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THERMAL BEHAVIOR OF SOME NEW ISATIN COMPLEXES[*]

C. Parnau, Rodica Olar[**], Mihaela Badea and A. Kriza

University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 90–92 Panduri Str., 050663 Sector 5, Bucharest, Romania

The complexes of the type $SnCl_4(HL)\cdot EtOH$ and $SnCl_2L_2$ (HL^1: the Schiff base resulted in 1:1 condensation of isatin and aniline; HL^2: the Schiff base resulted in 1:1 condensation of isatin and *p*-toluidine) have been synthesized and characterized. The thermal analysis of the new ligands and complexes has evidenced the thermal intervals of stability and also the thermal effects that accompany them. The Schiff bases thermal transformations consist in phase transitions, C_{arom}–N bond cleavage and thermolysis processes. The different nature of the complexes generates their different thermal behaviour. The complexes lead in three steps to SnO_2 and in all cases the Schiff bases degradation generates a pyrrolidone-coordinated derivative. As for the $SnCl_4(HL)\cdot EtOH$ complexes, the $SnCl_4$ formed during the last step is involved in two competitive processes, one consists in their volatilisation while the other one leads to SnO_2. As result the SnO_2 residue is smaller than the theoretically expected.

Keywords: *complexes, isatin, Schiff bases, thermal behaviour, tin(IV)*

Introduction

It is well known that the isatins have as well biological as coordinative properties [1]. Isatin (1H-indol-2,3-dione) is a synthetically versatile substrate, that can be used for synthesis of a large variety of heterocyclic compounds, such as indoles and quinolines, and as raw material for drug synthesis. Isatin has also been found in mammalian tissues [2]. There has been considerable interest showed in the coordination chemistry of transition metallic ions and isatin derivatives [3–7], but less attention has been accorded to complexation of main group of the metallic ions. Our interest in this category of ligands arises from their already proved medical and biological implications. Schiff bases derived from isatin showed anticonvulsant [1], tuberculostatic, antibacterial as well as antifungal activities [8, 9]. Moreover, complexes of some isatin derivatives with transition metals behave as antibacterial [7], antitubercular [10] and also antitumoral compounds [11]. Regarding the thermal behaviour of this kind of complexes there are a rather few information [12]. Schiff bases derived from isatin and aniline/*p*-toluidine/*m*-nitro aniline were obtained recently by direct condensation of organic derivatives. Using this ligand were also synthesised and characterised tin(IV) complexes that were formulated as mononuclear species of type $SnCl_4(HL)\cdot EtOH$ and $SnCl_2L_2$ [12].

In this paper we report the thermal behaviour of these derivatives in order to evidence the thermal intervals of their stability and also the thermodynamics effects that accompany them. The thermogravimetric analysis has shown that these compounds are stable up to 200–290°C. The thermal transformations are complex processes according to TG and DTG curves including phase transitions, C_{arom}–N bond cleavage (leading to the gaseous benzene, toluene or nitrobenzene formation) and then thermolysis processes. The products of the decomposition are nanometer-sized particles of tin(IV) oxide.

Experimental

The new ligands and complexes were synthesised and previously characterized by chemical analysis, IR, NMR, UV-vis spectroscopy as well as molar conductance measurements [13]. The chemical analysis and IR spectral data were used in order to confirm the nature of some intermediates and also the final products.

IR spectra were recorded in KBr pellets with a FTIR-BIORAD 135 instrument.

The heating curves (TG, DTA and DTG) were recorded in a static air atmosphere using a MOM Hungary derivatograph, type Paulik–Paulik–Erdey, with a sample mass between 34.8–50 mg over the temperature range of 20–1000°C, using a heating rate of 10°C min^{-1}.

