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MIXED LIGAND COMPLEXES OF TIN(II) & LEAD(II) METAL CHELATES OF SOME ORGANIC ACIDS WITH 2-HYDROXY-3-NAPHTHOIC 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), 8-hydroxyquinoline (8HQ), 1-nitroso-2-naphthol (1N2N) or o-amino-benzoic acid (OABA); HL' = 2-hydroxy-3-naphthoic acid (2H3NA) have been synthesized and characterized. The structure of these compounds were confirmed on the basis of chemical and spectral studies.

KEYWORDS : Mixed ligand complexes, 2-Hydroxy-3-naphthoic acid, Tin(II), Lead(II).

INTRODUCTION

Mixed ligand complexes are important in analytical, biochemical and pharmaceutical fields [1-3]. Several organo-tin derivatives of 1-hydroxy-2-naphthoic acid and 2-hydroxy-3-naphthoic acid have been reported by Manral *et al* [4]. Mixed ligand alkali metal complexes with 2-hydroxy-3-naphthoic acid as secondary ligand have been investigated by Banerjee *et al* [5]. Tiwary *et al* [6] have studied mixed ligand complexes of Rb(I) & Cs(I) chelates of some organic acids with 2-hydroxy-3-naphthoic acid. In the present paper, we report the synthesis of mixed ligand complexes of Sn(II) & Pb(II) metal chelates of organic acids with 2-hydroxy-3-naphthoic acid.

EXPERIMENTAL

O-nitrophenol(ONP), 2,4-dinitrophenol(DNP), 2, 4, 6-trinitrophenol(TNP), 1-nitroso-2-naphthol(1N2N), 8-hydroxyquinoline (8HQ), o-aminobenozic acid (OABA) and 2-hydroxy-3-naphthoic acid (2H3NA) 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 0.01 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 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	Ag
2-Hydroxy-3-naphthoic acid(2H3NA))	Cream	135m	---	---	---	---	---
$Sn(ONP)_2.2H3NA$	Brown	240d	7.5	47.30 (47.36)	2.65 (2.74)	4.70 (4.80)	20.17 (20.37)
$Sn(DNP)_2.2H3NA$	Pale yellow	112m	8.9	40.98 (41.02)	2.01 (2.08)	8.21 (8.32)	17.51 (17.64)
$Sn(TNP)_2.2H3NA$	Deep yellow	134m	9.1	36.02 (36.18)	1.43 (1.57)	10.85 (11.01)	15.38 (15.56)
$Sn(8HQ)_2.2H3NA$	Pale yellow	304md	7.9	58.40 (58.51)	3.18 (3.36)	4.52 (4.71)	18.05 (18.24)
$Sn(1N2N)_2.2H3NA$	Blackish green	130d	9.1	57.02 (57.16)	3.01 (3.07)	4.21 (4.30)	18.11 (18.24)
$Sn(OABA)_2.2H3NA$	Pale yellow	260d	8.9	51.75 (51.83)	3.32 (3.45)	4.71 (4.83)	20.15 (20.51)
$Pb(ONP)_2.2H3NA$	Pale yellow	273md	9.5	41.01 (41.12)	2.25 (2.38)	4.06 (4.17)	30.59 (30.87)
$Pb(DNP)_2.2H3NA$	Deep yellow	225d	10.3	36.15 (36.25)	1.68 (1.83)	7.21 (7.35)	27.05 (27.22)
$Pb(TNP)_2.2H3NA$	Deep yellow	170m	10.4	32.26 (32.42)	1.28 (1.41)	9.71 (9.86)	24.21 (24.34)
$Pb(8HQ)_2.2H3NA$	Pale yellow	240md	9.3	50.85 (50.93)	2.81 (2.93)	4.01 (4.10)	30.20 (30.32)
$Pb(1N2N)_2.2H3NA$	Deep brown	185md	7.5	50.25 (50.32)	2.56 (2.70)	3.58 (3.78)	27.85 (28.03)
$Pb(OABA)_2.2H3NA$	Cream	250d	11.1	44.81 (44.96)	2.75 (2.99)	4.02 (4.19)	30.85 (31.05)

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 2-hydroxy-3-naphthoic 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 2. Pertinent IR data for ligand (2-Hydroxy-3-naphthoic acid) & its mixed ligand complexes of Sn(II) & Pb(II)

Compound	υ_{O-H}	$\upsilon_{O-H\ ...O}$	Sym υ_{COO^-}	Antisym υ_{COO^-}	υ_{C-O} (phenolic)	$\upsilon_{M-O/M-N}$
2-Hydroxy-3-naphthoic acid(2H3NA)	3265br	----	----	1680, 1660	1320	----
$Sn(DNP)_2.2H3NA$	----	2557, 2362, 1827	1466	1665, 1603, 1568, 1533	1378, 1343	639, 580, 523, 476
$Sn(TNP)_2.2H3NA$	3284m	2569, 2362, 1870	1466	1668, 1633, 1562	1336	638, 599, 547, 522, 470
$Pb(1N2N)_2.2H3NA$	3423br	2363, 1898	1457	1642, 1576, 1533	1373, 1336	622, 595, 525, 476

Results & discussion

Some physical properties of the second ligand (2-hydroxy-3-naphthoic acid) and the mixed ligand complexes ($ML_2.HL'$) obtained are listed in Table-1.

