

SYNTHESIS & CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF Sn(II) & Pb(II) METAL CHELATES OF SOME ORGANIC ACIDS WITH GLYCINE

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Present investigation deals with synthesis and characterization of mixed ligand complexes of Sn(II) & Pb(II) using glycine and Sn(II)/Pb(II) metal chelates of some organic acids, viz. o-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol(1N2N) or 8-hydroxyquinoline (8HQ). The synthesized complexes have been characterized on the basis elemental analyses, conductance measurements and spectral methods such as IR, UV-Vis spectroscopy. The studies made are indicating towards octahedral geometry for these complexes.

KEYWORDS : Mixed ligand complexes, Glycine, Sn(II)/Pb(II) metal chelate, Infrared spectra.

INTRODUCTION

Glycine is an important amino acid and behaves as bidentate chelating ligand. Its complexes with alkali metals and some transition metals have well established [1-9]. In this communication, We have synthesized and characterized a number of mixed ligand complexes of Sn(II) and Pb(II) metal chelates of some organic acids with glycine of general formula $ML_2 \cdot HL'$, where M = Sn(II) or Pb(II), L = deprotonated ONP, DNP, TNP, 8HQ, or 1N2N and HL' = glycine.

EXPERIMENTAL

O-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ) and glycine of AnalaR (BDH or EMARK) grade were used as such.

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Preparation of Sn(II) & Pb(II) metal salts of organic acids : 95% Ethanolic solution of organic acid and suspension of dehydrated stannous chloride or lead acetate trihydrate in 95% ethanol were mixed in 2 : 1 (mole). The mixture was refluxed on hot plate with constant stirring at 80°C for 30 - 45 minutes. A clear solution was obtained which was made alkaline with ammonium hydroxide. Characteristic coloured Sn(II) or Pb(II) metal chelate was separated. It was filtered, washed with 95% ethanol and then dried in an electric oven at 100°C.

Preparation of Mixed ligand complexes : To a suspension of the Sn(II) or Pb(II) metal chelate(ML_2) in absolute alcohol in a conical flask and then to add second ligand (Glycine) in a ratio of 1 : 1 (mole), then stirring the mixture till all the solids went into solution. The contents were refluxed for about two hours, but in few cases the complexation completed within an hour. On cooling the resulting solution, the characteristic colour adduct separated which was filtered, washed

RESULTS & DISCUSSION

Physical properties : Some physical properties of second ligand (Glycine) and the new mixed ligand complexes obtained are listed in the Table 1.

Table 1

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
Glycine(Gly)	White	235m
[Sn(ONP) ₂ .Gly]	Pale green	254md	6.3	37.21 (37.36)	2.52 (2.70)	8.55 (8.72)	24.51 (24.64)
[Sn(DNP) ₂ .Gly]	Pale yellow	118m	7.2	31.35 (31.48)	1.85 (1.92)	12.14 (12.24)	20.52 (20.76)
[Sn(TNP) ₂ .Gly]	Pale green	198md	8.5	27.02 (27.20)	1.29 (1.36)	14.65 (14.81)	17.75 (17.94)
[Sn(1N2N) ₂ .Gly]	Light brown	260md	8.1	50.02 (50.20)	2.95 (3.09)	7.32 (7.64)	21.21 (21.59)
[Sn(8HQ) ₂ .Gly]	Pale yellow	232md	6.9	50.85 (51.04)	3.32 (3.44)	8.41 (8.51)	23.90 (24.04)
[Pb(ONP) ₂ .Gly]	Cream	290d	8.5	31.42 (31.56)	2.19 (2.28)	7.21 (7.36)	36.10 (36.30)
[Pb(DNP) ₂ .Gly]	Pale yellow	250md	9.3	27.11 (27.26)	1.56 (1.67)	10.42 (10.60)	31.21 (31.38)
[Pb(TNP) ₂ .Gly]	Yellow	198md	9.7	23.85 (23.99)	1.02 (1.20)	12.92 (13.06)	27.41 (27.62)
[Pb(1N2N) ₂ .Gly]	Brown	235d	7.9	43.14 (43.24)	2.51 (2.66)	6.32 (6.58)	32.15 (32.46)
[Pb(8HQ) ₂ .Gly]	Yellow	280d	8.8	43.20 (43.28)	2.85 (2.92)	7.12 (7.21)	35.32 (35.59)

Glycine is a white crystalline solid. The mixed ligand complexes are generally characteristic colours. 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 [10] whereas ideally molar conductance of a neutral compound should be zero. However, significantly low values (6.3 - 10.2) of molar conductance of the complexes indicate them to be covalent nature.

Infrared Spectra : Infrared measurements for the ligand(glycine) and its mixed ligand complexes were made between $4000 - 400 \text{ cm}^{-1}$ in KBr- phase with the help of JASCO-FTIR spectrophotometer model - 5300. Pertinent IR data for these complexes are shown in Table 2.

