Journal of Organometallic Chemistry, 90 (1975) 185—194
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SOLVENT EFFECTS ON THE PMR SPECTRA OF SOME BENZOATO AND OXINATO COMPLEXES OF DIMETHYLLEAD(IV)

MITSUTOSHI ARITOMI* and YOSHIKANE KAWASAKI

Department of Applied Chemistry, Osaka University, Yamadakami, Suita Osaka 565 (Japan)

(Received August 29th, 1974; in revised form November 25th, 1974)

Summary

The $J(^{207}Pb—CH_3)$ and δ (Pb—CH_3) values of some bezoato and oxinato complexes of dimethyllead(IV), $(CH_3)_2PbX_2$ (X = $OCOC_6H_4—Y$; Y = H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *p*-CH_3O, *p*-Cl, *p*-CO_2CH_3 and *p*-NO_2; X = ox—Y; Y = H and 7-CH_3 (ox = oxinato)), and the $J(^{205}Tl—CH_3)$ and δ(Tl—CH_3) values of dimethyl(oxinato)thallium(III), $(CH_3)_2Tl(ox)$, have been measured in various solvents. The solvents used in this experiment are classified into five groups: (I) non-coordinating solvents such as haloalkanes, (II) coordinating solvents except for heterocyclic solvents, (III) pyridine and its derivatives, (IV) quinoline and isoquinoline, and (V) benzene and its derivatives.

The $J(^{207}Pb—CH_3)$ values were found to increase with a decrease in the dielectric constant of the solvents of the first group, or with an increase in the donor strength of the solvents of the second group, and at the same time the chemical shifts of the methyl protons on the lead atom are displaced to higher field. The $J(M—CH_3)$ (M = ^{207}Pb and ^{205}Tl) values for the oxinato complexes were found to increase as the absorption maxima, λ_{max}, in the UV spectra shifted to red, and relations were obtained between these two quantities. These results seem to suggest that the mean singlet—triplet excitation energy, ΔE, in the Fermi contact term is mainly responsible for changes of the $J(^{207}Pb—CH_3)$ values for the dimethyllead compounds, which is produced by the induced quadrupolar reaction field or by the complex formation with the solvent molecule.

Introduction

In nuclear magnetic resonance spectroscopy, it has been observed that the metal—proton coupling constants of several organometallic compounds depend markedly on the solvent. The change of the $J(^{119}Sn—CH_3)$ values with solvent in some methyltin compounds has been interpreted in terms of the configurational change induced by coordination of the solvents to the tin atom, i.e., the $J(^{119}Sn—CH_3)$ values depend almost only on the *s* character of the tin orbitals used in the tin—carbon bonds [1-4], while the $J(M—CH_3)$ (M = ^{199}Hg and ^{205}Tl) values in methyl-mercury(II) and -thallium(III) compounds were correlated with both the configuration (s character) and positive charge density (hyperfine coupling constant, a_M (6s)) on the metal atom [5,6]. Recently we have found that the $J(^{207}Pb—CH_3)$ values increase with an increase in the stability constants of dimethyllead compounds, $(CH_3)_2PbX_2$ (X = oxinato [7] and benzoato [8]), with several donor molecules. In the present paper, we report the dependence of the PMR parameters of some benzoato and oxinato complexes of dimethyllead(IV), $(CH_3)_2PbX_2$ (X = $OCOC_6H_4$—Y; Y = H, o- and p-CH_3, p-CH_3O, p-Cl, p-CO_2CH_3 and p-NO_2; X = ox—Y; Y = H and CH_3 (ox = oxinate)) and dimethyl(oxinato)thallium(III), $(CH_3)_2Tl(ox)$, on the dielectric constant or the donor strength of the solvents and the absorption maxima in the UV spectra, in order to explain the dependence of the coupling constant $J(^{207}Pb—CH_3)$ on the nature of the solvent.

Experimental

Preparation of complexes

All of the benzoato and oxinato complexes of dimethyllead, $(CH_3)_2Pb(OCOC_6H_4—Y)_2$ (Y = H, o-CH_3, m-CH_3, p-CH_3, p-CH_3O, p-Cl, p-CO_2CH_3 and p-NO_2) and $(CH_3)_2Pb(ox—Y)_2$ (Y = H and 7-CH_3), were prepared by the method reported previously [7,9]. Dimethyllead dichloride [10] (3.1 g, 0.01 mol) was suspended in aqueous ammonia solution with an appropriate benzoic acid or oxine (0.02 mol), and stirred. The precipitates thus obtained in the case of the benzoato complexes were recrystallized from methylene chloride or dimethyl sulfoxide, and those in the case of the oxinato complexes from methanol. The crystalline complexes for the benzoato complexes (Y = p-CH_3, p-CH_3O, p-CO_2-CH_3 and p-NO_2) contain one molecule of water*. Dimethyl(oxinato)thallium, $(CH_3)_2Tl(ox)$, was prepared by the reaction of dimethylthallium carbonate and oxine in ethanol [11], crystalline complex was obtained from the reaction mixture. Analytical data for newly prepared complexes are shown in Table 1.

