Asian Journal of Chemistry Vol. 15, No. 1 (2003), 428–434

Preparation and Characterisation of Tin(II) and Tin(IV) Complexes with Some Morpholine-N-Thiocarbazones

R.R. JHA* and D.K. JHA†
Department of Chemistry, Ranchi University, Ranchi-834 008, India

Complexes of Sn(II) and Sn(IV) with benzaldehyde morpholine-N-thiocarbazone (Benzmtcz-H), cinnamaldehyde morpholine-N-thiocarbazone (Cinmtcz-H), Cyclohexanone morpholine-N-thio-carbazone (Cyclmtcz-H), isatine morpholine-N-thiocarbazone (Istmtcz-H), Salicylaldehyde morpholine-N-thiocarbazone (Salmtcz-H_2) and *o*-hydroxyacetophenone morpholine-N-thiocarbazone (Ohacetpmcz-H_2) of composition {Sn(II)$(LH)_2Cl_2$}; (LH = Benzmtcz-H, Cinmtcz-H, Istmtcz-H, Cyclmtcz-H), [Sn(II)$(LH)_2$]; (LH_2 = Salmtcz-H_2 or Ohacetpmtcz-H_2), [Sn(IV)L_2] and [Sn(IV)LI_2] (LH_2 = Salmtcz-H_2 or Ohacetpmtcz-H_2) and [Sn(IV)L_2I_2]; (LH = Benzmtcz-H, Cinmtcz H or Cyclmtcz H) have been prepared and characterised by elemental analysis, electrical conductance, IR and NMR spectral studies.

Key Words: Tin(II and IV), Complexes, Morpholine-N-thiocarbazones.

INTRODUCTION

The complexes of tin and its compounds have aroused considerable interest due to their application in agriculture and their uses as marine antifouling agent, wood preservatives, stabilizers for PVC and antihelmintics and studied extensively.[1–9] In spite of various positive uses it has been found that some tin compounds enter the food chain, that cause harmful effects like headache, nausea, abdominal pain, dehydration and photophobia.[1, 10] The complexes of Sn(II) and Sn(IV) with various ligands have been reported in detail[11–15]. In pursuance of our interest in tin complexes, we here report the preparation and characterisation of Sn(II) and Sn(IV) complexes with Schiff bases of morpholine-N-thiocarbazone derived from benzaldehyde (Benzmtcz-H), cinnamaldehyde (Cinmtcz-H), cyclohexanone (Cyclmtcz-H), isatine (Istmtcz-H), salicylaldehyde (Salmtcz-H_2) and *o*-hydroxyacetophenone (Ohacetpmtcz-H_2).

EXPERIMENTAL

The ligands were prepared[16] by refluxing aqueous ethanolic solution of morpholine-N-thiohydrazone with appropriate aldehyde or ketone in presence of 2–3 mL acetic acid. The ligands were recrystallised from hot ethanol and dried. The analytical results for Benzmtcz-H,N: found 16.77, required 16.85%; Cinmtcz-H,N: found 15.19, required 15.26%; Cyclmtcz-H,N: found 17.38, required 17.41%; Istmtcz-H,N: found 15.19, required 15.26%; Cyclmtcz-H,N: found 17.38, required 17.41%; Istmtcz-H,N: found 19.25, required 19.30%; Salmtcz-H_2,N: found 15.86, required 15.84%; Ohacetpmtcz-H_2,N: found 15.09, required 15.04%.

---

†Lunglai Government College, Lunglai (Mizoram), India.

Tin(II) chloride used was E. Merck, extra pure quality and Tin(IV) iodide was prepared by reported method.[17]

Preparation of Complexes

About 1 mmol of appropriate Sn(II) and Sn(IV) salt was dissolved in ethanol and treated with slight excess of requisite proportion (M : L = 1 : 1 or 1 : 2) of ethanolic solution of ligand and refluxed for 1–2 h, when the desired product separated either on standing or concentrating the refluxate to a small volume. For obtaining deprotonaled ligand complexes, the pH of refluxate was reduced by adding a few drops of morpholine. The complex was collected on a filter, washed with cold ethanol and purity of samples was checked by TLC. The composition and analytical results of complexes are shown in Table-1. Iodine was estimated as AgI. The complex was fused with AR Na_2CO_3, and NaI formed extracted and AgI was precipitated by adding $AgNO_3$ solution and acidifying the extract with dil. HNO_3. Sulphur was estimated as $BaSO_4$.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF TIN COMPLEX

