

## **MIXED LIGAND COMPLEXES OF Tl(I) METAL CHELATES OF SOME ORGANIC ACIDS WITH SALICYLIC ACID**

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A number of novel mixed ligand complexes of type ML.HL' have been synthesized and characterized, where M = Tl(I), L = deprotonated o-nitrophenol (ONP), 2, 4-dinitro-phenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline (8HQ); HL' = salicylic acid. All the complexes have been found to have 1 : 1 stoichiometric composition. The complexes have been characterized by elemental analysis, IR, UV-VIS spectral analysis and molar conductance measurements. IR spectral data show that the hydrogen bonding in these complexes is a dominant factor for their stability. Low value of their molar conductance would suggest them to be covalent nature.

### **INTRODUCTION**

**S**alicylic acid is an important hydroxy benzoic acid. Transition metal and alkali metal complexes with salicylic acid have been well investigated earlier [1-8]. In this communication, we have taken the salicylic acid as a secondary ligand to investigate the coordination behaviour towards Tl(I) metal salts of some organic acids and also to study whether it is selective in comparison to the other hydroxy acid complexes.

### **EXPERIMENTAL**

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

#### **Preparation 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 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.

#### Preparation of Mixed ligand complexes :

To a suspension of Tl(I) metal chelate of organic acid (ML) in absolute alcohol second ligand (Salicylic acid) was added in 1 : 1 mole ratio. 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 adduct 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 second ligand (SalA) 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.)			
					H	N	M
Salicylic acid (SalA)	Colourless	138m	---	---	---	---	
Tl(ONP).SalA	Greenish Yellow	>300	7.2	33.28 (33.59)	2.05 (2.15)	2.95 (3.01)	43.85 (44.01)
Tl(DNP).SalA	Pale cream	118m	9.5	29.52 (29.69)	1.60 (1.71)	5.21 (5.33)	38.63 (38.90)
Tl(TNP).SalA	Yellow	132md	8.0	27.19 (27.35)	1.35 (1.40)	7.18 (7.36)	35.77 (35.83)
Tl(1N2N).SalA	Deep brown	190md	10.5	39.54 (39.66)	2.15 (2.33)	2.57 (2.72)	49.66 (39.73)
Tl(8HQ).SalA	Yellow	298md	6.2	39.35 (39.47)	2.36 (2.47)	2.76 (2.88)	41.79 (42.02)

Salicylic acid is a colourless solid, insoluble in cold water but dissolves in hot water, ethanol and ether. The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc; but sparingly soluble in non-polar solvents, viz., chloroform, *n*-hexane, benzene, dioxane etc.

**Molar Conductance :** Molar conductance of all the compounds were measured in methanol at 27°C at a concentration of  $10^{-3}$  M. The values are given in Table - 1. The value of about  $35 - 40 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1}$  appears and characteristics of 1 : 1 electrolyte [9] whereas ideally molar conductance of a neutral compounds should be zero. However, significantly low values (6.2 - 10.5) of molar conductance of the compounds indicate them to be non-electrolyte.

#### Infrared spectra :

Infrared measurements for the ligand (salicylic acid) and its hitherto unknown mixed ligand complexes were made between  $4000 - 400 \text{ cm}^{-1}$  in KBr disc with the help of JASCO-FTIR spectrophotometer model – 5300. Pertinent infrared spectral data for these compounds are shown in Table 2.

**Table 2. Pertinent IR data for ligand (acetylsalicylic acid) & its mixed ligand Tl(I) complexes**

Compound	$\nu_{\text{O-H/O-H...O}}$	$\text{sym}\nu_{\text{COO}^-}$	$\text{asym}\nu_{\text{COO}^-}$	$\nu_{\text{CO(phenolic)}}$	$\nu_{\text{M-O/M-N}}$
Salicylic acid (SalA)	3240, 2596	1483	1660	1330	---
Tl(ONP).SalA	3468, 1830	1448	1607	1314	650, 563, 455
Tl(DNP).SalA	3276	1470	1602	1346	636, 575, 510, 485
Tl(TNP).SalA	3305	1466	1535	1337	635, 585, 530, 471
Tl(1N2N).SalA	3405	1459	1592	1348	668, 564
Tl(8HQ).SalA	3408	1485	1595	1382	668, 602, 561, 497

The broad band at  $3240\text{ cm}^{-1}$  in the spectra of the ligand point to intramolecular hydrogen bonding in it.

