X-Ray Diffraction, Mössbauer Spectral and Related Studies on some Tin(IV) Complexes with Various Nitrogen, Oxygen and Sulphur Donor Ligands

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A series of neutral adducts of tin(IV) chloride with various nitrogen donor ligands of general formula, $SnCl_4 \cdot L$ and $SnCl_4 \cdot L_2$ (where L = azines, semi- and thiosemi-carbazones) have been synthesized. The bonding in these compounds is discussed in terms of their i.r., n.m.r. and ^{119}Sn Mössbauer spectroscopic data. These data suggest that the ligands are functioning as mono- and bi-dentate ligands towards the metal atoms, which have coordination numbers of six in both the $SnCl_4 \cdot L$ and $SnCl_4 \cdot L_2$ complexes. The changes in Mössbauer parameters reflect the electronegative nature of the donor atoms.

Introduction

Azines, semi- and thiosemi-carbazones, are probably the most intriguing nitrogen donor ligands. Depending on reaction conditions, these compounds may act as ionic or neutral ligands [1]. A plethora of literature is available on their complexes with transition metals, whereas there has been almost no work on the corresponding neutral $SnCl_4$ adducts, notable exceptions being the $SnCl_4$ adduct of azine [2] and certain tin(IV) complexes with derivatives of these ligands [3, 4]. In view of the scanty information available on the addition complexes of tin(IV) halides and our interest in the coordination chemistry of tin(IV) complexes, a detailed study was carried out and our results are reported here.
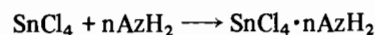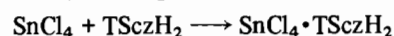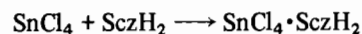
Experimental

All the chemicals were dried and distilled before use. All the ligands were prepared according to literature methods [4, 5]. Metal complexes were

prepared by mixing the calculated amounts of $SnCl_4$ and ligand in a medium of dry benzene. The products separated immediately as coloured solids but reaction mixtures were stirred for 1 h for completion of reaction. The solids were filtered and washed with solvents and dried *in vacuo*. They were analysed by methods similar to those reported in our earlier publication [6].

Infra red spectra were recorded as Nujol mulls, in KBr optics and in solution on a Perkin-Elmer 577 grating spectrophotometer in the range, 4000 - 200 cm^{-1}. ^1H n.m.r. spectra were recorded on a Perkin-Elmer RB-12 spectrometer operating at 90 MHz in DMSO-d_6 solutions using TMS as internal standard. ^{119}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A 15 mCi Ba^{119m}SnO$_3$ source was used at room temperature and samples were packed in perspex discs and cooled to 80 K using a liquid nitrogen cryostat. The experimental error in the measured values of isomer shift parameter (δ) was ± 0.05 mms^{-1}. X-ray powder diffractogram of the compound was obtained on a Philips PM 9929/O5 diffractometer with a FeK$_\alpha$ target. The structure was solved by Ito's [7] method.

Results and Discussion

Reaction of tin tetrachloride with these ligands in 1:1 and 1:2 molar ratios in the medium of benzene can be represented by following equations:

$$SnCl_4 + SczH_2 \longrightarrow SnCl_4 \cdot SczH_2$$
$$SnCl_4 + TSczH_2 \longrightarrow SnCl_4 \cdot TSczH_2$$
$$SnCl_4 + nAzH_2 \longrightarrow SnCl_4 \cdot nAzH_2$$

(where n = 1 or 2).

The reactions are quite facile and the yields are almost quantitative. The products are sparingly soluble in common organic solvents and show considerable thermal stability. All these complexes are

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monomeric in nature. Their physical characteristics are given in Table I.

The structures of the resulting compounds may be represented as shown right.

In the infra-red spectra of semi- and thiosemicarbazone ligands, νOH and νNH vibrations are observed in the region 3350–2850 cm^{-1}, whereas in the solution spectra of the ligands νNH is absent and νSH appears at 2500 cm^{-1}, due to tautomerisation. In the addition complexes of SnCl$_4$, broad bands have been observed in the region 3300–2900 cm^{-1}. It appears, therefore, that in these adducts the stretching vibrations of the νOH group overlap with the CH vibrations in this region [8]. Similar observations have also been reported by Srivastava et al. [9]. The asymmetric and symmetric bands of NH$_2$ appearing at ~3440 and 3360 cm^{-1} remain unchanged in the adducts as compared to their position in the free ligands.

