Inorganica Chimica Acta, 75 (1983) 21–27

Mercury(II) Halide Complexes of Tertiary Phosphines. Part VII.[#] Application of Spectra-Structure Correlations to $HgX_2(PPr_3)$, $HgX_2(PPh_2Me)$, $HgX_2(PPhMe_2)$, and some other 1:1 Complexes not Structurally Characterised Previously

NORMAN A. BELL, MICHAEL GOLDSTEIN*, TERRY JONES and IAN W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, U.K.

Received April 11, 1983

Correlations between solid state structure and vibrational spectra previously derived by the authors, and based upon full structure determination by X-ray methods, have been applied to the following 1:1 complexes which have not hitherto been adequately characterised structurally: $HgX_2(PPr_3)$ *[X = Cl, Br or I (α- and β-forms)],* $HgX_2(PPh_2Me)$ *[X = Cl (α- and β-forms), Br or I],* $HgX_2(PPhMe_2)$ *[X = Cl, Br or I],* $HgX_2(PEt_3)$ *[X = Br or I],* $HgX_2(PBu_3)$ *[X = Br or I] and* $HgI_2(PMe_3)$*. In the case of the* $HgX_2(PPr_3)$ *series, the studies were augmented by far-infrared, NMR and relative molecular mass data on solutions. While for some complexes structures have been proposed with a reasonable measure of confidence, for others only general indications of structural features can be made, and in a few cases entirely new (but uncharacterised) structures are probable. There is remarkable spectral variety even within such closely related series.*

TABLE I. Summary of Structures Determined for $HgX_2(PR_3)$ Complexes.[a]

PR_3[b]	Cl	Br	I
TPP	**Asymmetric dimer**[c] [2]	Asymmetric dimer [2]	[d]
PPh_3	**Symmetric dimer**[c] [2]	Symmetric dimer [2]	Symmetric dimer [2]
PPh_2Me	{α: *Chain polymer* β: *Symmetric dimer*}	*'Ionic chain'*	*Symmetric dimer*
$PPhMe_2$	*'Ionic chain'*	*'Ionic chain'*	*Symmetric dimer*
PMe_3	**'Ionic chain'** [3]	'Ionic chain' [3]	*New*[e]
PEt_3	**Chain polymer** [3]	*Chain polymer*	*Symmetric dimer*
PPr_3	*Dimer*[f]	*New*	{α: *New* β: *Symmetric dimer*}
PBu_3	{α: **'Pseudo-tetramer'** [2] β: **Symmetric dimer** [4]}	*'Pseudo-tetramer'*	*'Pseudo-tetramer'*
PCy_3	**Two dimers**[g]	*Symmetric dimer*[h] [7]	*Symmetric dimer*[h] [7]

[a] Structures in bold type have been determined by full X-ray analysis; structures in normal type have been deduced by comparison of preliminary single-crystal X-ray data; structures in *italics* are those proposed in the present work from comparative vibrational spectroscopy. [b] TPP = 1,2,5-triphenylphosphole; Cy = cyclohexyl. [c] The term 'Asymmetric dimer' refers to a halogen-bridged dimer *trans*-$(PR_3)XHgX_2HgX(PR_3)$ in which the bond lengths in the centrosymmetric $[HgX_2Hg]$ unit are distinctly unequal. Similarly, 'Symmetric dimer' refers to a *trans*- dimer with essentially equal bridging bond lengths. [d] All attempts to prepare this complex were unsuccessful. [e] Structure believed to be different to the various types determined previously, but not yet characterised. [f] Extent of asymmetry in the $[HgX_2Hg]$ bridge not clear. [g] Two independent centrosymmetric dimers in the unit cell, one with fairly equal $[HgX_2Hg]$ bridge bonds, the other with distinctly less symmetric bridging. [h] Symmetry of bridging now suggested.

[#] Part VI: see reference [1].

*Author to whom correspondence should be addressed at Lanchester Polytechnic, Priority Street, Coventry CV1 5FB, U.K..

