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SYNTHESIS AND CHARACTERISATION OF SOME NEW TIN METAL COMPLEXES [SnX_2L^{1-10}] WITH MACROCYCLIC LIGANDS: PHOTOELECTRON STUDY and HOMO-LUMO GAP

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ABSTRACT

Thirty tin (II) metal complexes of the type [SnX_2L^{1-10}] (where X= Cl or Br or I; L= macrocyclic ligands (L^1 to L^{10}) derived from thiodiglycolic acid and different aliphatic diamines were created and characterized using elemental analysis, X-ray photoelectron (XPS), Infrared, and molar conductivity spectra. An octahedral geometry was found for these compounds. Frontier molecular orbitals (FMO) analysis has been done to obtain the HOMO-LUMO gap.

Keywords: Tin (II), Macrocyclic Ligands, IR, XPS, Photoelectron Study, HOMO-LUMO Gap.

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INTRODUCTION

Throughout the last five, decade's macrocyclic chemistry of transition metals; lanthanides, and actinides has been thoroughly researched because of their importance and applications in coordination chemistry and biochemistry.[1-5] Various universal macrocyclic ligands such as Robson-type tetraiminodiphenol.[6-7] N_4S_2 donor macrocyclic[8-15], polyazamacrocyclic[16], polyphyrins[17], crown ethers[18], polyamines[19], have been mentioned in the written word. A number of macrocyclic Schiff bases containing various donor atom counts and size atoms have been reported in the last few decades.[20] In living systems, different transition metal ions function as carriers or enzymes in a macrocyclic environment[21] and have been employed as the active species of metalloenzymes.[2] When 1,3-diaminopropane, benzil, or m-phenylenediamine are utilized, it reacts with tindichloride and methyl tindichloride, but also acetylacetone in a nitrogen-free environment with THF serving as the reaction medium has led to the synthesis and characterization of numerous macrocyclic Schiff base compounds with tin(II). There have been these complexes characterized using a variety of physicochemical methods.[23] through the template. 1,3-diaminobutane condensation reactions with several dicarboxylic acids (malonic, succinic, glutaric, and adipic) when metal ions are present in a 2:2:1 molar ratio and characterized by various physicochemical techniques[24], by employing bis(3-oxo-2-butyldiene) propane-1-3-diamine as a precursor in the template method. The [Sn(N4mL)Cl_2] complexes are produced whenever the reaction of the tetradentate macrocyclic precursor [N4mL] with SnCl2 and different diamines occurs in a refluxing methanol solvent in a 1:1:1 molar ratio. Phthalic acid is used to condense 1,2-diaminoethane or 1,3-diaminopropane, dicyclohexyl-carbodiimide, and 4- methylamino pyridine and complexes characterized as [Sn(N_4L^n)Cl_2].[25] A literature survey of the past few decades reveals that very few Tin(II) complexes with macrocyclic ligands and reported.[26] In this research proper we have synthesized tin(II) complexes formed using macrocyclic ligands thioglycolic acid (2 mmol) and different aliphatic diamines (2 mmol) in methanol solvent and synthesized complexes have been characterized by various physicochemical techniques.

EXPERIMENTAL

Thiodiglycolic acid (Aldrich); $SnCl_2$ (Aldrich); $SnBr_2$ (Aldrich) and SnI_2 (Aldrich) were used. The solvent was distilled and dried before use. CH_3OH (BDH); $NH_2(CH_2)_{12}NH_2$(BDH); $NH_2(CH_2)_{10}NH_2$(BDH); $NH_2(CH_2)_9NH_2$(BDH); $NH_2(CH_2)_8NH_2$(BDH); $NH_2(CH_2)_7NH_2$(BDH); NH_2 $(CH_2)_6NH_2$(BDH); $NH_2(CH_2)_5NH_2$(BDH); $NH_2(CH_2)_4NH_2$(BDH); $NH_2(CH_2)_3NH_2$(BDH); $NH_2(CH_2)_2NH_2$(BDH) were utilised following purification and then dried in accordance with literature[27]. The digital melting point

