and $Fe(nic)_3 \cdot H_2O$, which we will term the "normal" values. (These δ values are among the largest observed for ferric ions and substantiate the primarily ionic character of the bonding.) Unfortunately, a comparative reproducible δ value for the parent compound, $Fe(bz)_3 \cdot 0.5H_2O$, cannot be cited until the question of a variable relaxation time is settled.

The difficulty encountered in obtaining reproducible data for the three compounds $Fe(bz)_3 \cdot 0.5H_2O$, $Fe(npbz)_3$, and $Na_3[Fe(bz\text{-}H)_3] \cdot 6H_2O$ may be morphological in origin, with the longest relaxation times characteristic of the most perfect crystals. Similar behavior has been noted for certain alums by Campbell and DeBenedetti.[5] The argument that loss of water of hydration leads to concentration of the iron ions and hence to reduced spin–spin relaxation time could be applied in that case and also to our hexahydrate case. There was a striking difference in the character of the spectra between the trihydrate and the hexahydrate. In the other two ill-behaved cases some explanation other than just concentration would seem to be required.

The compounds $Fe(nph)_3 \cdot 2H_2O$ and $Fe(npbz)_3$ contain secondary hydroxamate ligands. The δ value for the $Fe(nph)_3 \cdot 2H_2O$ complex was slightly less than normal. Despite the well-resolved spectra, the Mössbauer parameters are unusual in that (a) the temperature shift for δ is somewhat higher than expected and (b) the temperature dependence of Δ is large for a high-spin ferric complex. These values were confirmed by repeated syntheses and measurements of the complex. The spectra of $Fe(npbz)_3$ were dominated by relaxation effects but the various estimates for δ were notably lower than normal.

The $Fe(pto)_3$ complex was investigated to determine the effect of substituting sulfur for oxygen. The effect on δ was slight, considering both 300 and 77°K values, and suggests little if any additional covalency due to sulfur. The splitting, Δ, was the smallest, matched only by that of $Fe(ac)_3$.

The splitting in high-spin ferric complexes is dominated by the lattice contribution and in these complexes will depend on (a) departure from octahedral symmetry and (b) inequality of charge on the two coordinating atoms. Except for the nph and pto ligands, and possibly the salts, the chelating ring is the same, and large differences in the geometry are not expected. All of the Δ values are large compared to ferric complexes with six equivalent ligands because of the intrinsic difference between the bonding oxygens. From consideration of resonance structures, one might have expected the aromatic hydroxamates to have greater equality of charge on the coordinating oxygens, yet both $Fe(sal)_3 \cdot 3H_2O$ and $Fe(nic)_3 \cdot H_2O$ exhibited the largest splittings, the Δ values being near the limit observed for high-spin ferric ions. The trend in $Fe(bz)_3 \cdot 0.5H_2O$ results is toward a Δ value of about 0.8 mm/sec, still notably large. The very large Δ's for $Fe(sal)_3 \cdot 3H_2O$ and $Fe(nic)_3 \cdot H_2O$ may be related to the fact that they contain Lewis base groups in the ring.

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Vibrational Spectra and Structure of Organolead Compounds. II. Tetraphenyllead, Hexaphenyldilead, Triphenyllead Halides, and Diphenyllead Dihalides[1]

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The infrared and Raman spectra of tetraphenyllead and of hexaphenyldilead have been recorded over the range 4000–70 cm^{-1} and assignments for the various fundamentals have been made. The spectra have been recorded both in the solid state and in solution. Those of hexaphenyldilead are consistent with the staggered ethane-type structure; the Pb–Pb stretching frequency in this molecule is at 114 cm^{-1} in the solid state and at 109 cm^{-1} in solution. The triphenyllead halides and the diphenyllead dihalides, where soluble, are shown to behave as monomers in benzene solution, and their infrared and Raman spectra over the range 450–70 cm^{-1} have been assigned satisfactorily on this basis. In the solid state, however, the spectra, as well as other evidence, suggest that the mono- and dihalides are polymeric by way of halogen bridging. Triphenyllead chloride in benzene or in cyclohexane solution shows an isotopic splitting of the Pb–Cl stretching mode of ~ 6 cm^{-1}.

