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A Dimeric Structure of Dimethyllead(IV) Complexes with ONO Tridentate Schiff-base Ligands and the Interaction of These Complexes with Donor Solvents

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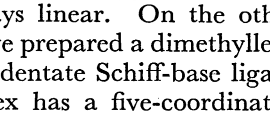
From measurements of the molecular weights, dimethyllead(IV) complexes with ONO tridentate Schiff-base ligands, 2-(2-oxidobenzylideneamino)phenolatos, were found to have dimeric six-coordinate structure in $CHCl_3$, in which either one of the two oxygen atoms in the ligands bridges the lead atoms. The $^2J(^{207}Pb–CH_3)$ values increase and the $\delta(Pb–CH_3)$ values shift to a higher magnetic field with an increase in the donor strength of the solvents. Linear relationships between the $^2J(^{207}Pb–CH_3)$ and $\delta(Pb–CH_3)$ values and Hammett's σ values of the substituents on the Schiff-base ligands were obtained. These results suggest that the complexes form monomerically as a result of coordination with one and/or two solvent molecules in such donor solvents as DMSO and HMPA, and that the $^2J(^{207}Pb–CH_3)$ values is dependent mainly on the change in the positive charge on the lead atom: the change in the mean excitation energy, ΔE, in the Fermi contact term.

In a series of spectroscopic studies of several dimethyllead(IV) complexes of 8-quinolinols,$^{1)}$ β-diketones,$^{2)}$ benzoates,$^{3)}$ and quadridentate Schiff bases,$^{4)}$ we have found that these dimethyllead(IV) complexes are monomeric and take a six-coordinate configuration in non-coordinating solvents, $CHCl_3$ and CH_2Cl_2, and that in such donor solvents as DMSO and HMPA, the lead atom is coordinated with a solvent molecule as the seventh ligand. In both types of solvents, the C–Pb–C skeleton is always linear. On the other hand, Bosco and Cefalù$^{5)}$ have prepared a dimethyllead(IV) complex with a ONO tridentate Schiff-base ligand and claimed that the complex has a five-coordinate configuration. The C–Pb–C skeleton of the complex is not linear, judging from the following observations: 1) the molecular weight in acetone shows a monomeric value, and 2) the spin-spin coupling constant, $^2J(^{207}Pb–CH_3)$, in $CDCl_3$ is very small (132 Hz) as compared with those of usual six-coordinate dimethyllead(IV) complexes (*ca.* 150 Hz) with the linear C–Pb–C skeleton.$^{1-4,6)}$ However, a possibility that the coordination of an acetone molecule to the lead atom gives the monomeric value can not be disregarded, since we have elucidated from spectroscopic studies$^{3)}$ that acetone interacts more or less strongly with dimethyllead(IV) complexes. Moreover, the configuration of the C–Pb–C skeleton in dimethyllead(IV) complexes, as ascertained in a series of our studies,$^{1-4,7,8)}$ is not correlated directly with the $^2J(^{207}Pb–CH_3)$ values. Therefore, we have reinvestigated the molecular weights of the some dimethyllead(IV) complexes with ONO tridentate Schiff-base ligands in $CHCl_3$, in which the possibility of the coordination of solvent molecules to the lead atom seems negligibly small.



	complex; $(CH_3)_2PbL$
L=**1**: X=Z=H, Y=NO_2	(complex I)
L=**2**: X=Y=H, Z=NO_2	(complex II)
L=**3**: X=Y=Z=H	(complex III)
L=**4**: X=Z=H, Y=CH_3	(complex IV)
L=**5**: X=OCH_3, Y=Z=H	(complex V)
L=**6**: X=OCH_3, Y=CH_3, Z=H	(complex VI)

We also wish to report on the effects of the substituents on the Schiff-base ligands and of the donor strength of solvents upon the $^2J(^{207}Pb–CH_3)$ and the $\delta(Pb–CH_3)$ values.

As the planar ONO tridentate Schiff-base ligands, 2-(2-oxidobenzylideneamino)phenolates, L=**1**—**6**, were used.

