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PREPARATION AND PROPERTIES OF SEVEN-COORDINATE DIMETHYLTIN(IV) AND DIMETHYLLEAD(IV) COMPLEXES: $(CH_3)_2M(pan)(acac)$ (M = Sn, Pb)

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Seven-coordinate dimethyltin(IV) and dimethyllead(IV) complexes, $(CH_3)_2M(pan)(acac)$ (M = Sn, Pb), were prepared. In these complexes the acetylacetonato ligand was found to become less labile as compared with that of six-coordinate complexes, $(CH_3)_2M(acac)_2$ (M = Sn, Pb).

Previously we have reported[1 - 3] that several six-coordinate dimethyllead(IV) complexes accept one donor molecule in solution and form seven-coordinate dimethyllead(IV) complexes. The isolated seven-coordinate dimethyllead(IV) complexes, however, are very limited.[4] In diorganotin(IV) compounds the seven-coordinate complexes are also few.[5] The present work reports the preparation and properties of seven-coordinate dimethyltin(IV) and dimethyllead(IV) complexes with a tridentate 1-(2-pyridilazo)-2-naphtholato ligand (pan) and a bidentate acetylacetonato ligand (acac), $(CH_3)_2M(pan)(acac)$ (M = Sn (**1a**) and Pb (**1b**)).

Equimolar amounts of $(CH_3)_2Sn(acac)_2$ (**2a**), prepared as described previously,[6] and Hpan were dissolved in methanol at room temperature. Red crystals of **1a** were obtained almost quantitatively by spontaneous evaporation of the solvent, m.p.

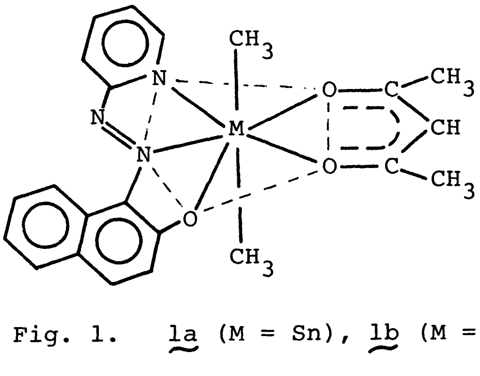
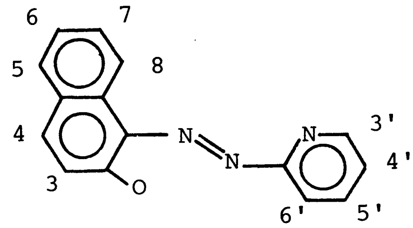


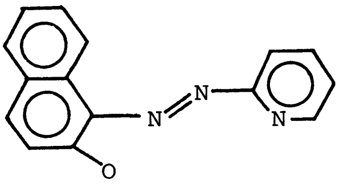
Fig. 1. **1a** (M = Sn), **1b** (M = Pb)

192 - 193°C. Found: C, 53.10; H, 4.69; N, 8.62%. Calcd for $C_{22}H_{23}N_3O_3Sn$: C, 53.26; H, 4.67; N, 8.47%. 1b was prepared by the same method from $(CH_3)_2Pb(acac)_2$ (2b)[6] and Hpan in methanol, m.p. 145°C. Found: C, 45.28; H, 4.12; N, 7.23%. Calcd for $C_{22}H_{23}N_3O_3Pb$: C, 45.20; H, 3.98; N, 7.19%.

The IR spectra of 1a and 1b in Nujol mulls showed the C=O stretching bands of the acetylacetonato ligand at 1590 and 1584 cm^{-1} respectively. Although the wave numbers of these bands are somewhat larger than those of the corresponding bisacetylacetonato complexes, 1566, 1559 cm^{-1} for 2a and 1575 cm^{-1} for 2b,[7] the values of 1a and 1b are smaller than that of the unidentate acetylacetonato ligand (1678 cm^{-1}) occurred in $(CH_3)_3Si(acac)$[8] and do not exceed the " chelate carbonyl " region.[9 - 11] Therefore, the acetylacetonato ligand of 1a and 1b is considered to act as a bidentate ligand. In visible spectra measured in CH_2Cl_2, absorption maxima of the longest wave length of 1a and 1b appeared at 536 nm($\varepsilon = 1.3 \times 10^4$) and 546 nm($\varepsilon = 2.4 \times 10^4$) respectively. The wave lengths of these bands are much longer than that of the free ligand (466 nm, $\varepsilon = 1.8 \times 10^4$)[12] with a conformation (I) and are close to that of $Cu(pan)^+$ (550 nm),[13] in which pan acts as a tridentate ligand with a conformation (II).[14] These IR and visible spectral reaults suggest that both 1a and 1b take a seven-coordinate configuration as shown in Fig. 1.



