

MIXED LIGAND COMPLEXES OF TIN(II) & LEAD(II) METAL CHELATES OF SOME ORGANIC ACIDS WITH N-PHENYLANTHRANILIC ACID

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RECEIVED : 31 December, 2015

Some novel mixed ligand complexes of type $ML_2.HL'$, 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); $HL' =$ N-phenylanthranilic acid (NPAA) have been synthesized. The complexes have been characterized by analytical, IR and UV-VIS spectral data. IR spectral data show that the hydrogen bonding in these complexes is a dominant factor for their stability.

KEYWORDS : Mixed ligand complexes, Metal chelates, Organic acid, N-phenylanthra-nilic acid, Infrared spectra.

INTRODUCTION

N-phenylanthranilic acid (Fenamic acid) serves as a parent structure for several non-steroidal anti-inflammatory drugs (NSAIDS). It widely used for treatment of inflammatory disorders and painful conditions such as rheumatoid arthritis, gout, painful menstruation and headache. Tin and lead compounds have analytical and technical importances [1]. Transition metal complexes with N-phenylanthranilic acid have been well investigated earlier [2-7]. In this communication, we have taken the N-phenylanthranilic acid as a secondary ligand to investigate the coordination behaviour towards Sn (II) and Pb (II) metal chelates of some organic acids and compare to the other amino acid complexes.

EXPERIMENTAL

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) and N-phenylanthranilic acid (NPAA) 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 0.01 mole of dihydrated stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) or 0.01 mole 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 Sn (II) or Pb (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 N-phenylanthranilic acid in 1 : 1 (mole) in absolute ethanol. The mixture was refluxed on magnetic hot plate with constant stirring at $70-80^\circ\text{C}$ 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 .

RESULTS & DISCUSSION

Some physical properties of the second ligand (N-phenylanthranilic acid) and the mixed ligand complexes ($\text{ML}_2 \cdot \text{HL}'$) obtained are listed in Table-1.

N-phenylanthranilic acid is a white crystalline solid, highly soluble in water, ethanol, sparingly soluble in ether, chloroform but insoluble in benzene, petroleum ether. The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc.; but sparingly soluble in non-polar solvents, viz., 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 $35-40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ appears and characteristics of 1 : 1 electrolyte [8] whereas ideally molar conductance of a neutral compounds should be zero. However, significantly low values (6.5 -10.4) of molar conductance of the compounds indicate them to be non-electrolyte.

Infrared Spectra : Infrared measurements for the ligand (N-phenylanthranilic acid) and its hitherto unknown mixed ligand complexes were made between $4000-400 \text{ cm}^{-1}$ in KBr disc with the help of JASCO-FTIR spectrophotometer model – 5300. Pertinent infrared spectral data for these compounds are shown 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 $3350-3310 \text{ cm}^{-1}$. This band represents the free N-H stretching modes [8].

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 $3446-3164 \text{ cm}^{-1}$. The shifting of this band suggests the coordination of the $-\text{NH}_2$ group to the tin or lead metal.

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

Table - 1

| Compound | Colour | M.P./ Decomp./ Trans. Temp. (°C) | Molar Conductance | Analysis % found/(calcd.) | | | |
|---------------------------------|----------------|---|----------------------|---------------------------|----------------|------------------|------------------|
| | | | | C | H | N | M |
| N-phenylanthranilic acid (NPAA) | White | 232m | --- | --- | --- | --- | |
| Sn(ONP) ₂ .NPAA | Brown | 240d | 7.1 | 49.30 (49.37) | 3.05 (3.13) | 8.80 (8.91) | 19.37 (19.53) |
| Sn(DNP) ₂ .NPAA | Pale yellow | 112m | 8.9 | 42.92 (43.00) | 2.35 (2.44) | 9.91 (10.03) | 16.91 (17.01) |
| Sn(TNP) ₂ .NPAA | Deep yellow | 134d | 9.1 | 38.01 (38.08) | 1.83 (1.90) | 12.35 (12.44) | 14.98 (15.07) |
| Sn(1N2N) ₂ .NPAA | Blackish green | 130d | 9.0 | 58.52 (58.60) | 3.31 (3.40) | 6.11 (6.21) | 17.41 (17.56) |
| Pb(ONP) ₂ .NPAA | Pale yellow | 273md | 9.5 | 43.00 (43.09) | 2.65 (2.73) | 5.96 (6.03) | 29.59 (29.76) |
| Pb(DNP) ₂ .NPAA | Deep yellow | 225d | 10.3 | 38.05 (38.16) | 2.08 (2.16) | 8.78 (8.90) | 26.25 (26.35) |
| Pb(TNP) ₂ .NPAA | Deep yellow | 170m | 10.4 | 34.16 (34.24) | 1.68 (1.71) | 11.11 (11.18) | 23.55 (23.65) |
| Pb(1N2N) ₂ .NPAA | Deep brown | 185md | 6.5 | 51.75 (51.82) | 2.96 (3.01) | 5.38 (5.49) | 27.02 (27.11) |

