

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

**BIRENDRA KUMAR, MANORANJAN MISHRA**

*P. G. Deptt. of Chemistry, Maharaja College, Ara – 802 301(INDIA)*

**AND**

**ASHOK KR. GUPTA, SALINI PRIYA**

*Deptt. of Chemistry, Sri Arvind Mahila College, Patna – 800 004 (INDIA)*

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Some noble mixed ligand complexes of Tl(I) metal chelates of different organic acids with acetylsalicylic acid of general formulae  $ML_n \cdot HL'$ , 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);  $HL' =$  acetylsalicylic acid have been synthesized by refluxing appropriate reagents in absolute ethanol. The newly synthesized complexes were characterized by elemental analysis, conductivity measurements, infrared and electronic absorption spectral data. The infrared spectral data suggest the coordination sites through the oxygen atom of  $-OH$  (phenolic) &  $-COOH$  (carboxyl) groups.

### **INTRODUCTION**

Acetylsalicylic acid (Aspirin) has pharmaceutical and analytical importances [1]. Banerjee *et al* [2] reported the synthesise of mixed ligand complexes with some acid salts with acetylsalicylic acid. Mixed ligand complexes of Rb(I) & Cs(I) with acetylsalicylic acid have been studied by Tiwari *et al* [3]. Prakash *et al* [4] synthesized and characterized some new mixed ligand Sn(II) & Pb(II) complexes. But literature survey revealed that no mixed ligand complexes of Tl(I) metal salts of some organic acids with acetylsalicylic acid have till been reported. Keeping this in mind and with a view to study more fully stereochemistry of Tl(I) metal complexes and their stability in aqueous and non-aqueous media. We have synthesized and characterized a number of Tl(I) complexes with above mentioned ligand.

### **EXPERIMENTAL**

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline (8HQ) and acetylsalicylic 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 (acetylsalicylic 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.

## RESULT & DISCUSSION

**S**ome physical properties of the ligand (HL') and the new mixed ligand complexes (ML.HL') are listed in Table 1.

Table 1

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
Acetylsalicylic acid (AcSalA)	Colourless	135 m	---	---	---	---	
$Tl(ONP).AcSalA$	Yellowish brown	>300	7.2	37.78 (37.94)	2.41 (2.53)	2.85 (2.95)	42.89 (43.08)
$Tl(DNP).AcSalA$	Pale cream	127m	9.5	31.62 (31.72)	1.80 (1.94)	4.81 (4.93)	35.83 (36.02)
$Tl(TNP).AcSalA$	Deep yellow	152m	8.0	29.28 (29.39)	1.55 (1.63)	6.78 (6.86)	33.17 (33.38)
$Tl(1N2N).AcSalA$	Deep brown	180md	10.2	40.84 (40.98)	2.35 (2.52)	2.41 (2.52)	36.56 (36.74)
$Tl(8HQ).AcSalA$	Light yellow	208m	6.5	40.75 (40.88)	2.56 (2.65)	2.50 (2.65)	38.51 (38.68)

Acetylsalicylic acid is a colourless solid, insoluble in cold water but soluble in hot water, ethanol and ether. It sublimes below its melting point and it is steam volatile.

The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvent like the methanol, ethanol, partly soluble in DMF, pyridine, acetone etc; but they are sparingly soluble in non-polar solvents, *e.g.* chloroform, *n*-hexane, benzene etc.

From Table-1, it is evident that most of complexes undergo a transformation at a higher temperature than the melting point of second ligand (acetylsalicylic acid), indicating their greater stability..

**Molar Conductance :** Molar conductance of all the compounds was 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  $ohm^{-1}cm^2mole^{-1}$  appears and characteristics of 1 : 1 electrolyte [5] 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 or covalent nature.

#### Infrared spectra :

Infrared spectra of the ligand (acetylsalicylic acid) and its hitherto unknown complexes were recorded in the region 4000-400  $\text{cm}^{-1}$  in KBr disc with the help of JASCO-FTIR spectrometer model 5300. The pertinent infrared data are listed in Table - 2.

