Vibrational and Nuclear Magnetic Resonance Studies of the Formation of Alkylmercury(II) Halide Complex Anions

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Vibrational-spectroscopic measurements show the formation of $[HgMeCl_2]^-$ from [HgMe(Cl)] and $[NBu^n_4]Cl$ in benzene, chloroform, dichloromethane, tetrahydrofuran, and acetonitrile but not in methanol or water. Similar formation of complex anions occurs for [HgMe(X)] (X = Br, I, or SCN) and for [HgR(X)] (RX = EtCl, Pr^{n}Cl, Bu^{n}Cl, EtBr, Pr^{n}Br, Bu^{n}Br, or EtI). The effects of the addition of halide ions on $\delta(^{199}Hg)$, measured by ^1H-$\{^{199}Hg\}$ INDOR, and $^2J(HgH)$ have been investigated and compared with the effects of solvents on these parameters. It is suggested that the complexes have an essentially linear RHgX group with the second halide much more weakly attached in the equatorial plane.

THE conclusions drawn from the several studies of the ability of organomercury(II) compounds to form anionic complexes with halides or pseudohalides are in conflict on many points. Thus Barbieri and Bjerrum,[1] from solubility measurements and polarographic studies on [HgEt(X)] (X = Cl, Br, I, or SCN) in the presence of additional X^-, concluded that in aqueous solution complexes were only formed when X = I or SCN. From similar studies on [HgR(SCN)] (R = Et or Bu^i) in 50% aqueous methanol they found that the favoured complex is $[HgR(SCN)_2]^-$ whereas in aqueous solution it is of the type $[HgEtX_3]^{2-}$. Further studies on [HgEt(Cl)] [2] and [HgEt(Br)] [3] using ion-exchange paper chromatography suggested some complex formation but with much lower stability constants than for iodide. Plazzogna *et al.*[4] made a spectrophotometric investigation of the ionization of Ph_3CCl in acetonitrile in the presence of [HgR(Cl)], to determine the formation constants of $[HgRCl_2]^-$. They concluded that higher complexes $[HgRCl_3]^{2-}$ were not formed, in contrast to the conclusions from studies in water.[2] They also found that, whilst complex formation occurred when R = Me or Et, it did not for R = Pr or Ph. This may be compared with the solubility studies of Toropova and Saikina [5] on [HgR(SCN)] in the presence of $[SCN]^-$ in aqueous solution which showed that complex formation was more complete when R = Pr^n than for Et or Me.

These stability-constant studies all employ methods in which the nature of the complex mercury species is implied indirectly. Vibrational and n.m.r. spectroscopic methods allow specific features of the organomercury complex to be observed. Although cyanide forms stronger complexes with Hg^{II} than halides or thiocyanate, addition of a large excess of cyanide has no effect on the Raman spectrum of [HgMe(CN)] in aqueous solution indicating that no complex anions are formed.[6] Indeed, only very minor changes in its spectrum were observed when dimethyl sulphide, a good ligand towards mercury, was used as solvent in place of water.[7] Relf *et al.*[8] studied the system [HgMe(SCN)] + $[SCN]^-$ in water and methanol. They found that, even under the most extreme conditions {1 : 8 for [HgMe(SCN)] : Li[SCN] in methanol and 1 : 40 for [HgMe(SCN)] : K[SCN] in water}, the maximum shift is only 5 cm^{-1} for the CN stretch and 9 cm^{-1} for the HgS stretch whilst the HgC stretching vibration is invariant. Furthermore, the changes in $^2J(^{199}Hg^1H)$ are very small and in the opposite sense to those predicted for the formation of a covalently bonded anion. They concluded that the mode of interaction which is deduced from the stability-constant studies is of the ion–dipole rather than covalent type. Recently,[9] we compared the vibrational spectra of [HgMe(X)] (X = Cl, Br, or I) in the solid state with those of benzene solutions. The lower HgC and HgX stretching wavenumbers observed for the solid can be interpreted as a result of the interaction between mercury and halide ions in adjacent molecules.

We felt that part of the confusion that exists between the various studies of the complexing of [HgMe(X)] resulted from the use of different media. In particular, where the solvent itself can act as a ligand or can effectively solvate X^- it may have a considerable influence on the nature and position of the equilibrium. We have used vibrational and n.m.r. spectroscopy to test this view. The chemical shifts of peripheral atoms and coupling constants over more than one bond can be influenced by factors other than the electronic state of the metal.[10] A better guide to the effect of added halide on [HgR(X)] might be the response of a metal nucleide, so in addition to the usual ^1H measurements we have studied the ^{199}Hg chemical shift by means of ^1H-$\{^{199}Hg\}$ INDOR. In the course of our studies, Lucchini and Wells [11] reported formation-constant studies on the complex formation between methylmercury(II) chloride and bromide and the appropriate lithium halide in ethanol

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[1] R. Barbieri and J. Bjerrum, *Acta Chem. Scand.*, 1965, **19**, 469.

