

MIXED LIGAND COMPLEXES OF THALLIUM(I) METAL CHELATES OF SOME ORGANIC ACIDS WITH ANTHRANILIC ACID

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Some new mixed ligand complexes of Thallium (I) metal chelates of different organic acids of general formula $ML.HL'$, where $M = Tl(I)$, $L = o$ -nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (1N2N) or o -nitrobenzoic acid (ONBA) and $HL' =$ Anthranilic acid have been synthesized and characterized by elemental analysis, molar conductance measurements, infrared and electronic spectral studies. On the basis of spectral studies, probable structures of the complexes have been proposed.

KEYWORDS : Mixed ligand complex, Anthranilic acid, Silver(I) metal chelate, Infrared spectra

INTRODUCTION

Amino acids play an important role in the metabolism of animal life and they form the units from which proteins are built. Anthranilic acid is used as an intermediate for production of dyes, pigments, and saccharin. It and its esters are used in preparing perfumes to imitate jasmine and orange, pharmaceuticals (loop diuretic, *e.g.*, furosemide) and UV-absorber as well as corrosion inhibitors for metals and mold inhibitors in soya sauce.

Thallium salts and complexes have been widely used in analytical laboratories, as powerful bacteriocides, and efficient catalyst in organic reactions [1, 2]. Literature survey [3-11], revealed that Tl(I) either received very little attention or have neglected towards its coordination behaviour. Realising these facts we propose to synthesise some mixed ligand Tl(I) complexes with various potential ligands containing hard atoms nitrogen and oxygen in order to study their stability in aqueous and non-aqueous media as well as their stereochemistry.

EXPERIMENTAL

Analar quality of ONP, DNP, TNP, 8HQ, 1N2N, ONBA and Anthranilic acid were used for the preparation of Thallium(I) metal chelates and adducts.

Preparation of Thallium(I) metal chelates :

Organic acid and sodium hydroxide were taken in 1 : 1 molar ratio in a clean and dry conical flask, and refluxed in 90% ethanol 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 90% ethanol and dried in an electric oven at 100°C.

Again sodium salt of organic acid was dissolved in 90% ethanol and an alcoholic solution of TlCl were mixed in 1 : 1 molar proportion. The mixture was refluxed on hot plate of magnetic stirrer at 60-70°C about half an hour, when coloured precipitate of Tl(I) metal chelate of organic acid was obtained. The precipitate was filtered, washed with 90% ethanol and dried in an electric oven at 100°C.

Preparation of Mixed ligand complexes : A suspension of Thallium(I) metal chelate of organic acid(ML) in absolute ethanol was taken in a conical flask and then second ligand (anthranilic acid) was added in 1 : 1 molar proportion. The mixture was stirred till all the solids went into solution. The contents were warmed with constant stirring at 80°C for about two hours, but in few cases the complexation completed within an hour. On cooling the resulting solution, the characteristic colour adduct separated which was filtered, washed with absolute ethanol with small amount of water and dried in an electric oven at 100°C.

RESULTS & DISCUSSION

Physical properties : Some physical properties and analytical data of the ligand-(Anthranilic acid) and the mixed ligand Tl(I) complexes are listed in Table -1.

Table - 1

Compound	Colour	M.P./ Decomp. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	Tl
Hippuric acid (HA)	White	232m	---	---	---	---	---
Tl(ONP).HA	Pale yellow	270d	10.0	34.45 (34.52)	2.42 (2.49)	5.29 (5.37)	39.05 (39.20)
Tl(DNP).HA	Pale yellow	215d	9.8	31.65 (31.78)	2.02 (2.12)	7.29 (7.41)	5.95 (36.08)
Tl(TNP).HA	Pale yellow	245md	10.5	29.35 (29.44)	1.72 (1.80)	9.09 (9.16)	33.35 (33.43)
Tl(1N2N).HA	Orange	210md	9.0	37.35 (37.45)	2.62 (2.70)	4.95 (5.04)	36.68 (36.80)
Tl(8HQ).HA	Light green	200md	8.5	40.85 (40.96)	2.76 (2.84)	5.24 (5.31)	38.65 (38.75)
Tl(ONBA).HA	Light brown	280d	7.0	34.85 (34.95)	2.32 (2.36)	4.96 (5.09)	37.05 (37.20)

Anthranilic acid is a white crystalline solid, highly soluble in water, ethanol but sparingly soluble in ether, chloroform and benzene but insoluble in CS₂ and petroleum ether. The mixed ligand complexes are generally coloured. 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 and dioxane. The complexes are stable under dry conditions. From Table-1, it is evident that most of complexes undergo a transformation at a higher temperature than the melting point of first ligand (Anthranilic acid), indicating their greater stability.