In part I of this series,[1] the infrared and Raman spectra of the trimethyllead halides and the dimethyllead dihalides were studied in the solid state as well as in solution. The compounds were shown to be monomeric in solution, but halogen-bridged polymeric in the solid state. The present investigation was aimed at making a similar study of the corresponding phenyl compounds, *viz.*, $(C_6H_5)_3PbX$ (X = F, Cl, Br,

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[1] Part I: R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Am. Chem. Soc.*, **90**, 6923 (1968).

or I) and $(C_6H_5)_2PbX_2$ (X = Cl, Br, or I). Diphenyllead difluoride is apparently not yet known. The melting points of the halides (Table I) suggest that they are associated in the solid state. Their precursors, tetraphenyllead and hexaphenyldilead, have also been studied as a prerequisite to the analysis of the spectra of the phenyllead halides. The PbPb stretching frequency in hexaphenyldilead has been located both in the solid state and in the solution Raman spectra.

Table I

Melting Points of the Group IV Triphenylmetal Halides and Diphenylmetal Dihalides (°C)

Compound	M			
	Si	Ge	Sn	Pb
$(C_6H_5)_4M$	237	230	225	225
$(C_6H_5)_3MF$	64	77	357 dec	318 dec
$(C_6H_5)_3MCl$	111	118	107	206
$(C_6H_5)_3MBr$	119	138	122	166
$(C_6H_5)_3MI$	156	157	121	139
$(C_6H_5)_2MF_2$	Liq[a]	Liq	>360	. . .
$(C_6H_5)_2MCl_2$	Liq	9	44	286 dec
$(C_6H_5)_2MBr_2$	3.8	Liq	38	250 dec
$(C_6H_5)_2MI_2$	. . .	71	72	103

[a] Liq = liquid of unknown melting point.

The results and discussion are most conveniently subdivided into (A) tetraphenyllead, (B) hexaphenyldilead, (C) triphenyllead halides, and (D) diphenyllead dihalides.

Experimental Section

Preparation of Compounds.—Tetraphenyllead, hexaphenyldilead, triphenyllead chloride, and diphenyllead dichloride were supplied by the International Lead-Zinc Research Organization and were used without further purification.

Triphenyllead bromide and triphenyllead iodide were prepared from triphenyllead hydroxide and the approprirate hydrogen halide in acetone solution.[2] They were purified by recrystallization from benzene. Triphenyllead fluoride was precipitated from solution when an aqueous solution of potassium fluoride was shaken with a benzene solution of triphenyllead chloride.[3]

Diphenyllead dibromide[4] and diphenyllead diiodide[5] were prepared by treating tetraphenyllead with the appropriate halogen. The iodide was purified by recrystallization from benzene.

Physical Measurements.—The infrared spectra in the region 4000–200 cm^{-1} were recorded on a Perkin-Elmer 225 spectrometer. Solids were run as Nujol or hexachlorobutadiene mulls while solution studies were carried out using carbon tetrachloride or benzene as solvents; potassium bromide, cesium iodide, or polythene plates or cells were used as appropriate. Low-frequency spectra of compounds were recorded using a Grubb-Parsons GM3 (200–70 cm^{-1}) instrument as Nujol mulls and, where possible, also as benzene solutions using polythene plates or cells. The spectra in this region were calibrated against the spectrum of water vapor. Solid-state spectra below 200 cm^{-1} were recorded at liquid nitrogen temperatures in order to improve resolution.

The Raman spectra were recorded using a Cary 81 spectrometer fitted with an He–Ne (6328-Å) source. Spectra were recorded on the solid powders, packed into the standard metal cone supplied with the instrument, or as benzene solutions sealed into glass capillaries. We are grateful to the University of London for making this instrument available.

The molecular weights were as follows: found for $(C_6H_5)_3PbCl$, 477 at 2.78×10^{-2} *M;* calcd for monomer, 474; found for $(C_6H_5)_3PbBr$, 498 at 4.78×10^{-2} *M;* calcd for monomer, 518; found for $(C_6H_5)_3PbI$, 549 at 4.87×10^{-2} *M;* calcd for monomer, 565; found for $(C_6H_5)_2PbI_2$, 610 at 4.99×10^{-2} *M;* calcd for monomer, 615.