[2] G. Rizzardi, R. Pietropaolo, and R. Barbieri, *Gazzetta*, 1966, **96**, 1371.

[3] G. C. Stocco, E. Rivarola, R. Romeo, and R. Barbieri, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2409.

[4] G. Plazzogna, P. Zanella, and L. Doretti, *J. Organometallic Chem.*, 1971, **29**, 169.

[5] V. F. Toropova and M. K. Saikina, *Russ. J. Inorg. Chem.*, 1965, **10**, 631.

[6] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1966, **62**, 1423.

[7] J. R. Hall and J. C. Mills, *J. Organometallic Chem.*, 1966, **6**, 445.

[8] J. Relf, R. P. Cooney, and H. F. Henneike, *J. Organometallic Chem.*, 1972, **39**, 75.

[9] P. L. Goggin, G. Kemeny, and J. Mink, *J.C.S. Faraday II*, 1976, 1025.

[10] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc. (A)*, 1969, 2134.

[11] V. Lucchini and P. R. Wells, *J. Organometallic Chem.*, 1975, **92**, 283.

using similarly obtained ^{199}Hg chemical shifts. Their work provides a useful complement to the results reported here.

RESULTS AND DISCUSSION

Vibrational Spectra.—The vibrations of [HgMe(X)] (X = Cl, Br, or I) which are most significantly affected by the intermolecular interaction in the solid state are the symmetrical methyl deformation, the HgC stretch, and the HgX stretch.[9] In view of the difficulties arising from interference by bands of the solvent and the tetra-alkylammonium cations, we have confined our attention to these vibrations.

TABLE 1

Some vibrational fundamental wavenumbers of [HgMe(X)] (X = Cl, Br, or I) in different environments [a]

System	Medium	Wavenumber/cm^{-1}			
		CH_3 sym def.	HgC str.	HgX str.	Low energy
[HgMe(Cl)]	$CDCl_3$	1 194	555	334	
[HgMe(Cl)] + [NBu$^{n}_{4}$]Cl		1 184	539	304	105
[HgMe(Cl)]	C_6H_6 or C_6D_6	1 196	554	335	
[HgMe(Cl)] + [NBu$^{n}_{4}$]Cl		*b*	535	305	
[HgMe(Cl)]	CH_2Cl_2	1 199	556	331	
[HgMe(Cl)] + [NBu$^{n}_{4}$]Cl		1 179	536	305	
[HgMe(Cl)]	thf [c]	1 194	553	330	
[HgMe(Cl)] + [NBu$^{n}_{4}$]Cl		1 174	533	304	
[HgMe(Cl)]	MeCN	1 196	555	328	
[HgMe(Cl)] + [NBu$^{n}_{4}$]Cl		1 178	536	305	
[HgMe(Cl)]	MeOH	1 196	554	327	
[HgMe(Cl)] + [NBu$^{n}_{4}$]Cl		1 196	553	325	
[HgMe(Cl)]	Water	1 198	555	313	
[HgMe(Cl)] + NaCl		1 197	555	313	
[HgMe(Cl)]	Solid	1 190	551	303	68
[HgMe(Br)]	$CDCl_3$	1 194	545	224	
[HgMe(Br)] + [NBu$^{n}_{4}$]Br		1 172	532	209	75
[HgMe(Br)]	Solid	1 180	543	208	51
[HgMe(I)]	$CDCl_3$	1 183	534	182	
[HgMe(I)] + [NBu$^{n}_{4}$]I		1 162	516	165	66
[HgMe(I)]	Solid	1 167	528	169	44
[HgMe(SCN)]	CH_2Br_2	1 185 [d]	540	287	
[HgMe(SCN)] + [NPr$^{n}_{4}$][SCN]		1 178 [e]	536	277	

[a] From Raman spectra for solutions except for the low-energy band which was observed in the i.r. For solids, values are the mean of Raman- and i.r.-active modes (which are not coincident for these centrosymmetric unit cells [9]), except for the low-energy band which is the Raman-active transverse translatory lattice mode. [b] Obscured by solvent. [c] thf = Tetrahydrofuran. [d] ν(CN) at 2 134 cm^{-1}. [e] ν(CN) at 2 128 cm^{-1}.

