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Preparation and characterization of diphenyllead(IV) and triphenyllead(IV) complexes with *N*-protected amino-acids and the dipeptides

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The diphenyllead(IV) derivatives of *N*-benzoyl--(glycine, DL-alanine); *N*-formyl and *N*-acetyl-L-phenylalanine; *N*-monochloroacetyl-L-phenylalanine; *N*-benzoyl-(glycylglycine,DL-alanylglycine), and *N*-formyl- *N*-acetyl- and *N*-monochloroacetyl-(L-phenylalanylglycine) have been prepared in 1:2 molar ratio by reaction of diphenyllead dichloride with the appropriate amino-acid or dipeptide. Corresponding triphenyllead(IV) derivatives have been prepared in 1:1 molar ratio by reaction of triphenyllead chloride with the thallium(I) salts of the amino-acid or the dipeptide. These complexes have been characterized by elemental analysis, IR and ^{1}H NMR spectral studies. A polymeric hexa-coordinated octahedral structure for diphenyllead(IV), and a five-coordinated distorted trigonal-bipyramidal chain-type structure for triphenyllead(IV), complexes is confirmed by IR spectra. The carboxylate group acts in a bidentate manner, not as in diorgano and triorganotin(IV) complexes with these acids, where it is monodentate. The available bonding sites such as amide and peptide carbonyl (CO) and amide and peptide nitrogen atoms are not involved in bonding with lead (IV) and thus are available for bonding with the biological systems. The presence of different *N*-protecting groups does not affect the coordination sites around lead(IV). The triphenyllead(IV) compounds are relatively more stable than the diphenyllead(IV) compounds.

Keywords: Organolead(IV), *N*-protected amino-acids and dipeptides, structures, complexes

INTRODUCTION

Rather few di- and tri-organolead(IV) derivatives of *N*-acylamino acids have been reported,[1–4] whilst derivatives of *N*-acyldipeptides are not known. In continuation of our earlier studies on triorganotin(IV),[5–8] di- and tri-organolead(IV)[9] derivatives of *N*-protected amino-acids and *N*-protected dipeptides, we report here the preparation and characterization of diphenyllead(IV) and triphenyllead(IV) derivatives with *N*-protected amino-acids and dipeptides. The bonding sites are definitely different for these organolead(IV) complexes as compared with the organotin(IV) complexes.[5–8] The carboxylate group is unidentate in the case of di- and tri-organotin(IV) complexes whereas it is bidentate in the di- and tri-organolead(IV) complexes. The antibacterial, antifungal and antitumour properties of these complexes will be reported later.

EXPERIMENTAL

Materials and methods

Literature procedures were used to prepare Ph_3PbCl,[10] Ph_2PbCl_2,[11] *N*-benzoylglycine,[12] *N*-benzoyl-DL-alanine,[13] *N*-acetyl-L-phenylalanine,[13] *N*-formyl-L-phenylalanine,[13] *N*-monochloroacetyl-L-phenylalanine,[14] *N*-benzoylglycylglycine,[15–17] *N*-acetyl-L-phenylalanylglycine,[17–19] *N*-formyl-L-phenylalanylglycine[17,19] and *N*-monochloroacetyl-L-phenyalanylglycine.[14,17,19]

Preparation of sodium and thallium(I) salts

The sodium salts of ligands were prepared for comparing their IR data with the IR data of complexes, whilst thallium(I) salts of ligands were used in the preparation of the triphenyllead(IV) complexes.