Results and Discussion

A. Tetraphenyllead.—On the basis of an X-ray diffraction analysis, tetraphenyllead is known[6] to have an exactly tetrahedral PbC_4 skeleton; however, the molecular symmetry is S_4 owing to the conformation of the phenyl groups relative to each other. (The tetraphenyl compounds of carbon, silicon, germanium, and tin are isostructural with it.) The lead compound is almost certainly also tetrahedral in solution, though it is insufficiently soluble to enable a molecular weight determination to be carried out. The infrared spectra of tetraphenyllead and of some other phenyllead compounds have previously[7,8] been measured down to 680 cm^{-1}. We have remeasured these spectra and extended the measurements to 70 cm^{-1}; we have also measured the Raman spectra, and the combined data are given in Table II. The assignments in this table are made by comparison of the spectra with those of the phenyl halides[9] and of phenyltin compounds.[10-16] Certain of these call for special comment.

The band at 997 cm^{-1} is assigned as the p mode (in Whiffen's nomenclature[9]); it is a ring deformation which is insensitive to the substituent. Of the bands associated with the $M-C_6H_5$ linkages (the so-called X-sensitive modes, *i.e.*, substituent-sensitive modes[9]), those of highest frequency are the q mode (at 1062 cm^{-1}) and the r mode (at 645 cm^{-1}). Bands between 986 and 726 cm^{-1}, which are all only weak in the Raman spectra, are assigned as CH out-of-plane deformations. The remaining X-sensitive modes, the y, t, u, and x modes,[9] together with the q and r modes, are illustrated below, and are assigned in Table III.

The bands associated with the y modes (~440 cm^{-1}) show some doubling owing to coupling between the same vibration of different phenyl groups. The bands near 200 cm^{-1} are described[9] as t modes and are very sensitive to M; for example, their values for C_6H_5F, C_6H_5Cl, C_6H_5Br, and C_6H_5I are 406, 297, 254, and 220

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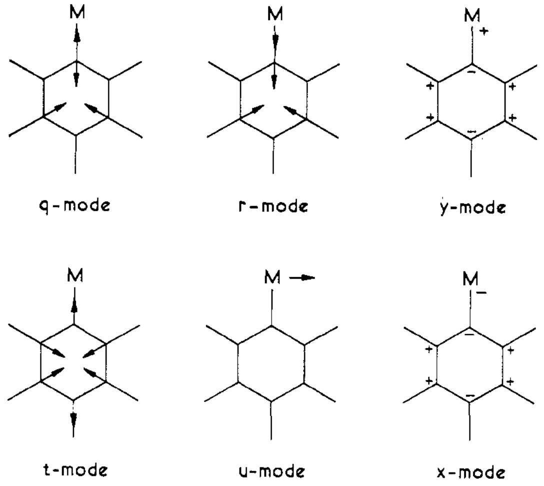
TABLE II[a]

