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THERMAL ANALYSIS OF SOME COMPLEXES $LH[Cr(NCS)_4L_2].xH_2O$ ($L=NH_3$ OR ORGANIC BASE)

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Data obtained by thermal analysis of $K_3[Cr(NCS)_6].4H_2O$ and some derivatives, $LH[Cr(NCS)_4L_2].xH_2O$, where $L=NH_3$ or an organic base, are reported. The TG, DTG and DTA curves show common behaviour (SCN^- ligand decomposition) as well as specific behaviour for each complex due to the base L, which complicates the thermal decomposition of the complexes. Some weak bases with low boiling points are easily eliminated, which determines the common thermal behaviour of the complexes.

A general mechanism of thermal decomposition is advanced involving dehydration and decomposition processes for both LH^+ and $[Cr(NCS)_4L_2]^-$. The apparent activation energies of different processes confirm the thermal decomposition mechanisms of the complexes under study.

Complexes derived from the Reinecke salt, $LH[Cr(NCS)_4L_2].xH_2O$, where L denotes an organic base, constitute a class of compounds showing both common properties and specific properties conferred by the base structure and nucleophilic character.

Correlations like that between the structure and properties can be demonstrated for complexes of Reinecke type by means of thermogravimetry and spectrophotometry concerning the substitution processes.

In the present paper, the results obtained by thermal analysis of some complexes $LH[Cr(NCS)_4L_2].xH_2O$, where L = ammonia, pyridine, 4-methylpyridine, 2-methylquinoline and 2,2'-dipyridyl, are reported.

Experimental

The complexes $LH[Cr(NCS)_4L_2].xH_2O$ were synthesized by the literature method [1] with the optimum reactant ratio for each product [2].

The quantitative analysis data are in good agreement with the chemical formulae of the complexes under study.

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Table 1 Thermogravimetric characteristics of the complexes under study

Complex	Process	Temperature range, °C	Product	*W* calculated for 1 mol product, %	*W* experimental	No. moles	Residue		
							Nature	*W* residue	
								calculated	experimental
1. $K_3[Cr(NCS)_6].4H_2O$	Dehydration	40–105	H_2O	3.05	9.10	3			
		105–170			3.2	1			
	Decomposition of coordination sphere (—NCS)	250–375	$(CN)_2$	8.81	14.3	1.5	CrS	63.62	63.50
		380–465	S	5.42	10.0	2	3KSCN		
2. $NH_4[Cr(NCS)_4(NH_3)_2].H_2O$	Dehydration	40–150	H_2O	5.08	5.1	1			
	NH_4^+ decomposition	190–235	NH_3	4.79	4.9	1			
	Decomposition of coordination sphere (—NH_3; —NCS)	235–335	$(CN)_2$	14.67	29.0	2	CrS	23.7	22.7
		335–415	NH_3	4.79	9.7	2			
		415–490	S	9.03	29.0	3			
3. $L_1H[Cr(NCS)_4(L_1)_2]$ L_1 = pyridine	Decomposition of L_1H^+	100–280	L_1	15.13	15.1	1			
	Decomposition of coordination sphere (—L_1; —NCS)	280–340	L_1	15.13	30.0	2	CrS	16.07	15.4
		340–410	$(CN)_2$	9.95	18.0	2			
		410–660	S	6.26	22	3.3			

4. $L_2H[Cr(NCS)_4(L_2)_2]$ L_2=4 methylpyridine	Decomposition of L_2H^+	180–285	L_2	16.49	27.0	1.63			
	Decomposition of coordination sphere (—L_2; —NCS)	285–335	L_2	16.49	20.0	1.12	CrS	14.88	15.0
		335–430	$(CN)_2$	9.21	23.0	2.55			
		430–515	S	5.67	17.2	3.13			
5. $L_3H[Cr(NCS)_4(L_3)_2].2H_2O$ L_3 = 2-methylquinoline	Dehydration	50–170	H_2O	2.4	4.5	2			
	Decomposition of L_3H^+	180–350	L_3	19.7	40	2	CrS	11.19	12.5
	Decomposition of coordination sphere (—L_3; —NCS)	350–400	L_3	19.7	8	0.4			
		400–550	$(CN)_2$	6.92	35	2			
		550–660	S	4.26		3			
6. $L_4H[Cr(NCS)_4L_4].H_2O$ L_4 = 2.2'-dipyridyl	Dehydration	50–140	H_2O	2.92	3	1			
	Decomposition of L_4H^+	140–295	L_4	25.38	25.5	1	CrS	13.65	12.7
	Decomposition of coordination sphere (—L_4; —NCS)	295–370	L_4	25.38	10.8	0.42			
		370–440			12.9	0.50			
		440–520	$(CN)_2$	8.45	16.9	2			
		520–610	S	5.21	15.6	3			

W— weight loss;
W residue — residue weight.

