Far-infrared and Raman Spectra of Crystalline Ammonium and Alkali-metal Trichloromercurate(II) Salts and Some Related Compounds

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A complete vibrational assignment has been made for the tetragonal (α) form of the salt $NH_4[HgCl_3]$ in terms of the known apex-shared octahedral polymeric sheet structure. The assignments have been aided by study of isomorphous ND_4^+ and Rb^+ analogues. An order–disorder phase transition in the NH_4^+ and ND_4^+ salts, similar to those in ammonium halides, has been found from observation of a cation librational mode at low temperatures. Another (β) form of the salt $NH_4[HgCl_3]$ has been characterized as having a double-rutile chain structure; vibrational assignments have been made by comparison with spectra of the isomorphous salts β-$ND_4[HgCl_3]$ and $M[CdCl_3]$ (M = NH_4, ND_4, K, or Rb). The previously described ' $Na[HgCl_3]$ ' has been shown not to exist; dehydration of the compounds $NaHgCl_3.2H_2O$ or $NaHgCl_3.2D_2O$ gives a physical mixture NaCl–$HgCl_2$. Vibrational spectra of the salts $NH_4[HgBr_3]$, $K[HgCl_3]$, $K_2[HgCl_4].H_2O$, and $K_2[HgCl_4].D_2O$ have also been studied.

ALTHOUGH there have been a number of vibrational spectroscopic studies on trihalogeno-complexes of mercury(II), the relation between spectra and crystal structure is not well defined. In particular, it is noteworthy that, whereas the ammonium and alkali-metal chloro-complexes have polymeric structures based on $[HgCl_6]$ octahedra, reported vibrational data,[1-4] which are notably incomplete, have largely been interpreted in terms of molecular [1,3] or quasi-molecular [4] $HgCl_2$ units. In the present work more complete assignments, which reflect more closely the crystallographic data, are reported and some structural anomalies explained.

RESULTS AND DISCUSSION

Ammonium and Tetradeuterioammonium Trichloromercurate(II).—We have recently shown [5] that, contrary to previous reports,[4,6] but in agreement with indications from phase-diagram studies,[7] ammonium trichloromercurate(II) exists in two crystalline forms, designated α (from a 1 : 1 $NH_4Cl:HgCl_2$ melt) and β modifications (from 1 : 1 $NH_4Cl:HgCl_2$ in aqueous solution). In acetone solution, both forms give Raman spectra characteristic of discrete trigonal-planar $[HgCl_3]^-$ ions [$\nu_1(a_{1g})$ at 294s, pol. cm^{-1}], but in the solid state they have different polymeric structures.

α *Forms*. The product obtained on cooling a melt consisting of equimolar quantities of NH_4Cl and $HgCl_2$ was found from single-crystal rotation *X*-ray photographs to have unit-cell dimensions $a = b = 420$ and $c = 790$ pm, and was therefore identified as having the

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[1] H. Poulet and J.-P. Mathieu, *J. Chim. phys.*, 1963, **60**, 442.

[2] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

[3] J. T. R. Dunsmuir and A. P. Lane, *J. Inorg. Nuclear Chem.*, 1971, **33**, 4361.

[4] D. E. Scaife, *Austral. J. Chem.*, 1971, **24**, 1753.

[5] R. M. Barr and M. Goldstein, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 33.

[6] H. F. McMurdie, J. de Groot, M. Morris, and H. E. Swanson, *J. Res. Nat. Bur. Stand., Sect. A*, 1969, **73**, 621.

[7] I. N. Beljaev and K. E. Mironov, *Zhur. obshchei Khim.*, 1952, **21**, 1484.

$P4/mmm$ (D_{4h}^1, $Z = 1$) structure deduced by Harmsen[8] [*cf.* $a = b = 419$ and $c = 794$ pm;[8] $a = b = 419{\cdot}8$ and $c = 793{\cdot}5$ pm (ref. 6)].

