			18				B_{2g}
73					38		A_g
78				22			B_{1g}
86					4		A_g
90			27				B_{2g}
124					15		A_g
129				39			B_{1g}
133		17				25	B_{3g}
179	5	29				46	B_{3g}
190			9		82		A_g
215		20		31		33	$B_{1g} + B_{3g}$
225	18		10		57		$A_g + B_{2g}$
300	173	9	20	20	210	34	A_g
371	31		4		28	5	A

TABLE 6

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $Rb_2[FeCl_5(H_2O)]$ at ambient temperature

Δ/cm^{-1}	$x(yy)z$	$x(zy)z$	$x(zx)z$	$x(yx)z$	$x(zz)y$	$x(yz)y$	D_{2h}
41			10				B_{2g}
65			9		42		$A_g + B_{2g}$
73			12		5		B_{2g}
94				23		6	B_{1g}
133				28	9		B_{1g}
136		13				21	B_{3g}
180	6	28		64	5	44	$B_{1g} + B_{3g}$
189			11		76		A_g
210		15		28		24	$B_{1g} + B_{3g}$
218	12		5		36		$A_g + B_{2g}$
272	7			4			$A_g + B_{1g}$
296	183	8	22	22	185	20	A_g
350	26		3		24		A_g

Since these are all chloro-complexes we can be quite sure (from comparison with simpler species) that none of the internal modes will lie below 100 cm^{-1}. We can be equally confident that for the K^+, Rb^+, and Cs^+ salts at least, none of the lattice modes will be much above 100 cm^{-1}. The spectra confirm this belief, showing a clear gap of 34 cm^{-1}

TABLE 7

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $(NH_4)_2[FeCl_5(H_2O)]$ at ambient temperature

Δ/cm^{-1}	$x(yy)z$	$x(zy)z$	$x(zx)z$	$x(yx)z$	$x(zz)y$	$x(yz)y$	D_{2h}
34	7				30		A_g
46			14				B_{2g}
50					16		A_g
71			6		42		A_g
82		5		30			B_{1g}
112	6						A_g
118		13	5		23	5	$A_g + B_{2g} + B_{3g}$
128				38			B_{1g}
138			10				B_{2g}
184		30				17	B_{3g}
187				44			B_{1g}
194					52		A_g
210		31		53		19	$B_{1g} + B_{3g}$
218	12				27		A_g
296	181		9	3	178	5	A_g
353	27				27		A_g

or more in the expected region. For the ammonium salts lattice modes will most probably rise above 100 cm^{-1}, and there is the additional complication that cation rotatory modes are allowed, although we have found no evidence of them.

For a single anion $[MCl_5(H_2O)]^{2-}$ of C_{4v} symmetry 11 internal modes are predicted; all are Raman-active.

TABLE 8

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $(ND_4)_2[FeCl_5(D_2O)]$ at ambient temperature

Δ/cm^{-1}	$z(xx)y$	$z(yx)y$	$z(yy)x$	$z(yx)x$	$x(zz)y$	$x(yz)y$	$x(zx)y$	$x(yx)y$	D_{2h}
34	6								A_g
46								18	B_{2g}
50	200	3		4					A_g
70					31		21		$A_g + B_{2g}$
81		12		10				22	B_{1g}
113			4						A_g
119	7						24		$A_g + B_{2g}$
126		18		21		10		32	B_{1g}
146						10			B_{3g}
184		28		24		35	45	71	$B_{1g} + B_{2g} + B_{3g}$
194	82				60		47		$A_g + B_{2g}$
200		30		27		42		72	$B_{1g} + B_{3g}$
210			12		25				A_g
269				3				4	B_{1g}
297	171	7	181	9	164	30	88	74	A_g
340	20		30		27	6	15	16	A_g

of intensity, but the pattern of behaviour is clear from the whole set. The spectra apparently show one third to one half the number of bands predicted by factor-group analysis [3] (Table 1).

[3] D. M. Adams and D. C. Newton, ' Tables for Factor Group and Point Group Analysis,' Beckman-RIIC Limited, Croydon, 1970; D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1970, 2282.

