

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

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RECEIVED : 15 October, 2015

A number of novel mixed ligand complexes of type $ML_2.HL'$ have been synthesized and characterized, 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' = Anthranilic acid. The complexes have been characterized by elemental analysis, IR, UV-VIS spectral analysis and molar conductance measurements. IR spectral data show that the hydrogen bonding in these complexes is a dominant factor for their stability. Low values of their molar conductance would suggest them to be non-electrolyte.

KEYWORDS : Mixed ligand complexes, Metal chelates, Organic acid, Anthranilic acid, Infrared spectra.

INTRODUCTION

Tin and lead compounds have analytical and technical importances [1]. Transition metal complexes with anthranilic acid have been well investigated earlier [2-8]. In this communication, we have taken the anthranilic acid as a secondary ligand to investigate the coordination behaviour towards Sn(II) and Pb(II) metal chelates of some organic acids and also to study whether it is selective in comparison 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 anthranilic acid (AnthA) 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 ($SnCl_2.2H_2O$) 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.

Table - 1

| Compound | Colour | M.P./ Decomp./ Trans. Temp. (°C) | Molar Conductance | Analysis % found/(calcd.) | | | |
|-----------------------------|-----------------|--|----------------------|---------------------------|----------------|------------------|------------------|
| | | | | C | H | N | M |
| O-aminobenzoic acid (OABA) | Colourless | 138m | --- | --- | --- | --- | |
| Sn(ONP) ₂ .OABA | Greenish yellow | >300 | 5.2 | 36.41 (36.48) | 1.99 (2.03) | 6.89 (7.09) | 29.95 (30.07) |
| Sn(DNP) ₂ .OABA | Pale cream | 118m | 7.1 | 29.65 (29.71) | 1.20 (1.24) | 11.48 (11.55) | 23.65 (23.79) |
| Sn(TNP) ₂ .OABA | Light brown | 112md | 7.8 | 24.98 (25.05) | 0.62 (0.69) | 14.56 (14.62) | 20.56 (20.62) |
| Sn(1N2N) ₂ .OABA | Light brown | >300 | 8.1 | 51.79 (51.86) | 2.51 (2.55) | 5.95 (6.05) | 25.56 (25.65) |
| Pb(ONP) ₂ .OABA | Yellowish cream | 232d | 8.5 | 29.74 (29.80) | 1.56 (1.65) | 5.65 (5.79) | 42.76 (42.88) |
| Pb(DNP) ₂ .OABA | Pale yellow | 200md | 9.1 | 25.05 (25.12) | 1.01 (1.05) | 9.71 (9.77) | 36.06 (36.15) |
| Pb(TNP) ₂ .OABA | Yellow | 164m | 9.8 | 21.65 (21.76) | 0.52 (0.60) | 12.56 (12.66) | 31.09 (31.24) |
| Pb(1N2N) ₂ .OABA | Dark brown | 190md | 10.1 | 43.49 (43.54) | 2.08 (2.15) | 5.00 (5.08) | 37.49 (37.59) |

Preparation of mixed ligand complexes :

The suspension of Sn(II) or Pb(II) metal chelate of organic acid (ML₂) was mixed with the solution of anthranilic 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.

RESULTS & DISCUSSION

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

Anthranilic 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 ohm⁻¹ cm² mole⁻¹ appears and characteristics of 1 : 1 electrolyte [9] whereas ideally molar conductance of a neutral compounds should be zero. However, significantly low values (5.2 -10.1) of molar conductance of the compounds indicate them to be non-electrolyte.

Infrared Spectra : Infrared measurements for the ligand (Anthranilic acid) and its hitherto unknown mixed ligand complexes were made between 4000-400 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.

