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SOLVATES OF SOME METHYLLEAD COMPOUNDS AND THEIR ^{207}Pb–CH$_3$ COUPLING CONSTANTS*

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Articles from this laboratory[2,3] have reported results on the addition compounds and solvates of $(CH_3)_3SnCl$ and various dialkylthallium compounds. The heavy metal–proton coupling constants were studied. In the case of the dialkylthallium compounds, changes in $J(Tl–CH_3)$ as a function of solvent were correlated with the solvent donor strength. It was of interest to extend these studies to a series of methyllead compounds.

EXPERIMENTAL

Preparations for methyllead perchlorate solvates were performed without rigorous exclusion of moisture. Dry solvents were employed and reactions were carried out in closed vessels, but the lead compounds seem to be much less sensitive to moisture than similar tin compounds which are extremely hygroscopic[1,4]. Analyses are calculated for the monohydrate of the two monosolvates of trimethyllead perchlorate and it can be seen that the analyses agree with that of the anhydrous compound.

Tetrakis(dimethylsulfoxide)dimethyllead(IV) diperchlorate

A slight excess of silver perchlorate in 3 cc of isopropanol was added to 1 g dimethyllead dichloride in 3 cc of dimethylsulfoxide, DMSO. The solution was allowed to stir for one minute, and the silver chloride was filtered off. The crystals that collected in the filtrate upon standing were washed with 2 cc portions of isopropanol three times and dried under vacuum at room temperature. The compound is initially white but soon darkens; it had a melting point of 66°. (Found: C, 16.06; H, 4.10. $C_{10}H_{30}Cl_2O_{12}PbS_4$ calcd.: C, 16.10; H, 4.02 %.)

Bispyridinedimethyllead(IV) diperchlorate

Tetrakis(dimethylsulfoxide)dimethyllead(IV) perchlorate was dissolved in a 10:1 molar excess of pyridine and 5 volumes of chloroform were added. Large, prismatic, nonhygroscopic crystals formed over a period of several days which had a melting point of 115°. (Found: C, 24.56; H, 2.84; N, 4.99. $C_{12}H_{16}Cl_2N_2O_8Pb$ calcd.: C, 24.30; H, 2.70; N, 4.73 %.)

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Attempted preparation of other dimethyllead compounds

Dimethyllead dichloride was crystallized from DMSO and the melting point behavior and analysis indicated some retention of DMSO. However, no definite stoichiometry was formed. Attempts to prepare a hexamethylphosphoramide, HMPA, solvate from the DMSO solvate led to an intractable oil.

Trimethyllead chloride and triethyllead chloride

The compounds were prepared by the method of Heap and Saunders[5]. Trimethyllead chloride (Found: C, 12.48; H, 3.11. C_3H_9PbCl calcd.: C, 12.55; H, 3.14%.) appeared to be stable, but triethyllead chloride (Found: C, 21.68; H, 4.59. $C_6H_{15}ClPb$ calcd.: C, 21.80; H, 4.58%.) decomposed slowly over a period of time. Triethyllead chloride was kept in the dark as much as possible and the purified crystals were stored in the dark at −78°.

Bis(hexamethylphosphoramide)trimethyllead(IV) perchlorate

One gram of trimethyllead chloride was dissolved in 20 cc of ethanol and a stoichiometric amount of silver perchlorate was added. The silver chloride was removed by filtration and two moles of HMPA were added to the filtrate. The solvent was partially removed by evaporation in a stream of air and ether was added to cause precipitation. The white solid had a melting point of 86°. (Found: C, 25.43; H, 6.41. $C_{15}H_{45}ClN_6O_6P_2Pb$ calcd.: C, 25.40; H, 6.43%.)

(Hexamethylphosphoramide)trimethyllead(IV) perchlorate

Trimethyllead perchlorate was made by double decomposition of trimethyllead chloride and silver perchlorate in isopropanol and one mole of HMPA was added. A precipitate formed slowly upon the addition of ether. The white solid had a melting point of 96°. (Found: C, 20.67; H, 5.18. $C_9H_{27}ClN_3O_5PPb$ calcd.: C, 20.55; H, 5.13. $C_9H_{27}ClN_3O_5PPb \cdot H_2O$ calcd.: C, 19.82; H, 5.32%.)

Pyridinetrimethyllead(IV) perchlorate

Trimethyllead perchlorate was made in isopropanol by double decomposition of trimethyllead chloride and silver perchlorate. One mole of pyridine was added to the isopropanol solution of trimethyllead perchlorate; addition of an excess of ether caused the precipitation of small white crystals with a melting point of 135°. (Found: C, 22.48; H, 3.36. $C_8H_{14}ClNO_4Pb$ calcd.: C, 22.55; H, 3.29. $C_8H_{14}ClNO_4Pb \cdot H_2O$ calcd.: C, 21.60; H, 3.60%.)

Attempted preparation of other trimethyllead compounds

The preparation of 2:1 complexes of trimethyllead perchlorate with pyridine, DMSO and tetramethylguanidine, TMG, was attempted. In all cases the analysis indicated a stoichiometry intermediate between a 1:1 and 2:1 composition.