Experimental

Materials. The dimethyllead dichloride was prepared by the chlorination of tetramethyllead in ethyl acetate at −10 °C.$^{9)}$ The Schiff bases, 2-(2-hydroxybenzylideneamino)phenols (H_2L), were prepared by dehydration reactions between the corresponding *o*-aminophenols and salicylaldehydes by refluxing in alcoholic solutions. The solvents were reagent grade and were purified according to the standard method except for $CDCl_3$, which was used as supplied.

Preparation of the Complexes, I—VI. The dimethyllead complexes, $(CH_3)_2PbL$, I—VI, with the corresponding ligands, **1**—**6** respectively, were prepared according to the following procedures. A dry methanol solution (20 dm) of sodium salts of an appropriate Schiff base (Na_2L), prepared from sodium methoxide in methanol (Na; 0.5 g, 20 mmol) and H_2L (10 mmol), was added, drop by drop, into dimethyllead dichloride (2.5 g, 10 mmol) in dry methanol (30 dm). The mixture was then stirred for a few hours. The precipitates were filtered, washed by benzene and methanol, and recrystallized from methanol (I and IV), *N*,*N*-dimethylformamide/methanol(II), or dichloromethane/hexane (III, V, and VI). Elemental analyses of the lead of all the complexes were carried out by decomposition with concentrated sulfuric and nitric acids.$^{10)}$

Molecular-weight and Conductivity Measurements. The molecular weights in $CHCl_3$ (0.5 wt %) were measured by means of a Mechrolab vapor pressure osmometer at 25 °C. The molar conductances in DMSO were measured by means of a Yokogawa F-225A Universal bridge and a cell with the cell constant of 0.377 cm^{-1} at 25±0.1 °C. The specific conductance of DMSO used was $\kappa=4.2\times10^{-7}\ \Omega^{-1}\ cm^{-1}$. The molar conductances (Λ_m) of IV—I in DMSO (10^{-3} mol·dm^{-3}) were 1.1—1.9 $\Omega^{-1}\ cm^2\ mol^{-1}$ (Table 1). All the complexes were found to be non-electrolytes.

Table 1. Analytical data, physical properties, and IR spectral data of $(CH_3)_2PbL$

Complex	Color	Mp (°C)	Found (Calcd) (%) C	H	N	Pb	Λ_m a) (Ω^{-1} cm^2 mol^{-1})	mol wt b) Found (Calcd)	ν(C=N) (cm^{-1}) in CH_2Cl_2 (in DMSO)
I	yellow-brown	230 c)	36.61 (36.51)	3.11 (2.86)	5.34 (5.68)	41.72 (41.99)	1.21	949 (493)	1606 (1595)
II	red	264 c)	36.30 (36.51)	2.81 (2.86)	5.83 (5.68)	42.11 (41.99)	1.17	977 (493)	1605 (1598)
III	yellow-red	252 d)	39.97 (40.17)	3.43 (3.37)	3.11 (3.12)	46.27 (46.20)	1.85	902 (449)	1600 e) (1597)
IV	yellow	190 c)	41.50 (41.55)	3.72 (3.70)	3.30 (3.03)	45.19 (44.80)	1.73	976 (463)	1602 (1597)
V	brown	223 c)	39.93 (40.16)	3.50 (3.58)	2.95 (2.93)	43.02 (43.30)	1.62	987 (479)	1603 (1595)
VI	red-brown	215 c)	41.44 (41.46)	3.59 (3.89)	2.71 (2.84)	41.78 (42.07)	1.96	962 (493)	1600 (1595)

a) In DMSO. b) In $CHCl_3$. c) Decomposed. d) Sublime. e) 1605 cm^{-1} in the solid state, reported by Bosco and Cefalù.[5]

IR and ^{1}H NMR Spectra. The IR Spectra were recorded on a Hitachi 225 spectrophotometer. ^{1}H NMR studies were carried out on a JEOL-PS-100 spectrometer operating at 100 MHz. All the data were obtained in 4 wt % or in saturated solutions. The chemical shifts were measured relative to TMS as the internal standard at the ambient temperature.