0020-1693/83/$3.00

TABLE II. Vibrational Assignments.[a]

Complex	Preparation		$\nu(HgX)_t$	$\nu(HgX)_b$	$\nu(HgP)$	Other bands
α-$HgCl_2(PPh_2Me)$	b,c	IR	286s, 281sh	203s, 132s, 110s		96w, 90w, 66m, 56w, 42ms
		Ra.	298mw, 283s			
β-$HgCl_2(PPh_2Me)$	b,c	IR[d]	310s	165s, 151s		111s, 105m, 79m, 56w, 44m
		Ra.	304s, 300sh			132mw, 114ms, 87s, 65s, 58m, 50s, 36m, 29m
$HgBr_2(PPh_2Me)$	b,c	IR	221s	122s, 112s, 99m	142wbr	76mw, 60w, 55w, 44w
		Ra.	216s			86sh, 74sh, 67s, 59s
$HgI_2(PPh_2Me)$	b,c	IR	165s	105s, 90s	149m	78w, 54m, 46w
		Ra.	164w	103m, 97sh, 89sh	146s	77w, 68w, 49m, 36s, 31w, 26s
$HgCl_2(PPhMe_2)$	[9, 10]	IR	312s, 302sh	120s, 107m, 93s		71s, 56s
		Ra.	318sh, 303s	129w, 97s		68s, 60w
$HgBr_2(PPhMe_2)$	[10]	IR	225s	129s, 120s, 99ms		88w, 76ms, 71sh, 59mw, 42w
		Ra.	223m	146w, 134m		96w, 71w, 61w, 50m
$HgI_2(PPhMe_2)$	b,e	IR	159m	112m, 105s	144ms	90sh, 73w, 62ms, 54sh, 44m
		Ra.	161s	114mbr	148m	66mw, 42m
$HgI_3(PMe_3)$	[3, 11]	IR	132s, 125s	112m		102w, 93w, 77w, 63m, 49m
		Ra.	124s			40s
$HgBr_2(PEt_3)$	[12]	IR	190s	144s, 84ms, 72ms		91sh, 57vw, 46mw
		Ra.	188s	164sh, 145m		55s, 45w, 41w, 30s
$HgI_2(PEt_3)$	[12]	IR	151s	93sh, 90s	132w	115wbr, 76w, 71sh, 62sh, 51m
		Ra.	143s	112m	134ms	47m, 34m, 22s
$HgCl_2(PPr_3)$	b	IR	305s	205m, 169ms, 144s		115ms, 98m, 83w, 61w, 49w
		Ra.	298s	208mw, 189s, 169w		81sbr
$HgBr_2(PPr_3)$	[12]	IR	203s, 181m	144s		112wbr, 88w, 76sh, 66ms
		Ra.	196sh, 179s	145m		113w, 104w
α-$HgI_2(PPr_3)$	[12]	IR	139s, 129m			88w, 76w, 71w, 61m, 51w
		Ra.	138s, 118m			
β-$HgI_2(PPr_3)$	[12]	IR	153s	90sbr	134ms	58w, 49w
		Ra.	157m	114m	138s	38s, 25s, 20m
$HgBr_2(PBu_3)$	[4, 12]	IR	188s, 166m	150ms, 127ms[f], 107s, 100m	127ms[f]	88ms, 75ms, 63m, 51m
		Ra	186mw, 172ms	166ms, 147w, 135w		82sh, 49s, 41s
$HgI_2(PBu_3)$	[4, 12]	IR	151s, 127s[f]	112m, 105m, 88msh, 78ms	127s[f]	66w, 49w
		Ra.	150mw, 129s	117sh		91w, 62w, 36s, 20w

[a] Data in cm^{-1}. Infrared spectra were recorded at *ca.* 50 K while Raman spectra were obtained at ambient temperature. Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Bands attributed to internal modes of the phosphine ligands have been eliminated and are not quoted. [b] This work (see Experimental). [c] Complex formation has been studied previously using calorimetry, but complex not isolated [8]. [d] Weak bands at 287, 205, 132, and 68 cm^{-1} are believed to be due to the presence of the α-form as impurity. [e] Relative molecular mass determined in benzene by cryoscopy, but complex not otherwise characterised [8]. [f] Coincident bands assumed.

Introduction

We have now determined the full crystal and molecular structure of a signficant number of 1:1 complexes of the type $HgCl_2(PR_3)$, and have deduced with little ambiguity (by comparative vibrational spectroscopy) or no ambiguity (by preliminary X-ray photographs) the structures of a few of their bromide and iodide analogues [2–6]. The structural variety summarised in Table I [2–5, 7] gives rise to differences in the vibrational spectra, and although a common feature can be identified it is evident that even small variations can give rise to significant effects on the spectra [6]. Thus although there are clearly difficulties and dangers in deducing the structures of related complexes, it should be possible, at least in principle, to elicit detailed structural features by careful analysis. Hence, at the risk of falling into a trap which we ourselves have warned others to avoid, we report here our attempts to apply our understanding of the spectra of structurally characterised $HgX_2(PR_3)$ complexes to the determination of the structures of some related complexes.

