

INTERACTION OF DIMETHYLLEAD(IV) BENZOATO COMPLEXES WITH SOME DONOR MOLECULES IN SOLUTION

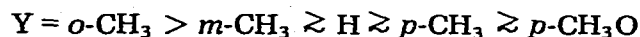
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Summary

The stability constants of some benzoato and oxinato complexes of dimethyllead(IV), $(\text{CH}_3)_2\text{PbX}_2$ ($\text{X} = \text{OCOC}_6\text{H}_4\text{Y}$; $\text{Y} = \text{H}, o\text{-CH}_3, m\text{-CH}_3, p\text{-CH}_3$ and $p\text{-CH}_3\text{O}$; $\text{X} = \text{oxinato}$), with donors (L): tertiary phosphine oxides, phosphates (R_3PO), hexamethylphosphortriamide (HMPA), dimethylsulfoxide (DMSO), dimethylformamide (DMF) and pyridines were determined in methylene chloride. The stability constants for the benzoato complexes were found to be larger than those for the oxinato complexes and in general decrease in the following order of Y:



The J_0 values, which are the $J(^{207}\text{Pb}-\text{CH}_3)$ values estimated for the hexacoordinate dimethyllead complexes, increase in the same order. Linear relationships were obtained in the plots of the stability constants against the basicity, the sum of the Taft's σ^* values of the R groups and the J_c values, which are the $J(^{207}\text{Pb}-\text{CH}_3)$ values estimated for the seven-coordinate complexes, $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_4\text{Y})_2 \cdot \text{L}$. The dependence of the stability constants on the Y and the R groups was found to be mainly due to the change of the electron density on the lead and the phosphoryl oxygen atom.

Introduction

The complex formation between several organometallic halide derivatives of Sn^{IV} , Pb^{IV} and Hg^{II} and donor molecules in solution has been quantitatively studied, and the configuration of the complexes and the nature of the metal—donor bonds have been discussed [1]. Recently we have reported that dimethylbis(benzoato)lead forms a seven-coordinate complex with HMPA, $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2 \cdot \text{HMPA}$, in solution [2]. In the present paper, we report the stability constants of some benzoato complexes of dimethyllead(IV),

$(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_4\text{Y})_2$ ($\text{Y} = \text{H}, o\text{-CH}_3, m\text{-CH}_3, p\text{-CH}_3$ and $p\text{-CH}_3\text{O}$), with several donor molecules, and correlations of these constants with the basicity, the Taft's σ^* values of the substituent groups of the donors and the $J(^{207}\text{Pb}-\text{CH}_3)$ values for the seven-coordinate dimethyllead complexes.

Experimental

Materials

Dimethyllead dichloride was prepared by the chlorination of tetramethyllead in ethyl acetate at about -10°C [3]. Tributyl-, triethyl- and trimethylphosphine oxides were prepared by the method reported previously [4]. Organic phosphates, HMPA and the other donors obtained from Nakarai Chemicals were stored over molecular sieves 4A 1/16 for several days and refluxed at reduced pressure over calcium hydride or lithium for a few hours. The middle fraction obtained by distillation was collected.

The specific conductances of HMPA and DMSO used in conductivity measurements were 1.23 and $1.03 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$, respectively.

Preparation of complexes

All $(\text{CH}_3)_2\text{PbX}_2$ compounds ($\text{X} = \text{OCOC}_6\text{H}_4\text{Y}$; $\text{Y} = \text{H}, o\text{-CH}_3, m\text{-CH}_3, p\text{-CH}_3$ and $p\text{-CH}_3\text{O}$; $\text{X} = \text{ox}$) were prepared by the reaction of dimethyllead dichloride (1.5 g, 5 mmol) and an appropriate benzoic acid or oxine (10 mmol) in aqueous ammonia solution, as reported in refs. 2, 5 and 6. The benzoato and oxinato compounds were purified by recrystallization from methylene chloride and methanol, respectively.