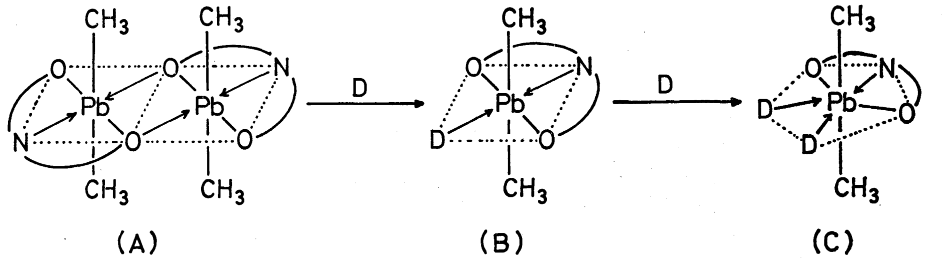
The analytical data, physical properties, and IR and ^{1}H NMR spectral data for the complexes, I—VI, are given in Tables 1 and 2.

Results and Discussion

The color, melting point, ν(C=N), and δ(Pb–CH_3) and $^2J(^{207}Pb–CH_3)$ values of III obtained by us (Tables 1 and 2) are in good agreement with those reported by Bosco and Cefalù.[5] As can be seen from Table 1, the molecular weights of I—VI were twice the values produces by the use of the $(CH_3)_2PbL$ formula. These results indicate that either one of the two oxygen atoms of the ligand bridges the lead atoms, resulting in the formation of a six-coordinate configuration (**A**), in which the C–Pb–C skeleton may be linear, although a distorted octahedral structure with a slightly bent C–Pb–C skeleton is possible. A similar dimeric structure is found in the case of $[(CH_3)_2Pb(ox)X]_2$ (ox=8-quinolinolato, X=Cl and Br), in which the halogen atoms bridge two lead atoms.[11] These results are in marked contrast to those for dimethyltin(IV) complexes; *i.e.*, the dimethyltin complexes of **1**, **3**, and **4**[12] and $(CH_3)_2Sn(ox)X$ (X=Cl and Br)[13] have the five-coordinate and distorted trigonal bipyramidal structures, with a bent C–Sn–C skeleton.

The bridging of the oxygen atom in Complex I—VI is weak and is easily severed by a solvent molecule, forming a six-coordinate configuration (**B**) in donor solvents, since a monomeric value was observed for III in such weak donor solvent as acetone.[5] The dimethyllead species may have a six-coordinate configuration with an acetone molecule as the sixth ligand (**B**). The existence of seven-coordinate ones (**C**) can not be excluded, especially in such strong donor solvents as DMSO and HMPA. The $^2J(^{207}Pb–CH_3)$ values of V and VI in DMSO and HMPA are comparable to those of $(CH_3)_2Pb(ox)_2$ in DMSO (176.4 Hz),[1] in which the seven-coordinate configuration was assumed, and of an isolated seven-coordinate complex, $(CH_3)_2Pb(gbha)(H_2O)$ (gbha=2,2′-(ethanediylidenediimino)diphenolato) (176—178 Hz).[8]

The $^2J(^{207}Pb–CH_3)$ values of III and IV in $CDCl_3$ (133.6 and 135.0 Hz respectively) are smaller than those of many other six-coordinate complexes (*ca.* 150 Hz).[1–4,6] Those of I and II with an electron-withdrawing nitro group on the ligands are much smaller: 120.7 and 123.1 Hz respectively. On the other hand, those of V and VI with an electron-releasing methoxyl group (155.0 and 156.7 Hz respectively) are larger than those of I—IV, and have values similar to that of $(CH_3)_2Pb(acac)_2$ (acac=acetylacetonato) (154.7 Hz), having a six-coordinate configuration with a linear C–Pb–C skeleton.[14] The independence of the $^2J(^{207}Pb–CH_3)$ values on the configuration of the C–Pb–C skeleton may better be understood by the linear relationship between these values and Hammett's σ values of the substituents on the phenyl ring of the ligands for I—IV (Fig. 1).