TABLE III. Relative Molecular Mass[a] and Far-infrared[b] Data for $HgX_2(PPr_3)$ and $HgX_2(PBu_3)$ Species in Benzene Solution.

Complex	M_r	M_r/F_r	$\nu(HgX)_t/cm^{-1}$	$\nu(HgX)_b/cm^{-1}$	Other bands/cm^{-1}
$HgCl_2(PPr_3)$	864	2.00	305s	156mbr, 144sh	100mwbr
$HgBr_2(PPr_3)$	1044	2.00	212ms	107svbr	75w, 64w
α-$HgI_2(PPr_3)$	1176	1.91	146m	88sbr	68sh, 59w, 51w
α-$HgCl_2(PBu_3)$	971	2.05	303s	163sbr	101mbr, 78w
$HgBr_2(PBu_3)$	1122	2.00	208s	109sbr	68m
$HgI_2(PBu_3)$	1252	1.91	149sbr	90sbr, 76brsh	61wbr

[a] M_r = experimentally determined value for relative molecular mass (estimated accuracy ±5%); F_r = relative formula mass of monomer. [b] Obtained at ambient; v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

Experimental

The preparation of many of the complexes have been adequately described in the literature, as indicated in Table II [3, 4, 8–12], but where details do not seem to be available, the following methods were adopted.

The complexes $HgX_2(PPh_2Me)$ [X = Cl(α-form), Br or I] were prepared on dropwise addition of a solution of the phosphine to a solution of the corresponding mercury(II) halide, each in minimal quantities of ethanol. The precipitates which formed immediately or on standing were collected, recrystallised from a formdimethylamide–water mixture and dried *in vacuo*. When α-$HgCl_2(PPh_2Me)$ was *rapidly* recrystallised in this way, the β-isomer was obtained. In the case of $HgCl_2(PPr_3)$ the same general procedure was used but recrystallisation was from ethanol. In attempts to obtain $HgI_2(PPhMe_2)$ analogously, a yellow oil was initially formed when the ethanolic solutions of HgI_2 and $PPhMe_2$ were mixed; on heating the whole mixture followed by decantation of the ethanolic solution, small white needles of the desired 1:1 adduct (which were separated off and dried *in vacuo*) were formed in the oil on standing, together with a yellow deposit of $(HgI_2)_3(PPhMe_2)_2$ [Found: C, 12.2; H, 1.5%. $C_{16}H_{22}P_2Hg_3I_6$ requires C, 11.7; H, 1.4%]. All complexes used gave satisfactory elemental analyses.

Infrared spectra in the 400–30 cm^{-1} range were obtained as described previously [6], with the samples as pressed discs in polyethene; benzene solutions (30–50 mg cm^{-3}) were studied using a demountable cell with polyethene windows [13]. The Raman method used has been described [6]. NMR data were obtained by standard techniques [14]. Relative molecular mass determinations were carried out ebullioscopically using a Hitachi-Perkin-Elmer model 115 apparatus standardised against benzil and using benzene as solvent; concentrations were in the range 3–16 mmol dm^{-3}.

Results and Discussion

Our general approach has been firstly to identify the infrared bands assignable as $\nu(HgX)_t$ and $\nu(HgX)_b$, and then to compare their patterns and positions with those of related compounds of known structure [6], and also within the series now studied. We have found the Raman spectra more difficult to deal with in this way, mainly because of the more marked variations in relative intensities of $\nu(HgX)$ and internal ligand modes. Therefore, the discussion throughout this paper is concerned with the far-infrared data; the Raman data given in Table II have simply been assigned by analogy with the infrared results.

In the case of PPr_3 and PBu_3 complexes, the interpretation has also been facilitated by the availability of data on solutions, and we consider this aspect first. The dimeric nature of $HgX_2(PBu_3)$ complexes in solution is now firmly established by NMR [15–17] and relative molecular mass (M_r) results [15 and Table III]. We can now report that the same situation obtains for the $HgX_2(PPr_3)$ series. Thus M_r data in Table III clearly show dimerisation, while the NMR results (Table IV) are closely analogous to those previously obtained for $HgX_2(PBu_3)$ [15–17]. These results enable use to fix 'typical' values for $\nu(HgX)_t$ and $\nu(HgX)_b$, and these are given in Table III. It should be noted, however, that most of these bands are broad and appear to show subsidiary maxima (Fig. 1). The implications of this are not certain, but it could mean that more than one structural form of the dimers, *i.e.* $(PR_3)_2HgX_2HgX_2$, is present.

