

IR and ¹H NMR Spectra of Tin(II) Complexes with 1-Substituted Tetrazoline-5-thiones

R.N. PANDEY

Post Graduate Centre of Chemistry, College of Commerce, Patna-800 020, India

Email: rameshwarnath.pandey@yahoo.com

Complexes of phenyl, *ortho*-tolyl, *meta*-tolyl and *p*-chlorophenyl derivatives of 1-substituted tetrazoline-5-thione have been prepared with Sn(II) and characterized on the basis of analytical, infrared, electronic and ¹H NMR spectral studies. All the complexes have general formula [Sn(ligand)₄(OH)₂] having *trans*- octahedral configuration. Metal-ligand vibrations in far IR have also been located and assigned.

Key Words: Tin(II) complexes, 1-Substituted Tetrazoline-5-thiones.

INTRODUCTION

1-Substituted tetrazoline-5-thiones forms stable complexes with many class 'a' and class 'b' metal ions¹⁻⁵. However, structural aspects of Sn(II) complexes have not been examined. The present paper reports the preparation, characterization and spectral studies of some solid stable complexes of Sn(II) with phenyl (1P T5TH), *o*-tolyl (1OTT5TH), *m*-tolyl (1MTT5TH) and *p*-chlorophenyl (1-PCIPT5TH) derivatives of 1-substituted tetrazoline-5-thione.

EXPERIMENTAL

All chemicals used were of AnalaR grade. The derivatives of 1-substituted tetrazoline-5-thione were prepared by the method of Lieber *et al.*⁶ All the tin(II) complexes were prepared using general method: 0.005 mol of stannous chloride was dissolved in minimum volume of moderately conc. HCl by warming and the solution was filtered. Methanolic hot solution of ligands (0.02 mol in 50 mL methanol) was mixed with tin(II) solution and pH was adjusted⁷ with the help of NH₄OH and dilute HCl solution. It was refluxed for 4 h on water bath. On cooling, light yellow complexes were precipitated out. [Sn₂(1P T5TH)(H₂O)₅Cl₄] was obtained from the filtrate on crystallization. The crystals were filtered, washed with methanol and dried at 110 °C in a electric oven. The analytical results are given in Table-1.

IR Spectra of ligands and complexes were recorded with Perkin-Elmer model-577 spectrophotometer in the range of 4000-200 cm⁻¹. Samples were prepared as KBr pellets. For UV spectral measurements 10⁻³ M solution of Sn(II) complexes were prepared by dissolving them into methanol adding one drop conc. HCl.

¹H NMR spectra of ligands and Sn(II) complexes were recorded with 90 MHz NMR spectrophotometer using TMS as internal indicator. The complexes were dissolved in CDCl₃ for recording their ¹H NMR spectra in the range of 0-10 ppm. The number of protons were obtained with the help of internal calibrator.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF TIN(II) COMPLEXES

Compound (colour)	pH of isolation	Analysis % found./calcd.				
		C	H	N	Cl	Sn
[Sn(1PT5TH) ₄ (OH) ₂] (Yellow)	7	38.3 (38.5)	2.85 (3.0)	26.2 (26.0)	–	13.6 (13.7)
[Sn ₂ (1PT5TH)(H ₂ O) ₅ Cl ₄] (Brick colour)	6	12.8 (12.9)	2.3 (2.4)	8.3 (8.6)	13.0 (12.9)	18.3 (18.2)
[Sn(1OTT5TH) ₄ (OH) ₂] (Light yellow)	7	41.5 (41.7)	3.6 (3.7)	24.2 (24.3)	–	13.1 (12.9)
[Sn(1MTT5TH) ₄ (OH) ₂] (Deep yellow)	7	41.4 (41.7)	3.6 (3.7)	24.4 (24.3)	–	12.8 (12.9)
[Sn(1PCl PT5TH) ₄ (OH) ₂] (Yellow)	7	33.2 (33.5)	2.3 (2.2)	22.1 (22.3)	–	11.6 (11.8)

RESULTS AND DISCUSSION

The four derivatives of 1-substituted tetrazoline-5-thione forms stable solid at pH 7. The analytical results indicate the stoichiometries [Sn(ligand)₄(OH)₂]. These complexes were shaken with aqueous Na₂CO₃ solution thoroughly and the aqueous extract was filtered, acidified with dilute HNO₃ and when treated with AgNO₃, no precipitate of AgCl occurred indicating the presence of covalent chloride. Other complexes contain covalently bonded hydroxyl group because they do not give brown precipitate of Ag₂O when shaken with AgNO₃ solution. Hence, covalently bonded hydroxyl group and chloride ion was assumed. The presence of coordinated hydroxyl group was further confirmed by the presence of a medium band in the infrared spectra at 545 cm⁻¹ corresponding to ν (Sn-O). The hydroxocomplexes have probably *trans*-octahedral configuration because only one ν (Sn-O) band is present. Similar observations have been reported by Kennedy *et al.*⁷ for *trans*-[Sn(OH)₂(*p*-thiocyanine)₂] which display only one ν (Sn-O) band at 563 cm⁻¹ in infrared spectrum. ν (Sn-O) band in many other Sn(II) complexes have been reported in the literature⁸⁻¹⁰.

Electronic spectra of all these complexes display charge transfer band around 330 nm indicating the presence of ligand in the complexes. All were non-conducting in DMF suggesting covalent chloride ions and hydroxide ions.

