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SYNTHESIS AND VIBRATIONAL SPECTRA OF SOME TRI- AND DI-PHENYLHALOPLUMBATES

IVOR WHARF, ROSANDA CUENCA, ERICA BESSO, and MARIO ONYSZCHUK
Department of Chemistry, McGill University, Montreal, PQ, H3A 2K6 (Canada)

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Summary

Phenylhaloplumbate salts of the type $[Et_4N][Ph_3PbXY]$ (X or Y = Cl, Br, I), $[Et_4N][Ph_6Pb_2X_2Y]$ (X or Y = Cl, Br), $[Et_4N][Ph_2PbX_3]$ (X = Cl, Br, I), and $[Me_4N]_2[Ph_2PbX_4]$ (X = Cl, Br) have been prepared and characterised in the solid state by infrared and Raman spectroscopy over the range 250–80 cm^{-1}. Similar vibrational data are reported for $[Me_4N][Ph_3PbX_2]$ (X = Cl, Br) and $[Me_4N][Ph_2PbCl_3]$ as well as new data for Ph_3PbX and Ph_2PbX_2 (X = Cl, Br, I). These infrared and Raman data are consistent with 5-coordinate, approximately trigonal-bipyramidal structures for triphenyllead systems (except Ph_3PbI) and 6-coordinate, approximately octahedral structures for diphenyllead systems (except Ph_2PbI_2), the required degree of coordination being achieved by halogen bridges where necessary. Stretching modes associated with halogen bridges are observed as strong, broad infrared bands only weakly Raman active, characteristics which suggest that these bonds have high ionic character.

Introduction

Arylhaloplumbates have not been as thoroughly examined as have their tin analogues [1]. Following the first report of $[Me_4N][Ph_3PbCl_2]$ [2], Huber et al. prepared several triaryl- and diaryl-haloplumbates [3,4] as well as a series of monophenylplumbates [5], but no structural information has yet appeared. Recently, a ^1H NMR spectrum of $[Et_4N][Ph_3PbCl_2]$ was published [6] as part of a study of pentacoordinate phenyl compounds of Main Group elements, but no other spectroscopic data of structural significance are available.

As part of our continuing interest in phenyllead halides and pseudohalides and their adducts [7], we now report the synthesis and vibrational spectra (in the skeletal region) of a number of tri- and di-phenylhaloplumbates, and these results are compared with those obtained recently for the tin analogues [8], following an earlier comparison made between hexamethylphosphoramide (HMPA) adducts of phenyl-tin and -lead halides [9]. To assist in the assignment of the spectra reported here, we have re-examined the vibrational spectra of several di- and tri-phenyllead halides, for some of which the structures are known, i.e. Ph_2PbCl_2 [10] and Ph_3PbX (X = Cl, Br) [11], thereby supplementing the previous spectral study of these compounds [12].

Experimental

All solvents were stored over molecular sieves before use, while tetraalkylammonium halides (Eastman or Aldrich) and triphenyl and diphenyllead chlorides (Alfa) were used as received. Triphenyllead bromide and iodide were previous preparations [9], while diphenyllead bromide and iodide were prepared from the acetate [14]. Other experimental details, e.g., micro-analyses, and Raman and far-infrared spectra were as described elsewhere [8], except that far-infrared spectra were measured using a 12.5 μm Mylar beam splitter.

Preparations

Method A. Equimolar quantities of triphenyllead chloride (1.75 g; 3.7 mmol) and tetraethylammonium halide were dissolved in hot acetonitrile (80–90 ml) and the solution evaporated to small bulk (20–30 ml). Adding benzene (30–40 ml) and then pentane (40–60 ml) dropwise to the cooled solution gave a flocculent precipitate which was filtered, washed with ether, and dried in vacuo at 65°C for several hours; yields 70–90% *. Recrystallisation from acetonitrile/benzene as above gave pure samples.