Complex	% Analysis: Found (Calcd.)			
	Sn	N	S	Halogen
[Sn(IV) (Benzmtcz)$_2$I$_2$]	13.31 (13.66)	9.31 (9.67)	7.31 (7.38)	28.91 (29.20)
[Sn(IV) (Cinmtcz)$_2$I$_2$]	13.01 (12.89)	8..92 (9.12)	7.01 (6.96)	27.37 (27.55)
[Sn(IV) (Cyclmtcz)$_2$I$_2$]	13.59 (14.21)	9.71 (10.06)	7.32 (7.68)	29.61 (29.20)
[Sn(IV) (Salmtcz)$_2$]	18.01 (18.39)	12.81 (13.02)	9.71 (9.94)	—
[Sn(IV) (Salmtcz)I$_2$]	18.34 (18.52)	6.41 (6.59)	4.99 (5.02)	39.51 (39.87)
[Sn(IV) (Ohacetpmtcz)$_2$]	17.31 (17.58)	12.01 (12.44)	9.31 (9.50)	—
[Sn(IV) [(Ohacetpmtcz)I$_2$)]	17.93 (18.13)	6.32 (6.45)	4.84 (4.92)	39.27 (39.02)
[Sn(II) (Benzmtcz-H)$_2$Cl$_2$]	16,91 (17.22)	12.11 (12.19)	9.11 (9.30)	10.11 (10.29)
[Sn(II) (Cinmtcz-H)$_2$Cl$_2$]	15.97 (16.08)	11.21 (11.38)	8.51 (8.69)	9.35 (9.60)
[Sn(II) (Cyclmtcz-H)$_2$Cl$_2$]	17.59 (17.71)	12.41 (12.54)	9.31 (9.57)	10.32 (10.58)
[Sn(II) (Istlmtcz-H)$_2$Cl$_2$]	15.41 (15.45)	14.08 (14.59)	8.01 (8.35)	9.11 (9.23)
[Sn(II) (Salmtcz-H)$_2$]	18.01 (18.33)	12.91 (12.98)	9.63 (9.90)	—
[Sn(II) (Ohacetpmtcz-H)$_2$]	17.30 (17.52)	12.11 (12.40)	9.60 (9.47)	—

RESULTS AND DISCUSSION

The analytical results of complexes correspond to composition [Sn(II)(LH)$_2$Cl$_2$] (LH = Benzmtcz-H, Cyclmtcz-H, Cinmtcz-H or Istmtcz H) and [Sn(IV)L$_2$I$_2$]; (LH = Benzmtcz-H, Cyclmtcz-H or Cinmtcz-H) suggest that the ligands Benzmtcz-H, Cinmtcz-H, Istmtcz-H and Cyclmtcz-H behave as neutral bidentate chelating molecules in neutral medium and monoanionic bidentate ligands at pH higher than 6. The ligands salmtcz-H$_2$ and Ohacetpmtcz-H$_2$ coordinate as monoanionic molecule and form complexes [Sn(II)(LH)$_2$ in neutral medium. In slightly basic medium Benzmtcz-H, Cinmtcz-H and Cyclmtcz-H form [Sn(IV) L$_2$I$_2$] at reflux temperature. The neutral inner chelate [Sn(IV)L$_2$]; and [Sn(IV)LI$_2$] (LH$_2$ = Salmtcz-H$_2$ or Ohacetpmtcz-H$_2$) are formed in slightly basic condition. The complexes of Sn(IV) are relatively more soluble in organic solvents than those of Sn(II) complexes. The electrical conductance value of complexes in DMF at room temperature (30–31°C) qualitatively display negligible electrical conductance value indicating non-ionic nature of complexes. The anions are coordinated to Sn(II) as well as Sn(IV) atom in dihalo complexes. In general, the complexes are quite stable in air but slowly decompose in aqueous suspension. As expected, the complexes are diamagnetic. Their ethanolic solutions do not display electronic absorption band in visible region, 400–850 nm. The strong absorption of complexes below 400 nm can be attributed to ligand absorption or charge transfer band.

