

CONTROLLED SYNTHESIS III. REACTION OF Sn(IV) AND Zr(IV) WITH ISATINS

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abstract: New metal chelates of Sn(IV) and Zr(IV) with isatins have been synthesized and characterized. Following the synthesis conditions, two types of complexes were obtained: $[M(HL^I)_2Cl_2]Cl_2$; $[ML^{II}_2Cl_2]Cl_2$ and $[ML^I_2Cl_2]$, where: HL^I = isatin; L^{II} = N-metil-isatin; $M=Sn(IV)$, $Zr(IV)$. The complexes were characterised by elemental analysis, IR and NMR spectroscopy, diffuse reflectance data and molar conductivity measurements. The experimental data suggest that the ligands acts as bidentate (OO), and in function of reaction system, can coordinates in two different forms.

Introduction

Isatin (1H-indol-2,3-dione) is a syntetically versatile substrate, where it can be used for synthesis of a large variety of heterocyclic compounds, such as indoles and quinolines, and a raw material for drug synthesis. Isatin has also been found in mammalian tissues [1]. There has been considerable interest show in the coordination chemistry of metal ions and isatins [1÷11], but less attention has been paid to complexation of main group metal ions. Isatin (1H-indol-2,3-dione, fig. 1) was first obtained by Erdman and Laurent in 1841 as a product from the oxidation of indigo by nitric and chromic acids.

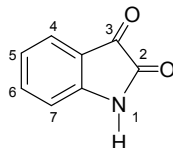


Fig. 1: Structure of 1H-indol-2,3-diona

Our interest in this category of ligands is justified by their already proved medical and biological implications [2÷12]. On the other hand, a great deal of our precedent work is focussed on the complex compounds generated by Group 14 metal halides [13÷19], also important in some biological processes.

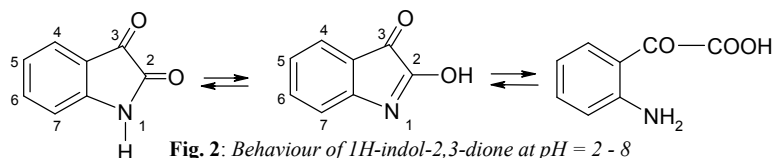


Fig. 2: Behaviour of 1H-indol-2,3-dione at pH = 2 - 8

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Isatin, due to its *cis* α -dicarbonyl moiety, is a potentially good substrate for the synthesis of metal complexes, either alone or deprotonated [1].

Experimental

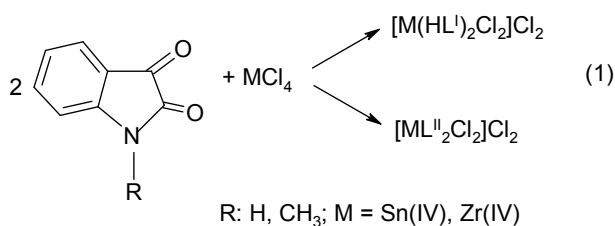
Materials and methods

All reagents used were of analytical grade and were used without further purification. SnCl_4 (Riedel), ZrCl_4 (Merck), isatin and *N*-methylisatin (Aldrich, 98%) and other chemicals employed were used as supplied by commercial sources. Solvents were purified by usual methods. *Chemical analysis* were performed by using the well-known micromethods. *The diffuse reflectance spectra* were recorded in range 250-800 nm 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. ^1H NMR data were recorded on Bruker Avance WH 2790 spectrometer in $\text{dms}\text{-d}_6$ using TMS as standard. *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.

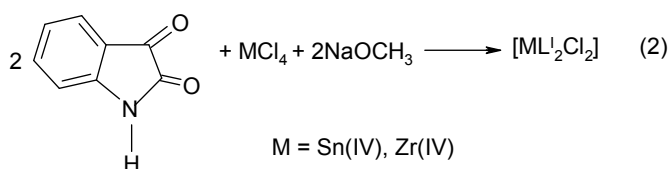
Synthesis of complexes $[\text{M}(\text{HL}^{\text{I}})_2\text{Cl}_2]\text{Cl}_2$ or $[\text{ML}^{\text{II}}_2\text{Cl}_2]\text{Cl}_2$; $[\text{MCl}_2\text{L}^{\text{I}}_2]$

All complexes were prepared by the following general procedure: a hot anhydrous ethanol solution of the ligand was added to the chlorides (1:2 molar ratio) of Sn(IV), Zr(IV) dissolved in anhydrous ethanol.