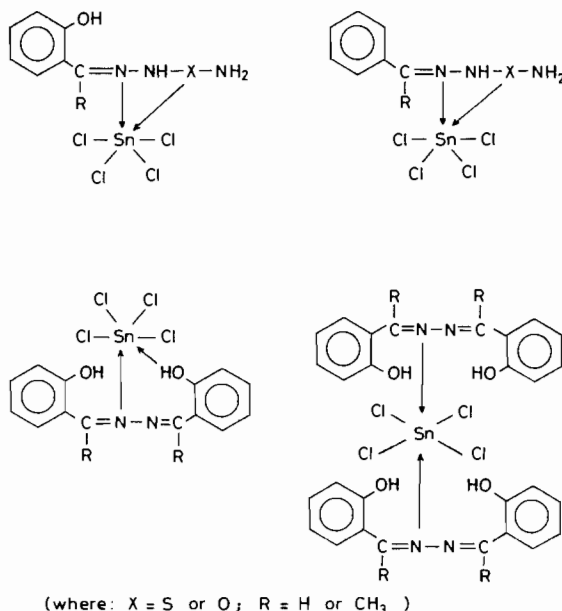In the case of azine ligands, a strong broad band due to νOH appears in the region, 3050–2650 cm^{-1}.

(where: X = S or O; R = H or CH$_3$)

TABLE I.

Reactants (g)		Molar Ratio	Yield %	Product and characteristics (Colour and State)	M.P. °C	ANALYSES %				Mol.wt.
SnCl$_4$	Ligand					Sn Found Calcd.	N Found Calcd.	Cl Found Calcd.	S Found Calcd.	Found Calcd.
1.16	C$_{14}$H$_{12}$O$_2$N$_2$ 0.94	1:1	93	SnCl$_4$(C$_{14}$H$_{12}$O$_2$N$_2$) Orange yellow solid	252	23.20 23.75	5.08 5.58	27.96 28.36		
0.63	C$_{14}$H$_{12}$O$_2$N$_2$ 1.17	1:2	94	SnCl$_4$(C$_{14}$H$_{12}$O$_2$N$_2$)$_2$ Yellow solid	282	16.06 16.07	8.12 7.75	18.82 19.16		
1.57	C$_{22}$H$_{16}$O$_2$N$_2$ 1.98	1:1	90	SnCl$_4$(C$_{22}$H$_{16}$O$_2$N$_2$) Maroon red solid	332	19.13 19.77	5.15 4.65	23.02 23.61		
0.67	C$_{22}$H$_{16}$O$_2$N$_2$ 1.74	1:2	91	SnCl$_4$(C$_{22}$H$_{16}$O$_2$N$_2$)$_2$ Orange red solid	310	12.29 12.63	6.58 5.94	14.62 15.08		
0.58	C$_{16}$H$_{16}$O$_2$N$_2$ 0.59	1:1	87	SnCl$_4$(C$_{16}$H$_{16}$O$_2$N$_2$) Yellow solid	197	21.63 22.48	6.10 5.29	26.10 26.84		
0.97	C$_{16}$H$_{16}$O$_2$N$_2$ 2.00	1:2	86	SnCl$_4$(C$_{16}$H$_{16}$O$_2$N$_2$)$_2$ Yellow solid	225	14.37 14.93	8.81 7.02	18.27 17.81		
2.53	C$_8$H$_9$N$_3$O$_2$ 1.73	1:1	90	SnCl$_4$(C$_8$H$_9$N$_3$O$_2$) Pinkish white solid	245*	25.71 27.04	– –	36.82 39.09	– –	482.0 439.98
1.11	C$_9$H$_{11}$N$_3$O 0.75	1:1	81	SnCl$_4$(C$_9$H$_{11}$N$_3$O) White solid	206	26.59 27.23	– –	41.53 39.27	– –	471.0 437.98
1.34	C$_8$H$_9$N$_3$O 0.83	1:1	85	SnCl$_4$(C$_8$H$_9$N$_3$O) White solid	211	27.65 28.06	– –	37.92 40.56	– –	450.0 423.98
1.15	C$_8$H$_9$N$_3$OS 0.86	1:1	86	SnCl$_4$(C$_8$H$_9$N$_3$OS) Yellowish white solid	–	25.38 26.09	– –	35.15 37.72	6.15 7.01	490.0 455.98
2.33	C$_9$H$_{11}$N$_3$OS 1.86	1:1	91	SnCl$_4$(C$_9$H$_{11}$N$_3$OS) Canary yellow solid	210*	25.02 25.37	– –	33.45 30.27	5.98 6.82	495.0 468.98
2.43	C$_8$H$_9$N$_3$S 1.65	1:1	90	SnCl$_4$(C$_8$H$_9$N$_3$S) White solid	181	26.59 27.23	– –	38.03 39.27	6.38 7.30	465.0 437.98
1.54	C$_9$H$_{11}$N$_3$S 1.14	1:1	87	SnCl$_4$(C$_9$H$_{11}$N$_3$S) Whitish yellow solid	215	25.52 26.21	– –	39.52 37.88	6.27 7.04	475.0 453.98

