

CONTROLLED SYNTHESIS I. REACTION OF Sn(IV) AND Zr(IV) WITH SCHIFF BASES DERIVED FROM 1-H-INDOL-2,3-DIONE AND DIAMINES

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

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 Sn(IV) and Zr(IV) complexation of Schiff bases derived from isatin with aliphatic and aromatic diamines. 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÷15] we herein, deemed desirable to report the synthesis and identification of the metal complexes of Sn(IV) and Zr(IV), with the Schiff base ligands formed by condensation of isatin with ethylenediamine, *o*-phenylenediamine and tolylene.

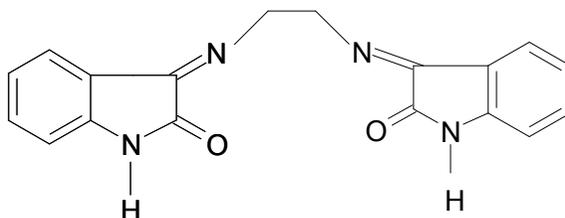


Fig. 1: Structure of ethylenediamine-bis(isatin)

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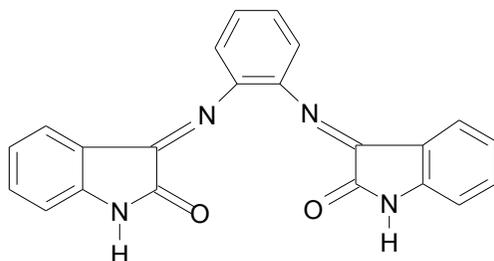


Fig. 2: Structure of *o*-phenylenediamine-bis(isatin)

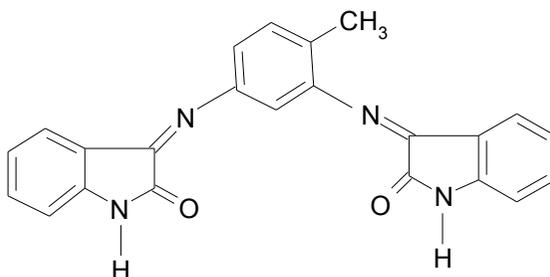


Fig. 3: Structure of tolylene-bis(isatin)

Experimental

All reagents used were of analytical grade and were used without further purification.

Synthesis of the ligands

Ethanol solutions of isatin (0.02 mol) in 100 ml and diamine (0.01 mol) in 50 ml were mixed and refluxed on steam bath for 2h, and then concentrated *in vacuo*. The resulting Schiff base ligand precipitated was filtered off, washed with ethanol and recrystallized from chloroform.

Synthesis of complexes

[MLCl₂] complexes were prepared by addition of metal salts (0.01 mol) in 50 ml anhydrous ethanol to a hot ethanolic solution of the ligand (0.01 mol / 50ml); then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added until pH reaches 7.3. The reaction mixture was refluxed on a steam bath for 4 hours.

Chemical analysis SnCl₂C₁₈H₁₂O₂N₄ *Requires:* Sn 23.47; Cl 14.04; N 11.07%. *Found:* Sn 23.52; Cl 14.11; N 11.11%. ZrCl₂C₁₈H₁₂O₂N₄ *Requires:* Zr 19.07; Cl 14.85; N 11.71%. *Found:* Zr 19.12; Cl 14.86; N 11.69%. SnCl₂C₂₂H₁₂O₂N₄ *Requires:* Sn 21.44; Cl 12.82; N 10.11%. *Found:* Sn 21.36; Cl 12.78; N 10.08. ZrCl₂C₂₂H₁₂O₂N₄ *Requires:* Zr 17.33; Cl 13.49; N 10.64%. *Found:* Zr 17.36; Cl 13.38; N 10.72%. SnCl₂C₂₃H₁₅O₂N₄ *Requires:* Sn 20.87; Cl 12.48; N 9.85%. *Found:* Sn 21.02; Cl 12.46; N 9.82%. ZrCl₂C₂₃H₁₅O₂N₄ *Requires:* Zr 16.85; Cl 13.12; N 10.35%. *Found:* Zr 16.90; Cl 13.14; N 10.38%.

The complexes were precipitated upon concentration. The compounds were filtered, washed with anhydrous ethanol and dried over P_2O_5 in vacuum.

Chemical analysis was performed by using the well-known micromethods.

The diffuse reflectance spectra were recorded in range 350-800 nm on a VSU2-P Zeiss Jena spectrophotometer, using MgO as standard.

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

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

Results and Discussion

In the systems $MCl_4 \cdot H_2L$ (where $M = Sn(IV); Zr(IV)$ and $H_2L =$ ethylenediamine-bis(isatin), *o*-phenylenediamine-bis(isatin), tolylene-bis(isatin)) the syntheses have been developed in the molar ratio 1:1 at $pH=7.3$. The complexes were isolated as sparingly soluble, beige coloured products from the reaction medium. These chelates are powders stable towards air and moisture. They decompose at higher temperature (270-320°C) and are insoluble in most common organic solvents.