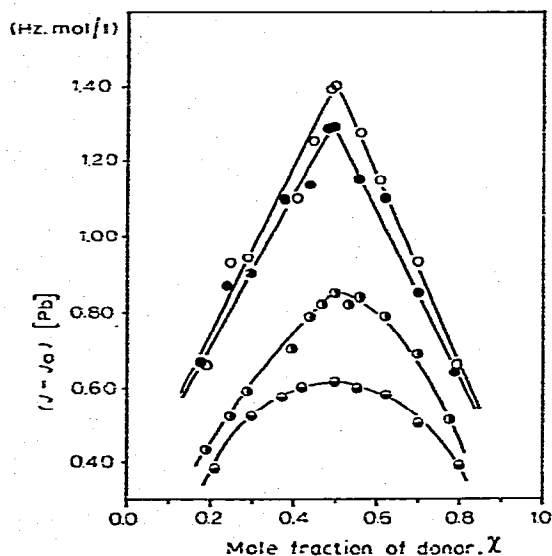


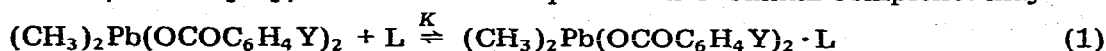
Fig. 1. Job's method of continuous variation applied for $J(^{207}\text{Pb}-\text{CH}_3)$ values of $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2$ at the total concentration (0.100 mol/l). Donors: $(\text{C}_2\text{H}_5)_3\text{PO}$ (\circ), $(\text{CH}_3)_3\text{PO}$ (\bullet), $[(\text{CH}_3)_2\text{N}]_3\text{PO}$ (\circ with a dot) (ref. 2) and $(\text{C}_6\text{H}_5)_3\text{PO}$ (\circ with a dot).

IR and PMR spectra

IR and PMR spectra were recorded on a Hitachi EPI-2G spectrometer with gratings and a JEOL model JNM-PS-100 spectrometer, operating at 100 MHz, respectively.

Determination of stoichiometry and stability constants of complexes

The application of the Job's method of continuous variation[7] for the $J(^{207}\text{Pb}-\text{CH}_3)$ values in some $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2$ -donor(L) systems is shown in Fig. 1. As can be seen from this figure, each curve has a maximum at χ (mole fraction of the donor) = 0.5. Thus, the stoichiometry of the complex formation between $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2$ and the donor molecules was found to be 1/1 in CH_2Cl_2 , as shown in the equilibrium 1. Similar complexes may be



formed for the other benzoato compounds in CH_2Cl_2 . However, in the case of HMPA, the curve is not symmetrical about the line corresponding to $\chi = 0.5$ and somewhat lifted in the region at $\chi > 0.5$. These facts seem to indicate that a 1/2 complex, $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2 \cdot 2\text{HMPA}$, makes some contributions to the equilibrium for the complex formation. For the equilibrium 1, the values of J for a series of solutions containing a constant amount of the lead compound (A_0) but varying amounts of donor molecules (D_0) is expressed by