We consider now the solid state results.

Chlorides

A comparison of the present results (Table II) with those obtained previously [6], illustrated in Fig. 2, suggests the occurrence of four different types of far-infrared spectra for the chloride series $HgCl_2(PR_3)$:

TABLE IV. NMR Parameters for $HgX_2(PPr_3)$ Complexes.[a]

Complex	$\delta(^{31}P)$/ppm[b]		$^1J(Hg-P)$/Hz[c]	
	300 K	183 K	300 K	183 K
$HgCl_2(PPr_3)$	33.0	32.7	7389	7524
$HgBr_2(PPr_3)$	27.2	27.7	6611	6836
α-$HgI_2(PPr_3)$	6.2	7.5	5071	5476
β-$HgI_2(PPr_3)$	6.9	7.5	5053	5481

[a] Solvent: 20% CD_2Cl_2 in CH_2Cl_2. [b] Relative to H_3PO_4 (±1 ppm). [c] ±5 Hz.

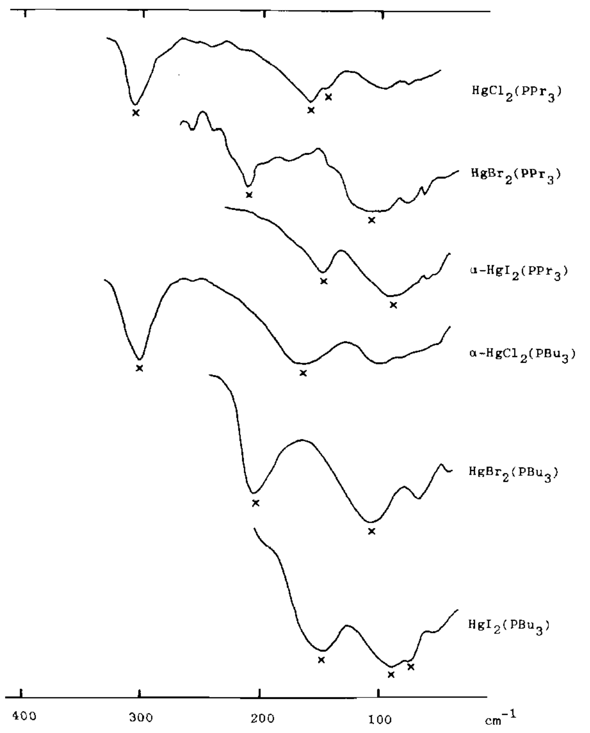

Fig. 1. Far-IR spectra (room temperature) of benzene solutions of 1:1 adducts of mercury(II) halides with tripropylphosphine and tributylphosphine.

(a) The $\nu(HgCl)_b$ bands consist of two closely spaced peaks, possibly unresolved (separation 0–23 cm^{-1}), in the range 190–150 cm^{-1}. This band pattern, with $\nu(HgCl)_t$ at 317–276 cm^{-1}, is characteristic of symmetrical (or near symmetrical) bridged dimers, and is typified by $HgCl_2(PPh_3)$ [2], $HgCl_2(PCy_3)$* [5], β-$HgCl_2(PBu_3)$ [4], and by the species present in benzene solutions of $HgCl_2(PPr_3)$ and $HgCl_2(PBu_3)$ (*vide supra*). We thus deduce that β-$HgCl_2(PPh_2Me)$ is of this type. Indeed, the correspondence between the spectrum of this complex and that of β-$HgCl_2(PBu_3)$ is remarkable (Fig. 2).