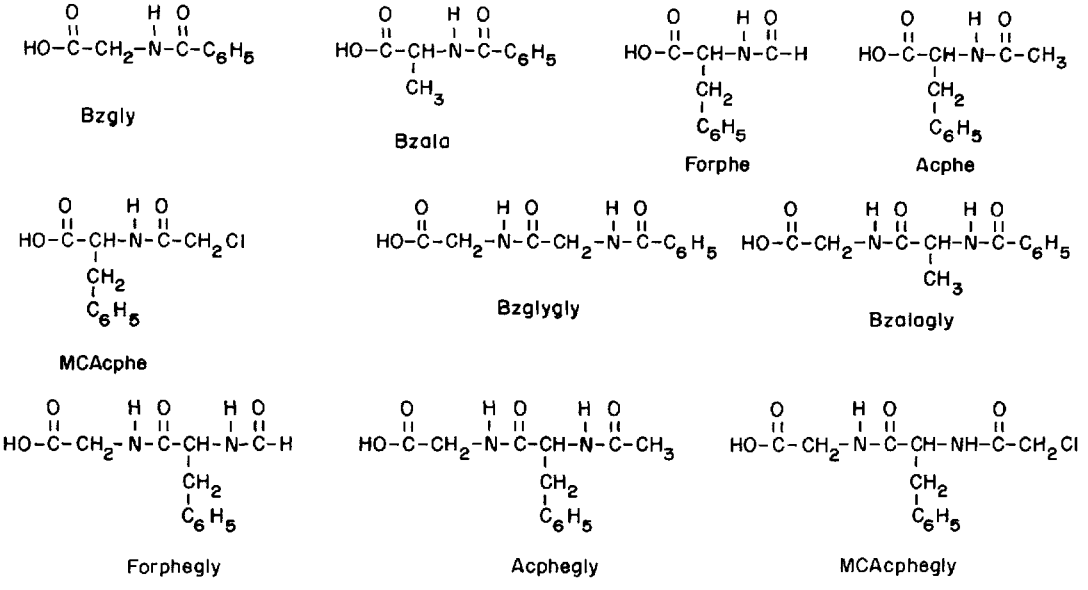


Figure 1

Table 1 Physical and analytical data of diorganolead(IV) and triorganolead(IV) complexes/ITH *N*-protected amino-acids and their dipeptides

No.	Complex[a]	Yield (%)	M.P. (°C)	Analysis(%), Found (calc.)			
				C	H	N	Pb
1	$Ph_2Pb(Bzgly)_2$	70	150[b]	50.54 (50.84)	3.51 (3.82)	3.80 (3.82)	—
2	$Ph_2Pb(Bzala)_2$	70	160[b]	50.91 (51.49)	3.91 (4.02)	3.41 (3.95)	27.35 (27.85)
3	$Ph_2Pb(Forphe)_2$	68	155[b]	50.97 (51.18)	39.2 (4.02)	3.15 (3.75)	—
4	$Ph_2Pb(Acphe)_2$	65	160[b]	52.20 (52.73)	4.12 (4.39)	3.55 (3.61)	—
5	$Ph_2Pb(MCAcphe)_2$	70	170[b]	47.89 (48.41)	3.77 (3.79)	2.95 (3.32)	24.12 (24.64)
6	$Ph_2Pb(Bzglygly)_2$	58	185[b]	48.71 (49.05)	3.62 (3.85)	6.21 (6.73)	24.22 (24.97)
7	$Ph_2Pb(Bzalagly)_2$	65	190[b]	49.75 (50.25)	4.15 (4.19)	6.10 (6.51)	—
8	$Ph_2Pb(Forphegly)_2$	75	190[b]	49.84 (50.25)	3.94 (4.19)	6.08 (6.51)	—
9	$Ph_2Pb(Acphegly)_2$	58	170[b]	51.21 (51.40)	4.11 (4.50)	5.81 (5.92)	—
10	$Ph_2Pb(MCAcphegly)_2$	60	180[b]	47.66 (47.69)	3.87 (3.97)	5.55 (5.85)	22.52 (23.39)
11	$Ph_3PbBzgly$	70	198–199	52.13 (52.53)	3.70 (3.72)	1.75 (2.27)	32.92 (33.67)
12	$Ph_3PbBzala$	75	202–203	52.74 (53.27)	3.90 (3.96)	1.72 (2.21)	—
13	$Ph_3PbForphe$	70	200–202	54.01 (54.00)	3.90 (3.94)	1.82 (2.18)	—
14	$Ph_3PbAcphe$	70	185–188	53.77 (53.97)	4.13 (4.18)	1.99 (2.19)	—
15	$Ph_3PbMCAcphe$	60	180–182	51.15 (51.73)	3.72 (3.71)	2.00 (2.08)	31.84 (32.21)
16	$Ph_3PbBzglygly$	57	182–183	51.45 (51.70)	3.70 (3.85)	3.53 (4.15)	—
17	$Ph_3PbBzalagly$	65	205–207	51.92 (52.34)	3.95 (4.07)	4.01 (4.07)	—
18	$Ph_3PbForphegly$	69	188–189	51.85 (52.30)	3.92 (4.07)	3.96 (4.07)	29.90 (30.20)
19	$Ph_3PbAcphegly$	70	203–205	52.91 (53.01)	4.03 (4.27)	3.47 (3.99)	—
20	$Ph_3PbMCAcphegly$	62	185–187	50.10 (50.52)	3.90 (3.93)	2.90 (3.80)	27.93 (28.21)