*Decomposition temperature.

However, in the spectra of adducts, two bands appear in the region 3500–2750 cm^{-1}. The presence of two bands in this region suggests that only one of the two OH groups coordinates with the metal atom, while the other one probably remains hydrogen-bonded to the nitrogen. A strong band due to $\nu(C{=}N)$ is observed in the ligands at ~1625 cm^{-1}. This band shifts to the lower frequency side in the spectra of semi- and thiosemi-carbazone adducts, but in the case of azine adducts [10] splits into two as only one of the two azomethine nitrogens can coordinate with metal ions.

The semi- and thiosemi-carbazone ligands show -OH proton signals at ~δ12.10 ppm (tridentate only), while all the ligands display N$\underline{H}$ proton signals at ~δ10.09 ppm. The signal due to O$\underline{H}$ remains unchanged in the compounds showing its non-involvement in coordination. However, the signal due to the N$\underline{H}$ proton shifts downfield indicating the involvement of O or S in bonding with the Sn atom and as a result of which the N$\underline{H}$ proton becomes less shielded. The signals at ~δ2.25 and 8.15 ppm are observed in the complexes due to -CH$_3$ and -H protons attached to a >C=N group. These signals are downfield in comparison with their original positions in the free ligands, thereby indicating the coordination of >C=N to the metal atom.

Both the asymmetric and symmetric tin–chlorine vibrations appear at ~315 and 285 cm^{-1} in semi- and thiosemi-carbazone adducts, while only one Sn–Cl vibration is observed at ~325 cm^{-1} in azine adducts [11]. In the infra-red spectra of these adducts, new bands appear at ~405, 370 and 310 cm^{-1} and these may be assigned to $N \rightarrow Sn$, $O \rightarrow Sn$ and $S \rightarrow Sn$ vibrations respectively [12].

Mössbauer parameters for these complexes are given in Table II.

The isomer shift values lie in the range prescribed for +4 oxidation state of tin and these values are lower than that of SnCl$_4$- i.e. 0.80 mm sec^{-1}. This reduction in isomer shift is due to the interaction between the tin and the donor atoms of the ligands. The thiosemi-carbazone adducts give the higher value, since their sulphur atoms possess a greater electron releasing tendency to the tin nucleus than do nitrogen or oxygen atoms.

Since these adducts do not show any quadrupole splitting the spherical charge distribution around the tin nucleus is unaltered on complexation. This also indicates that there is no marked difference in the polarities of the tin–ligand bonds. Similar trends have been observed in the complexes of Schiff bases [13] and 8-hydroxy quinoline [14] (I.S. = 0.45 mm sec^{-1}; Q.S. = 0 mm sec^{-1}).

The X-ray powder diffraction study of the compound, SnCl$_4$·(OHC$_{10}$H$_6$CHNNCHC$_{10}$H$_6$OH)$_2$, has been carried out to find out the unit cell dimensions. The observed 'd' values along with the calculated (indexed) and observed 'Q' values are given in Table III. The compound adopts a 'MONOCLINIC' lattice with the unit cell dimensions as below:

$a = 17.37$ Å

$\beta = 110° 83'$

$b = 11.87$ Å

$Z = 4$

$c = 10.25$ Å;

Acknowledgements

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TABLE II. Mössbauer Spectral Data of Tin Tetrachloride Adducts.