Assignments of the i.r. spectrum have been given[3] in terms of an interpretation of the crystal structure in which linear $HgCl_2$ molecules are surrounded by free chloride ions. Of the six i.r.-active unit-cell modes two were assigned to vibrations of the $HgCl_2$ units, the others being described just as lattice modes. However, the longer Hg–Cl distances [296 pm (ref. 8)], being appreciably less than the sum of the van der Waals radii [330 pm (ref. 9)], must represent significant covalent interaction, as evidenced from n.q.r. studies.[4] Moreover, a much more informative description of the assignments is obtained if these longer distances are not neglected, *i.e.* by considering the structure to consist of infinite sheets of edge-shared $[HgCl_6]$ octahedra with (disordered) NH_4^+ ions on four-fold axes between the sheets. Taking the NH_4^+ ions as point masses, a factor-group analysis (isomorphous point group D_{4h}) gives equation (1). (The same result is of course obtained for all

$$\Gamma_{\text{cryst}} = A_{1g}(\text{Raman}) + E_g(\text{Raman}) + 3A_{2u}(\text{i.r.}) + 3E_u(\text{i.r.}) \quad (1)$$

other descriptions of the structure; only the physical descriptions placed on the modes will vary.) Symmetry modes are shown in Figure 1, and the relation between this treatment and that obtained on the basis of a structure $[HgCl_2,Cl^-,NH_4^+]$ is shown in Tables 1 and 2.

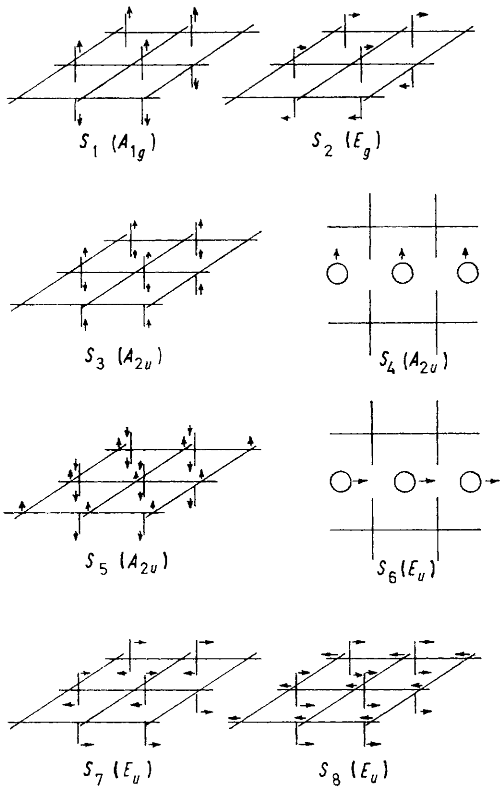

FIGURE 1 Symmetry modes of the salt α-$NH_4[HgCl_3]$. For S_4 and S_6 (only cation motion shown), views are parallel to the sheets; in the other cases the NH_4^+ ions (○) are omitted for clarity. Only one component of each degenerate mode is given

TABLE 1

Factor-group analysis[a] of the salt α-$NH_4[HgCl_3]$ for models (A) and (B)[b]

D_{4h}	n_{vib}	Model[b]	n_{rot}	n_{int}	n_{trans}
A_{1g}	1	(A)	0	1	0
		(B)	0	1	0
E_g	1	(A)	1	0	0
		(B)	0	1	0
A_{2u}	3	(A)	0	1	2
		(B)	0	2	1
E_u	3	(A)	0	1	2
		(B)	0	2	1

[a] n_{vib} = Total number of vibrational modes (other than acoustic), n_{rot} = number of rotational lattice modes, n_{int} = number of modes internal to $HgCl_2$ molecules [model (A)] or $[HgCl_3^-]_n$ sheets [model (B)], and n_{trans} = number of translational lattice modes. For both models the NH_4^+ ion is taken as a point mass. [b] Model (A), $[HgCl_2,Cl^-,NH_4^+]$; model (B), $[HgCl_3^-]_n,NH_4^+$.

TABLE 2

Description of modes of the salt α-$NH_4[HgCl_3]$ for structural models (A) and (B)[a]

Model (A)[b]	Species (D_{4h})	Model (B)	Symmetry co-ordinates
ν_{sym} ($HgCl_2$) [ν_1]	A_{1g}	ν_{sym} $(HgCl)_t$	S_1
$R_{x,y}$ ($HgCl_2$)	E_g	δ_{sym} $(HgCl)_t$	S_2
ν_{asym} ($HgCl_2$) [ν_3]	A_{2u}	ν_{asym} $(HgCl)_t$	S_3
Lattice	A_{2u}	$T_z(NH_4^+)$[d]	S_4
Lattice	A_{2u}	δ (sheet) out-of-plane	S_5
Lattice	E_u	$T_{x,y}$ (NH_4^+)[d]	S_6
δ ($HgCl_2$) [ν_2]	E_u	δ_{asym} $(HgCl)_t$	S_7
Lattice	E_u	δ (sheet) in-plane	S_8

[a] Model (A), $[HgCl_2,Cl^-,NH_4^+]$; model (B), $[HgCl_3^-]_n,NH_4^+$. [b] From ref. 3. [c] Shown in Figure 1. [d] Assuming no motion from $[HgCl_3^-]_n$ sheets.