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

Compound	$\nu_{\text{O-H/O-H...O}}$	$\text{sym}\nu_{\text{COO}^-}$	$\text{asym}\nu_{\text{COO}^-}$	$\nu_{\text{CO(phenolic)}}$	$\nu_{\text{M-O/M-N}}$
Acetylsalicylic acid (AcSalA)	3300 - 3100	1485	1680	1325	---
Tl(ONP).AcSalA	3397	1460	1742, 1598	1387, 1349	666, 531
Tl(DNP).AcSalA	3395	1464	1597, 1580	1390, 1316	666, 531, 490
Tl(TNP).AcSalA	3399	1461	1599, 1596	1376, 1325	626, 571, 525
Tl(1N2N).AcSalA	3409	1460	1597	1385, 1351	669, 626, 581, 480
Tl(8HQ).AcSalA	3405	1462	1585	1384, 1341	667, 578, 482

In infrared spectra of the ligand (AcSalA), a broad band of medium intensity appear in the region 3300-2400  $\text{cm}^{-1}$ , which indicates the intramolecular hydrogen bonding in the ligand. Bands in the region 3300-3100  $\text{cm}^{-1}$  show a higher shift of 90-140  $\text{cm}^{-1}$  in the infrared spectra of complexes, indicate presence of hydrogen bonding in the complexes.

The C-O (phenolic) stretching frequency appears at 1325  $\text{cm}^{-1}$  in the ligand which show a higher shift to 25-55  $\text{cm}^{-1}$  in the infrared spectra of mixed ligand complexes. The observation clearly indicate the mode of coordination of ligand (AcSalA) through oxygen atom of phenolic group with Tl(I) metal ion.

Secondly a sharp band at 1680  $\text{cm}^{-1}$ , in the ligand suggests the presence of antisym  $\text{COO}^-$  stretching frequency. On complexation, the spectra of mixed ligand complexes show negative shift of 79-100  $\text{cm}^{-1}$ . The symmetric  $\text{COO}^-$  stretching band at 1485  $\text{cm}^{-1}$  in the ligand has been shifted at region 1460-1464  $\text{cm}^{-1}$ . The above information indicate the coordination of Tl(I) metal ion through oxygen atom of  $\text{COOH}^-$  group.

The band in the region 480-537  $\text{cm}^{-1}$  in the spectra of all mixed ligand complexes may be assigned to M-O band frequency while medium bands in the region 574 – 669  $\text{cm}^{-1}$  is assigned to M-N band frequency [6]. These bands are absent in the second ligand, acetylsalicylic acid. These assignments are based on the assumption [7] 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  $-\text{NO}/-\text{NO}_2/ -\text{NH}_2$  group/quinoline ring 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 Perkin Elmer Lambda 15 UV-VIS spectrophotometer in methanol. The bands observed in electronic absorption spectra of the mixed ligand

complexes of Sn(II) & Pb(II) are given in Table - 3. Electronic absorption band observed at 484 nm in  $Tl(ONP)_2 \cdot AcSalA$  and 429 - 403 nm in  $Tl(DNP)_2 \cdot AcSalA$ . which indicates  $\pi-\pi^*$  transitions in aromatic ring.

Electronic spectra of the mixed ligand complexes show a charge transfer at 651-653 nm.

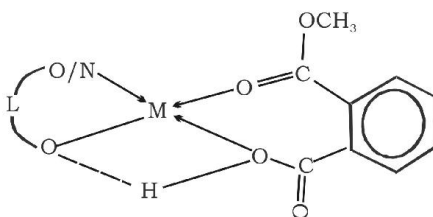
The shift in position of  $\pi-\pi^*$  and charge transfer bands of the ligand in the complexes show that there is a  $\pi$ -interaction between metal and ligand orbitals.

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

Compound	Diffuse reflectance ( in nm)
$Tl(ONP)_2 \cdot AcSalA$	658, 481
$Tl(8HQ)_2 \cdot AcSalA$	657
$Tl(DNP)_2 \cdot AcSalA$	652, 429, 427, 412, 408
$Tl(1N2N)_2 \cdot AcSalA$	658

## STRUCTURE & BONDING

On the basis of elemental analysis, the molecular formula of the mixed ligand complexes is found to be  $ML \cdot HL'$ , where  $M = Tl(I)$ ;  $L =$  deprotonated ONP, DNP, TNP, 8HQ or 1N2N;  $HL' =$  acetylsalicylic acid. Infrared and electronic absorption spectral studies revealed following structures for the complexes :



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

Fig. 1

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