For [HgMe(Cl)] in $CDCl_3$, these vibrations are observed as polarized Raman bands at 1 194, 555, and 334 cm^{-1} respectively. Addition of 1 mol equivalent of [NBu$^{n}_{4}$]Cl leads to a spectrum in which the major features now occur at substantially lower wavenumbers (1 184, 539, and 304 cm^{-1}) while weaker bands can still be observed in the original positions. The latter features completely disappear when another 2 equivalents of [NBu$^{n}_{4}$]Cl are added but no changes occur in the wavenumbers of the major bands. Where a sequence of anions of increasing negative charge has been studied, there is a progressive lowering of the wavenumbers of comparable modes as the charge increases {*e.g.* $[InCl_4]^-$, ν_1 at 321 cm^{-1};[12] $[InCl_5]^{2-}$, sym $InCl_4$ stretch at 294 cm^{-1};[13] $[InCl_6]^{3-}$, ν_1 at 257 cm^{-1} (ref. 13)}. Accordingly, we concluded that the only complex formed has the stoicheiometry $[HgMeCl_2]^-$. The findings for the systems [HgMe(Br)] + [NBu$^{n}_{4}$]Br and [HgMe(I)] + [NBu$^{n}_{4}$]I are entirely analogous (Table 1). Our attempts to isolate [NBu$^{n}_{4}$][HgMeX$_2$] from such solutions only resulted in the precipitation of [HgMe(X)].

In view of the conflicting aspects of previous work, we have investigated the methylmercury(II) chloride system in a number of solvents. The results (Table 1) indicate the formation of $[HgMeCl_2]^-$ in benzene, dichloromethane, tetrahydrofuran, and acetonitrile although there is some variation in the wavenumbers of its CH_3 deformation. Whilst the frequencies of [HgMe(Cl)] in methanol show no great differences to the other solvents, the addition of [NBu$^{n}_{4}$]Cl leaves them essentially unchanged. The same applies to the addition of sodium chloride to [HgMe(Cl)] in water, but in this case the HgCl stretch is substantially lower than in other solvents, perhaps as a result of hydrogen bonding between chloride and water. Thus complex formation with halide, at least of the type seen with the less-polar solvents, does not occur to any significant extent in these last two solvents. The results are summarized in Table 1 where values for solid [HgMe(X)] are included for comparison.

Whilst the vibrations of [HgMe(SCN)] in dichloro- or dibromo-methane solution also move to lower wavenumbers on addition of [NPr$^{n}_{4}$][SCN] (Table 1), the change is only about one third of that observed in the halide systems. The results were similar to those reported by Relf *et al.*[8] for the system [HgMe(SCN)] + Li[SCN] in methanol, but much lower relative concentrations of added $[SCN]^-$ were required. Like them, we observed indications of $[Hg(SCN)_4]^{2-}$ in the spectra [2 110(sh) and 236 cm^{-1}] implying an equilibrium such as

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[12] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 1960, 4473.

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

(1). In contrast, the vibrations of dimethylmercury(II) in dichloromethane were unaffected by the addition of an

$$2[\mathrm{HgMe(SCN)}] + 2[\mathrm{SCN}]^- \rightleftharpoons 2[\mathrm{HgMe(SCN)_2}]^- \rightleftharpoons [\mathrm{HgMe_2}] + [\mathrm{Hg(SCN)_4}]^{2-} \quad (1)$$

excess of $[\mathrm{NBu^n{}_4}]\mathrm{X}$ suggesting that it does not participate in complex formation with halide.

Since previous workers had proposed that there were marked differences in the complex formation between halides and alkylmercury(II) halides for different alkyl groups, we investigated the effect of $[\mathrm{NBu^n{}_4}]\mathrm{X}$ on the Raman spectra of [HgR(X)] (RX = EtCl, $\mathrm{Pr^nCl}$, $\mathrm{Bu^nCl}$, EtBr, $\mathrm{Pr^nBr}$, $\mathrm{Bu^nBr}$, or EtI) in halogenated hydrocarbon solvents. The results (Table 2) are entirely analogous to those for methylmercury(II) halides implying the formation of $[\mathrm{HgRX_2}]^-$ in all cases.

TABLE 2

The effect of the addition of 1 equivalent of $[\mathrm{NBu^n{}_4}]\mathrm{X}$ on the HgC and HgX stretching vibrations ($\mathrm{cm^{-1}}$) of [HgR(X)] (R = Et, $\mathrm{Pr^n}$, or $\mathrm{Bu^n}$; X = Cl, Br, or I) [a]