The simple two-line Raman spectrum obtained (see figure in ref. 5) is in strict accord with prediction, and assignments of the 298 [295 cm^{-1} (ref. 1)] and 81 cm^{-1} bands to A_{1g} ν_{sym} $(HgCl)_t$ and E_g $\delta_{\text{sym}}(HgCl)_t$, respectively, are unambiguous. The E_g deformation underwent a substantial shift to 94 cm^{-1} when the same was cooled with liquid nitrogen, but (in contrast to the i.r. spectrum see below) there were no other discernible spectral changes.

At room temperature, the far-i.r. spectrum showed only four of the expected six bands, in agreement with previous[3] transmission data. On cooling the sample to *ca.* 100 K, the broad band centred at *ca.* 150 cm^{-1} clearly resolved into three components (Figure 2), so that all modes predicted by factor-group analysis became observed. However, an additional feature appeared weakly at 270 cm^{-1} and became of significant intensity (at 276 cm^{-1}) when the sample was cooled to *ca.* 30 K

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[8] E. J. Harmsen, *Z. Krist.*, 1938, **100**, 208.

[9] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell Univ. Press, Ithaca, 1960.

(Figure 2). The behaviour and position of this band are just those expected of an NH_4^+ librational mode (not predicted by the factor-group analysis as the H atoms were ignored, their positions being unknown). This assignment has been unambiguously confirmed as follows: (*a*) the band is completely absent in the spectrum of the salt Rb[$HgCl_3$] even at low temperatures (Figure 2); (*b*) in the spectrum of the deuteriate α-ND_4[$HgCl_3$] (obtained from a melt), the band shifts by 71 cm^{-1} (calc.: 80 cm^{-1}) to lower wavenumbers (Table 3); and (*c*) the incoherent neutron inelastic scattering spectrum of the salt α-NH_4[$HgCl_3$] shows a strong peak at 280 cm^{-1} at 140 K, unequivocally arising from an NH_4^+ torsional motion. The barrier restricting reorientation of the NH_4^+ ion, calculated using an equation derived by Gutowsky *et al.*,[10] was found to be 12·1 kJ mol^{-1}, which compares favourably with data on ammonium halides.[11]

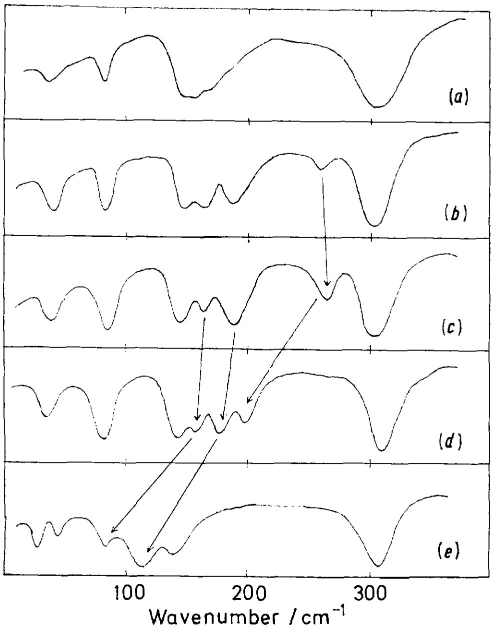

FIGURE 2 Far-i.r. spectra for the salts α-NH_4[$HgCl_3$] at 300 (*a*), 100 (*b*), and 30 K (*c*); α-ND_4[$HgCl_3$] (30 K) (*d*); and Rb[$HgCl_3$] (100 K) (*e*). Arrows indicate shifts in cation translations and NH_4^+ or ND_4^+ librations

TABLE 3

Vibrational assignments (cm^{-1}) for the salts α-NH_4[$HgCl_3$], α-ND_4[$HgCl_3$], and Rb[$HgCl_3$] in the solid state[a]

