Complex Mercury(II) Cations and their ^{1}H Nuclear Magnetic Resonance and Vibrational Spectra

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The cations, [HgXPMe$_3$]$^+$ (X = Cl, Br, I CN, or Me), [HgXAsMe$_3$]$^+$ (X = Cl or Me), [Hg(PMe$_3$)$_2$]$^{2+}$, [Hg(AsMe$_3$)$_2$]$^{2+}$, [HgMeSMe$_2$]$^+$, and [HgMepy]$^+$ have been characterised as their nitrate or fluoroborate salts. Their ^{1}H n.m.r. i.r. and Raman spectra are reported and discussed.

THERE have been a number of reports of cationic complexes [RHgL]$^+$ (R = alkyl or phenyl, L = PR$_3$, AsR$_3$, py, NR$_3$, SR$_2$ or H$_2$O) [1-3] but with the exception [3] of [HgMeSMe$_2$]$^+$ and [HgMeH$_2$O]$^+$, no detailed vibrational spectroscopic studies have been made. ^{1}H N.m.r. spectra have been recorded only for [HgMeD$_2$O]$^+$ and [HgMepy]$^+$.[4] There is even less information on the complexes [HgXL]$^+$ (X = halide or pseudohalide) or [HgL$_2$]$^{2+}$, the former having been shown to be present in the lattice of HgCl$_2$(SC$_4$H$_6$) [5] and the latter in the lattice of compounds HgX$_2$(NH$_3$)$_2$.[6] Hg{o-C$_6$H$_4$(Me$_2$As)$_2$}$_2$I$_2$ [7] contains a complex mercury(II) cation, but as all four arsenic atoms are co-ordinated to the metal it is better classified as [HgL$_4$]$^{2+}$. The high conductivity

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TABLE 1[a]

Infrared and Raman spectra (below 800 cm^{-1}) of complexes $[HgX(YMe_3)]^+$ [X = Cl, Br, I, CN or CH_3; Y = P or As]

	$[HgClPMe_3]^+[NO_3]^-$		$[HgClPMe_3]^+[BF_4]^-$			$[HgBrPMe_3]^+[NO_3]^-$		$[HgBrPMe_3]^+[BF_4]^-$	
	I.r.	R	I.r.	R	R in H_2O	I.r.	R	I.r.	R
YC_3 str. (asym) E	757s	761w	765s	763m	766m,p	757s	762w	768s	766m
YC_3 str. (sym) A_1	678m	677wm	674m	674m	677m,p	676m	676m	673m	675m
Hg–Y str. A_1	372m	369vw	378m	375vw	374vw,p		364w		364m
Hg–X str. A_1	319s	309s	328m	320s	324s,p	205wm	194s	204m	198s
YC_3 def. (asym) E		261w		266m	266w,dp		261wm		264w
YC_3 def. (sym) A_1	210vvw	207m	210vvw	211s		228m	222m	238m	234w
YC_3 rocking E		181vw		181vw					
{Y–Hg–X bend E	100s,vbd		90s,bd			118s,bd		106s,bd	
and lattice modes						53s		67s,bd	
Anion	1364vs,bd			[b]	766m,p	1368vs,bd			[b]
	1036m	1042s	525m			1036m	1040s	521m	
	816m					818m		353wm	
	716m	722w				716wm	721w		
Limit of study	(40)	(110)	(40)	(150)	(220)	(40)	(100)	(40)	(110)