System	ν(HgC)	ν(HgX)
[HgEt(Cl)] [b]	526	325
[HgEt(Cl)] + $[\mathrm{NBu^n{}_4}]\mathrm{Cl}$ [c]	514	299
$[\mathrm{HgPr^n(Cl)}]$ [b]	535	325
$[\mathrm{HgPr^n(Cl)}]$ + $[\mathrm{NBu^n{}_4}]\mathrm{Cl}$ [c]	524	300
$[\mathrm{HgBu^n(Cl)}]$ [b]	534	325
$[\mathrm{HgBu^n(Cl)}]$ + $[\mathrm{NBu^n{}_4}]\mathrm{Cl}$ [c]	525	300
[HgEt(Br)] [b]	518	217
[HgEt(Br)] + $[\mathrm{NBu^n{}_4}]\mathrm{Br}$ [d]	505	199
$[\mathrm{HgPr^n(Br)}]$ [b]	526	222
$[\mathrm{HgPr^n(Br)}]$ + $[\mathrm{NBu^n{}_4}]\mathrm{Br}$ [d]	514	196
$[\mathrm{HgBu^n(Br)}]$ [b]	525	211
$[\mathrm{HgBu^n(Br)}]$ + $[\mathrm{NBu^n{}_4}]\mathrm{Br}$ [d]	522	197
[HgEt(I)] [b]	509	173
[HgEt(I)] + $[\mathrm{NBu^n{}_4}]\mathrm{I}$ [d]	494	159

[a] Observed in Raman spectra. [b] In C_6H_6. [c] In CH_2Br_2. [d] In CH_2Cl_2.

Structure of the Complex Anions.—The quantitative n.m.r. measurements described below suggest that $[\mathrm{HgMeX_2}]^-$ is monomeric. If the two HgX bonds are of similar strength (*e.g.* a trigonal structure) then two HgX stretching vibrations should be observed in the region of the HgX stretch of [HgMe(X)]. In each case only one band is seen in the i.r. spectra corresponding exactly to the wavenumbers observed in the Raman spectra. The latter are highly polarized leaving very little residue in the perpendicularly polarized mode, yet there is no indication of a second band. The coincidence of the two HgX stretching vibrations for all the three halides seems improbable, *e.g.* the A_1 vibration of $[\mathrm{HgX_4}]^{2-}$ lies at greater wavenumbers than the T_2 by 38, 13, and 1 $\mathrm{cm^{-1}}$ for X = Cl, Br, and I respectively and the symmetric stretch of $\mathrm{HgX_2}$ in solution is at 50, 60, and 62 $\mathrm{cm^{-1}}$ respectively less than the asymmetric.[14] Furthermore, the requirement for very low Raman intensity for the asymmetric $\mathrm{HgX_2}$ vibration contrasts with the spectra of *cis*-$[\mathrm{PtX_2L_2}]$ where it is usually no less than half the intensity of the symmetric counterpart.[15] Accordingly, we conclude that the second HgX bond is considerably weaker than that in [HgMe(X)] and have looked for its stretching vibration at lower wavenumbers. The far-i.r. spectra in $CDCl_3$ showed relatively strong, fairly sharp, features at 105, 75, and 66 $\mathrm{cm^{-1}}$ (*e.g.* Figure 1) for Cl, Br, and I respectively, which are not apparent in the i.r. spectra of either [HgMe(X)] or $[\mathrm{NBu^n{}_4}]\mathrm{X}$ in solution, although the last species do give a less prominent and broader absorption in this wavenumber region. We believe that these bands arise from HgX stretching to the second, rather weakly bound, halide. They occur at considerably lower wavenumbers than those attributed to HgX bridge stretching [16] in $[\mathrm{Hg_2X_6}]^{2-}$ but *ca.* 50% higher than that assigned as the E_g translatory lattice mode of the solid methylmercury(II) halides. The latter mode is akin to a stretching vibration between mercury and the halogens of adjacent molecules which, in the case of [HgMe(Cl)], lie at the corners of a square plane at a distance of 3.27 Å.[17]

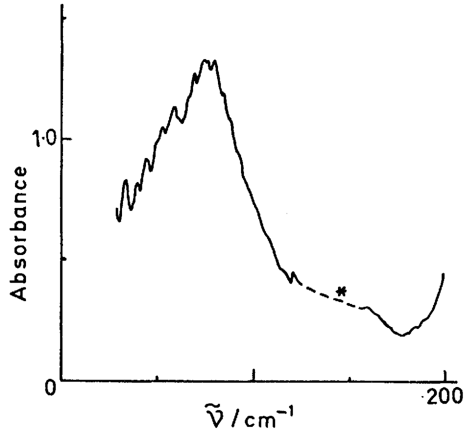

FIGURE 1 Far-i.r. interferometer spectrum of [HgMe(Br)] + $[\mathrm{NBu^n{}_4}]\mathrm{Br}$ (1 : 1 mol ratio) in $CDCl_3$ solution. The region marked with an asterisk was obscured by a beam-splitter interference fringe

