

## COMPLEXES OF Ti(IV) AND Zr(IV) WITH SOME BIDENTATE SCHIFF BASES DERIVED FROM ISATIN

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Six new metal chelates of Ti(IV) and Zr(IV) with the Schiff base ligands formed by condensation of isatin with aromatic amines (aniline, *p*-toluidine, *m*-nitro-aniline) have been synthesized and characterized by elemental analysis, infrared, electronic spectral data and molar conductivity measurements. In different conditions, two kinds of complexes of the same Schiff Base were obtained,  $TiCl_4(HL)$  and  $ZrCl_2L_2$ . The ligands behaves as NO bidentate. Conductance data reveal a non-electrolytic nature of the complexes.

### Introduction

Although much attention has been directed to study the metal complexes of the Schiff base ligands derived from isatin [1÷7], no investigations have appeared in literature to describe the M(IV) (M=Sn(IV), Ti(IV) and Zr(IV)) complexation of Schiff bases derived from isatin with aromatic amines. In view of versatile importance of isatins [8÷12], and in continuation of our previous work dealing with the Sn(IV) and Zr(IV) complexes of isatin Schiff bases [13÷16], we herein, deemed desirable to report the synthesis and identification of the metal complexes of Ti(IV) and Zr(IV), with Schiff Bases derived from isatin and aniline / *p*-toluidine / *m*-nitro- aniline, hereafter abbreviated: HIAN (isatin - aniline Schiff Base), HIPT (isatin - *p*-toluidine), HIMNA (isatin - *m*-nitro-aniline).

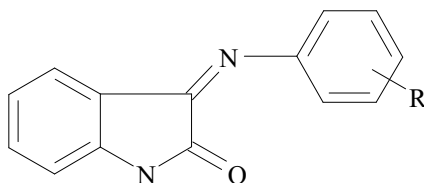


Fig. 1: Schiff bases

In different conditions, two kinds of complexes of the same Schiff Base were obtained,  $TiCl_4(HL)$  and  $ZrCl_2L_2$ , where HL are the Schiff Bases mentioned above.

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## Experimental

All reagents used were of analytical grade.  $\text{TiCl}_4$  (Riedel),  $\text{ZrCl}_4$  (Merck), aniline, *p*-toluydine *m*-nitro-aniline (Aldrich) were used without further purification. Anhydrous ethanol was obtained using the method presented in literature [17]. *Synthesis of the ligands* were made according to our previous work [14].

### Synthesis of complexes

$[\text{TiCl}_4(\text{HL})]$  complexes have been prepared by mixing anhydrous ethanolic solutions of Schiff Base and metal chloride in 1:1 molar ratio under nitrogen atmosphere at  $\text{pH}=6.5$ . The mixture was stirred during one hour under nitrogen atmosphere and than was refluxed on a water bath for 8 hours. The solvent excess was distilled.

$[\text{ZrCl}_2\text{L}_2]$  complexes were prepared by addition of metal chloride (0.01 mol) in 50 ml anhydrous ethanol to a hot ethanolic solution of the ligand (0.02 mol / 50ml); then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added until  $\text{pH}$  reaches 7.3. The reaction mixture was refluxed on a steam bath for 4 hours.

The complexes were precipitated upon concentration. The compounds were filtered, washed with anhydrous ethanol and dried over  $\text{P}_2\text{O}_5$  in vacuum.

### Chemical analysis

C, H and N were determined by micro-analytical methods. The metal and chloride were estimated gravimetrically [18].

$\text{TiCl}_4(\text{HIAN})$  *Calc*: Ti 11.75; Cl 34.51; N 6.78%. *Found*: Ti 11.62 ; Cl 34.47 ; N 6.80%.

$\text{TiCl}_4(\text{HIPT})$  *Calc*: Ti 11.22; Cl 33.50; N 6.76%. *Found*: Ti 11.24 ; Cl 33.34 ; N 6.80%.

$\text{TiCl}_4(\text{HIMNA})$  *Calc*: Ti 11.21; Cl 33.45; N 6.55%. *Found*: Ti 11.24 ; Cl 33.34 ; N 6.57%.

$\text{ZrCl}_2(\text{IAN})_2$  *Calc*: Zr 15.10 ; Cl 11.70; N 9.32%. *Found*: Zr 15.09 ; Cl 11.75; N 9.26%.