	$[HgIPMe_3]^+[NO_3]^-$		$[HgIPMe_3]^+[BF_4]^-$		$[HgCNPMe_3]^+[NO_3]^-$		$[HgCNPMe_3]^+[BF_4]^-$		$[HgMePMe_3]^+[NO_3]^-$		
	I.r.	R	I.r.	R	I.r.	R	I.r.	R	I.r.	R	R in H_2O
Hg–CH_3 rocking E									760s		
YC_3 str. (asym) E	769s		764s	767s	762s	760wm	760s	766m		758m	759w,dp
	765s	763wm									
YC_3 str. (sym) A_1	675m	674w	674m	677s	674m	674s	674m	676s	678m	676m	676m,p
Hg–Y str. A_1		359m		360s		347s		354s	358vvw	350m	347m,p
Hg–X str. A_1		166vs	173s	173vs	434m	399w	446m	422w	541s	538s	541s,p
Hg–C≡N bend E						273m		274m			
YC_3 def. (asym) E		262m		257m		257m		264m	260vw	262wm	261w,dp
YC_3 def. (sym) A_1		223w		234w		233wm		233m		190ms	188m,p
YC_3 rocking E						186s		193s		179sh,vw	
{Y–Hg–X bend E			100s,bd		108m,bd		115s		95s,vbd	109sh,vw	102sh,dp
and lattice modes			65s,bd		60m		78s				
							48s				
Anion	1355vs,bd			[b]	1345vs,bd			[b]			
	1029m		524m		1041vw	1039m	525m		1040wm		1044m,p
	814wm		355w		825m				826m		
	710wm				724w	725vw			716sh		
Limit of study	(200)	(120)	(40)	(130)	(40)	(100)	(40)	(140)	(40)	(100)	(90)
Other bands						2186[c] m					1187m,p[d]

	$[HgClAsMe_3]^+[NO_3]^-$		$[HgClAsMe_3]^+[BF_4]^-$		$[HgMeAsMe_3]^+[NO_3]^-$		
	I.r.	R	I.r.	R	I.r.	R	R in H_2O
Hg–CH_3 rocking E					762s		
YC_3 str. (asym) E	634s	635m	634s	639s	632s	632m	629m,dp
YC_3 str. (sym) A_1	598m	599m	597m	598s	598m	600s	595s,p
Hg–Y str. A_1	254m,bd	251m	254m	249ms		253wm	251wm,p
Hg–X str. A_1	333s	327m	345s	347ms	537s	536s	538s,p
Hg–C≡N bend E							
YC_3 def. (asym) E		215m,bd		228ms		219m	214wm,dp
YC_3 def. (sym) A_1		181s	183m	179vs		167ms	161s,p
YC_3 rocking E		138vw	134vw	143vw			
{Y–Hg–X bend E	112m,bd		104s	97ms	90vbd	101sh	95sh,dp
and lattice modes	47sh		78s				
Anion	1353vs,bd			771vw	1360vbd		
	1040m	1037m	524s		1038m	1040m	1046m,p
	823m		360m		824m		
	723m	723vw			720m	~718vw	
Limit of study	(40)	(110)	(40)	(70)	(40)	(90)	(80)
Other bands				183sh			1170m,p[d]
				296vw			
				327vw			

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[a] In all Tables of vibrational spectra the following abbreviations are used: w = weak, m = medium, s = strong, v = very, sh = shoulder, bd = broad, p = polarised, dp = depolarised. [b] ν_1 of BF_4^- doubtless makes a small contribution to the band near 760 cm^{-1}. [c] $\nu_{C\equiv N}$. [d] Symmetrical deformation of CH_3 group bonded to Hg.

of aqueous solutions of $HgCl_2(PEt_3)_2$ [2] was believed to be due to the cation $[Hg(PEt_3)_2(H_2O)_2]^{2+}$.

We wished to prepare some linear complexes of trimethylphosphine with mercury(II) in order to make comparisons with our spectroscopic results for complexes of other metals from this area of the Periodic Table.[8,9] In fact, we find that the complexes, $[HgXPMe_3][NO_3]$ (X = Cl, Br, I or CN) can be readily obtained from the reaction of a stoicheiometric quantity of $AgNO_3,PMe_3$ [10] with the appropriate mercuric halide. $[HgClAsMe_3][NO_3]$ was obtained similarly and all may be converted into the fluoroborate salts by the action of fluoroboric acid. The action of a further molar equivalent of $AgNO_3,PMe_3$ or $AgNO_3,AsMe_3$ gave the cations $[Hg(PMe_3)_2]^{2+}$ or $[Hg(AsMe_3)_2]^{2+}$ respectively. The molar conductivities of $[HgClPMe_3][BF_4]$ and $[Hg(PMe_3)_2][BF_4]_2$ were found to be 127·3 Ω^{-1} cm^{-1} (20·5 °C) and 244·4 Ω^{-1} cm^{-1} (22·0 °C) in aqueous solution in agreement with the ionic formulations. The complexes $[HgMeL][NO_3]$ (L = PMe_3, $AsMe_3$, SMe_2, or pyridine) were prepared either by the reaction of $AgNO_3L$ with HgMeI or of free ligand on $HgMeNO_3$. The action of trimethylstibine only gave metallic mercury.

