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The Preparation of a Seven-Coordinate Dimethyllead(IV) Complex, $(CH_3)_2Pb(gbha)(H_2O)$, and Ionic Dissociation of the Coordinated Water

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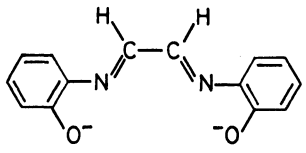
Synopsis. A seven-coordinate dimethyllead(IV) complex, $(CH_3)_2Pb(gbha)(H_2O)$, was prepared. From spectroscopic studies the water molecule in the complex was found to coordinate rather strongly to the lead atom as the seventh ligand. An interesting feature of the complex is that the dissociation of a proton from the coordinated water occurs in such coordinating solvents as DMSO and HMPA.

Although there are a great number of four- and six-coordinate dimethyllead(IV) complexes, seven-coordinate ones have not been reported. In a previous paper,[1] we reported on the interaction between a six-coordinate dimethyllead(IV) complex of *N,N'*-ethylenebis(salicylideneaminato); (saln), $(CH_3)_2Pb(saln)\cdot CH_3OH$, and donor-solvent molecules in solution. The formation of a seven-coordinate complex was assumed in the above experiments on the basis of the following data: 1) the $\delta(Pb-CH_3)$ value shifts to a higher magnetic field and 2) both the $^2J(^{207}Pb-CH_3)$ and $^3J(^{207}Pb-N=CH)$ values increase with an increase in the donor strength of the solvents. Similar observations have been reported for dimethyllead(IV) complexes of 8-qunolinolato,[2] β-diketonato,[3] and benzoato.[4]

We wish to report here on the first successful isolation of a seven-coordinate dimethyllead(IV) complex of bis(2-metidineaminophenolato); (gbha), $(CH_3)_2Pb(gbha)(H_2O)$; (**A**), and on the dissociation of a proton from the water molecule coordinated to the lead atom in such solvents as DMSO and HMPA.



gbha

Experimental

Preparation of $(CH_3)_2Pb(gbha)(H_2O)$. Dimethyllead dichloride was prepared by the chlorination of tetramethyllead in ethyl acetate at about −10 °C.[5] The *N,N'*-di(2'-hydroxyphenyl)-1,2-ethanediimine, H_2gbha, was prepared by a method reported previously.[6] $(CH_3)_2Pb(gbha)(H_2O)$[7] was prepared by the reaction of dimethyllead dichloride (2.5 g, 10 mmol) and Na_2gbha (Na; 0.5 g, 20 mmol and H_2gbha; 2.4 g, 10 mmol in 20 dm of methanol) in about 20 dm of methanol. The precipitates were recrystallized from a CH_2Cl_2/hexane (large excess) mixture. The complex was obtained as a black crystalline solid in a 78% yield and did not melt below 300 °C. Found: C, 38.68; H, 3.38; N, 5.77; Pb, 41.89%. Calcd for $C_{16}H_{18}N_2O_3Pb$: C, 38.94; H, 3.68; N, 5.68; Pb, 41.98%.

Measurements. The molar weight of the complex in $CHCl_3$ (0.72 wt%), established using a Mechrolab vapor-pressure osmometer at 25 °C, was found to be 514 (calcd 493). The molar conductances were measured by means of a Yokogawa F-255A Universal Bridge and a cell (cell constant; 0.377 cm^{-1}). The specific conductances of the solvents used, CH_2Cl_2, $(CH_3O)_3PO$, pyridine, DMSO, and HMPA, are $<10^{-7}$, 9.5×10^{-7}, 8.9×10^{-7}, 4.2×10^{-7}, and 4.8×10^{-7} Ω^{-1} cm^{-1} respectively.

The IR and ^1H NMR spectra of about a 4 wt% solution were recorded with a Hitachi EPI-2G Spectrophotometer and a JEOL-PS-100 Spectrometer operating at 100 MHz respectively. The chemical shifts were measured relative to TMS as an internal standard.

Results and Discussion

The ^1H NMR and IR spectral data and the molar conductance of the (**A**) complex in several solvents are summarized in Table 1. The $^3J(^{207}Pb-N=CH)$ value of the complex was observed in all the solvents. The stretching frequencies of the C–N double bond of the complex in CH_2Cl_2 (1712 cm^{-1}) and HMPA (1695 cm^{-1}) are almost the same and are different from that of free gbha (1640 cm^{-1} in Na_2gbha[8]). Therefore, gbha in the complex may be supposed to coordinate to the lead atom as an ONNO quadridentate ligand in all the solvents, according to the similar discussion of $(CH_3)_2Pb(saln)\cdot CH_3OH$.[1] The $^2J(^{207}Pb-CH_3)$ and

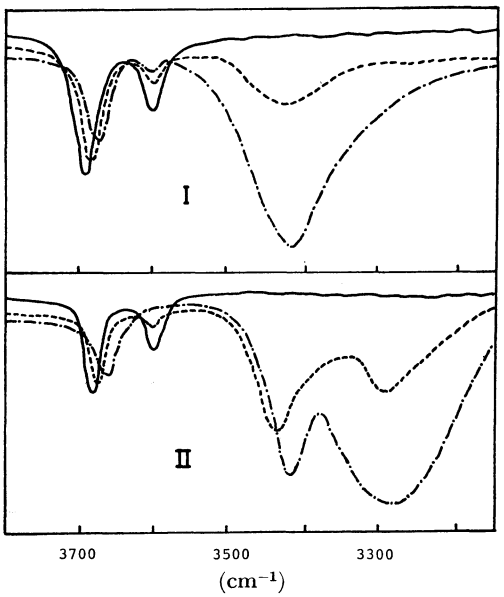


Fig. 1. IR spectra of free water molecule (I) and the gbha complex (II) in CH_2Cl_2–DMSO solutions (4 wt%). The concentration of DMSO added is 0(——), 0.8(– – –), and 7.8 wt%(-·-·-).