PMR spectra

The proton magnetic resonance measurements were made with JEOL spectrometers, models JNM-PS-100 and JNM-PMX-60, operating at 100 and 60 MHz, respectively. The chemical shifts δ (ppm) were measured relative to tetramethylsilane as internal standard. The concentration dependence of the coupling constants and the chemical shifts in the coordinating solvents (0.5-5.0 wt%) was within the limits of experimental error (±0.5 Hz and ±0.01 ppm, respectively). The $J(M—CH_3)$ and $\delta(M—CH_3)$ values for the dimethyl-lead and -thallium complexes, which were obtained in about 2.0 wt% solution for the coordinating solvents and in about 0.5 wt% solution for the other solvents, are summarized in Tables 2 and 3.

---

* From the fact that the $\nu(OH)$ stretching frequencies of $(CH_3)_2Pb(OCOC_6H_4—Y)_2 \cdot H_2O$ (Y = p-CH_3, p-CH_3O and p-CO_2CH_3) (about 3680 cm^{-1}) in CH_2Cl_2 are comparable with the frequency of water in the same solvent (3680 cm^{-1}), the crystal water is supposed to be completely free in solution.

TABLE 1

ANALYTICAL DATA OF $(CH_3)_2Pb(OCOC_6H_4-Y)_2 \cdot L$

Compound		M.p.(dec.)	Analysis found (calcd.)(%)		
Y	L	(°C)	C	H	N
o-CH_3		169-170	42.42 (42.60)	3.87 (3.97)	
m-CH_3		171-172	42.32 (42.60)	3.92 (3.97)	
p-CH_3	H_2O	172-173	41.13 (41.14)	4.31 (4.22)	
p-CH_3O	H_2O	171-172	38.50 (38.78)	3.94 (3.98)	
p-Cl		193-194	35.21 (35.05)	2.47 (2.57)	
p-CO_2CH_3	H_2O	203-204	38.97 (39.15)	3.53 (3.61)	
p-NO_2	H_2O	184-186	32.57 (32.71)	2.63 (2.75)	4.88 (4.77)

UV spectra

The ultraviolet spectra were recorded on a Hitachi model 356 spectrometer with 0.1 cm quartz cells. The absorption maxima for the oxinato complexes of dimethyl-lead and -thallium in various solvents are shown in Table 3.

TABLE 2

$J(^{207}Pb-CH_3)$ and $\delta(Pb-CH_3)$ VALUES OF $(CH_3)_2Pb(OCOC_6H_5)_2$ IN VARIOUS SOLVENTS

No.	Solvent	$J(^{207}Pb-CH_3)$ (Hz)	$\delta(Pb-CH_3)$ (ppm)	Group of solvent
1	CH_3NO_2	132.6	2.46	(I)
2	CH_2Cl_2	135.5	2.42	(I)
3	CH_2ClCH_2Cl	136.3	2.38	(I)
4	$CHCl_3$	136.6	2.40	(I)
5	CCl_2CHCl	139.3	2.37	(I)
6	CCl_4	140.1	2.36	(I)
7	Benzene	140.5	1.95	(V)
8	Chlorobenzene	140.6	2.17	(V)
9	o-Dichlorobenzene	140.4	2.37	(V)
10	α-Chloronaphthaline	139.0	2.20	(V)
11	CD_3CN	140.8	2.29	(II)
12	$(CD_3)_2CO$	144.7	2.29	(II)
13	CH_3OH	150.7	2.29	(II)
14	Quinoline	150.5	2.70	(IV)
15	α-Picoline(2-CH_3-Py)	152.3	2.35	(III)
16	Trimethylphosphate(TMP)	157.5	2.22	(II)
17	DMF	156.0	2.20	(II)
18	DMSO	159.6	2.15	(II)
19	Isoquinoline	163.6	2.85	(IV)
20	Pyridine(Py)	165.3	2.35	(III)
21	γ-Picoline(4-CH_3-Py)	167.2	2.37	(III)
22	HMPA	173.7	2.05	(II)