Vibrational Spectra.—Infrared and Raman spectra below 800 cm^{-1} of the trimethylphosphine complexes $[HgXPMe_3]^+$ (including X = Me) are given in Table 1. We could find no solvent suitable for solution i.r. studies but we have recorded Raman spectra of aqueous solutions of the methyl and chloro-derivatives; from polarisation measurements in these two cases, in conjunction with our previous investigations of trimethylphosphine complexes,[8] we can make definite assignments for all stretching and CPC deformation vibrations of the $HgXPC_3$ skeleton. The XHgP bending mode is likely to be strongly coupled to lattice vibrations in the solid state and only for the methyl compound have we observed it in solution. The PC_3 rocking mode may be associated with weak Raman features around 180 cm^{-1} in the chloro and methyl compounds and a strong Raman band in the cyanide, but no counterpart could be observed for the bromide or iodide, probably because it is obscured by strong skeletal stretching bands in these two cases.

A number of aspects of the solid-state spectra deserve comment. For all compounds except the chloride, features relating to Hg–P stretching are extremely feeble, if observed at all, in the i.r. spectra but the Raman counterpart is quite intense; for the chloro-derivative the reverse is true. Although there is a distinct band near 260 cm^{-1} in the Raman spectra, corresponding to the asymmetric deformation of the PC_3 group, a corresponding i.r. band was observed only in the methyl compound. For the cyanide, an additional band at 274 cm^{-1} probably arises from Hg–C–N bending; one such mode is identified at 276 cm^{-1} in $Hg(CN)_2$.[11]

Above 800 cm^{-1} the trimethylphosphine features closely resemble those in $AuXPMe_3$ and are not listed here. For $[HgMePMe_3]^+[NO_3]^-$, the features related to the nitrate ion in the i.r. spectrum are 1370 (very strong, broad), 1040 (weak) and 816 cm^{-1} (weak—medium). The 1040 cm^{-1} band relates to the symmetric stretching vibration which is not active in the free ion but can be rendered active in solids because of lattice symmetry. The other two bands are typical for ionic nitrates.[12] The spectra of the other nitrate salts studied here are closely comparable in this respect.

The Hg–Cl stretching bands observed in the i.r. and Raman spectra of solid $[HgClPMe_3]^+$ are not coincident within experimental error and both are some 10 cm^{-1} higher for the fluoroborate salt; for aqueous $HgClPMe_3BF_4$, the Raman spectrum shows the band at 324 cm^{-1}. We have remeasured the solid-state Raman spectrum of HgMeCl and find Hg–C and Hg–Cl stretching frequencies at 555 and 290 cm^{-1} respectively, essentially in agreement with Kohlrausch [13] but subsubstantially different from the solid-state infrared frequencies [14] 546 and 313 cm^{-1}. The crystal structure of this compound belongs to the space group D^7_{4h} (ref. 15) with two molecules per centrosymmetric unit cell; thus, theoretically there should not be coincidence between i.r. and Raman spectra and the observations are in accordance with this. It is worth noting that the effect on the Hg–Cl frequency is much greater than on the Hg–C frequency. We regard the non-coincidence observed here for $[HgClPMe_3]^+$ as being of similar crystal-structure origin and not as an indication of a more complex structure for the cationic unit such as a chloro-bridged dimer which would require two Hg–Cl stretching frequencies in both i.r. and Raman spectra. Similar instances of lack of coincidence can be found in most of the other compounds and are similarly explainable. Recognising its limitation, a C_{3v} description is employed in Table 1. We note that a 4 cm^{-1} discrepancy between i.r. and Raman Au–Cl stretching frequencies in solid $AuClPMe_3$ had been regarded by us previously [8] as experimental error, but is more probably an example of the same effect. In $[HgBrPMe_3]^+$ we describe the most intense Raman feature near 200 cm^{-1} as Hg–Br stretching, but as for $AuBrPMe_3$ [8] there must be considerable mixing between this and the symmetric deformation vibration of the ligand. The assignments for $[HgMeAsMe_3]^+[NO_3]^-$ clearly follow from the Raman spectrum in water and from previous work; [8] the only skeletal fundamental not identified is the ligand rocking

