

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

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Some nobel mixed ligand complexes of the general formula, ML.HL', where M = Tl (I); L = deprotonated o-nitrophenol (ONP), 2, 4-dinitro-phenol(DNP), 2, 4, 6-trinitro-phenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ) or o-nitrobenzoic acid (ONBA) and HL' = hippuric acid, have been synthesized, and characterized by elemental analysis, molar conductance measurements, infrared and electronic spectral studies. Their Infrared spectra suggest coordination of the hippuric acid with thallium metal through the nitrogen atoms of -NH₂(amino) group and oxygen atom of -COOH(carboxyl) group.

KEYWORDS : Mixed ligand complex, Hippuric acid, Silver(I) metal chelate, IR spectra

INTRODUCTION

Hippuric acid is an analogue of amino acid, glycine. High concentrations of hippuric acid can also indicate a toluene intoxication. It is excreted in small quantities in the urine of mammals as a means of elimination of the toxic benzoic acid and toluene [1]. Para-amino-hippuric acid (PAH), a derivative of hippuric acid, is a compound useful in medical tests involving the kidney [2]. Jankowski *et al* [3] characterise p-hydroxyhippuric acid as an inhibitor of Ca²⁺-ATPase in end-stage renal failure. The enzyme used for the Ca²⁺-ATPase assay system was isolated from red blood cells by crossflow filtration. The activity of the Ca²⁺-ATPase., Capllonch *et al* [4] studied the interactions of Zn(II), Cd(II) & Hg(II) with hippuric acid(hipH) and several novel compounds were synthesized and studied by NMR. Sadeek *et al* [5] have isolated hippurates of V(III), Cr(III) & Fe(III) as solids with the general formula; [V(hip)₃].15H₂O, [Cr(hip)₃].6H₂O & [Fe(hip)₃].1.5H₂O and characterized by elemental analysis, infrared, ¹H NMR, electronic spectra and thermogravimetric analysis. Rodríguez *et al* [6] have characterised the dimeric copper(II) complex of hippuric acid (Hhipp) of stoichiometry [Cu₂(hipp)₄-(H₂O)₄].2H₂O, thoroughly by means of its infrared,

Raman and electronic spectra, *Natarajan et al* [7] have prepared poly[triaquatri- μ -hippurato-hippuratodibarium] compound, $[\text{Ba}_2(\text{C}_9\text{H}_8\text{NO}_3)_4(\text{H}_2\text{O})_3]$. *Refat et al* [8] synthesised Mn(II), Au(III) & Zr(III) complexes with hippuric acid (N-benzoyl-glycine) and were characterised by elemental analysis, molar conductivity, magnetic measurements, spectral methods (mid-infrared, ^1H NMR, mass, X-ray powder diffraction and UV-Vis spectra) and simultaneous thermal analysis (TG and DTG) techniques.

In the light of above reports, we have synthesised and characterised mixed ligand complexes of thallium(I) metals with hippuric acid having general formula ML_2HL .

EXPERIMENTAL

Analar quality of o-nitrophenol(ONP), 2, 4-dinitro-phenol (DNP), 2, 4, 6-trinitro-phenol (TNP), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (1N2N), o-nitrobenzoic acid (ONBA) and hippuric 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 95% 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 95% 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 the 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 (Hippuric 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 1-2 hours. In the process of refluxing, the precipitation occurred immediately in the most of the cases. The characteristic coloured precipitate was filtered, washed with absolute ethanol and dried in an electric oven at 100°C.

RESULTS & DISCUSSION

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

Hippuric acid is a white crystalline solid, highly soluble in water, ethanol but sparingly soluble in ether, chloroform and benzene but insoluble in carbon disulphide 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 (Hippuric acid), indicating their greater stability.