TABLE 3

J(M—CH$_3$) AND δ(M—CH$_3$) VALUES AND ABSORPTION MAXIMA IN THE UV SPECTRA OF (CH$_3$)$_2$Pb(ox—Y)$_2$ AND (CH$_3$)$_2$Tl(ox) IN VARIOUS SOLVENTS

	Pb						Tl		
	Y = H			Y = 7-CH$_3$					
Solvent	J^a (Hz)	δ^b (ppm)	$\lambda_{max}{}^c$ (nm)	J^a (Hz)	δ^b (ppm)	$\lambda_{max}{}^c$ (nm)	J^a (Hz)	δ^b (ppm)	$\lambda_{max}{}^c$ (nm)
CH$_3$NO$_2$	147.2	2.20	377	147.8	2.16	392	^{d}	^{d}	^{d}
CH$_2$ClCH$_2$Cl	150.7	2.15	383	150.1	2.11	396	^{e}	^{e}	387
CH$_2$Cl$_2$	151.7	2.13	384	151.5	2.12	396	394	0.91	387
CHCl$_3$	152.3	2.14	385	151.3	2.12	397	388	0.97	385
CD$_3$CN	154.0	1.80	388	155.7	1.78	400	398	0.82	392
CCl$_2$CHCl	158.6	1.96	389	156.3	1.98	402	396	0.88	388
CCl$_4$	160.5	1.90	390	158.5	1.91	406	^{f}	^{f}	^{f}
(CD$_3$)$_2$CO	163.7	1.87	390	166.7	1.83	409	^{f}	^{f}	^{f}
2-CH$_3$-Py	166.5	2.02	394	165.2	2.00	408	408	1.06	396
Py	167.4	2.14	397	167.8	2.08	410	420	1.14	401
4-CH$_3$-Py	168.0	2.10	396	167.6	2.08	412	424	1.11	402
TMP	173.4	1.78	400	171.2	1.77	411	^{f}	^{f}	402
DMF	174.6	1.79	399	177.6	1.71	416	427	0.78	403
DMSO	176.4	1.70	398	178.8	1.68	415	434	0.72	403
HMPA	187.2	1.72	405	186.9	1.70	421	444	0.73	406

[a] *J*(M—CH$_3$) values (M = ^{207}Pb and ^{205}Tl). [b] δ (M—CH$_3$) values (M = Pb and Tl). [c] Absorption maxima at 2.0×10^{-3} (mol/l). [d] Oxinato ligands do not coordinate to the thallium atom as bidentate ligands, because of the absence of the absorption at 350 to 450 nm. [e] Obscured by the resonance peaks of the solvent. [f] Solubility is insufficient for the measurements.

Raman spectra

The Raman spectra were recorded on a JEOL model JRS-02AS spectrometer using 4880 Å light.

Results and discussion

As shown in Tables 2 and 3, there is a large variation in the *J*(M—CH$_3$) (M = ^{207}Pb and ^{205}Tl) values for (CH$_3$)$_2$Pb(OCOC$_6$H$_5$)$_2$, (CH$_3$)$_2$Pb(ox)$_2$ and

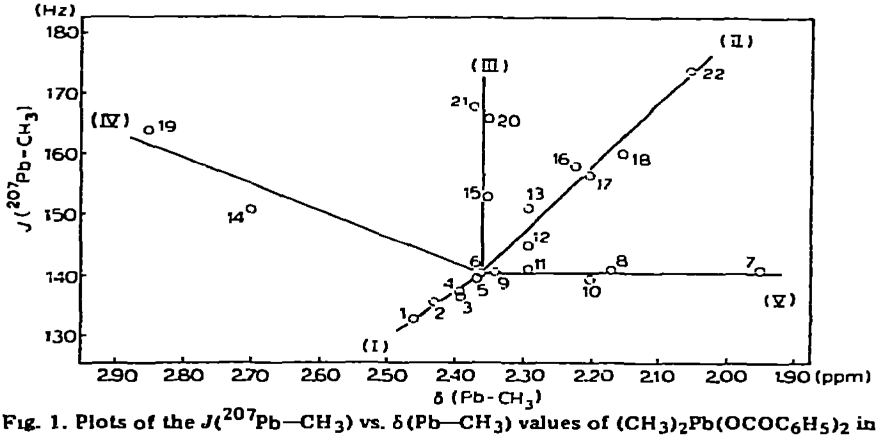
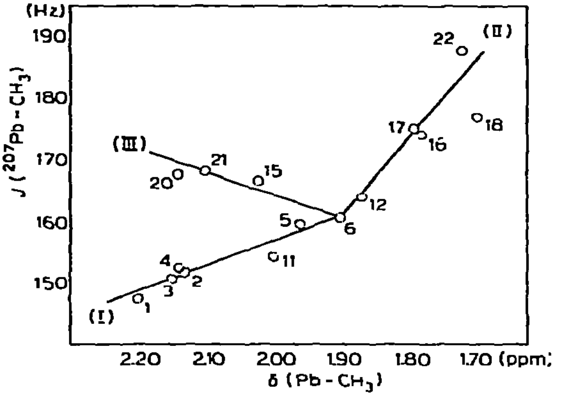


