THERMAL ANALYSIS OF Fe(III) COMPLEXES WITH SALICYLALDEHYDE SEMI-, THIOSEMI- AND S-METHYLISOTHIOSEMI-CARBAZONES[*]

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Abstract

The paper describes the results of differential thermal analysis of the octahedral Fe(III) complexes of the general formula $[Fe(HL^n)_2]Cl$ and $Fe(HL^3)L^3$, as well as of the corresponding ligands H_2L^n (H_2L^n – tridentate salicylaldehyde semi thiosemi- and S-methylisothiosemi-carabazones with $n=1$, 2 and 3 respectively). The decomposition of the complexes involving sulphur-containing ligands (H_2L^2 and H_2L^3) starts with sulphur elimination. In case of the complexes $[Fe(HL^2)]Cl$ and $[Fe(HL^3)]Cl$ sulphur evolves independently, whereas with $Fe(HL^3)L^3$ it is eliminated within the SCH_3 group. In the former case, sulphur elimination takes place at the same temperature for both complexes. The change in the coordination mode, being a consequence of the replacement of O by S, has no essential effect on thermal stability of the coordination polyhedron. The complexes involving ONN coordination, realized with the H_2L^3 ligand, exhibit a comparatively highest thermal stability of the coordination polyhedron.

Keywords: Fe(III) complexes, thermal analysis, thiosemicarbazide-based ligands

Introduction

The syntheses of salicylaldehyde semi- (H_2L^1), thiosemi- (H_2L^2) and S-methyl-isothiosemi-carbazone (H_2L^3), involving ONO, ONS and ONN as respective sets of donor atoms (Fig. 1), have been described in [1, 2]. The synthesis and voltammetric characteristics of their high-spin octahedral bis(ligand) complexes with iron(III) of the general formula $[Fe(HL_2^n)]Cl$ ($n=1,2,3$) and $(FeHL^3)L^3$ have been presented in [3]. With the objective of studying the effect of the nature of the atoms involved in coordination and the change of the complex moiety on thermal stability, a study has been carried out of thermal decomposition of these complexes and the corresponding free ligands. It should be mentioned that the decomposition of the H_2L^3 ligand and its complexes with other metals was partially analyzed in previous works [4, 5].

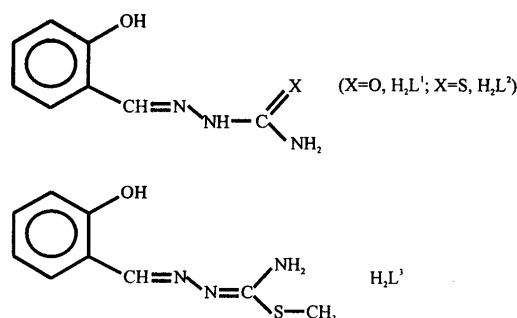[*] Part 36 of the series Transition metal complexes with the thiosemicarbazide-based ligands.

Fig. 1 Structural formula of H_2L^n

Experimental

Thermogravimetric measurements were carried out on a Paulik-Paulik-Erdey derivatograph (MOM, Hungary). The experiments were performed with samples of masses from 25 to 100 mg. The process was started in the air atmosphere, and the samples were heated to $1000^{\circ}C$ at a rate of $10^{\circ}C$ min^{-1}. Al_2O_3 served as standard. Analysis of the final decomposition product was carried out on an automatic PW 1373 (Philips) powder diffractometer using ASTM data.

Table 1 Characteristics of thermal decomposition of the ligand

H_2L^1				
Effect	Fragment eliminated	T/K	$\Delta m_{exp}/\%$	$\Delta m_{cal}/\%$
endo	NH_3	493	10	9.5
endo	$Sc-NH_3$	439–583	37.5	38.6
exo	Sal	583–973	52.5	51.9

H_2L^2				
Effect	Fragment eliminated	T/K	$\Delta m_{exp}/\%$	$\Delta m_{cal}/\%$
endo	NH_3	493	9	8.6
endo	$TSc-NH_2$	493–603	42	43.3
exo	Sal	603–1063	49	48

H_2L^3				
Effect	Fragment eliminated	T/K	$\Delta m_{exp}/\%$	$\Delta m_{cal}/\%$
endo	melting	430	–	
exo	SCH_3	503	22	22.5
endo	$TSc-SCH_3$	503–773	33	33
exo	Sal	773–1053	45	44.9