Table 2. Pertinent IR data for ligand (N-phenylanthranilic acid) and its mixed ligand Sn (II) and Pb (II) complexes

| Compound | ν_{N-H} | $\delta_{asym NH_2}$ | $\nu_{asym COO^-}$ | $\delta_{sym NH_2}$ | $\nu_{sym COO^-}$ | δ_{COO^-} | $\nu_{M-O/M-N}$ |
|---------------------------------|-------------|----------------------|--------------------|---------------------|-------------------|------------------|-----------------|
| N-phenylanthranilic acid (NPAA) | 3336 | 1665 | 1590 | 1515 | 1438 | 668 | --- |
| Sn(ONP) ₂ .NPAA | 3240 | 1695 | 1578 | 1509 | 1387 | 670 | 580, 520, 470 |
| Sn(1N2N) ₂ .NPAA | 3335 | 1658 | 1576 | 1512 | 1435 | 669 | 572, 531, 486 |
| Pb(DNP) ₂ .NPAA | 3305 | 1685 | 1610, 1580, 1560 | 1500, 1462 | 1421, 1410 | 670 | 555, 524, 472 |
| Pb(TNP) ₂ .NPAA | 3446, 3164 | 1640 | 1598, 1577 | 1512, 1506 | 1395, 1371 | 669 | 570, 501, 480 |

The strong band at 1590 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 $1610-1560\text{ cm}^{-1}$. The general shifting of the band to higher frequency by upto 20 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 hands below 1590 cm^{-1} may be appeared due to the presence of the functional groups of the first ligand.

The weak band at 1438 cm^{-1} , in the spectrum of the ligand represents symmetric $-COO^-$ stretching vibration. In the mixed ligand complexes, this band appear in the region

1435-1371 cm^{-1} . The shifting of this band to a lower frequency clearly indicates the involvement of $-\text{COOH}$ group of the ligand in complex formation and coordination of Sn (II) or Pb (II) metal ion through oxygen atom of $-\text{COOH}$ group of the ligand.

The strong band at 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 1695-1640 cm^{-1} . The fairly strong symmetrical N-H bending band in the spectrum of the ligand appears at 1515 cm^{-1} . In the mixed ligand complexes, this band appears in the region 1512-1462 cm^{-1} . The general shifting of these bands indicates the M-N interaction and these bands are metal sensitive.

The band in the region 531-470 cm^{-1} in the spectra of all mixed ligand complexes may be assigned to M-O band frequency [9] while medium bands in the region 580-550 cm^{-1} is assigned to M-N band frequency [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 Sn (II) or Pb (II) 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 Sn (II) and Pb (II) are given in Table-4.3.

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

Table 4.3. Major diffuse reflectance bands (in nm) for mixed ligand complexes of Sn (II) and Pb (II) with N-phenylanthranilic acid (NPAA)

| Compound | Diffuse reflectance (in nm) |
|---------------------------------|------------------------------|
| N-phenylanthranilic acid (NPAA) | 242, 275 |
| Sn(ONP) ₂ .NPAA | 232, 344, 386 |
| Sn(1N2N) ₂ .NPAA | 219, 344, 376 |
| Pb(DNP) ₂ .NPAA | 238, 344, 382 |
| Pb(TNP) ₂ .NPAA | 226, 350, 430 |

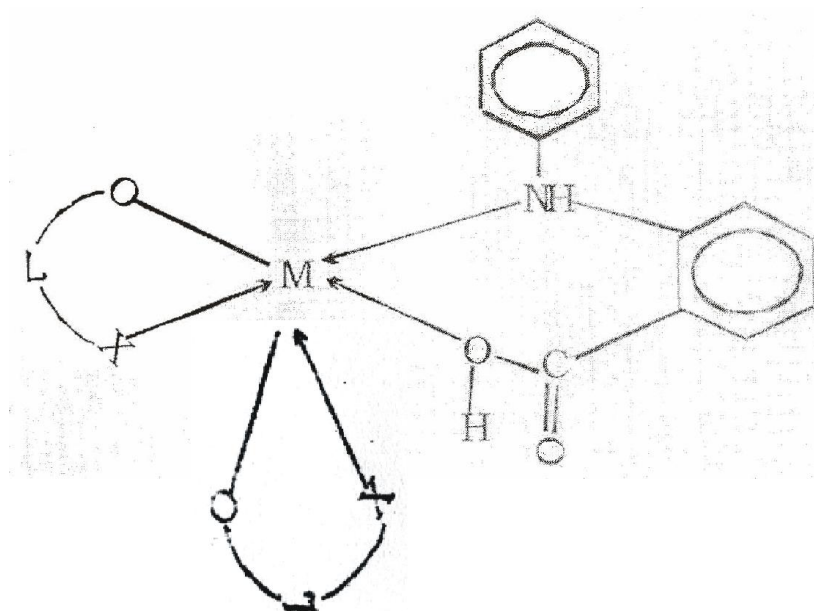
The electronic spectra of the mixed ligand complexes show bands in the region 219-350 nm which indicate the formation of $\pi-\pi^*$ complexes.

On electronic spectra of the mixed ligand complexes show a 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. Electronic spectra of some of the compounds are shown in Fig. 4.8 to 4.11.

STRUCTURE & BONDING

On the basis of analytical and spectral datas, following structures (Fig. 1) for the synthesized complexes are suggested :



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

Fig. 1

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