Their approximate forms are listed in Table 11, and correlated to factor-group symmetry species *via* the site group.

Factor-group analysis shows that each A_g mode should be accompanied by a B_{2g} mode and, similarly, that B_{1g} and B_{3g} modes should be equal in number. Two significant facts are immediately apparent: (i) There is a substantial deficit of lattice modes. The greatest number found is for $K_2[FeCl_5(H_2O)]$ which shows only 7 of the predicted 24!

However, this is the least interesting spectral region for our purpose as we are most concerned with the anion internal modes. The generally higher lattice modes found

TABLE 9

Observed Raman frequencies (cm^{-1}) and peak heights (arbitrary units) for crystals of $Cs_2[FeCl_5(H_2O)]$ at ambient temperature

$\Delta\nu$/ cm^{-1}	$x(yy)z$	$x(zy)z$	$x(zx)z$	$x(yx)z$	$x(zz)y$	$x(yz)y$	D_{2h}
37	6		6	75		4	B_{1g}
46			11				B_{2g}
53	14						A_g
57		8		15		8	$B_{1g} + B_{3g}$
63			9				B_{2g}
87				15			B_{1g}
115		4	24				B_{2g}
127	7			81		4	B_{1g}
167	53	11	92		49	4	$A_g + B_{2g}$
177				43	8		B_{1g}
224				8	12		$A_g + B_{1g}$
250			10				B_{2g}
278				8			B_{1g}
312	167	25	22	21	172	14	A_g

for the NH_4^+ and ND_4^+ salts strongly suggest that these modes are associated with translations of the cations.

(ii) A count of internal modes under D_{2h} symmetry (taking only K^+, Rb^+, and Cs^+ salts to avoid the complication of NH_4^+ modes) (Table 12) shows that whilst B_{1g} and B_{3g} modes occur in roughly equal numbers, there is a pronounced shortage of B_{2g} modes. This is so marked as to point to a general mechanism responsible for the vanishingly low intensities of these modes. Figure 2 shows how a set of four vectors along the C_{4v} principal

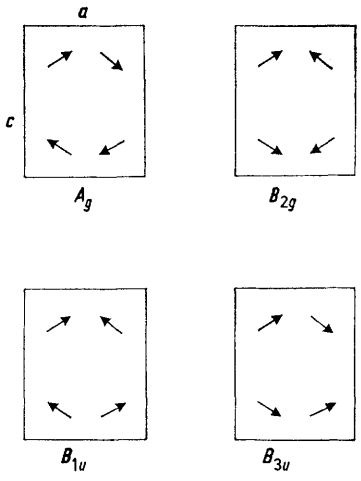


FIGURE 2 Coupling of four oriented vectors in the D_{2h}^{16} unit cell

axes of the anions couple (projected onto the crystallographic *ac* plane). It is seen that the motions associated with the

TABLE 10

Raman frequencies and principal symmetry species for the compounds $M^I_2M^{III}Cl_5(H_2O)$