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mode which may be obscured by the symmetric deformation feature. The interpretation of the spectrum of solid $[HgClAsMe_3]^+[NO_3]^-$ follows obviously; again Hg–Cl frequencies are not coincident between the i.r. and Raman spectra. The details for these compounds are included in Table 1.

TABLE 2

Infrared and Raman spectra (below 800 cm^{-1}) of $[HgMeSMe_2]^+[NO_3]^-$

	I.r.	R	R in H_2O
$Hg–CH_3$ rock $A' + A''$	790s,bd		
$S–C_2$ str (asym) A''	743m	731wm	729wm,dp
$S–C_2$ str (sym) A'	678s	680m	675m,p
Hg–C str	553s	554s	546vs,p
Hg–S str	302s	304m	302m,p
SC_2 def	279s	277m	291m,p
C–S–Hg bend	181vw	180wm,bd	179w,bd,dp
{S–Hg–C bend	120m,bd		125w,bd
{and lattice modes	80m,bd		
ν_4 NO_3^-	706s		
Limit of study	(40)	(100)	(100)

TABLE 3

Infrared and Raman spectra (below 600 cm^{-1}) of $[HgMe(C_5H_5N)]^+[NO_3]^-$

	I.r.	R	R in H_2O
ν(Hg–C)	562s	563s	561s,p
ν(Hg–N)	208wm	212m	206m,p
Other bands	556w,sh	182w	
	423s	160m	165m,bd,dp
	388ms	139m	
	358w	~90sh	
	98m	74s	
	60m,bd		
Limit of study	(40)	(50)	(120)

In Table 2 we record our observations for skeletal features of $[HgMeSMe_2]^+[NO_3]^-$: this is simply an amplification of previous work on an aqueous solution presumed to contain this species.[3]

TABLE 4

Infrared and Raman spectra (below 800 cm^{-1}) of complex cations $[Hg(YMe_3)_2]^{2+}$ [Y = P or As]

	$[Hg(PMe_3)_2][NO_3]_2$			$[Hg(PMe_3)_2][BF_4]_2$			$[Hg(AsMe_3)_2][NO_3]_2$		$[Hg(AsMe_3)_2][BF_4]_2$	
	I.r.	I.r. in $MeNO_2$	R	I.r.	R	R in H_2O	I.r.	R	I.r.	R
$Y–C_3$ str. (asym)	762s	†	766s	765s	769s	771s,p	630s	634m	634s	638m
$Y–C_3$ str (sym)	675m	†	679s	673s	676s	679s,p	594m	602s	594m	598s
$Hg–Y_2$ str (asym)		359								
$Hg–Y_2$ str (sym)			356s		355s	353s,p		250w		252w
YC_3 def (asym)			267m		266m	266m,dp		223m		221w
YC_3 def (sym)	213w		192s	214w	193s	186s,p		159m		159m
YC_3 rocking						183bd,dp				
{Y–Hg–Y bend	120s,bd		137w,bd	105s,bd			115s,bd		99s,bd	
{and lattice modes	87s,bd		98m	67sh			81s,bd		62m	
Anion	709w	†			*a*		708w	710vw		769w
				522s					522s	
				355vw					355vw	
Limit of study	(40)	(200)	(80)	(40)	(130)	(110)	(40)	(140)	(40)	(140)

Internal modes of the ligand are tabulated side by side although theoretically coincidence between infrared and Raman spectra is not predicted.

† Not investigated. [a] Probably contributes to band at 769 cm^{-1}.

In Table 3 our observations below 600 cm^{-1} for $[HgMepy]^+[NO_3]^-$ are recorded. The two features observed to be polarised in the Raman spectrum of the aqueous solution, 561 and 206 cm^{-1}, must be Hg–C and Hg–N stretching respectively.