Method B. Stoichiometric quantities, (1/1 or 2/1), of triphenyllead halide (1.4–2.0 g; 2.5–3.8 mmol) and tetraethylammonium halide (except for $[Et_4N][Ph_3PbBr_2]$ where 1/2 ratio was used) were dissolved in sufficient hot n-propanol or ethanol (50–100 ml) to give a clear solution. Evaporation of the solution followed by cooling in ice gave the crystalline product which was dried as above; yields 70–95%.

Method C. Stoichiometric quantities (1/2) of diphenyllead halide (1.0–1.6 g; 1.9–3.7 mmol) in acetone (100–200 ml) and tetramethylammonium halide in n-propanol (50–150 ml) were mixed and the fine precipitate produced was isolated as above; yields 85–92%.

Method D. Equimolar quantities of diphenyllead halide (1.5 g; 3.5–2.5 mmol) and tetraethylammonium halide were dissolved in hot acetonitrile (35–100 ml) and the clear solution evaporated to ~ 35 ml. Addition of ethyl acetate (35 ml) to the cooled solution gave the solid product; yields 50–90%.

The following were prepared by literature method [3]: $[Me_4N][Ph_2PbCl_3]$, dec. 310°C (lit. [3] 301°C); $[Me_4N][Ph_3PbCl_2]$, m.p. 307–309°C (dec.) (lit. [3] 298°C); $[Me_4N][Ph_3PbBr_2]$, m.p. 280°C (dec.) (lit. [3] 277°C).

Results

(a) Preparations

Since it was reported earlier [13] that no anionic species were detected in a study

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* Yields throughout this paper are based on the amount of phenyllead halide used.

of Ph_3Pb^+/X^- equilibria in methanol (containing 0.4% water), it is likely that the formation of solid triphenylhaloplumbates from solvents like ethanol or n-propanol reflects the stabilisation of a complex anion by ionic lattice formation. In the present case, counter-ion size appeared to determine the anion formed. Thus the smaller tetramethylammonium ion favoured the formation of $Ph_3PbX_2^-$ (X = Cl, Br), while the larger species $Ph_3PbI_2^-$ and $Ph_6Pb_2X_3^-$ (X = Cl, Br) were produced using the tetraethylammonium ion, even in the cases when equimolar quantities of Et_4NX and Ph_3PbX were used in early experiments. The bromide system is a borderline example of these effects since $[Et_4N][Ph_3PbBr_2]$ was obtained using a 2 to 1 ratio of Et_4NBr to Ph_3PbBr in ethanol, but in the chloride system a 10 to 1 ratio of the same components still gave the diplumbate ion in the solid state. Recently [6], $[Et_4N][Ph_3PbCl_2]$ was prepared using acetonitrile, the high dielectric constant of which probably favours complex anion formation in solution. In this connection, the reaction products were found to be very soluble in acetonitrile and the solid materials could only be isolated by addition of benzene and pentane to the reaction mixture.

The syntheses of diphenylhaloplumbates followed the same trends noted above. Thus, reacting stoichiometric quantities of Ph_2PbX_2 in acetone [14] with Me_4NX in ethanol or n-propanol gave the required products (although we were unable to repeat the preparation of $[Me_4N]_2[Pb_2PbI_4]$ [3]). However, the use of tetraethylammonium halides gave products of variable composition, which were deficient in nitrogen, i.e., in the Et_4N^+ ion. By using acetonitrile as the reaction solvent followed by the addition of ethyl acetate, $[Et_4N][Ph_2PbX_3]$ (X = Cl, Br, I) was obtained.

The compounds containing $Ph_3PbX_2^-$ and $Ph_6Pb_2X_3^-$ ions are crystalline, with sharp melting points consistent with weak ionic forces between large, singly charged ions. In contrast, the diphenylplumbates are microcrystalline, with the higher decomposition temperatures more characteristic of ionic compounds containing ions of higher charge, e.g., $Ph_2PbX_4^{2-}$ and $Ph_4Pb_2X_6^{2-}$, or possibly polymeric anions $(Ph_2PbX_3)_n^{n-}$. Consistent with this view, the dipenylhaloplumbates are soluble only in strong donor solvents, e.g. MeCN or DMF, but triphenylhaloplumbates dissolve also in weaker donors such as acetone and alcohols. All the compounds studied here are insoluble in non-coordinating solvents such as benzene, hexane, methylene chloride, etc., thus precluding molecular weight measurements.