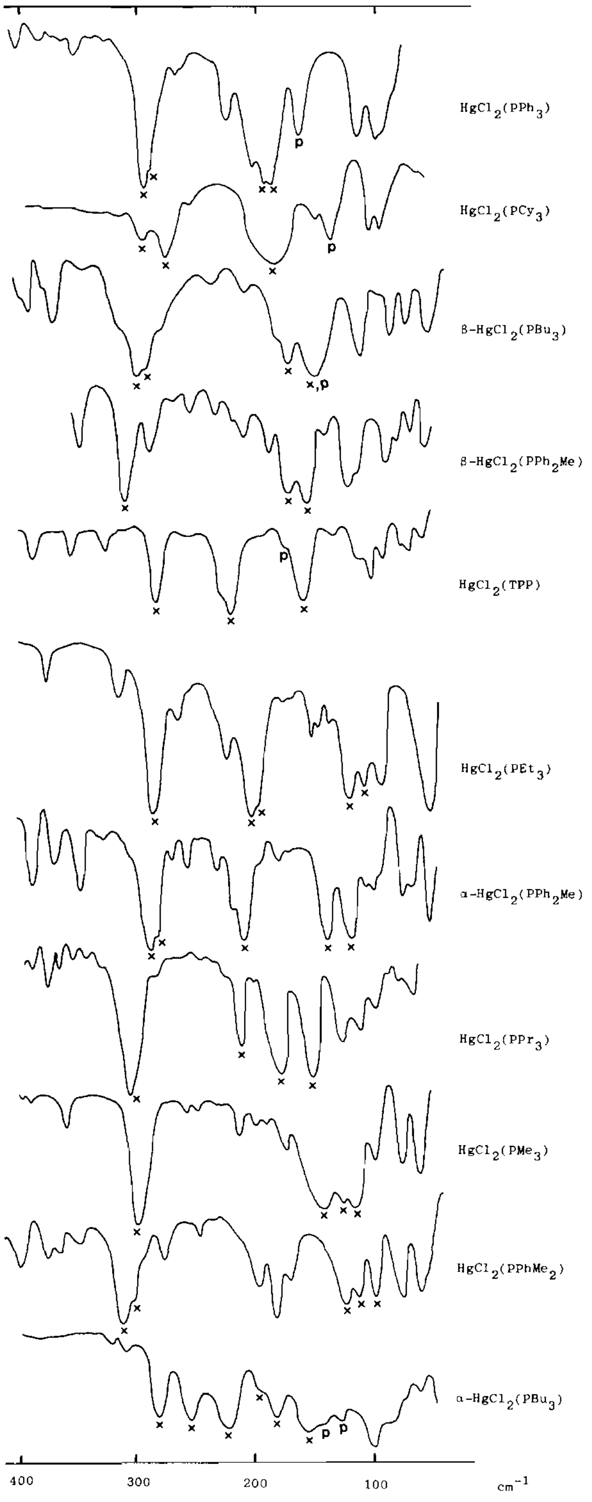

Fig. 2. Far-IR spectra (*ca.* 50 K) of 1:1 complexes of mercury(II) chloride with trialkylphosphines. Bands marked X or P are attributed to $\nu(HgX)$ or $\nu(HgP)$ modes respectively.

---

*Cy = cyclohexyl, C_6H_{11}.

(b) The $\nu(\mathrm{HgCl})_b$ modes are spread over the much wider range of 220 to 100 cm^{-1} (separation 100–60 cm^{-1}) in discrete dimers which are significantly distorted either inherently, as in $\mathrm{HgCl_2(TPP)}$* [2], or because of relatively weak association, as in $\mathrm{HgCl_2(PEt_3)}$ [3]. It thus seems fairly clear that α-$\mathrm{HgCl_2(PPh_2Me)}$ is of this latter type since its infrared spectrum (Fig. 2) closely resembles that of $\mathrm{HgCl_2(PEt_3)}$. We also believe $\mathrm{HgCl_2(PPr_3)}$, having $\nu(\mathrm{HgCl})_b$ at 205, 169 and 144 cm^{-1}, to be of this general type, but as its spectrum is not obviously that similar to any of the other complexes now studied (Fig. 2), a different *detailed* structure seems likely; certainly there are substantial differences between the spectra obtained for the solid and for benzene solution (Fig. 1).

(c) There are no significant skeletal bands between the strong $\nu(\mathrm{HgCl})_t$ mode at 310–280 cm^{-1} and an intense $\nu(\mathrm{HgCl})_b$ band complex starting below 150 cm^{-1}. This pattern is characteristic of a highly distorted dimeric species significantly associated into a polymeric arrangement with a near-linear P–Hg–Cl$_t$ angle, and typified by $\mathrm{HgCl_2(PMe_3)}$ [3]. On the assumption that the 183 cm^{-1} band is due to an internal mode of the phosphine ligand, we believe that the spectrum of $\mathrm{HgCl_2(PPhMe_2)}$ can be most satisfactorily interpreted in terms of this 'ionic polymer' type of structure.