Fig. 1. Plots of the *J*(^{207}Pb—CH$_3$) vs. δ(Pb—CH$_3$) values of (CH$_3$)$_2$Pb(OCOC$_6$H$_5$)$_2$ in various solvents. The numbers for the plots indicating solvents are referred to in Table 2.



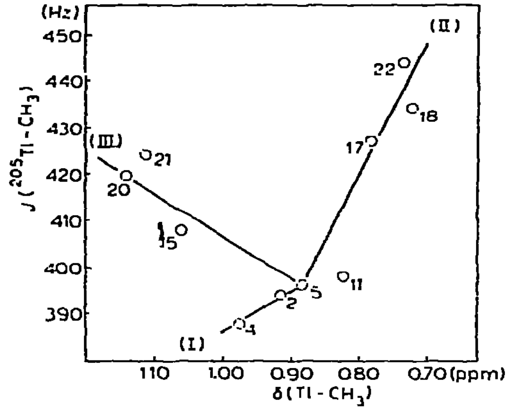


Fig. 2. Plots of the $J(^{207}Pb—CH_3)$ vs. $\delta(Pb—CH_3)$ values of $(CH_3)_2Pb(ox)_2$ in various solvents. The numbers for the plots indicating solvents are referred to in Table 2

Fig. 3. Plots of the $J(^{205}Tl—CH_3)$ vs. $\delta(Tl—CH_3)$ values of $(CH_3)_2Tl(ox)$ in various solvents. The numbers for the plots indicating solvents are referred to in Table 2.

$(CH_3)_2Tl(ox)$ as the solvent is changed. Figs. 1-3 show relations between the $J(M—CH_3)$ and $\delta(M—CH_3)$ values for these complexes. Similar relationships were also obtained in the other benzoato and 7-methyloxinato complexes of dimethyllead. As can be seen from these figures, the solvents used in this experiment can be classified into five groups*. The first group (I) consists of non-coordinating solvents such as haloalkanes and nitromethane. Coordinating solvents, except for heterocyclic solvents, belong to the second group (II). The third (III) consists of pyridine and its derivatives. The fourth (IV) consists of quinoline and isoquinoline, and benzene and its derivatives make up the fifth group (V). An analogous classification for $(CH_3)_2SnCl_2$ and $(CH_3)_3SnCl$ was reported previously [3].

Dependence of $J(^{207}Pb\text{-}CH_3)$ on dielectric constant

In the solvents of the first group, the methyl proton chemical shifts of the benzoato and oxinato complexes of dimethyllead are displaced to lower field by changing the solvent from CCl_4 to CH_3NO_2. Since the polarization of $(\text{lead})^{\delta+}—(\text{ligand})^{\delta-}$ bonds is amplified in solvents of the large dielectric constant, the amount of partial positive charge on the lead atom increases and causes the lower field shift for the methyl proton signals. The $J(^{207}Pb—CH_3)$ values for $(CH_3)_2Pb(OCOC_6H_4—Y)_2$ complexes in these solvents are shown in Table 4. As can be seen from Fig. 4, linear correlations were obtained between the $J(^{207}Pb—CH_3)$ values and $(\epsilon-1)/(3\epsilon+2)$ on which an induced quadrupolar reaction field of the solvent is linearly dependent [12] (see Fig. 5). Similar correlations for the other benzoato complexes were also obtained. This finding seems to indicate thet the $J(^{207}Pb—CH_3)$ values decrease as the partial pos-

---

* Solubility of the oxinato complexes of dimethyl-lead and -thallium is insufficient to measure the J and δ values in the solvents of the fourth and the fifth groups.