Analytical data and the preparative methods used for all new compounds are given in Table 1.

(b) Vibrational spectra

Raman and infrared peaks assigned to skeletal modes are listed in Tables 2 to 4. Weak to medium peaks in the 200–120 cm^{-1} range assigned to phenyl group (u) and (x) modes [15] have been omitted, as have unassigned deformation and/or lattice modes below 100 cm^{-1} *.

(i) Diphenyllead halide systems (Table 2). Data for diphenyllead iodide are very similar to those reported earlier [12] and the sharp infrared and Raman active ν(Pb–I) bands are consistent with strongly covalent lead–iodine bonds with the Ph_2PbI_2 molecules relatively weakly associated in the solid state. In contrast, our

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* Complete spectral data may be obtained by wnting to the authors of this paper.

TABLE 1

ANALYTICAL DATA

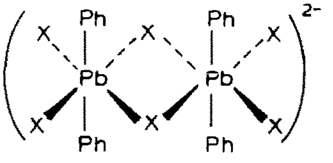
Compound	Method[a]	Colour	M.p. (°C)	Analysis (Found (calcd.) (%))		
				C	H	N
$[Et_4N][Ph_3PbCl_2]$	A	white	157–158[b]	48.9	5.3	2.1
				(48.8)	(5.5)	(2.2)
$[Et_4N][Ph_3PbBrCl]$	A	white	149–150	45.75	5.0	2.0
				(45.65)	(5.2)	(2.05)
$[Et_4N][Ph_3PbClI]$	A	white	176–179	41.7	5.05	2.3
				(42.7)	(4.8)	(1.9)
$[Et_4N][Ph_3PbBr_2]$	B	white	174–175	43.5	4.9	1.9
				(42.9)	(4.8)	(1.9)
$[Et_4N][Ph_3PbBrI]$	B	cream	195–197	39.9	4.6	1.75
				(40.3)	(4.55)	(1.8)
$[Et_4N][Ph_3PbI_2]$	B	pale-yellow	198–200	38.0	4.5	1.65
				(38.0)	(4.3)	(1.7)
$[Et_4N][Ph_6Pb_2Cl_3]$	B	white	181–183	47.3	4.6	1.1
				(47.4)	(4.6)	(1.3)
$[Et_4N][Ph_6Pb_2Cl_2Br]$	B	white	173–177	45.4	4.4	1.2
				(45.6)	(4.35)	(1.2)
$[Et_4N][Ph_6Pb_2ClBr_2]$	B	white	168–171	43.8	4.2	1.15
				(43.95)	(4.2)	(1.2)
$[Et_4N][Ph_6Pb_2Br_3]$	B	white needles	160–162	42.1	4.2	1.05
				(42.4)	(4.1)	(1.1)
$[Me_4N]_2[Ph_2PbCl_4]$	C	white	380	36.9	5.0	5.1
				(36.9)	(5.3)	(4.3)
$[Me_4N]_2[Ph_2PbBr_4]$	C	white	370–380	28.2	4.0	3.4
			(dec.)	(29.0)	(4.1)	(3.4)
$[Et_4N][Ph_2PbCl_3]$	D	white	222–223	39.4	4.9	2.15
			(dec.)	(40.2)	(5.1)	(2.3)
$[Et_4N][Ph_2PbBr_3]$	D	white	224–225	32.85	4.3	1.9
			(dec.)	(32.8)	(4.1)	(1.9)
$[Et_4N][Ph_2PbI_3]$	D	yellow	329–330	26.5	3.2	1.4
			(dec.)	(27.5)	(3.5)	(1.6)