Sl. No.	Compound	I.S.* mm. sec^{-1}	Q.S. mm. sec^{-1}
1	SnCl$_4$·(C$_6$H$_5$CHNNHCSNH$_2$)	0.56	0
2	SnCl$_4$·(C$_6$H$_5$C(CH$_3$)NNHCSNH$_2$)	0.63	0
3	SnCl$_4$·(C$_6$H$_5$·CHNNHCONH$_2$)	0.41	0
4	SnCl$_4$·(C$_6$H$_5$·C(CH$_3$)NNHCONH$_2$)	0.43	0
5	SnCl$_4$·(OHC$_6$H$_4$CHNNHCSNH$_2$)	0.53	0
6	SnCl$_4$·(OHC$_6$H$_4$C(CH$_3$)NNHCSNH$_2$)	0.56	0
7	SnCl$_4$·(OHC$_6$H$_4$CHNNHCONH$_2$)	0.41	0
8	SnCl$_4$·(OHC$_6$H$_4$CHNNCHC$_6$H$_4$OH)	0.30	0
9	SnCl$_4$·(OHC$_6$H$_4$CHNNCHC$_6$H$_4$OH)$_2$	0.35	0
10	SnCl$_4$·(OHC$_{10}$H$_6$CHNNCHC$_{10}$H$_6$OH)	0.43	0
11	SnCl$_4$·(OHC$_{10}$H$_6$CHNNCHC$_{10}$H$_6$OH)$_2$	0.51	0

*Isomer shift values are reported with respect to CaSnO$_3$.

TABLE III. X-Ray Powder Diffraction of $SnCl_4(C_{22}H_{16}O_2N_2)_2$.

Sl No.	$d_{obsd.}$	$Q_{obsd.}$	$Q_{calcd.}$	hkl	Sl. No.	$d_{obsd.}$	$Q_{obsd.}$	$Q_{calcd.}$	hkl
1	16.36	0.0037	0.0038	100	24	3.33	0.0897	0.0900	401
2	11.86	0.0071	0.0071	010	25	3.20	0.0971	0.0971	411
3	9.57	0.0109	0.0109	001	26	3.11	0.1033	0.1021	510
4	8.04	0.0154	0.0152	200	27	3.04	0.1069	0.1055	222
5	7.69	0.0169	0.0180	011	28	2.93	0.1164	0.1157	103
6	7.28	0.0189	0.0192	101	29	2.84	0.1232	0.1227	113
7	6.58	0.0230	0.0223	210	30	2.71	0.1357	0.1358	511
8	6.21	0.0259	0.0263	111	31	2.64	0.1430	0.439	610
9	5.92	0.0284	0.0284	020	32	2.54	0.1573	0.1571	521
10	5.34	0.0351	0.0352	201	33	2.41	0.1702	0.1644	422
11	5.09	0.0385	0.0390	021	34	2.38	0.1760	0.1757	601
12	4.98	0.0403	0.0413	310	35	2.34	0.1815	0.1815	014
13	4.74	0.0435	0.0436	002	36	2.26	0.1955	0.1965	104
14	5.50	0.0330	0.0342	300	37	2.16	0.2137	0.2127	522
15	4.55	0.0482	0.0477	121	38	2.02	0.2433	0.2432	800
16	4.37	0.0522	0.0507	012	39	1.98	0.2527	0.2546	224
17	4.14	0.0567	0.0565	102	40	1.93	0.2665	0.2665	061
18	3.98	0.0629	0.0639	030	41	2.28	0.1913	0.1907	242
19	3.80	0.0689	0.0679	410	42	1.82	0.3006	0.2992	105
20	3.64	0.0751	0.0748	031	43	1.78	0.3137	0.3149	910
21	3.49	0.0816	0.0813	131	44	1.77	0.3194	0.3191	821
22	3.42	0.0851	0.0850	122	45	1.74	0.3279	0.3276	125
23	3.36	0.0882	0.0875	321	46	1.73	0.3328	0.3327	262
					47	1.91	0.2730	0.2725	005
					48	1.83	0.2973	0.2978	811

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