Results and discussion

In this paper, we report the thermal behaviour of some complexes of $SnCl_4(HL)\cdot EtOH$ and $SnCl_2L_2$ type

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[**] Author for correspondence: rodica_olar@yahoo.co.uk; olar.marioara@unibuc.ro

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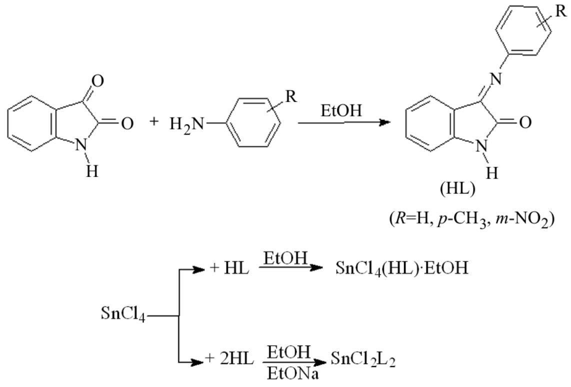
Akadémiai Kiadó, Budapest, Hungary

Springer, Dordrecht, The Netherlands

(HL^1: the Schiff base resulted from 1:1 condensation of isatin and aniline and respectively HL^2: the Schiff base resulted from 1:1 condensation of isatin and *p*-toluidine). The Schiff bases were synthesised by direct condensation of isatin and aromatic amines as it is shown in Scheme 1. The tin(IV) complexes with neutral and respectively anionic Schiff bases derived from isatin and aniline/*p*-toluidine/*m*-nitroaniline were characterised as mononuclear species on the basis of the chemical analysis as well as the physico-chemical data that was previously reported (Scheme 1) [13].



Scheme 1

It is worth mentioning that in neutral forms the Schiff bases are coordinated through azomethinic nitrogen and carbonyl oxygen atoms respectively through azomethinic nitrogen and oxygen atoms in the enolic form of deprotonated ligands. The following solid compounds have been studied from the point of view of their thermal behaviour:

HL^1 or $C_{14}H_{10}N_2O$ (**1**)

HL^2 or $C_{15}H_{12}N_2O$ (**2**)

$[SnCl_4(HL^1)]\cdot EtOH$ or $SnC_{16}Cl_4H_{16}N_2O_2$ (**3**)

$[SnCl_4(HL^2)]\cdot EtOH$ or $SnC_{17}Cl_4H_{18}N_2O_2$ (**4**)

$[SnCl_2(L^1)_2]$ or $SnC_{28}Cl_2H_{18}N_4O_2$ (**5**)

$[SnCl_2(L^2)_2]$ or $SnC_{30}Cl_2H_{22}N_4O_2$ (**6**)

The results concerning the organic ligands and their Sn(IV) complexes decomposition are comparatively discussed below.

Thermal behaviour of Schiff bases and of tin(IV) complexes

Thermal decomposition of $C_{14}H_{10}N_2O$ (HL^1) (**1**) and $C_{15}H_{12}N_2O$ (HL^2) (**2**)

The TG, *T*, DTG and DTA curves corresponding to the organic compound (**1**) heating in the 20–1000°C temperature range are presented in Fig. 1.

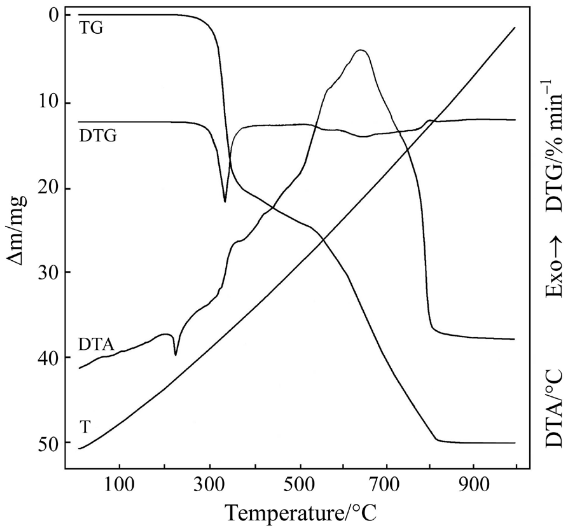
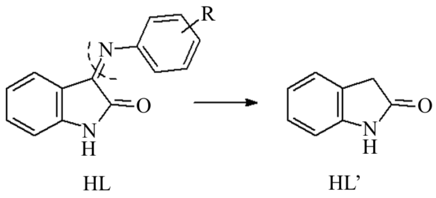


