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SHORT COMMUNICATION

Proton magnetic resonance spectra of some dimethyllead(IV) complexes

Recently Holmes and Kaesz[1] have pointed out that there is a linear relationship between the value of the spin–spin coupling constant $J(^{119}Sn–CH_3)$ and the per cent *s* character of the hybridized tin orbital used in the Sn–C bond for several methyltin(IV) compounds. A *trans*-configuration has been deduced for bis(acetylacetonato)-dimethyltin[2] when the observed value of the coupling constant ($J(^{119}Sn–CH_3)$ 99.3 cps, which is almost twice the value of tetramethyltin) has been applied to this relation. This configuration is consistent with that obtained from the infrared and Raman spectra[2,3]. On the other hand, for bis(oxinato)dimethyltin[2,4], bis(picolinato)dimethyltin[2], bis(tropolonato)dimethyltin[5] and dimethyltin diacetate[6], the values of spin–spin coupling constant $J(^{119}Sn–CH_3)$ are rather smaller than those for bis-(acetylacetonato)dimethyltin[2] and the aquodimethyltin(IV) cation[7] and are comparable to that for dimethyltin dimethoxide[8]. If the Holmes–Kaesz relation holds also in these complexes, these small spin–spin coupling constants may be indicative of a bent $CH_3–Sn–CH_3$ moiety. Among these complexes, a distorted *trans*-configuration having the bent $CH_3–Sn–CH_3$ moiety has been suggested for dimethyltin diacetate, because the infrared spectrum of this molecule has shown both antisymmetric and symmetric Sn–C stretching vibrational bands at 574 cm^{-1} and 528 cm^{-1}, respectively.

In the case of dimethyllead diperchlorate[9,10], the value of spin–spin coupling constant $J(^{207}Pb–CH_3)$ has been found to be more than twice the value for tetramethyllead[11,12,13], although the value in water[9] is not the same with that in dimethyl sulfoxide[10]. It seems, therefore, interesting to study spin–spin coupling $J(^{207}Pb–CH_3)$ in dimethyllead(IV) complexes.

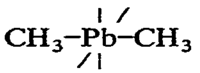
The τ values of methyl groups attached to the lead atom and the values of spin–spin coupling constant $J(^{207}Pb–CH_3)$ in bis(acetylacetonato)dimethyllead, bis(oxinato)dimethyllead and bis(tropolonato)dimethyllead observed in chloroform

TABLE 1

CHEMICAL SHIFT OF THE METHYL PROTONS ATTACHED TO LEAD AND SPIN–SPIN COUPLING CONSTANT $J(^{207}Pb–CH_3)$ IN SOME DIMETHYLLEAD(IV) COMPOUNDS

Compound	*Solvent*	*τ (ppm)*	*$J(^{207}Pb–CH_3)$ (cps)*
$(CH_3)_2Pb(acac)_2$	$CHCl_3$	7.95	154.7
$(CH_3)_2Pb(Tr)_2$	$CHCl_3$	7.95	154.7
$(CH_3)_2Pb(Ox)_2$	$CHCl_3$	7.86	152.3
$(CH_3)_2PbCl_2$	DMSO (ref. 10)		154.5
$(CH_3)_2Pb(ClO_4)_2$	DMSO (ref. 10)		150
	H_2O (ref. 9)		135.1
$(CH_3)_2Pb(OH)_2$	H_2O (ref. 9)		128.3
$(CH_3)_4Pb$	toluene (ref. 13)	9.35	62

are shown in Table 1. The corresponding values in some other dimethyllead(IV) compounds and tetramethyllead are added in this Table for comparison. One of remarkable results for the values of spin–spin coupling constant $J(^{207}Pb–CH_3)$ in dimethyllead(IV) complexes studied in this note is that the values are larger than twice the value for tetramethyllead[11,12,13] and also larger than that for dimethyllead diperchlorate in aqueous perchloric acid[9]. The values are comparable to those for dimethyllead dichloride and dimethyllead diperchlorate in dimethyl sulfoxide[10]. The other notable result is that the values of spin–spin coupling constant $J(^{207}Pb–CH_3)$ are almost the same for all dimethyllead(IV) complexes. The configuration for these complexes, therefore, seems to be the same one, probably the *trans*-configuration (I) which has been suggested for bis(acetylacetonato)dimethyllead on the basis of infrared spectral data[3]. These results thus are in marked contrast to those for dimethyltin(IV) complexes.