In the spectra of the mixed ligand complexes, broad bands appear in the region  $3276 - 3408\text{ cm}^{-1}$ . The shifting of the band in the above region indicates presence of hydrogen bonding in the complexes. Further, the free salicylic acid gave hydrogen bonded O-H stretching band at  $2596\text{ cm}^{-1}$ . The strong band at  $1330\text{ cm}^{-1}$  in the ligand clearly shows the presence of C-O (phenolic) in the ligand. In the complexes, this band shows a higher shift of  $13 - 52\text{ cm}^{-1}$ . This fact indicates the involvement of phenolic oxygen in complex formation.

The antisymmetric stretching frequency of  $\text{COO}^-$  group ( $1660\text{ cm}^{-1}$ ) in the ligand has been shifted in the region  $1592 - 1607\text{ cm}^{-1}$ . The symmetric stretching frequency of  $\text{COO}^-$  group observed at  $1483\text{ cm}^{-1}$  in the ligand. But in the complexes lower shift of  $13 - 27\text{ cm}^{-1}$  have been observed. The above information suggests the involvement of oxygen atom of  $-\text{COOH}$  group in the complex formation with Tl(I) metal ion.

The bands in the region  $485 - 564\text{ cm}^{-1}$  in the spectra of all mixed ligand complexes may be assigned to M - O band frequency while medium bands in the region  $575 - 668\text{ cm}^{-1}$  is assigned to M - N band frequency [10]. These bands are not present in the ligand. These assignments are based on the assumption [11] that since oxygen atom is more electronegative than nitrogen, the M - O bond tends to be more ionic than the M - N bond. Consequently M - O vibrations are expected to appear at lower frequencies. The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of nitroso (in case of 1N2N) or nitro (in case of ONP, DNP, TNP) or pyridine ring (in case of 8HQ) to metal in all the mixed ligand complexes.

**Electronic spectra :** Electronic spectra were recorded on Perkin Elmer Lambda 15 UV-VIS spectrophotometer in methanol. The bands observed in electronic spectra of the mixed ligand complexes of Tl(I) are given in Table - 3.

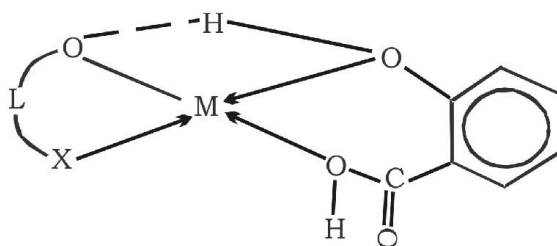
**Table 3. Major diffuse reflectance bands(in nm) for mixed ligand Tl(I) complexes with salicylic acid(SalA)**

Compound	Diffuse reflectance ( in nm)
Tl(ONP) <sub>2</sub> .SalA	658
Tl(DNP) <sub>2</sub> .SalA	657
Tl(1N2N) <sub>2</sub> .SalA	654
Tl(8HQ) <sub>2</sub> .SalA	651

On electronic spectra of the mixed ligand complexes show a charge transfer band at 651 - 658 nm. The charge transfer bands in the complexes show that there is a  $\pi$ -interaction between metal and ligand orbitals.

## STRUCTURE & BONDING

On the basis of quantitative analysis, IR, UV-VIS spectral data and conductivity measurements suggest the probable structure for these complexes (Fig.1).



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

Fig. 1

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