Molar conductance : Molar conductances of all the compounds were measured in methanol at 30°C at a concentration of 10^{-3} M with the help of Systronics Digital Direct Reading Conductivity Meter - 304. The values are given in Table - 1. The significantly low values ($5.8 - 11.0 \text{ ohm}^{-1}\text{cm}^2 \text{mole}^{-1}$) of molar conductance of the compounds indicate them to be non-electrolyte.

Infrared spectra : Infrared spectral measurements were made in PERKIN-ELMER Spectrum RX1 for the ligand (anthranilic acid) and its mixed ligand Tl(I) complexes between $4000 - 450 \text{ cm}^{-1}$ in KBr -phase, Selected absorption bands in different regions are given in Table-2.

Table 2. Pertinent infrared data bands for anthranilic acid & its mixed ligand Tl(I) complexes

Compound	$\nu_{\text{N-H}}$	$\delta_{\text{asv}}(\text{NH}_2)$	$\nu_{\text{asv}}(\text{COO}^-)$	$\delta_{\text{sym}}(\text{NH}_2)$	$\nu_{\text{sym}}(\text{COO}^-)$	δCOO^-	$\nu_{\text{M-O/M-N}}$
Anthranilic acid (AnthA)	3472, 3374, 3324	1669	1589, 1564	1531, 1485	1445, 1417	668	—
Tl(ONP).AnthA	3429, 3375, 3345	1684	1615, 1579	1519, 1495	1453	669	550, 524, 470
Tl(DNP).AnthA	3446, 3318	1630	1601, 1560	1522	1479, 1418	669	590, 529, 489
Tl(TNP).AnthA	3425, 3145	1634	1553	1511	1427	670	530, 490
Tl(1N2N).AnthA	3439, 3316, 3277	1697	1610, 1560	1517	1416	670	565, 520, 480
Tl(8HQ).AnthA	3390	1635	1598, 1571	1528, 1510	1472	673	530, 475
Tl(ONBA).AnthA	3444, 3375, 3143	1640	1598, 1576	1505	1426	670	595, 501, 475

Anthranilic acid is an aromatic amino acid and aromatic amino acids are not zwitter ions. It contains primary amino group. Primary amines display two weak absorption bands, one near 3500 cm^{-1} and the other near 3400 cm^{-1} . These bands represent respectively the free asymmetrical and symmetrical N-H stretching modes [12].

The spectrum of the anthranilic acid shows three medium, well resolved absorption bands at $3472, 3374$ & 3323 cm^{-1} . These bands may be due to asym. & sym. N-H stretching modes which is extended by combination band at the region $2401 - 2361 \text{ cm}^{-1}$.

In the mixed ligand complexes, two medium or weak absorption bands: one near $3454 - 3418 \text{ cm}^{-1}$ and the other below 3400 ($3395 - 3159$) cm^{-1} are observed. These bands represent respectively the free asym. and sym. N-H stretching modes. The shift of the absorption range of N-H has been observed in the thallium metal anthranilates which might be due to coordination of $-\text{NH}_2$ group to the thallium metal. The spectra of the ligand show several bands between $3240-2511 \text{ cm}^{-1}$. These bands may be due to the presence of H-bonded $-\text{COOH}$ group. But in the spectra of the mixed ligand complexes of the anthranilic acid, these bands are found to be absent indicating the absence of H-bonding.