THE INFRARED AND RAMAN SPECTRA (4000–500 CM^{-1}) OF SOME PHENYLLEAD COMPOUNDS IN THE SOLID STATE

Probable assignments	$(C_6H_5)_4Pb$		$(C_6H_5)_6Pb_2$		$(C_6H_5)_3PbF$	$(C_6H_5)_3PbCl$	$(C_6H_5)_3PbBr$	$(C_6H_5)_3PbI$	$(C_6H_5)_2PbCl_2$	$(C_6H_5)_2PbBr_2$	$(C_6H_5)_2PbI_2$
	R	Ir	R	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir
ν(CH)	3061 s	3059 m	3062 s	3058 m	3068 m	3059 sh	3062 m	3060 m		3064 vw	
					3053 m		3048 m	3050 m	3050 w		
	3041 vs	3037 m	3040 vs	3035 w	3046 m	3042 m		3038 m	3037 w, sh	3042 m	3041 m
	3021 w	3016 w	3007 w	3007 w							
	2987 w	2981 w	2985 w		2990 w	2980 w					
		1955 w		1955 w	1958 w	1953 w		1945 w	1949 w	1947 w	1963 vw
		1895 w		1892 w	1901 w	1897 w	1888 w	1890 vw	1895 vw	1894 vw	1891 vw
		1875 w		1872 w	1885 w	1866 w	1864 w	1864 w	1867 w	1863 w	1863 vw
		1818 w		1815 w	1820 w	1815 w	1798 w	1804 w	1783 w	1773 vw	
		1762 w			1769 w	1744 w	1740 w	1740 w	1735 vw		1739 vw
		1640 w			1647 w	1630 w	1626 w				
ν(CC)	1570 vs	1569 ms	1570 vs	1568 ms	1576 m	1565 ms	1564 m	1565 m	1558 m	1556 ms	1566 m
							1558 m				1550 w
	1474 s	1475 ms	1476 s	1474 ms	1479 ms	1474 ms	1474 ms	1474 ms	1474 ms	1471 ms	1466 ms
	1432 m	1428 s	1431 m	1429 s	1434 ms	1428 s	1429 ms	1431 ms	1440 ms	1438 ms	1429 ms
	1397 w	1377 w	1395 w	1375 w	1378 w	1375 m	1375 m	1376 m	1379 m, br	1380 m, br	1365 m, br
	1331 m	1328 m	1330 m	1326 w	1330 w	1324 m	1325 m	1325 m	1323 m	1321 m	1315 m
		1299 m		1296 w	1301 w	1297 m	1296 m	1297 m			1297 m
β(CH)	1262 w	1258 m	1261 w	1258 w		1256 w	1257 w		1255 w	1251 w	
	1190 ms	1213 vw	1188 ms	1183 w		1182 w	1180 w	1184 w			1183 w
		1172 w		1168 w	1173 w	1168 w	1167 w	1170 w	1170 vw		
	1159 s	1149 m	1158 s	1156 w	1161 w	1152 m	1154 m	1155 m	1162 m	1161 w	1154 m
	1153 sh								1087 w	1086 w	1083 m
										1059 w	1053 m
q mode	1063 m	1061 s	1062 s	1057 ms	1068 m	1058 ms	1057 ms	1060 ms	1052 w	1046 w	1042 m
β(CH)	1019 s	1018 s	1018 m	1014 s	1023 ms	1015 s	1013 ms	1012 ms	1014 ms	1013 m	1010 m
p mode	998 vs	997 s	1000 vs	996 s	995 s	995 s	994 s	994 s	990 s	987 s	992 s
γ(CH)	986 w	984 vw		983 vw		984 vw	982 vw	984 vw	986 s	982 s	982 s
		974 m				973 vw	967 vw	967 w			
	915 w	907 m	913 w		914 w	906 w	910 vw		912 w	910 w	898 w
	856 vw	851 w	856 vw	852 vw		846 w	853 w	846 w			
						839 w	844 w				
	740 w	754 m, br	731 w	734 w		794 w	838 w				808 w
		726 vs		723 vs	732 vs	727 vs	728 vs	729 sh			728 sh
					722 vs	720 vs	720 vs	722 vs	719 vs	717 vs	720 vs
φ(CC) v mode	700 w	697 vs	700 w	695 vs	694 vs	691 vs		696 m			685 m
						687 vs	686 vs	686 vs	673 s	672 s	672 m
		668 m			667 w			668 w	668 sh	664 sh	668 m
r mode	645 vs		648 vs						652 m	650 m	643 m
α(CCC)	617 m	617 vw	618 w	614 vw	614 w	612 vw	612 w	613 w			618 vw
s mode											607 vw

[a] Abbreviations: ν, stretching vibration; β, in-plane deformation; γ, out-of-plane deformation; φ, out-of-plane ring deformation; α, in-plane ring deformation (*cf.* ref 9).



cm^{-1}, respectively. The t modes, which are essentially M–C_6H_5 stretching vibrations, show the fall in frequency down group IV, *viz.*, ν(Si–Ph)[16,17] ~430, ν(Ge–Ph)[18] ~320, ν(Sn–Ph)[11] ~250 cm^{-1}, expected from mass and bond strength considerations.

On the basis of S_4 selection rules, the Pb–C_6H_5 stretching frequencies belong to the symmetry species a, b, and e, all of which are Raman active but only the b and e modes of which are infrared active. However, as the PbC_4 skeleton does not differ significantly from tetrahedral, the b and e modes are expected to be nearly degenerate (they both correlate with t_2 in T_d symmetry). The asymmetric stretching modes are considered to give rise to the bands near 220 cm^{-1}, which are very strong in the infrared spectra and medium in the Raman spectra. The band at ~200 cm^{-1} is assigned as the symmetric (a) Pb–C_6H_5 stretching mode on the grounds that it occurs as a strong, polarized band in the Raman spectrum. It is, however, also active in the solid-state infrared spectrum.

The two lowest frequency X-sensitive modes, namely, the u mode (an in-plane PbC deformation) and the x mode (an out-of-plane ring-buckling mode), are considered to give rise to the bands at ~182 and ~150 cm^{-1}, respectively, by analogy with the spectra of other substituted benzene molecules.[9-16]

The skeletal bending modes occur at or below 100 cm^{-1}.

