

Structural Aspects of some Tin(II) and Tin(IV) Complexes with some Thiocarbohydrazones

(MISS) PRAJNA KUMARI and L. K. MISHRA*

Department of Chemistry, Patna University, Patna-800 005

Manuscript received 3 December 1991, revised 17 December 1993, accepted 13 January 1994

Coordination complexes of Sn^{II} and Sn^{IV} adopt a wide variety of geometry^{1,2} and a number of organotin as well as Sn^{II} complexes of sulphur, oxygen and nitrogen donor Schiff bases are potent antifungal and antibacterial substances^{2,3}. We report here the preparation and characterisation of the complexes of Sn^{II} and Sn^{IV} with dibenzaldehyde thiocarbohydrazone (dibenzthchH), diacetophenonethiocarbohydrazone (diacettchH), dicyclohexanonethiocarbohydrazone (dicycltchH), disalicylaldehyde thiocarbohydrazone (disaltchH₃), dicinnamaldehyde thiocarbohydrazone (dicintchH) and di-*o*-hydroxyacetophenonethiocarbohydrazone (dihacettchH₃) of general formula $[\text{Sn}(\text{LH})_2\text{Cl}_2]$ (LH = dibenzthchH, diacettchH, dicintchH and dicycltchH), $[\text{Sn}(\text{L}'\text{H}_2)_2]$ (L'H₃ = disaltchH₃ and di-hacettchH₃), $[\text{SnL}_2\text{I}_2]$ (LH = dibenzthchH, diacettchH, dicycltchH or dicintchH) and $[\text{SnL}'\text{I}]$ (L'H₃ = dibenzthchH₃ or di-*o*-hacettchH₃).

Results and Discussion

The complexes of both Sn^{II} and Sn^{IV} are slightly soluble in methanol but dissolve appreciably in DMF and dioxan. They are stable in air and decompose gradually on heating above 130–50°. Very low conductance values (4–9 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) in DMF solution indicate their non-electrolytic nature.

The electronic absorption spectrum of dibenzthchH displays strong bands at 225 (ϵ_{max} 11 244) and 315 nm (24 340) assignable to $\delta-\delta^*$ and $\pi-\pi^*$ transitions. In the complexes these bands are shifted to higher wavelength near 235 and 335 nm. The bands of dicycltchH at 205 (ϵ_{max} 6 310) and 250 nm (10 466) attributed for $\delta-\delta^*$ and $\pi-\pi^*$ transitions, are also affected and observed near 215 and 270 nm in the complexes. The diiodo complex $\text{Sn}(\text{dicycltch})_2\text{I}_2$ displays a new band at 390 nm attributable to charge transfer transition from iodine to metal. Di(*o*-hydroxyacetophenone)-

thiocarbohydrazone displays bands at 250 (ϵ_{max} 12 335), 288 (9 935) and 325 nm (7 850) assignable to $\delta-\delta^*$, $n-\pi^*$ and $\pi-\pi^*$ transitions, and these are observed near 255, 305 and 335 nm respectively, in the complexes. The band at 390 nm in the iodo complexes is attributed to charge transfer band. DisaltchH₃ displays bands at 210 (ϵ_{max} 18 290), 250 (21 840), 290 (13 920) and 325 nm (9 632) attributable to $\delta-\delta^*$, $n-\pi^*$ and $\pi-\pi^*$ transitions respectively. The complexes of disaltchH₃ display these bands at higher wavelength located near 215, 260 and 320(br) nm. In case of the iodo complex $[\text{Sn}(\text{disaltch})\text{I}]$, the extra band at 390 nm is attributed to charge transfer transition. The shift of the bands of the ligands in their complexes suggests the bonding of ligands to metal atom.