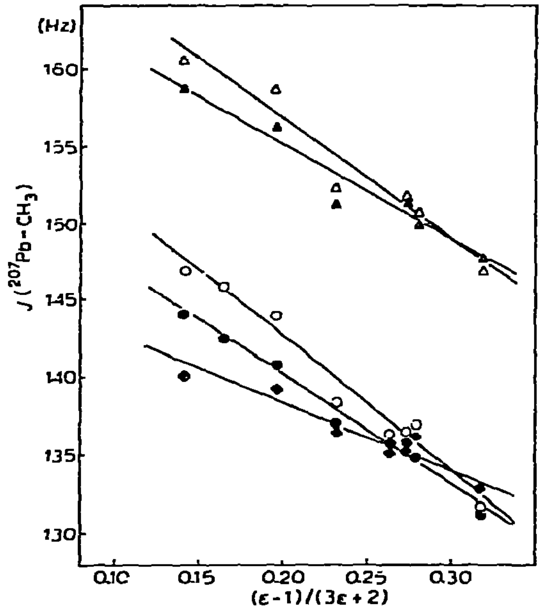
TABLE 4

$J(^{207}Pb—CH_3)$ VALUES OF $(CH_3)_2Pb(OCOC_6H_4\text{-}Y)_2$ IN SEVERAL SOLVENTS OF THE FIRST GROUP[a] (IN Hz)

Solvent	Y *m*-CH$_3$	*p*-CH$_3$	*p*-CH$_3$O	*o*-CH$_3$	H	*p*-Cl	*p*-CO$_2$CH$_3$
CH_3NO_2	131.5	131.0	131.8	130.4	132.6	*b*	*b*
CH_2ClCH_2Cl	137 8	134.7	*b*	133.3	136.3	*b*	*b*
CH_2Cl_2	136.2	135.9	136.9	131.3	135.5	129.3	128.1
CH_2Br_2	136.4	135.9	136.2	133.7	135.1	130.0	*b*
$CHCl_3$	138.3	136.9	136.8	137.3	136.6	131.3	130.5
CCl_2CHCl	143.9	140.8	140.3	137.1	139.3	133.8	131.4
CS_2	145.8	142.5	*b*	141.0	*b*	*b*	*b*
CCl_4	146.9	144.0	*b*	140.4	140.1	*b*	*b*
	160.3[c]	154.0[c]	152.4[c]	150.1[c]	147.6[c]	144.4[c]	140.8[c]

[a] Values for *p*-NO$_2$ could not be observed because of poor solubility. [b] Solubility is insufficient for the measurement. [c] Value at $\epsilon = 1$.

itive charge on the lead atom increases. In Table 4, the $J(^{207}Pb—CH_3)$ values extrapolated to $\epsilon = 1$, at which point the reaction field should vanish, are shown for the *para*-substituted-benzoato complexes. These values thus obtained are linearly reduced with increasing electron attracting power of the substituent on the benzoato ligands($Y = p\text{-}CH_3O, p\text{-}CH_3$, H, p-Cl and $p\text{-}CO_2CH_3$) [13] (see Fig. 6). This relation also shows that a decrease of the electron



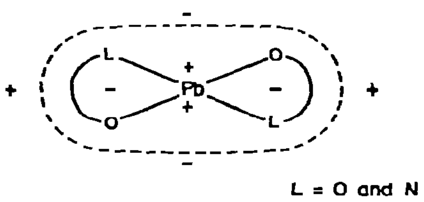


Fig. 4. Correlations of the $J(^{207}Pb—CH_3)$ values with $(\epsilon-1)/(3\epsilon+2)$ for $(CH_3)_2Pb(OCOC_6H_4—Y)_2$ (Y = m-CH$_3$(-○-), p-CH$_3$(-●-) and H(-◆-)) and $(CH_3)_2Pb(ox—Y)_2$ (Y = H(-△-) and 7-CH$_3$(-▲-)).

Fig. 5. Quadrupolar reaction field for $(CH_3)_2Pb(OCOC_6H_5)_2$ and $(CH_3)_2Pb(ox)_2$. The two methyl groups on the lead atom are occupied up and down with respect to the paper.

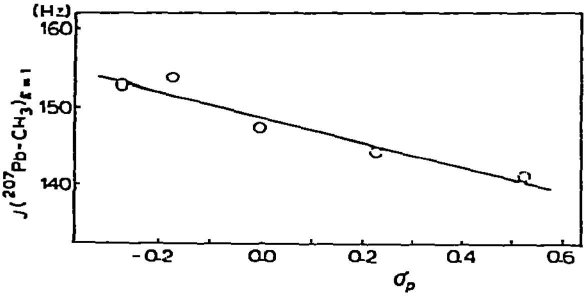


Fig. 6. Plot of the $J(^{207}Pb{-}CH_3)_{\epsilon=1}$ values vs. Hammett's constant σ_p for $(CH_3)_2Pb(OCOC_6H_4\text{-}Y)_2$ (Y = p-CH_3O, p-CH_3, H, p-Cl and p-CO_2CH_3).

density around the lead atom results in a reduction of the $J(^{207}Pb{-}CH_3)$ values for the benzoato complexes.