B. Hexaphenyldilead.—The structure of hexaphenyldilead has not yet been determined, but, on the basis of electron diffraction work,[19] that of hexamethyldilead was found to be of the ethane type, with D_{3d} symmetry. The C–Pb and Pb–Pb bond lengths were found to be 2.25 and 2.88 Å, respectively. It seems probable that hexaphenyldilead has the same structure.

The internal vibrations of the phenyl groups (Table II) occur at virtually the same frequencies as for tetraphenyllead and do not call for further comment. On the basis of D_{3d} selection rules, the Pb–C_6H_5 stretching modes belong to the following types: a_{1g}(R), e_g(R), a_{2u}(IR), and e_u(IR).

Table III

The Infrared and Raman Spectra (500–70 cm^{-1}) of Tetraphenyllead and Hexaphenyldilead in the Solid State and in Benzene Solution

	$(C_6H_5)_4Pb$				$(C_6H_5)_6Pb_2$			
	Solid		Soln		Solid		Soln	
Assignment	R	Ir	R	Ir	R	Ir	R	Ir
y mode	447 w	450 s			447 m	447 m	445 m	
	437 w	440 s	*a*	440 s		441 s		438 s
						433 m		
ν_a(Pb–C_6H_5)	224 m	223 s		221 s	233 w	223 sh	230 m	
	214 m				220 m	218 s	217 m	219 s
ν_s(Pb–C_6H_5)	199 vs	201 s	196 s, p		204 vs		203 vs, p	
u mode	184 w	181 s			171 m	181 s		
x mode	152 s	147 m			150 w	144 w		
ν(Pb–Pb)					114 vs		109 vs, p	
Skeletal bends	110 m							
	87 vs							
	72 m				74 m			

[a] Compound insufficiently soluble to observe more than a single Raman band in solution.

The very strong, polarized band at 203 cm^{-1} in the solution Raman spectrum of the compound is assigned unambiguously as the a_{1g} totally symmetric Pb–C_6H_5 stretching mode; its absence in the infrared spectrum confirms that the molecule is centrosymmetric (Table III).

The very strong, polarized band in the solution Raman spectrum of the compound at 109 cm^{-1} is assigned as the Pb–Pb stretching vibration. It thus lies, as expected, well below the SnSn stretching frequency of hexamethylditin (190 cm^{-1}).[10]

The solid-state spectra of the compound in the 200-cm^{-1} region are appreciably more complicated than in solution, and it is clear that, in this state, crystal field effects are important.

C. Triphenyllead Halides.—With the exception of the fluoride, which in any case has a high decomposition point of over 300°, the melting points of the triphenyllead halides are all appreciably higher than those of the

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analogous tin compounds (Table I). Triphenyltin fluoride is polymeric in the solid state,[11] but the other phenyltin halides are monomeric both in the solid state and in solution.[11,12] On the other hand, although triphenyllead chloride, bromide, and iodide are monomeric in benzene solution (this work) and nonelectrolytes when dissolved in N,N-dimethylformamide,[20] in the solid state their melting points suggest that they are all polymeric. We set out to study this apparent dependence of the structures of the compounds on their phase by measurements of their vibrational spectra.

Solution Spectra.—The solution infrared and Raman spectral measurements have been confined to the region below 450 cm^{-1}, because little or no structural information can be derived from a study of the internal vibrations of the phenyl groups. The band maxima, together with their assignments, are in Table IV.

The y mode discussed above for tetraphenyllead and hexaphenyldilead occurs near 440 cm^{-1} in the spectra of the halides. No solution measurements could be made for the fluoride owing to its low solubility in all convenient solvents.

The skeletal stretching modes in C_{3v} symmetry belong to the species $a_1 + e$ (Pb–C_6H_5) and a_1 (Pb–X); both a_1 and e modes are infrared as well as Raman active. The a_1 (ν_s) Pb–C_6H_5 stretching mode occurs at 200 cm^{-1} as a strong, polarized band in the Raman spectra and also as a strong band in the infrared spectra. The asymmetric stretching mode (ν_a) occurs as a strong to very strong band in the infrared spectra but as a medium band in the Raman spectra, near 224 cm^{-1} in each case. Both the symmetric and the asymmetric stretching vibrations in these compounds lie very close to their values in tetraphenyllead and in hexaphenyldilead.