Abbreviations: gly, glycine; ala, DL-alanine; phe, L-phenylalanine; Bz, *N*-benzoyl; For, *N*-formyl; Ac, *N*-acetyl; MCAc, *N*-monochloroacetyl.

[a] All complexes are white; cpds **1–10** prepared by method I and crystallized from ethanol (95%), cpds **11–20** prepared by method II and crystallized from dry methanol.

[b] Complexes decomposed.

Table 2 Infrared spectral data (KBr 4000–200 cm^{-1}) of *N*-protected amino-acids, dipeptides with their sodium salts and esters

Compound		ν(N–H) amide/peptide	Amide I ν(CO) amide/peptide	Amide II $\nu[\nu(CN+\delta(NH)]$	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$
Bzgly		3324s	1645	1545m	1730sb	1180s	550
Bzala		3250s	1625s	1545m	1720s	1210s	300
Forphe		3360s	1710s	1515m	1710s	1260s	450
Acphe		3335s	1620s	1540m	1695s	1240s	455
MCAcphe		3320vs	1630s	1530m	1700s	1250s	550
Bzalagly		3305s	1660s 1620s	1560s 1570s	1750s	1230s	520
Bzglygly		3350s	1670s 1625s	1530s 1550s	1722s	1220s	502
Forphegly		3325s	1610b,s	1540s	1732s	1230s	502
Acphegly		3360s 3280bs	1650b	1550w	1740s	1205s	535
MCAcphegly		3410s 3300s	1660s 1630s	1540s	1735s	1205s	530
BzglyNa		3320b	1635s,b	1545m,b	1590s,b	1400s	190
BzalaNa		3440,b 3305b	1630s,b	1520m,b	1595s	1405s	190
ForpheNa		3370mb, 3300m,b	1660s,b	1510m,b	1615s	1390s	225
AcpheNa		3280s,b	1640m	1520m	1620s	1395s	225
BzglyglyNa		3360m,b 3280m,b	1675s 1650s	1542b	1600m,b	1390m,b	210
BzalaglyNa		3360m,b	1630m	1530m,b	1600s	1390s	210
ForpheglyNa		3320m,b	1650m,b 1660m,b	1530m,b	1593m,b	1385s,b	208
AcpheglyNa		3390m,b	1633s,b	1540m,b	1600m,b	1400m,b	200
MCAcpheglyNa			1655s 1640s	1520m,b	1600s	1390n,b	210
Bzgly ester	k	3340s	1640s	1530s	1757s	1190s	567
	c	3440m	1645s	1540m	1730s	1220s	510
Bzala ester	k	3340s	1658m	1516vs	1740s	1160s	580
	c	3420s,b	1658m	1516vs	1730s	1165s	575
Acphe ester	k	3315s	1640s	1525s,b	1730s	1220s	510
	c	3420m	1660s	1510s	1735s		
Bzglygly ester	k	3360s	1660s 1635s	1535s	1735s	1200s	535
	c	3320m,b 3420m,b	1650s	1520s	1740s	1195s	545
Bzalagly ester	k	3260m,b	1620–1670 m,b	1515m,b	1730s	1190s	560
	c	3410s,b 3310s,b	1630–1660 s,b	1510m,b	1725s	1195s	530
Forphegly ester	k	3280s	1640s	1555s,b	1730s	1290s	440
	c	3410m 3310m	1670s	1520m,b	1740s	1295s	445
Acphegly ester	k	3285s	1675b 1640s	1540s	1743s	1200s	543
	c	3420m,b 3310m,b	1660s,b	1520m,b	1740s	1230s	510
MCAphegly ester		3295s	1659s 1640s	1565s	1750s	1225s	425

