Far-infrared and Raman Spectra of Crystalline Tetra-alkylammonium Trihalogenomercurate(II) Salts. Evidence for Monomeric or Halogen-bridged Associated Anions depending on the Cation

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A study has been made of the far-infrared (20—400 cm^{-1}) and Raman spectra of eight compounds of type $[NR_4][HgX_3]$ (R = Me, Et, Pr^n, or Bu^n; X = Cl, Br, or I) and of $[SMe_3][HgI_3]$ in the solid state. Solution-phase Raman data have also been obtained. For R = Et and X = Cl two crystalline modifications have been identified. The low-temperature α form has vibrational spectra explicable in terms of an essentially monomeric anionic structure, whereas the β form, stable above 71 °C, clearly contains strong halide-bridged groups. The structures of the other compounds have been deduced by comparison with the data on α- and β-$[NEt_4][HgCl_3]$. Thus associated anionic structures are present also in $[NEt_4][HgX_3]$ (X = Br or I), $[NPr^n_4][HgCl_3]$, and $[NBu^n_4][HgI_3]$. Evidently the weak halogen bridging found in the crystal structures of $[SMe_3][HgI_3]$ and $[NMe_4][HgCl_3]$ may be disregarded in qualitative interpretation of the vibrational data; the spectra of $[NMe_4][HgX_3]$ (X = Br or I) may similarly be described in terms of monomeric anionic structures.

We recently reported on the vibrational spectra and structures of anhydrous trichloromercurate(II) salts of ammonium and alkali-metal cations, and noted that in all known cases the structures are best described in terms of condensed $[HgCl_6]$ octahedral units in the solid state.[1] Rather different arrangements obtain in other trihalogenomercurate(II) salts. In $K[HgBr_3]\cdot H_2O$, strong bromine bridging results in the formation of chains containing distorted tetrahedral co-ordination about mercury.[2] In the only tri-iodomercurate(II) whose structure has been described, $[SMe_3][HgI_3]$, approximately trigonal-planar anions are loosely linked by long contacts to give a trigonal-bipyramidal environment for each metal atom.[3] Weak interactions are also present in $[NMe_4][HgBr_3]$, which may be described as containing near-trigonal anions with one further fairly close bromine-mercury contact from a neighbouring anion resulting in a ' two-anion ' asymmetric unit;[4] the chloride[4] is isomorphous with the bromide (but interatomic distances are not known), whereas the iodide is not.[5] In contrast, strong bromine bridging to form a dimeric anion exists in the unusual $[H(AsPh_3O)_2][Hg_2Br_6]$.[6]

Partly in an attempt to rationalise these structural variations, and partly to place spectra–structure correlations involving mercury halogen-bridged systems on a firmer basis, we undertook a systematic study of the far-i.r. and Raman spectra of several compounds of type $[NR_4][HgX_3]$ (R = Me, Et, Pr^n, or Bu^n; X = Cl, Br, or I). Some of these compounds have been studied in less detail previously.[7,8] Hooper and James[8] based their assignments on the crystal structure of $[NMe_4][HgBr_3]$, in which there is known[4] to be a bridging interaction. They made their assignments on the assumption that the other three tetra-alkylammonium trihalogenomercurate(II) salts for which they report bridging modes, $\nu(HgX)_b$ (strictly, in-plane deformations of $Hg{-}X\cdots Hg$ units), have a similar structure. It is noteworthy, but not inconsistent with our results, as we shall show, that a $\nu(HgBr)_b$ mode was not assigned for $[NMe_4][HgBr_3]$ itself.