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

| Compound | $\nu_{\text{N-H}}$ | δ_{asymNH_2} | ν_{asymCOO^-} | δ_{symNH_2} | ν_{symCOO^-} | δ_{COO^-} | $\nu_{\text{M-O/M-N}}$ |
|-----------------------------|--------------------|----------------------------|--------------------------|---------------------------|-------------------------|-------------------------|------------------------|
| O-aminobenzoic acid(OABA) | 3472, 3374, 3324 | 1669 | 1589, 1564 | 1531, 1485 | 1445, 1415 | 668 | --- |
| Sn(ONP) ₂ .OABA | 3447, 3317, 3143 | 1685 | 1601, 1561 | 1525 | 1434, 1418 | 670 | 591, 530, 490 |
| Sn(TNP) ₂ .OABA | 3439, 3318, 3275 | 1695 | 1609, 1560 | 1520 | 1417 | 673 | 566, 519, 480 |
| Pb(DNP) ₂ .OABA | 3428, 3375, 3342 | 1681 | 1616, 1578 | 1519 | 1452 | 670 | 555, 524, 472 |
| Pb(1N2N) ₂ .OABA | 3424, 3150 | 1684 | 1560 | 1519 | 1428 | 673 | 535, 485 |

Anthranilic acid is an aromatic amino acid. 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 sym-metrical N—H stretching modes [10]. The spectrum of the ligand shows three medium, well resolved absorption bands at 3472, 3374 & 3324 cm^{-1} . These bands may be due to asym. and sym. N—H stretching modes which is extended by combination band at the region 2401-2361 cm^{-1} .

In the spectra of mixed ligand complexes, two medium or weak absorption bands, one near 3454-3418 cm^{-1} and other band in the region 3375-3150 cm^{-1} are observed. The shift of the absorption range of N—H has been observed in the tin and lead metal chelates, which might be due to coordination of $-\text{NH}_2$ group to the tin and lead metal. The spectra of the ligand show several bands between 3240-2511 cm^{-1} . These bands may be due to the presence of hydrogen bonded $-\text{COOH}$ group.

The strong band between 1589-1564 cm^{-1} in the spectra of ligand is in all probably due to the asymmetric $-\text{COO}^-$ stretching vibration. The weak bands between 1445-1415 cm^{-1} represents symmetric $-\text{COO}^-$ stretching vibration. In the complexes, the $\nu_{\text{as}(\text{COO}^-)}$ band appear in the region 1620-1597 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 Sn(II) or Pb(II) metal ion through oxygen atom of the ligand. The strong band at 667 cm^{-1} in the spectra of ligand may be due to $-\text{COO}^-$ bending vibration. In the complexes, this band appears in the region 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 ($-\text{NH}_2$) N—H bending band in the spectra of the ligand appears at 1669 cm^{-1} . In the spectra of 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 1531 & 1485 cm^{-1} . In the complexes, this band appears in the region 1540-469 cm^{-1} . The shifting of these bands indicates the M—N interaction and these bands are metal sensitive.

The bands in the region 530-470 cm^{-1} in the spectra of the mixed ligand complexes may be assigned to M—O band frequency while medium bands in the region 550-595 cm^{-1} is assigned to M—N band frequency [10]. These bands are not present in the ligand. These assignments are based on the assumption [11] 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.

Electronic spectra : Electronic spectra were recorded on Perkin Elmer Lambda 15 UV-VIS spectrophotometer in methanol. The bands observed in electronic spectra of the 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) and Pb(II) with Anthranilic acid(AnthA)

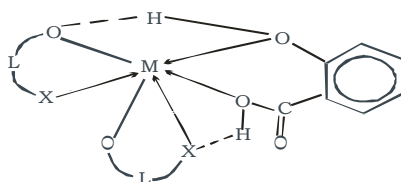
| Compound | Diffuse reflectance (in nm) |
|------------------------------|------------------------------|
| Anthranilic acid(AnthA) | 240, 280 |
| Sn(ONP) ₂ .AnthA | 248, 382 |
| Sn(TNP) ₂ .AnthA | 225, 347, 402 |
| Pb(DNP) ₂ .AnthA | 241, 283, 376 |
| Pb(1N2N) ₂ .AnthA | 235, 347, 392 |

The ligand (AnthA) exhibits sharp intense bands at 240 nm and 280 nm, These bands indicate $\pi-\pi^*$ transition as well as charge transfer in aromatic ring.

Electronic absorption spectra of the mixed ligand complexes show bands in the region 225-347 nm, which indicate $\pi-\pi^*$ transitions in aromatic ring.

On electronic spectra of the mixed ligand complexes show a charge transfer band at 376-402 nm. The charge transfer bands of the ligand in the complexes show that there is a π -interaction between metal and ligand orbitals.

On the basis of quantitative analysis, IR, UV-VIS spectral data and conductivity measurements suggest the probable structure for these complexes (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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