$[\text{M}(\text{HL}^{\text{I}})_2\text{Cl}_2]\text{Cl}_2$; $[\text{ML}^{\text{II}}_2\text{Cl}_2]\text{Cl}_2$ MCl_4 (0,002 mol in 50 mL anhydrous ethanol) was treated with 0,004 mol ligand (HL^{I} = isatin; L^{II} = *N*-methylisatin) dissolved in 50 mL anhydrous ethanol. The mixture was stirred during 1 h under nitrogen atmosphere and then was refluxed on a steam bath for 6 h. The solvent excess was distilled.



$[\text{ML}^{\text{I}}_2\text{Cl}_2]$ The ligand in 50 mL anhydrous ethanol was added drop wise to MCl_4 under nitrogen atmosphere; then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added (M:ligand: CH_3ONa 1:2:2). The reaction mixture was refluxed on a steam bath for 8 h.



The complexes were crystallized upon concentration. The compounds were filtered, washed with anhydrous ethanol and dried over P₂O₅ in vacuum.

[M(HL^I)₂Cl₂]Cl₂ SnCl₄C₁₆H₁₀O₄N₂ Requires: Sn 21.40; Cl 25.60; N 5.05%. Found for brick solid: Sn 21.46; Cl 25.68; N 4.80%. ZrCl₄C₁₆H₁₀O₄N₂ Requires: Zr 17.30; Cl 26.93; N 5.31%. Found for brick solid: Zr 17.36; Cl 27.00; N 5.20%. **[ML^I₂Cl₂]Cl₂** SnCl₄C₁₈H₁₄O₄N₂ Requires: Sn 20.37; Cl 24.37; N 4.80%. Found for pink solid: Sn 20.42; Cl 24.40; N 4.52%. ZrCl₄C₁₈H₁₄O₄N₂ Requires: Zr 16.43; Cl 25.57; N 5.04%. Found for pink solid: Zr 16.56; Cl 25.68; N 5.95%. **[ML^I₂Cl₂]** SnC₁₆H₈O₄N₂Cl₂ Requires: Sn 24.45; Cl 14.67; N 5.78%. Found for beige-maron solid: Sn 24.67; Cl 14.63; N 5.70%. ZrC₁₆H₈O₄N₂Cl₂ Requires: Zr 20.12; Cl 15.63; N 6.16%. Found for beige-maron solid: Zr 20.18; Cl 15.98; N 6.05%.

Results and Discussion

The analytical data show different stoichiometries in dependence of organic anion and in function of reaction system (*i.e.* CH₃ONa), ligands can coordinates in two diferent forms.

The complexes were isolated as sparingly soluble, coloured products from the reaction medium. These chelates are powders stable towards air and moisture. They decompose at >260 °C and are insoluble in most common organic solvents but soluble in dmf and dmsol.

On the basis of *chemical analysis* the minimal formula correspond to [M(HL^I)₂Cl₂]Cl₂ and [ML^I₂Cl₂], M=Sn(IV), Zr(IV).

The conductivity values for the [ML^I₂Cl₂] complexes (6.5-8.9 Ω⁻¹.cm².mol⁻¹) indicate that the complexes are non-electrolytes in solution. For the [M(HL^I)₂Cl₂]Cl₂ and [ML^{II}₂Cl₂]Cl₂ the conductivity values (65-82 Ω⁻¹.cm².mol⁻¹) indicate that the complexes are electrolytes in dmf solutions.

