



Synthesis and Characterization of Complexes of Tin(IV) and Zirconium(IV) with Tetradentate Ligands (ONNO)

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A series of new metal chelates of Sn(IV) and Zr(IV) with the Schiff bases formed by the condensation of isatin with diamines have been synthesized and characterized by elemental analyses, infrared, electronic ¹H NMR spectroscopy and molar conductivity measurements. The data suggest a 1:1 metal to ligand stoichiometry for all isolated complexes. They behave as dibasic ONNO tetradentate ligands.

Key Words: Isatin, Tin(IV), Zirconium(IV) diamines and tetradentate ligands.

INTRODUCTION

In continuation of our previous work¹⁻³ on Sn(IV) and Zr(IV) complexes of isatin Schiff bases, we report here the synthesis and identification of the complexes of Sn(IV) and Zr(IV) with Schiff bases formed by the condensation of isatin with ethylenediamine-*o*-phenylenediamine or tolylene, thereafter, abbreviated as HL₁: 2IZTen (ethylene diamine-*bis*isatin) HL₂: 2IZTfen: (*o*-phenylenediamine-*bis*isatin); HL₃: 2IZTtol (tolylene-*bis*isatin). The proposed structure of various ligands have been shown in Fig. 1.

The synthesized compounds were characterized by elements analysis, IR, ¹H NMR and electronic spectroscopy as well as by conductance measurements. The correlation of the experimental data allows to assign an octahedral stereochemistry to all the reported complexes⁴⁻⁷.

EXPERIMENTAL

All the reagents, tin tetrachloride (Merck), zirconium tetrachloride (Merck), ethylenediamine, *o*-phenylenediamine and tolylene (Aldrich) were of AR grade and were used without further purification.

Synthesis of the ligands: Solution of isatin (0.02 mol) in 100 mL ethanol and diamine (0.01 mol) in 50 mL ethanol were mixed and refluxed on steam both for 2 h and then the reaction mixture was allowed to concentrate in vacuum. The precipitated Schiff base was washed with ethanol and recrystallized from chloroform.

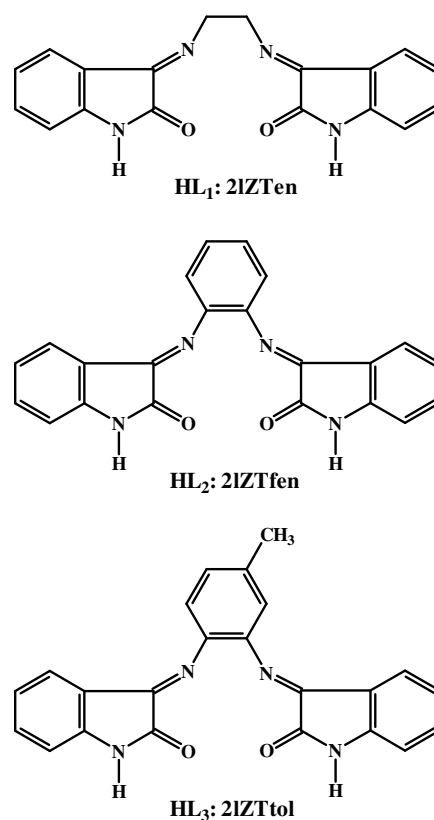


Fig. 1. Proposed structure of synthesized ligand

TABLE-1
ANALYTICAL AND PHYSICO-CHEMICAL DATA OF THE SYNTHESIZED COMPLEXES OF TIN(IV)
AND ZIRCONIUM(IV) WITH SCHIFF BASES DERIVED FROM ISATIN DIAMINES