The PbX stretching vibrations in these compounds lie at 290, 191, and 150 cm^{-1} for X = Cl, Br, and I, respectively (*cf.* the SnX stretching vibrations of the analogous tin compounds which are at 342, 231, and 170 cm^{-1} for X = Cl, Br, and I, respectively).[11,12] They occur as strong to very strong bands in both the infrared and the Raman spectra, being polarized in the latter as expected for a_1 vibrations. The frequencies in each case are nearly identical with those found for the corresponding trimethyllead halides,[1] which also exist as monomers with C_{3v} symmetry in solution. The PbX stretching frequencies in the triphenyl derivatives are actually 0–7 cm^{-1} higher than those for the corresponding trimethyl derivatives; as this trend is the opposite to that expected from mass considerations, it suggests that phenyl groups have a slightly higher electronegativity than methyl groups when attached to lead, leading to a higher effective positive charge on the lead atoms and hence higher PbX stretching frequencies.

The infrared-active band attributed to the PbCl

TABLE IV

THE INFRARED AND RAMAN SPECTRA (500–70 CM^{-1}) OF THE TRIPHENYLLEAD HALIDES IN THE SOLID STATE AND IN BENZENE SOLUTION

	$(C_6H_5)_3PbF$		$(C_6H_5)_3PbCl$				$(C_6H_5)_3PbBr$				$(C_6H_5)_3PbI$			
	Solid		Solid		Soln		Solid		Soln		Solid		Soln	
Assignment	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir
y mode	445 w	446 s		448 m										
			443 w	441 s	435 w	440 s			435 w	441 s	442 m	444 s	442 w	441 s
				438 s			443 m	438 s						
w mode							390 w				394 w			
ν_a(Pb–C_6H_5)	233 m	234 s	236 m	234 m			236 m	234 m			235 m	233 m		
		209 m	228 m	224 s		222 s	228 m	224 s	228 m	225 s	213 sh	225 s	227 m	224 s
ν_s(Pb–C_6H_5)	200 s	194 s	199 vs	203 m	200 vs	200 s	208 m	200 s	200 sh, p	201 vs	198 vs	195 s	200 s, p	202 vs
							196 vs					189 s		
ν(Pb–X)		343 s, br		180 s	291 s	290 s		121 vs, br	191 vs, p	191 sh	121 vvs	122 vs	151 vs, p	149 s
		299 m, br				284 sh								
u mode	170 m	167 w	175 m			181 ms	175 m	175 m			174 m			
x mode		150 w	152 w	164 s		166 m	156 w				156 m			
		142 m		143 s								131 sh		
Skeletal bends				128 s										
				112 s		110 m					97 s			
	80 s		78 s			92 m	76 vs				69 sh			

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stretching vibration of triphenyllead chloride in benzene or cyclohexane solutions (290 cm^{-1}) has a shoulder 6 cm^{-1} to lower energy. It is considered that this shoulder arises from the $PbCl^{37}$ stretching vibration, the Cl^{37} being present in its natural abundance (24.47%).

In benzene solution, the PbBr and the symmetric $Pb-C_6H_5$ stretching vibrations of triphenyllead bromide are nearly coincident, as might have been expected from mass considerations. As both vibrations have a_1 symmetry, they are likely to be appreciably mixed. Similar effects have been noted previously in the spectra of triphenylgermanium bromide[18] and triphenyltin bromide.[11]

The skeletal bending modes could not be located in solution.

Solid-State Spectra.—The solid-state infrared and Raman spectra of the compounds are in Tables II and IV. The y modes occur at nearly the same frequencies in the solid state as in solution; so do the symmetric and asymmetric $Pb-C_6H_5$ stretching modes, although both of these vibrations are doubled in most of the solid-state spectra.

The PbX stretching vibrations are more difficult to assign in the solid-state spectra, since bands due to the phenyl groups often interfere. However, it is clear that they are depressed by 28–100 cm^{-1} from their values in solution and hence that the compounds are polymeric in the solid state (Figure 1). The iodide, which shows the lowest drop in the PbX stretching frequency in going from solution to the solid state, is probably least strongly associated in the solid state. The PbF stretching frequencies occur at 299 and 343 cm^{-1} in the infrared spectrum of triphenyllead fluoride but were unobserved in the Raman spectrum. The same situation prevails for triphenyltin fluoride,[11,12] for which ν(SnF) was found at 372 cm^{-1} in the infrared spectrum but was not observed in the Raman spectrum. The PbCl stretching vibration is probably associated with the band at 180 cm^{-1} in the infrared spectrum of the solid chloride, while the PbI stretching frequency is at 122 cm^{-1}.

