

COMPLEXES OF TIN (IV) WITH SOME BIDENTATE SCHIFF BASES DERIVED FROM 1-*H*-INDOL-2,3-DIONE

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Abstract

A series of new metal complexes of tin (IV) with Schiff bases of isatin (1-*H* - indol -2,3-dione) with aniline, *p*-toluidine and *m*-nitro aniline have been synthesized and characterized by elemental analysis, IR, NMR and electronic spectroscopy and conductance measurements.

Two types of such complexes were been synthesized: SnCl₄(HL) and SnCl₂(L)₂. Electronic, IR and NMR spectral data agree with the coordination of the metallic center through nitrogen and oxygen donor atoms. Conductance data reveal a non-electrolytic nature of the complexes.

Introduction

Containing different donor atoms, the Schiff bases are an important class of ligands in the coordination chemistry, widely reported.¹⁻³ Nevertheless, a survey of the literature reveals that no work treating complexes of tin(IV) with Schiff bases derived from 1-*H* - indol -2,3-dione (isatin) were since reported.

Our interest in this category of ligands is justified by their already proved medical and biological implications.⁴⁻⁶ On the other hand, a great deal of our precedent work is focused on the complex compounds generated by Group 14 metal halides,⁷⁻¹⁷ also important in some biological processes.

Our purpose was to synthesize and characterize some metal complexes of tin (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).

In different conditions, two kinds of complexes of the same Schiff base were obtained, SnCl₄(HL) and SnCl₂(L)₂, where HL are the Schiff bases mentioned above.

Results and discussion

The Schiff bases under present consideration react with tin(IV) chloride in anhydrous ethanol medium, to give colored amorphous compounds, stable in air and insoluble in most common organic solvents.

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

Table 1: Analytical and physical data of the synthesized compounds

Compound	Empirical formula*	Melting point ($^{\circ}\text{C}$)	Color	Λ_{M}^{**} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
$\text{SnCl}_4(\text{HIAN})$	$\text{SnCl}_4(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O})$	207	Pale brown	6.5
$\text{SnCl}_2(\text{IAN})_2$	$\text{SnCl}_2(\text{C}_{14}\text{H}_9\text{N}_2\text{O})_2$	250	Beige	-
$\text{SnCl}_4(\text{HIPT})$	$\text{SnCl}_4(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O})$	170	Reddish brown	8.8
$\text{SnCl}_2(\text{IPT})_2$	$\text{SnCl}_2(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O})_2$	250	Beige	-
$\text{SnCl}_4(\text{HIMNA})$	$\text{SnCl}_4(\text{C}_{14}\text{H}_9\text{N}_3\text{O}_3)$	90	Dark brown	10.4
$\text{SnCl}_2(\text{IMNA})_2$	$\text{SnCl}_2(\text{C}_{14}\text{H}_8\text{N}_3\text{O}_3)_2$	211 ^d	Pale brown	-

*: The elemental analysis data were in good agreement with the calculated percentages of Sn, C, H, N and Cl for all the synthesized compounds.

** : The conductance was recorded in DMF solutions.

^d: The compound decompose at 211 $^{\circ}\text{C}$.

Spectral data

In order to clarify the manner of the ligand coordination at the metallic center IR spectra on the 400 - 4000 cm^{-1} range were recorded.

The most important IR bands, presented and assigned in table 2 show the following characteristics:

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

In the cases of the $\text{SnCl}_4(\text{HL})$ compounds, the spectra reveal that the band having a maximum at 1740 cm^{-1} in the free ligands is shifted to lower wave numbers with a $\Delta\nu$ between 26 - 37 cm^{-1} . This shift indicates the implication of carbonyl oxygen in the coordination at the metallic center.