$$K = C/[(A_0 - C)(D_0 - C)] \quad (2)$$

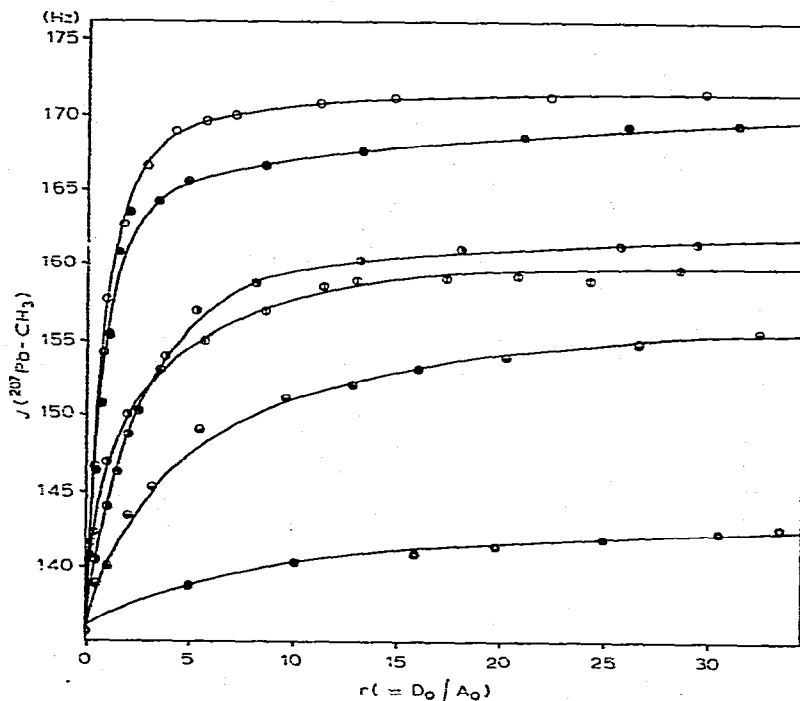


Fig. 2. $J(^{207}\text{Pb}-\text{CH}_3)$ values for $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2$ (2.00×10^{-2} mol/l) in CH_2Cl_2 solutions containing varying amounts of donor molecule: $(\text{C}_2\text{H}_5)_3\text{PO}$ (○), $[(\text{CH}_3)_2\text{N}]_3\text{PO}$ (●), Pyridine (◐), $(\text{CH}_3)_2\text{SO}$ (◑), $(\text{CH}_3\text{O})_3\text{PO}$ (◒) and $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ (◓).

$$J = [J_0 \cdot (A_0 - C) + J_c \cdot C] / A_0 \quad (3)$$

eqn. 3, where J_0 and J_c are the $J(^{207}\text{Pb}-\text{CH}_3)$ values of the uncomplexed and the complexed lead compounds, respectively and C is the amount of the complex formed in solution. By using eqns. 2 and 3, we have obtained eqn. 4:

$$J = J_0 + \frac{(J_c - J_0)}{2} \left[(r + 1 + 1/A_0K) - \sqrt{(r + 1 + 1/A_0K)^2 - 4r} \right] \quad (4)$$

$(r = D_0/A_0)$

The changes of the J values for $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2$ with varying amounts of donor are shown in Fig. 2. The solid lines indicate the J values calculated by the least-squares method [8] by using eqn. 4, in which J_0 , J_c and K were used as parameters. The values thus obtained were found to agree well with those obtained by using a constant value for J_0 but changing the values for J_c and K . The calculations have been done with a NEAC model 700 computer at the Calculation Center of Osaka University.

Results and discussion

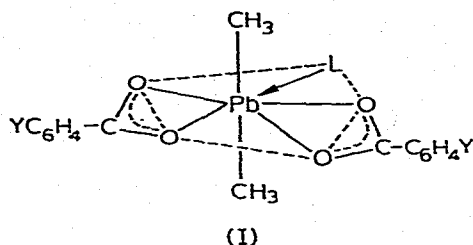
As shown in Table 1, the benzoato compounds of dimethyllead, $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_4\text{Y})_2$ ($\text{Y} = \text{H}$, $o\text{-CH}_3$, $m\text{-CH}_3$, $p\text{-CH}_3$ and $p\text{-CH}_3\text{O}$), were found to be non-electrolytes in HMPA and in CH_2Cl_2 solution containing $(\text{CH}_3)_3\text{PO}$. The

TABLE I
MOLAR CONDUCTANCES AND STRETCHING FREQUENCIES OF CARBOXYL GROUPS FOR $(\text{CH}_3)_2\text{PbX}_2$ COMPOUNDS IN SEVERAL SOLVENTS