On the basis of *chemical analysis* the minimal formula correspond to $[MLCl_2]$, $M=Sn(IV)$, $Zr(IV)$.

The conductivity values for the $[MLCl_2]$ complexes ($6.5-10.4 \Omega^{-1}.cm^2.mol^{-1}$) indicate that the complexes are non-electrolytes in solution. 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 3190-3235, 1740-1715 and 1652-1619 cm^{-1} in the ligands spectra, were assigned to stretching vibration modes ν_{NH} , $\nu_{C=O}$ and $\nu_{C=N}$ respectively.

All the bands assigned to stretching vibration modes ν_{NH} , $\nu_{C=O}$ and $\nu_{C=N}$ in the free ligands disappear in the spectra of the $[MLCl_2]$ compounds, but new bands are recorded at 1583-1572 and 1225-1233 cm^{-1} . These new bands, assigned to the $\nu_{C=N^*}$ (new azomethine bond) and ν_{C-O} vibration modes respectively, suggest the enolysation of NH hydrogen of isatin and the coordination at tin/zirconium through the oxygen of the C-O group.

The formation of M-O and M-N bonds is further supported by the appearance of ν_{M-O} and ν_{M-N} in the regions 480-515 and 440-470 cm^{-1} respectively in the spectra of chelates.

The most important conclusions 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 of isatin residues forming three five-membered chelating rings.

Electronic spectra were recorded in diffuse reflectance spectra (MgO). The Sn(IV) and Zr(IV) chelates are diamagnetic with no ligand field transition. Their diffuse reflectance

spectra manifest two bands at 430-441 and 579-604 nm for $[MLCl_2]$. These bands may probably be attributed to intraligand transitions.

Table 1. Infrared spectra (cm^{-1})

Compound	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$	ν	ν_{C-O}	ν_{M-N}	ν_{M-O}
$H_2L'=2IZTen$	3190 m,br	1740 s	1652 s-m	–	–	–	–
$[SnCl_2L']$	–	–	1620 m	1575 m	1230 m-w	440 w	515 w
$[ZrCl_2L']$	–	–	1600 m	1583 m	1225 m-w	448 w	500 w
$H_2L''=2IZTfen$	3219 m,br	1715 s	1650 s-m	–	–	–	–
$[SnCl_2L'']$	–	–	1615 m	1583 m	1228 m-w	468 w	481 w
$[ZrCl_2L'']$	–	–	1610 m	1572 m	1233 m-w	460 w	480 w
$H_2L'''=2IZTtol$	3235 m,br	1733 s	1619 s-m	–	–	–	–
$[SnCl_2L''']$	–	–	1606 m	1574 m	1229 m-w	441 w	511 w
$[ZrCl_2L''']$	–	–	1603 m	1582 m	1228 m-w	440 w	514 w

The correlation of the experimental data allows assigning a octahedral stereochemistry to all the reported complex compounds. The proposed structural representations are presented in Figs. 4 and 5:

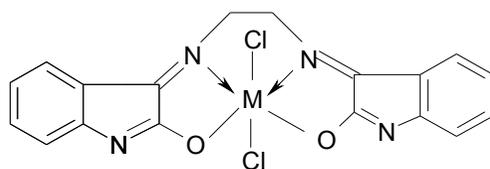


Fig. 4: Proposed structures of complex compounds $[MCl_2L]$; $M=Sn(IV), Zr(IV)$; $H_2L=2IZTen$

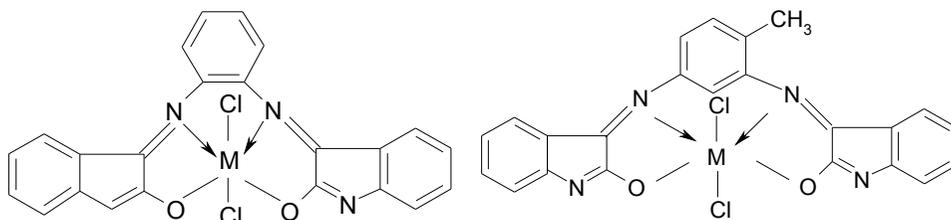


Fig. 5: Proposed structures of complex compounds $[MCl_2L]$ $M=Sn(IV), Zr(IV)$; $H_2L=2IZTfen, 2IZTtol$

Conclusion

We report here the synthesis and the characterization of new complexes of Sn(IV) and Zr(IV) with the Schiff Base ligands derived from isatin and aliphatic and aromatic diamines. The syntheses were conducted in conditions allowing the tetradentate bi-basic function of the ligands and the stability of Sn/Zr(IV). The synthesized compounds were characterized by elemental analysis, IR and electronic spectroscopy, as well as by conductance measurements. The correlation of the experimental data allows assigning an octahedral stereochemistry to all the reported complex compounds.

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