Cs_2InCl_5-(H_2O)	Cs_2InCl_5-(D_2O)	K_2FeCl_5-(H_2O)	K_2FeCl_5-(D_2O)	Rb_2FeCl_5-(H_2O)	$(NH_4)_2FeCl_5$-(H_2O)	$(ND_4)_2FeCl_5$-(D_2O)	Cs_2FeCl_5-(H_2O)
	36 A_g* + B_{3g}	38 A_g			34 A_g	34 A_g	
44 B_{1g}							37 B_{1g}
		47 $A_g + B_{2g}$	48 B_{2g}	41 B_{2g}	46 B_{2g}	46 B_{2g}	46 B_{2g}
48 B_{3g}	50 A_g* + B_{3g}						53 A_g*
52 A_g					50 A_g	50 A_g	
66 A_g*	66 A_g*						57 $B_{1g} + B_{3g}$
		70 A_g	73 A_g	65 A_g	71 $A_g + B_{2g}$	70 $A_g + B_{2g}$	63 B_{2g}
76 B_{3g}							
		77 B_{1g}	78 B_{1g}		82 B_{1g}	81 B_{1g}	87 B_{1g}
		85 A_g	86 A_g		112 A_g*	113 A_g*	
90 A_g	90 A_g	89 B_{2g}	90 B_{2g}	73 B_{2g}	118 $A_g + B_{2g}$	119 $A_g + B_{2g}$	115 B_{2g}
				94 B_{1g}			
124 $B_{1g} + B_{3g}$	126 $B_{1g} + B_{3g}$	124 A_g	124 A_g				
		129 B_{1g}	129 B_{1g}	133 B_{1g}	128 B_{1g}	126 B_{1g}	127 B_{1g}
		132 B_{3g}	133 B_{3g}	136 B_{3g}	138 B_{2g}		
149 A_g* + B_{3g}	148 A_g* + B_{3g}	174 B_{3g}				146 B_{3g}	
		177 B_{1g}					
162 $A_g + B_{1g}$ + B_{3g}	160 $A_g + B_{1g}$	180 B_{3g}	179 B_{3g}	180 $B_{1g} + B_{3g}$	184 B_{3g}	184 $B_{1g} + B_{3g}$	177 B_{1g}
		183 A_g			187 B_{1g}		
174 B_{3g}	168 B_{3g}						
178 B_{1g}	174 B_{1g}	222 $B_{1g} + B_{3g}$	215 $B_{1g} + B_{3g}$	210 $B_{1g} + B_{3g}$	210 $B_{1g} + B_{3g}$	200 $B_{1g} + B_{3g}$	224 $A_g + B_{1g}$
184 A_g*	186 A_g*	190 A_g	190 A_g	189 A_g	194 A_g	194 $A_g + B_{2g}$	167 A_g* + B_{2g}
190 B_{2g}	191 B_{2g}						
215 A_g*	213 A_g	226 A_g* + B_{2g}	225 A_g* + B_{2g}	218 A_g* + B_{2g}	218 A_g*	210 A_g*	
256 B_{1g}		276 A_g* + B_{1g}		272 A_g* + B_{1g}		269 B_{1g}	278 B_{1g}
271 A_g*	270 A_g*						250 B_{2g}
280 A_g*	282 A_g*	300 A_g*	300 A_g*	296 A_g*	296 A*	297 A_g*	312 A_g*
310 A_g*	300 A_g*	384 A_g*	371 A_g*	350 A_g*	353 A*	340 A_g*	

Frequencies in Δ cm^{-1}. * Indicates a non-zero *yy* component.

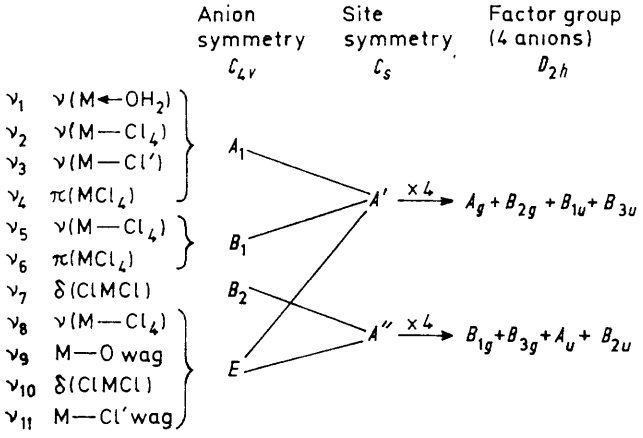
B_{2g} mode are largely self-cancelling and can be expected to be associated with very small changes in polarisability.

Taking $K_2[FeCl_5(H_2O)]$ as typical of the series we consider its spectrum in detail.

B_2 and E *Modes.*—Seven of the predicted 10 A_g/B_{2g}

modes and 4 of the expected 5 B_{1g}/B_{3g} modes are found. Closer examination shows that each B_{1g} is accompanied by a B_{3g} band which is either close to or coincident with it, except for the 180 (B_{3g}) and 276 cm^{-1} (B_{1g}) bands. However,

TABLE 11



comparison with others of the series shows that the equivalent of the 180 cm^{-1} band does often show a B_{3g} component. We are forced to conclude that the 276 cm^{-1} B_{3g} component is vanishingly weak.