Spectra

Infrared spectra in the KBr region were run on a Beckman IR-5A instrument with CsBr optics. Infrared spectra in the NaCl region were run on a Perkin-Elmer 21 instrument. A Varian Associates A-60 spectrometer was used for determination of PMR spectra. Solvents were either reagent grade or distilled prior to use.

RESULTS

The results from infrared spectra in the 600 to 250 cm^{-1} region are contained in Table 1 and the results from NMR studies in Table 2.

TABLE 1

FREQUENCIES IN THE INFRARED[a]

Compounds	*Solvent*[b]	*Frequencies (cm^{-1})*		
		Asym. str.	*Sym. str.*	*Other bands*
$(CH_3)_3PbCl$		493		
$(CH_3)_2PbCl_2$		493		
$[(CH_3)_3Pb(HMPA)_2]ClO_4$		500		452 (s), 380 (m)
$[(CH_3)_3Pb(pyridine)]ClO_4$		497	460 (w)	417 (m)
	$(CH_2Cl)_2$	497	465 (w)	
	pyridine	493		
$[(CH_3)_2Pb(pyridine)_2](ClO_4)_2$		465		415 (vs), 338 (s)
$[(CH_3)_2Pb(DMSO)_4](ClO_4)_2$				625 (vs), 457 (vw) 421 (m), 404 (s), 342 (s), 313 (m)

[a] The asymmetric stretching frequency is assigned a qualitative intensity of strong (s) and other bands are assigned a qualitative intensity of very strong (vs), strong (s), medium (m), weak (w) or very weak (vw). [b] Compounds are mulled in nujol where no solvent is listed.

TABLE 2

$J(^{207}Pb–CH_3)$ FOR METHYL CATION IN VARIOUS SOLVENTS

Compound	*Solvent*	*Concentration*[c]	*$J(^{207}Pb–CH_3)$ (cps)*
$(CH_3)_3PbF$[a]	$CHCl_3$	saturated	81
$(CH_3)_3PbCl$[a]	$CHCl_3$	saturated	70
$(CH_3)_3PbBr$[a]	$CHCl_3$	saturated	68
$(CH_3)_3PbI$[a]	$CHCl_3$	saturated	63
$(CH_3)_3PbOH$[a]	$CHCl_3$	saturated	76
$(CH_3)_4Pb$[a]	toluene	80%	62
$(CH_3)_3PbCl$[b]	benzene	saturated	69.5
$(CH_3)_3PbCl$	$MeNO_2$	saturated	73.5
$(CH_3)_3PbCl$	MeCN	20%	77.5
$(CH_3)_3PbCl$	Me_2CO	20%	78.0
$(CH_3)_3PbCl$	MeOH	30%	79.5
$(CH_3)_3PbCl$	pyridine	30%	81.0
$(CH_3)_3PbCl$	DMSO	30%	83.0
$(CH_3)_3PbCl$[b]	DMA	saturated	83.5
$(CH_3)_3PbCl$[b]	DMF	saturated	83.5
$(CH_3)_3PbCl$	HMPA	30%	87.5
$(CH_3)_3PbBF_4$	H_2O	30%	77.5
$(CH_3)_3PbClO_4$	pyridine	saturated	78.0
$[(CH_3)_3Pb(pyridine)]ClO_4$	CH_2Cl_2	33%	74.5
$(CH_3)_3PbClO_4$	DMSO	33%	80.5
$(CH_3)_3PbClO_4$	HMPA	30%	85.0
$[(CH_3)_3Pb(HMPA)_2]ClO_4$	$C_2H_4Cl_2$	55%	83.0
$(CH_3)_2PbCl_2$	DMSO	33%	154.5
$(CH_3)_2Pb(ClO_4)_2$	DMSO	40%	150.0

[a] From ref. 6. [b] From ref. 2. [c] Concentration by weight.