$\text{ZrCl}_2(\text{IPT})_2$  *Calc*: Zr 16.98 ; Cl 13.42; N 10.47%. *Found*: Zr 17.14 ; Cl 13.34; N 10.52%.

$\text{ZrCl}_2(\text{IMNA})_2$  *Calc*: Zr 13.20 ; Cl 9.82; N 12.25%. *Found*: Zr 13.14 ; Cl 10.23; N 12.10%.

*Electronic spectra* were recorded in range 230-800 nm on a UNICAM UV/VIS Spectrometer UV 4.

*The IR spectra* were recorded in range 400-4000  $\text{cm}^{-1}$  with a BIO-RAD FTS 135 spectrophotometer, using KBr pellets.

*Molar conductivities* were measured in freshly prepared  $10^{-3}$   $\text{mol}\cdot\text{dm}^{-3}$  solutions in DMF at room temperature with a digital conductivity meter Consort C 533.

## Results and Discussion

The Schiff Bases under present consideration react with titanium(IV) and zirconium(IV) chlorides in anhydrous ethanol medium, to give colored amorphous compounds, stable in air. They decompose at higher temperature (240-270°C) and are insoluble in most common organic solvents.

*Elemental analysis* data suggest 1:1 or, respectively 1:2 metal : ligand stoichiometries, the general formula, in each being  $\text{TiCl}_4(\text{HL})$ , respectively  $\text{ZrCl}_2(\text{L})_2$ .

*The conductivity values* for the  $[\text{TiCl}_4(\text{HL})]$  complexes (in DMF,  $10^{-3}$  mol, 25 °C), ranging in the 6.5-10.4  $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  region, indicate that the non-electrolytic nature of the compounds. This suggests that the anions are covalently bonded.

The *most important IR bands*, presented and assigned in Table 1 show the following characteristics:

The three bands appearing at 3190, 1740 and 1654  $\text{cm}^{-1}$  in the ligands spectra, were assigned to stretching vibration modes  $\nu_{\text{NH}}$ ,  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  respectively.

In the cases of the  $[\text{TiCl}_4(\text{HL})]$  compounds, the spectra reveal that the band having a maximum at 1740  $\text{cm}^{-1}$  in the free ligands is shifted to lower wave numbers. This shift indicates the implication of carbonyl oxygen in the coordination at the metallic center.

The band appearing at 1650  $\text{cm}^{-1}$  in the free ligands, assignable to the  $\nu_{\text{C=N}}$  vibration mode, is shifted to lower wave numbers with a  $\Delta\nu = 35$   $\text{cm}^{-1}$  in the complexes spectra, this indicating the participation of azomethinic nitrogen atom in coordination.

The band due to the  $\nu_{\text{NH}}$  vibration mode in isatin, having the maximum at 3190  $\text{cm}^{-1}$  in the free ligands, remains largely unaffected in the chelates.

**Table 1. Infrared spectra ( $\text{cm}^{-1}$ )**

Compound	$\nu_{\text{NH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=N}^*}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
HIAN	3191 m,br	1743 s	1654 s-m	-	-	-	-
$[\text{TiCl}_4(\text{HIAN})]$	3190	1708 m	1616 m	-	-	522 w	445 w
$[\text{ZrCl}_2(\text{IAN})_2]$	-	-	1617 m	1570 m	1226 m-w	500 w	448 w
HIPT	3180 m,br	1744 s	1654 s-m	-	-	-	-
$[\text{TiCl}_4(\text{HIPT})]$	3180	1710 m	1616 m	-	-	531 w	454 w
$[\text{ZrCl}_2(\text{IPT})_2]$	-	-	1615 m	1566 m	1224 m-w	520 w	440 w
HIMNA	3192 m,br	1737 s	1653 s-m	-	-	-	-
$[\text{TiCl}_4(\text{HIMNA})]$	3190	1717 m	1618 m	-	-	529 w	449 w
$[\text{ZrCl}_2(\text{IMNA})_2]$	-	-	1620 m	1570 m	1226 m-w	514 w	445 w

The most important conclusion drawn from this discussion is that the HL Schiff Base ligand is coordinated to the central metal ion as **NO bidentate ligand**. The free bonding sites are the central azomethine nitrogen atom and the oxygen of the carbonyl groups.