(d) The complex pattern of $\nu(\mathrm{HgCl})$ infrared bands throughout the range 280–140 cm^{-1} shown by α-$\mathrm{HgCl_2(PBu_3)}$, arising from association of dimers to form a 'pseudo-tetrameric' structure [2], is not found in any other spectrum obtained for a chloride. This structure thus appears to be unique to α-$\mathrm{HgCl_2(PBu_3)}$, among the chlorides studied.

Bromides

Although a full X-ray structural analysis has not been reported for any bromide complex $\mathrm{HgBr_2(PR_3)}$, preliminary single-crystal studies have shown that three members of this series studied in the present work are isostructural with their chloride analogues (Table I) [2, 3] and the vibrational spectra have been previously interpreted in such terms [6]. The spectra of the remaining bromide complexes can thus be approached by analogy, and also by comparison with the spectra of corresponding chlorides. These approaches lead to the deductions:

(a) $\mathrm{HgBr_2(PEt_3)}$ is structurally the same as its chloride analogue, with $\nu(\mathrm{HgBr})_b$ at 144 and 84, 72 cm^{-1};

(b) $\mathrm{HgBr_2(PBu_3)}$ is much more likely to be a 'pseudo-tetramer' than an isolated dimer as previously [4] inferred. This is even more apparent when spectra of the solid state (Fig. 3) and solution (Fig. 1) are compared. Association beyond the dimer stage in benzene solution has been suggested before [18].

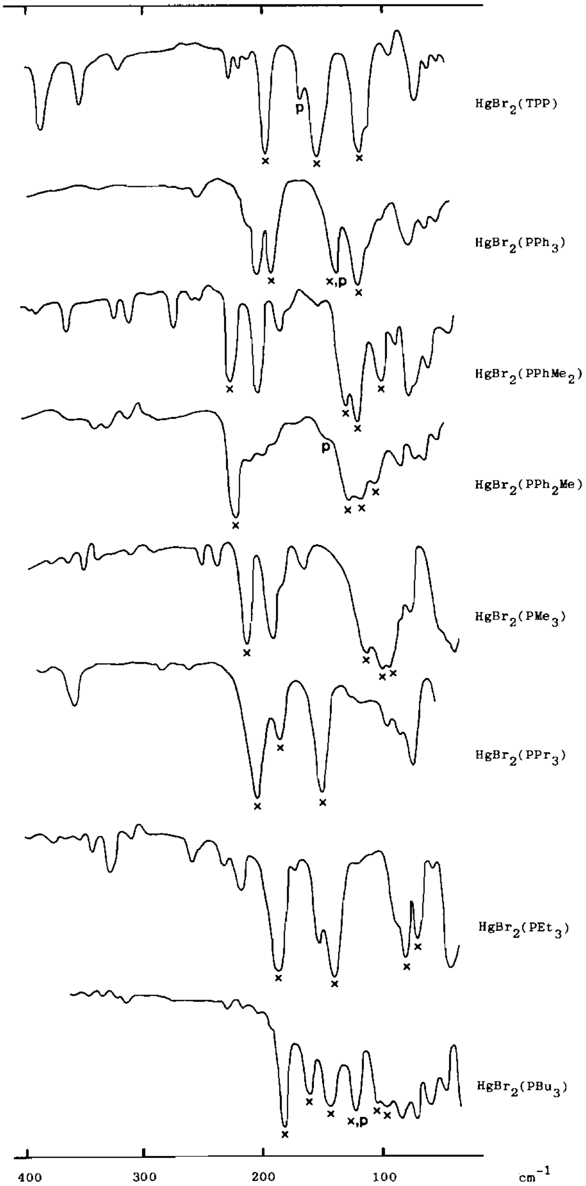

Fig. 3. Far-IR spectra (*ca.* 50 K) of 1:1 complexes of mercury(II) bromide with trialkylphosphines. (X and P as in Fig. 2).

Interpretation of the spectra of the other bromide complexes is much more problematical. Whereas the spectrum of the discrete dimer $\mathrm{HgBr_2(PPh_3)}$ is significantly different to that of the 'ionic chain' $\mathrm{HgBr_2(PMe_3)}$ (dimers linked by longer bridges), the data for $\mathrm{HgBr_2(PPhMe_2)}$ and $\mathrm{HgBr_2(PPh_2Me)}$ appear to show a general gradation between the two (Fig. 3), so that some sort of intermediate structures would seem to be likely. However, the spectra are clearly not characteristic of the 'pseudo-tetramer' arrangement typified by $\mathrm{HgBr_2(PBu_3)}$, and the

---

*TPP = 1,2,5-triphenylphosphole.

