

MIXED LIGAND COMPLEXES OF THALLIUM (I) METAL CHELATES OF SOME ORGANIC ACIDS WITH N-PHENYLANTHRANILIC ACID

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RECEIVED : 15 October, 2015

A number of mixed ligand thallium (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), 8-hydroxyquinoline (8HQ) or o-nitro-benzoic acid (ONBA); $HL =$ N-phenylanthranilic acid (NPAA) have been synthesized. On the basis of various physico-chemical investigations, it has been found that N-phenylanthranilic acid behaves as monoprotic bidentate ligand coordinating through oxygen atom of $-COOH$ group and nitrogen atom of $-NH_2$ group.

KEYWORDS : Mixed ligand complexes, N-phenylanthranilic acid, Thallium (I) metal chelates, Electronic absorption spectra.

INTRODUCTION

N-phenylanthranilic acid (NPAA) or Fenamic acid is a molecule which serves as a parent structure for several non-steroidal anti-inflammatory drugs, including mefenamic acid, tolfenamic acid, flufenamic and meclofenamic acid. Attali *et. al.* [1] have invented derivatives of it which is used as potassium channel &/or cortical neutron activity modulators. Ros *et al* [2] have synthesized the complexes of rhodium with NPAA and their structure was investigated by IR spectra. Yan *et. al.* [3] have studied the thermal decomposition and mechanism of lanthanide complexes with NPAA. Mixed ligand alkali metal complexes with NPAA as secondary ligand have been investigated by Banerjee *et. al.* [4]. Barai *et. al.* [5, 6] have studied mixed ligand complexes of Tl (I) chelates of some organic acids with anthranilic acid & hippuric acid. In continuation, we report the synthesis of mixed ligand complexes of Tl(I) metal chelates of some organic acids with N-phenylanthranilic acid.

EXPERIMENTAL

O-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ) or o-nitro-benzoic acid (ONBA) and N-phenylanthranilic acid (NPAA) of AnalaR grade were used as such.

Table 1

27/C015

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
N-phenylanthranilic acid (NPAA)	White	184m	---	---	---	---	
Tl(ONP).NPAA	Pale yellow	275d	10.0	40.95 (41.05)	2.62 (2.70)	4.95 (5.04)	36.68 (36.80)
Tl(DNP).NPAA	Pale yellow	260d	9.5	37.90 (37.97)	2.25 (2.33)	6.86 (6.99)	33.98 (34.04)
Tl(TNP).NPAA	Pale yellow	265d	6.0	35.25 (35.33)	1.95 (2.01)	8.62 (8.68)	31.52 (31.67)
Tl(1N2N).NPAA	Yellowish green	280d	11.0	46.73 (46.83)	2.82 (2.88)	4.67 (4.75)	34.62 (34.68)
Tl(8HQ).NPAA	Yellowish green	285d	6.5	46.92 (47.02)	2.95 (3.03)	4.89 (4.99)	36.35 (36.47)
Tl(ONBA).NPAA	Bottle green	290d	7.8	46.02 (46.14)	2.54 (2.57)	4.71 (4.80)	34.91 (35.03)

Table 2. Pertinent IR data for ligand(N-phenylanthranilic acid) & its mixed ligand Tl(I) complexes

Compound	ν_{N-H}	δ_{asymNH_2}	$\nu_{asymCOO^-}$	δ_{symNH_2}	ν_{symCOO^-}	δ_{COO^-}	$\nu_{M-O/M-N}$
N-phenylanthranilic acid (NPAA)	3336	1665	1590	1516	1438	697, 668	---
Tl(ONP).NPAA	3291	1690	1613	1545, 1508, 1476	1417	669	578, 525, 492
Tl(DNP).NPAA	3445	1680	1613, 1564	1509	1418	670	589, 500, 475
Tl(TNP).NPAA	3335	1658	1576	1512	1435	670	529, 496
Tl(1N2N).NPAA	3305	1689, 1653	1580	1532, 1499, 1462	1421	670	572, 512, 486
Tl(8HQ).NPAA	3240	1683, 1647	1578	1509, 1450	1388	670	580, 520, 480
Tl(ONBA).NPAA	3446	1695, 1639	1598, 1577	1530, 1505	1395	669	580, 501, 472

Preparation of Tl(I) metal chelates :

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 chelate 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 (N-phenylanthranilic 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 ligand (N-phenylanthranilic acid) and the mixed ligand complexes (ML.HL') obtained are listed in Table -1.

N-phenylanthranilic acid is a white crystalline solid, highly soluble in water, ethanol etc., sparingly soluble in ether, chloroform, benzene etc. and insoluble in CS₂, petroleum ether. The mixed ligand complexes are of characteristic colours. They are appreciably soluble in polar solvents like water, 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 33°C at a concentration of 10⁻³ M. The values are given in Table -1. The value of about 35-40 ohm⁻¹cm²mole⁻¹ is characteristic of 1 : 1 electrolyte [7] whereas ideally molar conductance of neutral compound should be zero. However, significantly low values (6.0 - 11.0) of molar conductance of the compounds indicate them to be covalent nature.

Infrared Spectra : Infrared spectral measurements were made in PERKIN-ELMER Spectrum RX1 for the ligand (N-phenylanthranilic acid) and mixed ligand Tl (I) complexes between 4000-450 cm⁻¹ in KBr-phase. Selected absorption bands are given in Table 2.