α-NH_4[$HgCl_3$] (*ca.* 30 K)	α-ND_4[$HgCl_3$] (*ca.* 30 K)	ν_D/ν_H obs.	ν_D/ν_H calc.	Rb[$HgCl_3$] (*ca.* 100 K)	Activity	Assignment[b]
309vs	309vs	1	1	320vs	I.r.	A_{2u} (S_3) $\nu_{asym}(HgCl)_t$
298s[c]	298s[c]	1	1	299s[c]	Raman	A_{1g} (S_1) $\nu_{sym}(HgCl)_t$
276m[d]	205m[d]	0·74	0·71		I.r.	NH_4^+ Libration
195s	184s	0·94	0·91	108s[e]	I.r.	A_{2u} (S_4) and E_u (S_6)
168s	154m	0·92	0·91	78ms[f]	I.r.	NH_4^+ or Rb^+ Translations
142s	142s	1	1	154ms	I.r.	E_u (S_7) $\delta_{asym}(HgCl)_t$
92s	92s	1	1	52m	I.r.	A_{2u} (S_5) δ_{oop} (sheet)
81mw[c]	81mw[c]	1	1	84w[c]	Raman	E_g (S_2) $\delta_{sym}(HgCl)_t$
40ms	40m	1	1	34ms	I.r.	E_u (S_8) δ_{ip} (sheet)

[a] v = Very, s = strong, m = medium, and w = weak. [b] Symmetry co-ordinates in Figure 1. [c] Ambient-temperature value. [d] Intensity is temperature dependent (see text). [e] ν_{Rb}/ν_{NH_4} = 0·55 (calc.: 0·46). [f] ν_{Rb}/ν_{NH_4} = 0·46 (calc.: 0·46).

The observation of the librational mode shows that at low temperatures the NH_4^+ ion is fixed in position. This automatically implies that under such conditions the space group is not *P4/mmm*, since the tetrahedral NH_4^+ ion cannot lie on a four-fold axis, and hence the factor-group analysis predictions given strictly speaking should not apply. That they do is acceptable because the spatial distribution of the four hydrogen atoms will not significantly affect the vibrational spectrum of what is otherwise a regular array of Hg, Cl, and N atoms.

The effect of deuteriation is also to shift i.r. bands at 195 and 168 to 184 and 154 cm^{-1} respectively, clearly identifying these as the A_{2u} and E_u NH_4^+ ion translations (Table 3). These assignments are supported by comparison with the i.r. spectrum of the salt Rb[$HgCl_3$]. Bands unaffected by deuterium substitution are at 309 [unambiguously the A_{2u} $\nu_{asym}(HgCl)_t$ mode], 142, 92, and 40 cm^{-1}. Assignment of the lowest three bands is equivocal, but, using the symmetry labels tentatively suggested from a polarized-reflection study[3] on a polycrystalline boule containing partially oriented regions of the salt NH_4[$HgCl_3$], we suggest the assignments given in Table 3. Although the value for E_u $\delta_{asym}(HgCl)_t$ is high by comparison with the equivalent mode in crystalline $HgCl_2$,[12] these proposals are supported by studies on Rb[$HgCl_3$] (see below).

β *Forms*. When stoicheiometric quantities of NH_4Cl and $HgCl_2$, each in the minimum amount of water, were mixed together the product crystallizing out on slow evaporation was found to be of formula NH_4[$HgCl_3$] but differed from the α form. We designated this compound β-NH_4[$HgCl_3$].[5] Single-crystal *X*-ray examination (see Experimental section) uniquely identified the salt as belonging to the same space group (*Pnma*; D_{2h}^{16}) as M[$CdCl_3$] (M = K, Rb, or NH_4)[6] with very similar unit-cell dimensions to these;[5] isomorphism was verified by comparison of the *X*-ray powder patterns of the salts β-NH_4[$HgCl_3$] and NH_4[$CdCl_3$]. It is therefore clear that the frequently quoted difference between the structures of the salts NH_4[$HgCl_3$] and NH_4[$CdCl_3$] is

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[10] H. S. Gutowsky, G. E. Pake, and R. Bersohn, *J. Chem. Phys.*, 1954, **22**, 643.