2-Hydroxy-3-naphthoic acid is a cream colour solid, insoluble in cold water but dissolves in hot water, ethanol and ether. It sublimes below its melting point and steam volatile. 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 they are sparingly soluble in non-polar solvents, namely chloroform, n-hexane, benzene and dioxane.

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 $ohm^{-1}\ cm^2\ mole^{-1}$ is characteristic of 1:1 electrolyte [7] whereas ideally molar conductance of a neutral compound should be zero. However, significantly low values (7.5-11.1) of molar conductance of the compounds indicate them to be covalent nature.

Infrared Spectra :

Infrared measurements for the ligand (2-Hydroxy-3-naphthoic acid) and its mixed ligand complexes were made between 4000-400 cm^{-1} in KBr-phase with the help of JASCO-FTIR spectrophotometer model – 5300. Pertinent IR data for these compounds are shown in Table 2.

The OH stretching band appears at 3265 cm^{-1} in the ligand 2-hydroxy-3-naphthoic acid. The presence of band in this region indicates the strong intramolecular hydrogen bonding in the ligand. In the mixed ligand complexes of Sn(II) and Pb(II), broad bands appear in the region ~3400-1800 cm^{-1} indicate the presence of strong hydrogen bonding.

The strong band at 1320 cm^{-1} in the spectra of the ligand is, in all probability due to the C—O (phenolic) stretching vibration. In the spectra of mixed ligand complexes, a higher shift of bands to 16-58 cm^{-1}, suggests the participation of oxygen atom of phenolic group in complexation.

Further the antisym COO^- stretching frequencies, appear at 1680 cm^{-1} and 1660 cm^{-1} in the ligand. In the mixed ligand complexes the lower shifting of the bands in the above region clearly indicate the involvement of –COOH group in complex formation. Coordination of Sn(II) or Pb(II) metal ion through oxygen atom of –COOH group of the ligand.

The band in the region 525-470 cm^{-1} in the spectra of all mixed ligand complexes may be assigned to M—O band frequency while medium bands in the region 639-547 cm^{-1} is assigned to M—N band frequency [8].

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. The electronic absorption bands are observed at region 420-404 nm in the complex $Sn(TNP)_2.2H3NA$ which indicates π-π^* transition in aromatic ring.

Electronic spectra of the mixed ligand complexes show a charge transfer band at 650-653 nm.

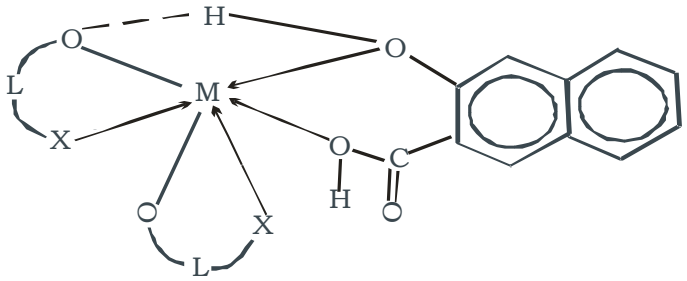
The shift in position of π-π^* in $Sn(TNP)_2.2H_3NA$ and charge transfer bands of the ligand in the complexes show that there is a π-interaction between metal and ligand orbitals.

Table 3. Major diffuse reflectance bands (in nm) for mixed ligand complexes of Sn(II) and Pb(II) with 2-Hydroxy-3-naphthoic acid (2H3NA)

Compound	Diffuse reflectance (in nm)
$Sn(DNP)_2$. 2H3NA	650
$Sn(TNP)_2$. 2H3NA	651, 420, 411, 404
$Pb(1N2N)_2$. 2H3NA	653
$Pb(8HQ)_2$. 2H3NA	651

Structure & bonding

On the basis of quantitative analysis, the molecular formula of the mixed ligand complexes of tin (II) and lead (II) salts of some organic acids with 2-hydroxy-3-naphthoic acid is found to be $ML_2.HL'$, where M = Sn or Pb, L = deprotonated ONP, DNP, TNP, 8HQ, 1N2N or OABA, HL′ = 2-hydroxy-3-naphthoic 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, 8HQ, 1N2N or OABA ; X = O or N

Fig. 1

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