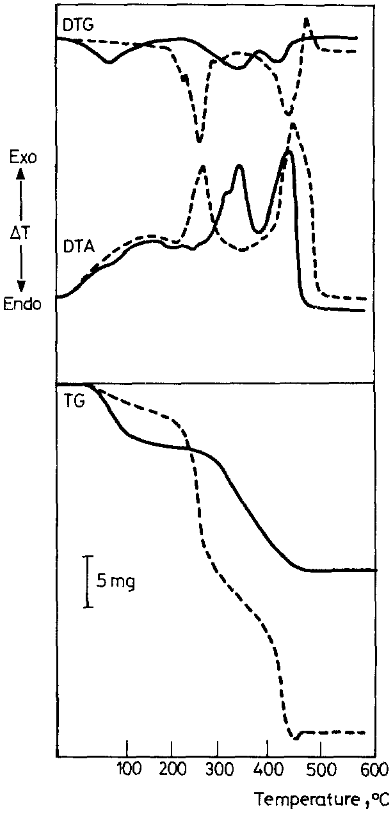

Fig. 1 TG, DTG and DTA curves of complexes 1 (———) and 2 (– – –)

The thermal behaviour in the nonisothermal regime was followed by means of a MOM (Budapest) derivatograph of Paulik–Paulik–Erdey type under the following conditions: sample amount—50 mg; heating rate—9 or 12 deg/min, maximum temperature—600° or 900°; ambient atmosphere.

Results and discussion

The thermal curves show that the decompositions of the complexes $LH[Cr(NCS)_4L_2].xH_2O$ proceed in several steps, with both common and specific stages.

The estimation of weight losses and the natures of the decomposition products and residues confirmed the chemical compositions of the complexes and afforded some considerations on the thermal decomposition mechanisms. In some cases the thermal processes in the coordination sphere of the complex, as well as the behaviour of the cation LH^+ and the crystallization water, were made evident.

The thermal behaviour of these complexes was analysed starting from the initial synthesis compound, $K_3[Cr(NCS)_6].4H_2O$ and the Reinecke salt, $NH_4[Cr(NCS)_4(NH_3)_2].H_2O$. The literature data on the thermal behaviour of the ligand SCN^- in complexes [3–7], the cation NH_4^+ and the ligand NH_3 [8, 9] were also taken into account.

The TG, DTG and DTA curves for complexes 1 and 2 indicate common behaviour, associated with the thermal decomposition of the ligand SCN^- into $(CN)_2$ and S. These products are eliminated within the ranges 235–375° and 380–630° respectively, along with thermooxidative processes with specific exothermic effects in the DTA curves.

Up to SCN^- decomposition, complex 1 undergoes dehydration, while complex 2 eliminates NH_3 from NH_4^+. Complex 1 leaves a KSCN—CrS residue between 470 and 610°, while a CrS residue remains from complex 2 at about 630°. At higher temperatures CrS transforms into Cr_2O_3.

The TG, DTG and DTA curves for complexes 2–6 in Fig. 2 show both common and specific processes for each complex in the series.

The common thermal processes are associated with SCN^- decomposition and elimination of the products by thermooxidative processes. Among these products the sulphur is eliminated constantly between 410 and 520° or higher, while $(CN)_2$ is eliminated before S by thermooxidative processes influenced by the organic base L.

The thermal processes specific for each complex are due to the ligand L. It is often eliminated stepwise, either as a free base or as decomposition products over a wide temperature range. Its influence on the common thermal processes depends on its structure and basic character (involving the metal-ligand bond strength, electronic effects, etc.), boiling point, reactivity and stability against heat.

In this connection it is evident that the weak organic bases with low boiling points are eliminated easily, therefore having little influence on the common thermal behaviour of the complexes $LH[Cr(NCS)_4L_2].xH_2O$. Thus, complex 3, containing a weak base L_1 (b.p. = 115.5°), eliminates it completely within the range 100–340°, thereafter showing thermal behaviour similar to that of SCN^-. Instead, the complexes 4, 5 and 6 eliminate the organic base (1.63 L_2, 2 L_3, 1 L_4) only partially till ligand decomposition, whose thermal processes are evidenced with difficulty. Only the thermooxidative elimination of S appears regularly within the range 410–520° or higher. The residue formed on the decomposition of these compounds at about 650° is CrS.