The ir spectra of ligands and complexes show phenyl ring skeletal vibrations at 1 650–1 050 cm^{-1} . Di(ortho-hydroxyphenyl)thiocarbohydrazone (disaltchH₃) displays ν_{OH} vibration at 3 320 cm^{-1} which disappears in its Sn^{IV} complex $[\text{SnL}\text{I}]$ (LH₃ = disaltchH₃) indicating the deprotonation of phenolic OH in its complexes. The ν_{OH} of the ligand (1 368 cm^{-1}) disappears in the spectrum of the complex supporting the deprotonation of phenolic OH. In the Sn^{II} complex $[\text{Sn}(\text{disaltchH}_2)_2]$, ν_{OH} is observed as weak broad band at 2 950–3 300 cm^{-1} indicating that at least one of the phenolic OH of the ligand is retained in its Sn^{II} complex which is involved in hydrogen bonding. The $\nu_{\text{C}=\text{O}}$ band of the ligand (1 150 cm^{-1}) is raised to higher energy (1 270–1 290 cm^{-1}) on complexation supporting coordination of phenolic oxygen. The thioamide bands I, II, III (1 255–1 535 cm^{-1}) are shifted to higher frequencies while thioamide band IV (970 cm^{-1}) is shifted to lower frequencies, indicating the involvement of thioamide group in bond formation⁴. The $\nu_{\text{C}=\text{N}}$ band of azomethine group (1 590 cm^{-1}) is shifted to higher frequency, indicating the coordination through nitro-

group of the azomethine group.

The IR spectrum of di(*o*-hydroxyacetophenone)-thiocarbohydrazone displays ν_{OH} vibration at $3\,340\text{ cm}^{-1}$ which disappears in its Sn^{IV} complex, suggesting the deprotonation of phenolic OH and coordination of ligand through oxygen atom of phenolic OH group. The $\nu_{\text{C-N}}$ stretch ($1\,590\text{ cm}^{-1}$) is shifted to higher frequency in almost all the complexes suggesting that the second bonding site of the ligand is azomethine nitrogen. The ligand and its complexes display a number of similar bands in finger-print region. In the Sn^{II} and Sn^{IV} complexes the thioamide bands I, II and III are shifted

to higher frequencies while thioamide band IV shifts to lower frequency by $40\text{--}20\text{ cm}^{-1}$ in the complexes. In case of Sn^{IV} complex $[\text{Sn}(\text{diohacettch})\text{I}]$ a large shift in thioamide band IV (by 210 cm^{-1}) indicates that the thioamide sulphur is bonded to metal atom^{4,5} by deprotonation of thiol SH of the ligand also. In far-infrared region, the ligand and its complexes display four to five bands whose positions are not very different.

Dicyclohexanonethiocarbohydrazone displays NH and CH_2 stretching vibrations as strong bands at $3\,260$, $3\,170$, $3\,130$, $2\,920$ and $2\,838\text{ cm}^{-1}$. In the complexes, the NH vibrations are observed with reduced intensity with slight change in wavenumber. The complex $[\text{Sn}(\text{dicycltchH})_2\text{Cl}_2]$ displays thioamide band IV at 940 cm^{-1} but band IV suffers a major change in Sn^{IV} complex $[\text{SnL}_2\text{I}_2]$ and it is observed around 720 cm^{-1} . The thioamide bands I, II and III are shifted to higher frequencies in all the complexes suggesting the coordination of thioamide group in all the complexes.