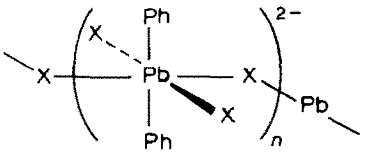
[a] These are given in the experimental section. [b] Lit. [6], 158–159°C.

infrared data for Ph_2PbX_2 (X = Cl, Br) which differ considerably from those previously reported [12] show the halogen-dependent absorption to be a very strong, broad, low frequency band which is not Raman active. This is consistent with the structure of the chloride [10] having chains of Ph_2Pb units linked by pairs of chlorine atoms forming symmetric bridges, while the long lead–chlorine bonds (d(Pb–Cl) 2.80 Å) show them to have low covalent character. Thus, broad, low-frequency, strongly infrared but very weakly Raman active lead-halogen modes may be taken as diagnostic for bridging Pb–X–Pb (X = Cl or Br), with the bonds having high ionic character.

For $Ph_2PbX_4^{2-}$, the halogen-dependent modes are observed as strong, broad infrared absorptions which are only Raman active in the spectrum of the bromo-complex. While the ν(PbX) values are somewhat lower than those found for $Ph_2PbX_2 \cdot 2HMPA$ species [9], the spectra are generally consistent with a six-coordinated *trans*-Ph_2Pb structure, with the four equatorial lead–halogen bonds having more ionic character than in the neutral HMPA adduct. In addition, the Raman and infrared intensities in the lead-phenyl stretch region agree with the ions being fairly centrosymmetric, although some correlation splitting may be present.

Vibrational data for $[R_4N][Ph_2PbX_3]$ (X = Cl, Br) show the terminal and bridging lead-halogen bonds which are formed by the breaking of only half the Pb–X–Pb units in Ph_2PbCl_2 and Ph_2PbBr_2. However, as found for $Ph_2PbX_2 \cdot HMPA$ [9], the data do not permit the two possible six-coordinated anionic structures, Ia or Ib, to be distinguished. Clearly X-ray diffraction studies are required to resolve this question. Although infrared data for $[Et_4N][Ph_2PbI_3]$ are consistent with the presence of a strong lead-iodine bridge similar to the other $Ph_2PbX_3^-$ ions in contrast to the situation found with Ph_2PbI_2, the Raman spectrum of this compound could not be obtained; thus, the assignment in Table 2 must be considered tentative.


(Ia)


(Ib)

Inspection of vibrational data for Ph_2PbX_2, $Ph_2PbX_4^{2-}$, $Ph_2PbX_3^-$, $Pb_2PbX_2 \cdot$ 2HMPA [9], and $Ph_2PbX_2 \cdot HMPA$ [9] suggests an unperturbed $\nu_s(Ph_2Pb)$ value of 194–198 cm^{-1} for the linear diphenyllead moiety. For $Ph_2PbCl_4^{2-}$ and $Ph_2PbCl_3^-$ higher values (~ 210 cm^{-1}) are observed, presumably caused by the interaction of symmetric $\nu(Ph_2Pb)$ and $\nu(PbCl_n)$ modes, as was suggested earlier for the analogous tin systems [8].

(ii) Triphenyllead halide systems (Tables 3 and 4). Infrared and Raman data for triphenyllead iodide are very similar to those reported earlier [12]. The strong sharp lead-iodine stretching mode which is both Raman and infrared active shows that this compound is only weakly associated in the solid state and has a mainly covalent lead–iodine bond. In contrast, our improved infrared spectra for Ph_3PbCl and Ph_3PbBr show strong, broad halogen-dependent absorptions which are only very weakly Raman active, while in the lead-phenyl stretching region (190–240 cm^{-1}) the spectra of both chloride and bromide are very similar. These results are consistent with the structures of these compounds as determined by X-ray diffraction [11], that is, they are isomorphous with chains of distorted trigonal-planar Ph_3Pb groups joined by slightly asymmetric halogen bridges, the lead–halogen bonds having low covalent-bond character.

