

CONTROLLED SYNTHESIS II. REACTION OF Sn(IV) AND Zr(IV) WITH ISATIN-3-TIOSEMICARBAZONE AND *n*-METIL ISATIN-3-TIOSEMICARBAZONE

Elena Cristurean, Carmen Părnău*, Mihaela Badea and Rodica Olar

abstract: A series of new metal chelates of Sn(IV) and Zr(IV) with the thiosemicarbazones formed by condensation of isatin with thiosemicarbazides have been synthesized and characterized. Following the synthesis conditions, two types of complexes were obtained: $[M(HL^I)_2]$; $[ML^II_2]Cl_2$, where: H_2L^I = isatin 3-thiosemicarbazona; HL^II = N-metil-isatin 3-thiosemicarbazona; $M=Sn(IV)$, $Zr(IV)$. The complexes were characterised by IR, diffuse reflectance data, elemental analyses and molar conductivity measurements. The experimental data suggest that the ligand acts as tridentate, and in function of reaction system, can coordinates in two different forms.

Introduction

In view of versatile importance of isatins [1÷5] and in continuation of our previous work dealing with the Sn(IV) and Zr(IV) complexes of isatin Schiff bases [6÷8] and looking for greater carcinostatic activity, we have now turned our attention to TSCs derived from isatin (1-*H*-indole-2,3-dione) which was recently found to be endogenous in mammalian tissues and body fluids [9÷16]. There has been considerable interest show in the coordination chemistry of metal ions and isatin-thiosemicarbazones, but less attention has been paid to complexation of main group metal ions.

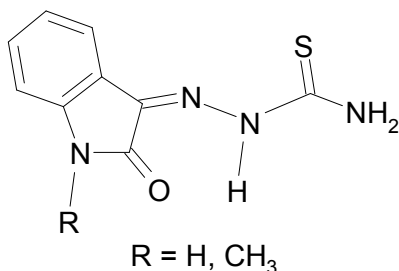


Fig. 1: Structure of ligands (H_2L^I :R=H, HL^II :R=CH₃)

* Faculty of Chemistry, Department of Inorganic Chemistry, University of Bucharest

Isatin-thiosemicarbazone may act as chelating agent coordinating to the central metal ions through azomethine nitrogen, carbonyl oxygen and thiolato sulphur atoms (mono- or dibasic NOS tridentate ligands) (Fig. 2).

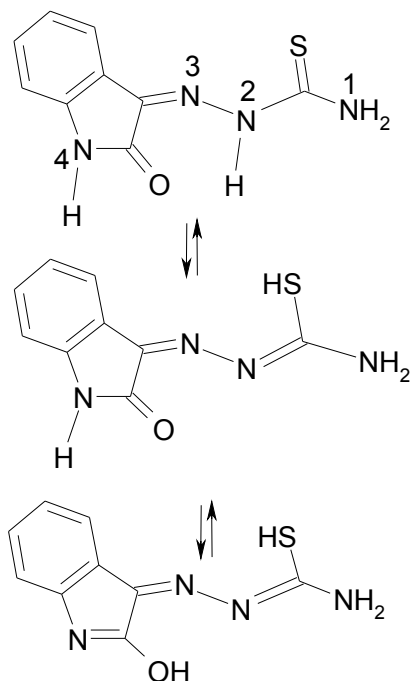


Fig. 2: Tautomer structures of isatin 3-thiosemicarbazone (H_2L^I)

Experimental

Materials and methods

All reagents used were of analytical grade and were used without further purification. $SnCl_4$ (Riedel), $ZrCl_4$ (Merck), isatin (Aldrich, 98%), thiosemicarbazide (Merck) and other chemicals employed in the preparation of the TSCs were used as supplied by commercial sources. Solvents were purified by usual methods. *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.