$\nu(\mathrm{HgBr})_t$ positions of the PMe_3, $PPhMe_2$ and PPh_2Me adducts (225–216 cm^{-1}) are quite different to those of the discrete dimers $HgBr_2(PPh_3)$ and $HgBr_2$(TPP), at 195–190 cm^{-1}. On balance, therefore, we suggest 'ionic chain' structures for the $PPhMe_2$ and PPh_2Me complexes.

A further problem exists with $HgBr_2(PPr_3)$, which is plainly different in the solid state to the species present in benzene solution (Fig. 1). Although there is clearly a strong, single $\nu(\mathrm{HgBr})_b$ band at 144 cm^{-1}, exactly as in $HgBr_2(PEt_3)$, there are no other bands at lower wavenumbers that are obviously other $\nu(\mathrm{HgBr})_b$ modes. Moreover, $\nu(\mathrm{HgBr})_t$ appears to be split by 22 cm^{-1} – far more than can be attributed to correlation field effects. This situation is similar to that found for the 'pseudo-tetramer' $HgBr_2(PBu_3)$, yet the spectrum of $HgBr_2(PPr_3)$ is not otherwise at all similar to that of the latter (Fig. 3). Hence we suggest that $HgBr_2(PPr_3)$ is of a different and as yet uncharacterised structure.

Iodides

Very little indeed is known crystallographically about the $HgI_2(PR_3)$ series, other than the fact that $HgI_2(PPh_3)$ is isostructural with the discrete dimeric chloride and bromide analogues [2]. There can be little doubt, from the spectra shown in Fig. 4, that $HgI_2(PPh_2Me)$ also has a discrete dimeric structure in the solid state, despite appearing to be a monomer in solution [8], and judging from the small separation between the two $\nu(\mathrm{HgI})_b$ bands (105, 90 cm^{-1}), this dimer must be fairly symmetrically bonded. It is also reasonably certain that $HgI_2(PPhMe_2)$, $HgI_2(PEt_3)$, and β-$HgI_2(PPr_3)$ are all also discrete and highly symmetrical dimers; in the first two cases the two $\nu(\mathrm{HgI})_b$ bands are incompletely resolved (112, 105 cm^{-1} and 93, 90 cm^{-1}, respectively), while in the PPr_3 complex they are accidentally coincident at 90 cm^{-1}. The band of medium-weak intensity found in these spectra at 149–132 cm^{-1}, between the $\nu(\mathrm{HgI})_t$ and $\nu(\mathrm{HgI})_b$ bands, is very probably the elusive $\nu(\mathrm{HgP})$ mode.

As in the case of the bromide analogue, $HgI_2(PBu_3)$ can now be reassigned a 'pseudo-tetrameric' structure (see Fig. 1 of [4]).

The spectra of $HgI_2(PMe_3)$, contrary to previous assertions [11], and α-$HgI_2(PPr_3)$ do not admit of simple interpretation in terms of discrete dimeric structures. The spectra are similar to each other but do not resemble the spectra of any of the other iodide complexes studied (Fig. 4). Moreover, there is no analogous pattern of bands in the chloride and bromide series, a situation at least for the PMe_3 complex compatible with results of preliminary single-crystal X-ray data [3]. It thus seems probable that these complexes, $HgI_2(PMe_3)$ and α-$HgI_2(PPr_3)$ both have a structure which is yet different to any of the several structures so far characterised.