In dibenzaldehyde thiocarbohydrazone, the aldimine (CH=N) group CH stretch is observed at $2\,970\text{ cm}^{-1}$. In the Sn^{II} and Sn^{IV} complexes, the $\nu_{\text{C-H}}$ band is not affected while in the inner neutral chelates SnL_2I_2 ($\text{LH} = \text{dibenztchH}$), NH stretches are affected appreciably. The $\nu_{\text{C=N}}$ band of the free ligand ($1\,580\text{ cm}^{-1}$) is shifted to higher frequency in the complexes, suggesting the involvement of C=N nitrogen in bond formation. In far-infrared region, the ligand displays prominent bands at 500 , 430 , 410 , 330 , 300 and 250 cm^{-1} . The complexes display four or five broad bands but these are not well resolved indicating that ligand band couples with (M-L) bands giving broad bands. The thioamide band IV of the ligand is not affected appreciably in the Sn^{II} complexes indicating that the ligand has coordinated in thione form. In the Sn^{IV} complexes, the thioamide band IV is shifted to lower frequency (710 cm^{-1}) while the thioamide bands I, II, III are shifted to higher frequencies, indicating the coordination of ligand to metal atom. A major shift of thioamide band IV supports the deprotonation of ligand in thiol form. The bonding site of the ligand is C=N nitrogen and thioamide sulphur. The $\nu_{\text{C=N}}$ is broad and in some cases resolved into two bands indicating that both the azomethine nitrogens are not involved in bonding. In the complexes, the far-infrared bands are observed with

TABLE I - ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compd./ (Colour)	Analysis % : Found/(Calcd.)		
	M	N	Cl/I
$[\text{Sn}(\text{dibenztch})_2\text{I}_2]$ (Yellow)	12.41 (12.66)	11.69 11.95	26.91 27.08
$[\text{Sn}(\text{diacettch})_2\text{I}_2]$ (Yellow)	11.69 (11.94)	11.11 11.28	25.41 25.55
$[\text{Sn}(\text{acettch})_2\text{I}_2]$ (Cream)	14.86 (15.04)	13.98 14.20	32.01 32.16
$[\text{Sn}(\text{dicycltch})_2\text{I}_2]$ (Brown)	12.81 (13.11)	12.12 12.37	27.96 28.03
$[\text{Sn}(\text{cintch})_2\text{I}_2]$ (Brown)	14.26 (14.59)	13.61 13.78	31.01 31.21
$[\text{Sn}(\text{disaltch})\text{I}]$ (Dark yellow)	20.91 (21.19)	9.91 10.00	22.61 22.66
$[\text{Sn}(\text{diohacettch})\text{I}]$ (Yellow)	19.82 (20.18)	9.32 9.52	20.96 21.58
$[\text{Sn}(\text{diacettchH})_2\text{Cl}_2]$ (Cream)	14.51 (14.64)	13.67 13.82	8.56 8.74
$[\text{Sn}(\text{acettchH})_2\text{Cl}_2]$ (Cream)	19.36 (19.54)	18.41 18.45	11.01 11.67
$[\text{Sn}(\text{dicycltchH})_2\text{Cl}_2]$ (Pale yellow)	16.31 (16.42)	16.12 15.51	9.81 9.81
$[\text{Sn}(\text{cintchH})_2\text{Cl}_2]$ (Yellow)	18.56 (18.83)	17.61 17.78	11.01 11.25
$[\text{Sn}(\text{disaltchH}_2)_2]$ (Bright yellow)	15.61 (15.88)	15.21 14.99	-
$[\text{Sn}(\text{diohacettchH}_2)_2]$ (Light brown)	14.52 (14.77)	13.81 13.94	
$[\text{Sn}(\text{dibenztchH})_2\text{Cl}_2]$ (Light yellow)	15.31 (15.73)	14.61 14.85	9.21 9.39

reduced intensity but the (M-N) or (M-S) stretches could not be distinguished due to a number of ligand vibrations. In case of the Sn^{II} complexes with (dihacettch H_3) and (disaltch H_3) complexes $[\text{Sn}(\text{L}'\text{H}_2)_2]$ ($\text{L}'\text{H}_3 = \text{disaltchH}_3$ or dihacettchH_3), a broad and medium band at 2 950–3 300 cm^{-1} indicates that at least one of phenolic OH is retained in complexes. The ν_{OH} band of these ligands does not vanish at 1 370–1 390 cm^{-1} , supporting the presence of at least one uncoordinated phenolic OH. The ir data indicate that these ligands are acting as monoanionic tridentate (O-N-S) donor molecules with Sn^{II} . In Sn^{IV} complexes $[\text{SnL}'\text{I}]$ ($\text{L}'\text{H}_3 = \text{disaltchH}_3$ or dihacettchH_3), ν_{OH} and δ_{OH} vibrations disappear completely. Thus with Sn^{IV} these ligands are bonded as quinquedentate trianionic ligands in $[\text{SnL}'\text{I}]$ ($\text{L}'\text{H}_3 = \text{disaltchH}_3$ or dihacettchH). The bonding pattern of these ligands suggests distorted octahedral structure for the Sn^{II} and Sn^{IV} complexes.

