

Complexes of tin(IV) and zirconium(IV) with Schiff bases derived from isatin and diamines

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

In continuation of our previous work 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 Sr^{IV} with Schiff bases formed by condensation of isatin with ethylenediamine, *o*-phenylenediamine or tolylene, hereafter abbreviated as : HL' : 2IZTen : ethylenediamine-bis(isatin), HL'' : 2IZTfen : *o*-phenylenediamine-bis(isatin), HL''' : 2IZTtol : tolylene-bis(isatin) (Fig. 1).

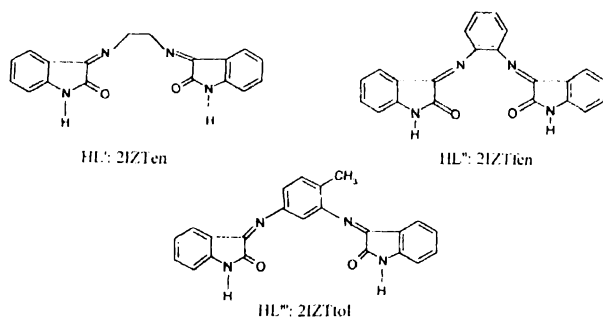


Fig. 1. Structure of ligands.

The synthesized compounds were characterized by elemental 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 complexes.

Results and discussion

In the systems MCl₄-H₂L (where M = Sn^{IV}, Zr^{IV} and

H₂L = 2IZTen, 2IZTfen, 2IZTtol) the syntheses have been carried out in the molar ratio 1 : 1 at pH 7.3. The complexes were isolated as sparingly soluble, coloured products from the reaction medium. These chelates are powders stable in moist air. They decompose at higher temperature (260–310°C) and are insoluble in most common organic solvents.

On the basis of chemical analysis, the minimal formulae correspond to [MCl₂L], M = Sn^{IV}, Zr^{IV}.

Molar conductivities for the [MCl₂L] complexes, 4.3–10.6 Ω⁻¹ cm² mol⁻¹, measured in freshly prepared 10⁻³ mol dm⁻³ solutions in DMF at room temperature, indicate that the complexes are non-electrolytes in solution. This suggests that the anions are covalently bonded (Table 1).

Spectral data :

In order to ascertain the manner of the ligand coordina-

Table 1. Analytical and physical data of the synthesized compounds

Compd.	Empirical formula ^a	M.p. ^b °C	Colour	Λ _M ^c Ω ⁻¹ cm ² mol ⁻¹
SnCl ₂ L'	SnCl ₂ C ₁₈ H ₁₂ N ₄ O ₂	280	Pale brown	10.6
ZrCl ₂ L'	ZrCl ₂ C ₁₈ H ₁₂ N ₄ O ₂	267	Beige	8.6
SnCl ₂ L''	SnCl ₂ C ₂₂ H ₁₂ N ₄ O ₂	292	Brick	8.0
ZrCl ₂ L''	ZrCl ₂ C ₂₂ H ₁₂ N ₄ O ₂	283	Beige	10.2
SnCl ₂ L'''	SnCl ₂ C ₂₃ H ₁₅ N ₄ O ₂	305	Reddish brown	4.3
ZrCl ₂ L'''	ZrCl ₂ C ₂₃ H ₁₅ N ₄ O ₂	294	Pink-beige	6.8

^aThe elemental analyses were in good agreement with the calculated percentages of Sn/Zr, C, H, N and Cl for all the synthesized compounds.

^bThe compounds decompose.

^cThe conductance was recorded in DMF (10⁻³ M solutions).

tion to the metallic centre IR spectra in the 400–4000 cm^{-1} range were recorded.

Table 2. IR data (cm^{-1})

Compd.	ν_{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': 2IZTen	3190	1740	1652	–	–	–	–
$\text{SnCl}_2\text{L}'$	–	–	1620	1575	1230	440	515
$\text{ZrCl}_2\text{L}'$	–	–	1600	1583	1225	448	500
HL'': 2IZTfen	3219	1715	1650	–	–	–	–
$\text{SnCl}_2\text{L}''$	–	–	1615	1583	1228	468	481
$\text{ZrCl}_2\text{L}''$	–	–	1610	1572	1233	460	480
HL''': 2IZTtol	3235	1733	1619	–	–	–	–
$\text{SnCl}_2\text{L}'''$	–	–	1606	1574	1229	441	511
$\text{ZrCl}_2\text{L}'''$	–	–	1603	1582	1228	440	514

* New azomethine band.

The most important IR bands, presented and assigned in Table 2, show the following characteristics :

The three bands appearing at 3190–3235, 1740–1715 and 1652–1619 cm^{-1} in the ligand spectra, were assigned to stretching vibration modes ν_{NH} , $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$, respectively.

All the bands assigned to stretching vibration modes ν_{NH} , $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$ in the free ligands disappear in the spectra of the $[\text{MCl}_2\text{L}]$ compounds, but new bands are recorded at 1583–1572 and 1225–1233 cm^{-1} . These new bands, assigned to the $\nu_{\text{C=N}^*}$ (new azomethine bond) and $\nu_{\text{C-O}}$ vibration modes respectively, suggest the enolisation of the NH hydrogen of isatin and the coordination at tin/zirconium through the oxygen of the C–O group.