Table 1. Infrared spectra (cm⁻¹)

Compound	ν _{NH}	ν _{C=O(2)}	ν _{C=O(3)}	ν _{C=N*}	ν _{C-O}	ν _{M-O}
HL ^I	3190 br	1730 s	1620 vs	-	-	-
[Sn(HL ^I) ₂ Cl ₂]Cl ₂	-	1720 m	1609 m	-	-	420 w
[Zr(HL ^I) ₂ Cl ₂]Cl ₂	-	1718 m	1603 m	-	-	430 w
[SnL ^I ₂ Cl ₂]	-	1721 m	-	1582 s, sh	1249 s, sh	527 w
[ZrL ^I ₂ Cl ₂]	-	1700 m	-	1575 s,sh	1228 s, sh	500 w
L ^{II}	-	1744 s	1725 vs	-	-	-
[SnL ^{II} ₂ Cl ₂]Cl ₂	-	1730 m	1609 m	-	-	427 w
[ZrL ^{II} ₂ Cl ₂]Cl ₂	-	1720 m	1606 m	-	-	430 w

The infrared spectrum of isatin shows two strong bands at 1730 and 1620 cm⁻¹ corresponding to the carbonyl stretching vibrations (see table 1).

A broad band occurs at 3190 cm^{-1} due to the N-H stretching, and it is accompanied by many sub-bands; the several bands in the region $1400\text{--}1100\text{ cm}^{-1}$ are associated with N-H in-plane bending. The $\nu_{\text{C=O}}$ values are not modified by N-alkylation.

All the bands assigned to stretching vibration modes ν_{NH} and $\nu_{\text{C=O(3)}}$ in the free isatin disappear in the spectra of the compounds $[\text{ML}^{\text{II}}_2\text{Cl}_2]$, but new bands are recorded at $1585\text{--}1575$ and $1250\text{--}1230\text{ cm}^{-1}$, respectively. 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.

The formation of M-O bonds is further supported by the appearance of $\nu_{\text{M-O}}$ in the regions $400\text{--}500$ in the spectra of chelates.

The highest energy $\pi\rightarrow\pi^*$ band at 35780 cm^{-1} (279 nm) in the *UV-VIS spectra* of ligands, in ethanol, is at higher energy in the spectra of complexes, suggesting it likely arises from one of the functional groups that coordination rather the aromatic ring.

The diffuse reflectance spectra were recorded in range $250\text{--}800\text{ nm}$ (MgO). In the spectra of ligands the band at 27820 cm^{-1} (359 nm) is very broad and likely involves $n\rightarrow\pi^*$ transitions for the C=O functions. The Sn(IV) and Zr(IV) chelates are diamagnetic with no ligand field transition. The lowest energy bands of the complexes $[\text{ML}^{\text{II}}_2\text{Cl}_2]$ at $430\text{--}441\text{ nm}$ are assigned to charge transfer transitions of hydroxylato donor (see fig.3).

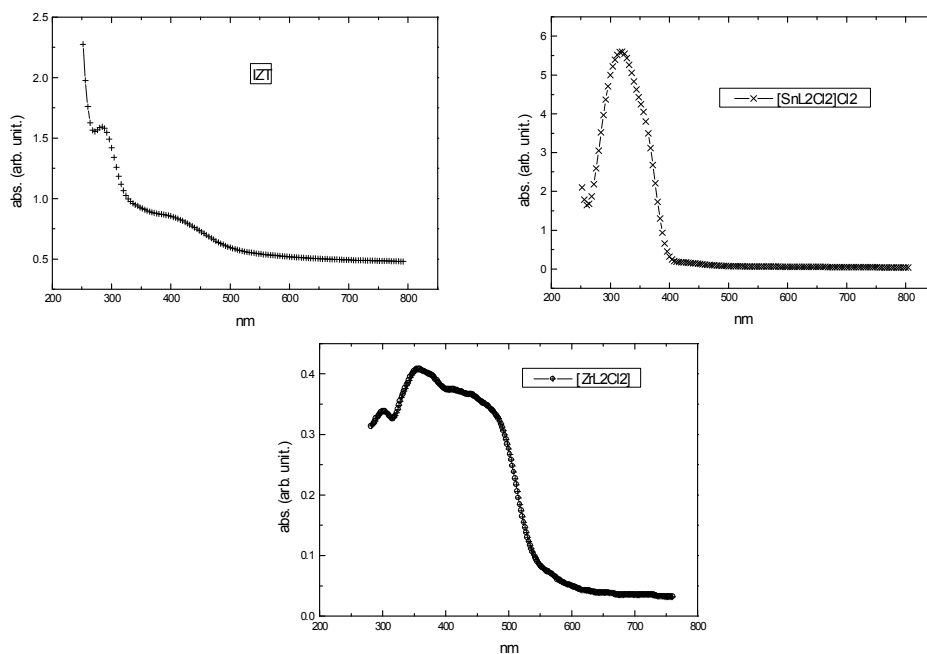


Fig. 3: The diffuse reflectance spectra: isatin (HL^{I}), $[\text{SnL}^{\text{II}}_2\text{Cl}_2]\text{Cl}_2$ and $[\text{ZrL}^{\text{II}}_2\text{Cl}_2]$