$CH_3-\overset{|\ /}{\underset{/\ |}{Pb}}-CH_3$ (I)

There are three contributions to spin–spin coupling[14,15]: (*i*) the Fermi contact term. (*ii*) Coupling via electron orbital motion. This term is normally very small and negligible for the discussion of spin–spin coupling[14,16]. (*iii*) Dipole–dipole coupling of the nuclear spin and electronic spins. The contribution of this term to the observed spin–spin coupling constant seems also to be small[12]. The Fermi contact term appears to dominate spin–spin coupling between heavy metal nuclei and protons[12,16–19].

The Fermi contact term is expressed by equation (1), provided the fractional *s* character of the bond involved in the coupling is taken into account[18,20]:

$$J(\text{M–C–H}) = \text{const}\cdot\alpha_M^2\cdot a_M(ns)\cdot a_H(1s)/\Delta E_M \qquad (1)$$

where α_M^2 is the *s* character of the M orbitals in the M–C bond, $a_M(ns)$ and $a_H(1s)$ is hyperfine coupling constant (hfs) of the *ns* electron in an M atom and the 1*s* electron of proton, respectively. ΔE_M is the mean singlet–triplet excitation energy. If both the hfs $[a_M(ns)]$ and the ΔE_M are assumed to be constant in a series of compounds, the constant J(M–C–H) depends probably on the *s* character of the M orbitals in the M–C bonds and therefore on the configuration of the compounds. These conditions seem to hold for almost all methyltin(IV) compounds, because there is a linear relationship between the *s* character and the value of coupling constant $J(^{119}Sn–CH_3)$[1]. These conditions, however, do not hold for organomercury(II)[18] and organothallium(III)[19] compounds. The coupling constant $J(^{205}Tl–CH_3)$ for a series of compounds R_3Tl, R_3Tl^+ and RTl^{2+} can be explained only when changes of both $a_{Tl}(6s)$ and α_M^2 terms are taken into consideration. This is due to the fact that the $a_{Tl}(6s)$ term increases when the net positive charge which the 6*s* valence electrons see becomes large[18,21,22].

The rather large values of the spin–spin coupling constant $J(^{207}Pb–CH_3)$ observed in dimethyllead complexes could not be accounted only by a change of hybridization of the lead orbital, because in this explanation the coupling constant $J(^{207}Pb–CH_3)$ in dimethyllead(IV) complexes, which have probably *sp*-hybridized lead orbitals, is at most twice the value for tetramethyllead which has sp^3-hybridized lead orbitals. For a satisfactory explanation of these large coupling constants for dimethyllead(IV) complexes, increases of both the *s*-character of the lead orbitals and the hfs term $a_{Pb}(6s)$ seem to be neccessary. The increase of the hfs term may be accomplished by increase of net positive charge on the lead nucleus. If this assumption is accepted, the lead-ligand bonds in these dimethyllead(IV) complexes can be considered to have a rather large ionic character. The infrared spectra also seem to indicate that the Pb–O bond is rather ionic in bis(acetylacetonato)dimethyllead compared to the Sn–O bond in bis(acetylacetonato)dimethyltin, because the Pb–O stretching vibrational frequency (390 cm^{-1}) in the former is lower than that of the Sn–O (406 cm^{-1}) in the latter[23].

Experimental

Bis(oxinato)dimethyllead. Dimethyllead dichloride was suspended in an aqueous solution of 8-hydroxyquinoline. By adding aqueous ammonia to this solution with stirring, yellow precipitates were obtained. Recrystallization from chloroform and ligroin gave greenish yellow powder. Decomposition begins at 147°. (Found C, 45.11; H, 3.47; N, 5.86. $C_{20}H_{18}N_2O_2Pb$ calcd.: C, 45.70; H, 3.45; N, 5.33%.)

Bis(tropolonato)dimethyllead. The same method used for preparing bis(oxinato)dimethyllead was employed for obtaining this compound. Recrystallization from chloroform and ligroin gave pale yellow solid. Decomposition begins at 191°. (Found C, 39.51; H, 3.39. $C_{16}H_{16}O_4Pb$ calcd.: C, 40.05; H, 3.39%.)

Bis(acetylacetonato)dimethyllead. The compound was prepared by the method reported elsewhere[24].

Proton magnetic resonance spectra. The proton magnetic resonance spectra were measured in chloroform using a Japan Electron Optics model JNM-3H-60 spectrometer operating at 60 Mc/sec. Tetramethylsilane was used as an internal standard.

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