

COMPLEXES OF Sn(IV) AND Zr(IV) WITH A SCHIFF BASE LIGAND DERIVED FROM ISATIN AND O-AMINOPHENOL

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A series of new metal chelates of Sn(IV) and Zr(IV) with a Schiff base ligand formed by condensation of isatin with *o*-aminophenol have been synthesized and characterized via elemental analyses, infrared, electronic spectral data and conductivity measurements.

Introduction

Metal complexes of the Schiff bases formed by condensation of the active ketonic and aldehydic compounds with aromatic amines have been reported [1÷4]. However, no investigations are known on the study of Sn(IV) and Zr(IV) complexes of Schiff bases derived from isatin with aromatic amines. Isatin and its derivatives have an important biological activity (like anticonvulsive action, antiviral activity, insecticide and fungicide etc.) [5÷7]. These organic compounds can act as ligands, having functional groups with nitrogen and oxygen as donor atoms [8÷10]. The study of ligand formed by condensation of *o*-aminophenol with isatin, hereafter abbreviated as HIAP, gave us the possibility to isolate and characterized new complexes of Sn(IV) and Zr(IV).

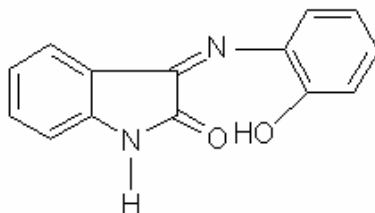


Fig. 1: Structure of HIAP Schiff base ligand.

Experimental

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

Synthesis of the ligand

The Schiff Base ligand HIAP was prepared by reacting equimolar amounts of *o*-aminophenol (0.02 mol; 2.18 g) and isatin (0.02 mol; 2.94 g) in 150 ml absolute methanol. The reaction mixture was refluxed on a steam bath for 4 hours. The excess of

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solvent was partially evaporated and the brownish mass product was precipitated by cooling and filtered off, washed with methanol and dried over P_4O_{10} in vacuo at room temperature.

Synthesis of complexes

$[M(IAP)_2]Cl_2$ complexes were prepared by addition of metal salts (0.01 mol) in 50 ml anhydrous methanol to a hot methanolic solution of the ligand (0.02 mol / 50ml), under nitrogen atmosphere and continuous stirring. The reaction mixture was refluxed on a steam bath for 4 hours.

Chemical analysis. Found: Sn 18.02 ; Cl 10.76 ; N 8.32% . $SnCl_2C_{28}H_{18}O_4N_4$ *Requires:* Sn 17.89; Cl 10.68; N 8.44%. *Found:* Zr 14.40 ; Cl 11.34; N 8.68% . $ZrCl_2C_{28}H_{18}O_4N_4$ *Requires:* Zr 14.34 ; Cl 11.14; N 8.80% .

$[M(IAP)_2]$ complexes: the ligand Schiff Base (0,02mol in 50 ml anhydrous methanol) was added drop wise, under nitrogen atmosphere, to metal (IV) chloride (0,01 mol MCl_4 in 25 ml anhydrous methanol); then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added until pH reaches 7,4. The reaction mixture was refluxed on steam bath for 8 hours.

Chemical analysis. Found: Sn 20.22 ; N 9.40%. $SnC_{28}H_{16}O_4N_4$ *Requires:* Sn 20.10; N 9.48%. *Found:* Zr 16.38; N 9.87%. $ZrC_{28}H_{16}O_4N_4$ *Requires:* Zr 16.20; N 9.94% .

The complexes were precipitated upon concentration. The compound was 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.

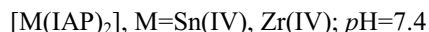
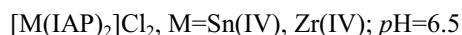
The IR spectra were recorded in range 400-4000 nm with a BIO-RAD FTS 135 spectrophotometer, using KBr pellets.

Molar conductivities were measured in freshly prepared 10^{-3} mol.dm⁻³ solutions in DMF at room temperature with a digital conductivity meter Consort C533.

Results and Discussion

In the systems MCl_4 -HIPA (where M = Sn(IV) and Zr(IV)) the syntheses have been developed in the molar ratio 1:2, in different conditions of pH. The complexes were isolated as sparingly soluble, brown (pH=6.5) and beige (pH=7.4), respectively, coloured products from the reaction medium. These chelates are powders stable in atmospheric conditions and insoluble in most common organic solvents.

On the basis of *chemical analysis* the minimal formula correspond to:



The conductivity values for the $[M(IAP)_2]$ complexes ($6.5 \div 10.4 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) indicate that the complexes are non-electrolytes in solution. This suggests that the anions are covalently bonded. On the other hand conductivity values measured under same conditions for the $[M(IAP)_2]Cl_2$ complexes ($60 \div 65 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) indicate their electrolytic behaviour. This suggests that the anion (Cl^-) is ionically bonded in the outer sphere of coordination.

