

## Mercury(II) Halide Complexes of Tertiary Phosphines. Part V. Correlations between Crystallographically Determined Structures and the Vibrational Spectra of Complexes $\text{HgX}_2(\text{PR}_3)$

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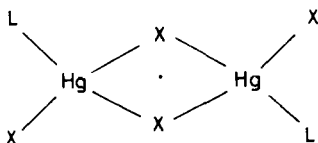
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A critical appraisal has been made of the far-infrared and Raman spectra ( $40\text{--}450\text{ cm}^{-1}$ ) of the complexes  $\text{HgX}_2(\text{PR}_3)$  of crystallographically known structure:  $\text{HgX}_2(\text{PPh}_3)$  [ $X = \text{Cl}, \text{Br}$  or  $\text{I}$ ],  $\text{HgX}_2(1,2,5\text{-triphenylphosphole})$  [ $X = \text{Cl}$  or  $\text{Br}$ ],  $\alpha$ - and  $\beta$ - $\text{HgCl}_2(\text{PBu}_3)$ ,  $\text{HgCl}_2(\text{PCy}_3)$  [ $\text{Cy} = \text{cyclohexyl}$ ],  $\text{HgCl}_2(\text{PEt}_3)$ , and  $\text{HgX}_2(\text{PMe}_3)$  [ $X = \text{Cl}$  or  $\text{Br}$ ]. Remarkably, although the known structures are apparently quite varied, and the spectra similarly diverse, it is shown that the gross features of the spectra can be explained, to first order, in terms of a common centrosymmetric halogen-bridged dimeric unit. However, there are subtleties in the structures which can have very significant influence on the spectral patterns, and this makes structural elucidation from spectroscopic data fraught with difficulty.

### Introduction

A very large number of complexes of stoichiometry  $\text{HgX}_2(\text{L})$  has been described in the literature. On the basis of some very early preliminary crystallographic work [1], a centrosymmetric dimeric structure of the type:



has generally been supposed to be the prevalent arrangement in such complexes. In recent years, far-infrared spectroscopy has been used to 'substantiate' this structural assignment. The essence of the arguments put forward is that for this structure (of idealised  $C_{2h}$  point group symmetry), one  $\nu(\text{HgX})$  band is allowed in the infrared spectrum due to

stretching of the terminal bonds ( $B_u$ ) whereas two infrared bands originate in  $[\text{HgX}_2\text{Hg}]$  bridging motions ( $A_u + B_u$ ). Most of the work reported relates to chlorides, for which  $\nu(\text{HgCl})_t$  is known to occur in the  $270\text{--}310\text{ cm}^{-1}$  range, with  $\nu(\text{HgCl})_b$  expected at significantly lower wavenumbers (*ca.*  $200\text{ cm}^{-1}$  often being quoted). However, the latter assignment is not always obvious from the spectra, and indeed much of the literature relates to studies restricted to the spectral region above  $200\text{ cm}^{-1}$ . Consequently, there are several instances where the essential and reliable evidence for a bridging structure is the observation of a terminal stretching mode!

Recognising these inadequacies some years ago, we have initiated a programme of determination of the crystal and molecular structures of a series of complexes of the type  $\text{HgX}_2(\text{PR}_3)$ . Our results so far [2–5], summarised in Table I and Fig. 1, demonstrate that a variety of structures is possible even within a closely related series, and that the presence

TABLE I. Known Structures of  $\text{HgX}_2(\text{PR}_3)$  Complexes.