The IR spectra of ligands in KBr disc or Nujol mull display NH stretches in the region 3180–3110 cm^{-1} (Table-2). The NH stretches of ligands are not affected appreciably in complexes with neutral ligands, but disappear in bis-ligated complexes [Sn(IV)L$_2$I$_2$]; (LH = Benzmtcz-H, Cinmtcz-H or Cyclmtcz-H). The ligand Salmtcz-H$_2$ displays phenolic (OH) stretch at 3280 cm^{-1} and ν(OH) of Ohacetpmtcz-H$_2$ at 3370 cm^{-1} which disappear in their complexes [Sn(II)(LH)$_2$], [Sn(IV)L$_2$] and [Sn(IV)LI$_2$] indicating deprotonation of phenolic OH on complexation. The Salmtcz-H$_2$ and Ohacetpmtcz-H$_2$ complexes [Sn(II)(LH)$_2$] and [Sn(IV)L$_2$] display NH stretches at 3120 and 3140 cm^{-1} respectively, but these disappear in [Sn(IV)L$_2$] and [SnIH$_2$]complexes indicating deprotonation of both NH and OH protons in bis-complexes [Sn(IV)L$_2$] and [Sn(IV)LI$_2$]. The thioamide bands[18, 19] (I, II, III) of ligands (Table-2) are raised to higher wavenumber in their complexes while the thioamide band (IV) shifts to lower frequency by 20–25 cm^{-1} in complexes containing neutral Benzmtcz-H, Cinmtcz-H, Cyclmtcz-H and Istmtcz-H and complexes [Sn(II)(LH)$_2$] (LH$_2$ = Salmtcz-H$_2$ or Ohacetpmtcz-H) as well as in [Sn(IV)L$_2$I$_2$] suggesting the bonding of thioamide group in complexes[20, 21]. The thioamide IV, however, shift to lower frequency and observed near 725–690 cm^{-1} in [Sn(IV)L$_2$] and [SnLI$_2$] ([LH$_2$ = Salmtcz H$_2$ or Ohacetpmtcz-H$_2$) or (Sn(IV)L$_2$I$_2$); (LH = Benzmtcz-H, Cinmtcz-H or Cyclmtcz-H). A large shift of thioamide band suggests coordination of ligand through deprotonated thiol sulphur also[20–22]. The ligands display azomethine (C=N) stretch near 1635–1590 cm^{-1}, which shifts to lower frequencies and observed near 1612–1585 cm^{-1}, suggesting that second donor sites of Benzmtcz-H, Cynmtcz-H or Istmtcz-H is azomethine nitrogen. The ν(CO) of Istmtcz-H observed at 1690 cm^{-1} is not affected appreciably in complexes suggesting that carbonyl oxygen is not involved in coordination. The phenolic ν(C—O) of ligand in Salmtcz-H_2 and Ohacetpmtcz-H_2 is observed at 1160–1153 cm^{-1} respectively which is raised to higher frequency and observed at 1390, 1385 and 1360 cm^{-1} indicating coordination of phenolic oxygen on deprotonation. Thus Salmtcz-H_2 and Ohacetpmtcz-H_2 are coordinated as tridentate mono or dianionic molecule in Sn(II) and Sn(IV) complexes. In far IR region ligands as well as their complexes display a number of IR bands between 535 and 300 cm^{-1}; therefore definite M—L band could not be suggested. Thus it is suggested that Sn(II) complexes $[Sn(II)(LH)_2Cl_2]$; (LH = Benzmtcz-H, Cinmtcz-H, Cyclmtcz-H or Istmtcz-H), and $[Sn(II)(LH)_2]$; (LH_2 = Salmtcz-H_2 and Ohacetpmtcz-H_2) are six-coordinated complexes with sp^3d^3 hybrid bonding in which lone pair of electrons of Sn(II) occupy one hybrid orbital and complexes are distorted octahedral, Sn(IV) complexes are all octahedral with sp^3d^2 hybrid bonding but $[Sn(IV)LI_2]$ are five-coordinated with sp^3d hybrid bonding.

NMR-study

The NMR spectrum of salicylaldehyde morpholine-N-thiocarbazone (H_2-Salmtcz) shows dianionic nature of ligand in $SnLI_2$ complex.

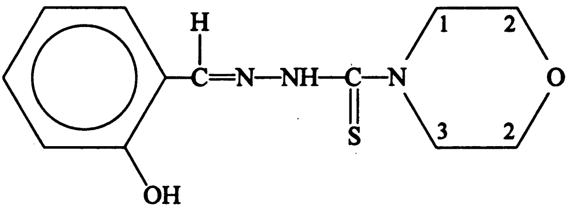
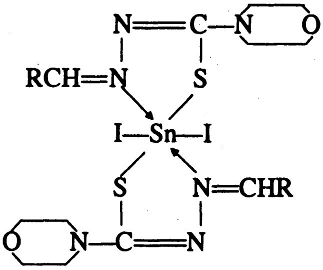