The frequencies found for complex cations $[Hg(PMe_3)_2]^{2+}$ and $[Hg(AsMe_3)_2]^{2+}$ are given in Table 4. The solid-state Raman spectrum of $[Hg(PMe_3)_2][BF_4]_2$ shows no major difference from that of an aqueous solution. Our previous work has shown that the asymmetric PC_3 stretching frequencies are higher than the symmetric ones and hence we attribute the partially polarised nature of the Raman band at 771 cm^{-1} to the contribution from the spherically symmetrical BF_4^- stretching vibration. The 186 cm^{-1} band is polarised but there is a change of contour between the spectra under the different polarisation conditions, suggesting that the depolarised rocking vibration underlies the polarised, more intense symmetric deformation feature. From selection rules and from observations on *cis*- and *trans*-square planar complexes $MX_2(YMe_3)_2$ (M = Pt or Pd; X = Cl, Br, or I; Y = P or As) we expect the number of YC_3 symmetric stretching and M–Y stretching bands to provide clear distinction between linear and bent MY_2 structures. Only a single YC_3 symmetric stretching feature and never more than one feature reasonably assignable as MY_2 stretching is observed. This is strong indication of linearity. The $Hg–P_2$ symmetric stretching frequency is at 353 cm^{-1} in aqueous $[Hg(PMe_3)_2][BF_4]_2$. Although the solid salts did not clearly show HgY_2 stretching features in the i.r. region, a nitromethane solution of $[Hg(PMe_3)_2][NO_3]_2$ showed a band at 359 cm^{-1} which must be due to this vibration. In spite of anion and solvent differences this seems to be sufficiently different from the Raman frequency to add support for the conclusion of linearity about mercury.

^1H *N.m.r. Spectra.*—The n.m.r. parameters derived from ^1H n.m.r. studies of 0·2M-solutions of the complexes in D_2O are given in Table 5. The cations $[HgXPMe_3]^+$ show the expected doublet with ^{199}Hg (17% abundance) satellites except that the spectrum of the methyl derivative is rather broad at 30° but is much better resolved at 0 °C suggesting that exchange of phosphines is occurring. The cyanide and iodide derivatives had a marked tendency to disproportionate in solution to give $[Hg(PMe_3)_2]^{2+}$ and presumably HgX_2.

The values for $[HgPhPMe_3][NO_3]$ were obtained for a solution of stoicheiometric quantities of $AgNO_3,PMe_3$ and HgPhCl in deuterionitromethane which had been heated for 5 min and filtered. This also showed the presence of $[Hg(PMe_3)_2]^{2+}$ which probably explains why the desired product could not be isolated. The ion $[Hg(PMe_3)_2]^{2+}$ shows a triplet, typical of a system containing two strongly coupled phosphine ligands.[16] However, the central line is much broader than in complexes such as *trans*-$PtX_2(PMe_3)_2$ [9] indicating that $^2J_{PP}$ is significantly less in this linear mercury system. The ^{199}Hg satellites of the $AsMe_3$ resonances are very broad, *e.g.* for $[HgClAsMe_3]^+$, the satellites have a width at half height of 3 Hz compared with that of the main peak of 0·8 Hz. A similar, but less marked, effect occurs with the ^{195}Pt satellites of $[PPh_4][PtCl_3AsMe_3]$ for which measurements at various magnetic fields showed that the broadening increased at lower magnetic fields.[17] The effect is, therefore, ascribed to relatively rapid relaxation of ^{195}Pt spin *via* scalar coupling to the ^{75}As nucleus.[18] This is effective because the relaxation time of the quadrupolar arsenic nucleus is very short (*ca.* 10^{-6} s), its coupling to ^{195}Pt is large and the frequency difference between ^{75}As and ^{195}Pt, even at 23·5 kgauss, is not too large (4 MHz). The coupling of arsenic to ^{199}Hg should be greater than to ^{195}Pt (*cf* ^{31}P) [19] and the frequency difference between ^{75}As and ^{199}Hg is only 0·75 MHz at 23·5 kgauss, so that the effect should be greater for ^{199}Hg. As the frequency difference between ^{127}I and ^{199}Hg is 2·1 MHz, the same process can explain the broadening of the satellites in the ^1H n.m.r. of $[HgIPMe_3][NO_3]$ and may apply to HgIMe instead of, or as well as, exchange of methyl groups.[4,20] The values for $HgPMe_3AsMe_3{}^{2+}$ were obtained from a 1 : 1 solution of $[Hg(PMe_3)_2]^{2+}$ and $[Hg(AsMe_3)_2]^{2+}$. The $AsMe_3$ features are very broad due to exchange between $HgPMe_3AsMe_3$ and $[Hg(AsMe_3)_2]^{2+}$ so that data were only obtainable for the PMe_3 resonance. For the latter, the ^{199}Hg satellites are broad because of the relaxation of ^{199}Hg by ^{75}As.