The splitting of $\nu_{as}(Ph_3Pb)$ and $\nu_s(Ph_3Pb)$ is consistent with vibrational coupling between adjacent Ph_3Pb units in each unit cell, but since this also occurs with Ph_3PbI, the effect clearly does not depend on the nature of the interaction between Ph_3Pb units in the same unit cell.

The spectra of $[Me_4N][Ph_3PbX_2]$ (X = Cl, Br) and $[Et_4N][Ph_3PbX_2]$ (X = Cl, Br, I) suggest that the anions, like the corresponding tin species [8], are trigonal-bipyramidal with axial lead–halogen bonds. However, the extensive splitting of the lead-phenyl stretching modes indicates that the Ph_3Pb unit has lower symmetry than trigonal-planar, as was found in the triphenyllead halides. While spectra of both

(Continued on p. 253)

TABLE 2

VIBRATIONAL SPECTRA (250–80 cm^{-1}) OF DIPHENYLLEAD HALIDES

Ph_2PbCl_2		Ph_2PbBr_2		Ph_2PbI_2		$[Me_4N]_2$ $[Ph_2PbCl_4]$		$[Me_4N]_2$ $[Ph_2PbBr_4]$		$[Me_4N]$ $[Ph_2PbCl_3]$		$[Et_4N]$ $[Ph_2PbCl_3]$		$[Et_4N]$ $[Ph_2PbBr_3]$		$[Et_4N]$ $[Ph_2PbI_3]$ [b]	Assignment
IR	R [a]	IR	R [a]	IR	R [a]	IR	R	IR	R	IR	R	IR	R	IR	R	IR	
237m		232sm		243s		238w		230sm		237wm	239vw					242m	
				218sm			220m		216wm		218vs	222m	225m	220sm	222wm		$\nu_{as}(Ph_2Pb)(t)$ [c]
										212sh				216m		216vs	
	210s		209m	206m	208w		210vs	206wm			209vs	208sh	211s				
196m	197s	199m	194vs			202w			197vs	193s		203m	205s	203wm	196vs	197wm	$\nu_s(Ph_2Pb)(t')$ [c] $+ \nu_t(PbCl_2)$
				187s	186s					187sh	187m		187vs				
										163m	162vw	158m	158m				
										140vs		137vs		140vs	145vm	139m	$\nu_b(PbCl_2)$ or
				137s	140m	160sh		117vs	110m					107sh		122sm	$\nu_t(PbX_2)$ or
99vs		87vs		122vs	118s	144vs		102vs	104w					95vs		83vs	$\nu(PbX_4)$
													112s				
						116m	119sh			123w	128m						$\delta(PbCl_2)$ or
						110m	115m			116w	121sh						$\delta(PbCl_4)$

[a] Data from ref. 12 [b] Sample decomposed under 488.0 nm Ar^+ irradiation. [c] Whiffen's notation [15].