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device used to calculate the melting points was incorrect. The elements C, H, N, and Sn underwent semi-micro-sized elemental studies at the Central Drug Research Institute (CDRI), Lucknow (UP), India. All of these produced compounds' molar conductivities were calculated in DMF using the Design Electronic Conductivity Bridge at room temperature. Infrared all of these compounds' spectra were captured in KBr/CsI using a Shimudzu-170-IR spectrophotometer of 4000-200cm^{-1}. The Kratos analytical Axis Supra ESCA equipment used a monochromatized AlKα (1486.6 eV) source to record the X-ray photoelectron spectra (XPS). Using the ESCApe program, all of these peaks were filled with Shirley background and adjusted for the charge using the C1s peak (284.08 eV) Lorentzian line shape.[28]

Preparation of [$SnX_2.L^{1-10}$] Complexes

In thioglycolic acid (2 mmol) in 50 ml various aliphatic diamines were introduced to dry methanol (2mmol) i.e., $NH_2(CH_2)_2NH_2$ or $NH_2(CH_2)_4NH_2$ or $NH_2(CH_2)_3NH_2$ or $NH_2(CH_2)_5NH_2$ or $NH_2(CH_2)_6NH_2$ or $NH_2(CH_2)_7NH_2$ or $NH_2(CH_2)_8NH_2$ or $NH_2(CH_2)_9NH_2$ or $NH_2(CH_2)_{10}NH_2$ or $NH_2(CH_2)_{12}NH_2$ and refluxed for about 3 hrs. and after that SnX2 (where X= Cl or Br or I) (1 mmol) and refluxed once again for three hours. After filtration, the outcome was precipitate air dried and recrystallized into benzene: pet ether (9:1).

RESULTS AND DISCUSSION

Any of these synthesized macrocyclic ligands i.e., L^1 or L^2 or L^3 or L^4 or L^5 or L^6 or L^7 or L^8 or L^9, or L^{10}, and prepared their metal complexes [SnX_2L^{1-10}] were white-yellowish. Within 0.5%, It must have been noted that the elemental investigation indicated C, H, N, and X=Cl or Br or I. The molar conductivity of all these prepared complexes was observed below 20-40 ohm^{-1}cm^{2}mol^{-1} in DMF solvent at 25° C (room temperature) which concluded these are all prepared complexes are nonelectrolyte[28], Sn-N, and Sn-Cl fundamental modes of vibration were found to have They have respective infrared frequency bands of 435–480 cm-1 and 485–964 cm-1 connected with them.[29]

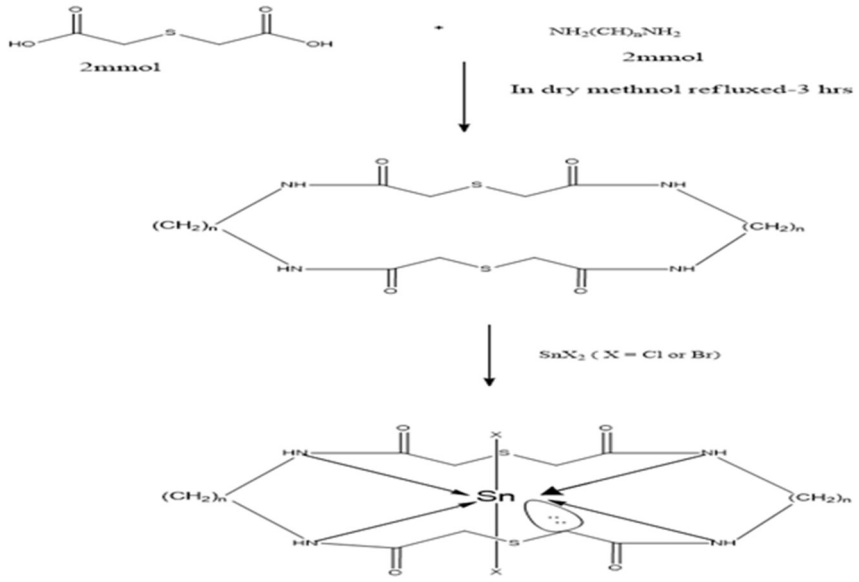

Fig.-1: Preparation of [SnX_2. L^{1-10}] Complexes (where X=Cl or Br or I, n=2 or 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 12)