TABLE 5

^1H N.m.r. parameters of PMe_3 and $AsMe_3$ mercury complexes

	τ_{YMe_3}	$^2J_{PH}$	$^3J_{HgH}$
$[HgClPMe_3][BF_4]$	8·08	13·8	121·9
$[HgBrPMe_3][BF_4]$	8·10	13·7	117·0
$[HgIPMe_3][BF_4]$	8·13	13·7	106·4
$[HgCNPMe_3][BF_4]$	8·16	13·6	99·6
$[HgPhPMe_3][NO_3]$	8·19	12·5	50·8
$[HgMePMe_3][NO_3]$	8·28	12·2	43·9
$[Hg(PMe_3)_2][BF_4]_2$	8·15	10·6 [c]	84·3
$[HgPMe_3AsMe_3][BF_4]_2$	8·14	13·3	*ca.* 92
$[HgClAsMe_3][BF_4]$	8·08		91·9
$[HgCH_3AsMe_3][NO_3]$	8·32		
$[Hg(AsMe_3)_2][BF_4]_2$	8·16		*ca.* 64

^1H N.m.r. parameters of $HgMeL{\cdot}NO_3$

L	τ_{HgMe}	$^2J_{HgH}$
PMe_3 [a]	9·26	167·3
$AsMe_3$	9·09	*ca.* 180
SMe_2 [b]	8·94	220·7
py	8·97	226·0

[a] $^3J_{PH} = 5{\cdot}2$ Hz. [b] $\tau_{SMe_2} = 7{\cdot}23$. [c] $|^2J_{PH} + {}^4J_{PH}|$.

DISCUSSION

For comparison of the *trans*-influence of different ligands in a given situation, linear complexes of Hg^{II} provide examples in which there are no influences from other groups present to confuse observations. Hatton, Schneider, and Siebrand [4] have previously studied a fairly wide range of complexes HgMeX and discussed trends in $^2J_{HgH}$ and chemical shift. Their series only included two neutral donors, D_2O and pyridine and adding our results for the wider set of neutral donors, we have the following order for $^2J_{HgH}$: $CH_3{}^- < Ph^- \ll PMe_3 < CN^- \approx AsMe_3 < I^- < OH^- < Br^- < Cl^- < SMe_2 < py < D_2O$. As for $^3J_{Pt-H}$ in trimethylphosphine complexes,[9] $^2J_{HgH}$ seems to give a measure of the metal–ligand bond strength or at least the *s*-orbital contribution to it. The values of ν(Hg–C) generally follow this series but with some marked exceptions, *e.g.* CN which can be explained as the result of mixing of $\nu(Hg-CH_3)$ with ν(Hg–CN). The possibility of such mixing makes quantitative discussions on ν(Hg–C) difficult but some deductions are valid. Thus, since PMe_3 cannot have an effective mass greater than Br^-, the value of 541 cm^{-1} for ν(Hg–C) *trans* to PMe_3 compared to 546 cm^{-1} *trans* to Br must imply a weaker Hg–C bond in the former case. Since the methyl group can only be σ-bonded to the metal, the σ contribution to the Hg–X bond is likely to affect it most. Thus the trend in $^2J_{HgH}$ should be the reverse of the σ-donor abilities of the group X.