RESULTS AND DISCUSSION

α- and β-$[NEt_4][HgCl_3]$.—During the course of this study it became apparent that $[NEt_4][HgCl_3]$ could be obtained in two forms, since the far-i.r. spectrum obtained for the sample dispersed at room temperature in polyethylene was markedly different to that recorded for a pressed wax disc which had been softened by heating to *ca.* 80 °C. {It is noteworthy that the spectrum previously reported[8] for ' $[NEt_4][HgCl_3]$ ' (erroneously listed in Table 2 of ref. 8 as $[NEt_4][HgBr_3]$) differs substantially from the spectra of both forms obtained by us (Figure 1), but we have not obtained evidence for more than two forms.} Further investigation revealed the existence of two distinct phases: that obtained at room temperature is designated α-$[NEt_4][HgCl_3]$, whereas the higher-temperature phase (see Experimental section), stable on cooling to room temperature for at least a few days, is designated the β form. Differential thermal analysis (d.t.a.) of the α form revealed a small endotherm at 71 °C, the β form then melting at 117 °C.

The spectra of the α form can be fairly easily interpreted in terms of essentially monomeric anionic units. Thus the strong Raman line at 269 cm^{-1} corresponds to a polarised Raman line at 288 cm^{-1} in MeCN solution (Table) and is clearly a terminal stretching mode $\nu_{sym}(HgCl)_t$, whereas the intense i.r. band at 252 cm^{-1} is obviously $\nu_{asym}(HgCl)_t$, *cf.* ref. 8. At low temperatures the symmetric mode appeared as a weak shoulder in the i.r. spectrum at 274 cm^{-1}, attributable to slight distortion from planarity or to a site-symmetry effect. The next-highest wavenumber bands appeared at 101 (Raman) or 98 cm^{-1} (i.r.). These are too low in value to be described as arising from

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Vibrational spectra (cm^{-1}) of trihalogenomercurate(II) salts [a]

Compound	Method [b]	$\nu_{sym}(HgX)_t$	$\nu_{asym}(HgX)_t$	$\nu(HgX)_b$	$\delta(XHgX)$	Other
$[NMe_4][HgCl_3]$	Raman, solid	276s				
	Raman, MeCN	293s,p				
	I.r., solid (r.t.)		260sbr		108sbr	
	I.r., solid (l.n.)	278(sh)	258s		112sbr	78m, 52m
α-$[NEt_4][HgCl_3]$	Raman, solid	269s			101s	81s
	Raman, MeCN	288p				
	I.r., solid (r.t.)		252sbr		96s	
	I.r., solid (l.n.)	274(sh)	252s		98s	65m
β-$[NEt_4][HgCl_3]$	Raman, solid	288s		230m		
	Raman, Me_2CO	290s,p				
	I.r., solid (r.t.)		281s	184s	110(sh), 100s	44w
	I.r., solid (l.n.)	288s	280s	188s	112s, 100s	76m, 66m, 51w
$[NPr^n_4][HgCl_3]$	Raman, solid	291s		227m		80m
	Raman, Me_2CO	290s				
	I.r., solid (r.t.)		288s	170mbr		
	I.r., solid (l.n.)		292s	178s, 170s	124s, 109s	83s
$[NMe_4][HgBr_3]$	Raman, solid (r.t.)	177s				46w, 33w
	Raman, solid (l.n.)	178s	160m(sh)			46w, 34w
	Raman, Me_2CO	181s,p				
	I.r., solid (r.t.)		185sbr		90sbr	
	I.r., solid (l.n.)	178s	191s, 161s		85sbr	110m, 60m
$[NEt_4][HgBr_3]$	Raman, solid	186s		160w		78w
	Raman, Me_2CO	184s,p				
	I.r., solid (r.t.)	180s	192s	129s, 120s	80s	60s, 40m
	I.r., solid (l.n.)	180s	195s	128s, 123s	96m, 86s	80m, 70m, 62s, 40s
$[SMe_3][HgI_3]$	Raman, solid	126s				
	Raman, MeCN	135s,p				
	I.r., solid (r.t.)		144s,p			
	I.r., solid (l.n.)	136s	156s		64m	110m, 80s
$[NMe_4][HgI_3]$	Raman, solid	134s	152w			112w
	Raman, Me_2CO	135s,p				
	I.r., solid (r.t.)	130m	152s			80s
	I.r., solid (l.n.)	135m	155s, 128m		54m	110m, 84s
$[NEt_4][HgI_3]$ [c]	Raman, solid	137s				69w
	Raman, Me_2CO	135s,p				
	I.r., solid (r.t.)	135s	152s	92w	50m	75w, 69w
	I.r., solid (l.n.)	135s	154s	98s	54s	80m, 70m
$[NBu^n_4][HgI_3]$	Raman, solid	135s	154w			
	Raman, Me_2CO	136s,p				
	I.r., solid (r.t.)	134s	148s		54m	
	I.r., solid (l.n.)	133s	154s	93s	58m	78m, 48w, 40w