Fig. (H_2-Salmtcz)

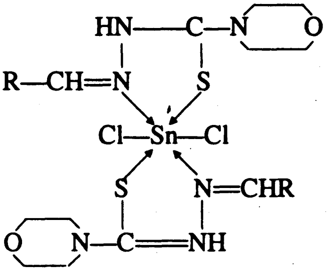
The signals of the protons at C_1, (2H) and C_2, (4H) and C_3, (2H) are observed at 2.40, 3.42 and 3.82 ppm respectively. The phenyl ring signals for 4 protons are observed between 6.70 and 7.38 ppm. The (HC═N) proton signal is located at 8.2 ppm. Thiocarbazone N_3 proton signal has been observed as sharp signal for one proton at 10.8 ppm and phenolic OH proton signal at 11.3 ppm. The NH and phenolic proton signals disappear in complex $[Sn(Salmatcz)I_2]$ and CH═N proton singlet down shifted to 8.6 ppm. The morpholine ring proton signals are observed between 2.75–3.75 ppm. The PMR spectral pattern clearly indicates bonding of Sn(IV) through O, N and S atoms of ligand. A large downfield shift of (HC═N) proton signal clearly indicates the coordination of aldimine nitrogen with Sn(IV) atom, as shown in Fig. 1 (d).



R = C_6H_5—
= $C_6H_5CH{=}CH$—
= Isatinyl
= Cyclohexyl

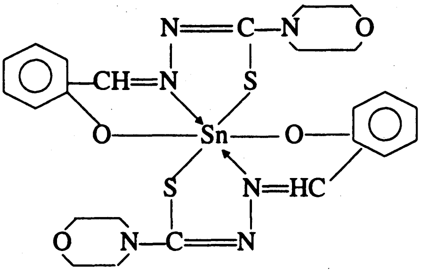
[SnL_2I_2]

Fig. 1 (a)



[$Sn(LH)_2Cl_2$]

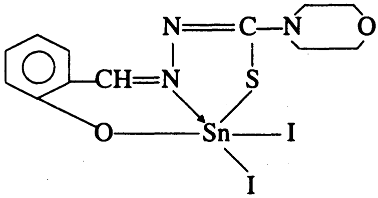
Fig. 1 (b)



M : L = 1 : 1

[SnL_2]

Fig. 1 (c)



M : L = 1 : 1

[$SnLI_2$]

Fig. 1 (d)

TABLE-2

PROMINENT IR BANDS (cm^{-1}) OF LIGANDS AND THEIR METAL COMPLEXES

Compound	ν(OH) + ν(NH)		ν(C=N)	Thioamide bands				ν(C—O)	ν(M—L) + Ligand
				I	II	III	IV		
Benzmtcz-H		3150 b	1590 m	1455 s	1415 s	1325 s	885 s	—	505 m, 380 w, 365 w, 310 w
[Sn(IV) (Benzmtcz)$_2$I$_2$]		3140 bs	1600 s	1500 s	1450 s	1360 m	700 m	—	515 m, 475 w, 380 w, 373 m
[Sn(II) (Benzmtcz)$_2$Cl$_2$]		3105 b	1600 s	1510 s	1455 s	1370 m	875 s	—	505 m, 470 w, 380 w, 340 w
Cinmtcz-H		3110 s	1620 s	1525 s	1405 s	1295 s	925 s	—	520 s 505 s, 410 w, 375 w
[Sn(IV) (Cinmtcz)$_2$I$_2$]		3140 b	1605 m	1535 s	1460 s	1365 s	905 s	—	465 m, 430 w, 415 w, 340 w
Cyclmtcz-H		3130 m	1630 s	1460 s	1448 m	1260 s	980 s	—	518 s, 442 w, 390 m
[Sn(IV) (Cyclmtcz)$_2$I$_2$]		3210	1612 s	1520 s	1460 s	1300 w	690 m	—	505 m, 475 w
[Sn(II) (Cyclmtcz)$_2$Cl$_2$]		3040 m	1615 s	1490 s	1460 m	1315 w	905 s	—	510 m, 455 w, 420 vw, 265 m
Salmtcz-H	3280 s	3076 m	1624 s	1478 s	1394 s	1275 s	920 m	1153 m	515 m, 485 w, 430 w
[Sn(II) (Salmtcz-H)$_2$]		3370 s	1595 m	1550 s	1365 s	1355 m	890 vs	1360 m	525 s, 490 s, 435 s, 353 w, 345 w, 330 w
[Sn(IV) (Salmtcz)$_2$]	3110 vs	3080 ms	1600 m	1550 s	1465 s	1375 vs	720 s	1390 s	495s, 442 m, 405 s, 345, 330 w
[Sn (Salmtcz)I$_2$]		3140 s	1632 m	1543 s	1405 s	1272 m	710 s	1360 s	515 s, 440 m 405 s, 335 w
Istmtcz-H	3320 s	3140 s	1635 s	1505 s	1380 m	1285 m	895 s	1690 m	525 w, 490 w, 375 w
[Sn(II) (Istmtcz-H)$_2$Cl$_2$]	3310 s	3150 m	1585 s	1550 m	1452 s	1320 m	885 s	1690 m	485 w, 405 w, 390 w
Ohacetpmtcz-H$_2$	3370 s	3150 m	1590 m	1480 s	1365 s	255 ms	890 vs	1160 m	535 m, 500 w, 455w, 345w, 310 b
[Sn(II) (Ohacetpmtcz-H)$_2$]		3140 m	1595 s	1525 m	1435 m	1312 w	865 s	1385 m	525 m, 490 w, 436 w, 345 m
[Sn(IV) (Ohacetpmtcz)$_2$]		3120 m	1600 m	1525 m	1440 m	1328w	725 w	1360 m	535 m, 485 w, 440 m, 340 m
[Sn(IV) (Ohacetpmtcz)I$_2$]		3135 m	1605 m	1515 m	1405 s	1320 w	715 w	1370 m	535 m, 480 w, 435 m, 320 m