Fig. 1 TG, DTG and DTA curves of (**1**)

According to the TG curve at progressive heating, before the two decomposition steps, there has been evidenced at 225°C the melting of the Schiff base. The first decomposition step occurred in the temperature range 260–370°C (the maximum rate corresponds to the 335°C temperature) and it has been accompanied by a weak exothermic effect. This step corresponds to the azomethinic bond cleavage, leading to the α-benzopyrrolidone as it is shown in the Scheme 2. Regarding the gaseous residue, this could be a mixture of benzene, nitrobenzene as well as CO_2, NO_2 and H_2O (the exo effect indicates that the thermal degradation of organic leaving fragments is accompanied by these derivatives volatilisation).

The chemical elemental analysis was used in order to confirm the composition of the solid residue (found: C, 72.14; N, 10.42; H, 5.27%; requires for C_8H_7NO: C, 72.18; N, 10.53; H, 5.26%). The absence in IR spectrum of the reaction product (Fig. 2b), of the band corresponding to the stretching vibration $\nu_{C=N}$, that appears at 1654 cm^{-1} in the spectrum of (**1**) (Fig. 2a), represents a proof of the α-benzopyrrolidone formation.

The second decomposition step (370–800°C) is accompanied by a strong exothermal effect and it corresponds to the oxidative degradation of the previous compound ($HL^{1'}$). During this transformation at least two thermochemical processes occur according to DTG and DTA curves.



Scheme 2

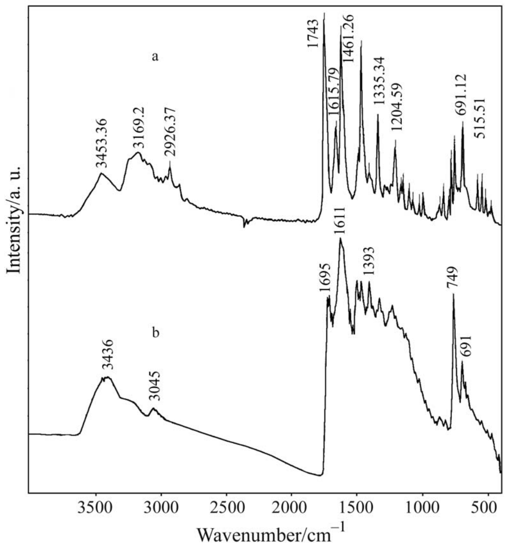


Fig. 2 IR spectra of HL^1 (a) and the intermediate resulted from thermal degradation at 370°C (b)

For the HL^2 (**2**), the melting point has been evidenced at 230°C. The decomposition occurs also in two steps as it is shown in Fig. 3. First one, with a mass loss of 43.82% (calculated 43.64%) corresponds to the cleavage of azomethinic bond and α-benzopyrrolidone formation (270–400°C). The thermochemical degradation of this derivative (400–820°C) occurs in the second step with a mass loss of 56.18% (calculated 56.36%). The step occurs in several reactions that are difficult to separate; all exhibit an exothermal effect.

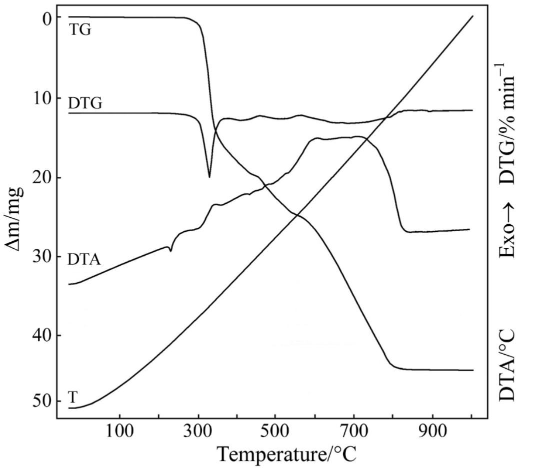


Fig. 3 TG, DTG and DTA curves of (**2**)

Thermal decomposition of $SnC_{16}Cl_4H_{16}N_2O_2$ (3) and $SnC_{17}C_{14}H_{18}N_2O_2$ (4)

Complexes (**3**) and (**4**) have the same thermal behaviour and the general aspect of the DTG, DTA and TG curves as it is shown for (**3**) (Fig. 4). The thermal decomposition occurs in three steps.