The coupling mechanism for $J(M{-}CH_3)$ has been considered to be governed by the Fermi contact term as expressed by eqn. 1 [14] (although some questions about this model were raised [15,16]) where α_M^2 is the s character

$$J(M{-}CH_3) = \text{const} \times \alpha_M^2 \times a_M(ns) \times a_H(1s)/\Delta E \qquad (1)$$

of the metal orbitals in the metal—carbon bonds, $a_M(ns)$ and $a_H(1s)$ are the hyperfine coupling constants of the *ns* electron in a metal atom and the 1*s* electron of proton, respectively. ΔE is the mean singlet—triplet excitation energy. The C—Pb—C moiety for several dimethyllead compounds is supposed to be linear in all the solutions studied here, on the basis of the selection rule for the C—Pb—C stretch in the Raman spectra [17,19], while the $J(^{207}Pb{-}CH_3)$ values were found to change from about 135 to 182 Hz (see Table 5). Thus, the change of the $J(^{207}Pb{-}CH_3)$ values for the dimethyllead compounds is independent of the configuration of the C—Pb—C moiety. This fact implies that factors other than the α_{Pb}^2 in eqn. 1 make significant contributions to the change of the $J(^{207}Pb{-}CH_3)$ values in the dimethyllead compounds, in contrast to that of the $J(^{119}Sn{-}CH_3)$ values in a series of methyltin compounds [1-4]. As has been observed in many organometallic compounds [5,6,14,20], the increment of the $a_M(ns)$, which is induced when the positive charge density on the metal atom increases, is a factor which enlarges the $J(M{-}CH_3)$ values. How-

TABLE 5

C—Pb—C STRETCHING FREQUENCIES IN THE RAMAN SPECTRA AND $J(^{207}Pb{-}CH_3)$ VALUES FOR SOME $(CH_3)_2PbX_2$ COMPOUNDS[a]

X	Solvent	ν_s (cm^{-1})	ν_{as}[b] (cm^{-1})	$J(^{207}Pb{-}CH_3)$ (Hz)
NO_3	H_2O	475[c]		135.1
acac[d]	CH_2ClCH_2Cl	474	541[f,g]	153.6
bzac[e]	DMSO	476		170.8
bzac[e]	HMPA	480		181.8
Cl[h]		460	534[f]	

[a] About 20 wt%. [b] No lines attributable to the ν_{as} could be detected. [c] 480 cm^{-1} in ref. 17. [d] Acetylacetonato complex. [e] Benzoylacetonato complex. [f] By IR in the solid state. [g] Ref. 18. [h] Ref. 19.

ever, our observation in the solvents of the first group is that the $J(^{207}Pb{-}CH_3)$ values become smaller with an increase in partial positive charge on the lead atom, which is a direction of enlarging the $a_{Pb}(6s)$ value. As can be seen from eqn. 1, the increase of the ΔE is a reasonable factor to account for the dependence of the $J(^{207}Pb{-}CH_3)$ value on the dielectric constant, because the ΔE value may be increased as the partial positive charge on the lead atom increases. A recent MO study of methylmercury(II) compounds has also indicated that the ΔE value is increased with increasing positive charge on the mercury atom [21].

Dependence of $J(^{207}Pb{-}CH_3)$ on donor strength

The solvents of the second and the third groups have the ability to coordinate to the metal atom. In methyltin compounds, $(CH_3)_2SnCl_2$ [3], $(CH_3)_3SnCl$ [2,3] and $(CH_3)_2Sn(OCOC_6H_5)_2$ [4], the $J(^{119}Sn{-}CH_3)$ values have been reported to increase with increasing donor strength of the solvents as a result of the coordination of the solvent molecules to the tin atom. Previously we have reported that $(CH_3)_2Pb(OCOC_6H_5)_2$ forms a seven-coordinate complex with HMPA in CH_2Cl_2 [9]. Subsequent studies have also shown that the benzoato [8] and oxinato [7] complexes are non-electrolytes and form seven-coordinate complexes with several donor molecules in the solvents of the second and the third groups. As shown in Tables 2 and 3, the $J(M{-}CH_3)$ (M = ^{207}Pb and ^{205}Tl) values of the benzoato and oxinato complexes increase with an increase in the donor strength of the solvents [22]. The chemical shifts of the methyl protons on the metal atom are also displaced to higher field (see Figs. 1-3). The upfield shift of the methyl proton signals in the solvents of the second group can be explained by a decrease in partial positive charge around the metal atom which interacts with the better donor solvents. The above results seem to show that the increase of the $J(M{-}CH_3)$ (M = ^{207}Pb and ^{205}Tl) values for $(CH_3)_2Pb(OCOC_6H_4{-}Y)_2$, $(CH_3)_2Pb(ox{-}Y)_2$ and probably $(CH_3)_2Tl(ox)$ in the donor solvents is governed mainly by the decrease of ΔE, because in the other factors, α_M^2 and $a_M(6s)$, the first was found to be almost constant on the basis of the Raman spectra for the dimethyllead compounds and the second results in the change of the $J(M{-}CH_3)$ values in the wrong direction.