[11] J. R. Durig and D. J. Antion, *J. Chem. Phys.*, 1969, **51**, 3639; J. R. Durig and C. B. Pate, *Spectrochim. Acta*, 1972, **A28**, 1031.

[12] Y. Mikawa, R. J. Jakobsen, and J. W. Brasch, *J. Chem. Phys.*, 1966, **45**, 4528.

simply a consequence of the different preparative methods used.

Factor-group analysis for β-$NH_4[HgCl_3]$ can be carried out by taking the Wyckoff sites for the atoms as being the same as in the isomorphous cadmium salt. For point-mass NH_4^+ groups equation (2) is obtained,*

$$\Gamma_{\mathrm{chain}} = 10A_g(\mathrm{Raman}) + 5B_{1g}(\mathrm{Raman}) + 10B_{2g}(\mathrm{Raman}) + 5B_{3g}(\mathrm{Raman}) + 5A_u(\mathrm{inactive}) + 9B_{1u}(\mathrm{i.r.}) + 4B_{2u}(\mathrm{i.r.}) + 9B_{3u}(\mathrm{i.r.}) \qquad (2)$$

while the internal modes of the two double-rutile chains in the unit cell reduce as in (3).* Following Adams and

$$\Gamma_{\mathrm{chain}} = 8A_g + 3B_{1g} + 7B_{2g} + 4B_{3g} + 3A_u + 6B_{1u} + 2B_{2u} + 7B_{3u} \qquad (3)$$

Newton[13] in their single-crystal Raman spectral study of the salt $NH_4[CdCl_3]$, we find the line-group approach in equation (4) for an isolated chain adequate in describing the number of modes observed for β-$NH_4[HgCl_3]$.

$$\Gamma_{\mathrm{chain}} = 7A_g + 4B_g + 3A_u + 6B_u \qquad (4)$$

Similarity of the Raman (see figure in ref. 5) and i.r. spectra of the salts β-$NH_4[HgCl_3]$ and $NH_4[CdCl_3]$, if due allowance is made for greater covalence in the former salt, leads to the assignments in Table 4. Spectra of the deuteriates β-$ND_4[HgCl_3]$ and $ND_4[CdCl_3]$ showed slight differences to their NH_4^+ analogues, particularly in the 100—200 cm^{-1} region, but, because of extensive overlap, band positions could not be located accurately enough for specific assignments to be made of NH_4^+ translations; no cation librations were observed at temperatures down to *ca.* 30 K.

TABLE 4

Vibrational spectra (cm^{-1}) of trichloro-mercurate(II) and -cadmate(II) salts having the double-rutile chain structure

β-$NH_4[HgCl_3]$		β-$ND_4[HgCl_3]$		$NH_4[CdCl_3]$		$ND_4[CdCl_3]$		$K[CdCl_3]$		$Rb[CdCl_3]$		
I.r. (30)	Raman (100)	I.r. (100)	Raman (300)	I.r. (30)	Raman (300)	I.r. (30)	Raman (300)	I.r. (100)	Raman (300)	I.r. (100)	Raman (300 K)	Assignment[a]
309s		315sbr		246s		243m		254s		247s		$B_u\ \nu_{\mathrm{asym}}(\mathrm{MCl})_{\mathrm{t}}$
	297s		300s		244s		245s		253s		252s	$A_g\ \nu_{\mathrm{sym}}\ (\mathrm{MCl})_{\mathrm{t}}$
	262s		265s		219s		220s		226s		222s	$A_g\ \nu_{\mathrm{sym}}(\mathrm{MCl})_{\mathrm{b}}$
					217 [b]				202w			$B_g\ \nu_{\mathrm{sym}}(\mathrm{MCl})_{\mathrm{b}}$
222m				228s		228m		227m		222s		$B_u\ \nu_{\mathrm{asym}}(\mathrm{MCl})_{\mathrm{b}}$
198s		180sbr		195s		192s		184s		182s		
172s		164s		172s		170sbr		175s		173s		
165s		154s		155s		163br		150m		150s		
						153br		138m		130m		
	158w		154wbr		181w				164w			B_g (chain)
145sh		145s		122m		122m		124m		118s		
	117m		114wbr		157w		152wvbr		142w		142m	A_g (chain)
115m		103m		104m		102mw		114w				
	110m				121m		120wvbr		124w			B_g (chain)
								92m		91m		
96w				80mw		78m [c]		77m		77w		
	94w		100wbr		110 [b]							A_g (chain)
	86m		82mbr		106ms		103w		105m		100w	B_g (chain)
										73m		
82s		83s		70mw		68mw [c]		70m		70m		
								65m		62m		
	72w				86m		85mw		88w		84w	B_{2g} Translation [d]
	54m				63s		63wvbr		70w		68w	$A_g + B_{1g} + B_{3g}$ Translations [d]
									56w			
52m		51m		42w [c]				54w		50w		
42m [c]		43s										
	35w				41w							