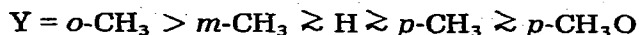
X	Y		Solvent		
			CH_2Cl_2	HMPA(DMSO) ^d	$\text{CH}_2\text{Cl}_2/\text{TMPO}^e$
$\text{OCOC}_6\text{H}_4\text{Y}$	H	Λ_m^a	<0.1	0.53(0.55)	0.23
		$\nu_{\text{asym}}(\text{CO}_2)^b$	1525	1525	1523
		$\nu_{\text{sym}}(\text{CO}_2)^c$	1370	1375	1370
	$o\text{-CH}_3$	Λ_m	<i>f</i>	0.27	0.41
		$\nu_{\text{asym}}(\text{CO}_2)$	1532	1537	1530
		$\nu_{\text{sym}}(\text{CO}_2)$	1370	1382	1375
	$m\text{-CH}_3$	Λ_m	<i>f</i>	0.23	0.33
		$\nu_{\text{asym}}(\text{CO}_2)$	1535	1538	1532
		$\nu_{\text{sym}}(\text{CO}_2)$	1382	1383	1380
	$p\text{-CH}_3$	Λ_m	<i>f</i>	0.60	0.32
		$\nu_{\text{asym}}(\text{CO}_2)$	1523	1537	1527
		$\nu_{\text{sym}}(\text{CO}_2)$	1372	1392	1373
	$p\text{-CH}_3\text{O}$	Λ_m	<i>f</i>	0.49	0.27
		$\nu_{\text{asym}}(\text{CO}_2)$	1525	1532	1525
		$\nu_{\text{sym}}(\text{CO}_2)$	1376	1386	1377
ox		Λ_m	<0.1	0.36(0.51)	<i>f</i>
acac ^g		Λ_m	<0.1	0.57(0.44)	<i>f</i>
hfacac ^h		Λ_m	<0.1	28.1(57.8)	<i>f</i>
NO_3		Λ_m	<i>f</i>	29.0(58.0)	<i>f</i>

^a Molar conductances ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) at 1.0×10^{-3} ($25 \pm 0.1^\circ\text{C}$). ^b In cm^{-1} at about 2.0 wt%. ^c In cm^{-1} at about 8.0 wt%. ^d Figures in parentheses are obtained in DMSO. ^e Λ_m and ν_{asym} , ν_{sym} values are obtained in the CH_2Cl_2 solution containing about 0.1 mole/l and 8.0 wt% of $(\text{CH}_3)_3\text{PO}$, respectively. ^f Not measured. ^g Acetylacetonato complex (see ref. 9). ^h Hexafluoroacetylacetonato complex.

$J(^{207}\text{Pb}-\text{CH}_3)$ values of $(\text{CH}_3)_2\text{PbX}_2$ ($\text{X} = \text{benzoato}$ [5], oxinato [5,6] and acetylacetonato [9]) in DMSO have been recently reported to be larger by about 25 Hz than those in CH_2Cl_2 or CHCl_3 . On the other hand, the increment of the $J(^{207}\text{Pb}-\text{CH}_3)$ value of dimethylbis(hexafluoroacetylacetonato)lead, $(\text{CH}_3)_2\text{Pb}(\text{hfacac})_2$, in DMSO (148.5 Hz), in which this compound is electrolyte as in $[(\text{CH}_3)_2\text{Pb}(\text{DMSO})_4]^{2+}2\text{X}^-$ ($\text{X} = \text{ClO}_4$ and NO_3) [$J(^{207}\text{Pb}-\text{CH}_3)$: about 149 Hz] [10] (see Table 1), was found to be small relative to the value in CH_2Cl_2 (144.5 Hz). These findings seem to show that the benzoato and oxinato compounds studied in this work do not form ion pairs in the solutions containing strongly donor molecules. Two benzoato ligands are assumed to coordinate to the lead atom as bidentate ligands both in CH_2Cl_2 and HMPA, and also in CH_2Cl_2 solution containing excess $(\text{CH}_3)_3\text{PO}$, since the stretching frequencies of the carboxyl groups in these solvents are almost the same (see Table 1). It seems evident from the above results together with the stoichiometry for the complex formation that seven-coordinate dimethyllead complexes with one donor molecule exist in solution, and they may take a distorted pentagonal bipyramid configuration (I) around the central lead atom.