ACKNOWLEDGEMENT

One of the authors (DKJ) is thankful to UGC for financial support.

REFERENCES

1. D. Patris, T. Barcas, A. Simopoulos and N.H.J. Gangas, *Inorg. Chem.*, **28**, 2439 (1989).
2. B.N. Binddle, J.S. Gray and A.J. Crowe, *J. Chem. Soc. Dalton Trans*,.,419 (1990).
3. A. Fargasova, *Chem. Abstr.*, **122**, 8683q (1995).
4. J.A. Zufita and J.J. Juckerman, *Prog. Inorg. Chem.*, **24**, 251 (1978).
5. P.G. Harrison,*Coord. Chem. Rev.*, **20**, 1 (1976).
6. M.N. Karayannis, L.L.Pytewski and C.M. Mikulski, *Coord. Chem. Rev.*, **11**, 93 (1973).
7. A. Chakrabarti, T.K. Chattopadhyaya and A. Roy, *Indian J. Chem.*, **35A**, 621 (1996).
8. J.C. Trehan, R.K. Sharma and C.P. Sharma, *Polyhedron*, **5**, 1227 (1986).
9. C.I.F. Denekep, D.F. Evans, J. Parr and J.D. Woolings, *J. Chem Soc., Dalton Trans.*, 1489 (1993).
10. Hillwings, K. Havms and K. Dehricke, *Organomet. Chem. J.*, **501**, 327 (1995).
11. P.J. Smith and L. Singh, *Inorg. Chem. Acta (Rev.)*, **7**, 11 (1973).
12. C.I.P. Denekamp, D.P. Evans, J. Parr and J.D. Woolwings, *J. Chem. Soc., Dalton Trans.*, 1489 (1993).
13. A.E. Merbach, *J. Chem Soc., Dalton Trans.*, 804 (1984).
14. S. Sen Gupta and N.K. Kausik, *Indian J. Chem.*, **26A** ,175 (1987).
15. K. Dey, S. Roy, P.K. Bhattacharya and A. Gangopadhyay, *J. Indian Chem. Soc.*, **62**, 809 (1985).
16. P. Kumari and L.K. Mishra, *J. Indian Chem. Soc.*, **72**, 463 (1995).
17. G.A.Brauer, Hand Book of Preparative Inorganic Chemistry, Academic Press (1963).
18. C.N.R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).
19. C.N.R. Rao, R. Venkataraghavan and T.R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).
20. M.R. Gajendragad and U. Agrawal, *Z. Anorg. Allg. Chem.*, **415**, 84 (1975).
21. M. Marcotrigeano, G. Poyronel and R. Bettistuze, *J. Inorg. Nucl. Chem.*, **37**, 1675 (1975).
22. M.A. Ali and S.E. Livingstone, *Coord. Chem. Rev.*, **13**, 101 (1974).

(*Received:* 5 August 2002; *Accepted:* 20 September 2002) AJC-2856