Abbreviations: k, in KBr disc; s, strong; b, broad; m, medium; c, in $CHCl_3$.

Sodium salt

Sodium hydroxide (0.1 mol) was added to a solution of *N*-protected amino-acid or dipeptide (0.1 mol) in ethanol (95%, 50 cm^3) with refluxing until a clear solution resulted (pH 7–7.2). After refluxing, the excess of alcohol was removed by distillation, dry benzene (20 cm^3) was added to remove water azeotropically using Dean and Stark trap. The sodium salt of the amino-acid separated out and was filtered, washed several times with dry ether and dried *in vacuo*.

Thallium(I) salt

Solid thallium carbonate (0.1 mol) was added to a solution of *N*-protected amino acid or dipeptide (0.1 mol) in ethanol (95%, 50 cm^3); evolution of CO_2 took place. The reaction mixture was refluxed on a water bath until a clear solution resulted. After removing excess alcohol by distillation, dry benzene (20 cm^3) was added to remove water azeotropically using a Dean and Stark trap. The thallium(I) salt was obtained in the form of a jelly, which was dried first in vacuo and then in a sulphuric acid desiccator. The solid obtained after one month was crystallized from absolute methanol.

Preparation of complexes

Diphenyllead(IV) and triphenyllead(IV) complexes have been prepared by two different methods. The complexes **1–10** have been prepared by method I and complexes **11–20** by method II.

Method I

To a suspension of diphenyllead dichloride (0.1 mol) in ethanol (95%, 30 cm^3) was added triethylamine (0.2 mol) followed by a solution of *N*-protected amino-acid or dipeptide (0.2 mol) in ethanol (95%, 10 cm^3) and the mixture was refluxed on a water bath. The solution became clear after half an hour of refluxing at 80–90°C and was then filtered. The filtrate was allowed to stand until white crystals of the complexes appeared which were filtered. Triethylamine hydrochloride which was formed as a side product remained dissolved in ethanol. Solid complexes were recrystallized from fresh ethanol (95%).

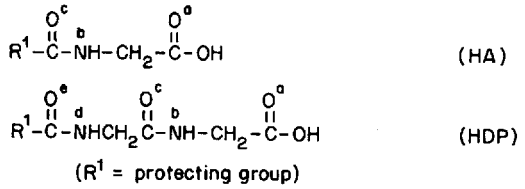


Figure 2

Method II

A solution of triphenyllead chloride (0.1 mol) in absolute methanol (20 cm^3) was added to a solution of the thallium(I) salt of the *N*-protected amino-acid or dipeptide (0.1 mol) in absolute methanol (30 cm^3). The resulting solution was stirred on a magnetic stirrer at room temperature for half an hour and then refluxed with stirring at 50°C for 2 h. Thallium(I) chloride separated during reaction and was filtered off; the complex was obtained from the filtrate. It was crystallized from fresh absolute methanol. Note: complexes **1–10** can also be prepared by neutralization of triphenyllead hydroxide with the corresponding *N*-protected amino-acid or dipeptide but the yield obtained was less compared with that obtained by method II. The diorganotin(IV) and the triorganotin(IV)[5–8] compounds can be prepared by the reaction of the sodium salt of the amino-acid or dipeptide with organotin(IV) chlorides. However, no reaction takes place between organolead(IV) chlorides and sodium salts of corresponding *N*-protected amino-acids or dipeptides.