D=HMPA, DMSO, Pyridine, $(CH_3O)_3PO$, CH_3OH, $(CH_3)_2CO$

TABLE 2. THE ^{1}H NMR

Solvent	I				II				III		
	δ_1	δ_2	^2J	^3J	δ_1	δ_2	^2J	^3J	δ_1	δ_2	^2J
$CDCl_3$	2.13	8.12	120.7	5.0	2.10	—$^{b)}$	123.1	—$^{b)}$	2.07 2.05$^{c)}$	8.32 8.20$^{c)}$	133.6 132$^{c)}$
CH_2Cl_2	2.12	8.59	120.8	5.2	—$^{b)}$	—$^{b)}$	—$^{b)}$	—$^{b)}$	2.05	8.39	135.9
CH_3OH	2.00	8.48	138.0	5.6	2.02	—$^{b)}$	140.0	—$^{b)}$	1.91	8.41	138.6
$(CH_3O)_3PO$	1.98	8.66	150.9	10.8	1.94	8.56	154.8	—$^{b)}$	1.81	8.47	141.2
Pyridine	2.18	—$^{d)}$	151.8	—$^{d)}$	—$^{b)}$	—$^{b)}$	—$^{b)}$	—$^{b)}$	2.04	—$^{d)}$	144.5
DMSO	1.81	8.60	160.5	14.7	1.84	8.64	164.7	13.1	1.74	8.56	152.4
HMPA	1.77	8.95	166.6	15.5	1.82	9.19	165.6	15.2	1.70	8.75	158.0

a) δ_1, δ_2, ^2J, and ^3J are δ(Pb–CH_3) (ppm), δ(Pb–N=CH) (ppm), $^2J(^{207}Pb–CH_3)$ (Hz), and $^3J(^{207}Pb–N=CH)$
d) Obscured by the solvent peaks.

This relationship indicates that the $^2J(^{207}Pb–CH_3)$ values decrease with an increase in the electron-withdrawing character of the substituent on the ligand. The electron-withdrawing group leads to an increase in the polarization in $Pb^{\delta+}–O^{\delta-}$ bonds, resulting in an increase in the positive charge on the lead atom. Indeed, the δ(Pb–CH_3) values are found to shift to a lower magnetic field in this order: IV, III, II, and I (Fig. 1). Similarly, an increase in the $^2J(^{207}Pb–CH_3)$ values and a higher magnetic-field shift of the δ(Pb–CH_3) values with an increase in the donor strength of the solvents (Table 2) can also be explained by the decrease in the positive charge on the lead atom with the increase in the donor strength of the solvents. These results are consistent with our previous assumption[1,3,4,7,15] that the change in the mean excitation energy, ΔE, in the Fermi contact term plays a dominant role in determining the $^2J(^{207}Pb–CH_3)$ value for dimethyllead(IV) complexes. Therefore, the small $^2J(^{207}Pb–CH_3)$ value can not be connected directly with the conclusion that the C–Pb–C skeleton is bent in the dimethyllead(IV) complexes. This is substantiated by the observation that the $^2J(^{207}Pb–CH_3)$ values of the dimethyllead(IV) cation, $(CH_3)_2Pb^{2+}$, with a linear C–Pb–C skeleton, are very smaller, ranging from 101 to 132 Hz in several strong acids.[7]

It should also be noted that the amount of variation in the $^2J(^{207}Pb–CH_3)$ values upon a change in the solvent from $CDCl_3$ to HMPA are in this order: I, II (*ca.* 50 Hz)>III, IV (*ca.* 30 Hz)>V, VI (*ca.* 20 Hz). These values are attributable to the fact that the strength of coordination of the solvent molecule to the lead atom differs from complex to complex, probably increasing with an increase in the positive charge on the lead atom.