Since $B_{1g} + B_{3g}$ pairs can only derive from B_2 and E modes in C_{4v} we have identified exactly the five required. In principle the single B_2 mode [δ(ClMCl) in the ($FeCl_4$) plane, and hence expected below 190 cm^{-1}] can be detected because, unlike the E modes, it should not have A_g and B_{2g} components. Thus far we have concluded that in terms of anion symmetry the five $B_2 + E$ modes are at 276 (E), 222 (E), 180 (E or B_2), 177/174 (E or B_2) and 132/129 cm^{-1} (E or B_2). Being the highest of the E modes the 276 cm^{-1} band is ν_8, ν(Fe–Cl). It is equivalent to an E_u mode in a D_{4h} square-planar species (*i.e.*, Raman-*in*active) and is only allowed in the present complexes by virtue of the relatively small distortion from D_{4h}. It was found to be extremely weak throughout the aquohalogeno-series and vanishingly weak in three of them.

TABLE 12

Band count (internal modes only)

	$Cs[InCl_5-(H_2O)]$	$Cs_2[InCl_5-(D_2O)]$	$K_2[FeCl_5-(H_2O)]$	$K_2[FeCl_5-(D_2O)]$	$Rb_2[FeCl_5-(H_2O)]$
A_g	7	7	7	5	5
B_{1g}	4	3	4	2	4
B_{2g}	2	1	1	1	1
B_{3g}	4	3	4	3	3

On deuteriation, the band at 384 cm^{-1} is lowered by 13 cm^{-1} and must be assigned as ν(Fe←OH_2). The only other affected band is at 222 cm^{-1}; equivalent bands are seen to shift similarly in the indium salts and in the ammonium aquopentachloroferrates. ν(Fe←OH_2), ν_1, and the M–O wag, ν_9, are of A_1 and E symmetry respectively.

The 132/129 cm^{-1} pair are accompanied by an A_g band, and the 180 cm^{-1} B_{3g} band has an A_g component at 183 cm^{-1}; both therefore originate in E species. In contrast the 177/174 cm^{-1} pair have no A_g component, as required for a B_2 mode.

A_1 and B_1 Modes.—Both A_1 and B_1 modes should give $A_g + B_{2g}$ doublets but we have only the A_g evidence in nearly all cases. In principle the relative intensities of the various derived tensor components should allow differentiation (Table 13) but in practice this has not occurred probably owing to inadequacy of the oriented gas model. Being deserted by group theory we have recourse to other arguments. We note that ν_2, ν_3, and ν_5 are all ν(Fe–Cl) modes and may reasonably be expected above 250 cm^{-1}; indeed ν_8, the E-species ν(Fe–Cl) mode, has been located at 276 cm^{-1}. Only one band, at 300 cm^{-1}, was found in this region for the iron salts; therefore either ν_2, ν_3, and ν_5 are coincident or one or more of these vibrations is vanishingly weak. One of the A_1 modes is certainly likely to be weak. However, for the indates a second band is found (*i.e.*, 280 and 271 cm^{-1}). For the latter compound we place ν_3 below ν_2 in recognition of the greater length of the unique In–Cl bond compared with the other four. The possibility remains that the 271 cm^{-1} band is the B_1 mode and that the second A mode is missing.

TABLE 13

Rotation of the polarisability tensor for $FeCl_5(H_2O)^{2-}$ by 45° about y

C_{4v} → D_{2h}

$$A_1 \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \longrightarrow \begin{bmatrix} \frac{a+b}{2} & 0 & \frac{b-a}{2} \\ 0 & a & 0 \\ \frac{b-a}{2} & 0 & \frac{a+b}{2} \end{bmatrix}$$

$$B_1 \begin{bmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{bmatrix} \longrightarrow \begin{bmatrix} \frac{1}{2}c & 0 & \frac{1}{2}c \\ 0 & -c & 0 \\ \frac{1}{2}c & 0 & \frac{1}{2}c \end{bmatrix}$$

$$B_2 \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \longrightarrow \begin{bmatrix} 0 & \sqrt{\frac{1}{2}}d & 0 \\ \sqrt{\frac{1}{2}}d & 0 & \sqrt{\frac{1}{2}}d \\ 0 & \frac{1}{2}\sqrt{d} & 0 \end{bmatrix}$$

$$E \begin{cases} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{bmatrix} \longrightarrow \begin{bmatrix} 0 & \sqrt{\frac{1}{2}}e & 0 \\ \sqrt{\frac{1}{2}}e & 0 & \sqrt{\frac{1}{2}}e \\ 0 & \sqrt{\frac{1}{2}}e & 0 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{bmatrix} \longrightarrow \begin{bmatrix} -e & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & e \end{bmatrix} \end{cases}$$