Physical measurements

Melting points were determined in open capillaries. The elemental analysis was carried out by Regional Sophisticated and Instrumentation Centre, Punjab University, Chandigarh. The lead content was determined in a UV–Vis spectrophotometer UV-240. Absorption of a lead dithizone complex solution in chloroform was measured at 510 nm.[20,21] IR spectra were recorded on a Pye–Unicam P321 spectrometer in KBr discs and chloroform solutions. ^1H NMR spectra were recorded on a JEOL–JNM–PMX 60SI spectrometer using tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

The twenty complexes of *N*-benzoyl-(glycine, DL-alanine); *N*-formyl- and *N*-acetyl-L-phenylalanine; *N*-monochloroacetyl-L-phenylalanine; *N*-benzoyl-(glycylglycine, DL-alanylglycine); *N*-ormyl-, *N*-acetyl- and *N*-monochloroacetyl-L-phenylalanylglycine (Fig. 1) have been prepared with diphenyllead(IV) and triphenyllead(IV) in

Table 3 Infrared spectral data (KBr 4000–200 cm^{-1}) of complexes of diorganolead(IV) and triorganolead(IV) with *N*-protected amino-acids and the dipeptides

No.	Compound		ν(NH) amide/ peptide	ν(CO) amide/ peptide	[ν(CN) + δ(NH)]	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$[a]
1	$Ph_2Pb(Bzgly)_2$		3400b	1640m	1530bs	1595s	1395s	200
2	$Ph_2Pb(Bzala)_2$		3380b	1655s	1550s,b	1550s	1380s	170
3	$Ph_2Pb(Forphe)_2$		3365s	1635s	1505s	1600sh	1380s	220
4	$Ph_2Pb(Acphe)_2$		3260bs	1635s	1545s	1610s	1390s	220
5	$Ph_2Pb(MCAcphe)_2$		3280s	1655s	1540s	1565s	1390sh	175
6	$Ph_2Pb(Bzglygly)_2$		3320s	1660s 1640s	1555s 1545s	1580s	1400s	180
7	$Ph_2Pb(Bzalagly)_2$		3360s 3305s	1660s 1645s	1555s 1540s	1590s	1380s	170
8	$Ph_2Pb(Forphegly)_2$		3260s	1655s 1605s	1540s,b	1570s	1385m	195
9	$Ph_2Pb(Acphegly)_2$		3305bs 3310bs	1660sh 1645s	1555s 1540s	1580s	1380s	200
10	$Ph_2Pb(MCAcphegly)_2$		3320bs 3380b	1675ms 1640vs	1530sh 1540s	1590s	1395s	195
11	$Ph_3PbBzgly$		3440s,b	1660s	1540s	1595s	1400s	195
12	$Ph_3PbBzala$	k	3440bs	1660s, 1655s	1525s	1600s	1398s	198
		c	3400–3340bs	1655s, 1650s	1515s	1600s	1420s	180
13	$Ph_3PbForphe$	k	3300b	1660, 1650s	1535s	1580s	1405s	175
		c	3440, 3400b	1665, 1655s	1520s	1600	1420s	180
14	$Ph_3PbAcphe$		3280s	1640s	1530s	1580s	1412s	168
15	$Ph_3PbMCAcphe$		3280s	1650s	1540s	1580sh	1415s	175
16	$Ph_3PbBzglygly$		3320s,b	1660s 1650s	1530s	1590s	1385a	205
17	$Ph_3Pbzalagly$		3300s,b	1665s 1650s	1540s	1580s	1408s	172
18	$Ph_3PbForphegly$	k	3290s	1635, 1620mb	1520b	1600s	1380s	220
		c	3420, 3390b	1640s, 1625mb	1525m,b	1605s	1390s	215
19	$Ph_3PbAcphegly$		3280s	1650s, 1630s	1555s	1575s	1420s	155
20	$Ph_3PbMCAcphegly$		3370bs	1635s, 1625ms	1540s	1580s	1375s	205

Abbreviations: k, in KBr disc; c, in chloroform solution; mb, medium broad; s, strong; s,b, strong broad.
[a] $\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}$.