Supplementary data have been obtained by $^1\text{H NMR spectroscopy}$, recorded for the ligands and for their complexes of Sn(IV). The $^1\text{H NMR}$ spectrum of isatin shows the signals of the aromatic nucleus at δ 6.86 (d), 7.00 (t), 7.47 (d) and 7.53 (t) (DMSO-d_6), corresponding to H-7, H-5, H-4 and H-6 respectively. N-alkylation not alter this pattern (see table 2). The only $^1\text{H NMR}$ signal displaying a down field shift in complex compounds $[\text{Sn}(\text{HL}^I)_2\text{Cl}_2]\text{Cl}_2$ is those associated with the hydrogen (NH) of the isatin. This behavior is related with a decrease of the electron density and a deshielding of the NH proton, as a result of the participation of the adjacent carbonyl group in coordination. This behavior is in good agreement with IR spectra of complexes where the maximum of the $\nu_{\text{C=O}(2)}$ vibration mode appears at lower frequencies as in the corresponding free ligand. This $^1\text{H NMR}$ signal (NH) disappear in the spectrum of $[\text{SnL}^I_2\text{Cl}_2]$.

Table 2. $^1\text{H NMR}$ spectra (δ , ppm)

Compound	N-H	H-4	H-5	H-6	H-7
HL^I	11.03s	7.50d	7.07t	7.60t	6.92d
$[\text{Sn}(\text{HL}^I)_2\text{Cl}_2]\text{Cl}_2$	11.63s	7.53d	7.10t	7.62t	6.93d
$[\text{SnL}^I_2\text{Cl}_2]$	-	7.50d	7.07d	7.60t	6.92d
L^{II}	-	7.59d	7.12t	7.61t	6.91t
$[\text{SnL}^{II}_2\text{Cl}_2]\text{Cl}_2$	-	7.56d	7.10t	7.61t	6.93t

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

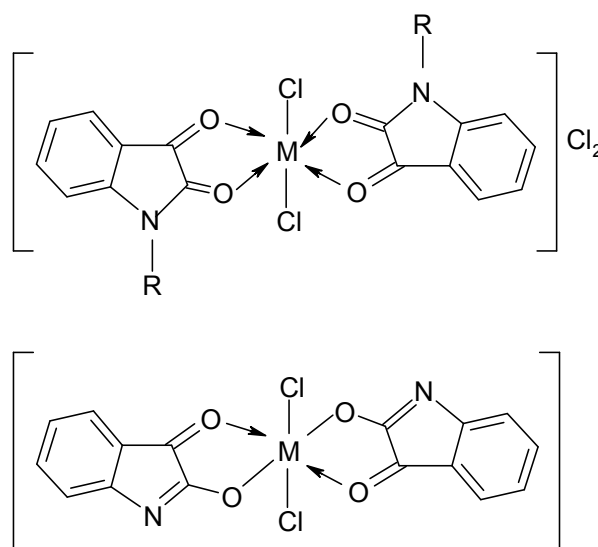


Fig. 4: Propose structures of complex compounds $[\text{M}(\text{HL}^I)_2\text{Cl}_2]\text{Cl}_2$, $[\text{ML}^{II}_2\text{Cl}_2]\text{Cl}_2$ and $[\text{ML}^I_2\text{Cl}_2]$; $\text{M}=\text{Sn(IV)}$, Zr(IV)

Conclusion

We report here the synthesis and the characterization of new complexes of Sn(IV) and Zr(IV) with "isatins". The syntheses were conducted in conditions allowing the bidentate in dependence of organic anion and in function of reaction system (*i.e.* CH₃ONa, stability of Sn/Zr(IV)). 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 assigning an octahedral stereochemistry to all the reported complex compounds.

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