The strong bands between $1588 - 1564 \text{ cm}^{-1}$ in the spectra of ligand is in all probably due to the asymmetric $-\text{COO}^-$ stretching vibration. The weak bands between $1441 - 1416 \text{ cm}^{-1}$, represents symmetric $-\text{COO}^-$ stretching vibration. In the mixed ligand complexes, the $\nu_{\text{as}(\text{COO}^-)}$ band appear in the region $1620 - 1597 \text{ cm}^{-1}$ and the $\nu_{\text{s}(\text{COO}^-)}$ band appear in the region $1465-$

1371 cm^{-1} . The general shifting of the $\nu_{\text{as}(\text{COO}^-)}$ band to higher frequency and $\nu_{\text{s}(\text{COO}^-)}$ band to lower frequency clearly indicates the involvement of $-\text{COOH}$ group of the ligand in complex formation and coordination of Tl(I) ion through oxygen atom of $-\text{COOH}$ group of the ligand (anthranilic acid).

The strong band at 667 cm^{-1} in the spectra of the ligand may be due to $-\text{COO}^-$ bending vibration. In the complexes this band appears in the region of 670 - 668 cm^{-1} . The shifting of this band by a very low frequency suggests that $-\text{COO}^-$ bending vibration is not metal sensitive.

A weak asymmetrical N-H bending band in the spectra of the ligand (anthranilic acid) appears at 1669 cm^{-1} . In the mixed ligand complexes this band appears in the region 1697 - 1634 cm^{-1} . The fairly strong symmetrical ($-\text{NH}_2$) N-H bending bands in the spectra of ligand appear at 1536 and 1484 cm^{-1} . In the mixed ligand complexes this band appears in the region 1540 - 1469 cm^{-1} . The shifting of these bands indicates the metal - nitrogen interaction and these bands are metal sensitive.

In all the mixed ligand complexes, the bands with medium to strong absorption in the far infrared region 591 - 540 cm^{-1} and 525 - 446 cm^{-1} are tentatively assigned to M-O and M-N modes [13, 14].

Electronic spectra : Electronic spectra were recorded on Systronic Double Beam Spectrophotometer - 2201 in methanol. The bands observed in electronic spectra of the mixed ligand Tl(I) complexes are given in Table - 3.

Table – 3. Major diffuse reflectance bands (in nm) for mixed ligand complexes of Tl(I) with Anthranilic acid

Compound	Diffuse reflectance (in nm)
Anthranilic acid (AnthA)	280, 240
Tl(ONP).AnthA	248, 382
Tl(DNP).AnthA	254, 376
Tl(TNP).AnthA	267, 386
Tl(1N2N).AnthA	248, 382
Tl(ONBA).AnthA	242, 283, 376
Tl(8HQ).AnthA	248, 309

The electronic spectra of the mixed ligand Tl(I) complexes show bands at the region 242 - 309 nm which indicates $\pi-\pi^*$ transition in the complexes. Most of the mixed ligand complexes also show a charge transfer bands in the region 376 - 386 nm.

The shift in position of $\pi-\pi^*$ transition and charge transfer bands in the mixed ligand Tl(I) 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 thallium(I) complexes is found to be $\text{ML.HL}'$, where M = Tl(I), o-nitrophenol(ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol(1N2N) or o-nitrobenzoic acid(ONBA) and $\text{HL}' = \text{Anthranilic acid}$. Infrared spectra

indicate that the Tl(I) metal replaces the H-atom of the hydroxyl or carboxyl group and through the N/O-atom of the $-\text{NO}_2/-\text{NO}$ group or N-atom of quinoline ring of the first ligand(HL) forming two six membered chelates and the coordination of second ligand (anthranilic acid) through nitrogen atom of $-\text{NH}_2$ group and oxygen atom of $-\text{COOH}$ group with Tl(I) metal ion. The probable structure of the complexes is shown in Fig. 1.

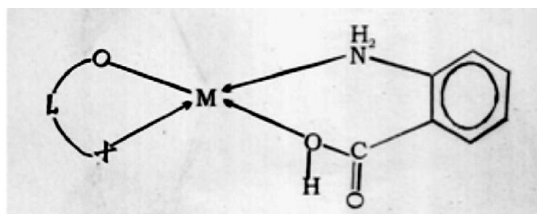


Fig. 1

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