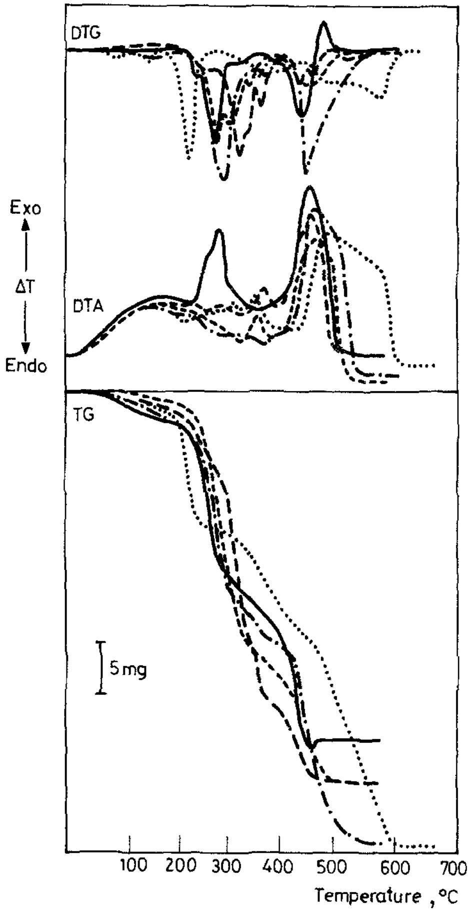

Fig. 2 TG, DTG and DTA curves of complexes 2 (———), 3 (– – –), 4 (- - - -), 5 (·—·—·—·) and 6 (······)

The thermal decompositions of the complexes under study take place according to mechanisms involving dehydration and decomposition processes of both LH^+ and $[Cr(NCS)_4L_2]^-$, with a disturbing influence of the organic base L.

The apparent activation energies of some processes in the general thermal decomposition mechanism were estimated by the Freeman–Carroll [10] method (Table 2).

Thus, the dehydration processes take place with characteristic low energies of activation (40–80 kJ/mol).

The decomposition process with ligand L elimination involves activation energies within a wide range of values as a consequence of differences in both the

Table 2 Activation energies of decomposition processes

Complex	Process	Temperature range, °C	E_a, kJ/mol
1 $K_3[Cr(NCS)_6].4H_2O$	I	40–105	51.7
	II	105–170	—
	III	250–375	72.7
	IV	380–465	199.9
2 $NH_4[Cr(NCS)_4(NH_3)_2].H_2O$	I	40–150	—
	II	190–235	—
	III	235–335	89.3
	IV	335–415	202.0
	V	415–610	198.9
3 $L_1H[Cr(NCS)_4(L_1)_2]$	I	100–280	91.8
L_1 = pyridine	II	280–340	191.5
	III	340–410	—
	IV	410–660	287.2
4 $L_2H[Cr(NCS)_4(L_2)_2]$	I	180–285	100.5
L_2 = 4 methylpyridine	II	285–335	765.9
	III	335–430	—
	IV	430–515	199.1
5 $L_3H[Cr(NCS)_4(L_3)_3].2H_2O$	I	50–170	27.2
L_3 = 2 methylquinoline	II	180–350	106.6
	III	350–400	—
	IV	400–550	218.8
	V	550–660	—
6 $L_4H[Cr(NCS)_4L_4].H_2O$	I	50–120	—
L_4 = 2,2′-dipyridyl	II	120–280	—
	III	295–370	131.6
	IV	370–440	239.3
	V	440–520	287.2
	VI	520–610	287.2

metal-ligand bond strengths and the mechanisms of base elimination from the complexes under study (Fig. 3).

The elimination of sulphur released from the coordination sphere along with the SCN^- decomposition proceeds with similar energies of activation for the complexes under study, due to its state of non-combined sulphur (Fig. 4) with the exception of complexes 3, 5 and 6 for which the stages do not separate quite well.