Compounds	Colour	m.p. (°C)	Elemental analysis (%): Calcd. (Found)					λ_M (Ω^{-1} $\text{cm}^2 \text{mol}^{-1}$)
			C	H	N	Cl	M	
$\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_2$ (L ₁)	Pale yellow	–	67.86 (67.92)	4.42 (4.40)	17.58 (17.61)	–	–	–
$\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_2$ (L ₂)	Pale yellow	–	72.10 (72.13)	3.78 (3.82)	15.36 (15.30)	–	–	–
$\text{C}_{23}\text{H}_{17}\text{N}_4\text{O}_2$ (L ₃)	Pale yellow	–	72.64 (72.63)	4.23 (4.21)	14.80 (14.74)	–	–	–
$\text{SnCl}_2\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_2$	Pale brown	280	42.52 (42.48)	2.36 (2.42)	11.11 (11.07)	14.11 (14.04)	23.52 (23.47)	10.6
$\text{SnCl}_2\text{C}_{22}\text{H}_{12}\text{N}_4\text{O}_2$	Brick red	292	47.82 (47.76)	2.17 (2.20)	10.08 (10.11)	12.78 (12.82)	21.36 (21.44)	8.0
$\text{SnCl}_2\text{C}_{23}\text{H}_{15}\text{N}_4\text{O}_2$	Reddish brown	305	48.50 (48.52)	2.64 (2.58)	9.82 (9.85)	12.48 (12.46)	21.02 (20.87)	4.3
$\text{ZrCl}_2\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2$	Brick red	267	45.00 (45.04)	2.50 (2.48)	11.69 (11.71)	14.86 (14.85)	19.12 (19.07)	8.6
$\text{ZrCl}_2\text{C}_{22}\text{H}_{12}\text{N}_4\text{O}_2$	Red	283	50.38 (50.34)	2.29 (2.32)	10.72 (10.64)	13.38 (13.49)	17.36 (17.33)	8.0
$\text{ZrCl}_2\text{C}_{23}\text{H}_{15}\text{N}_4\text{O}_2$	Pinkish brown	294	51.07 (51.04)	2.77 (2.80)	10.38 (10.35)	13.14 (13.12)	16.90 (16.85)	6.8

Synthesis of metal complexes: $[\text{MCl}_2]$ complexes were prepared by the addition of metal salts (0.01 mol) in 50 mL anhydrous ethanol under nitrogen atmosphere to a hot ethanol solution of the ligand (0.01 mol/50 mL). Sodium methoxide was added in portionwise to the reaction mixture under nitrogen atmosphere with continuous stirring until pH reaches to 7.3. Then, the reaction mixture was heated on water steam bath for 4 h. A brown coloured product was settled down after the completion of reaction, that was filtered and recrystallized using solvent mixture of anhydrous ethanol and chloroform (20:30) and finally dried over P_2O_5 in vacuum.

RESULTS AND DISCUSSION

In the system $\text{MCl}_2\cdot\text{H}_2\text{L}$, where $\text{M} = \text{Sn(IV)}$ and Zr(IV) and $\text{H}_2\text{L} = 2\text{IZTen}$, 2IZTfen and 2IZTtol , the synthesis have been carried out in the molar ratio of 1:1 at pH 7.30. Complexes were isolated as sparingly soluble coloured product from the reaction mixture. These chelates are powder inform, which were recrystallized using proper solvents and precipitants. Complexes are stable even in moist air and decompose at higher temperature *ca.* 260-310 °C and are insoluble in most common organic solvents.

On the basis of elemental analysis the empirical formula of this complexes is $\text{MCl}_2\cdot\text{H}_2\text{L}$ where $\text{M} = \text{Sn(IV)}$ and Zr(IV) .

Molar conductivities for the MCl_2L complexes is 4.3-10.6 $\text{cm}^2 \text{mol}^{-1}$ measured in the freshly prepared 10^{-3} mol/L solution in DMF at room temperature. This suggests that anions are mostly covalently bonded. The physical data of the synthesized complexes have been presented in Table-1.

In order to ascertain the manner of the ligand coordination to the metallic centre IR spectra were recorded in the range of 4000-400 cm^{-1} in KBr, pellets (Table-2).

All three bands appearing at 3190-3235, 1740-1715 and 1652-1619 cm^{-1} in the ligand spectra were assigned to the stretching vibrational modes for $\nu(\text{N-H})$, $\nu(\text{C=O})$ and $\nu(\text{C=N})$, respectively.

All the bands assigned to the stretching vibrational modes for $\nu(\text{N-H})$, $\nu(\text{C=O})$ and $\nu(\text{C=N})$, in the free ligands disappear in the spectra of $[\text{MCl}_2\text{L}]$ compounds, but new bands are recorded at 1583-1572 and 1233-1225 cm^{-1} . These new bands have been assigned to the $\nu(\text{C=S})$ (new azomethine band) and $\nu(\text{C-O})$ vibrational modes, respectively, suggest the enolization of the NH hydrogen of isatin and the coordination of the zirconium through the oxygen of the C-O group.