As in the case of $(CH_3)_2Pb(saln)\cdot CH_3OH$,[4] we have also obtained the spin-spin coupling constants between the lead nucleus and the azomethine proton, $^3J(^{207}Pb–N=CH)$, in the case of I and II, although Bosco and Cefalù did not report these values.[5] The couplings were not detected in the other complexes, since the azomethine proton signals of the complexes are broad (with a half-height width of 4—8 Hz). The broadenings are presumed to be due to the coupling with the lead nucleus. By comparison with the values of $(CH_3)_2Pb(saln)\cdot CH_3OH$ (23.4—29.3 Hz),[4] those of I and II (5.0—15.5 Hz) are quite small and change remarkably along with the coordinating ability of the solvents. Therefore, the above results suggest that the coordination of the nitrogen atom to the lead atom in I—VI is weaker than in $(CH_3)_2Pb(saln)\cdot CH_3OH$. On the other hand, the $^3J(^{119}Sn–N=CH)$ values of $(CH_3)_2SnL$ (L=**3**) decrease with an increase in the donor strength of the solvents, although the $^2J(^{119}Sn–CH_3)$ values increase.[11]

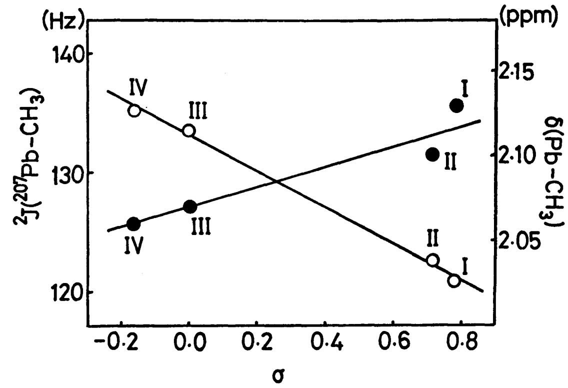


Fig. 1. Plots of the $^2J(^{207}Pb–CH_3)$ (—○—) and the δ(Pb–CH_3) values (—●—) in $CDCl_3$ *vs.* Hammett's σ for $(CH_3)_2PbL$, I—IV.

In conclusion, Complexes I—VI have a dimeric six-coordinate structure (**A**) in such non-coordinating solvents as $CHCl_3$ and CH_2Cl_2. On the other hand, in such donor solvents as DMSO and HMPA the complexes form a monomeric six- and/or seven-coordinate structure, (**B**) and/or (**C**), with one or two donor solvent molecules. In either solvent, the C–Pb–C skeleton is linear and is perpendicular to the coordination plane. Therefore, the results are fundamentally different from those for the dimethyltin(IV) complexes, in which the C–Sn–C skeleton is quite flexible.

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DATA OF $(CH_3)_2PbL$a)

Complex								
IV			V			VI		
δ_1	δ_2	^2J	δ_1	δ_2	^2J	δ_1	δ_2	^2J
2.06	8.32	135.0	2.05	8.35	155.0	2.04	8.34	156.7
2.01	8.32	138.5	2.01	8.38	157.5	2.00	8.36	159.7
1.94	8.48	145.2	1.96	8.48	158.7	1.93	—b)	166.4
1.83	8.50	149.6	—b)	—b)	—b)	1.89	8.47	167.1
2.11	—d)	155.4	2.00	—d)	157.6	2.02	—d)	159.0
1.75	8.43	156.1	1.87	8.47	167.4	1.87	8.46	168.8
1.70	8.72	166.8	1.83	8.84	172.8	1.83	8.78	178.3

(Hz) respectively. b) The solubility is insufficient for measurements. c) Reported by Bosco and Cefalù.5)

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11) $[(CH_3)_2Pb(ox)X]_2$ (X=Cl and Br) were prepared by a photoreaction of $(CH_3)_2Pb(ox)_2$ in CHX_3 or CH_2X_2. The $^2J(^{207}Pb\text{-}CH_3)$ values are 148—152 Hz in $CDCl_3$ or CH_2Cl_2: Y. Kawasaki, to be published.

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