It remains to locate the two $\pi(MCl_4)$ modes, $\nu_4(A_1)$ and $\nu_6(B_1)$. As only the 190 and 226 cm^{-1} bands remain they are accordingly assigned jointly to these species. However, in a recent single-crystal study of the square-pyramidal $[InCl_5]^{2-}$ the B_1 $\pi(MCl_4)$ mode was found to be above the A_1 mode.[4] We assume the same order for the aquo-complexes. The assignments are summarised in Table 10.

DISCUSSION

Although there are four formula units in the unit cells of these crystals it has still proved feasible to discuss the spectra in terms of the full factor-group predictions so far as internal modes are concerned. We are now becoming familiar in Raman spectroscopy with the situation that some species tend to be vanishingly weak although formally allowed (the B_{2g} species in this case). Making allowance for this, we have seen

[4] D. M. Adams and R. R. Smardzewski, *J. Chem. Soc.* (*A*), 1971, 714.

that the Raman results bear out factor-group predictions rather well. It remains to be seen whether the i.r. spectra fit this picture. Some molecular crystals having four molecules to the unit cell also show (even more clearly) the full factor-group splitting, although for tin tetraiodide with $z = 8$ the limit seems to have been reached.[5]

TABLE 14

Comparison of vibrational frequencies (cm^{-1}) of $[InCl_5]^{2-}$ and $[InCl_5(H_2O)]^{2-}$

		$[InCl_5]^{2-}$ [a]	$[InCl_5(H_2O)]^{2-}$
ν(In–Cl)	$\nu_2(A_1)$	294	280
	$\nu_3(A_1)$	283	271
	$\nu_5(B_1)$	287	280
	$\nu_8(E)$	274	256
$\pi(InCl_4)$	$\nu_6(B_1)$	193	215
	$\nu_4(B_1)$	140	187
$\delta(InCl_4)$	$\nu_{10}(E)$	143	162
	$\nu_7(B_2)$	165	149
δ(In–Cl)	$\nu_{11}(E)$	108	124

[a] Ref. 4.

In Table 14 we compare single-crystal assignments for $(Et_4N)_2[InCl_5]$ [4] and $Cs_2[InCl_5(H_2O)]$ as both have C_{4v} symmetry. The order of the stretching modes is similar in each case, with the E modes coming lowest, and there is a general drop in ν(In–Cl) upon aquation. The X-ray data show that the Cl′–In–Cl angles, θ, are 103·9 ($[InCl_5]^{2-}$) and 87·5° $\{[InCl_5(H_2O)]^{2-}\}$ respectively. $\nu_8(E)$ will be *lowered* by increasing θ owing to the form of the corresponding G-matrix element [6] but $\nu_5(B_1)$ is independent of θ; we note that the difference in the ν_5 modes is the least of all the ν(In–Cl) modes. Since ν_8 is *raised* upon increasing θ we conclude that the effect of decreasing the co-ordination number outweighs this effect, although it is possible that interaction with $\nu_9(E)$ has some influence upon ν_8.

Among the bending modes the B_1 out-of-plane deformation is the highest in each case, and the lowest mode remains of E symmetry (probably the unique In–Cl wag). The most notable difference is the A_1 out-of-plane bend which rises *ca.* 50 cm^{-1} upon aquation, probably owing to the relative ease with which this mode is executed in the absence of a sixth ligand.

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[5] D. M. Adams and W. S. Fernando, to be published.
[6] J. N. Murrell, *J. Chem. Soc.* (*A*), 1969, 297.