Table 2. IR data (cm^{-1})

Compound	ν_{NH}	$\nu_{\text{C=O}}$	ν_{skeleton}	$\nu_{\text{C=N}}$	$\nu_{\text{C=N}}^*$	$\nu_{\text{C-O}}$
HIAN	3191	1743	1614	1654	-	-
$\text{SnCl}_4(\text{HIAN})$	3180	1706	1617	-	-	-
$\text{SnCl}_2(\text{IAN})_2$	-	-	1606	-	1572	1224
HIPT	3180	1744	1614	1654	-	-
$\text{SnCl}_4(\text{HIPT})$	3173	1711	1615	-	-	-
$\text{SnCl}_2(\text{IPT})_2$	-	-	1606	-	1568	1232
HIMNA**	3196	1737	1617	1653	-	-
$\text{SnCl}_4(\text{HIMNA})^{**}$	3180	1717	1620	-	-	-
$\text{SnCl}_2(\text{IMNA})_2^{**}$	-	-	1606	-	1582	1227

*: New azomethine band

**.: Supplementary intense bands assigned to $\nu(\text{NO}_2 \text{ asym})$ and $\nu(\text{NO}_2 \text{ sym})$ at 1526, respectively 1348 cm^{-1} were recorded.

In the cases of the $\text{SnCl}_4(\text{HL})$ compounds, the spectra reveal that the band having a maximum at 1740 cm^{-1} in the free ligands is shifted to lower wave numbers with a $\Delta\nu$ between 26 - 37 cm^{-1} . This shift indicates the implication of carbonyl oxygen in the coordination at the metallic center.

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

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.

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 $\text{SnCl}_2(\text{L})_2$ compounds, 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 and the coordination at tin through the oxygen of the C-O group.

Identification of the bands assignable to the Sn - O, respectively Sn - N vibration modes was rather difficult, because in the corresponding region the ligands display quite intense bands.

NMR data

Supplementary data have been obtained by ^1H - and ^{13}C -NMR spectroscopy, recorded for the ligands and for their $\text{SnCl}_4(\text{HL})$ chelate compounds.

The ^1H spectra of the ligands can be resolved into three distinct regions. The spectra exhibit two multiplets at 7,0 - 7,3 and 6,3 - 6,8 ppm (corresponding to the isatin and amine aromatic rings) and one singlet at 10,3 ppm (corresponding to the isatin NH residue).

The only ^1H -NMR signal displaying a down field shift in complex compounds (from 10,3 to 10,9 ppm) is those associated with the hydrogen of the isatin NH residue. 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^{18, 19}. This behavior is in good agreement with IR spectra of complexes where the maximum of the $\nu_{\text{C=O}}$ vibration mode appears at lower frequencies as in the corresponding free ligands.

UV-VIS spectra were recorded in the region 200 - 1000 nm.

The electronic spectra of the ligands in ethanol exhibit mainly three bands at 230 nm($\pi \rightarrow \pi^*$), 290 nm($n \rightarrow \pi^*$) and 396 nm.

The reflectance spectra are similar and shifted toward lower frequencies.

In the visible region, the bands of the ligands, appearing at 415-420 nm, are less intense.

In the $\text{SnCl}_4(\text{HL})$ complexes spectra the bands are shifted with about 20 nm to lower frequencies, proving the ligands coordination at metallic centers. In the cases of the $\text{SnCl}_2(\text{L})_2$ compounds the shift is even greater (of 35-40 nm), indicating a more accentuated conjugation between the azomethine group and the aromatic ring (see table 3).

Table 3. UV-VIS data

Compound	Absorption maxima (nm/cm ⁻¹)		
HIAN	250(40000)	300(33333)	415(24096)
SnCl ₄ (HIAN)	245(40816)	340(29411)	430(23255)
SnCl ₂ (IAN) ₂	260(38461)	352(28409)	445(22471)
HIPT	248(40322)	290(34482)	420(23809)
SnCl ₄ (HIPT)	243(41152)	343(29154)	460(21739)
SnCl ₂ (IPT) ₂	250(40000)	350(28571)	480(20833)
HIMNA	242(41322)	290(34482)	420(23809)
SnCl ₄ (HIMNA)	240(41666)	332(30120)	440(22727)
SnCl ₂ (IMNA) ₂	245(40816)	341(29325)	460(21739)

Conductance data for the SnCl₄(HL) compounds (in DMF, 10⁻³ mol, 25⁰C), ranging in the 6,5 - 10,4 Ω⁻¹cm²mol⁻¹ region, indicate the non-electrolytic nature of the compounds.