The stability constants (K), the J_0 and the J_c values for the dimethyllead benzoato and oxinato complexes with some tertiary phosphine oxides, phosphates and HMPA in CH_2Cl_2 are summarized in Table 2. The value of $\Delta\nu(\text{OH})$ in this Table indicate the frequency shifts of the O—H stretching band of phenol by the hydrogen bonding with the donors [11]. The K values of $(\text{CH}_3)_2\text{Pb}(\text{OCCOC}_6\text{H}_4\text{Y})_2 \cdot \text{R}_3\text{PO}$ complexes were found to be larger than those for $(\text{CH}_3)_2\text{Pb}(\text{ox})_2 \cdot \text{R}_3\text{PO}$ complexes. Table 2 also shows that there is a general drift of the K values against the Y for most of the above R_3PO donors.



The decrease of the K values is probably associated with the decrease of the amount of positive charge on the lead atom, because the J_0 values, which have been shown to increase with decreasing positive charge on the lead atom for some dimethyllead compounds [5,6], become larger in this order.

In a series of the benzoato complexes $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2 \cdot \text{R}_3\text{PO}$, the K values increase with an increase in the $\Delta\nu(\text{OH})$ values for the R_3PO donors, which are associated with the electron density on the phosphoryl oxygen. The results are analogous to that in some dimethyllead oxinato complexes [6]. The plots of the values of $\log K$ vs. the $\Delta\nu(\text{OH})$ values, the J_c values and the sum of the Taft's σ^* values of the R groups ($\Sigma\sigma^*$) are shown in Figs. 3 and 4. The correlations between these quantities are expressed by eqns. 5-7, where r is the correlation coefficient. The stability constants, $\log K_{\text{phenol}}$, for the

TABLE 2

STABILITY CONSTANTS (K) AND $J(^{207}\text{Pb}-\text{CH}_3)J_0$ VALUES FOR $(\text{CH}_3)_2\text{PbX}_2 \cdot \text{R}_3\text{PO}$ COMPLEXES IN METHYLENE CHLORIDE AT 24°C^a

R	$\Delta\nu(\text{OH})^b$	X = OCOC ₆ H ₄ Y						X = ox					
		Y = o-CH ₃		Y = m-CH ₃		Y = H		Y = p-CH ₃		Y = p-CH ₃ O		Y = p-CH ₃ O	
		K	J_0	K	J_0	K	J_0	K	J_0	K	J_0	K	J_0
C ₂ H ₅	510	181.9	170.2	145.0	170.3	108.4	171.4	82.0	171.7	77.9	170.6	2.8	182.0
CH ₃	470	421.0	172.0	144.9	170.5	86.8	173.6	164.6	171.6	247.0	171.6	5.3	181.0
n-C ₄ H ₉	488 ^c	114.6	171.5	126.3	173.0	95.2	173.1	82.8	173.3	64.1	171.2	2.2	179.6
(CH ₃) ₂ N	450	137.0	171.8	54.3	171.4	53.4	169.6	55.8	171.2	44.6	171.8	1.0	180.6
C ₆ H ₅	480	39.4	165.7	22.8	164.4	32.3	163.4	21.6	164.4	14.6	164.7	0.5	175.2
C ₂ H ₅ O	345	10.9	157.1	7.6	157.6	8.8	160.7	5.5	161.9	5.1	155.4	e	e
CH ₃ O	315	7.0	157.2	5.9	157.8	6.1	157.4	5.4	158.0	3.3	155.8	e	e
p-CH ₃ C ₆ H ₄ O	245 ^d	2.5	154.0	2.4	150.9	2.3	150.3	1.8	155.6	2.1	148.0	e	e
C ₆ H ₅ O	210	1.6	152.4	1.6	147.1	1.4	146.9	1.3	153.0	0.9	148.5	e	e
		131.0 ± 0.5 ^f		135.8 ± 0.5 ^f		135.9 ± 0.5 ^f		136.4 ± 0.5 ^f		137.2 ± 0.5 ^f		151.0 ± 0.5 ^f	
		(131.3) ^g		(136.2) ^g		(135.5) ^g		(135.9) ^g		(136.9) ^g		(151.7) ^g	