N-phenylanthranilic acid is an aromatic amino acid and aromatic amino acids are not zwitter ions. It contains 2° - amino group. Secondary amines display a single weak absorption bands in the region 3350-3310 cm⁻¹. This band represents the free N—H stretching modes.

The spectrum of the ligand shows a weak poorly resolved absorption bands at 3336 cm⁻¹ which is extended by combination band at the region of 2357 cm⁻¹. This band may be due to N-H stretching modes.

In the mixed ligand complexes, the —NH stretching band appear in the region of 3446-3239 cm⁻¹. The shifting of this band suggests the coordination of the —NH₂ group to the tin or lead metal.

The spectra of the ligand show several bands between 2857-2500 cm⁻¹. These bands may be due to the presence of H-bonded —COOH group. But in the spectra of mixed ligand complexes, these bands are found to be absent indicating the absence of H-bonding.

The strong band at 1589 cm⁻¹ in the spectrum of the ligand is in all probably due to the asymmetric —COO⁻ stretching vibration. In the mixed ligand complexes, this band appears in the region 1615 - 1557 cm⁻¹. The general shifting of the band to higher frequency by upto 26 cm⁻¹; suggest the interaction of oxygen atom of —COOH group with the metal atoms. Since the —COOH group becomes more asymmetrical as the M—O interaction become stronger. The other bands below 1589 cm⁻¹ may be appeared due to the presence of the functional groups of the first ligand.

The weak band at 1433 cm⁻¹, in the spectrum of the ligand represents symmetric —COO⁻ stretching vibration. In the mixed ligand complexes, this band appear in the region 1435-1363 cm⁻¹. The shifting of this band to a lower frequency clearly indicates the involve-ment of —COOH group of the ligand in complex formation and coordination of Sn(II) or Pb(II) metal ion through oxygen atom of —COOH group of the ligand.

The strong band between 696-668 cm^{-1} in the spectrum of the ligand may be due to $-\text{COO}^-$ bending vibration. These bands appear in the region of 706-663 cm^{-1} in the mixed ligand complexes. There is no appreciable shifting of the band frequency which suggests that $-\text{COO}^-$ bending vibration is not metal sensitive.

A weak asymmetrical N-H bending band in the spectra of the ligand appears at 1665 cm^{-1} . In the mixed ligand complexes, this band appears in the region 1694-1633 cm^{-1} . The fairly strong symmetrical N—H bending band in the spectrum of the ligand appears in the region 1515-1482 cm^{-1} . In the mixed ligand complexes, this band appears in the region 1544–1450 cm^{-1} . The general shifting of these bands indicates the M—N interaction and these bands are metal sensitive.

The band in the region 589-462 cm^{-1} in the spectra of all mixed ligand complexes may be assigned to M—O/M—N band frequency [8, 9]. 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 (N-phenylanthranilic acid) and the mixed ligand complexes of Tl(I) are given in Table - 3.

The ligand (NPAA) exhibits sharp intense bands at 242 nm & 275 nm, These bands indicate $\pi-\pi^*$ transition as well as charge transfer in aromatic ring.

Table 3. Major diffuse reflectance bands (in nm) for mixed ligand complexes of Tl(I) with N-phenylanthranilic acid (NPAA)

Compound	Diffuse reflectance (in nm)
N-phenylanthranilic acid (NPAA)	242, 275
Tl(ONP).NPAA	226, 347, 402
Tl(DNP).NPAA	222, 344, 389
Tl(TNP).NPAA	232, 344, 386
Tl(1N2N).NPAA	238, 344, 382
Tl(8HQ).NPAA	235, 347, 392
Tl(ONBA).NPAA	226, 350, 430

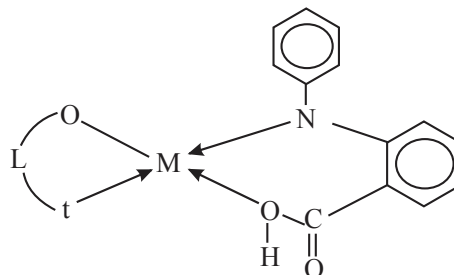
The electronic spectra of the mixed ligand complexes show bands in the region 219-350 nm, which indicate $\pi-\pi^*$ transition in the complexes. The mixed ligand complexes also show charge transfer bands in the region 376-430 nm.

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

STRUCTURE & BONDING

On the basis of quantitative analysis, the molecular formula of the mixed ligand complexes of Tl (I) metal chelates of some organic acids with N-phenylanthranilic acid is found to be $\text{ML.HL}'$, where $\text{M} = \text{Tl (I)}$, $\text{L} =$ deprotonated ONP, DNP, TNP, 1N2N, 8HQ or ONBA; $\text{HL}' =$ N-phenylanthranilic acid. IR data suggest that the Tl(I) metal replaces the H-atom of the hydroxyl group and through the N/O of the $-\text{NO}_2/-\text{NO}$ of the first ligand. The Tl(II) metal chelates thus formed combine with second ligand (N-phenyl-anthranilic acid)

through the O-atom of carboxyl and N-atom of amine groups giving a six membered chelate. Probable structures of the complexes are shown in Fig. 1.



where M = Sn(II) or Pb(II); L = deprotonated ONP, DNP, TNP or 1N2N; X = O or N

(Fig. 1)

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