Table - 1

Compound	Colour	M.P./ Decomp. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	TI
Hippuric acid (HA)	White	232m	---	---	---	---	---
TI(ONP).HA	Pale yellow	270d	10.0	34.45 (34.52)	2.42 (2.49)	5.29 (5.37)	39.05 (39.20)
TI(DNP).HA	Pale yellow	215d	9.8	31.65 (31.78)	2.02 (2.12)	7.29 (7.41)	35.95 (36.08)
TI(TNP).HA	Pale yellow	245md	10.5	29.35 (29.44)	1.72 (1.80)	9.09 (9.16)	33.35 (33.43)
TI(1N2N).HA	Orange	210md	9.0	37.35 (37.45)	2.62 (2.70)	4.95 (5.04)	36.68 (36.80)
l(8HQ).HA	Light green	200md	8.5	40.85 (40.96)	2.76 (2.84)	5.24 (5.31)	38.65 (38.75)
TI(ONBA).HA	Light brown	280d	7.0	34.85 (34.95)	2.32 (2.36)	4.96 (5.09)	37.05 (37.20)

Molar conductance : Molar conductances of all the compounds were measured in methanol at 32°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 ($7.0 - 10.5 \text{ ohm}^{-1}\text{cm}^2 \text{mole}^{-1}$) 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 TI(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 hippuric acid & its mixed ligand TI(I) complexes

Compound	$\nu_{\text{N-H}}$	$\delta_{\text{asv}}(\text{NH}_2)$	$\nu_{\text{asv}}(\text{COO}^-)$	$\delta_{\text{sym}}(\text{NH}_2)$	$\nu_{\text{sym}}(\text{COO}^-)$	δ_{COO^-}	$\nu_{\text{M-O/M-N}}$
Hippuric acid (HA)	3325, 3209	1665	1599	1528, 1482	1410	669	----
TI(DNP).HA	3426	1661	1609, 1560	1515, 1484	1418	669	560, 510, 470
TI(TNP).HA	3353	1630	1612, 1558	1510, 1480	1422	670	533, 490
TI(8HQ).HA	3300	1654	1608, 1578	1502, 1467	1424, 1382	670	570, 512, 470
TI(1N2N).HA	3309	1632	1574, 1517	1488	1417	670	588, 485
TI(ONBA).HA	3443	1637	1598, 1557	1504	1430	670	585, 502, 480

Hippuric acid is an aromatic amino acid and aromatic amino acids are not zwitterions [9]. It contains 2° -amino group. Secondary amines display a single weak absorption bands in the $3350-3310 \text{ cm}^{-1}$ region. This band represents the free N-H stretching modes [9].

The spectrum of the hippuric acid shows a weak poorly resolved absorption bands at 3325 cm^{-1} which is extended by combination band at the region of $2399 - 2356\text{ cm}^{-1}$. These bands may be due to N-H stretching modes.

In the mixed ligand complexes, the -NH stretching band appear in the region of $3406 - 3209\text{ cm}^{-1}$. The shifting of this band suggests the coordination of the -NH_2 group to the thallium metal.

The spectra of the ligand (hippuric acid) show several bands between $3209 - 2474\text{ cm}^{-1}$. These bands may be due to the presence of H-bonded -COOH group. But in the spectra of the mixed ligand complexes, these bands are found to be absent indicating the absence of H-bonding.

The strong band at 1599 cm^{-1} in the spectra of ligand is in all probably due to the asymmetric -COO^- stretching vibration. In the mixed ligand complexes, the bands appear in the region $1622 - 1551\text{ cm}^{-1}$. The general shifting of the bands suggest the interaction of O-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 1599 cm^{-1} may be appeared due to the presence of the functional groups of the first ligands.

The weak band at 1410 cm^{-1} , in the spectra of the ligand represents symmetric -COO^- stretching vibration. In the mixed ligand complexes, this band appears in the region $1430\text{-}1363\text{ cm}^{-1}$. The shifting of this band indicates the involvement of -COOH group of the ligand in complex formation and coordination of Tl(I) ion through O- atom of -COOH group of the ligand.

The strong band at 668 cm^{-1} , in the spectra of the ligand may be due to -COO^- bending vibration. This band appears in the region of $670\text{-}668\text{ cm}^{-1}$ in the mixed ligand complexes. There is no appreciable shifting of the band which suggests that -COO^- bending vibration is not metal sensitive.