^a Concentration of the lead compound (A_0) is 2.00×10^{-2} (mol/l); K in l/mol and J_0 in Hz. ^b Frequency shift of the O—H stretching vibration of phenol; $\Delta\nu(\text{OH}) = \nu(\text{OH})_{\text{free}} - \nu(\text{OH})_{\text{complex}}$ (cm⁻¹). ^c Obtained in this work. ^d Ref. 6. ^e Could not be obtained because of too small stability constant. ^f Estimated value of J_0 (Hz). ^g Observed value of J_0 (Hz).

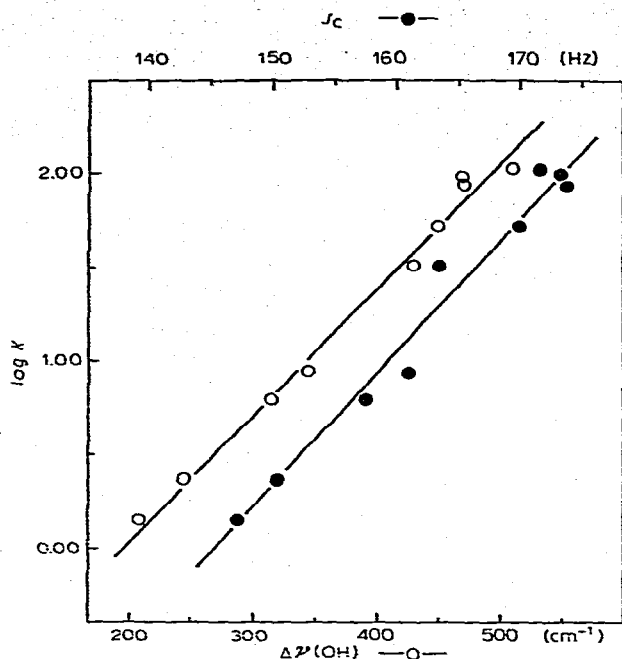


Fig. 3. Plots of $\log K$ vs. $\Delta\nu(\text{OH})$ and J_c for $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2 \cdot \text{R}_3\text{PO}$ complexes.

phenol- R_3PO system [11,12]* were correlated with $\Delta\nu(\text{OH})$ and $\Sigma\sigma^*$ by eqns. 8 and 9.

$$\log K = 6.70(\pm 0.19) \times 10^{-3} \Delta\nu(\text{OH}) - 1.30(\pm 0.08); \quad r = 0.994 \quad (5)$$

$$\log K = -2.71(\pm 0.25) \times 10^{-1} \Sigma\sigma^* + 2.06(\pm 0.09); \quad r = 0.990 \quad (6)$$

$$J_c = 8.97(\pm 0.53) \times 10^{-2} \Delta\nu(\text{OH}) + 128.6(\pm 2.1) (\text{Hz}); \quad r = 0.974 \quad (7)$$

$$\log K_{\text{phenol}} = 6.52(\pm 0.23) \times 10^{-3} \Delta\nu(\text{OH}) + 0.23(\pm 0.08); \quad r = 0.997 \quad (8)$$

$$\log K_{\text{phenol}} = -2.74(\pm 0.15) \times 10^{-1} \Sigma\sigma^* + 3.37(\pm 0.17); \quad r = 0.945 \quad (9)$$

Since the coefficients of $\Delta\nu(\text{OH})$ in eqns. 5 and 8, and those of $\Sigma\sigma^*$ in eqns. 6 and 9 are almost the same, respectively, the electronic effect of the R group on the $\log K$ values is comparable with that on the $\log K_{\text{phenol}}$ values. The major factor which differentiates the $\log K$ values from the $\log K_{\text{phenol}}$ values may be a steric factor. Equation 7 shows that the J_c values increase linearly with an increase in the electron density on the phosphoryl oxygen and the value of its intercept is almost the same as the J_0 value. This finding suggests that the J_c values become larger as the electron density on the lead atom is increased by the coordination of the good donor molecules, as have been reported for the dimethyllead oxinato compounds [6]. The other benzoato compounds were found to behave in a similar manner.