Relation of $J(^{207}Pb{-}CH_3)$ with absorption maxima in the UV spectra

Metal complexes which contain the bidentate oxinato ligands have been well known to have the absorption maxima, λ_{max}, near 400 nm in the UV spectra [23]. The λ_{max} for our oxinato complexes shifts to red with a decrease in the dielectric constant of the non-coordinating solvents or with an increase in the donor strength of the coordinating solvents (see Table 3), and was found between 377 and 421 nm, while the λ_{max} of $(CH_3)_2Sn(ox)_2$, the $J(^{119}Sn{-}CH_3)$ values which are independent of the solvents, was reported to be almost constant [7]. These findings indicate that the positions of the λ_{max} are closely related to the change of the electron density around the metal atom; the λ_{max} shifts to longer wavelength as the amount of partial positive charge on the metal atom decreases. One probable explanation for the red shift in the donor solvents is an increase in a contribution of the charge transfer from metal to the oxinato ligands to this band with a decrease in partial positive charge, which

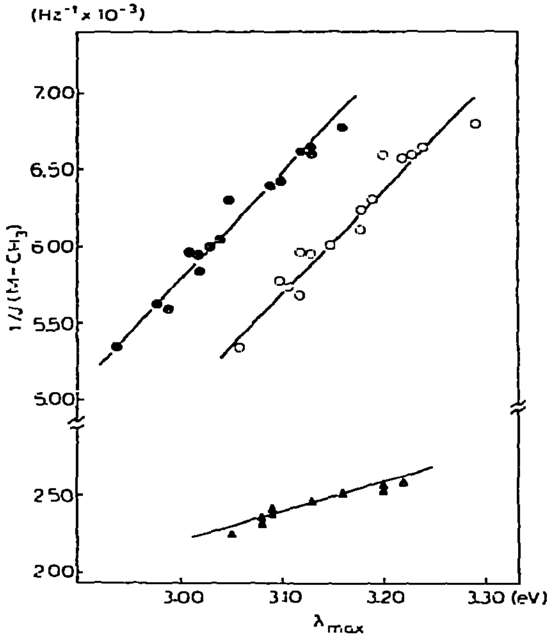


Fig. 7. Correlations of $1/J(M{-}CH_3)$ ($M = {}^{207}Pb$ and ${}^{205}Tl$) with λ_{max} for $(CH_3)_2Pb(ox)_2$ (-○-), $(CH_3)_2Pb(ox\text{-}CH_3\text{-}7)_2$ (-●-) and $(CH_3)_2Tl(ox)$ (-▲-).

is produced by interaction with donor solvents, while the blue shift in the solvents of large dielectric constant is probably a result of the stabilization of the ground states for the complexes rather than the excited states in these solvents. As shown in Fig. 7, we have obtained linear correlations between $1/J(M{-}CH_3)$ and λ_{max} (in eV) for the oxinato complexes of dimethyl-lead and -thallium, and the coupling constants were found to be expressed by eqns. 2-4:

$(CH_3)_2Pb(ox)_2$:

$$J({}^{207}Pb{-}CH_3) = 147.5/(\lambda_{max} - 2.27) \quad (Hz) \qquad (2)$$

$(CH_3)_2Pb(ox\text{-}CH_3\text{-}7)_2$:

$$J({}^{207}Pb{-}CH_3) = 144.9/(\lambda_{max} - 2.16) \quad (Hz) \qquad (3)$$

$(CH_3)_2Tl(ox)$:

$$J({}^{205}Tl{-}CH_3) = 540.8/(\lambda_{max} - 1.82) \quad (Hz) \qquad (4)$$

Either way, it seems evident that the $J(M{-}CH_3)$ values for these oxinato complexes depend on the λ_{max}. The above correlations suggest indirectly that the changes of the $J(M{-}CH_3)$ values for the dimethyl-lead and -thallium compounds depend on the change of the excitation energy, ΔE.