Synthesis of the ligands (H_2L^I , HL^{II})

Isatin-2,3-indolinedione or *N*-methylisatin and thiosemicarbazide, taken with 1:1 molar ratio, were dissolved in aqueous ethanol in presence of a few drops of acetic acid. The mixture

was refluxed over water bath for 1 h. After cooling at room temperature, the yellow microcrystalline solid was separated, washed with ethanol, diethylether and dried under vacuum. *M.p.* $\text{H}_2\text{L}^{\text{I}}$ 240 °C; HL^{II} 257 °C. $\text{H}_2\text{L}^{\text{I}}$ IR (cm^{-1} , KBr): 3322m, 3206m,br, 3086m,br, 3086m (NH_2+NH); 1699s (C=O); 1622s (C=N); 830m (C=S); HL^{II} IR (cm^{-1} , KBr): 3426s, 3247m,br, 3150m (NH_2+NH); 1676s (C=O); 1607s,br (C=N); 832m (C=S).

Synthesis of complexes

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.

$[\text{ML}^{\text{I}}_2]$ The reaction mixture were refluxed on a steam bath for 12 h; then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added (M:ligand: CH_3ONa 1:2:4). $[\text{M}(\text{HL}^{\text{II}})_2]\text{Cl}_2$ The reaction mixture were refluxed on a steam bath for 6 h; then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added (M:ligand: CH_3ONa 1:2:2).

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

$[\text{ML}^{\text{I}}_2]$ $\text{SnC}_{18}\text{H}_{12}\text{O}_2\text{S}_2\text{N}_8$ Requires: Sn 21.29; N 20.08%. Found for beige-maroon solid: Sn 23.12; N 20.11%. $\text{ZrC}_{18}\text{H}_{12}\text{O}_2\text{S}_2\text{N}_8$ Requires: Zr 17.20; N 21.12%. Found for beige-maroon solid: Zr 17.12; N 21.19%. $[\text{M}(\text{HL}^{\text{II}})_2]\text{Cl}_2$ $\text{SnCl}_2\text{C}_{20}\text{H}_{18}\text{O}_2\text{S}_2\text{N}_8$ Requires: Sn 18.11; Cl 10.83; N 17.08%. Found for maroon solid: Sn 18.06; Cl 11.08; N 17.00. $\text{ZrCl}_2\text{C}_{20}\text{H}_{20}\text{O}_2\text{S}_2\text{N}_8$ Requires: Zr 14.52; Cl 11.30; N 17.83%. Found for maroon solid: Zr 14.36; Cl 11.38; N 17.70%.

Results and Discussion

The analytical data show different stoichiometries in dependence of organic anion and in function of reaction system (*i.e.* CH_3ONa), ligands can coordinates in two different 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 >300 °C and are insoluble in most common organic solvents but soluble in dmf.

On the basis of *chemical analysis* the minimal formula correspond to $[\text{ML}^{\text{I}}_2]$ and $[\text{M}(\text{HL}^{\text{II}})_2]\text{Cl}_2$, M=Sn(IV), Zr(IV).

The conductivity values for the $[\text{ML}^{\text{I}}_2]$ complexes ($6.5\text{-}10.4 \Omega^{-1}.\text{cm}^2.\text{mol}^{-1}$) indicate that the complexes are non-electrolytes in solution. For the $[\text{M}(\text{HL}^{\text{II}})_2]\text{Cl}_2$ the conductivity values ($62\text{-}80 \Omega^{-1}.\text{cm}^2.\text{mol}^{-1}$) indicate that the complexes are electrolytes in solution.

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

The bands at 3150, 1700-1680 and 1620-1610 cm^{-1} in the ligands spectra, were assigned to stretching vibration modes $\nu_{\text{N}(2)\text{H}+\text{N}(4)\text{H}}$, $\nu_{\text{C}=\text{O}}$ and $\nu_{\text{C}=\text{N}}$, respectively.

All the bands assigned to stretching vibration modes $\nu_{\text{N}(2)\text{H}}$, $\nu_{\text{C}=\text{O}}$ and $\nu_{\text{C}=\text{S}}$ in the free ligands disappear in the spectra of the compounds, but new bands are recorded at 1595-1570,

1310-1270 and 500-600 cm^{-1} , respectively. These new bands, assigned to the $\nu_{\text{C=N}^*}$ (new azomethine bond), $\nu_{\text{C-O}}$ and $\nu_{\text{C-S}}$ vibration modes respectively, suggest the enolisation and/or thiolysation of NH hydrogen of isatin and/or of NH thiosemicarbazide and the coordination at tin/zirconium through the oxygen/sulphur of the C-O/C-S group.