For $[HgXPMe_3]^+$, $^3J_{HgH}$ follows the same order as $^2J_{HgH}$ of the methyl-mercury derivatives. In fact, considering the sensitivity of $^2J_{HgH}$ to solvent changes *etc*,[4] there is a surprisingly good linear relationship between $^2J_{HgH}$ and $^3J_{HgH}$, namely $^3J_{HgH} = (0{\cdot}67 \pm 0{\cdot}03)\ ^2J_{HgH} - (24{\cdot}3 \pm 5{\cdot}4)$. This implies that changes in the mercury–donor atom bond dominate both couplings and that the Hg–C and Hg–P bonds respond in a similar way to the *trans*-ligand. The behaviour of ν_{HgP} is in agreement with that of $^3J_{HgH}$. Thus whilst $^3J_{HgH}$ will only directly be related to the σ-part of the Hg–P bond, the similarity to the behaviour of the Hg–C bond suggests that the Hg–P bond is primarily a σ bond.

From the vibrational spectra we can compare the isoelectronic species $[HgClPMe_3]^+$ and $[AuClPMe_3]$;[8] the difference in the mass of the central atoms is so

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small that we can directly compare the vibrational frequencies. Of particular note is that the M–Cl frequencies for solutions are **326** cm^{-1} for M = Au and **325** for M = Hg and M–P frequencies **383** for M=Au and **374** for M=Hg. The disparity between these two sets of figures suggests that the metal–phosphorus bond is significantly weakened by substituting Hg^{II} for Au^{I}. Since the increased positive charge might have been expected to enhance σ-accepting power for mercury, this observation suggests that there is a significant π contribution to the Au–P bond. We are a little surprised that the M–Cl frequencies are not more sensitive to this change and indeed that there appears to be a very slight frequency lowering. In the case of the i.r. spectrum of solid $[HgClPMe_3][BF_4]$ the frequencies were fairly close to those observed for solution. In solid $[HgClAsMe_3][BF_4]$, Hg–As was **251** and Hg–Cl **347** cm^{-1} compared with solution i.r. values for $AuClAsMe_3$ of Au–As **269** and Au–Cl **335** cm^{-1} and this, if anything, implies more significant contribution from π bonding in the trimethylarsine–gold complexes than in the trimethylphosphine ones.

TABLE 6

Characterising data for complexes containing $[HgXL]^+$ or $[HgL_2]^{2+}$ ion

Compound	% C Calc.	% C Obs.	% H Calc.	% H Obs.	% N Calc.	% N Obs.	% Yield	M.p. °C
$[HgMePMe_3][NO_3]$	13·55	13·85	3·4	3·45	3·95	3·85	*ca.* 100	185—186
$[HgMeAsMe_3][NO_3]$	12·05	12·45	3·05	3·0	3·5	3·7	*ca.* 100	159—160
$[HgMeSMe_2][NO_3]$	10·6	10·6	2·65	3·0	4·1	3·8	*ca.* 90	116—118(d.)
$[HgMePy][NO_3]$	20·2	20·25	2·25	2·6	7·85	7·6	*ca.* 100	193—195
$[HgClPMe_3][NO_3]$	9·6	9·65	2·4	2·35	3·75	3·6	26	178—180
$[HgClPMe_3][BF_4]$	9·0	9·15	2·25	2·55			71	275—278
$[HgBrPMe_3][NO_3]$	8·6	8·65	2·15	2·25	3·35	3·6	81	187—190
$[HgBrPMe_3][BF_4]$	8·1	8·2	2·05	1·9			91	266—269
$[HgIPMe_3][NO_3]$	7·75	7·95	1·95	2·0	3·0	3·0	41	156—159
$[HgIPMe_3][BF_4]$	7·35	7·35	1·85	1·8			87	238—240
$[HgCNPMe_3][NO_3]$	13·15	13·25	2·5	2·45	7·7	7·8	50	198—200
$[HgCNPMe_3][BF_4]$	12·3	12·25	2·35	2·3	3·6	3·8	81	249—251
$[HgClAsMe_3][NO_3]$	8·6	8·6	2·15	2·2	3·35	3·3	42	215—217
$[HgClAsMe_3][BF_4]$	8·15	8·0	2·05	2·1			85	187—190(d.)
$[Hg(PMe_3)_2][NO_3]_2$	15·1	15·1	3·8	3·8	5·9	5·75	61	168—170
$[Hg(PMe_3)_2][BF_4]_2$	13·7	13·85	3·45	3·4			88	290—292
$[Hg(AsMe_3)_2][NO_3]_2$	12·75	12·55	3·2	3·1	4·95	4·9	52	175—177
$[Hg(AsMe_3)_2][BF_4]_2$	11·7	11·4	2·95	2·7			78	283—285