In view of the relatively small perturbation of the wavenumbers of [HgMe(X)] on attachment of the second X and the weakness of this attachment, we suggest that the second X is held by a comparatively polar (rather than covalent) bond as shown below. There is likely to be a small amount of bending of the primary CHgX axis as proposed by Brown *et al.*[18] on the basis of the effect of solvents on the value of ^1J(HgC) in [HgMe(X)]. We did not observe the low-energy HgX feature in the Raman spectra. The solvents which promote complex formation all have intense Raman scattering at low Raman shifts which obscures all but the strongest bands, whereas the low-wavenumber HgX stretch would be expected to be rather weak if the bond is relatively polar.[19]

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[14] N. W. Hurst, Ph.D. Thesis, University of Bristol, 1975.

[15] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

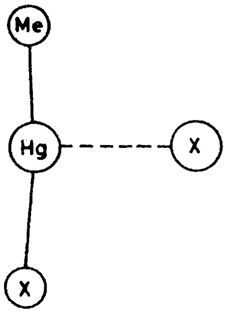
[16] R. M. Barr and M. Goldstein, *J.C.S. Dalton*, 1976, 1593.

[17] D. R. Grdenić and A. I. Kitaigorodski, *Zhur. fiz. Khim.*, 1949, **23**, 1161.

[18] A. J. Brown, O. W. Howarth, and P. Moore, *J.C.S. Dalton*, 1976, 1589.

[19] J. H. B. George, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, 1953, **49**, 375.

N.M.R. Spectra.—The ^{199}Hg chemical shift of [$HgMe_2$] ranges over *ca.* 100 p.p.m. according to the solvent, more-polar media giving shifts to lower frequency.[20]



Kennedy and McFarlane [21] ascribed this to co-ordination of the solvent on the basis that this would reduce imbalance in the *p*-electron distribution and thereby produce a shift to low frequency. However, the term P_u of Jameson and Gutowsky to which they refer has a maximum value of 1 for linearly bonded mercury and $\frac{2}{3}$ when the metal is three- or four-co-ordinate.[22] Consequently, co-ordination of solvent molecules should increase the paramagnetic term causing a shift to high frequency.

The greater tendency of [HgMe(Cl)] towards additional co-ordination does not lead to a greater variation of $\delta(^{199}Hg)$ with solvent (Table 3) than for [$HgMe_2$]. Again the more-polar solvents give the more-negative values with the notable exception of pyridine. In Table 3 the mercury shift is also given for [HgMe(Cl)] in the presence of 1 equivalent of [NBu^n_4]Cl in each of these solvents. For solvents where vibrational spectra show significant formation of [$HgMeCl_2$]$^-$ (benzene, chloroform, dichloromethane, tetrahydrofuran, and acetonitrile) there is a change in $\delta(^{199}Hg)$ of 100—200 p.p.m. to high frequency, the direction predicted by alteration in the value of P_u. For solutions in methanol and water, where there is little if any formation of [$HgMeCl_2$]$^-$, there is only a small change in $\delta(^{199}Hg)$, still to high frequency. In all the cases only one resonance is seen because interconversion between [HgMe(Cl)] and [$HgMeCl_2$]$^-$ is fast on the n.m.r. time scale. We feel confident in associating a change in $\delta(^{199}Hg)$ of the order of 100 p.p.m. to high frequency with co-ordination of an additional halide, and conclude that formation of [$HgMeCl_2$]$^-$ also occurs to a significant extent in dimethyl sulphoxide and pyridine for which we do not have vibrational results.

TABLE 3

Effect of the medium on $\delta(^{199}Hg)$ and ^2J(HgH) of [HgMe(Cl)]

	$\delta(^{199}Hg)$ [b]			^2J(HgH)/Hz		
Solvent [a]	[HgMe(Cl)]	[HgMe(Cl)] + [NBu^n_4]Cl	[HgMe(Cl)] + 2[NPr^n_4][BF_4]	[HgMe(Cl)]	[HgMe(Cl)] + [NBu^n_4]Cl	[HgMe(Cl)] + 2[NPr^n_4][BF_4]
C_6H_6	−813	−625	−814	203.8	217.6	204.2
$CDCl_3$	−810	−715	−856	202.1	214.7	202.5
CH_2Cl_2	−814	−702	−874	205.0	216.0	207.4
thf	−861	−568	−861	208.4	219.4	208.8
MeCN	−862	−691	−847	214.0	220.5	214.7
MeOH	−856	−846	−929	211.5	212.4	207.7
Pyridine	−782	−734	−839	216.5	217.3	212.6
SMe_2O	−853	−739	−867	221.2	222.6	219.4
H_2O–D_2O	−885	−872 [c]	−888 [d]	223.6	225.7 [c]	224.9 [d]

[a] Concentration of Hg was 0.2 mol dm^{-3} except in benzene (0.1 mol dm^{-3}) and water (saturated at 360 K, *ca.* 0.05 mol dm^{-3}). [b] In p.p.m. to high frequency of [$HgMe_2$]. [c] With 5NaCl. [d] With 5 Na[BF_4].