1:2 and 1:1 molar ratio (metal:ligand) respectively. Diphenyllead(IV) carboxylates **1–10** were prepared by method I and triphenyllead(IV) carboxylates **11–20** by method II. The analytical and physical data are given in Table 1. All the complexes 1–20 are white solids which decompose before melting and which have high melting points. As regards the relative stability of the complexes with amino-acids and dipeptides, the diphenyllead(IV) amino-acid complexes have lower decomposition temperature than the corresponding dipeptide complexes. The corresponding triphnenyllead(IV) complexes of amino-acids and dipeptides have stability almost in the same range. The triphenyllead(IV) complexes are relatively more stable than the diphenyllead(IV) complexes. Variation of the *N*-protecting groups does not affect the stability of the complexes to any significant extent. Complexes of triphenyllead(IV) are soluble in polar organic solvents, e.g. $CHCl_3$, DMSO, CH_2Cl_2, on warming, and are insoluble in CCl_4, diethyl ether, light petroleum ether, pentane, benzene and nitrobenzene. Diphenyllead(IV) derivatives are soluble only in DMSO and ethanol (95%). Due to insolubility of the complexes in benzene and nitrobenzene, molecular weights could not be determined cryoscopically. All these complexes react with camphor to give a black melt (Rast method not applicable).

Infrared spectra

Infrared spectra of the amino-acids, sodium salts, and ethyl esters have been recorded in KBr and in $CHCl_3$ solution and are given in Table 2. These

Table 4 ^{1}H NMR data (scale, δ ppm) of diorganolead (IV) and triorganolead(IV) complexes

No.	Compound	PhCONH/Ph–CH_2/ Ph–Pb		NH	–CH–	$-CH_2CO$/$-CH_2C_6H_5$		CH_3CO	$-CH_3$
5	$Ph_2Pb(MCAcphe)_2$[c,b]	6.80 (m, 14H)	7.30 (bm, 10H)	7.89 (bs, 2H)	4.41 (m, 2H)	—	3.75 (s, 4H)	—	—
6	$Ph_2Pb[Bzglygly)_2$[d]	7.25–8.00 (m, 24H)		a	—	3.88 (m, 4H)		—	—
7	$Ph_2Pb(Bzalagly)_2$[c]	7.25–8.25 (m, 24H)		a	4.62 (bm, 2H)	3.75 (d, 4H)		—	1.32 (d, 6H)
9	$Ph_2Pb(Acphegly)_2$[c]	8.00–7.25 (m, 14H)	7.18 (s, 10H)	a	4.65 (m, 2H)		3.78 (d, 4H)	1.87 (s, 6H)	—
11	$Ph_3PbBzgly$[d]	6.62–8.25 (m, 21H)		a	—	4.25 (bm, 2H)		—	—
12	$Ph_3PbBzala$[d]	7.37–8.10 (bm, 21H)		a	4.81 (bm, 1H)	—		—	1.50 (d, 3H)
14	$Ph_3PbAcphe$[d]	7.25–8.10 (bm, 16H)	7.12 (s, 5H)	a	4.65 (bm, 1H)	—		1.87 (s, 3H)	—
15	$Ph_3PbMCAcphe$[d,b]	6.75–7.87 (bm, 21H)		a	3.25 (m, 3H)	—		—	—
18	$Ph_3PbForphegly$[d]	7.18–8.10 (bm, 20H)		6.13–6.48 (bm, 2H)	4.73 (bm, 1H)	4.00 (d, 2H)	3.12 (d, 2H)	—	—

Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; bm, broad multiplet.

[a] –NH proton overlapping phenyl proton.

[b] $-CH_2Cl$ proton overlapping phenyl protons in compd **5** and in compd **15** a singlet at 4.00 ppm (2H).

[c] Spectra were recorded in $CDCl_3$ + 1 drop of DMSO.

[d] Spectra were recorded in $CDCl_3$.

data have been included in order to compare the ν(NH), ν(COO), ν(CO) (both amide and peptide) values in acids, sodium salts and esters with those in the case of the complexes. The metal ion, Pb(IV), can bind to the carboxylate group in a unidentate, a bidentate, or a bridging bidentate manner. The IR data help to identify the various possible bonding sites, such as abc in the *N*-protected amino-acid (HA) and abcde in the *N*-protected dipeptide (HDP) (Fig. 2).