Table-1: $Sn3P_{1/2, 3/2}$: N1s, O1s and S2p Binding Energies (eV) in Ligand, SnX_2 and [SnX_2L^{1-10}] Complexes.

S.No.	Ligand and Complexes	Sn3p ½, 3/2		N1s		O1s	$S2p_{1/2, 3/2}$
		$Sn3p_{1/2}$	$Sn3p_{3/2}$	Uncoord.	Coord.		
1.	L^1	-	-	400.8	-	531.0	166.0
2.	L^2	-	-	400.8	-	531.0	166.0

3.	L^3	-	-	400.8	-	531.0	166.0
4.	L^4	-	-	400.8	-	531.0	166.0
5.	L^5	-	-	400.8	-	531.0	166.0
6.	L^6	-	-	400.8	-	531.0	166.0
7.	L^7	-	-	400.8	-	531.0	166.0
8.	L^8	-	-	400.8	-	531.0	166.0
9.	L^9	-	-	400.8	-	531.0	166.0
10.	L^{10}	-	-	400.8	-	531.0	166.0
11.	$SnCl_2$	758.8	716.8	-	-	-	-
12.	$SnCl_2L^1$	756.8	714.8	400.8	402.8	531.0	166.0
13.	$SnCl_2\ L^2$	756.8	714.8	400.8	402.8	531.0	166.0
14.	$SnCl_2\ L^3$	756.8	714.8	400.8	402.8	531.0	166.0
15.	$SnCl_2\ L^4$	756.8	714.8	400.8	402.8	531.0	166.0
16.	$SnCl_2\ L^5$	756.8	714.8	400.8	402.8	531.0	166.0
17.	$SnCl_2\ L^6$	756.8	714.8	400.8	402.8	531.0	166.0
18.	$SnCl_2\ L^7$	756.8	714.8	400.8	402.8	531.0	166.0
19.	$SnCl_2\ L^8$	756.8	714.8	400.8	402.8	531.0	166.0
20.	$SnCl_2\ L^9$	756.8	714.8	400.8	402.8	531.0	166.0
21.	$SnCl_2\ L^{10}$	756.8	714.8	400.8	402.8	531.0	166.0
22.	$SnBr_2$	758.6	716.6	-	-	-	-
23.	$SnBr_2L^1$	756.6	714.6	400.8	402.6	531.0	166.0
24.	$SnBr_2L^2$	756.6	716.6	400.8	402.6	531.0	166.0
25.	$SnBr_2L^3$	756.6	714.6	400.8	402.6	531.0	166.0
26.	$SnBr_2L^4$	756.6	716.6	400.8	402.6	531.0	166.0
27.	$SnBr_2L^5$	756.6	714.6	400.8	402.6	531.0	166.0
28.	$SnBr_2L^6$	756.6	716.6	400.8	402.6	531.0	166.0
29.	$SnBr\ L^7$	756.6	714.6	400.8	402.6	531.0	166.0
30.	$SnBr_2L^8$	756.6	716.6	400.8	402.6	531.0	166.0
31.	$SnBr_2L^9$	756.6	714.6	400.8	402.6	531.0	166.0
32.	$SnBr_2L^{10}$	756.6	716.6	400.8	402.6	531.0	166.0
33.	SnI_2	758.4	716.4	-	-	-	-
34.	SnI_2L^1	756.2	714.2	400.8	402.6	531.0	166.0
35.	SnI_2L^2	756.2	714.2	400.8	402.6	531.0	166.0
36.	SnI_2L^3	756.2	714.2	400.8	402.6	531.0	166.0
37.	SnI_2L^4	756.2	714.2	400.8	402.6	531.0	166.0
38.	SnI_2L^5	756.2	714.2	400.8	402.6	531.0	166.0
39.	SnI_2L^6	756.2	714.2	400.8	402.6	531.0	166.0
40.	SnI_2L^7	756.2	714.2	400.8	402.6	531.0	166.0
41.	SnI_2L^8	756.2	714.2	400.8	402.6	531.0	166.0
42.	SnI_2L^9	756.2	714.2	400.8	402.6	531.0	166.0
43.	SnI_2L^{10}	756.2	714.2	400.8	402.6	531.0	166.0