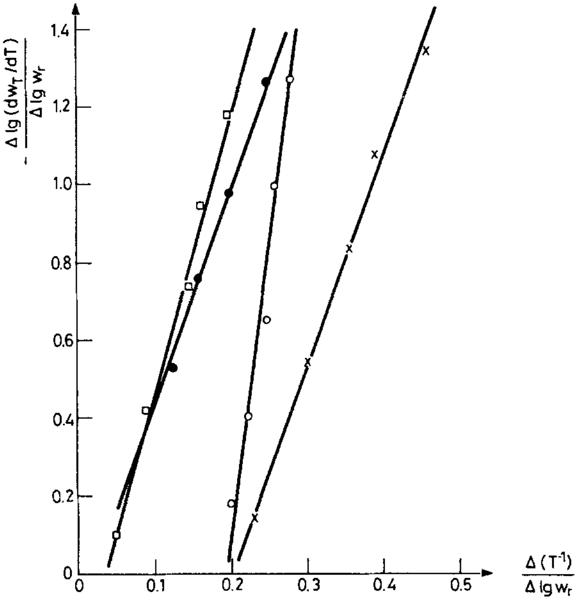

Fig 3 Freeman–Carroll diagrams for the first process of ligand elimination from complexes 3 (×), 4 (●), 5 (□) and 6 (○)

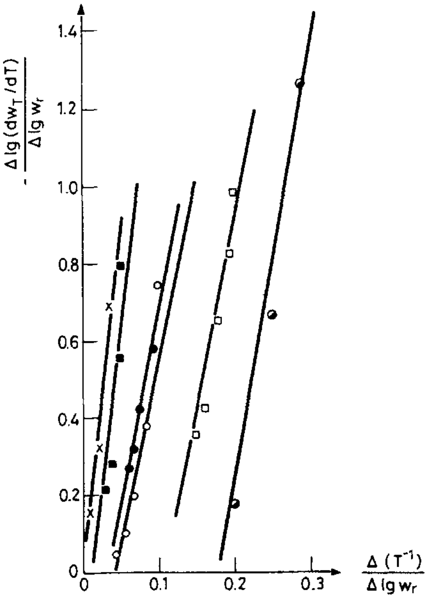

Fig. 4 Freeman–Carroll diagrams for the process of sulphur elimination from complexes 1 (●), 2 (○), 3 (×), 4 (□), 5 (◑) and 6(■)

The complexes $LH[Cr(NCS)_4L_2].xH_2O$ exhibit both common and specific thermal decomposition processes. The general mechanism of thermal decomposition involves dehydration and decomposition of LH^+ and $[Cr(NCS)_4L_2]^-$, with different disturbing influences by the organic base L.

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Zusammenfassung — Die thermische Analyse von $K_3[Cr(NCS)_6].4H_2O$ und einigen Derivaten der allgemeinen Formel $LH[Cr(NCS)_4L_2].xH_2O$ ($L = NH_3$ oder eine organische Base) betreffende Daten werden angegeben. Die TG-, DTG- und DTA-Kurven zeigen sowohl gemeinsame Charakteristika (Zersetzung des Liganden SCN^-) als auch für jeden Komplex spezifische, durch die Base L bedingte Züge, die die thermische Zersetzung der Komplexe komplizieren. Einige schwache Basen mit niedrigen Siedepunkten werden leicht eliminiert, was ein gleiches thermisches Verhalten dieser Komplexe zur Folge hat. Ein allgemeiner Mechanismus der thermischen Zersetzung wird angegeben, der die Dehydratisierung und die Zersetzungsprozesse sowohl für LH^+ als auch für $[Cr(NCS)_4L_2]^-$ in sich einschließt. Die scheinbaren Aktivierungsenergien der verschiedenen Prozesse sind mit dem Mechanismus der thermischen Zersetzung der Untersuchten Komplexe im Einklang.

Резюме — Проведен термический анализ соединения $K_3[Cr(NCS)_6].4H_2O$ и некоторых его производных типа $LH[Cr(NCS)_4L_2].xH_2O$, где $L = NH_3$ или какое-либо органическое основание. ТГ, ДТГ и ДТА-кривые показали как общее, так и специфическое поведение каждого комплекса, обусловленное характером лиганда и усложняющего термическое разложение комплексов. Некоторые слабоосновные лиганды с низкой точкой кипения легко выделяются, что и определяет общее термическое поведение комплексов. Выдвинут общий механизм термического разложения, включая процесс дегидратации и разложения обоих LH^+ и $[Cr(NCS)_4L_2]^-$. Кажущиеся энергии активации различных процессов подтверждают механизм термического разложения исследованных комплексов.