Complex <sup>a</sup>	Structure	Ref.
$\text{HgCl}_2(\text{PPh}_3)$	Centrosymmetric dimer	[2] <sup>b</sup>
$\text{HgBr}_2(\text{PPh}_3)$	Centrosymmetric dimer	[2] <sup>c</sup>
$\text{HgI}_2(\text{PPh}_3)$	Centrosymmetric dimer	[2] <sup>c</sup>
$\text{HgCl}_2(\text{TPP})$	Centrosymmetric dimer	[2] <sup>b</sup>
$\text{HgBr}_2(\text{TPP})$	Centrosymmetric dimer	[2] <sup>c</sup>
$\alpha$ - $\text{HgCl}_2(\text{PBu}_3)$	'Tetramer'	[2, 4] <sup>b</sup>
$\beta$ - $\text{HgCl}_2(\text{PBu}_3)$	Centrosymmetric dimer	[4] <sup>b</sup>
$\text{HgCl}_2(\text{PCy}_3)$	Two independent centrosymmetric dimers	[5] <sup>b</sup>
$\text{HgCl}_2(\text{PEt}_3)$	Chain polymer	[3] <sup>b</sup>
$\text{HgCl}_2(\text{PMe}_3)$	'Ionic' polymer	[3] <sup>b</sup>
$\text{HgBr}_2(\text{PMe}_3)$	'Ionic' polymer	[3] <sup>c</sup>

<sup>a</sup>(TPP) = 1,2,5-triphenylphosphole; (PCy<sub>3</sub>) = tricyclohexylphosphine. <sup>b</sup>Full X-ray structure determination. <sup>c</sup>Preliminary X-ray photographs show structure to be the same as that of the corresponding chloride.

† Part IV: See reference [5].

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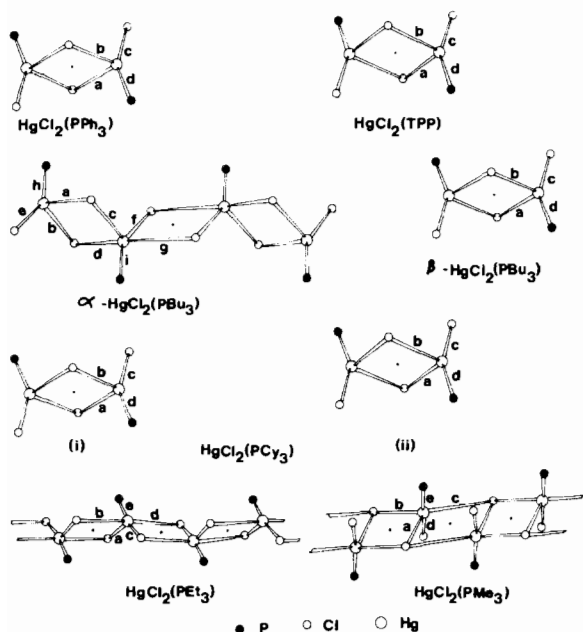


Fig. 1. Summary of structural data for  $\text{HgCl}_2(\text{PR}_3)$  complexes.  $\text{HgCl}_2(\text{PPh}_3)$ :  $a = 2.623(8)$ ,  $b = 2.658(8)$ ,  $c = 2.370(10)$ ,  $d = 2.406(7)$  Å; angle  $c-d = 128.7(4)^\circ$ .  $\text{HgCl}_2(\text{TPP})$ :  $a = 2.542(13)$ ,  $b = 2.747(14)$ ,  $c = 2.404(11)$ ,  $d = 2.438(10)$  Å; angle  $c-d = 127.8(5)^\circ$ .  $\alpha\text{-HgCl}_2(\text{PBu}_3)$ :  $a = 2.626(19)$ ,  $b = 2.709(20)$ ,  $c = 2.895(21)$ ,  $d = 2.664(18)$ ,  $e = 2.289(21)$ ,  $f = 2.304(21)$ ,  $g = 3.375(25)$ ,  $h = 2.363(21)$ ,  $i = 2.337(19)$  Å; angle  $e-h = 147.8(7)$ , angle  $f-i = 150.6(7)^\circ$ .  $\beta\text{-HgCl}_2(\text{PBu}_3)$ :  $a = 2.720(6)$ ,  $b = 2.736(6)$ ,  $c = 2.348(8)$ ,  $d = 2.377(6)$  Å; angle  $c-d = 150.9(3)^\circ$ .  $\text{HgCl}_2(\text{PCy}_3)$ : [two independent dimers] (i)  $a = 2.641(4)$ ,  $b = 2.665(4)$ ,  $c = 2.391(5)$ ,  $d = 2.416(3)$  Å; angle  $c-d = 139.6(2)^\circ$ ; (ii)  $a = 2.602(4)$ ,  $b = 2.779(4)$ ,  $c = 2.413(3)$ ,  $d = 2.412(3)$  Å; angle  $c-d = 132.0(1)^\circ$ .  $\text{HgCl}_2(\text{PEt}_3)$ :  $a = 2.56(1)$ ,  $b = 3.04(1)$ ,  $c = 2.42(1)$ ,  $d = 3.21(1)$ ,  $e = 2.35(1)$  Å; angle  $c-e = 145.4(3)^\circ$ .  $\text{HgCl}_2(\text{PMe}_3)$ :  $a = 2.782(4)$ ,  $b = 2.941(4)$ ,  $c = 3.489(4)$ ,  $d = 2.355(4)$ ,  $e = 2.365(3)$  Å; angle  $d-e = 162.1(1)^\circ$ .