Whilst the low shift of [$HgMe_2$] in pyridine [20] is in keeping with the values for other polar solvents, this solvent results in a particularly high frequency shift for [HgMe(Cl)]. Paralleling the behaviour with added chloride ions, these shifts could be the consequence of co-ordination of pyridine to [HgMe(Cl)] which evidently does not occur with the much weaker acceptor [$HgMe_2$]. Since the other solvents are unlikely to be significantly better ligands towards [$HgMe_2$], it seems unlikely that the shift to low frequency with increasing polarity of the medium is due to co-ordination, at least in the same sense as for halide ions. A possible source is the interaction (*e.g.* of the quadrupole) with the fields produced by the polar solvent molecules in a solvation shell, but there is no simple correlation with dielectric constant or dipole moment. The increases in the magnitudes of ^2J(HgH) and ^1J(HgC) which occur with increasing polarity of the medium [8] presumably have a similar cause rather than co-ordination of the solvent (at least in the case of [$HgMe_2$]). From the similarity of the behaviours of $\delta(^{199}Hg)$ of [$HgMe_2$] and [HgMe(Cl)] in solvents other than pyridine, we feel that these solvents are not co-ordinating significantly to [HgMe(Cl)] either.

With the intention of providing a set of ' control experiments ', we also measured the shift of [HgMe(Cl)] in the presence of [BF_4]$^-$. The results in Table 3 are somewhat baffling. For solutions in benzene, tetrahydrofuran, and water there was no significant effect on $\delta(^{199}Hg)$ as might have been anticipated. However, in chloroform, dichloromethane, pyridine, and methanol there is quite a large shift to low frequency. In these solvents and dimethyl sulphoxide there is also a marked increase in the width of the ^{199}Hg satellites (but not the main resonance), implying a reduction in the mercury spin–lattice relaxation time.

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[20] M. A. Sens, N. K. Wilson, P. D. Ellis, and J. D. Odom, *J. Magnetic Resonance*, 1975, **19**, 323.

[21] J. D. Kennedy and W. McFarlane, *J.C.S. Faraday II*, 1976, 1653.

[22] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.

As expected from the vibrational studies, $\delta(^{199}\text{Hg})$ of $[\text{HgMe}_2]$ was only slightly affected by the presence of chloride ions and then in the sense produced by increased polarity of the media as opposed to co-ordination (Table 4). On addition of 1 equivalent of the appropriate halide, the mercury resonances of [HgMe(Br)], [HgMe(I)], and [HgMe(SCN)] in dichloromethane move to high frequency by a similar amount to that of [HgMe(Cl)]. In contrast to the behaviour of [HgMe(Cl)] but in keeping with previous reports,[1,8] the changes in $\delta(^{199}\text{Hg})$ of [HgMe(SCN)] on addition of $[\text{SCN}]^-$ suggest some formation of a complex anion in aqueous methanol and possibly even in water. The differences in the mercury chemical shifts of [HgR(X)] and [HgR(X)] + $[\text{NBu}^n_4]$X (X = Cl or Br) are similar for R = Me, Et, Pr^n, or Bu^n (Table 5), emphasizing the conclusion from the vibrational experiments that the length of the alkyl chain does not significantly affect the degree of formation of $[\text{HgRX}_2]^-$.

TABLE 4

Effect on $\delta(^{199}\text{Hg})$ and $^2J(\text{HgH})$ of addition of anions to [HgMe(X)] (X = Me, Br, I, or SCN)

System	Solvent [a]	$\delta(^{199}\text{Hg})$ [b]	$^2J(\text{HgH})$/Hz
$[\text{HgMe}_2]$	CH_2Cl_2	−46	104.0
$[\text{HgMe}_2]$ + 4$[\text{NBu}^n_4]$Cl		−48	104.0
[HgMe(Br)]		−915	199.8
[HgMe(Br)] + $[\text{NBu}^n_4]$Br		−782	212.8
[HgMe(I)]		−1 097	188.8
[HgMe(I)] + $[\text{NBu}^n_4]$I		−989	200.9
[HgMe(SCN)]		−705	193.5
[HgMe(SCN)] + $[\text{NPr}^n_4]$[SCN]		−570	203.8
[HgMe(SCN)]	MeOH–D_2O (1 : 1)	−763	*ca.* 204
[HgMe(SCN)] + 5K[SCN]		−679	*ca.* 208
[HgMe(SCN)]	D_2O, *ca.* 360 K	−770	210.8
[HgMe(SCN)] + 5K[SCN]		−722	211.4

[a] Concentration of Hg was 0.2 mol dm^{-3} except for [HgMe-(SCN)] (0.1 mol dm^{-3}) in D_2O. [b] As in Table 3.