Results and discussion

In Fig. 2 is presented the course of thermal decomposition for the above ligands, and in Figs 3–6 the same for their complexes with Fe(III). Table 1 gives a survey of particular fragments eliminated at characteristic temperatures, along with the observed and calculated values of mass loss for free ligands, while analogous quantities for complexes are presented in Table 2. Thermal decomposition of all three ligands has a similar course in its final part, the difference being observed only in the initial stage. With H_2L^3 the decomposition is preceded by melting of the substance at 430 K, which was not observed with the other two ligands. The endothermic effects occurring with H_2L^1 and H_2L^2 at the same temperature (493 K) are accompanied by evolution of NH_3, which represents the beginning of the compound decomposition. In contrast to this, in case of H_2L^3 the melting is followed by an exothermic effect (503 K) due to elimination of the SCH_3 group. The further course of decomposition of all the three ligands is characterized by an endothermic effect accompa-
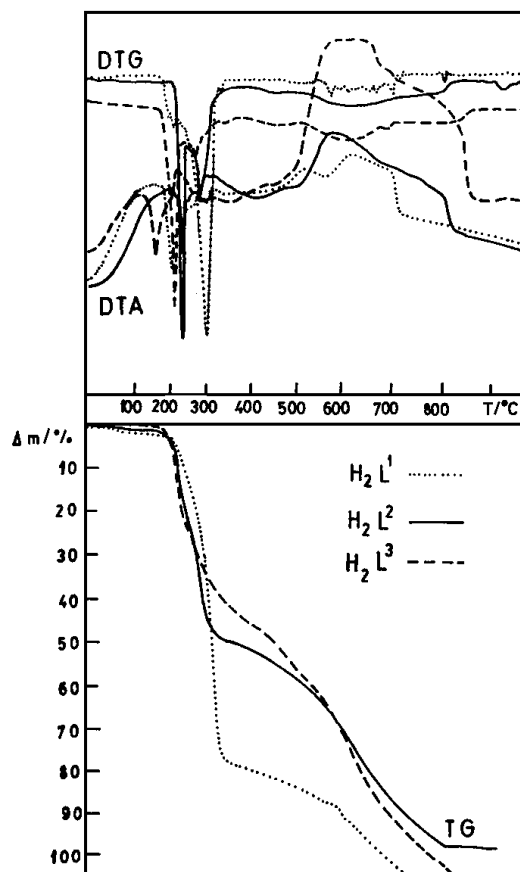

Fig. 2 TG, DTG and DTA curves of H_2L^n

nied by elimination of the semicarbazide (Sc) and thiosemicarbazide (Tsc) moiety, respectively (Table 1). The process of elimination of Sc and Tsc moieties from all three ligands begins at similar temperatures (493–503 K). However, with H_2L^3 the process takes place in a wider temperature interval, so that the elimination of the corresponding fragment ends up at a significantly higher temperature compared to that for the other two ligands.

The differences in bond strength and surroundings about the sulphur in H_2L^2 and H_2L^3 are straightforward, implying the different courses of their thermal decompo-
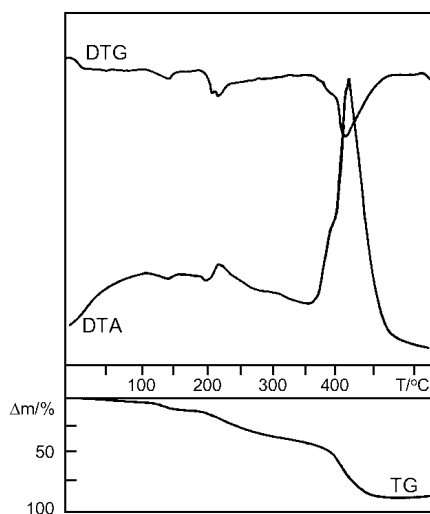