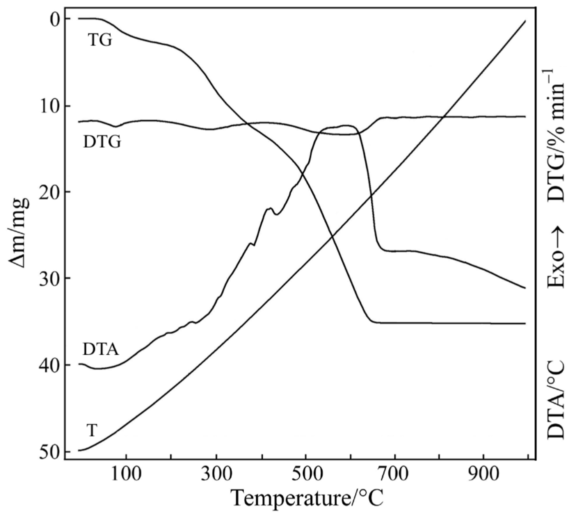


Fig. 4 TG, DTG and DTA curves of (**3**)

The decomposition of the complexes starts at a lower temperature with the ethanol loss in an endothermic process that occurs with maximum rate at 80°C (Table 1).

The second step, a weak exothermic one, occurs in the temperature range 200–370°C and corresponds to the azomethinic bond cleavage as it was also observed for the organic uncoordinated Schiff base. The α-benzopyrrolidone resulted after this process remains coordinated to tin(IV). The last step is very complex and it is an overlapping of the thermal decomposition of complex leading to $SnCl_4$ and the organic part, which simultaneously suffers an oxidative degradation; a part from the resulted $SnCl_4$ is volatilised. In the same time the water developed from thermal decomposition of the α-benzopyrrolidone leads to the hydrolysis of the $SnCl_4$ remaining part. The final product of the thermal decomposition is SnO_2 that represent 47 and respectively 45% from the entire quantity that should be obtained according to the complex formula. Such behaviour was observed also for other tin(IV) species with a high covalence degree [14, 15]. The nature of the final product was established by chemical elemental analysis and powder-XRD determination.

Thermal decomposition of $SnC_{28}Cl_2H_{18}N_4O_2$ (5) and $SnC_{30}Cl_2H_{22}N_4O_2$ (6)

The different nature of the ligand and the coordination mode generates the different thermal behaviour for $[SnL_2Cl_2]$ complexes (Fig. 5). Excepting this, the two complexes have a similar behaviour. The two complexes are very stable and the thermal decomposition begins at 200 and 210°C, respectively. The first step corresponds to the chlorine loss and the

Table 1 Thermal behaviour of the complexes (**3**) and (**4**)

Complex	Step	Thermal effect	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%	intermediate/final product nature
$[SnCl_4(HL^1)]\cdot EtOH$ (**3**)	1	endothermic	50–140	8.53	8.70	$[SnCl_4(HL^1)]$
	2	exothermic	200–370	17.07	17.02	$[SnCl_4(HL^{1'})]$
	3	exothermic	370–650	60.97	45.77	SnO_2
		residue (SnO_2)		13.43	28.51	
$[SnCl_4(HL^2)]\cdot EtOH$ (**4**)	1	endothermic	50–140	8.63	8.47	$[SnCl_4(HL^2)]$
	2	exothermic	210–390	18.74	19.05	$[SnCl_4(HL^{2'})]$
	3	exothermic	390–660	62.47	44.59	SnO_2
		residue (SnO_2)		10.16	27.89	