[a] s = Strong, m = medium, w = weak, br = broad, sh = shoulder, and p = polarised. [b] All the Raman data were obtained at room temperature (r.t.) unless otherwise indicated; l.n. = sample cooled (to *ca.* 100 K) with liquid nitrogen. [c] Bands due to $[NEt_4]_2[Hg_3I_8]$ contaminant were excluded (see text).

motions of possible bridging chlorine atoms, but are reasonably attributed to $\delta(ClHgCl)$, since any alternative would place this deformation at the unacceptably low value of 65 cm^{-1} (i.r.) {*cf.* 89 cm^{-1} for $PO(OBu^n)_3$ solutions of $[HgCl_3]^-$ (ref. 9)}. It may be concluded that if halogen bridging is present in α-$[NEt_4][HgCl_3]$ it is so weak that it has little influence on the vibrational spectra.

In contrast to the α phase, β-$[NEt_4][HgCl_3]$ does not have spectra characteristic of a monomeric anion. Thus both the symmetric and asymmetric $\nu(HgCl)_t$ modes are intense in the i.r. (resolved only at low temperature). Of greater significance (Figures 1 and 2) are the bands at 230 (Raman) and 188 cm^{-1} (i.r.). These are clearly at too high a wavenumber to be assigned to $\delta(ClHgCl)$ or lattice modes, and must therefore be associated with motions which are essentially stretching vibrations. They are, however, some 60 (Raman) or 100 cm^{-1} (i.r.) lower than the other stretching modes and thus surely arise from a bridging structure, *i.e.* $\nu(HgCl)_b$. Furthermore, as will be seen from the following discussion, the effects on the spectra are so marked that this bridging interaction must be far more significant than obtains in $[SMe_3][HgI_3]$ or $[NMe_4][HgBr_3]$.[3,4]

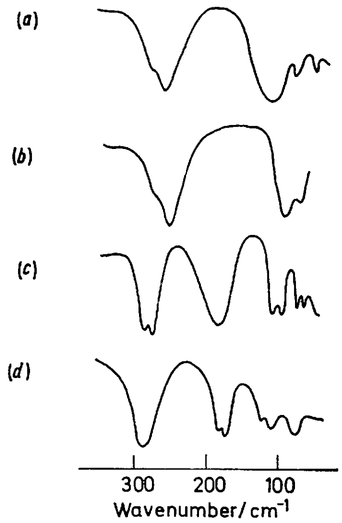

FIGURE 1 Far-i.r. spectra at *ca.* 100 K of (*a*) $[NMe_4][HgCl_3]$, (*b*) α-$[NEt_4][HgCl_3]$, (*c*) β-$[NEt_4][HgCl_3]$, and (*d*) $[NPr^n_4]$-$[HgCl_3]$