[a] Following ref. 13 for the salt $NH_4[CdCl_3]$; C_{2h} line-group analysis (other than for lattice modes). [b] From ref. 13 (300 K). [c] 100 K value. [d] Under D_{2h} unit-cell factor group.

Rubidium Trichloromercurate(II).—Isomorphism between this salt and α-$NH_4[HgCl_3]$, confirmed in the present work, has been demonstrated by *X*-ray powder studies.[3] The Raman spectra of the two salts are virtually identical, as expected because the cations are primitively related and, being on centres of symmetry, do not contribute to the Raman spectrum. The i.r. spectra are also seen to be analogous when the difference in mass of the cations is taken into account. The shifts to lower wavenumbers of one of the cation translations (Table 3) was somewhat less than that calculated from the inverse relation $(\nu_T)^2 \propto m^{-1}$, as the latter assumes no contribution from the motion of other atoms.

Comparison of the i.r. data in Table 3 shows that the A_{2u} $\nu_{\mathrm{asym}}(\mathrm{HgCl})_{\mathrm{t}}$ and E_u $\delta_{\mathrm{asym}}(\mathrm{HgCl})_{\mathrm{t}}$ modes are at somewhat higher wavenumbers in the Rb salt, while the reverse trend is found for the A_{2u} and E_u sheet deformations. These effects are self consistent since shortening of the $Hg-Cl_t$ distance will result in weakening of the bridging interaction; they therefore support the assignments proposed for the three lowest-frequency bands.

Ammonium Tribromomercurate(II).—The product obtained from a 1 : 1 $NH_4Br : HgBr_2$ melt was found to be identical to that obtained from aqueous solution, but the data do not allow unambiguous structural assignment. Thus although only one prominent Raman band is found in the ν(HgBr) region (at 178 cm^{-1}), as expected for the α-$NH_4[HgCl_3]$ structure, there are other, albeit

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* Analyses previously given [13] are in error.

[13] D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1971, 3499.

very weak, features (196sh, 139vw, and 109vw cm^{-1}). I.r. data (255m, 243mw, 224sh, 201ms, 176m, 154sbr, and 117m cm^{-1} at *ca.* 100 K) do not provide satisfactory evidence on which to suggest a structure. The *X*-ray powder photograph shows no obvious relation to those of the salts α- or β-$NH_4[HgCl_3]$.

$MCdCl_3$ (M = NH_4, ND_4, K, *or* Rb).—These salts are isomorphous[6] and have closely similar spectra (Table 4). Raman line assignments follow single-crystal data.[13] In each i.r. spectrum, the band at highest wavenumber (243—254 cm^{-1}) is certainly the single $\nu(CdCl)_t$ mode (B_u) predicted on line-group analysis, and the 222—228 cm^{-1} band is probably associated with singly bridging Cd–Cl–Cd groups. There are no obvious candidates for cation translatory modes.

TABLE 5

Vibrational spectra (cm^{-1}) of the salts $K_2[HgCl_4],H_2O$, $K_2[HgCl_4],D_2O$, and $K[HgCl_3]$

Raman[a]			I.r.[b]		
$K_2[HgCl_4],H_2O$	$K_2[HgCl_4],D_2O$	$K[HgCl_3]$	$K_2[HgCl_4],H_2O$	$K_2[HgCl_4],D_2O$	$K[HgCl_3]$
264s[c]	263s[c]	280s	308s[d]	307s[d]	326s
157wbr[e]	153wbr[e]		202m[e]	196m[e]	
125m	124m	116m	168s	168s	170msh
104s	104s	97s	140s	140s	148s
91m	89m	83m	118s	118s	127s
82m	80m	71m	110s	110s	118sh
57w	57w		100m	100m	
53ms	53m	59m	76m	76m	92m
41m	40m	*f*	66m	66m	69m
26w	25w		44w	43w	*f*
21w	19w		34m	34m	

[a] Ambient temperature. [b] *ca.* 100 K. [c] A_g $\nu_{sym}(HgCl)_t$. [d] A_u $\nu_{asym}(HgCl)_t$. [e] H_2O (or D_2O) Translational mode. [f] Limit of study 50 cm^{-1}.