Unidentate bonding of the carboxylate group will correspond to an ester-type carboxylate. Bidentate bonding of the carboxylate group will closely correspond to that of the sodium carboxylate. Bridging bidentate carboxylate will result in polymeric structures. Non-participation of the amide C=O and the peptide C=O in bond formation with lead(IV) in the complexes would correspond to that found in the esters of the *N*-protected amino-acids or the dipeptides. The ν(NH) values (both amide and peptide) in the case of both HA and HDP, sodium salt and ester, when compared with those of the complexes, helps in identifying the nature of the coordination of the amide NH to the lead(IV) atom, or alternatively to its intermolecular hydrogen bonding with the amide C=O or the peptide C=O of the neighbouring molecules. Infrared spectra of the complexes have been recorded in KBr discs and chloroform solutions and are given in Table 3. In the spectra of both diphenyllead(IV) and triphenyllead(IV) compounds, vibrations associated with the OH part of the COOH group of the *N*-protected amino-acids have disappeared, and so it can be concluded that Ph_2Pb(IV) and Ph_3Pb(IV) groups are bonded through carboxylate groups of the *N*-protected amino-acid or the dipeptide.

The ν(NH) absorptions (3240–3440 cm^{-1}) in complexes **1–20** generally remain at the same position or shift to a higher value than the corresponding HA and HDP (3260–3360 cm^{-1}), suggesting that the amide and the peptide nitrogens are not coordinating to lead(IV). The solution spectra ($CHCl_3$) of compounds **12**, **13** and **18** showed an upward shift (3400–3440 cm^{-1}) of ν(N–H) vibration consistent with the loss of hydrogen bonding in solution.[22,23]

In complexes **1–5** and **11–15**,- the amide I band is in the range 1635–1660 cm^{-1} and remains in the same position or slightly shifts upward with respect to that found in the corresponding ethyl ester of the HA (1640–1658 cm^{-1}). This suggests the non-participation of the amido C=O in coordination to lead(IV) and further indicates the presence of a hydrogen-bonding association of

the amide NH with the amido C=O group of the neighbouring molecule in the solid state. In complexes **6**–10 and **16**–20 the amide I band is in the range 1635–1660 cm^{-1}, which is again at the same position with respect to that found in the corresponding ethyl ester of the dipeptides (1640–1660 cm^{-1}). The peptide C=O band is in the range 1620–1655 cm^{-1} in complexes **1**–**20** and is at the same position as is found in the corresponding dipeptides (1620–1640 cm^{-1}). This implies neither the amide C=O nor the peptide C=O coordinate to lead(IV). The rise of the amide and the peptide C=O in complexes **12**, **13** and **18** in solution again confirms loss of hydrogen bonding in the solution state. The amide II band [ν(CN) + δ(NH)] in compounds **1**–**20** is comparable with those of the corresponding sodium salts, which again confirms the non-participation of the amido C=O and the peptido C=O in bond formation with lead(IV).

In the present series of diorganolead(IV) complexes **1**–**10**, carboxylate groups absorb in the range of 1550–1610 cm^{-1} which is the region for bridging bidentate carboxylates. The absence of a strong band (1700 cm^{-1}) in all the complexes as compared with the esters of *N*-protected amino-acids and the dipeptides (1725–1757 cm^{-1}) shows the absence of a monodentate bonding for the carboxylate group. The $\nu(COO)_{asym}$ band (1550–1610 cm^{-1}) in the diorganolead(IV) complexes is slightly lower than the corresponding sodium salts (1570–1620 cm^{-1}), which is again indicative of a bidentate carboxylate group. Triorganolead(IV) complexes **11**–**20** also absorb in the same region (1575–1600 cm^{-1}) as in diorganolead(IV) complexes, indicating the presence of a bidentate carboxylate group. The $\nu(COO)_{sym}$ band (1375–1420 cm^{-1}) in all the complexes **1**–**20** is comparable with the corresponding sodium salts (1385–1405 cm^{-1}), while it is quite different from the $\nu(COO)_{sym}$ band (1240–1260 cm^{-1}) in the corresponding amino-acid esters. The rise of $\nu(COO)_{sym}$ bands in all the complexes **1**–**20** from the $\nu(COO)_{sym}$ band in esters confirms the absence of a monodentate carboxylate group.