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$[NMe_4][HgX_3]$ (X = Cl, Br, *or* I) *and* $[SMe_3][HgI_3]$.—These compounds fall into the same structural category as α-$[NEt_4][HgCl_3]$, since their i.r. and Raman spectra are readily interpreted in terms of monomeric anionic units. This is most clearly illustrated for $[NMe_4][HgCl_3]$ in Figure 1, where the i.r. spectra arising from the two types of structure are compared. For $[NMe_4][HgBr_3]$, apart from splitting of ν$(HgBr)_t$ into three i.r. bands at low temperature (two of which are also found in the Raman spectrum), arising from the asymmetric $[HgBr_3]^-$ units in low-symmetry sites in the structure,[4] the spectra are analogous to those of $[NMe_4][HgCl_3]$, so that comparable structures obtain. The compounds $[NMe_4][HgI_3]$ and $[SMe_3][HgI_3]$ have very similar spectra in the range studied, and although i.r. bands are present in the region where ν$(HgI)_b$ modes might be expected to occur, the sulphonium salt is known[3] not to have Hg · · · I contacts substantially shorter than the sum of the van der Waals radii. Certainly, these bridging interactions are less significant than those which obtain in $[NMe_4][HgBr_3]$, so that the spectra are determined by a structure containing essentially monomeric $[HgI_3]^-$ anions. The likely origin of the i.r. bands at *ca.* 100 cm^{-1} is cation lattice modes (internal modes are otherwise accounted for), since analogous bands are found for $[NMe_4]X$ and $[SMe_3]X$ salts (X = I or HgI_3) (very similar cationic mass). These bands shift to *ca.* 60 cm^{-1} in $[NEt_4]^+$ salts, supporting the assignment.

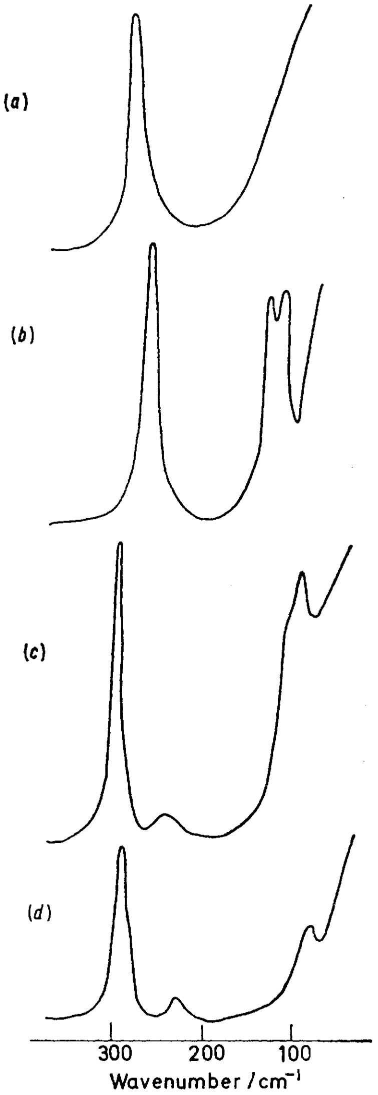

FIGURE 2 Raman spectra at *ca.* 300 K of (*a*) $[NMe_4][HgCl_3]$, (*b*) α-$[NEt_4][HgCl_3]$, (*c*) β-$[NEt_4][HgCl_3]$, and (*d*) $[NPr^n_4]$-$[HgCl_3]$

$[NEt_4][HgX_3]$ (X = Br *or* I), $[NPr^n_4][HgCl_3]$, *and* $[NBu^n_4][HgI_3]$.—It is obvious from Figures 1 and 2 that $[NPr^n_4][HgCl_3]$ has the same chlorine-bridged structure as the β-$[NEt_4]^+$ salt. Similarly, $[NEt_4][HgBr_3]$ is markedly different from $[NMe_4][HgBr_3]$ (Figure 3) but closely analogous to β-$[NEt_4][HgCl_3]$ (*cf.* Figures 1 and 3), classifying it as halogen bridged. The compound $[NEt_4][HgI_3]$ was always obtained contaminated with $[NEt_4]_2[Hg_3I_8]$ (itself an aggregate of $[HgI_3]^-$ ions and HgI_2) and (assumed) $[NEt_4]I$. However, its spectra could be deduced by a subtraction procedure, and are indicative of strongly halogen-bridged anions. The same conclusion is reached for $[NBu^n_4][HgI_3]$.