' $Na[HgCl_3]$ ' *and* $Na[HgCl_3],2H_2O$.—A compound of composition ' $Na[HgCl_3]$ ' has been described[14] as having a double-rutile chain structure analogous to that of the salt $NH_4[CdCl_3]$. However, the existence of this compound has been questioned by Malcic[15] who, in determining the structure of the salt $Na[HgCl_3],2H_2O$, failed to isolate anything but the dihydrate using the preparative method previously described[14] for ' $Na[HgCl_3]$ ', a result which we have confirmed for a variety of conditions. Scrutiny of the available data reveals that unit-cell dimensions given for ' $Na[HgCl_3]$ ' (a = 948, b = 416, and c = 1 835 pm, with uncertainty in the last digits)[14] are effectively the same as those of the salt $Na[HgCl_3],2H_2O$ (a = 937·2, b = 403·7, and c = 1 871 pm).[15] Our attempts to prepare the anhydrous salt by gentle heating of $Na[HgCl_3],H_2O$ *in vacuo* always gave a product identified, by *X*-ray powder photography and i.r. and Raman spectroscopy, as being a simple physical mixture NaCl–$HgCl_2$. The same product was obtained from a 1 : 1 NaCl : $HgCl_2$ melt. In none of the systems so far examined has any clear evidence been obtained for the existence of anhydrous sodium trichloromercurate(II), and the reported crystal structure[14] is clearly in error.

Our spectra of the salt $Na[HgCl_3],2H_2O$ always contained bands arising from impurities $HgCl_2$ (i.r. and Raman) and NaCl (i.r. only as this salt shows no first-order Raman spectrum), and are therefore not reported; the same problem arose with the salt $Na[HgCl_3],2D_2O$. It has previously been noted[4] that $Na[HgCl_3],2H_2O$ (unwittingly described as the anhydrous salt) is difficult to obtain pure.

Dipotassium Tetrachloromercurate(II) *Hydrate and Deuteriate*.—These salts contain infinite chains formed by *trans* edge-shared distorted $[HgCl_6]$ octahedra,[16,17] and are therefore structurally related to the trichloromercurate(II) salts. As the primitive unit cell contains four formula units, full factor-group analysis will be of limited use in understanding the vibrational spectra (*e.g.* it predicts 57 optically active modes due to the anionic chains alone), and a line-group approach (C_{2h}) is probably more appropriate [equation (5)]. Deuteriation

$$\Gamma_{chain} = 2A_g(\text{Raman}) + 3B_g(\text{Raman}) + 2A_u(\text{i.r.}) + 4B_u(\text{i.r.}) \quad (5)$$

shifts of the 157 (Raman) and 202 cm^{-1} (i.r.) bands (ν_D/ν_H = 0·97, calc.: 0·95) identify these as H_2O translational modes [rather than librations (ν_D/ν_H, calc.: 0·71—0·74)]. Assuming that bands below *ca.* 80 cm^{-1} are lattice modes of the anions and cations, the numbers of observed i.r. and Raman bands (Table 5) are therefore almost in accord with line-group predictions. Bands at 264 (Raman) and 308 cm^{-1} (i.r.) are certainly the A_g and A_u $\nu(HgCl)_t$ modes, respectively, while the next-highest-wavenumber internal-chain bands [125 (Raman) and 168 cm^{-1} (i.r.)] are attributed to $\nu(HgCl)_b$ modes (more correctly, in-plane chain deformations). Symmetry labels can be placed on the other Raman bands by comparison with results of single-crystal studies,[1] but no further assignments can be made.