TABLE 3

VIBRATIONAL SPECTRA (250–80 cm^{-1}) OF TRIPHENYLLEAD HALIDES

Ph_3PbCl		Ph_3PbBr		Ph_3PbI		$[Me_4N][Ph_3PbCl_2]$		$[Me_4N][Ph_3PbBr_2]$		$[Et_4N][Ph_3PbCl_2]$		$[Et_4N][Ph_3PbBr_2]$		$[Et_4N][Ph_3PbI_2]$		Assignment
IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	
232vs	229sh	233vs	235vw	233m	234w	229s	229m	229vs		231sm		231vs	230sh			$\nu_{as}(Ph_3Pb)(t)$ [a]
	226wm	226vs	226vw	226vs					226wm	228sm	228m	227sh	226wm	226vs	228w	
								211vs				217s				
212wm	209w	211sm	208w	210m		208sm	208vs	209vw	208wm	217vw	217vs	211m	210w	212s	207w	$\nu_s(Ph_3Pb)(t')$ [a]
202w	198vs	201s	196vs	196wm	197m		192m		197vs	206m			198vs		194s	
						192m					201sh					$\nu_s(PbCl_2)$
						174vs				195vs						$\nu_{as}(PbCl_2)$
										174vs						
						148s				149sm						$\delta(PbCl_2)$
										134sm						
145vs		121vs		123vs	122vs											
136sh			113wm									121sm	120m		91vs	$\nu_b(PbXPb)$ or $\nu_s(PbX_2)$ or $\nu(PbI)$
		100m														
								117vs				109vs		89vs		$\nu_{as}(PbX_2)$
				93w	96s	115s	109vs	96sm	98vs	117sm			95m			$\delta(PbI)$ or $\delta(PbX_2)$
				87vw								88sm	86m			

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[a] Whiffen's notation [15].

TABLE 4

VIBRATIONAL SPECTRA (250–280 cm^{-1}) OF TRIPHENYLLEAD MIXED HALIDE SALTS

[Et$_4$N] [Ph$_3$PbClBr]		[Et$_4$N] [Ph$_3$PbClI]		[Et$_4$N] [Ph$_3$PbBrI]		[Et$_4$N] [Ph$_6$Pb$_2$Cl$_3$]		[Et$_4$N] [Ph$_6$Pb$_2$Cl$_2$Br]		[Et$_4$N] [Ph$_6$Pb$_2$Br$_2$Cl]		[Et$_4$N] [Ph$_6$Pb$_2$Br$_3$]		Assignment
IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	
231vs		231vs	231wm					233s	232wm	231sh	233sh	230sh	232sh	$\nu_{as}(Ph_3Pb)(t)$ [a]
228vs	227wm		228wm	228vs	229w	228s				226vs		226vs		
217w	221sh		218w			221s		220sm	218m	218sh	223m	218sm	222m	
212m				214sm										
203w	200vs	206sm	201vs		208w		217s		208sh		208s	204m	207s	$\nu_s(Ph_3Pb)(t')$ [a]
			196vs		196vs	198sh	193vs	199m	196vs	199w	194vs	199sh	196vs	
						209sm		208vs	(208sh)	205sm				$\nu_t(PbCl)$
180m		175sm				192s	(193vs)							
155m		150wm												$\delta(PbBr)$
						146vs								$\nu_b(PbClPb)$
						132m								
												143m	144sm	$\nu_t(PbBr)$
109sm				106sm	102w						140m	137m	138sh	
								127vs		126vs				$\nu_b(PbBr)$
								114sh		113m		109s		
		85sm		87sm										$\nu(PbI)$

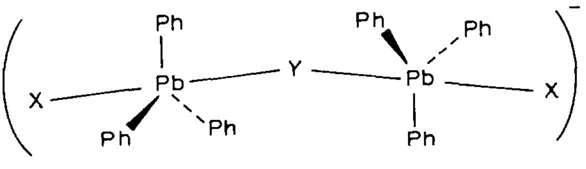
[a] Whiffen's notation [15].

$Ph_3PbBr_2^-$ salts are very similar, those for the corresponding chloro-anions show some differences. In particular, infrared absorptions for $[Et_4N][Ph_3PbCl_2]$ at 195 and 134 cm^{-1} are much more intense than expected for (u) and (x) modes; indeed, that at 195 cm^{-1} is as strong as $\nu_{as}(PbCl_2)$ at 174 cm^{-1}. Thus, we assign these peaks to $\nu_{as}(PbCl_2)$ and $\delta(PbCl_2)$, respectively for a second, structurally distinct $Ph_3PbCl_2^-$ ion in the unit cell, with $\nu_s(PbCl_2)$ for this species coincident with the strong Raman band at 217 cm^{-1}.

