

## **SYNTHESIS & CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF Tl(I) METAL SALTS OF SOME ORGANIC ACIDS WITH 2-AMINOTHIOPHENOL**

**ASHOK KUMAR GUPTA**

*Deptt. of Chemistry, Sri Arvind Mahila College (Patliputra Univ.), Patna - 800004 (India)*

**SHALINI PRIYA**

*Research Scholar, B.I.T. Mesra (Jharkhand)*

**AND**

**BIRENDRA KUMAR**

*Deptt. of Chemistry, Maharaja College (VKS Univ.), Ara - 802301 (India)*

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Some new mixed ligand Tl(I) complexes having general formula  $ML.HL'$ , where  $M = Tl(I)$ ;  $L =$  deprotonated o-nitrophenol (ONP), 2,4-dinitrophenol(DNP), 2,4,6-trinitrophenol(TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline(8HQ);  $HL' =$  2-Amino-thiophenol (OATP) have been synthesized. On the basis of various physico-chemical investigations, it has been found that 2-Aminothiophenol behaves as bidentate ligand coordinating through N-atom of  $-NH_2$  group and S-atom of  $-SH$  group.

**KEYWORDS** : Mixed ligand complexes, 2-Aminothiophenol, Thallium(I) metal salt, Infrared spectra, Electronic absorption spectra.

### **INTRODUCTION**

Thallium metal and its compounds find applications in analytical, industrial, pharmaceutical and medicinal field [1-3]. 2-Aminothiophenol is an important bidentate chelating ligand. It forms more stable five membered ring with thallium metal ions. It has been well investigated for its coordinating behaviour towards alkali and alkaline earth metals [4-8]. Extending our investigation to synthesize some new mixed ligand complexes of Tl(I) metal salts of some organic acids with 2-aminothiophenol..

### **EXPERIMENTAL**

O-nitrophenol(ONP), 2,4-dinitrophenol(DNP), 2,4,6-trinitrophenol(TNP), 1-nitroso-2-naphthol(1N2N) or 8-hydroxyquinoline(8HQ) and 2-aminothiophenol(OATP) of AnalaR grade were used as such.

#### **Synthesis of Tl(I) metal salts :**

Organic acid and sodium hydroxide were taken in 1 : 1 molar ratio in 95% ethanol, and refluxed on hot plate with constant stirring at 80°C for about one hour. The solution was

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concentrated and cooled, when the sodium salt of organic acid precipitated out. It was filtered, washed with 95% ethanol and then dried in an electric oven at 100°C.

Again sodium salt of organic acid was dissolved in 95% ethanol and an alcoholic solution of TlCl were mixed in 1 : 1 molar ratio. The mixture was refluxed on hot plate of magnetic stirrer at 60 – 70°C for about half an hour, when coloured precipitate of Tl(I) metal salt of organic acid was obtained. It was filtered, washed with 95% ethanol and then dried in an electric oven at 100°C.

#### Synthesis of Mixed ligand complexes :

To a suspension of Tl(I) metal salt of organic acid(ML) in absolute alcohol, second ligand (2-aminothiophenol) was added in 1 : 1 mole proportion. The mixture was refluxed on magnetic hot plate with constant stirring at 80°C for about two hours. On cooling the resulting solution, the characteristic colour complex got separated. It was filtered, washed with absolute ethanol and then dried in an electric oven at 100°C.

## RESULTS & DISCUSSION

Some physical properties of the ligand(2-aminothiophenol) and the mixed ligand complexes(ML.HL') obtained are listed in Table 1.