The bands assigned to stretching vibration modes  $\nu_{\text{NH}}$  and  $\nu_{\text{C=O}}$  in the free ligands disappear in the spectra of the  $[\text{ZrCl}_2\text{L}]$  compounds, but new bands are recorded at 1570 and 1225  $\text{cm}^{-1}$ . 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 NH hydrogen of isatin and the coordination at titanium/zirconium through the oxygen of the C-O group.

The band appearing at 1650  $\text{cm}^{-1}$  in the free ligands, assignable to the  $\nu_{\text{C=N}}$  vibration mode, is shifted to lower wave numbers in the complexes spectra, this indicating the participation of azomethinic nitrogen atom in coordination.

In this case the HL, Schiff Base ligand, is coordinated to the central metal ion as ***uninegative NO bidentate ligand***.

The formation of M-O and M-N bonds is further supported by the appearance of  $\nu_{\text{M-O}}$  and  $\nu_{\text{M-N}}$  in the regions 440÷450 and 500÷530  $\text{cm}^{-1}$  respectively in the spectra of chelates [19].

The *electronic spectra* of the ligands in ethanol exhibit three bands at 230 nm ( $\pi \rightarrow \pi^*$ ), 290 nm ( $n \rightarrow \pi^*$ ) and 380 nm. The *diffuse reflectance spectra* are similar and shifted toward lower frequencies..

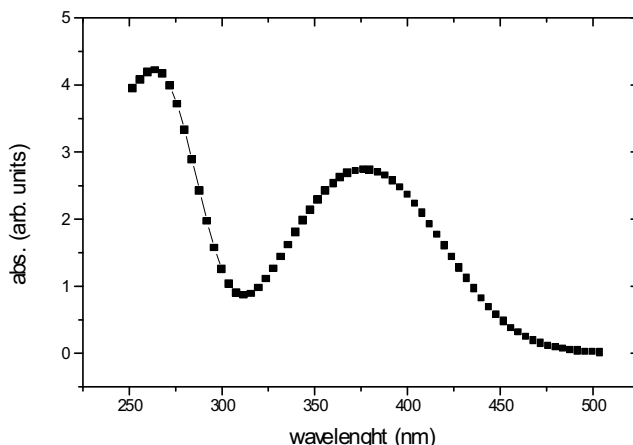


Fig. 2: Electronic spectrum (diffuse reflectance technique) of HIAN.

In the visible region, the bands of the ligands, appearing at  $\sim 400$  nm, are less intense.

The Ti(IV) and Zr(IV) chelates are diamagnetic with no ligand field transition. In the  $[\text{TiCl}_4(\text{HL})]$  complexes spectra the bands are shifted with about 20 nm to lower frequencies, proving the ligands coordination at metallic center (Fig. 3). In the  $\text{ZrCl}_2\text{L}_2$  complexes spectra these bands are shifted toward lower frequencies or is replaced by more complicated bands of different intensities [20], indicating a more accentuate conjugation between the azomethine group and the aromatic ring (Fig. 4).