The energy that binds (eV) of $Sn3p_{1/2,3/2}$, N1s, O1s, and $S2p_{1/2,3/2}$ A list of photoelectron peaks is provided in Table-I. This was observed that binding energies (eV) of $Sn3p_{1/2,3/2}$ in starting material $SnCl_2$ or $SnBr_2$ or SnI_2 were for $Sn3p_{1/2}$ 758.8 eV to 758.4 eV and for $Sn3p_{3/2}$ were 716.8 eV to 716.4 eV which were higher than in complexes [$SnX_2\ L^{1-10}$] $Sn3p_{1/2}$ 756.8 eV to 756.2 eV and $Sn3p_{3/2}$ 714.8 eV to 714.2 eV. These XPS results suggest that the electron density of the tin metal ion in [SnX_2L^{1-10}] is more than in SnX_2 due to coordination (Fig.-2 and Table-1).[30-32] Moreover, in all these [SnX_2L^{1-10}] metal complexes two N1s photoelectron peaks have been shown in intensity ratio 1:3, one weak intensity near the ligand and a second peak with a larger intensity pointing in the direction of binding energy greater than the photoelectron peak of the ligand, concluded act of four nitrogen atoms only three are coordinated and one nitrogen atom is uncoordinated are shown in (Fig.-3 and Table- 1).[31-32]

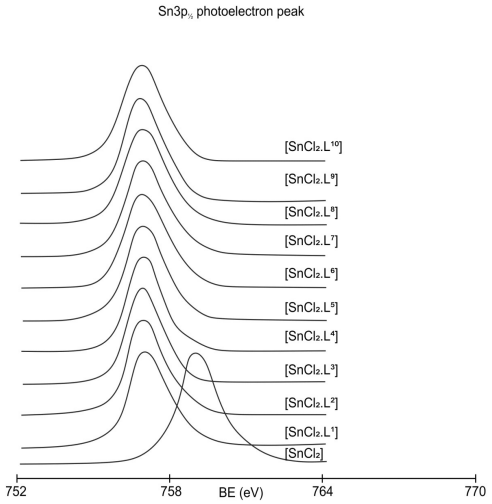

Fig.-2: Sn3p½ Photoelectron Peak Binding Energies (eV) in $SnCl_2$ and $[SnCl_2.L^{1\text{-}10}]$ Complexes

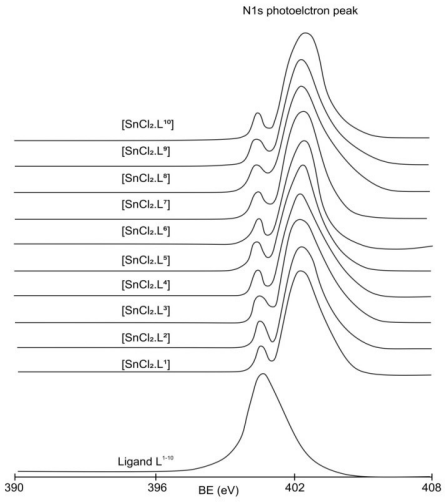

Fig.-3: N1s Photoelectron Peak Binding Energies(eV) in ligand and $[SnCl_2.L^{1\text{-}10}]$ Complexes