of a prominent absorption in the  $270\text{--}310\text{ cm}^{-1}$  range is not characteristic of any of the individual structures. The purpose of the present paper is thus to rationalise the observed spectral features in terms of the crystallographically determined structures, and thereby to establish the validity of spectra–structure correlations for complexes of this type.

## Results and Discussion

The general approach used to establish the band assignments was to make comparisons of the spectra within a corresponding chloro/bromo/iodo series, and by reference to the spectra of the phosphine ligands in the unco-ordinated state and/or co-ordinated to other metal compounds [6–10]. As has been found previously [11, 12], the Raman scattering ability of the  $\nu(\text{HgX})$  modes increases markedly in the sequence

of  $\text{X}$ :  $\text{Cl} < \text{Br} < \text{I}$ . Consequently, the internal ligand modes tend to dominate the Raman spectra of the complexes with the lighter halides, with the effect that the  $\nu(\text{HgX})_b$  modes are often not readily detectable in these cases. Additionally, it should be noted that the spectra of the iodides are rather crowded in the region below  $150\text{ cm}^{-1}$ , making their assignment rather difficult. Location of  $\nu(\text{HgP})$  has also been problematical, but in agreement with other studies [5, 9, 11] has been easier in the Raman spectra than in the infrared.

Our results are summarised in Table II, and representative spectra are shown in Fig. 2.<sup>†</sup>

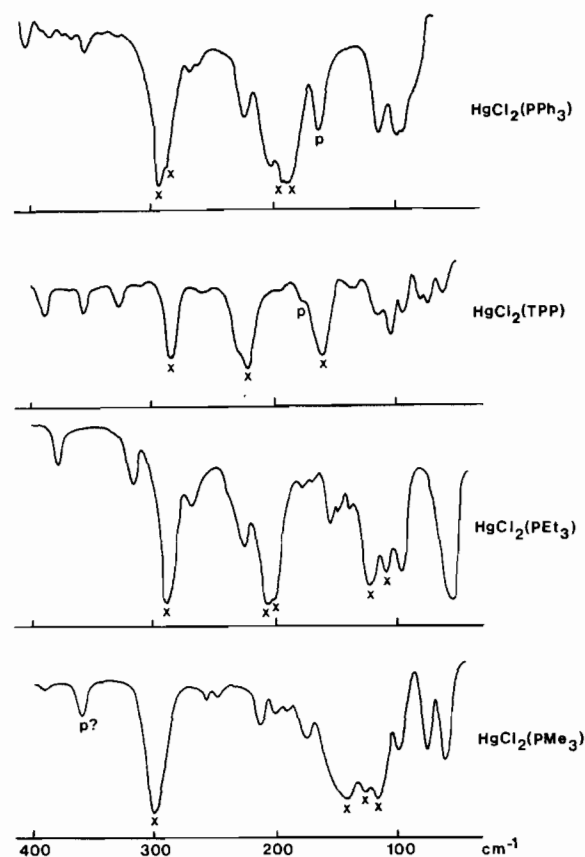


Fig. 2. Far-infrared spectra of some  $\text{HgX}_2(\text{PR}_3)$  complexes. Bands marked X are assigned as  $\nu(\text{HgX})$ , while those marked P are attributed to  $\nu(\text{HgP})$  modes (see Table II). For spectra of  $\alpha$ - and  $\beta$ - $\text{HgCl}_2(\text{PBu}_3)$  and  $\text{HgCl}_2(\text{PCy}_3)$ , see refs. [4] and [5] respectively.