The formation of the M–O and M–N bonds is further supported by the appearance of $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ bands in the regions 480–515 and 440–470 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 ligand is acting as chelating agent towards the central metal ions as a dibasic ONNO tetradentate ligand, via the two coordinating sites of azomethine nitrogen atoms and the two negatively charged oxygen atoms of isatin residues, forming three five-membered chelating rings³.

Electronic spectra were recorded by diffuse reflectance technique. The free ligands exhibit two bands at 300 and 260 nm. These bands may be assigned to an allowed π - π^* electronic transition resulting from the local excitation of the π -system. The bands at 340 nm suggest an n - π^* electronic transition. The Sn^{IV} and Zr^{IV} chelates are diamagnetic with no ligand field transition. Their diffuse

reflectance spectra display two bands at 430–441 and 579–604 nm for $[\text{MLCl}_2]$. These bands may probably be attributed to intra-ligand transitions⁴.

NMR data :

The ^1H NMR spectra of the ligands and metal chelates were recorded in $(\text{CD}_3)_2\text{CO}$ solutions.

The ^1H spectra of the ligands can be resolved into three distinct regions. The ^1H NMR spectrum of ethylenediamine-bis(isatin) exhibits two multiplets at 2.9–3.6 and 7.3–7.8 ppm and a doublet at 11.6–11.8 ppm corresponding, respectively, to the resonance of the aliphatic protons of ethylenic chain, the protons of the condensed aromatic nuclei of isatin residues and the NH proton belonging to isatin. 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 7.2–7.8, a triplet at 8.1–8.5 ppm and a doublet at 11.8 ppm corresponding, respectively, to the resonances resulting from the condensed aromatic ring protons of isatin, the aromatic ring protons belonging to *o*-phenylenediamine and the NH protons of the isatin. The integration of the ^1H NMR signals yields the proton ratio 4 : 2 : 1, respectively, which is consistent with the assignments.

The ^1H NMR spectra of the neutral diamagnetic chelates of the type MCl_2L ($\text{M} = \text{Sn}^{\text{IV}}$ and Zr^{IV}) are similar to those of the ligands, excepting that the signal due to NH proton of isatin disappears. This proves the deprotonation of the NH group upon complexation and supports the above infrared spectral data suggesting that the ligand acts as dibasic chelating agent.

The correlation of the experimental data allows assigning an octahedral stereochemistry to all the reported complexes (Fig. 2).

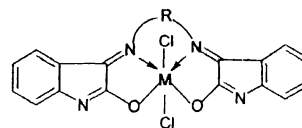


Fig. 2. Propose structures of complex compounds $[\text{MCl}_2\text{L}]$.

($\text{R} = \text{C}_2\text{H}_4, \text{C}_6\text{H}_4, \text{C}_7\text{H}_6$; $\text{M} = \text{Sn}^{\text{IV}}, \text{Zr}^{\text{IV}}$)

Experimental

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

Note

Synthesis of the ligands : Solutions of isatin (0.02 mol) in 100 ml ethanol and diamine (0.01 mol) in 50 ml ethanol were mixed and refluxed on steam bath for 2 h, and then concentrated in vacuum. The precipitated Schiff base, was washed with ethanol and recrystallized from chloroform (Found : C, 67.92; H, 4.40; N, 17.61. Calcd. for $C_{18}H_{14}N_4O_2$: C, 67.86; H, 4.42; N, 17.58%); (Found : C, 72.13; H, 3.82; N, 15.30. Calcd. for $C_{22}H_{14}N_4O_2$: C, 72.10; H, 3.78; N, 15.36%); (Found : C, 72.63; H, 4.21; N, 14.74. Calcd. for $C_{23}H_{17}N_4O_2$: C, 72.64; H, 4.23; N, 14.80%).

[MCl₂L] complexes were prepared by addition of metal salts (0.01 mol) in 50 ml anhydrous ethanol, under nitrogen atmosphere, to a hot ethanolic solution of the ligand (0.01 mol/50 ml); then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added until pH reaches 7.3. The reaction mixture was refluxed on water steam bath, for 4 h. The complexes were washed with anhydrous ethanol and dried over P₂O₅ in vacuum (Found : Sn, 23.52; Cl, 14.11; N, 11.11. Calcd. for $SnCl_2C_{18}H_{12}N_4O_2$: Sn, 23.47; Cl, 14.04; N, 11.07%); (Found : Zr, 19.12; Cl, 14.86; N, 11.69. Calcd. for $ZrCl_2C_{18}H_{12}N_4O_2$: Zr, 19.07; Cl, 14.85; N, 11.71%); (Found : Sn, 21.36; Cl, 12.78; N, 10.08. Calcd. for $SnCl_2C_{22}H_{12}N_4O_2$: Sn, 21.44; Cl, 12.82; N, 10.11%); (Found : Zr, 17.36; Cl, 13.38; N, 10.72. Calcd. for

$ZrCl_2C_{22}N_4O_2$: Zr, 17.33; Cl, 13.49; N, 10.64%); (Found : Sn, 21.02; Cl, 12.46; N, 9.82. Calcd. for $SnCl_2C_{23}H_{15}N_4O_2$: Sn, 20.87; Cl, 12.48; N, 9.85%); (Found : Zr, 16.90; Cl, 13.14; N, 10.38. Calcd. for $ZrCl_2C_{23}H_{15}N_4O_2$: Zr, 16.85; Cl, 13.12; N, 10.35%).

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