EXPERIMENTAL

I.r. spectra were recorded as Nujol mulls from 4000—200 cm^{-1} on a Perkin-Elmer 225 grating spectrophotometer, and below 200 cm^{-1} as Nujol/vaseline mulls on a Grubb-Parsons I.R.I.S. interferometer. The frequencies are accurate to ±1 cm^{-1} except where bands are broad.

The Raman spectra were recorded, in the main, on a Cary 81 Raman spectrophotometer with 632·8 nm Spectrophysics Model 125 helium–neon laser excitation. Some were measured using a Spex Ramalog Raman spectrophotometer with 488·0 nm Spectrophysics model 140 argon ion laser excitation, or with a Coderg PHO spectrophotometer with 647·1 or 568·2 nm excitation from a Coherent Radiation Laboratories Model 52MG krypton–argon ion laser. Frequencies are accurate to ±2 cm^{-1}.

The ^{1}H n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer in HA mode at 30 °C unless otherwise indicated. For D_2O solutions HDO was used as lock and the internal reference used was sodium 3-(trimethylsilyl)-1-propanesulphonate; tetramethylsilane was used as reference for the investigation in CD_3NO_2. Chemical shifts and large coupling constants were measured with the aid of a frequency counter and are accurate to ±0·2 Hz.

Preparations.—Complexes of the type $[LHgX]^+[NO_3]^-$. These complexes were prepared by treatment of the appropriate mercuric halide (cyanide) with an equimolar quantity of trimethylphosphine (arsine)–silver nitrate in ethanol.

The product in all cases except the iodo-complex was precipitated with the silver halide (cyanide), from which it was separated by continuous extraction with acetone. The complexes were recrystallised from acetone and dried *in vacuo*.

The iodo-complex was soluble in warm ethanol and was, therefore, separated from the silver iodide by filtration, and recrystallised from ethanol. This complex decomposed *in vacuo*.

Complexes of the type $[LHgX]^+[BF_4]^-$. The fluoroborates were prepared by treatment of a suspension of the appropriate nitrate complex, in acetone, with a slight excess of aqueous fluoroboric acid. The fluoroborates were crystallised from acetone, after filtration, by the addition of ether. All except the iodo-complex were dried *in vacuo*.

Ions of the type L_2Hg^{2+} ($L = PMe_3$ or $AsMe_3$). The bistrimethylphosphine (arsine) complexes were prepared, as their nitrates, by stirring a suspension of $LHgClNO_3$ in ethanol, overnight, with an equimolar solution of the corresponding silver nitrate adduct. The products, being soluble in ethanol, were recrystallised from it after removing silver chloride by filtration.

The fluoroborates were prepared, as before, by treatment of the nitrates in acetone with an excess of aqueous fluoroboric acid. All complexes were dried *in vacuo*.

Complexes of type $LHgMeNO_3$ ($L = PMe_3$, $AsMe_3$). An excess of MeHgI was stirred with trimethylphosphine (arsine)–silver nitrate in water for 3 h. The solution was filtered to remove silver iodide and excess of MeHgI; the compound was crystallised by removal of water at room temperature under reduced pressure. It was washed with acetone and dried in air.

Complexes of type $LHgMeNO_3$ ($L = SMe_2$, py). An acetone solution of $MeHgNO_3$ was treated with a slight excess of dimethyl sulphide (pyridine) also in acetone. The white precipitate formed was separated by decantation and then washed with acetone and ether.

Characterising data are presented in Table 6. For the methylmercury compounds, agreement between observed and calculated analytical data is not always very good but in the cases where sharp n.m.r. spectra are obtained (the py, SMe_2, and PMe_3 compounds) there are no features additional to those of the compound in question and integration ratios are consistent with the formulation given, within the accuracy of this method ($\pm 3\%$).

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