

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

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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), 1-nitroso-2-naphthol (1N2N), 8-hydroxy-quinoline (8HQ) or o-aminobenzoic acid; HL' = Salicylic acid. All the complexes have been found to have 1 : 1 stoichiometric composition. 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 value of their molar conductance would suggest them to be non-electrolyte.

INTRODUCTION

Tin & lead compounds have analytical and technical importances [1]. Transition metal and alkali metal complexes with salicylic acid have been well investigated earlier [2-8]. In this communication, we have taken the salicylic acid as a secondary ligand to investigate the coordination behaviour towards tin(II) and lead(II) metal salts of some organic acids and also to study whether it is selective in comparison to the other hydroxy acid complexes.

EXPERIMENTAL

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitro-phenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), o-aminobenzoic acid (OABA) and salicylic acid (Sala) of AnalaR grade were used as such.

Preparation of metal chelates of tin(II) and lead(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 0.01mole 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.

Table 1

Compound	Colour	M.P./ Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
Salicylic acid (SalA)	Colourless	138m	---	---	---	---	
Sn(ONP) ₂ .SalA	Greenish yellow	>300	6.2	42.78 (42.80)	2.54 (2.63)	5.19 (5.26)	22.19 (22.28)
Sn(DNP) ₂ .SalA	Pale cream	118m	8.1	36.55 (36.61)	1.85 (1.93)	8.89 (8.99)	18.85 (19.06)
Sn(TNP) ₂ .SalA	Light brown	112md	8.8	31.86 (31.99)	1.25 (1.40)	11.65 (11.78)	16.55 (16.65)
Sn(8HQ) ₂ .SalA	Pale yellow	298md	7.9	53.88 (55.07)	2.81 (3.30)	4.58 (5.14)	19.65 (21.79)
Sn(1N2N) ₂ .SalA	Light brown	>300	9.1	53.87 (53.93)	2.91 (2.99)	4.55 (4.66)	19.65 (19.76)
Sn(OABA) ₂ .SalA	White	262md	8.9	47.59 (47.66)	3.26 (3.40)	5.15 (5.29)	22.21 (22.45)
Pb(ONP) ₂ .SalA	Yellowish cream	232d	8.5	36.65 (36.70)	2.19 (2.25)	4.42 (4.50)	33.21 (33.35)
Pb(DNP) ₂ .SalA	Pale yellow	200md	9.5	31.95 (32.06)	1.59 (1.69)	7.78 (7.87)	29.02 (29.13)
Pb(TNP) ₂ .SalA	Yellow	164m	10.2	28.38 (28.46)	2.19 (1.25)	10.21 (10.48)	25.71 (25.86)
Pb(8HQ) ₂ .SalA	Yellow	202m	9.9	46.92 (47.38)	2.56 (2.84)	3.98 (4.42)	29.95 (32.72)
Pb(1N2N) ₂ .SalA	Dark brown	190md	10.5	46.81 (47.01)	2.58 (2.61)	3.96 (4.06)	31.65 (30.06)

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

Compound	ν_{O-H}	$\nu_{O-H...O}$	Sym ν_{COO^-}	Antisym ν_{COO^-}	ν_{C-O} (phenolic)	$\nu_{M-O/M-N}$
Salicylic acid (SalA)	3240br	2596	1483	1660	1330	----
Sn(DNP) ₂ .SalA	3276br	1831	1470	1702, 1607	1346	636, 575, 510, 485
Sn(1N2N) ₂ .SalA	3405br	-----	1459	1592	1343	668, 564
Pb(8HQ) ₂ .SalA	3408br	-----	1485, 1456	1595	1382	668, 602, 561, 497

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 salicylic 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 (SalA) and the mixed ligand complexes ($ML_2.HL'$) obtained are listed in Table-1.

Salicylic acid is a colourless solid, insoluble in cold water but dissolves in hot water, ethanol and 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 [9] whereas ideally molar conductance of a neutral compounds should be zero. However, significantly low values (6.2-10.5) of molar conductance of the compounds indicate them to be non-electrolyte.

Infrared Spectra : Infrared measurements for the ligand (Salicylic 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.

The broad band at 3240 cm^{-1} in the spectra of the ligand point to intramolecular hydrogen bonding in it.

In the spectra of the mixed ligand complexes, broad bands appear in the region $3276-3408 \text{ cm}^{-1}$. The shifting of the band in the above region indicates presence of hydrogen bonding in the complexes. Further, the free salicylic acid gave hydrogen bonded O-H stretching band at 2596 cm^{-1} . The lower value 1831 cm^{-1} of the band in the $Sn(DNP)_2$. SalA indicates presence of strong hydrogen bonding.

The strong band at 1330 cm^{-1} in the ligand clearly shows the presence of C—O (phenolic) in the ligand. In the complexes, this band shows a higher shift of $13-52 \text{ cm}^{-1}$. This fact indicates the involvement of phenolic oxygen in complex formation.

The antisymmetric stretching frequency of COO^- group (1660 cm^{-1}) in the ligand has been shifted in the region $1592-1607 \text{ cm}^{-1}$. The symmetric stretching frequency of COO^- group observed at 1483 cm^{-1} in the ligand. But in the complexes lower shift of $13-27 \text{ cm}^{-1}$ have been observed. The above information suggests the involvement of oxygen atom of $-COOH$ group in the complex formation with Sn(II) or Pb(II) metal ion.

The bands in the region $485-564 \text{ cm}^{-1}$ in the spectra of all mixed ligand complexes may be assigned to M—O band frequency while medium bands in the region $575-668 \text{ cm}^{-1}$ 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. The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of nitroso (in case of 1N2N) or nitro (in case of ONP, DNP, TNP) or pyridine ring (in case of 8HQ) to metal in all the mixed ligand complexes.

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) and Pb(II) are given in Table-3.

On electronic spectra of the mixed ligand complexes show a charge transfer band at 651-654 nm.

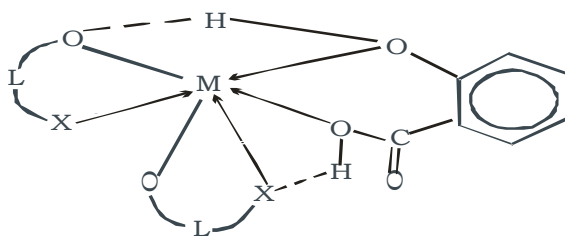
The charge transfer bands in the complexes show that there is a π -interaction between metal and ligand orbitals.

Table 3. Major diffuse reflectance bands (in nm) for mixed ligand complexes of Sn(II) and Pb(II) with Salicylic acid (SaLA)

Compound	Diffuse reflectance (in nm)
Sn(DNP) ₂ .SaLA	654
Sn(1N2N) ₂ .SaLA	651
Pb(8HQ) ₂ .SaLA	651

STRUCTURE & BONDING

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, 8HQ, 1N2N or OABA ; X = O or N

Fig. 1

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