TABLE 5

Effect on $\delta(^{199}\text{Hg})$ of addition of halide ions to [HgR(X)] (R = Et, Pr^n, or Bu^n; X = Cl or Br)

	$\delta(^{199}\text{Hg})$ [a]	
System	[HgR(X)] [b]	[HgR(X)] + $[\text{NBu}^n_4]$X [c]
[HgEt(Cl)]	−978	−878
$[\text{HgPr}^n(\text{Cl})]$	−947	−856
$[\text{HgBu}^n(\text{Cl})]$	−944	−848
[HgEt(Br)]	−1 071	−933
$[\text{HgPr}^n(\text{Br})]$	−1 039	−910
$[\text{HgBu}^n(\text{Br})]$	−1 036	−901

[a] As in Table 3. [b] In benzene (saturated). [c] In CH_2Cl_2 (0.2 mol dm^{-3}).

The observation of a single set of resonances with parameters equal to the weighted means of those of the components suggests that the formation constant for $[\text{HgMeX}_2]^-$ can be evaluated from the results for various ratios of [HgMe(X)] to $[\text{NBu}^n_4]$X. However, in view of the sensitivity of the n.m.r. parameters, especially $\delta(^{199}\text{Hg})$, to the medium, there must be considerable uncertainty in the value of a parameter for an individual component in the mixture as opposed to in the pure state. The resulting errors are likely to be greater when the degree of formation is low as for the measurements of Lucchini and Wells[11] on [HgMe(X)] in ethanol. So as to obtain a measure of the magnitude of the formation constant and its variation with halide, we have measured $(\delta^{199}\text{Hg})$ and $^2J(\text{HgH})$ for [HgMe(X)] (X = Cl, Br, I, or SCN) at constant concentrations of mercury in dichloromethane in the presence of various amounts of $[\text{NBu}^n_4]$X. Figure 2 shows a typical plot of the variation of these parameters with added halide. The tangents to the initial and final parts of the curves intersect near to the ratio corresponding to a 1 : 1 adduct, in agreement with the conclusions of the vibrational studies. Assuming the equilibrium (2), we have found the values

$$[\text{HgMe(X)}] + \text{X}^- \rightleftharpoons [\text{HgMeX}_2]^- \qquad (2)$$

of the formation constant, K, which give the best (least-squares) fit to the values of $\delta(^{199}\text{Hg})$ and $^2J(\text{HgH})$ separately. The results are given in Table 6 together with the n.m.r. parameters derived for $[\text{HgMeX}_2]^-$. An almost equally good fit could be achieved assuming the formation of a dimeric anion *via* equation (3). However, the behaviour on dilution in the case of [HgMe(Br)] was

$$2[\text{HgMe(X)}] + 2\text{X}^- \rightleftharpoons [\text{Hg}_2\text{Me}_2\text{X}_4]^{2-} \qquad (3)$$

in accord with the formation of a monomeric adduct rather than a dimer. The values of K derived from $^2J(\text{HgH})$ for a particular system are two to three times those obtained from $\delta(^{199}\text{Hg})$. Qualitatively, this is

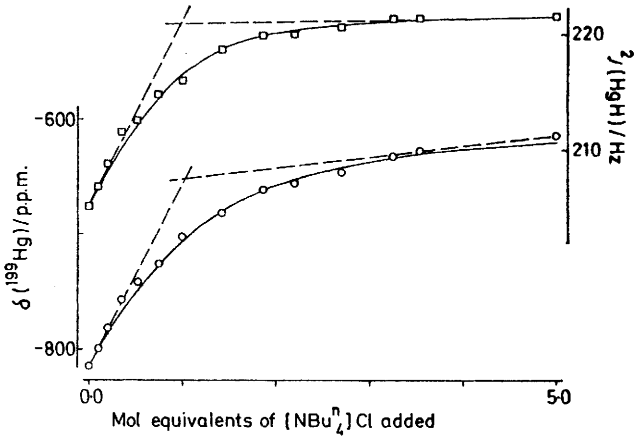

FIGURE 2 Plot of $\delta(^{199}\text{Hg})$ (○) and $^2J(\text{HgH})$ (□) of [HgMe(Cl)] against mol equivalents of $[\text{NBu}^n_4]$Cl added

TABLE 6

Formation constants for $[\text{HgMeX}_2]^-$ (X = Cl, Br, I, or SCN)