Table 1

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
2-Aminothiophenol (OATP)	Colourless	116.5b	...	...	...	...	...
Tl(ONP).OATP	Greenish yellow	>300	10.2	23.78 (23.86)	2.91 (2.98)	10.35 (10.44)	50.65 (50.79)
Tl(DNP).OATP	Deep yellow	275d	9.5	21.32 (21.46)	2.40 (2.46)	12.41 (12.52)	45.33 (45.68)
Tl(TNP).OATP	Deep yellow	265d	8.0	12.39 (12.50)	1.95 (2.03)	14.08 (14.22)	41.37 (41.51)
Tl(IN2N).OATP	Light brown	298d	10.5	32.24 (32.32)	3.35 (3.43)	10.11 (10.28)	49.86 (50.03)
Tl(8HQ).OATP	Light yellow	262d	6.2	32.85 (33.00)	3.06 (3.21)	9.50 (9.62)	46.71 (46.84)

2-Aminothiophenol is a cream coloured solid, insoluble in cold water but soluble in hot water, ethanol and ether. It is steam volatile. The mixed ligand complexes are of characteristic colours. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc; but they are sparingly soluble in non-polar solvents, namely, chloroform, *n*-hexane, benzene dioxane etc.

**Molar Conductance :** Molar conductance of all the compounds were measured in methanol at 30°C at a concentration of  $10^{-3}$  M. The values are given in Table -1. The value of about 35 - 40  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  is characteristic of 1 : 1 electrolyte [9] whereas ideally molar

conductance of neutral compound should be zero. However, significantly low values (6.2 - 10.5) of molar conductance of the compounds indicate them to be covalent nature.

**Infrared Spectra :** Infrared spectra of the ligand(2-Aminothiophenol) and its mixed ligand Tl(I) complexes were recorded in KBr phase between 4000 - 450  $\text{cm}^{-1}$  with the help of JASCO - FTIR spectrophotometer model - 5300. Pertinent IR data for ligand (OATP) and its mixed ligand Tl(I) complexes are listed in Table 2.

**Table 2. Pertinent IR data for ligand(o-aminophenol) & its mixed ligand Tl(I) complexes**

Compound	$\nu_{\text{N-H}}$	$\nu_{\text{S-H}}$	$\nu_{\text{NH}_2}$	$\nu_{\text{M-O/M-N}}$
2-Aminothiophenol (OATP)	3400, 3300	2550	1610	---
Tl(ONP).OATP	3380, 3290	2480	1605, 1575	654, 568, 532, 455
Tl(DNP).OATP	3390, 3280	2490	1600, 1580	668, 546, 521
Tl(TNP).OATP	3380, 3290	2510	1600, 1560	635, 585, 530, 471
Tl(1N2N).OATP	3360, 3270	2500	1600, 1580	637, 585, 476
Tl(8HQ).OATP	3350, 3275	2510	1600, 1575	649, 560, 546, 455

2-Aminothiophenol(OATP) acts as chelating ligand towards transition metal ions, coordinating both through the  $-\text{NH}_2$  and  $-\text{SH}$  groups [10-11]. The ligand (OATP) has two strong absorption bands at 3400  $\text{cm}^{-1}$  and 3300  $\text{cm}^{-1}$  respectively. For this reason a well defined trend in the  $-\text{NH}_2$  frequency is not observable for their transition metal complexes although there is a general lowering of the absorption bands. Similar shift of the absorption range of NH has been observed in the complexes, which might be due to coordination of  $-\text{NH}_2$  to the Tl(I) metal. The medium intensity of  $-\text{NH}_2$  bending vibration occurring at 1610  $\text{cm}^{-1}$  in the ligand has also shifted down by 5 - 10  $\text{cm}^{-1}$  and other band appearing in the region 1580 - 1560  $\text{cm}^{-1}$  is due to the presence of different functional group present in the first ligand.

The spectra of mixed ligand Tl(I) complexes differ from that of the acid metal salts and the second ligand (OATP). While the spectra of the ligand a moderately medium absorption band at 2550  $\text{cm}^{-1}$ , the region of S-H vibration frequency. This band has shifted down by 70 - 40  $\text{cm}^{-1}$  in the complexes, indicating thereby that coordination has taken place through S-atom of  $-\text{SH}$  group. Extra bands are due to presence of  $-\text{NO}_2$ ,  $-\text{NH}_2$ ,  $-\text{NO}$  of first ligand (organic acids) very much overlap with other ligand vibration. These complexes also show one or two peaks between 1170 - 1114  $\text{cm}^{-1}$ .