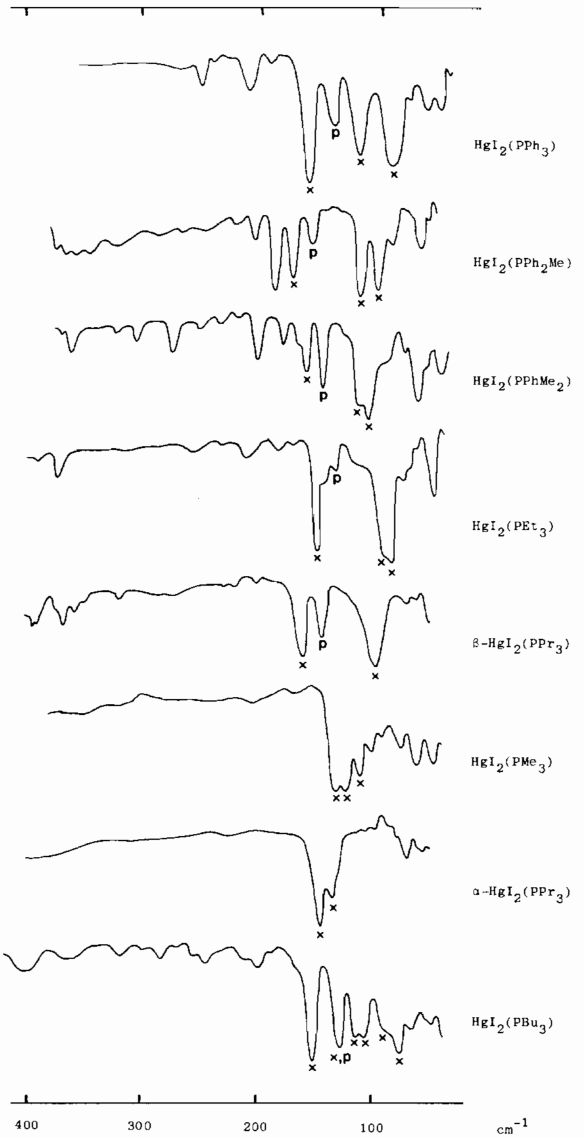

Fig. 4. Far-IR spectra (*ca.* 50K) of 1:1 complexes of mercury(II) iodide with trialkylphosphines. (X and P as in Fig. 2).

Summary

The structures suggested in the present work are listed in Table I in italics to distinguish them from those determined unambiguously by single-crystal X-ray methods. Clearly, some of the suggestions are more tentative than others, and we would not be entirely surprised if subsequent X-ray studies showed one or more of our descriptions to be less than precise. What is truly remarkable about the $HgX_2(PR_3)$ series is that there is great structural variety based on a simple dimeric unit, and this variety is reflected in the range of spectral patterns in the low-frequency vibrational spectra. It does not seem certain by any means that all possible structural types have yet been identified, and we have suggested some likely candidates for further study.

The rationale which we previously proposed for structural variations among $HgX_2(PR_3)$ complexes [3] is now in need of refinement, particularly if variations in structure with changing halide ligand are verified, but it is by no means clear what the new rationale should be.

Acknowledgements

We thank the Science and Engineering Research Council for a Studentship (to T. J.), an equipment grant and computing facilities. We are grateful to the University of Leicester (Department of Chemistry) and University College Cardiff (Department of Chemistry) for Raman facilities, and the University of Bristol for NMR measurements.

References

1 N. A. Bell, T. D. Dee, M. Goldstein, P. J. McKenna and I. W. Nowell, *Inorg. Chim. Acta, 71*, 135 (1983).

2 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 43*, 87 (1980).

3 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 48*, 185 (1981).

4 N. A. Bell, M. Goldstein, T. Jones, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 61*, 83 (1982).

5 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta, 70*, 215 (1983).

6 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 69*, 155 (1983).

7 T. Allman, R. G. Goel and P. Pilon, *Spectrochim. Acta, 35A*, 923 (1979).

8 M. J. Gallagher, D. P. Graddon and A. R. Sheikh, *Austral. J. Chem., 29*, 759 (1976).

9 G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).

10 R. C. Cass, G. E. Coates and R. G. Hayter, *J. Chem. Soc.*, 4007 (1955).

11 H. Schmidbaur and K. H. Rathlein, *Chem. Ber., 106*, 2491 (1973).

12 R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, *J. Chem. Soc.*, 1209 (1940).

13 M. Goldstein, and H. A. Willis, *Lab. Practice, 19*, 808 (1970).

14 N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. W. Nowell, *J. Chem. Res.* (S) 2, (M) 0201 (1981).

15 K. Kessler, *Ph.D. Thesis*, University of Bristol (1977).

16 S. O. Grim, P. J. Lui and R. L. Keiter, *Inorg. Chem., 13*, 342 (1974).

17 A. Yamasaki and E. Fluck, *Z. anorg. Chem., 396*, 297 (1973).

18 Y. Farhangi and D. P. Graddon, *Austral. J. Chem., 26*, 983 (1973).