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

Compound	$\nu_{\text{N(2)H}}$	$\nu_{\text{N(4)H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$ ν	ν	$\nu_{\text{C-S}}$	$\nu_{\text{C-S}}$	$\nu_{\text{M-O/M-S}}$
HL ^I	3158 s, br	–	1699 s	1622 s 1609	–	830 m	–	–
[SnL ₂]	–	–	1662 w-m	1595 s	1310 s, sh	–	550 m	470/420 w
[ZrL ₂]	–	–	1660 w-m	1603 m	1310 s,sh	–	610 m	472/430 w
HL ^{II}	3145 m,br	–	1681 s	1613 vs 1609	–	830 m	–	–
[Sn(HL ^{II}) ₂]Cl ₂	–	–	1664 w-m	1570 s	1270 s	–	550 m	481/427 w
[Zr(HL ^{II}) ₂]Cl ₂	–	–	1660 w-m	1610 m	1270 s	–	598 m	480/430 w

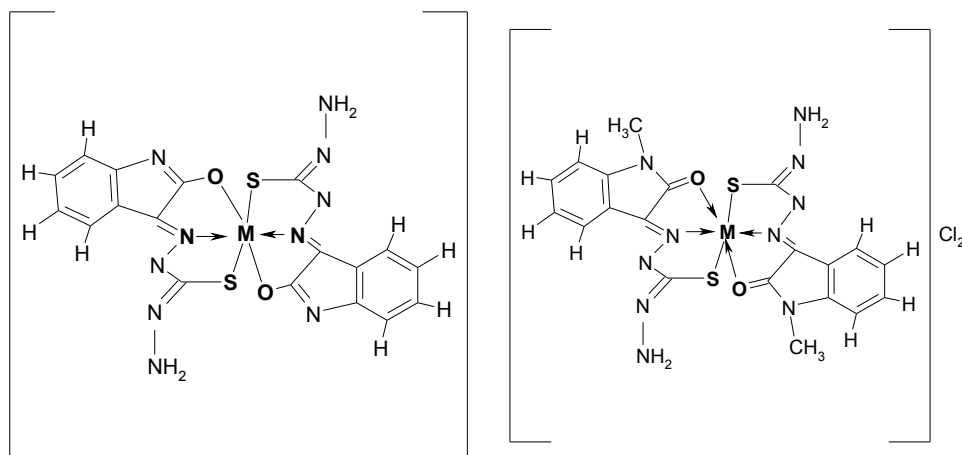


Fig. 3: Proposed structures of complex compounds $[\text{ML}_2]$, $[\text{M}(\text{HL}^{\text{II}})_2]\text{Cl}_2$; $\text{M}=\text{Sn}(\text{IV})$, $\text{Zr}(\text{IV})$

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 480-470 and 430-420 cm^{-1} , respectively, in the spectra of chelates.

The most important conclusions drawn from the infrared spectral evidence is that the thiosemicarbazones (TSCs) is acting as chelating agent towards the central metal ions as a mono- or dibasic NOS tridentate ligand forming two five-membered chelating rings.

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 350-800 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, C=N and C=S functions. The Sn(IV) and Zr(IV) chelates are diamagnetic with no ligand field transition. The two lowest energy bands in the diffuse reflectance spectra of the complexes are assigned to charge transfer transitions (430-441 nm) with the lowest energy band (579-604 nm) hydroxylato/thiolato donor.

The proposed structural representations are presented in Fig. 3.

Conclusion

We report here the synthesis and the characterization of new complexes of Sn(IV) and Zr(IV) with the thiosemicarbazones derived from "isatins" and thiosemicarbazide. The syntheses were conducted in conditions allowing the tridentate mono- or di-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 a octahedral stereochemistry to all the reported complex compounds.

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