Table 1. The ^1H NMR and IR data and the molar conductance of $(CH_3)_2Pb(gbha)(H_2O)$ in several solvents

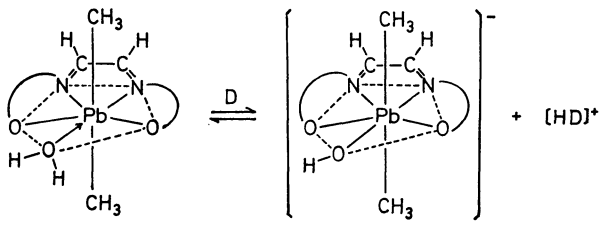
Solvent	δ(Pb–CH_3) (ppm)	δ(Pb–N=CH) (ppm)	$^2J(^{207}Pb–CH_3)$ (Hz)	$^3J(^{207}Pb–N=CH)$ (Hz)	ν(OH) (cm^{-1})	Λ_m[a] (Ω^{-1} cm^2 mol^{-1})
$CDCl_3$	1.96	8.65	176.4	37.8	—[b]	—[b]
CH_2Cl_2	1.94	8.67	178.9	37.9	3680 3600	0.1
$(CH_3O)_3PO$	1.75	8.68	177.6	36.8	3407 3270	10.0
Pyridine	1.85	8.66	180.5	38.4	3400[c] 3275	11.0
DMSO	1.68	8.84	179.0	38.0	3418 3280	15.2
HMPA	1.69	8.64	179.5	36.6	3425 3240	2.5

a) At 10^{-3} mol dm^{-3} (25±0.1 °C). b) Not measured. c) This peak may come from  .

$^3J(^{207}Pb–N=CH)$ values in $CDCl_3$ are much larger than those of $(CH_3)_2Pb(saln)\cdot CH_3OH$ with the six-coordinate structure ($^2J(^{207}Pb–CH_3)=157.8$ Hz and $^3J(^{207}Pb–N=CH)=23.4$ Hz in $CDCl_3$) and do not change even in such highly coordinating solvents as DMSO and HMPA. The $^2J(^{207}Pb–CH_3)$ value of $(CH_3)_2$-(gbha)Pb(H_2O) is similar to that of $(CH_3)_2Pb(saln)\cdot CH_3OH$ in DMSO. The above results suggest that the water molecule coordinates, as the seventh ligand, to the lead atom rather strongly in the (**A**) complex.

The IR spectrum of the (**A**) complex in CH_2Cl_2 showed two peaks, at 3680 and 3600 cm^{-1}, assigned to the O–H antisymmetric and symmetric stretching vibrations respectively. Figure 1 shows the IR spectra for free water (I) and the gbha complex (II) in CH_2Cl_2–DMSO solutions of the O–H stretching vibrational region. The frequencies and shapes of the O–H bands change continuously with the concentration of DMSO added. The changing features of the spectra for (I) and (II) are quite different and suggest that the water molecule in the complex is not free.

The molar conductance shows that the complex is an electrolyte in the coordinating solvents, but not in CH_2Cl_2 (Table 1). On the other hand, the free water does not show any electric conductivity even in DMSO and HMPA. Therefore, the appearance of the conductances in the complex suggests the presence of an ionic species, $[(CH_3)_2Pb(gbha)(OH)]^-$; (**B**), in the coordinating solvents. The values of the conductances are smaller than those for usual 1:1 electrolytes (for example, 25—40 Ω^{-1} cm^2 mol^{-1} for 1:1 electrolytes in DMSO at a concentration of *ca.* 10^{-3} mol dm^{-3} [9]). Consequently, the following equilibrium may occur in coordinating solvents, in which the dissociation of a proton takes place instead of the replacement of the coordinated water molecule by a solvent molecule. The existence of the anionic hydroxo complex (**B**) and the protonated solvent molecule ($[HD]^+$) is substantiated by the appearance of two peaks (at *ca.* 3270 and *ca.* 3400 cm^{-1}) in the IR spectra of the complex in coordinating solvents.



(**A**) (**B**)

D=HMPA, DMSO, pyridine, $(CH_3O)_3PO$.

In the conclusion, $(CH_3)_2Pb(gbha)(H_2O)$ may be supposed to take the seven-coordinate structure (**A**), with the water molecule coordinating to the lead atom rather strongly in non-coordinating solvents. On the other hand, in coordinating solvents, a partial dissociation of a proton from the coordinated water occurs, resulting in an equilibrium between **A** and the ionic species **B** and $[HD]^+$.

References

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