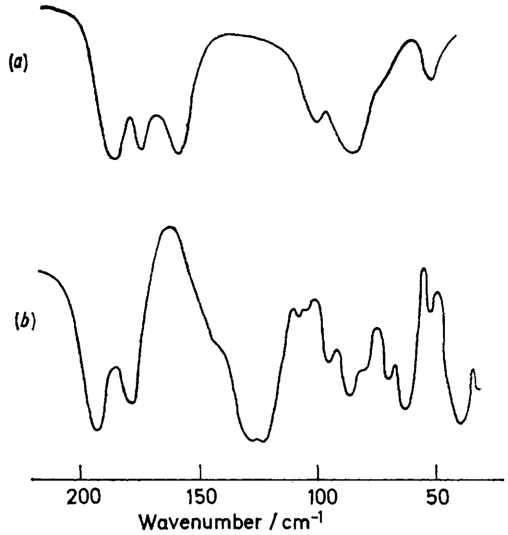

FIGURE 3 Far-i.r. spectra at *ca.* 100 K of (*a*) $[NMe_4][HgBr_3]$ and (*b*) $[NEt_4][HgBr_3]$

General Discussion.—The highest wavenumber bands identified in the spectra are appropriately described as ν$(HgX)_t$ by reference to solution-phase data (Table and ref. 9). Bands assigned at 170—230 (Cl), 120—160 (Br), or 90—100 cm^{-1} (I) as ν$(HgX)_b$ are clearly of complex origin, but their wavenumbers warrant such description rather than as translatory lattice modes. Indeed, $[NMe_4][HgBr_3]$ and $[SMe_3][HgI_3]$, where long Hg · · · X interactions are found (292—294 and 352—369 pm, respectively),[3,4] do not show these ν$(HgX)_b$ bands. Evidently, the compounds falling into the structural class typified by β-$[NEt_4][HgCl_3]$ comprise strongly halogen-bridged anions while still containing terminal

Hg–X bonds. Their actual structures cannot be unambiguously deduced from the vibrational spectra, but they are clearly different from those of the ammonium or alkali-metal trichloromercurates (sheet or double-rutile chains).[1] Preliminary *X*-ray crystallographic data[10] suggest a centrosymmetric dimeric structure for $[NEt_4][HgBr_3]$, and the spectral data for the associated species can reasonably well be rationalised in such terms. Thus up to two $\nu(HgX)_t$ and two $\nu(HgX)_b$ modes are observed in the i.r., in agreement with predictions for D_{2h} dimeric structures; further assignment would be premature.

The general trend deduced in the present work is that with the smaller $[NMe_4]^+$ or $[SMe_3]^+$ cations essentially monomeric $[HgX_3]^-$ anions are formed, while with larger cations associated structures obtain. The 'change over' occurs at $[NEt_4][HgCl_3]$, where both types of structure are formed. This trend is the opposite to that which is commonly believed to occur in halogenometallates.

EXPERIMENTAL

Except for β-$[NEt_4][HgCl_3]$, all the trihalogenomercurate(II) salts studied were prepared by mixing stoicheiometric quantities of the mercury(II) halide and tetra-alkylammonium (or trimethylsulphonium) halide, each dissolved in the minimum quantity of hot acetone. The products, which crystallised immediately or on cooling, were filtered off and dried *in vacuo* over silica gel. The compound β-$[NEt_4][HgCl_3]$ was obtained either by heating the α form at *ca.* 90 °C for 30 min, or by suspending it in boiling light petroleum (b.p. 100—120 °C) and filtering off. All the compounds gave satisfactory C, H, and N analyses. The sample analysing as $[NEt_4][HgI_3]$, which was found spectroscopically to contain $[NEt_4]_2[Hg_3I_8]$, is thus assumed also to contain $[NEt_4]I$.

Far-i.r. spectra were obtained using RIIC FS-520 (50—450 cm^{-1}) or FS-720 (10—200 cm^{-1}) interferometers with the samples as pressed discs in polyethylene or wax (softened at *ca.* 80 °C). Low temperatures were achieved using an RIIC VLT-2 cryostat. Raman spectra were recorded on Cary 81 or 82, Spex Ramalog, or Coderg PH1 spectrometers using 488.0-, 514.5-, or 647.1-nm Ar^+–Kr^+ laser excitation.

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