Effects of the ring current of solvents on $\delta(Pb{-}CH_3)$

As the $J(M{-}CH_3)$ values become larger, the methyl proton signals of $(CH_3)_2Pb(OCOC_6H_5)_2$ in the solvents of the fourth group and of $(CH_3)_2Pb(ox)_2$ and $(CH_3)_2Tl(ox)$ in the solvents of the third group shift to lower field, while those of $(CH_3)_2Pb(OCOC_6H_5)_2$ in the solvents of the third group are almost constant, contrary to those in the solvents of the first and the second groups (see Figs. 1-3). The large paramagnetic effect due to the ring current of the pyridine and quinoline rings of the solvents seems to contribute significantly to the methyl proton chemical shifts in addition to the diamagnetic effect due to the reduction of positive charge on the metal atom, which is produced by the coordination of the solvent molecule. The difference between pyridines and quinolines for the above paramagnetic shifts in $(CH_3)_2Pb(OCOC_6H_5)_2$ is probably due to a difference in magnetic anisotropy of the ring current as reported in the polynuclear aromatic hydrocarbons [24].

As shown in Fig. 1, the $J(^{207}Pb—CH_3)$ values of $(CH_3)_2Pb(OCOC_6H_5)_2$ in the solvents of the fifth group are almost constant, while the $\delta(Pb—CH_3)$ values vary by about 0.40 ppm. The higher field shift of the methyl proton signals may be explained by the diamagnetic effect of the solvents, analogous to the results reported previously [25,26].

On the basis of the dependence of the $J(^{207}Pb—CH_3)$ values on the dielectric constant or the donor strength of the solvents and the absorption maxima in the UV spectra for some benzoato and oxinato complexes of dimethyllead(IV), we indicate that the excitation energy, ΔE, which is closely related to the electron density around the lead atom, is a major factor affecting the change of the $J(^{207}Pb—CH_3)$ values for the dimethyllead compounds and probably that of the $J(^{205}Tl—CH_3)$ values for dimethyl(oxinato)thallium(III), rather than the hyperfine coupling constant, $a_M(6s)$.

Acknowledgements

We wish to express our hearty thanks to Professor Rokuro Okawara for his continuous encouragement throughout this study. We are also grateful to Dr. Teizo Kitagawa of Osaka University for the measurements of the Raman spectra.

References

1 M.M. McGrady and R.S. Tobias, Inorg Chem., 3 (1964) 1157.
2 T.F. Bolles and R.S. Drago, J. Amer. Chem. Soc., 88 (1966) 5730
3 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Japan, 40 (1967) 1566.
4 Y. Kawasaki, J. Inorg. Nucl. Chem., 30 (1968) 377.
5 J.V. Hatton, W.G. Schneider and W. Siebrand, J. Chem. Phys., 39 (1963) 1330.
6 J.V. Hatton, J. Chem. Phys., 40 (1964) 933.
7 M. Aritomi and Y. Kawasaki, J. Organometal. Chem., 81 (1974) 363.
8 M. Aritomi, K. Hashimoto and Y. Kawasaki, to be published.
9 M. Aritomi, Y. Kawasaki and R. Okawara, Inorg. Nucl. Chem. Lett., 8 (1972) 1053.
10 G. Grüttner and E. Kraus, Ber., 49 (1916) 1415.
11 H. Kurosawa, K. Yasuda and R. Okawara, Inorg. Nucl. Chem. Lett., 1 (1965) 131.
12 A.D. Buckingham, Can. J. Chem., 38 (1960) 300.
13 M.S. Newman(Ed.), Steric Effect in Organic Chemistry, John Wiley, New York, 1356.
14 G.W. Smith, J. Chem. Phys., 42 (1965) 435.
15 W. McFarlane, J. Chem. Soc., (1967) 725.
16 P.T. Narasimhan and M.T. Rogers, J. Chem. Phys., 34 (1961) 1049.
17 C.E. Freidline and R.S. Tobias, Inorg. Chem., 5 (1966) 354.
18 Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Japan, 37 (1964) 903.
19 R.J.H. Clark, A.G. Davies and R.J. Puddephatt, J. Amer. Chem. Soc., 90 (1968) 6923.
20 D.K. Dalling and H.S. Gutowsky, J. Chem. Phys., 55 (1971) 4959.
21 H.F. Henneike, J. Amer. Chem. Soc., 94 (1972) 5945.
22 V. Gutmann, Coordination Chemistry in Nonaqueous Solutions, Springer, New York, 1968.
23 Y. Kawasaki, Org. Mag. Resonance, 2 (1970) 165, and refs. therein.
24 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Ed., Pergamon Press, London, 1969.
25 Y. Kawasaki, Mol. Phys., 12 (1967) 287; M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, J. Inorg. Nucl. Chem., 30 (1968) 3231.
26 E.M. Engler and P. Laszlo, J. Amer. Chem. Soc., 93 (1971) 1317.