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# Tin(IV) Complexes with 2-Methoxy-2'-Hydroxy Chalkones

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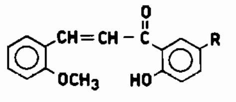
*Tin(IV) complexes with 2-methoxy-2'-hydroxy-5'-methyl and 2-methoxy-2'-hydroxy-5'-chloro chalkones have been prepared in benzene medium. The elemental analyses indicate $Sn\cdot L\cdot Cl_3$ stoichiometry (where LH is the ligand). They appear to be non-electrolytes in DMF. They are insoluble in most of the common organic solvents indiating the extended polymeric chain structure. The infrared spectral studies in the region 4000–200 $cm^{-1}$ suggest that tin(IV) has coordination number six in these complexes.*

## Introduction

In the previous paper we have reported the magnetic and spectral properties of a few nickel(II) complexes with 2,2'-dihydroxy chalkones [1]. Now we have extended this study to the synthesis and spectral properties of Tin(IV) [2] and titanium(IV) complexes [3].

In this present communication we report the synthesis and i.r. spectral study of tin(IV) complexes with 2-methoxy-2'-hydroxy-5'-methyl and 2-methoxy-2'-hydroxy-5'-chloro chalkones.



| | R |
|---|---|
| I | $CH_3$ |
| II | Cl |

## Experimental

### Materials and Methods

Chalkones I and II were prepared by the known method [1] using 2-OH-5-Me-acetophenone, 2-OH-5-Cl-acetophenone and 2-methoxybenzaldehyde.

### Preparation of Complexes

Anhydrous tin(IV) chloride was of Riedel make and used as such for the complexation.

Commercial grade benzene was purified by repeated distillation and stored over sodium metal.

Tin(IV) chloride (0.01 mol) was treated with 0.012 mol of chalkone in benzene medium with vigorous shaking. The reaction mixture was refluxed in an oil bath till the evolution of HCl gas ceased. The complex which a separated out was filtered, washed with little benzene, then with n-hexane and dried under vacuum.

The dry complex was powdered and extracted in a Soxlet thimble to remove excess of the reagent with n-hexane. The complex was then dried under vacuum.

The complexes were analysed for their metal and chloride contents.

| Lig. | | |
|---|---|---|
| I–$(C_{16}H_{12}O_3)SnCl_3$* | 23.74% Sn,<br>(24.16) | 21.5% Cl<br>(21.68) |
| II–$(C_{16}H_{11}ClO_3)SnCl_3$ | 22.90% Sn,<br>(23.20) | 20.45% Cl<br>(20.82) |

### Physical Measurements

The molar conductivities of the complexes in DMF were measured on an ELICO CM-82 conductivity bridge having a cell of cell constant 0.829 $cm^{-1}$ at the concentration $10^{-3}$ *M*.

The infrared spectra of the complexes in nujol mull were recorded on a Perkin–Elmer 220 instrument in the region 4000–200 $cm^{-1}$.

## Results and Discussion

These two complexes are brownish red in colour and not soluble in common organic solvents. However, they are soluble to a limited extent in DMF. This insolubility of the complexes in common organic solvents has prevented a determination of molecular weights. The elemental analysis is in favour of the $Sn\cdot L\cdot Cl_3$ (where LH is the ligand) formulation.

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*The values in parenthesis are the calculated values.

TABLE I. Infrared Frequencies (in cm$^{-1}$) of Chalkones and Their Tin(IV) Complexes.$^{a}$

| S. No. | Assignments | | | | |
|---|---|---|---|---|---|
| 1 | Aromatic CH and =CH stretching vibration | 2900 | 2940 | 2900 | 2940 |
| | | | | | 2840 |
| 2 | Intramolecular H-bonded OH stretching vibration | 2667br, w | – | 2650br, w | – |
| 3 | C=O stretching vibration | 1650s | 1630s | 1650s | 1635s |
| 4 | HC=CH stretching vibration | 1600m | 1605s | 1587s | 1610s |
| 5 | Aromatic C=C stretching vibration | – | 1580s | – | 1595s |
| | | | 1550s | 1558sh | 1570br, s |
| | | 1525w | 1540s | 1546m | 1540m |
| | | 1470s | 1500s | 1520m | – |
| 6 | Phenolic C–O stretching vibration | 1287s | 1300m | 1287s | 1360s |
| 7 | Sn–O stretching vibration | – | 495s | – | 485w |
| | | | 460m | | – |
| | | | 440w | | 440m |
| 8 | Sn–Cl stretching vibration | – | 330s | – | 340br, s |
| | | | 320sh | | – |

$^{a}$s = strong; m = medium; w = weak; br = broad; sh = shoulder.

The molar conductance values determined at the concentration ~10$^{-3}$ *M* in DMF are too low to account for any dissociation of the complexes in that solvent. Hence these can be looked upon as non-electrolytes.

The infrared frequencies of the ligands (I and II) and the complexes (III and IV) are listed in Table I along with their assignments.

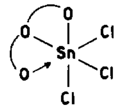
The broad weak band in the region 2667–2650 cm$^{-1}$ due to intramolecular H-bonded OH [6] vanishes in the complexes, indicating the involvement of the OH group in the bond formation.

The phenolic C–O stretching vibration at 1287 cm$^{-1}$ moves to higher frequency (Table I) supporting the above conclusion. The C=O stretching of the ligands at 1650 cm$^{-1}$ is observed in the region 1635–1630 cm$^{-1}$. This indicates the formation of coordination bond between metal ion and C=O through oxygen. The band of medium to high intensity appearing in the region 1600–1587 cm$^{-1}$ is assigned to the HC=CH stretching vibration in view of the previous assignments [7–9].

The bands of medium to strong intensity observed in the region 495–440 cm$^{-1}$ are assigned to the $\nu$(Sn–O) vibrations in view of the previous assignments [10–18].

The previous studies have established that the $\nu$(M–X) vibrations are quite sensitive to the oxidation state and coordination number of the central metal ion [19–23]. Fay and Pinnavaia [15] have assigned $\nu$(Zr–Cl) and $\nu$(Hf–Cl) bands in the region 361–273 cm$^{-1}$ for Zr(IV) and Hf(IV) acetylacetonates. Recently, Jones and Fay [22] and Ohkaku and Nakamoto [23] have assigned a strong band in the vicinity of 340 cm$^{-1}$ to the $\nu$(Sn–Cl) in tin(IV) acetylacetonates and adducts respectively. In view of these assignments a strong band in the region 330–340 cm$^{-1}$ has been assigned to the $\nu$(Sn–Cl) vibration.

The analytical results, conductance values and spectral evidence make us to suggest the following structure for these complexes, in which tin(IV) exhibits coordination number six:



The construction of the models for these complexes suggests that the attachment of the ligand to the single metal ion is sterically not favoured. These observations and the insolubility of the complexes in the common organic solvents makes us to suggest a polymeric extended chain structure rather than a monomeric one, in which tin(IV) displays the same coordination number.

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