The band in the region 521 - 455  $\text{cm}^{-1}$  in the spectra of all mixed ligand Tl(I) complexes may be assigned to M - O band frequency while medium bands in the region 668 - 530  $\text{cm}^{-1}$  assigned to M - N band frequency [12-13]. The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of  $-\text{NO}/-\text{NO}_2$  of first ligand, *i.e.*, organic acid to Tl(I) metal ion in all the mixed ligand complexes.

**Electronic Spectra :** Electronic spectra were recorded on Systronic Double Beam UV-VIS spectrophotometer - 2201 in methanol. The bands observed in electronic spectra of ligand (2-Aminothiophenol) and the mixed ligand Tl(I) complexes are given in Table 3.

The electronic absorption bands of the mixed ligand Tl(I) complexes are observed in the region 233 - 269 nm, which indicate  $\pi-\pi^*$  transition in the complexes. The mixed ligand complexes also show charge transfer bands in the region 328 - 390 nm.

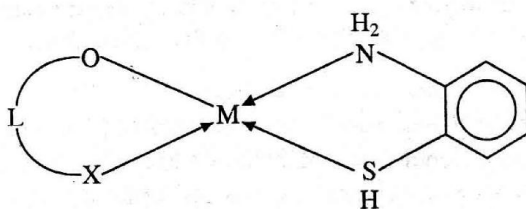
**Table 3. Major diffuse reflectance bands(in nm) for mixed ligand Tl(I) complexes with 2-aminothiophenol (OATP)**

Compound	Diffuse reflectance ( in nm)
Tl(ONP).OATP	353, 250, 236
Tl(DNP).OATP	390, 351, 339, 240
Tl(TNP).OATP	371, 328, 248
Tl(1N2N).OATP	358, 373, 233
Tl(8HQ).OATP	364, 269, 251

The shift in position of  $\pi$ - $\pi^*$  and charge transfer bands of the ligand in the complexes show that there is a  $\pi$ -interaction between metal and ligand orbitals.

## STRUCTURE & BONDING

On the basis of quantitative analysis and spectral data the probable structures of the complexes are shown in Fig. 1.



where M = Tl(I), L = deprotonated ONP, DNP, TNP, 8HQ or 1N2N; X = N or O  
(Fig. 1)

## REFERENCES

1. Watt, G. N. and Knifton, J. F., *Inorg. Chem.*, **7**, 1443 (1968).
2. Hieber, W and Bruck, R., *Nature Wissenschafte*, **36**, 312 (1949).
3. Livingstone, S. E., *J. Chem. Soc.*, **437**, 1042 (1956).
4. Olszewski, E. J. and Albinak, M. J., *J. Inorg. Nucl. Chem.*, **27**, 1431 (1961).
5. Shyamal, A. and Singhal, O. P., *Trans. Met. Chem.*, **4**, 179 (1995)
6. Stiefel, R. I., Waters, J.H., Billigs, E. and Gray, H. B., *J. Amer. Chem. Soc.*, **87**, 3016 (1965).
7. Shyamal, A. and Gupta, B. K., *Rev. Chem Miner.*, **20**, 123 (1983).
8. Prakash, D. Hussain, A. S., Yadav, S. P. and Gupta, A. K., *Asian J. Chem.*, **12(4)**, 1135 (2000).
9. Banerjee, A. K., Layton, A. J. and Nyholm, R. S., *J. Chem. Soc.(A)*, 2536 (1969)
10. Livingstone, S. E. and John. D. N., *Inorg. Chem.*, **7**, 1443 (1968).
11. Korobkov, V. S., Kuzin, I. V. and Artamonov, E. P., *Akad. Nauk SSSR, Sibirsk, Otd.*, **161**, 472 (1964).
12. Shyamal, A. and Singhal, O. P., *Trans. Met. Chem.*, **4**, 179 (1995)
13. Condrate, R. A. & Nakamoto, K., *J. Chem. Phys.*, **42**, 2590 (1965).

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