### $\text{HgX}_2(\text{PPh}_3)$ [ $\text{X} = \text{Cl}, \text{Br}$ or $\text{I}$ ]

These complexes have been subject to more detailed studies hitherto than any other compounds of this type [11, 13, 14] and the essential features of the spectra, with which we concur, are readily under-

<sup>†</sup>Further details are available on request to the authors.

TABLE II. Summary of Vibrational Spectral Assignments ( $cm^{-1}$ ).

Complex <sup>a</sup>	Method <sup>b</sup>	$\nu(HgX)_t$	$\nu(HgX)_b$	$\nu(HgP)$
$HgCl_2(PPh_3)_2$	I.r.	291s, 288sh	188s, 183s	157m
	Ra.	286s		156s
$HgBr_2(PPh_3)_2$	I.r.	203s <sup>c</sup> , 190s	137s <sup>d</sup> , 117s	137s <sup>d</sup>
	Ra.	200sh, 192s <sup>c</sup>		150s <sup>d</sup>
$HgI_2(PPh_3)_2$	I.r.	163s, 139m <sup>d</sup>	117s, 89s	139m <sup>d</sup>
	Ra.	160m, 143s <sup>d</sup>		125ms
$HgCl_2(TPP)_2$	I.r.	283s	219s, 156s	168sh
	Ra.	278m <sup>c</sup>		
$HgBr_2(TPP)_2$	I.r.	195s	151s, 117s	164mw
	Ra.	198m, 194m		
$\alpha$ - $HgCl_2(PBu_3)_2$	I.r.	278s, 252s <sup>e</sup>	218s, 190sh, 179m, 149mbr	138sh, 122w
	Ra.	280s, 252s <sup>e</sup>		
$\beta$ - $HgCl_2(PBu_3)_2$	I.r.	301s, 295sh	173m, 150s <sup>d</sup>	150s <sup>d</sup>
	Ra.	298s <sup>f</sup>		
$HgCl_2(PCy_3)_2$	I.r.	293m <sup>g</sup> , 276s <sup>h</sup>	183sbr	139m
	Ra.	280sh <sup>g</sup> , 270s <sup>h</sup>		184m <sup>c</sup>
$HgCl_2(PEt_3)_2$	I.r.	286s	203s, 198sh, 117s, 105s	
	Ra.	270s, 260s		
$HgCl_2(PMe_3)_2$	I.r.	300s	141s, 124s, 115s	361mw <sup>i</sup>
	Ra.	291s		142sh, 136m, 112m
$HgBr_2(PMe_3)_2$	I.r.	216s	116s, 102s, 96s	351w <sup>i</sup>
	Ra.	208sh, 193s		106mbr

<sup>a</sup>(TPP) = 1,2,5-triphenylphosphole; (PCy<sub>3</sub>) = tricyclohexylphosphine. <sup>b</sup>I.r. = infrared data at ca. 50 K; Ra. = Raman data at ambient temperature. <sup>c</sup>Some contribution from internal mode of the phosphine ligand. <sup>d</sup>Coincident bands. <sup>e</sup>The particularly low wavenumber is discussed in ref. [4]. <sup>f</sup>Alternative assignment is discussed in ref. [4]. <sup>g,h</sup>Sets of bands corresponding to the two independent dimers [5]. <sup>i</sup>The particularly high wavenumber is discussed in the text.