Conclusions

We report here the synthesis and the characterization of six new complexes of tin(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 and the stability of tin(IV). Varying the conditions under these requirements, two kinds of complexes of the same Schiff base were obtained, SnCl₄(HL) and SnCl₂(L)₂, where HL are the Schiff bases mentioned above.

The synthesized compounds were characterized by elemental analysis, IR, NMR 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. The proposed structural representations are presented in figure 1:

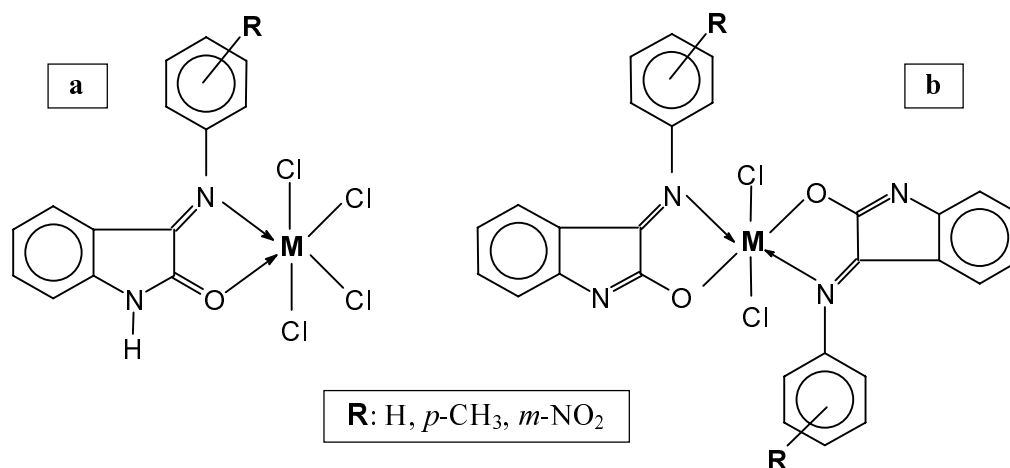


Figure 1. Proposed structures of complex compounds; **a**: SnCl₄(HL); **b**: SnCl₂(L)₂

Experimental

Reagents and methods. All the reagents were AR grade. Tin tetrachloride (Riedel), aniline, *p*-toluidine and *m*-nitro-aniline (Aldrich) were used without further purification. Anhydrous ethanol was obtained using the method presented in literature.²⁰ Tin and chlorine content was determined by a conventional method²¹ and C, H, and N were determined by micro-analytical methods. The IR spectra were recorded in KBr pellets, using a BIO-RAD FTS 135 spectrometer. The reflectance UV-VIS spectra were recorded with a VSU 2P spectrometer, at room temperature. ¹H- and ¹³C-NMR data were recorded on VARIAN T 60 and BRUKER WH 2790 spectrometers. Digital conductivity meter K 612 was used to measure the molar conductivities in DMF solutions.

Schiff bases preparation. The preparation of the Schiff Bases was conducted as follows: an ethanol solution of isatin (0,001 mol, 25 ml) was added to an ethanol solution of aromatic amine (0,001 mol, 25 ml) and refluxed for four hours on a water bath. After solution concentration, the precipitate was separated by suction filtration, washed with ethanol and dried over CaCl₂ in vacuum. **HIAN**: Anal. C₁₄H₁₀N₂O: Calc: C, 75.67; H, 4.50; N, 12.61. Found: C, 75.5; H, 4.7; N, 12.4. ¹H NMR: δ₁ = 10.0(s); δ₂ = 7.3(m); δ₃ = 6.8(m). ¹³C NMR: δ₁ = 165.8 (C=O); δ₂ = 154.5 (C=N). **HIPT**: C₁₅H₁₂N₂O: Calc: C, 76.27; H, 5.08; N, 11.86. Found: C, 76.2; H, 5.0; N, 12.0. ¹H NMR: δ₁ = 10.4(s); δ₂ = 7.3(m); δ₃ = 6.9(m); δ₄ = 2.41(s, CH₃); ¹³C NMR: δ₁ = 165.6; δ₂ = 154.4; δ₃ =

21(CH₃). **HIMNA**: C₁₄H₉N₃O₃: Calc: C, 62.92; H, 3.37; N, 15.73. Found: C, 62.8; H, 3.5; N, 15.72. ¹H NMR: δ₁ = 10.7(s); δ₂ = 7.3(m); δ₃ = 6.7(m). ¹³C NMR: δ₁ = 165.7; δ₂ = 154.5.

