

MIXED LIGAND COMPLEXES OF Sn(II) & Pb(II) METAL CHELATES OF SOME ORGANIC ACID WITH HIPPURIC ACID

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Mixed ligand Sn(II) & Pb(II) complexes having general formula $ML_2.HL'$, where $M = Sn(II)$ or $Pb(II)$, $L =$ deprotonated o-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol(TNP) or 1-nitroso-2-naphthol (1N2N); $HL' =$ Hippuric acid (HA) have been synthesized and characterized. The structure of these complexes have been confirmed on the basis of chemical and spectral studies.

INTRODUCTION

Mixed ligand complexes of Sn(II) & Pb(II) are of analytical, biochemical and pharmaceutical importances [1-3]. Transition metal and alkali/alkaline earth metal complexes with hippuric acid have been well investigated earlier [4-10]. In the present paper, we report the synthesis of mixed ligand complexes of Sn(II) & Pb(II) metal chelates of some organic acids with Hippuric acid.

EXPERIMENTAL

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) and hippuric acid (HA) of AnalaR grade were used as such.

Preparation of metal chelates of Sn(II) and Pb(II) :

95% Ethanolic solution of 0.02 mole of organic acid and suspension of 0.01mole of dihydrated stannous chloride ($SnCl_2 \cdot 2H_2O$) or 0.01mole of lead acetate trihydrate in 95% ethanol were mixed. The mixture was refluxed on magnetic hot plate with constant stirring for 30-45 minutes. A clear solution was obtained which was made alkaline with ammonium hydroxide, characteristic colour chelate of tin (II) or lead (II) was separated. It was filtered, washed with solvent and finally dried in an electric oven at 80°C.

Preparation of mixed ligand complexes :

The suspension of Sn (II) or Pb (II) metal chelate of organic acid (ML_2) was mixed with the solution of hippuric acid in 1 : 1 (mole) in absolute ethanol. The mixture was refluxed on magnetic hot plate with constant stirring at 70-80°C for 2-3 hours and cooled. The

characteristic colour precipitate of adduct got separated. It was filtered, washed with absolute ethanol and finally dried in an electric oven at 80°C.

Table - 1

Compound	Colour	M.P./ Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
Hippuric acid (HA)	Colourless	232m	---	---	---	---	
Sn(ONP) ₂ .HA	Yellowish brown	>300	7.1	43.75 (43.90)	2.86 (2.93)	5.01 (5.12)	21.55 (21.71)
Sn(DNP) ₂ .HA	Pale cream	127 m	8.5	37.85 (37.97)	2.10 (2.26)	10.28 (10.54)	17.71 (17.88)
Sn(TNP) ₂ .HA	Pale yellow	303d	6.9	33.35 (33.43)	1.65 (1.72)	12.89 (13.00)	15.65 (15.75)
Sn(1N2N) ₂ .HA	Light brown	>300	8.0	54.18 (54.23)	3.69 (3.72)	6.49 (6.54)	18.36 (18.50)
Pb(ONP) ₂ .HA	Pale yellow	170 md	8.6	37.71 (37.78)	2.41 (2.52)	4.25 (4.41)	32.57 (32.62)
Pb(DNP) ₂ .HA	Pale rose	186 md	9.3	33.41 (33.50)	1.85 (1.99)	9.22 (9.31)	27.41 (27.54)
Pb(TNP) ₂ .HA	Deep yellow	152 m	9.8	29.85 (29.92)	1.47 (1.54)	11.49 (11.64)	24.45 (24.60)
Pb(1N2N) ₂ .HA	Deep brown	180 md	10.5	47.61 (47.66)	2.79 (2.87)	5.68 (5.75)	28.32 (28.37)

Table 2. Pertinent IR data for ligand (Hippuric acid) & its mixed ligand Sn (II) & Pb (II) complexes

Compound	ν_{N-H}	δ_{asymNH_2}	$\nu_{asymCOO^-}$	δ_{symNH_2}	ν_{symCOO^-}	δ_{COO^-}	$\nu_{M-O/M-N}$
Hippuric acid(HA)	3325, 3209	1665	1599	1528, 1482	1410	669	---
Sn(TNP) ₂ .HA	3443	1637	1598, 1557	1504, 1480	1431	671	585, 505, 485
Sn(1N2N) ₂ .HA	3300	1660	1610, 1570	1502, 1467	1429, 1381	670	575, 511, 472
Pb(ONP) ₂ .HA	3439	1639	1598, 1565	1515, 1504	1415, 1400	670	535, 502, 485
Pb(DNP) ₂ .HA	3425	1662	1608, 1575	1516, 1481	1414	670	559, 509, 472

RESULTS & DISCUSSION

Some physical properties of the second ligand (Hippuric acid) and the mixed ligand complexes (ML₂.HL') obtained are listed in Table-1.

Hippuric acid is a white crystalline solid, highly soluble in cold water, ethanol, sparingly soluble in ether, chloroform and benzene but insoluble in CS₂ and petroleum ether. The mixed ligand complexes are of characteristic colours. They are appreciably soluble in polar solvents like 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 27°C at a concentration of 10⁻³ M. The values are given in Table-1. The value of about 35-40 ohm⁻¹ cm² mole⁻¹ is characteristic of 1 : 1 electrolyte [11] whereas ideally molar conductance of a neutral compounds should be zero. However significantly low values (7.1-10.5) of molar conductance of the compounds indicate them to be covalent nature.