A broad, strong $^+\text{NH}_3$ stretching band in the region $3100 - 2600 \text{ cm}^{-1}$ observed in the ligand (glycine). Multiple combination and overtone bands extend the absorption to about 2000 cm^{-1} . This overtone region usually contains a prominent band near $2222 - 2000 \text{ cm}^{-1}$ assigned to a combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillation of the NH_3^+ group. Above observation is due to free glycine exists in zwitter ion ($^+\text{NH}_3\text{-CH}_2\text{COO}^-$) form [11].

In the mixed ligand complexes, two weak absorption bands : one near 3500 cm^{-1} and the other near 3400 cm^{-1} are observed. These bands represent, respectively, the free asymmetrical and symmetrical N-H stretching modes. This observation is probably conversion of Zwitter ion form into original form after mixed ligand complex formation.

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

Compound	$\nu_{\text{N-H}}$	ν_{asymCOO^-}	ν_{symCOO^-}	$\nu_{\text{M-O/M-N}}$
Glycine(Gly)	3100 - 2600, 2220	1595	1399	---
[Sn(ONP) ₂ .Gly]	3444, 3350	1597	1353	640, 570, 540, 485
[Sn(8HQ) ₂ .Gly]	3413	1640, 1582	1379, 1349, 1314	598, 497, 469
[Pb(TNP) ₂ .Gly]	3378, 3310	1613, 1591	1372, 1334	630, 590, 568, 519
[Pb(1N2N) ₂ .Gly]	3343, 3256, 3263	1591, 1541	1360	619, 565, 531, 485

The strong band at 1399 cm^{-1} in the spectra of ligand(glycine) is, in all probably due to the symmetric COO^- stretching vibration. In the mixed ligand complexes the lower shifting of the above band to $20 - 85 \text{ cm}^{-1}$, suggest the participation of oxygen atom of COO^- (carboxylate).

Further asymmetric COO^- stretching frequency appears at 1595 cm^{-1} in the ligand and the bands appear in the region $1541 - 1640 \text{ cm}^{-1}$ in all the mixed ligand complexes. The shifting of the band clearly indicates the involvement $-\text{COOH}$ 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 (glycine). The bands in the region $469 - 540 \text{ cm}^{-1}$ in the spectra of all the mixed ligand complexes may be assigned to M-O band frequency [12] while the medium bands in the region $565 - 640 \text{ cm}^{-1}$ is assigned to M-N band frequency [13].

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.

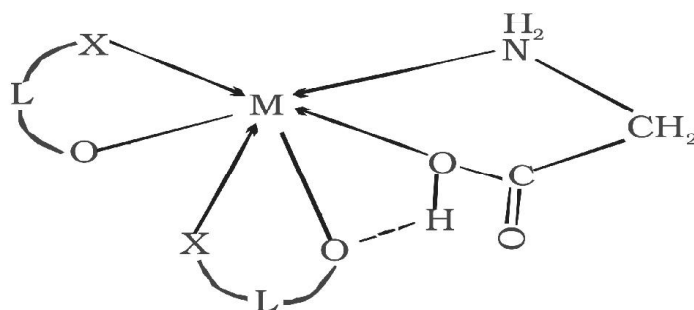
Table 3

Compound	Diffuse reflectance (in nm)
Sn(OABA) ₂ . Gly	649
Pb(8HQ) ₂ . Gly	650
Pb(1N2N) ₂ . Gly	652
Pb(OABA) ₂ . Gly	652

In electronic spectra of the mixed ligand complexes show a charge transfer band at the region 649-652 nm. The charge transfer bands of the ligand in the complexes show that there is a π -interaction between metal & ligand orbitals.

STRUCTURE & BONDING

On the basis of quantitative analysis, the molecular formula of the mixed ligand complexes of Sn(II) and Pb(II) chelates of some organic acids with glycine is found to be $ML_2.HL'$, where M = Sn(II) or Pb(II), L = deprotonated ONP, DNP, TNP, 8HQ or 1N2N, HL' = glycine. IR data suggest that the tin or lead metal replaces the hydrogen atom of the hydroxyl or carboxyl group and through the N/O atom of the $-NO_2/-NO/-NH_2$ group/quinoline ring of the first ligand, *i.e.*, organic acid. The Sn(II) or Pb(II) metal chelates thus formed combine with second ligand, *i.e.*, glycine through coordination with the oxygen atom of carboxyl($-COOH$) group and the nitrogen atom of amino (NH_2) group giving a five membered chelate. It also indicates presence of hydrogen bond, which is one of dominant factors of stabilizing these complexes. Probable structures of the complexes are shown in Fig.1.



where M = Sn(II) or Pb(II); L = deprotonated ONP, DNP, TNP, 8HQ or 1N2N; X = O/N

Fig. 1

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