The stability constants with several donor molecules, the J_c values and the $J(^{207}\text{Pb}-\text{CH}_3)$ values obtained when such donor molecules were used as a solvent for $(\text{CH}_3)_2\text{PbX}_2$ ($\text{X} = \text{OCOC}_6\text{H}_5$ and ox) are shown in Table 3. The J_c values

* Regression analysis was made by using the data in ref. 11.

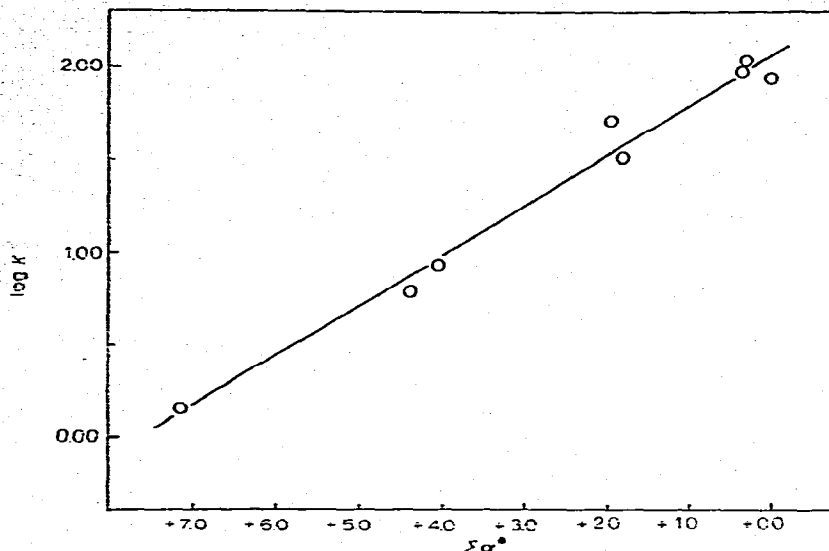


Fig. 4. Plots of $\log K$ vs. $\Sigma\sigma^*$ for $(\text{CH}_3)_2\text{Pb}(\text{OCOC}_6\text{H}_5)_2 \cdot \text{R}_3\text{PO}$ complexes.

TABLE 3

STABILITY CONSTANTS AND J_c VALUES FOR $(\text{CH}_3)_2\text{PbX}_2 \cdot \text{L}$ COMPLEXES AND $J(^{207}\text{Pb}-\text{CH}_3)$ VALUES IN THE DONOR SOLVENTS

Compound		K (l/mol)	J_c (Hz)	J^a (Hz)
X	L			
OCOC ₆ H ₅	$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	53.0	169.6	173.7
	$(\text{CH}_3)_2\text{SO}$	20.4	160.4	159.6
	HCON(CH ₃) ₂	12.5	155.5	156.0
	pyridine	11.5	165.3	165.3
	α -picoline	2.6	153.1	152.3
ox	$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	1.0	180.6	187.2

^a Value obtained in the donor as the solvent (see refs. 5 and 6).

were found to become larger with increasing K values and to be almost identical with the $J(^{207}\text{Pb}-\text{CH}_3)$ values in the donor solvents, except for those in HMPA. From this table, we consider that one of major factors affecting the change of the $J(^{207}\text{Pb}-\text{CH}_3)$ values with the solvent donor strength is the amount of positive charge on the lead atom, which is produced mainly by the formation of seven-coordinate dimethyllead complexes with the solvent molecules, as reported previously [5,6]. The larger $J(^{207}\text{Pb}-\text{CH}_3)$ values in HMPA, compared with the J_c values, may be due to the formations of some 1/2 complexes in addition to 1/1 complexes of the dimethyllead benzoato and oxinato compounds with HMPA, as discussed from the results for the application of the Job's method.

Acknowledgement

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