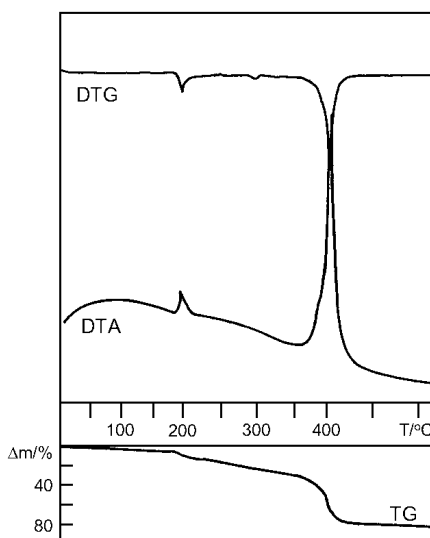
Fig. 3 TG, DTG and DTA curves of $[Fe(HL^1)_2]Cl$
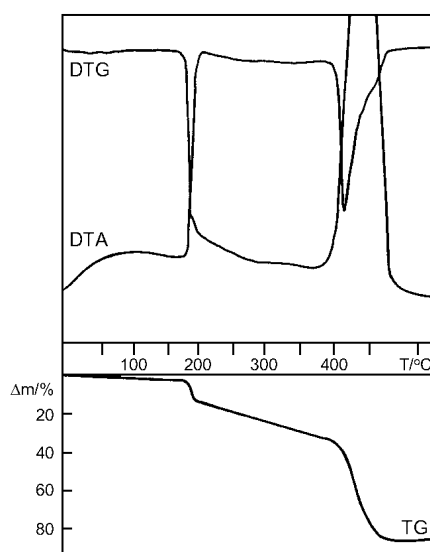

Fig. 4 TG, DTG and DTA curves of $[Fe(HL^2)_2]Cl$

Fig. 5 TG, DTG and DTA curves of $[Fe(HL^3)_2]Cl$

sition. Thus, in case of H_2L^3 the SCH_3 group is eliminated first, which is in contrast to H_2L^2, from which sulphur is eliminated along with the Tsc-NH_2 fragment.

The decomposition process of all the three ligands ends up with elimination of the salicylaldehyde (Sal) moiety, which is accompanied by a pronounced exothermic effect. Decomposition of H_2L^3 starts at a somewhat higher temperature, and the process for all the three ligands is completed to about 1000 K.

Thermal decomposition of the investigated complexes takes also place in several endothermic and exothermic processes. In case of the complexes with H_2L^2 and H_2L^3, the first exothermic effect is due to sulphur elimination. This effect for the complexes $[Fe(HL^2)_2]Cl$ and $[Fe(HL^3H)_2]Cl$ has its maximum at a similar temperature of ca. 460 K. Although in the former complex sulphur is coordinated whereas in the latter is not, this has no effect on the temperature of sulphur elimination, which is practically identical for both compounds. The mentioned exothermic effect of the $[Fe(HL^3)_2]Cl$ decomposition is followed by another exothermic effect, probably due to elimination of the CH_3 group. In contrast to this, in case of $Fe(HL^3)L^3$ the methyl group is eliminated together with sulphur, the same being observed in the decomposition of the H_2L^3 ligand and complexes of some other 3d with this and some similar ligands [6, 7]. In our case, the presence of Cl was obviously the reason of the independent sulphur elimination. It is interesting to notice that sulphur alone is eliminated at somewhat lower temperature. Also, when S and CH_3 are eliminated together, as in the case of the free H_2L^3 ligand and $Fe(HL^3)L^3$, it can be said that the methyl group, having somewhat higher cleavage temperature (Table 1), hinders somehow sulphur elimination. Elimination of the SCH_3 fragment takes practically place at the same temperature with both the ligand and the complex.

However, decomposition of the only complex containing no sulphur-
$[Fe(HL^1)_2]Cl$, starts with an endothermic effect related to elimination of HCl. With
the other two complexes of this type, $[Fe(HL^2)_2]Cl$ and $[Fe(HL^3)_2]Cl$, the elimina-
tion of this fragment occurs after the mentioned exothermic effects, taking place at
somewhat higher temperatures (Table 2). The elimination of HCl from $[Fe(HL^2)_2]Cl$
is accompanied by a simultaneous elimination of the rest of the thiosemicarbazide
fragment (Tsc-S). In case of $[Fe(HL^3)_2]Cl$, together with hydrochloride is eliminated
NH_2 group, which has also been observed with the vanadium complexes containing
NH_2 and Cl [5].

The respective fragments Sc and Tsc are eliminated from $[Fe(HL^1)_2]Cl$ and
$[Fe(HL^2)_2]Cl$ over a close temperature interval, beginning at a somewhat lower and
ending up at somewhat higher temperatures than in the case of decomposition of the
corresponding free ligands.

The final exothermic effect in the decomposition process of $[Fe(HL^1)_2]Cl$ and
$[Fe(HL^2)_2]Cl$ is due to elimination of the salicylaldehyde moiety.