A weak asymmetrical N-H bending band in the spectra of ligand appears at 1666 cm^{-1} . In the few mixed ligand complexes this band appears in the region $1697\text{-}1653\text{ cm}^{-1}$. The fairly strong symmetrical N-H bending band in the spectra of ligand appears in the region $1527\text{-}1482\text{ cm}^{-1}$. In the mixed ligand complexes this band appears in the region $1540\text{-}1459\text{ cm}^{-1}$. The shifting of these bands indicates the metal – nitrogen interaction and these bands are metal sensitive.

The bands in region $591\text{-}457\text{ cm}^{-1}$ in the spectra of all the mixed ligand complexes may be assigned to M-O/M-N band frequency [10].

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 Hippuric acid

Compound	Diffuse reflectance (in nm)
Hippuric acid (HA)	268, 245
Tl(ONP).HA	248, 392
Tl(DNP).HA	251, 386, 498
Tl(TNP).HA	264, 344, 395
Tl(1N2N).HA	254, 315
Tl(8HQ).HA	254, 344, 376
Tl(ONBA).HA	248

The electronic spectra of the mixed ligand Tl(I) complexes show bands in the region 248 - 344 nm which indicates π - π^* transition in the complexes. The mixed ligand complexes also show charge transfer bands in the region 376-395 nm.

The shift in position of π - π^* 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 complexes of Tl(I) metal chelates of some organic acids with hippuric acid is found to be $ML.HL'$, 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 $HL' =$ Hippuric 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 $-NO_2/-NO$ group or N-atom of quinoline ring of the first ligand (HL) forming a six membered chelate and the coordination of second ligand (hippuric acid) through nitrogen atom of $-NH_2$ group and oxygen atom of $-COOH$ group with Tl(I) metal ion forming a five membered chelate. The probable structure of the complexes is shown in Fig. 1.

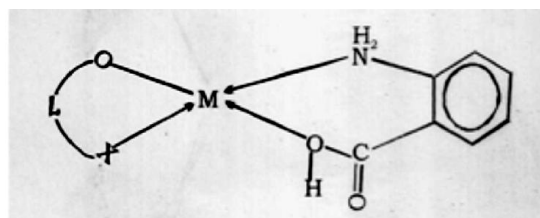


Fig. 1

REFERENCES

1. Costanzo, L., *Physiology*, 4th edn., Philadelphia Lippincott Williams & Wilkins, p.156 (2007)
2. American Psychosomatic Society, *Psychosomatic Medicine*, **14**, 34 (1952)
3. Jankowski, J., Tepel, M., Stephan, N., Vander Giet, M., Breden, V., Zidek, W. and Schluter, H., *Kidney International*, **59(78)**, 584 (2001).
4. Capllonch, M. C., Garca Raso, A., Terron, A., Apella, M.C., Espinosa, E. and Molins, E., *J. Inorg. Biochem.*, **85(2)**, 173 (2001)
5. Sadeek, S. A., Refat, M.S., Teleb, S.M. and El-Megharbel, S.M., *J. Mol. Str.*, **737(2-3)**, 139 (2005)
6. Rodriguez, M. I., Manca, S.G., Totaro, R.M. and Baran, E.J., *Acta Farm. Bonaerense*, **25(1)**, 71 (2006).
7. Natarajan, S., Dhas, S.A.M.B., Suresh, J. and Krishnakumar, R.V., *Acta Crystallographica*, Sec.E, **63(5)** (2007).
8. Refat, M.S., El-Korashy, S.A. and Ahmed, A. S. *Spectrochimica Acta*, Part A, **70**, 840 (2008).
9. Condrate, R. A. and Nakamoto, K., *J. Chem. Phys.*, **42**, 2590 (1965).
10. Shyamal, A. and Singhal, O. P., *Trans. Met. Chem.*, **4**, 179 (1979).

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