Infrared spectra and nature of bonding: The IR spectrum of 1-substituted tetrazoline-5-thione, display two distinct broad absorption bands in the range 3090-3020 cm⁻¹ are assigned to superimposed bands of ν (N-H) and ν (C-H) vibrations. These ligand bands are observed at higher frequency (Table-2) suggest the absence of bonding through imino nitrogen. Thus N-H group of ligands is intact in solid complexes. All ligands display weak broad band at 2350-2340 cm⁻¹ assigned to ν (S-H) is not observed on coordination indicating the presence of thione tautomeric form in the complexes and metal-sulphur bond is assumed. The formation of metal-sulphur bond is also supported by the systematic change in position of all four

TABLE-2
 KEY IR SPECTRAL BAND OF LIGANDS

Compound [#]	ν(N-H)	Thioamide bands*				ν(Sn-S)/ν(Sn-O)
		I	II	III	IV	
1PT5TH	3050 m	1512 s	1280 s	1058 s	785 m	–
Compound -1	3100 m	1510 m	1240 m	1030 m	765 m	400w (455w)
Compound-2	3100 m	1505 s	1241 m	1020 m	760 m	420w (450w)
	3080 m		1235 m			
1OTT5TH	3090 sb	1500 m	1300 m	1055 m	810 m	–
	Compound-3		1495 s			
1MTT5TH	3050 m	1500 s	1285 m	1052 m	790 m	–
Compound-4	3070 mb	1500 m	1260 m	1040 m	710 m	410w (450w)
1PCIPT5TH	3080 mb	1498 s	1280 s	1055 m	780 m	–
	Compound-5					
	3080 m					

#Compound nos. correspond to the complexes in Table-1. *Band-I (ν(NH) + ν(CH) + ν(C=N)); Band II [ν(C-N) + ν(NH) + ν(CH) + ν(C=S)]. Band III [ν(C-N) + ν(C-S)]; Band IV [ν(C-S)].

thiomide bands of ligands. The thiomide band II undergoes red shift of 25-40 cm⁻¹, band III undergoes red shift of *ca.* 40 cm⁻¹ and band IV 40-20 cm⁻¹ due to increase in CN bond order and decrease of CS bond order resulting bonding through thione sulphur¹¹⁻¹³. New band at 400-410 cm⁻¹ in far infrared spectra assigned to ν(Sn-S) mode also suggests formation of Sn-S bond. The non-ligand bands at 3330, 1610 and 830 cm⁻¹ in aquo complex [Sn₂(1PT5TH)(H₂O)₅Cl₄] are assigned to νH₂O, δH₂O and πH₂O, respectively of coordinated water molecules. All hydroxo complexes lack of δH₂O at 1610 cm⁻¹ and exhibit δH₂O near 1150 cm⁻¹ indicating coordinated hydroxo group¹⁴. The νOH band is found to be considerably shifted to *ca.* 3100 cm⁻¹ suggesting strong H-bonding of hydroxyl hydrogen atom in the solid complexes.

Far IR spectrum of [Sn₂(1PT5TH)(H₂O)₅Cl₄] contains non-ligand bands at 430 and 310 cm⁻¹ of medium intensity assigned to tin-chlorine terminal and bridging stretching modes in dimeric octahedral structure.

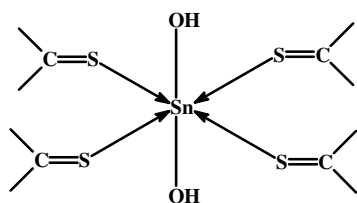
¹H NMR Spectra: To substantiate further bonding in these complexes ¹H NMR spectra of free ligands and their complexes were compared. 1-Phenyl-tetrazoline-5-thione contains multiplet signals centred at δ7.7 ppm due to 5 phenyl protons¹⁵. However, multiplet centred at δ7.4 and δ8.2 ppm (1PCIPT5TH), δ7.95 ppm (1pT5TH) and at δ 7.4 ppm (MTT5TH) suggest 4-phenyl protons in two different magnetic environment and singlet signal at δ 2.25 ppm (1mtT5TH) and at δ 2.3 ppm (1otT5TH) arises due to 3-methyl protons.

The position of signals due to phenyl protons of ligands are almost unchanged in position but show broad multiplet propably due to the presence of four nitrogen

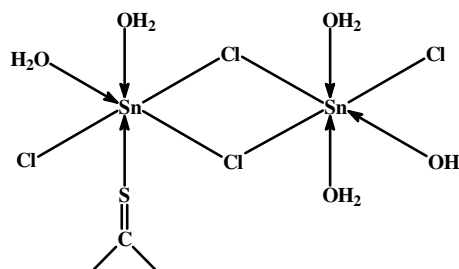
atoms which may cause large quadrupole resonance broadening effect or ligand exchange reaction occurring in solution¹⁶. Similar broadening of the phenyl proton bands have been observed in literature¹⁷.

Since the ligand is monodentate, one should expect a proton signal from the N-H protons as well. Generally, the signal of the N-H proton is weak and broad and appears around δ 8-6 ppm. This is the same region as the protons of the phenyl protons of the ligands are absorbing. So, it appears that the N-H signal is masked by the strong and broad signal due to the phenyl protons. This is also indicated by the relative area of the phenyl proton peak which is greater than required for phenyl protons. Thus, the ¹H NMR spectra are also compatible with bonding through thiocarbonyl sulphur and no deprotonation of the N-H group of ligands.

Thus, on the basis of aforesaid physico-chemical and spectral data *trans*-octahedral structure of all Sn(II) complexes may be tentatively assigned.



Tentative *trans*-octahedral structure of $[\text{Sn}(\text{OH})_2(\text{Ligand})_4]$



Octahedral structure of $[\text{Sn}_2(1\text{PT5TH})(\text{H}_2\text{O})_5\text{Cl}_4]$

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