DISCUSSION

Complexes of the type $[(CH_3)_3PbL]^+ClO_4^-$ have been isolated when L is hexamethylphosphoramide and pyridine. The absence of perchlorate coordination is indicated by the infrared spectra of nujol mulls in the region 900 cm^{-1} to 1200 cm^{-1} (ref. 4). The infrared spectra of trimethyllead chloride and dimethyllead dichloride have strong bands at 493 cm^{-1}, and this is the only band that appears in the infrared in the region of the lead–carbon stretching frequency. If the band at 493 cm^{-1} is the asymmetric stretch, then the absence of the symmetric stretch in the infrared can be accounted for if the trimethyllead species is nearly planar and the dimethyllead species nearly linear in the solid state. This would imply that the chloride ions in both compounds were bridging, the trimethyllead species being trigonal bipyramidal and coordinated to two bridging chlorides and the dimethyllead species being octahedral and coordinated to four bridging chlorides. This proposal finds some support in the insolubility of dimethyllead dichloride in any but strongly donors solvents like DMSO. The infrared bands between 490 cm^{-1} and 500 cm^{-1} may then be assigned to the asymmetric stretch for the trimethyllead perchlorate solvates. Pyridinetrimethyllead perchlorate has a weak band in the infrared spectrum at 460 cm^{-1} which is also present in a methylene chloride solution of the complex and absent in a pyridine solution. This is assigned to the lead–carbon symmetric stretch, which should be observable in the infrared for a non-planar trimethyllead cation. Disappearance of the lead–carbon symmetric stretch in a pyridine solution of the complex indicates that the $(CH_3)_3Pb^+$ ion adopts a planar configuration in pyridine solution, and it is probable that two molecules of pyridine are coordinated to the lead in solution. The trimethyllead cation has been shown by Raman spectroscopy to have a planar structure in aqueous solutions of its nitrate and perchlorate salts[7]. This structure is similar to that proposed for $(CH_3)_3Sn^+$ (Ref. 1). The solid complex bis(hexamethylphosphoramide)-trimethyllead(IV) perchlorate has been isolated. The infrared spectrum shows hexamethylphosphoramide to be complexed through the phosphoryl oxygen[8], and a planar $(CH_3)_3Pb^+$ group in the complex. Unsuccessful attempts were made to isolate complexes of the type $[(CH_3)_3PbL_2]^+$ with other ligands.

Both four-coordinate and six-coordinate complexes of the dimethyllead cation have been obtained. Except for bispyridinedimethyllead(IV) perchlorate, which did not show any signs of decomposition after several months, the complexes of $(CH_3)_2Pb^{++}$ were quite unstable. The tetrakis(dimethylsulfoxide)dimethyllead perchlorate was the only one for which a satisfactory analysis was obtained. The structure of the two dimethyllead complexes is unknown, but it is likely that the bispyridine complex has a pseudotetrahedral configuration with local C_{2v} symmetry. The tetrakis(dimethylsulfoxide) complex is most probably six-coordinate with *cis*- or *trans*-methyl groups, but no band in the infrared spectrum of this complex could be assigned with certainty to a lead–carbon stretch.

The lead–proton coupling constants given in Table 2 for solutions of trimethyllead halides in chloroform show increasing $J(^{207}Pb\text{–}CH_3)$ with increasing electronegativity of the halide. Bent[9] has proposed that the *s* orbital of an atom forming two or more bonds will tend to concentrate in the bonding orbitals directed toward the least electronegative ligands. This provides an acceptable explanation of the observed trend in $J(Pb\text{–}CH_3)$ in the trimethyllead halides since *s* orbital character has been correlated with $J(\text{Sn–CH}_3)$ in the similar methyl tin compounds[2,10].

It has been demonstrated that trimethyllead chloride acts as a Lewis acid toward donor molecules[2], and the structure of the adduct was proposed to be trigonal bipyramidal with three methyl groups in the equatorial plane and a chloride and a donor ligand on the vertical axis. Table 2 shows that $J(^{207}\text{Pb–CH}_3)$ increases as the donor character of the solvent increases from benzene to hexamethylphosphoramide. A very similar solvent effect on the coupling constant has been found for $J(\text{Tl–CH}_3)$ of dimethylthallium salts in various solvents[3].

Changes in the hybridization of lead involving changes in the bond angles at the lead atom have an important effect on $J(^{207}\text{Pb–CH}_3)$, since the configuration of the trimethyllead entity changes from pseudotetrahedral in the free acid to near trigonal bipyramidal in the adduct. However, $J(^{207}\text{Pb–CH}_3)$ changes from 77.5 cps for $(CH_3)_3PbBF_4$ dissolved in water to 85.0 cps for $(CH_3)_3PbClO_4$ dissolved in hexamethylphosphoramide and this change in $J(^{207}\text{Pb–CH}_3)$ is independent of any apparent geometrical change in the planar $(CH_3)_3Pb^+$ ion. A similar situation involving a change in heavy metal–proton coupling constant without any corresponding change in the configuration of the heavy metal alkyl cation was found for dimethylthallium salts[3], and the phenomenon has been more thoroughly discussed in conjunction with this work.

The coupling constant data for dimethyllead compounds are sparse and the only conclusion that may be drawn is that they appear to be quite sensitive to the environment of the lead atom. $J(^{207}\text{Pb–CH}_3)$ does seem to fall in definite and mutually exclusive ranges for complexes of $(CH_3)_3Pb^{++}$ and $(CH_3)_3Pb^+$.

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SUMMARY

Some solvates of the trimethyllead(IV) cation and dimethyllead(IV) cation have been prepared and their structures investigated by infrared and nuclear magnetic resonance spectroscopy. Solvates have been isolated with one or two solvent molecules coordinated to trimethyllead(IV) cation and two or four solvent molecules coordinated to dimethyllead(IV) cation. The effect of solvent on $J(^{207}\text{Pb–CH}_3)$ in the trimethyllead cation has been found to be similar to the effect of solvent on $J(\text{Tl–CH}_3)$ in the dimethylthallium(III) cation.

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