The $\Delta\nu$ value, [$\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}$], can be used to determine the mode of coordination of the carboxylate group.[23] The $\Delta\nu$ values (170–220 cm^{-1}) of the complexes **1**–**10** and (155–220 cm^{-1}) of the complexes **11**–**20** are lower than the corresponding sodium salts (190–225 cm^{-1}), which shows the presence of a bridging bidentate carboxylate.[4] The $\Delta\nu$ values of all the complexes **1**–**20** are much lower as compared with the corresponding amino-acid esters (425–580), so absence of a monodentate carboxylate is confirmed.

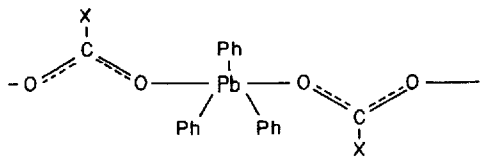


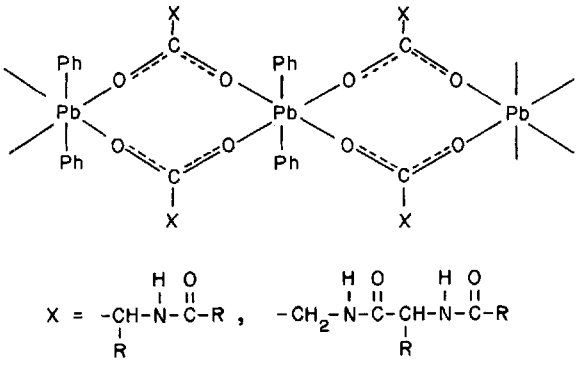
Figure 3

^{1}H NMR spectra

The ^{1}H NMR spectra of the soluble complexes **11**, **12**, **14**, **15** and **18** have been recorded in $CDCl_3$ and of complexes **5**, **6**, **7** and **9** have been recorded in $CDCl_3$ + one drop of DMSO and are given in Table 4. The COOH signal (9.00–10.00 ppm) of the free acids in trifluoroacetic acid is missing in the case of the spectra of all the soluble complexes. The NH signal could not be detected in all the cases as it is superimposed by the signal of the phenyl protons. The complex pattern in the range 6.62–8.25 ppm of the phenyl protons indicated the asymmetric position of the phenyl groups both in the diphenyl- and the triphenyl-lead(IV) complexes. The position of the –CH– and $-CH_2-$ signals are shifted to a higher field compared with that in *N*-protected amino-acids and dipeptides respectively. The shift in –CH– protons and $-CH_2-$ protons and the absence of a signal due to the COOH group confirms the coordination of the carboxylate group to lead(IV). The total number of protons calculated from the molecular formula of the complex agrees with that from the integration curve.

CONCLUSIONS

The polymeric nature of the diphenyl- and triphenyl-lead(IV) compounds of both the *N*-protected amino-acids and the dipeptides indicates the presence of bridging bidentate carboxylate groups, which is supported by earlier work.[9] The C=O and NH (amide and peptide) do not coordiate to lead(IV). A pentacoordinated chain-type structure (Fig. 3) having a distorted trigonal-bipyramidal geometry is proposed for compounds **11**–**20** in which all phenyl groups lie in the plane



R = side chain of the amino-acid and dipeptide

COR = *N*-protecting group

Figure 4

of the molecule while oxygen atoms of the carboxylate group lie in the axial position linking lead atoms in a chain-type structure.[9] A hexacoordinated polymeric structure (Fig. 4) having distorted octahedral geometry is proposed for compounds **1–10** in which four oxygen atoms lie in one plane while two phenyl groups lie in the axial positions linking the lead atoms in a chain-type structure.

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