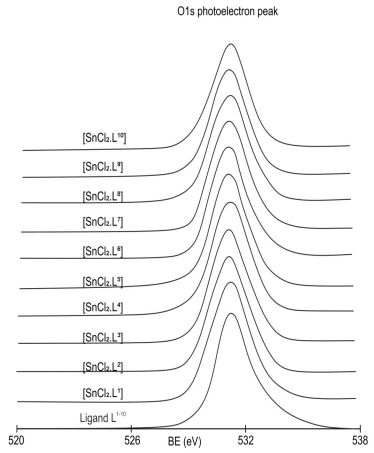

Fig-4: O1s Photoelectron Binding Energies (eV) in Ligand and $[SnCl_2.L^{1\text{-}10}]$ Complexes

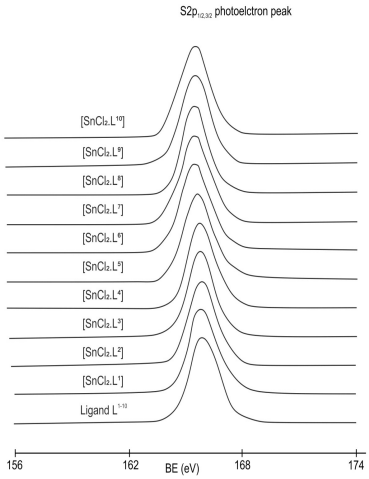

Fig-5: S2p½,3/2 Binding Energies (eV) in Ligand and $[SnCl_2.L^{1\text{-}10}]$ Complexes

The O1s and $Snp_{1/2,3/2}$ photoelectron peaks in $[SnX_2L^{1\text{-}10}]$ complexes were observed at the same binding energies position as in ligands, suggested not involvement of oxygen and sulphur atom in coordination (Fig.-4, 5 and Table-1).[31-32] In each $[SnX_2L^{1\text{-}10}]$ metal complex Sn3s photoelectron peaks have not demonstrated repeated splitting, indicating each complex is diamagnetic.[32]

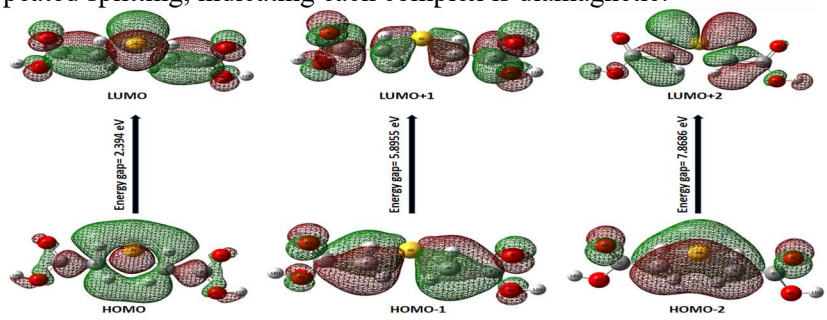

Fig.-6: Diagrammatic Representation of HOMO–LUMO Surfaces of Ligand L

FMO analysis was performed using the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO energy is related to the Ionization Potential (IP), whereas the LUMO energy is utilized to calculate electron affinity (EA). If $E_{HOMO} \approx IP$ and $E_{LUMO} \approx EA$ The average value of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are then related to electronegativity.[32] The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Ligand L is 2.394eV,5.8955eV, and 7.8686Ev are shown in Fig.-6.

CONCLUSION

On the basis of physicochemical techniques data i.e., of molar conductance, IR, XPS, and elemental analysis, the composition of each complex may be proposed as $[SnX_2L^{1\text{-}10}]$ and an octahedral geometry may be established. The energy gap of 2.394eV, 5.8955Ev, and 7.8686eV between HOMO-LUMO for L suggested that the molecule is active and stable.

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CONFLICT OF INTERESTS

The authors confirm that none of their known financial conflicts of interest or close personal connections might have seemed to have influenced the research presented in this study.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this work, took part in its reviewing, editing, and characterizing, and gave their final approval for publication. The author's ORCID IDs which are listed below can be used to confirm their research profile.

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