stood in terms of the centrosymmetric dimer structure (Fig. 1). Splitting of the  $\nu(HgX)_t$  modes (evident at low temperatures) can only be due to correlation field effects ( $A_g + A_u \rightarrow 2A_g + 2A_u$  under the  $C_{2h}^5$  factor group;  $P2_1/n$ ,  $Z = 2$ ). The only contentious aspect of the assignments is the location of the lower wavenumber  $\nu(HgX)_b$  mode. According to Deacon *et al.* [13] this mode is at 97, 83  $cm^{-1}$  for  $HgCl_2(PPh_3)_2$ , whereas Adams *et al.* [14] proposed assignment to a band at 150  $cm^{-1}$ ; no comment was made on this discrepancy in the most recent paper [11]. However, data in the literature suggest that the separation between the two infrared-active stretching modes of planar  $[MX_2M]$  bridges (strictly, in-plane deformations) will be small when the bridge angles are close to  $90^\circ$  and the bridge bond lengths nearly equal [4, 12, 15, 16]. Hence for  $HgX_2(PPh_3)_2$  we suggest that the two  $\nu(HgX)_b$  infrared bands will be

close together in each case. We thus propose assignments (Table II) which differ from those previously put forward [13, 14] and which are only possible because of the improved resolution and definition obtained in the present work (samples cooled to ca. 50 K).

#### $HgX_2(1,2,5\text{-triphenylphosphole}) [X = Cl \text{ or } Br]$

These complexes are also halogen-bridged dimers, but the  $[HgX_2Hg]$  ring is distinctly asymmetric (Fig. 1). The effect of this is markedly to increase the separation between the two infrared-active  $\nu(HgX)_b$  bands (*cf.* Fig. 2). Furthermore, the presence of only one dimeric molecule in the primitive unit cell means that there can be no correlation field effects. Consequently, although these complexes are clearly of the same general structural type as the  $PPh_3$  analogues, their spectra appear to be distinctly different.

*$\alpha$ - and  $\beta$ -HgCl<sub>2</sub>(PBu<sub>3</sub>)*

The detailed assignments reported by us recently [4] are summarised in Table II. The essential point to make in the present context is that although the spectra of the two forms are markedly different [4], the best interpretation of the spectra is in terms of similar dimeric structures for each isomer. In the case of the  $\alpha$ -form there is inter-dimer association which leads to the 'tetramer' description used earlier [2], but the effect of this is merely to perturb the spectral pattern. It is thus apparent that, in these cases also, relatively small structural effects give rise to markedly different spectra.

*HgCl<sub>2</sub>(PCy<sub>3</sub>)*

Earlier interpretation of the vibrational spectrum of this complex was based upon a non-centrosymmetric dimeric structure [17], but later workers disputed this [11]. We have recently resolved this matter by determination of the crystal and molecular structure of the complex [5]. The presence of two independent centrosymmetric dimers in the unit cell results in a multiplicity of  $\nu(\text{HgCl})_t$  bands, so that more bands are observed than is expected for a single centrosymmetric dimer [5]. Hence without a detailed knowledge of the complete structure, an incorrect [17] or incomplete [11] deduction would be made from the spectrum.

*HgCl<sub>2</sub>(PEt<sub>3</sub>)*

This complex comprises a polymeric chain in which the mercury atoms are in a pentaco-ordinate environment [3] (Fig. 1). A reasonable approach to interpretation of the spectra would be in terms of the appropriate line group symmetry. However, there is a very striking similarity between the infrared spectrum of this compound and that of HgCl<sub>2</sub>(PPh<sub>3</sub>) (Fig. 2). Indeed, the strong bands at 286 and 203, 198 cm<sup>-1</sup> are typical of (respectively)  $\nu(\text{HgCl})_t$  and  $\nu(\text{HgCl})_b$  modes, and in the absence of knowledge of the structure would be interpreted in terms of a simple dimeric arrangement with considerable confidence. Close scrutiny of the crystallographic results provides the solution to this anomaly. If the longest Hg–Cl interactions (3.21 Å) are disregarded, then the structure appears as consisting of distorted centrosymmetric dimers (PEt<sub>3</sub>)ClHgCl<sub>2</sub>HgCl(PEt<sub>3</sub>), and it is evident that the main features of the spectra can satisfactorily be accounted for on this basis. The wide spread of the  $\nu(\text{HgCl})_b$  bands is attributable to the high asymmetry of the [HgCl<sub>2</sub>Hg] bridges (*vide supra*), and their multiplicity results from the presence of more than one 'dimer' in the unit cell. This approach to spectral interpretation is analogous to that used in the case of  $\alpha$ -HgCl<sub>2</sub>(PBu<sub>3</sub>) in which the 3.375 Å inter-dimer interaction was disregarded, but the result is in contradistinction to that obtained in the former case, in that (apparently) substantial

structural differences (compared with simple dimers) have relatively small effects on the infrared spectra.