I



II

In the PMR spectrum of 1b in $CDCl_3$, the methyl groups attached to the lead atom gave a signal at $\delta = 1.81$ and the $^2J(^{207}Pb\text{-}CH_3)$ value was found to be 177.3 Hz. The J value is appreciably larger than that of 2b in $CDCl_3$ (154.7 Hz) and is rather close to that of 2b in HMPA (182.7 Hz).[15] In HMPA 2b has been assumed to have a seven-coordinate configuration with a linear $CH_3\text{-}Pb\text{-}CH_3$ skeleton. The large J value of 1b, therefore, is in agreement with the assumption that 1b has the configuration shown in Fig. 1. The $^2J(^{119}Sn\text{-}CH_3)$ value of 1a in $CDCl_3$ (115.8 Hz, $\delta(Sn\text{-}CH_3) = 0.52$) was found to be somewhat larger than that of 2a (99.3 Hz ($CDCl_3$)[16] or 98.4 Hz (HMPA)[15]) in which the trans configuration of the $CH_3\text{-}Sn\text{-}CH_3$ moiety was assumed.6,16) The CH_3-Sn-CH_3 moiety of **1a**, therefore, may also take the trans configuration (Fig.1). Although two methyl groups of the acetylacetonato ligand were found to give different chemical shifts for **1a** (δ= 2.04 and 2.11), only one methyl signal was observed for **1b** (δ= 2.04). The coordination of two oxygen atoms of the acetylacetonato ligand may be more unsymmetrical in **1a** as compared with **1b**. This explanation is not inconsistent with the fact that **1a** showed higher C=O stretching frequency than **1b**. One notable result in the PMR spectrum of **1b** is that long range spin-spin couplings with the lead nucleus were observed for the methyl and methine protons of the acetylacetonato ligand: $^4J(^{207}Pb\text{-}O\text{-}C\text{-}CH_3) = 4.5$ Hz and $^4J(^{207}Pb\text{-}O\text{-}C{=}CH) = 6.8$ Hz. These couplings have not been obtained in **1a**, **2a**16) and **2b**.15) H_8 and H_3 of the naphthol ring and H_6' of the pyridine ring (numbering of the protons is shown in **I**) gave resonance lines at δ= 9.75, 7.10 and 9.20 for **1a** and 10.00, 7.07, and 9.19 for **1b** respectively, whereas the free ligand exhibited the corresponding signals at $\delta = < 8.4$, 6.64, and < 8.4 respectively. The remarkable down field shift of H_8 upon complex formation of pan is due to conformational change from **I** to **II**. In **II** the close proximity of H_8 to the nitrogen atom attached to the pyridine ring (2.31 Å) was reported for Cu(pan)Cl from the X-ray crystallographic analysis.17) This value is less than the sum of van der Waals radius of each atom (~2.7 Å). The down field shifts of H_3 and H_6' may be explained by the coordination of naphthol oxygen and pyridine nitrogen respectively to the lead atom.

The PMR spectra of **1a** and **1b** were not changed by addition of Hacac, although each of the acetylacetonato methyl and methine proton signal has been reported to

$$(CH_3)_2M(acac)_2 \quad + \quad Hacac^* \xrightleftharpoons{\text{fast}} (CH_3)_2M(acac)(acac^*) \quad + \quad Hacac$$

$$(CH_3)_2M(pan)(acac) \quad + \quad Hacac^* \xrightleftharpoons{\text{slow}} (CH_3)_2M(pan)(acac^*) \quad + \quad Hacac$$

coalesce to a single line in a mixture of **2a** and Hacac as a result of rapid exchange of the acetylacetonato ligand at the room temperature.18) In **2b** and Hacac system similar coalescence was also observed. These results suggest that in the seven-coordinate complexes, **1a** and **1b**, the acetylacetonato ligand becomes less labile than that of six-coordinate complexes, **2a** and **2b**.

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