A specific feature of the decomposition of the complex involving H_2L^3 is that in
its final stage is eliminated the whole ligand moiety, so that it is not possible to sepa-
rate elimination of the Tsc and Sal fragments. However, with both complexes involv-
ing this ligand, the NH_2 group is missing from the Tsc moiety, as it has already been
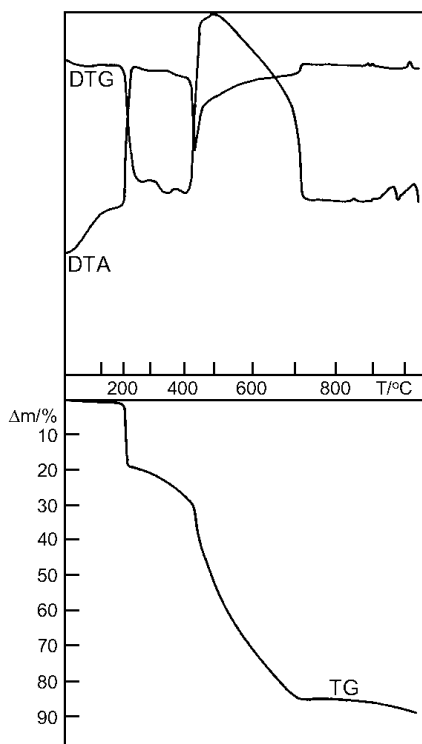eliminated either alone or together with HCl (Table 2). In contrast to this, in case of

Fig. 6 TG, DTG and DTA curves of Fe(HL^3)L^3

decomposition of the H_2L^3 ligand itself a successive elimination of the Tsc and Sal fragments is observed, the NH_2 being eliminated within Tsc. It should also be noticed that the decomposition of the H_2L^3 complexes involving Cl is completed at a significantly lower temperature compared to that of the ligand itself and the complexes containing no this halogen.

Table 2 The characteristics of thermal decomposition of the complex

	$[Fe(HL^1)_2]Cl$			
Effect	Fragment eliminated	T/K	Δm_{exp}/%	Δm_{cal}/%
endo	HCl	408–453	8.3	8.1
endo	$2S_c^*$	453–631	30	30.8
exo	2(Sal+0.25O)	631–746	45	43.4
residue	Fe_2O_3	746	16.6	17.8
	$[Fe(HL^2)_2]Cl$			
Effect	Fragment eliminated	T/K	Δm_{exp}/%	Δm_{cal}/%
exo	2S	458–483	14	13.3
endo	2(TSc–S)+HCl	483–673	36	36.4
exo	2(Sal–0.75O)	673–773	34	33.8
residue	Fe_2O_3	773	16	16.6
	$[Fe(HL^3)_2]Cl$			
Effect	Fragment eliminated	T/K	Δm_{exp}/%	Δm_{cal}/%
exo	2S	463	13	12.6
exo	$2CH_4$	463–533	6	5.1
endo	$HCl+2NH_3$	533–678	16	13.9
exo	$2(L^3–NH_2–0.75O)$	678–773	52	52.7
residue	Fe_2O_3	773	13	15.7
	$[Fe(HL^3)L^3$			
Effect	Fragment eliminated	T/K	Δm_{exp}/%	Δm_{cal}/%
exo	$2SCH_3$	508	19	19.1
endo	$2NH_3$	508–693	9	7.2
exo	$2(L^3–NH_2–0.75O)$	693–993	56	56.8
residue	Fe_2O_3	993	16	16.9

The final decomposition product of all the investigated complexes was Fe_2O_3. It is known that breaking up of the coordination polyhedron in the case of $[Fe(HL^2)_2]Cl$ takes already place in the first exothermic effect at about 460 K, involving elimination of the coordinated sulphur. In view of the fact that Cl does not take part in coordination, its elimination does not affect the coordination polyhedron of the corresponding compound. The coordination polyhedron of $[Fe(HL^1)_2]Cl$ is stable to the beginning of elimination of the Sc fragment at 453 K, and in case of $[Fe(HL^3)_2]Cl$ and $[Fe(HL^3)]L^3$ to the respective temperatures of 533 and 508 K, corresponding to elimination of the coordinated NH_2 group. On the basis of this it can be concluded that the replacement of one oxygen atom in the coordination polyhedron with sulphur (which is equivalent to the replacement of the H_2L^1 with H_2L^2) does not lead to essential changes in its thermal stability. On the other hand, the formation of an octahedral coordination involving the ONN set of atoms, which is the case with the H_2L^3 complexes, enhances thermal stability of the corresponding polyhedron.

In view of the fact that other analogous fragments from the complexes involving H_2L^1 and H_2L^2 are also eliminated at close temperatures, it can be generally stated that these compounds exhibit quite similar thermal stability. Finally, it can be concluded that of all the investigated complexes $Fe(HL^3)L^3$ exhibits the highest thermal stability.

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