Table 2 Thermal behaviour of the complexes (**5**) and (**6**)

Complex	Step	Thermal effect	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%	intermediate/final product nature
$[SnCl_2(L^1)_2]$ (**5**)	1	exothermic	200–280	8.62	8.70	$[SnO(L^1)_2]$
	2	exothermic	280–550	44.93	44.03	$[SnO(L^{1'})_2]$
	3	exothermic	550–775	23.00	23.41	SnO_2
		residue (SnO_2)		23.45	23.86	
$[SnCl_2(L^2)_2]$ (**6**)	1	exothermic	210–290	8.44	8.51	$[SnO(L^2)_2]$
	2	exothermic	290–570	45.52	45.24	$[SnO(L^{2'})_2]$
	3	exothermic	570–780	22.64	22.91	SnO_2
		residue (SnO_2)		23.40	23.34	

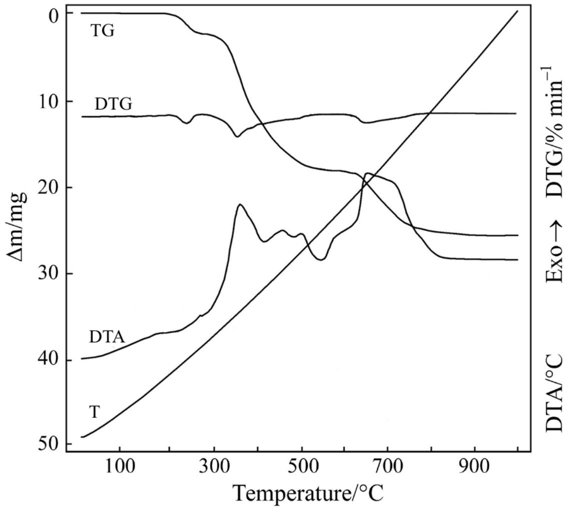
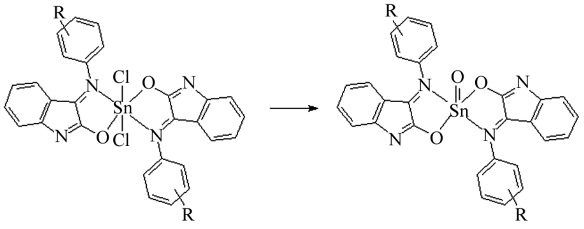


Fig. 5 TG, DTG and DTA curves of (**5**)

oxotin(II) complex formation in an exothermic process as it is shown in Scheme 3. After the chlorine atoms elimination the coordinative saturation of tin(IV) occurs through the oxygen bonding. The next step, exothermic also, corresponds to the ligand thermolysis with the α-pyrrolidone generation that is coordinated to the oxotin(II) in the anionic form. The oxidative degradation of the organic remaining part leads to powder tin(IV) oxide occurs as the final step. The thermal behaviour data for these complexes are shown in Table 2.

Regarding these species it can be mentioned that the final residue contains the whole initial quantity of tin. This behaviour is a consequence of the fact that the intermediate compound formed after the second step has a smaller covalence degree.



Scheme 3

Conclusions

A series of complexes of tin(IV) with Schiff bases derived from isatin and aniline respectively *p*-toluidine (both in neutral and anionic form, respectively) were characterised as mononuclear species.

The Schiff bases are melting before decomposition process, which occurs in two steps.

The $[SnCl_4(HL)]\cdot EtOH$ species suffer two exothermic processes after ethanol elimination. The final residue, that is SnO_2, is in a smaller quantity in comparison with the expected theoretic one. This behaviour could arise from lower lattice energy and a higher covalence degree for $SnCl_4$ that is formed as intermediate.

The complexes with the higher molecular mass $[SnCl_2L_2]$ display a thermal behaviour more complex, the steps of the degradation being not well delimited.

In these cases the final product is the SnO_2 which corresponds to the entire quantity of tin from the complex compound; this is a consequence of the fact that oxotin(II) species formed as intermediates have a smaller covalence degree and are less volatile.

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