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

HIAP	$[Sn(IAP)_2]Cl_2$	$[Sn(IAP)_2]$	$[Zr(IAP)_2]Cl_2$	$[Zr(IAP)_2]$	Assignments
-	464w	445w	472w	454w	ν_{M-N}
-	556w	545w	530w	556w	ν_{M-O}
1295m	1270m	1243m	1265m	1235m	ν_{C-O}
-	-	1580m-s	-	1578m-s	$\nu_{C=N^*}$
1617s	1618s	1619s	1616s	1618s	ν_{sch}
1670m	1649m	1649m	1644s-m	1648m	$\nu_{C=N}$
1726vs	1710s	-	1712s	-	$\nu_{C=O}$ cyclic ketones
3136m	3130m,br	-	3135m,br	-	ν_{NH}
3249m	-	-	-	-	ν_{OH}

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

The three bands appearing at 3190, 1726 and 1670 cm^{-1} in the ligands spectra, were assigned to stretching vibration modes ν_{NH} , $\nu_{C=O}$ and $\nu_{C=N}$ respectively.

In the cases of the $[M(IAP)]Cl_2$ compounds (**1:2**, $pH=6.5 \div 7$) the band appearing at 1670 cm^{-1} in the free ligands, assignable to the vibration mode, undergoes shift to lower wave numbers in the complexes spectra, this indicating the participation of azomethinic nitrogen atom in coordination.

The band at 1726 cm^{-1} in spectrum of the free ligand, assignable to $\nu_{C=O}$ of isatin moiety, shifts towards lower values in chelates (1710 cm^{-1}) indicating that the carbonyl oxygen atom of the isatin residue is one of the coordinating sites.

The band due to the ν_{NH} vibration mode in isatin, having the maximum at 3190 cm^{-1} in the free ligands, remains largely unaffected in the chelates proving evidence for its non-coordination.

The band observed at 1295 cm^{-1} in the IR spectrum of the HIAP Schiff Base ligand is ascribed to the phenolic C-O stretching vibration [11]. This band is found in the region 1260-1280 cm^{-1} in the IR spectra of the complexes, thus indicating that the deprotonated hydroxylic oxygen anion of o-aminophenol moiety takes part in complexation.

The most important conclusion drawn from this discussion is that the HIAP Schiff Base ligand is coordinated to the central metal ions as **uninegative ONO tridentate ligand**. The free bonding sites are the central azomethine nitrogen atom and two oxygens of the hydroxyl and the carbonyl groups.

All the bands assigned to stretching vibration modes ν_{NH} , $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$ respectively in the free ligands disappear in the spectra of the $[\text{M}(\text{IAP})_2]$ compounds (**1:2**, $\text{pH}=7.4$), but new bands are recorded at 1580 and 1220 - 1230 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 tin/zirconium through the oxygen of the C-O group.

In this case the HIAP Schiff Base ligand is coordinated to the central metal ions as **binegative ONO tridentate 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 530-565 and 470-490 cm^{-1} respectively in the spectra of chelates.

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 $[\text{M}(\text{IAP})_2]\text{Cl}_2$ and 380÷413 and 584÷587 for $[\text{M}(\text{IAP})_2]$. These bands may probably be attributed to intraligand transitions.

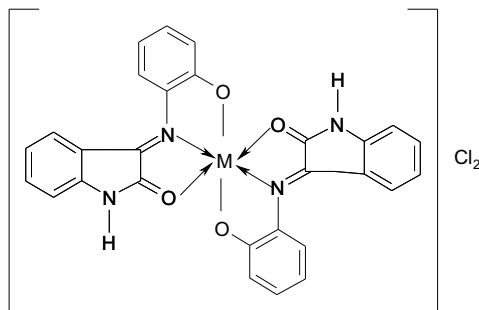


Fig. 2: Structure of $[\text{M}(\text{IAP})_2]\text{Cl}_2$.

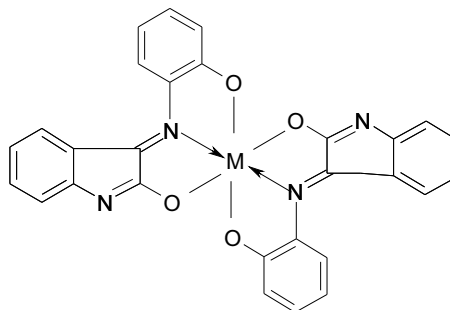


Fig. 3: Structure of $[\text{M}(\text{IAP})_2]$.

The correlation of the experimental data allows assigning an octahedral stereochemistry to all the reported complex compounds. The proposed structural representations are presented in Figs. 2 and 3.

Conclusions

We report here the synthesis and the characterization of new complexes of Sn(IV) and Zr(IV) with a Schiff Base derived from isatin and o-aminophenol. The syntheses were conducted in conditions allowing the tridentate (mono-basic or bi-basic) function of the ligands and the stability of Sn/Zr(IV). Varying the conditions under these requirements, two kinds of complexes of the same Schiff Base were obtained, $[\text{M}(\text{IAP})_2]\text{Cl}_2$ and $[\text{M}(\text{IAP})_2]$, where HIAP are the Schiff Base mentioned above.

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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