*HgX<sub>2</sub>(PMe<sub>3</sub>) [X = Cl or Br]*

The chain structure adopted by these complexes (Fig. 1) is significantly different to that shown by HgCl<sub>2</sub>(PEt<sub>3</sub>). The presence of a large Cl–Hg–P angle involving a short *terminal* Hg–Cl bond has led to an 'ionic' description [Cl–Hg–PMe<sub>3</sub>]<sup>+</sup>Cl<sup>-</sup> [3] and from preliminary X-ray data the bromide is evidently analogous. However, bearing in mind the relative insignificance (in spectroscopic terms) of the 'inter-dimer' interactions in  $\alpha$ -HgCl<sub>2</sub>(PBu<sub>3</sub>) (3.375 Å) and in HgCl<sub>2</sub>(PEt<sub>3</sub>) (3.21 Å) (*vide supra*), it is reasonable to suppose that the longest chain interactions in HgCl<sub>2</sub>(PMe<sub>3</sub>) (3.49 Å) can, to first approximation, be ignored. If this is done, then the structure can also be described as consisting of centrosymmetric (L)-ClHgCl<sub>2</sub>HgCl(L) dimers, and spectral interpretation can be effected in such terms. The relatively high wavenumbers of the  $\nu(\text{HgCl})_t$  modes, 300 cm<sup>-1</sup> (infrared) and 291 cm<sup>-1</sup> (Raman), and the significantly low wavenumbers for  $\nu(\text{HgCl})_b$ , 141–115 cm<sup>-1</sup> (infrared) and 142–112 cm<sup>-1</sup> (Raman), arise from the short Hg–Cl terminal distances and the long Hg–Cl bridges (Fig. 1).

The assignment of  $\nu(\text{HgP})$  in HgX<sub>2</sub>(PMe<sub>3</sub>) warrants further comment. Earlier studies on these complexes [18] and on [HgCl(PMe<sub>3</sub>)]<sup>+</sup> salts [7] placed  $\nu(\text{HgPMe}_3)$  at ca. 360 cm<sup>-1</sup>. This is in marked contrast to values of 120–170 cm<sup>-1</sup> given for complexes of HgX<sub>2</sub> with heavier phosphine ligands (Table II and [9, 11]). We note, however, that in the HgX<sub>2</sub>(PMe<sub>3</sub>) series there must be significant formal positive charge on mercury (*cf.* the 'ionic' formulation previously given [3]), and that, for the chloride at least, the Hg–P distance is particularly short (Fig. 1). A  $\nu(\text{HgP})$  position substantially higher than for the other complexes described in the present work is thus to be expected, although whether a value more than twice the norm is correct must await further analysis.

**Conclusions**

The wide variety of structural arrangements found in complexes of formula HgX<sub>2</sub>(PR<sub>3</sub>) is reflected in the range of vibrational spectral patterns shown by these species. However, a careful analysis allows an interpretation to be made in terms of a common structural feature, namely a centrosymmetric halogen-bridged dimeric arrangement (PR<sub>3</sub>)XHgX<sub>2</sub>-HgX(PR<sub>3</sub>). It is essential to note though that small structural differences may result in considerable changes in the spectral pattern. Conversely, it is found that apparently major structural variations can have very little influence on the spectra. The study

shows quite vividly the caution which must be taken in interpreting spectra of such species in detailed structural terms.

### Experimental

The complexes were prepared as described previously [2–5] and were recrystallised to high purity as shown by elemental analysis. Far-infrared spectra were obtained using a Beckman-RIIC FS-720 interferometer, with the samples studied as pressed discs in polyethylene cooled to *ca.* 50 K using a CTi model 20 closed cycle helium cryostat. Raman spectra were recorded on a Coderg T-800 triple monochromator spectrophotometer using  $\text{Ar}^+$  (488.0 nm) laser excitation, with  $90^\circ$  collection from powdered samples in capillary tubes.

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