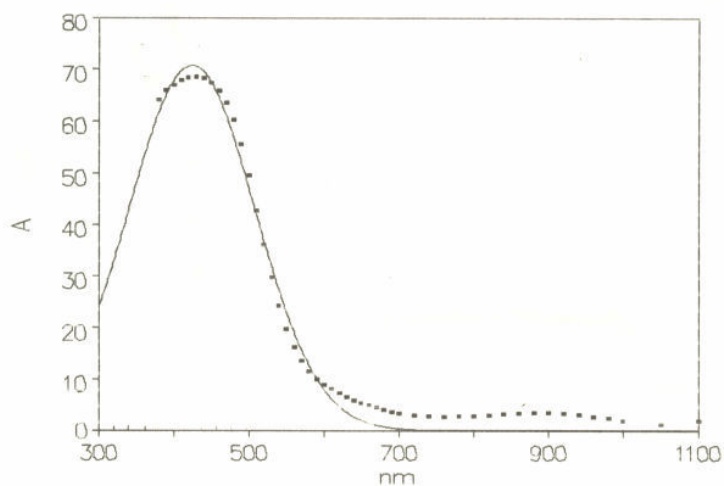


Fig. 3: Electronic spectrum (diffuse reflectance technique) of  $TiCl_4(HIAN)$

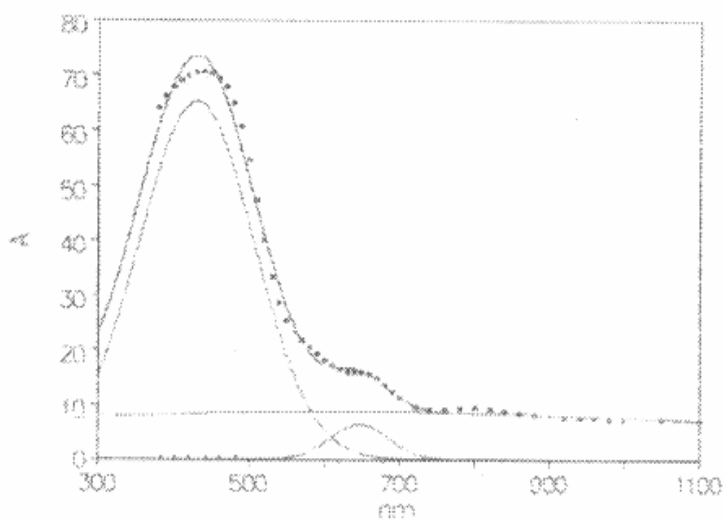


Fig. 4: Electronic spectrum (diffuse reflectance technique) of  $ZrCl_2(IAN)_2$

The correlation of the experimental data allows assigning an octahedral stereochemistry to all the reported complex compounds. The proposed structural representations are presented in Fig. 5:

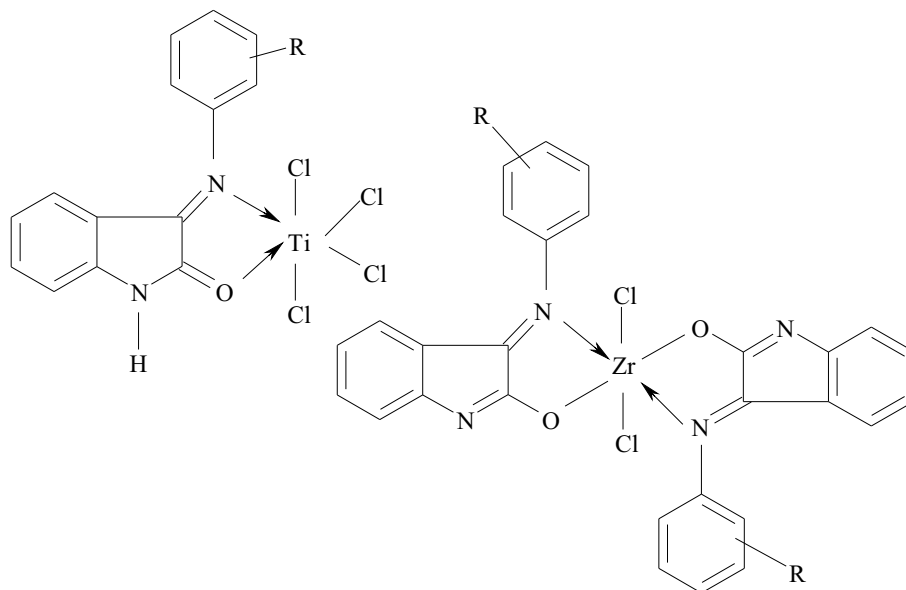


Fig. 5: Propose structures of complex compounds:  $TiCl_4(HL)$  and  $ZrCl_2L_2$

## Conclusion

We report here the synthesis and the characterization of six new complexes of titanium (IV) and zirconium (IV) with Schiff Bases derived from isatin and aniline / *p*-toluidine / *m*-nitro- aniline. The syntheses were conducted in conditions allowing the bi-dentate (neutral or mono-basic) function of the ligands. Varying the conditions under these requirements, two kinds of complexes of the same Schiff Base were obtained,  $[TiCl_4(HL)]$  and  $[ZrCl_2L_2]$ , where HL are the Schiff Bases mentioned above.

The synthesized compounds were characterized by elemental analysis, IR, electronic spectroscopy, as well as by conductance measurements.

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