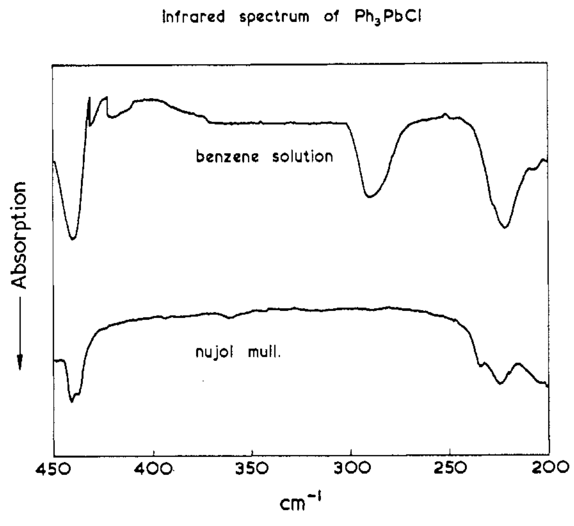

Figure 1.—Infrared spectrum of triphenyllead chloride in benzene solution and in the solid state.

While the skeletal stretching and bending frequencies could not be completely assigned, it seems likely that the structures of the compounds in the solid state are similar to that proposed[1] for the solid trimethyllead halides, *viz.*, nearly planar PbC_3 skeletons, joined together by chains of the type –X–Pb–X–, this being the known structure of trimethyltin fluoride.[21]

D. Diphenyllead Dihalides.—The crystal structure of diphenyllead dichloride has recently been determined.[22] The compound consists of planar Cl_2PbCl_2 chains containing equivalent Pb–Cl bonds mutually perpendicular, with the phenyl groups normal to the chain axis and with the Pb–C bonds nearly perpendicular to the plane of the chain (Figure 2). The Pb–C and Pb–Cl bond lengths are 2.12 and 2.80 Å, respectively. The polymeric nature of the solid dichloride and dibromide is also suggested by the high melting points of the compounds (Table I) and their low solubilities in usual solvents.

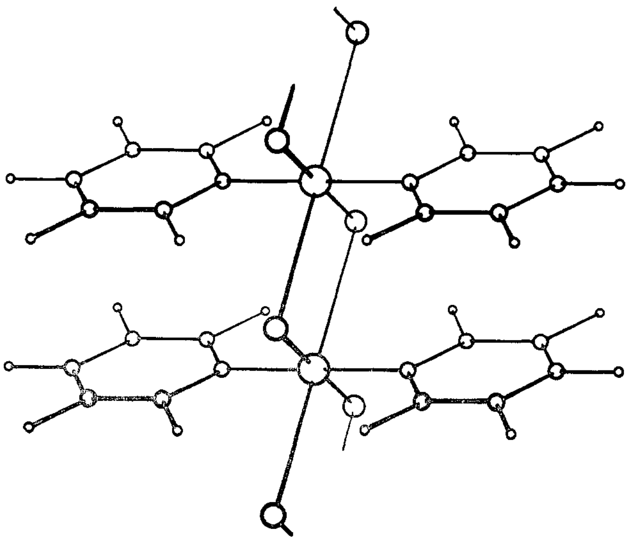

Figure 2.—Structure of diphenyllead dichloride.

On the other hand, in solution it is clearly impossible that the dihalides retain the same structure, and molecular weight measurements (this work) have indeed shown that the diiodide is a monomer in benzene solution. Accordingly, we first discuss the solution spectra of the diiodide, the only dihalide for which the solubility is sufficient for such measurements.

Solution Spectra of the Diiodide.—The band maxima and assignments for this molecule are in Table V. On the basis of a skeletal symmetry of C_{2v} for the monomeric molecule, the two $Pb-C_6H_5$ stretching frequencies and the two Pb–I stretching frequencies have the symmetries $a_1 + b_1$ and $a_1 + b_2$, respectively (PbC_2 in $\sigma_v(zx)$, PbI_2 in σ_v (zy)). All of these bands should be both infrared and Raman active.

The former occur at $\sim$204 cm^{-1} (a_1, strong and polarized in the Raman spectrum and strong in the

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(21) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 85 (1963).