Experimental

The ligands were prepared by condensing thiocarbohydrazide with appropriate aldehydes and ketones in methanolic acetic acid solution⁶.

$[\text{Sn}(\text{LH})_2\text{Cl}_2]$ ($\text{LH} = \text{dibenzthH}$, dicyclthH , diacettchH or dicintchH) and $[\text{Sn}(\text{L}'\text{H}_2)_2]$ ($\text{L}'\text{H}_3 = \text{disaltchH}_3$ or dihacettchH_3): A mixture of stannous chloride (0.005 mol) dissolved in dry methanol (50 ml) and the ligand (0.01 mol) dissolved in hot methanol (or 1:1 methanol-DMF) (40 ml) was refluxed for 30 min when the bis-ligated complexes separated out. The complexes in some cases were highly soluble and that required concentration and cooling of the refluxate to a small volume to yield the products. The products were washed with methanol and dried over CaCl_2 .

$[\text{SnL}_2\text{I}_2]$ ($\text{LH} = \text{dibenzthH}$, diacettchH , dicintchH or dicyclthH): A mixture of dry methanolic solutions of stannic iodide (0.005 mol), ligand (0.01 mol) and a few drops of dry morpholine was refluxed for 30 min and then concentrated to a small volume when a yellow orange product separated out gradually. The complexes were washed with cold methanol and dried in a desiccator over CaCl_2 .

$[\text{SnL}'\text{I}]$ ($\text{L}'\text{H}_3 = \text{disaltchH}_3$ or dihacettchH_3): The monoiodo complexes were prepared by refluxing SnI_4 (0.01 mol) with the ligand (0.01 mol) in dry methanol (50 ml) containing dry morpholine (2–3 drops). The mixture was then filtered and the filtrate concentrated to yield orange-yellow product which was dried in a desiccator.

References

1. J. A. ZUBIETA and J. J. JUCKERMAN, *Prog. Inorg. Chem.*, 1978, **24**, 251; B. Y. K. HO and J. J. JUCKERMAN, *J. Organomet. Chem.*, 1973, **42**, 1; P. G. HARRISON, *Coord. Chem. Rev.*, 1976, **20**, 1.
2. S. VASNINE and R. A. GEANANGEL, *Inorg. Chim. Acta*, 1989, **160**, 43.
3. T. TANAKA, *Organomet. Chem. Rev.*, 1970, **45**, 1; F. W. B. E. INSTEN and B. C. PENFOLD, *Chem. Commun.*, 1966, 780; *J. Chem. Soc., Sect. A*, 1968, 3019; P. G. HARRISON, "Organotin Compounds", American Chemical Society, 1976, pp. 157, 258.
4. C. N. R. RAO and R. VENKATARAGHAVAN, *Spectrochim. Acta*, 1962, **18**, 541; C. N. R. RAO, R. VENKATARAGHAVAN and F. R. KASTURI, *Can. J. Chem.*, 1964, **42**, 36; M. R. GAJENDRAGAD and U. AGARWALA, *Z. Anorg. Allgem. Chem.*, 1975, **415**, 84.
5. M. A. ALI and S. E. LIVINGSTONE, *Coord. Chem. Rev.*, 1974, **13**, 101.
6. L. F. AUDRIETH, E. S. SCOTT and P. S. KIPPUR, *J. Org. Chem.*, 1954, **19**, 733.