SnCl₄(HL) complexes: 0,002mol SnCl₄ in 50 ml anhydrous ethanol was treated with 0,002 mol ligand dissolved in 50 ml anhydrous ethanol. The mixture was stirred during one hour under nitrogen atmosphere and than was refluxed on a water bath for eight hours. The solvent excess was distilled. The compound was filtered, washed with anhydrous ethanol and dried over P₂O₅ in vacuum. Anal. **SnCl₄(HIAN)**: Calc: Sn, 24.59; C, 34.80; H, 2.07; N, 5.80; Cl, 29.42. Found : Sn, 24.60; C, 34.70; H, 2.10; N, 5.90; Cl, 29.5. ¹H NMR (DMSO+CDCl₃): δ₁=11.0; δ₂= 7.0-7.3; δ₃ = 6.3-6.8. ¹³C NMR (DMSO+CDCl₃): δ₁=178.3(C=O); δ₂=163.4(C=N). **SnCl₄(HIPT)**: Calc: Sn, 23.90; C,36.24; H,2.41; N,5.64; Cl, 28.59. Found: Sn, 23.89; C, 36.20; H, 2.40; N,5.60; Cl, 28.49. **SnCl₄(HIMNA)**: Calc: Sn, 22.49; C, 31.84; H,1.70; N, 7.96;Cl, 26.91. Found: Sn, 22.40;C, 31.90;H, 1.90;N, 8.01;Cl, 26.40.

SnCl₂(L)₂ complexes: appropriate Schiff base (0,002mol in 50 ml anhydrous ethanol) was added drop wise, under nitrogen atmosphere, to tin (IV) chloride (0,001mol SnCl₄ in 25 ml anhydrous ethanol); then, under nitrogen atmosphere and continuous stirring, sodium methoxide was added until pH reaches 7,4. The reaction mixture was refluxed on water bath, for eight hours. The compound was filtered, washed with anhydrous ethanol and dried over P₂O₅ in vacuum. The compounds are insoluble in most common organic solvents, so that their NMR and conductance measurement were not available. Anal. **SnCl₂(IAN)₂**: Calc: Sn, 18.79; C, 53.19; H, 2.84; N, 8.86; Cl, 11.24. Found: Sn, 18.81; C, 53.17; H, 2.90; N, 8.82; Cl, 11.24. **SnCl₂(IPT)₂**: Calc: Sn, 17.99; C, 54.57; H, 3.33; N, 8.49; Cl, 10.76. Found: Sn, 18.01; C, 54.60; H, 3.35; N, 8.49; Cl, 10.80. **SnCl₂(IMNA)₂**: Calc: Sn, 16.44; C, 46.56; H, 2.22; N, 11.64; Cl, 9.84. Found: Sn, 16.50; C, 46.58; H, 2.23; N, 11.50; Cl, 9.80.

References and Notes

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Povzetek

Pripravili smo serijo kompleksov kositra(IV) s Schiffovimi bazami, pripravljenimi iz izatina in anilina, *p*-toluidina oziroma *p*-nitroanilina. Strukture spojin smo potrdili z elementno analizo, IR, NMR, UV/Vis spektroskopijami in z merjenjem prevodnosti. Izolirali smo dve vrsti kompleksov in sicer: SnCl₄(HL) ter SnCl₂(L)₂. Spektroskopski podatki potrjujejo koordinacijo ligandov preko dušikovih in kisikovih atomov, merjenje prevodnosti pa ne-elektrolitske lastnosti.