Infrared Spectra : Infrared spectra of the ligand (Hippuric acid) and mixed ligand complexes of Sn (II) & Pb (II) were recorded in KBr phase between 4000-400 cm^{-1} with the help of PERKIN-ELMER Spectrum RX1 spectrophotometer. Selected absorption bands are shown in Table-2.

Hippuric 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 [12]. The spectrum of the ligand shows a weak poorly resolved absorption bands at 3325 cm^{-1} which is extended by combination band at the region of 2399-2356 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 3439-3300 cm^{-1} . The shifting of this band suggests the coordination of the $-\text{NH}_2$ group to the tin or lead metal.

The spectrum of the ligand show several bands between 3209-2474 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, these bands are found to be absent indicating the absence of H-bonding.

The strong band at 1599 cm^{-1} in the spectrum of the ligand is in all probably due to the asymmetric $-\text{COO}^-$ stretching vibration. In the mixed ligand complexes, the bands appear in the region 1610-1557 cm^{-1} . The general shifting of the bands suggest the interaction of oxygen atom of $-\text{COOH}$ group with the metal atom. Since the $-\text{COOH}$ 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 spectrum of the ligand represents symmetric $-\text{COO}^-$ stretching vibration. In the mixed ligand complexes, this band appears in the region 1431-1381 cm^{-1} . The shifting of this band indicates the involvement of $-\text{COOH}$ group of the ligand in complex formation and coordination of Sn (II) or Pb (II) ion through oxygen atom of $-\text{COOH}$ group of the ligand.

The strong band at 669 cm^{-1} , in the spectrum of the ligand may be due to $-\text{COO}^-$ bending vibration. This band appears in the region of 671-670 cm^{-1} in the mixed ligand complexes. There is no appreciable shifting of the band which suggests that $-\text{COO}^-$ bending vibration is not metal sensitive.

A weak asymmetrical N—H bending band in the spectra of ligand appears at 1665 cm^{-1} . In the few mixed ligand complexes, this band appears in the region 1662-1637 cm^{-1} . The fairly strong symmetrical N—H bending band in the spectrum of the ligand appears in the region 1528-1482 cm^{-1} . In the mixed ligand complexes, this band appears in the region 1516-1467 cm^{-1} . The shifting of these bands indicates the M—N interaction and these bands are metal sensitive.

The band in the region 472-511 cm^{-1} in the spectra of all mixed ligand complexes may be assigned to M—O band frequency while medium bands in the region 535-585 cm^{-1} is assigned to M—N band frequency [12]. These bands are absent in the second ligand, hippuric acid. These assignments are based on the assumption [13] 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 $-\text{NO}/-\text{NO}_2$ of first ligand, *i.e.*, organic acid, to Sn (II) or Pb (II) metal ion in all the mixed ligand complexes.

Electronic Spectra : Electronic spectra were recorded on Systronics Double Beam UV-VIS spectrophotometer – 2201 in methanol. The bands observed in electronic absorption spectra of the ligand and mixed ligand complexes of Sn (II) & Pb (II) are given in Table-3.

Table 3. Major diffuse reflectance bands(in nm) for mixed ligand complexes of Sn(II) & Pb(II) with Hippuric acid(HA)

Compound	Diffuse reflectance (in nm)
Hippuric acid(HA)	245, 268
Sn(TNP) ₂ .HA	248, 392
Sn(1N2N) ₂ .HA	254, 334, 376
Pb(ONP) ₂ .HA	254, 395
Pb(DNP) ₂ .HA	264, 344, 395

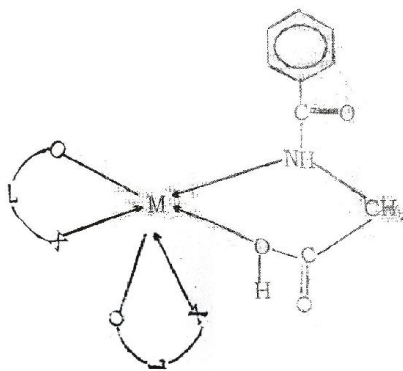
The ligand(HA) exhibits sharp intense bands at 245 nm and 268 nm, These bands indicate π - π^* transition as well as charge transfer in aromatic ring.

Electronic absorption spectra of the mixed ligand complexes show bands in the region 245-344 nm, which indicate π - π^* transitions in aromatic ring. 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 complexes show that there is a π -interaction between metal and ligand orbitals.

STRUCTURE & BONDING

On the basis of qualitative analysis, the molecular formula of the mixed ligand complexes of Sn (II) & Pb (II) metal chelates of some organic acids with hippuric acid is found to be $ML_2.HL'$, where M = Sn or Pb, L = deprotonated ONP, DNP, TNP or 1N2N, HL' = Hippuric acid. Infrared and electronic absorption spectral studies revealed the structure and bonding of these complexes as given below (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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