TABLE-2
INFRARED DATA (cm^{-1}) OF LIGANDS AND
SYNTHESIZED COMPLEXES

Compd.	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=N}^-)$	$\nu(\text{C=O})$	$\nu(\text{M-N})$	$\nu(\text{M=O})$
HL ₁	3190	1740	1652	–	–	–	–
SnCl_2L_1	–	–	1620	1575	1230	440	515
ZrCl_2L_1	–	–	1600	1583	1225	448	500
HL ₂	3219	1715	1650	–	–	–	–
SnCl_2L_2	–	–	1615	1583	1228	468	481
ZrCl_2L_2	–	–	1610	1572	1233	460	480
HL ₃	3235	1733	1619	–	–	–	–
SnCl_2L_3	–	–	1606	1574	1229	441	511
ZrCl_2L_3	–	–	1603	1582	1228	440	514

The formation of the M-O and M-N bands is further supported by the appearance of $\nu(\text{M-O})$ and M-N bands is further supported by the appearance of $\nu(\text{M-O}')$ and $\nu(\text{M-N})$ bands in the regions 515-480 and 470-440 cm^{-1} , respectively in the spectra of the chelates.

The most important conclusion drawn from the infrared spectral evidence is that the diamine *bis(isatin)* Schiff base ligands is acting as chelating agent towards the central metal ions as dibasic ONNO tetradentate ligands *via* the two coordinating sites of azomethine nitrogen atoms and the two negatively charged oxygen atoms of isatin residue forming three five membered chelating ring^{8,9}.

Electronic spectral data: The electronic spectra were recorded by diffuse reflectance technique. The free ligands exhibit two bands at $\lambda = 300$ nm and $\lambda = 260$ nm. These bands may be assigned to an allowed $\pi\text{-}\pi^*$ electronic transition resulting from the local excitation of the π -system. The bands at $\lambda = 340$ nm suggests an $n\text{-}\pi^*$ transition. The Sn(IV) and Zr(IV) chelates are diamagnetic with no ligands field transition. Their diffuse reflectance spectra display two bands at $\lambda = 430$ -441 nm and $\lambda = 579$ -604 nm for $[\text{MCl}_2\text{L}]$ complexes. These bands may probably be attributed to the intra-ligand transition¹⁰.

NMR data: The ^1H NMR spectra of ligands and metal chelates were recorded in $(\text{CD}_3)_2\text{CO}$ solutions. The ^1H NMR spectra of ligands can be resolved into three distinct regions. The ^1H NMR spectrum of ethylenediamine-*bis(isatin)* exhibits two multiplies at $\delta = 2.9$ -3.6 and $\delta = 7.3$ -7.8 ppm and a doublets at $\delta = 11.6$ -11.8 ppm corresponding to the resonance of the aliphatic protons of ethylenic chain, the protons of the condensed aromatic nucleus of isatin residues and the NH proton belonging

to isatin, respectively. The integration of the ^1H NMR signals yields the proton ratio 2:4:1, respectively, which is consistent with the above assignments.

The ^1H NMR spectrum of *o*-phenylenediamine *bis*(isatin) exhibits a multiplet at $\delta = 7.2\text{--}7.8$, a triplet at $\delta = 8.6\text{--}8.5$ ppm and a doublet at $\delta = 11.8$ ppm corresponding to the resonance resulting from the condensed aromatic ring of isatin, the aromatic ring protons belonging to *o*-phenylenediamine and the π -H proton of the isatin. The integration of the ^1H NMR signals fields the proton ratio 4:2:1, respectively which is consistent with the assignments.

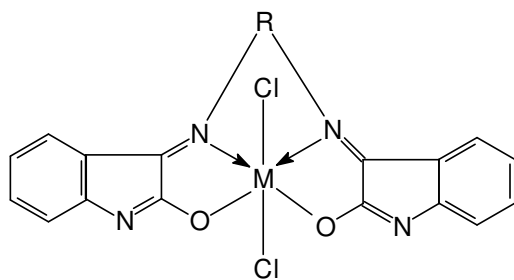


Fig. 2. Proposed structure of synthesized compounds $[\text{MCl}_2\text{L}]$ where $\text{R} = \text{C}_2\text{H}_2, \text{C}_6\text{H}_4, \text{C}_7\text{H}_6$ and $\text{M} = \text{Sn(IV)}$ and Zr(IV)

The ^1H NMR spectra of the neutral diamagnetic chelates of the type MCl_2L [$\text{M} = \text{Sn(IV)}$ and Zr(IV)] are similar to those of the ligands, expecting that the signal due to NH proton of isatin disappears. This proved the de-protonation of the NH group upon coordination and support the above infrared spectral data suggesting that the ligand acts as dibasic chelating agents.

Thus, the correlation of the experimental data allows the assignment of an octahedral stereochemistry to all the reported complexes (Fig. 2).

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