X	$\delta(^{199}\text{Hg})$ $[\text{HgMeX}_2]^-$	$\frac{K\,^a}{\text{dm}^3\,\text{mol}^{-1}}$	$^2J(\text{HgH})$/Hz $[\text{HgMeX}_2]^-$	$\frac{K\,^b}{\text{dm}^3\,\text{mol}^{-1}}$
Cl [c]	−596	10.2	222.2	32.5
Br [c]	−688	14.8	219.0	33.3
I [c]	−889	12.2	208.1	28.6
SCN [c]	−506	31.1	206.6	85.6
Cl [d]	−586	18.2	223.5	56.8

[a] From measurements of $\delta(^{199}\text{Hg})$. [b] From measurements of $^2J(\text{HgH})$. [c] In CH_2Cl_2. [d] In CD_3CN.

understandable since addition of $[NBu^n_4]X$ should also increase the polarity of the medium. The resulting trend of $\delta(^{199}Hg)$ to low frequency would counteract the shift produced by complexation, giving an apparently low value of *K*, whereas the two effects are in the same sense for $^2J(HgH)$ resulting in a high value of *K*. The discrepancies are a good illustration of the errors that can arise from the assumption that the parameters of individual components do not alter as the composition of the mixture is varied.

The true value of the formation constant should lie between the values obtained from $\delta(^{199}Hg)$ and $^2J(HgH)$. Within this range of uncertainty there is no difference in the degree of formation for $X = Cl^-$, Br^-, and I^- but it is significantly greater for $[SCN]^-$ or when the solvent is acetonitrile in place of dichloromethane. The values of *K* are at least an order of magnitude greater than those obtained by Lucchini and Wells [11] for ethanol solutions. Since solvents such as pyridine or acetonitrile which are relatively good ligands do not seem to impede the formation of $[HgMeX_2]^-$, we presume that hydrogen bonding of the halide ions to the protons of alcohols and water is the cause of the much lower degree of formation in the latter solvents.

EXPERIMENTAL

The i.r. spectra were recorded as described in ref. 9, using a Perkin-Elmer model 225 double-beam spectrophotometer and a Grubb–Parsons I.R.I.S. interferometer for measurements above and below 200 cm^{-1} respectively. The Raman spectra were obtained with a Coderg PHO double monochromator, with excitation from a Coherent Radiation Laboratories model 52 krypton-ion laser. Solutions were prepared by adding solvent to the solid components until all the material had dissolved and were somewhat more concentrated than those used for n.m.r. studies in most cases. Wavenumbers are accurate to ±1 cm^{-1}, except for the bands of solutions below 110 cm^{-1} which are relatively broad but their maxima are accurate to better than ±3 cm^{-1}.

The n.m.r. spectra were recorded with a modified Varian Associates HA 100 spectrometer as described in ref. 23. However, $SiMe_4$ was not used as a reference or lock since it is apt to obscure the low-frequency satellite of methylmercury(II) compounds. Instead, a band of the solvent (adding some hydrogen-containing material in the case of deuterio-solvents) was used. There is some uncertainty as to the shift of such bands from internal $SiMe_4$, *e.g.* the addition of $[NBu^n_4]Cl$ to CH_2Cl_2 caused a change in the solvent resonance of 0.12 p.p.m. mol^{-1} to high frequency. In view of this we have not quoted proton shifts or used them to evaluate formation constants. The uncertainty in the theoretical frequency for $SiMe_4$ is not sufficient to produce any significant error in the conversion of $\nu(^{199}Hg)$ into $\Xi(^{199}Hg)$. Since the individual lines due to Hg–H coupling were observed and measured in the INDOR spectra, the values of $\delta(^{199}Hg)$ are accurate to better than 1 p.p.m.

Although dimethylmercury(II) is the generally accepted reference for mercury shifts, there is some disagreement in its value of $\Xi(^{199}Hg)$. Because of the likelihood of interference in the proton spectrum from $SiMe_4$, the internal reference used has often been benzene, but from the solvent studies of Sens *et al.*[20] addition of even a small percentage of benzene should alter $\Xi(^{199}Hg)$ significantly from the value for neat $[HgMe_2]$. To avoid this we measured the ^1H-$\{^{199}Hg\}$ INDOR spectrum of the neat liquid (with no internal reference) in a capillary surrounded by CH_2Cl_2 which provided the lock signal. No correction for bulk susceptibility was made. The value $\Xi(^{199}Hg) = 17\,910\,840.6$ Hz (at 305 K) is close to that of Johannesen and Duerst [24] where $SiMe_4$ was added as a reference, but is *ca.* 60 Hz greater than when benzene was added.[21,25]

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