Raman and infrared data for $[Et_4N][Ph_3PbXY]$ (Table 4) show that these compounds contain true mixed halo-anions. Of particular interest is the lack of Raman activity of the lead-halogen stretching modes. Presumably, the fact that both ν(Pb–X) modes require movement of the central-lead atom reduces their similarity to $\nu_s(PbX_2)$ in $Ph_3PbX_2^-$ species.

Most triphenyldihaloplumbate spectra show correlation splitting in the lead-phenyl stretching region. The effect appears to depend on cation-anion sizes, i.e., being smallest when the ions are perhaps of similar size, e.g., $[Me_4N][Ph_3PbCl_2]$ and $[Et_4N][Ph_3PbI_2]$, and greatest when they are more disparate, e.g., $[Et_4N][Ph_3PbX_2]$ (X = Cl, Br).

The Raman and infrared spectra of $[Et_4N][Ph_6Pb_2X_3]$ (X = Cl, Br) are consistent with the structure II, derived from that of Ph_3PbX (X = Cl, Br) by the replacement of each alternate halogen bridge with a coordinating halide ion. Thus both $Ph_6Pb_2Cl_3^-$ and $Ph_6Pb_2Br_3^-$ spectra have relatively sharp, higher frequency infrared and Raman bands indicative of terminal Pb–X bonds and the broad, lower frequency infrared absorptions required for a Pb–X–Pb bridge. However, an X-ray diffraction study is required to show whether the halogen bridge is symmetric or asymmetric. The spectra of $[Et_4N][Ph_6Pb_2Cl_2Br]$ show this to be a true mixed halo-species. The existence of ν_t(Pb–Cl) and ν_b(PbBrPb) modes with corresponding lack of peaks assigned to ν_t(Pb–Br) and ν_b(PbClPb) suggests that the anion has a bridging bromine and terminal chlorine atoms (II; X = Cl, Y = Br). In contrast, the data for $[Et_4N][Ph_6Pb_2ClBr_2]$ are more consistent with a double salt containing equal numbers of $(Ph_6Pb_2Br_3)^-$ and $(Ph_6Pb_2Cl_2Br)^-$ ions. The doubling of lead-phenyl stretching modes, particularly $\nu_s(Ph_3Pb)$, is also consistent with vibrational coupling between pairs of strongly connected triphenyllead moieties.



(II)

Raman data for Ph_3PbX, $Ph_3PbX_2^-$, $Ph_6Pb_2X_3^-$, and $Ph_3PbX\cdot HMPA$ [9] suggest 195–200 cm^{-1} as the range for an unperturbed $\nu_s(Ph_3Pb)$ mode, but for $Ph_3PbCl_2^-$ and $Ph_6Pb_2Cl_3^-$ values are shifted to significantly higher frequency, up to 217 cm^{-1}. Although the effect is less pronounced than that observed for the $Ph_3SnX_2^-$ species [8], the reason is presumably the same, i.e., interaction of modes with the same symmetry and similar frequency values, $\nu_s(PbCl_2)$ and $\nu_s(Ph_3Pb)$, causes $\nu_s(Ph_3Pb)$ to be shifted from its unperturbed value.

Discussion

The effects of adduct formation on lead–halogen bonding as shown by changes in ν(Pb–X) values are evident in Table 5 which lists root-mean-square (RMS) lead-halogen stretching frequencies for the phenyllead halide systems reported here and earlier [9]. Although in some cases the data are incomplete, we believe the overall trends are sufficiently clear for the qualitative discussion in this paper.