Potassium Trichloromercurate(II).—The structure of this salt is not known, but we find (*X*-ray powder photography) that it is not isomorphous with any of the other salts described herein. In addition, the i.r. and Raman spectra do not resemble those of the salts $Cs[HgX_3]$

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(X = Cl or Br)[3] or other A$[MX_3]$ perovskites,[18] $K[HgX_3],H_2O$ (X = Br or I),[19] or $R_4N[HgX_3]$ (R = Me, Et, Pr^n, or Bu^n; X = Cl, Br, or I).[20] However, there is a remarkable similarity of the spectra with those of the salt $K_2[HgCl_4],H_2O$ (Table 5 and Figure 3). Apart from frequency differences (substantiating the individuality of the salts), the only bands which are clearly not common to both the salts $K[HgCl_3]$ and $K_2[HgCl_4],H_2O$ are those in the latter identified above as H_2O translations. The data do not allow unambiguous structural assignment for the salt $K[HgCl_3]$, but it seems most probable that $[HgCl_6]$ octahedra are present. Observation of single i.r. (326) and Raman (280 cm^{-1}) $\nu(HgCl)_t$ modes, which are mutually exclusive, indicates that these octahedra contain two short Hg–Cl bonds which are mutually *trans*.

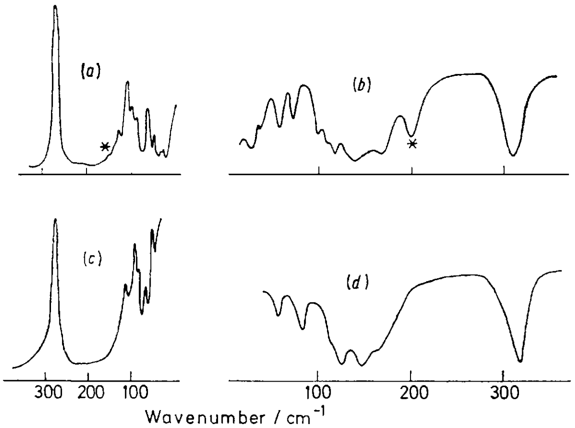

FIGURE 3 Vibrational spectra of the salts $K_2[HgCl_4],H_2O$ [(*a*), Raman; (*b*), i.r.] and $K[HgCl_3]$ [(*c*), Raman; (*d*), i.r.]. Bands marked with an asterisk are H_2O translations (see text)

EXPERIMENTAL

Salts α-$NH_4[HgCl_3]$, α-$ND_4[HgCl_3]$, $K[HgCl_3]$, and $Rb[HgCl_3]$ were obtained by heating (*ca.* 300 °C) a sealed glass ampoule containing stoicheiometric quantities of mercury(II) chloride and appropriate ammonium or alkali-metal chloride; the tube was then cooled and opened, and the product ground. All the other salts described in this work were prepared by mixing stoicheiometric quantities of mercury(II) or cadmium(II) chloride and ammonium or alkali-metal chloride, each in the minimum amount of water (or D_2O as appropriate); the solutions were allowed to evaporate in a stream of nitrogen (or in a desiccator in the case of the deuteriates) until crystallization commenced, and the product filtered off and dried *in vacuo* over silica gel. The salt $NH_4[HgBr_3]$ was prepared by both methods. All salts gave satisfactory elemental analysis.

Single-crystal *X*-ray studies on the salt β-$NH_4[HgCl_3]$ were carried out using Pye–Unicam rotation and Weissenberg cameras and Cu-K_α radiation. Zero- and first-level Weissenberg photographs showed the following systematic absences:

hkl	No conditions
0*kl*	$k + l = 2n$
*h*0*l*	No conditions
*hk*0	$h = 2n$
*h*00	$(h = 2n)$
0*k*0	$(k = 2n)$
00*l*	$(l = 2n)$

These conditions assign the structure uniquely to space group *Pnma* (No. 62, D_{2h}^{16}). *X*-Ray powder photographs were taken on a Phillips 11·46 cm camera using Cu-K_α radiation. Far-i.r. spectra were obtained using R.I.I.C. FS-520 (50—450 cm^{-1}) or FS-720 (10—200 cm^{-1}) interferometers. Samples were studied as polyethylene (B.D.H.) or wax discs. Low temperatures were achieved using R.I.I.C. VLT-2 (*ca.* 100 K) or CTi Cryodyne model 20 (*ca.* 30 K) cryostats. Raman spectra were recorded on Cary 81, Cary 82, Spex Ramalog, or Coderg PH1 spectrometers using 488·0, 514·5, or 647·1 nm Ar$^+$–Kr$^+$ laser excitation; all low-temperature Raman spectra were obtained on the Coderg PH1 instrument.

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