(22) M. Mammi, V. Busetti, and A. Del Pra, *Inorg. Chim. Acta*, 1, 419 (1967).

TABLE V

THE INFRARED AND RAMAN SPECTRA (500–70 CM^{-1}) OF THE DIPHENYLLEAD DIHALIDES IN THE SOLID STATE AND IN BENZENE SOLUTION (FOR DIPHENYLLEAD DIIODIDE ONLY)

	$(C_6H_5)_2PbCl_2$		$(C_6H_5)_2PbBr_2$		$(C_6H_5)_2PbI_2$			
	Solid		Solid		Solid		Soln	
Assignment	R	Ir	R	Ir	R	Ir	R	Ir
y mode		446 s		446 s		440 s	441 m	437 s
		256 m		252 m		242 ms		
$\nu_a(Pb–C_6H_5)$		236 s		230 s		232 ms	235 m	229 s
	210 s		209 m			217 s		
$\nu_s(Pb–C_6H_5)$	197 s	194 s	194 vs	197 s	208 w	205 m	208 s, p	205 s
					186 s	186 s		
$\nu(Pb–X)$				122 s	140 m	136 s?	162 sh	160 s
					118 s	121 s	152 vs, p	144 s
u mode	167 m		168 m			177 sh		
					158 m			
x mode		139 s		138 s		136 s		
Skeletal bends		105 sh						
	90 m	95 s	92 s	89 s	94 s			
			71 s					

infrared spectrum) and at ~230 cm^{-1} (b_1, medium in the Raman spectrum and strong in the infrared spectrum).

The PbI stretching frequencies are at ~148 cm^{-1} (a_1, very strong and polarized in the Raman spectrum and strong in the infrared spectrum) and 161 cm^{-1} (b_2, shoulder in the Raman spectrum and strong in the infrared spectrum). The average PbI stretching frequency in this compound (~155 cm^{-1}) is slightly (~5 cm^{-1}) above that found for triphenyllead iodide in solution, consistent with the thesis advanced previously[1,23] that replacement of organo groups attached to a metal atom by more electronegative halogen atoms results in a higher effective nuclear charge on the metal atom and hence higher metal–ligand stretching frequencies.

Solid-State Spectra.—It seems probable that all of the diphenyllead dihalides, with the exception of the apparently unknown difluoride, have the diphenyllead dichloride structure in which the local symmetry of the lead atoms is D_{2h}. On this basis, four PbX stretching vibrations are possible, those of symmetry a_g and b_{1g} being Raman active only and those of symmetry b_{2u} and b_{3u} being infrared active only.

Both the out-of-plane PbC deformation frequencies as well as the $Pb–C_6H_5$ symmetric and asymmetric stretching frequencies show shifts up to 22 cm^{-1} on passing from solution to the solid state. Moreover, the PbI stretching frequencies show similar shifts, to lower frequencies, on change of state. Thus it is clear that the diiodide is polymeric in the solid state. However, owing to the number of phenyl vibrations occurring below 200 cm^{-1}, it did not prove possible confidently to interpret the solid-state spectra of this compound. The PbCl stretching frequencies of solid diphenyllead dichloride lie well below the values found for monomeric tetrahedral[24] and monomeric octahedral[25] chloro species of lead(IV) consistent with the longer Pb–Cl bonds expected for bridging ClPbCl groups; *cf.* data in ref 26. Further interpretation of these spectra did not prove possible, owing to their relatively poor resolution. The solid-state spectra are therefore included in Table V simply with suggested assignments.

Conclusion

It has been shown that whereas tetraphenyllead, hexaphenyldilead, triphenyllead chloride, triphenyllead bromide, triphenyllead iodide, and diphenyllead diiodide are monomers in solution and whereas their vibrational spectra may be satisfactorily interpreted on this basis, in the solid state the triphenyllead halides and the diphenyllead dihalides are polymeric by way of halogen bridging. As the triphenyltin halides (X = Cl, Br, or I) are monomers both in the solid state as well as in solution, the present results indicate a greater tendency for the larger lead atoms to achieve a coordination number higher than 4. The lead atoms are probably five-coordinate in the triphenyllead halides and six-coordinate in the diphenyllead dihalides. Diphenyllead diiodide is probably less strongly associated than the corresponding chloride and bromide.

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[24] J. T. Neu and W. D. Gwinn, *J. Am. Chem. Soc.*, **70**, 3463 (1948).

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