Adduct formation by monomeric $\mathrm{Ph_3PbX}$ (X = Cl, Br, I) and $\mathrm{Ph_2PbI_2}$ shows the lower ν(PbX) values caused by the increase in coordination from 4 to 5, as was observed earlier with adducts of phenyltin halide [8]. When HMPA replaces a halide in a linear X-Pb-X unit, increased ν(PbX) values show that the *trans*-influence of HMPA strengthens the lead–halogen bond opposite. It is of equal if not greater interest to consider adduct formation by polymeric $\mathrm{Ph_3PbX}$ and $\mathrm{Ph_2PbX_2}$ (X = Cl, Br) in terms of the breaking of mainly ionic $\mathrm{Pb}\overset{\mathrm{X}}{\diagup\ \diagdown}\mathrm{Pb}$ units and the formation of the more covalent lead–halogen terminal bonds with no change in coordination number. For $\mathrm{Ph_6Pb_2X_3^-}$, half the bridging units in solid $\mathrm{Ph_3PbX}$ have been broken with the halogen bridges remaining relatively unaffected, while the terminal bonds appear to be stronger than in $\mathrm{Ph_3PbX_2^-}$.

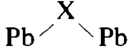
When all bridges in $\mathrm{Ph_2PbX_2}$ (X = Cl, Br) are broken to form $\mathrm{Ph_2PbX_4^{2-}}$, the terminal lead–halogen bonds appear to retain considerable ionic character, perhaps because steric or interionic repulsions between chlorine atoms in a square planar arrangement cause the Pb–X bonds to be longer than those in $\mathrm{Ph_3PbX_2^-}$. In

TABLE 5

RMS STRETCHING FREQUENCIES ($\mathrm{cm^{-1}}$) ν(Pb–X)[a] FOR VARIOUS PHENYLLEAD HALIDE SYSTEMS

	X = Cl	X = Br	X = I
$\mathrm{Ph_3PbX}$(solution)[b]	291	191	150
$\mathrm{Ph_3PbX}$(solid)	141	112	123
$\mathrm{Ph_3PbX_2^-}$	183	115	90
$\mathrm{Ph_3PbX\cdot HMPA}$	217	140	108
$\mathrm{Ph_6Pb_2X_3^-}$			
terminal	201	140	–
bridging	139	109	–
$\mathrm{Ph_2PbX_2}$(solution)[b]	–	–	156
$\mathrm{Ph_2PbX_2}$(solid)	99	87	130
$\mathrm{Ph_2PbX_4^{2-}}$	152	108	–
$\mathrm{Ph_2PbX_2\cdot 2HMPA}$	211	140	114
$\mathrm{Ph_2PbX_3^-}$			
terminal	193	143	131
bridging	152	101	83
$\mathrm{Pb_2PbX_2\cdot HMPA}$			
terminal	–	156	129
bridging	–	121	100

[a] Values from this work and ref. 9; values for some species are estimates since not all ν(Pb–X) bands required for a given species may be identified or only one broad band is observed. [b] Benzene solution data [12].

contrast, Pb–X bonds in $Ph_2PbX_2 \cdot 2HMPA$ appear to resemble those in $Ph_3PbX \cdot HMPA$, in both cases HMPA is *trans* to a halogen. Presumably the small oxygen donor atom in HMPA reduces steric crowding in the di-adduct, and we note that $Ph_2PbI_2 \cdot 2HMPA$ is easily prepared, but all our attempts to prepare $[Me_4N]_2[Ph_2PbI_4]$ have failed. When half the bridges in Ph_2PbX_2 are broken to form $Ph_2PbX_3^-$, the remaining bridging units have similar ν(PbX) values to those found for $Ph_6Pb_2X_3^-$, but it would be premature to suggest this supports the polymeric structure Ib with single  $\mathrm{Pb}\overset{\mathrm{X}}{\diagup\;\diagdown}\mathrm{Pb}$ units for $Ph_2PbX_3^-$ compounds. When a terminal halogen is replaced by HMPA to form $Ph_2PbX_2 \cdot HMPA$, both terminal and bridging ν(Pb–X) values increase, as would be expected from either structure Ia or Ib. Clearly, the wide range of ν(Pb–X) values for lead–halogen bonds show that these bonds vary greatly in the nature of their bonding, and it is unfortunate that organolead halide compounds have received much less attention from X-ray crystallographers than have the corresponding organotin species. In this respect, we hope that some of the compounds reported will be the subject of X-ray diffraction studies in the near future.

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