

THERMAL DECOMPOSITION OF OCTAHEDRAL Ni(II) COMPLEXES WITH ACETONE 1-NAPHTHOYLHYDRAZONE

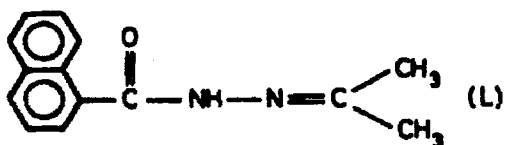
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The thermal decompositions of acetone 1-naphthoylhydrazone (L) and its octahedral complexes with Ni(II), with the general formula NiL_2X_2 ($X = Cl, Br, NO_3$ and NCS), were studied in air and nitrogen atmospheres. It was established that the organic ligand is decomposed in an exothermic processes, which is followed by oxidation of the decomposition fragments by atmospheric oxygen. At temperatures below 640° , all the complexes decompose completely, yielding NiO as the final product, which was confirmed by its X-ray analysis. From the difference between the enthalpy changes for the decompositions of the complexes and of the ligand itself, the nature of the final oxide, and the crystal field splitting parameters obtained from optical measurements, the corresponding stabilization energies were determined.

This work is a continuation of studies of the octahedral Ni(II) complexes of the dehydrazides and hydrazones of some carboxylic acids [1]. Their synthesis and spectral and magnetic properties have already been described [2, 3]



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Analysis of the thermal decomposition was carried out for the complexes NiL_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ and NO_3) and for the ligand, acetone 1-naphthoylhydrazone.

Experimental

Thermogravimetric investigations were carried out with a derivatograph. Each sample was heated from room temperature to 1000° at a rate of 10

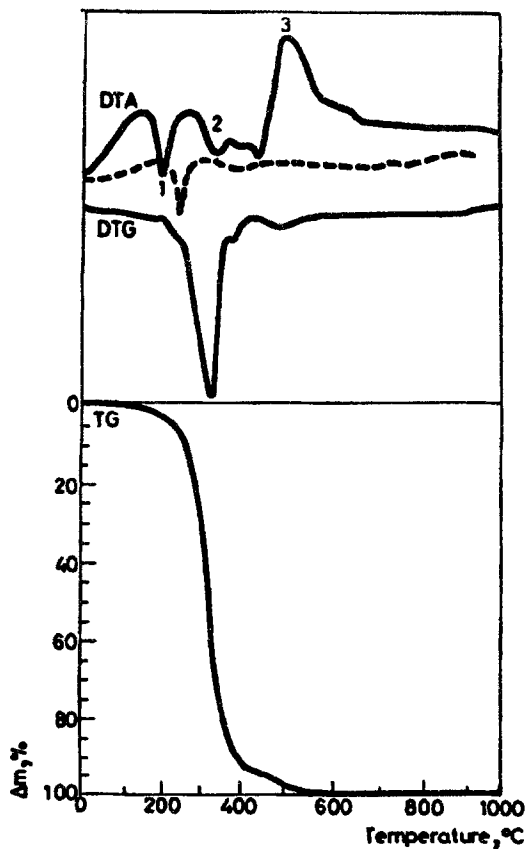


Fig. 1 TG, DTG and DTA curves of L (----- air, nitrogen)

deg/min. The processes were carried out both in air and in nitrogen atmosphere. Al_2O_3 was used as the reference material.

The DSC analysis was carried out in air with Du Pont Instrumental Thermal Analyser 1090, 910 DSC Pressure Cell. The calorimeter was calibrated

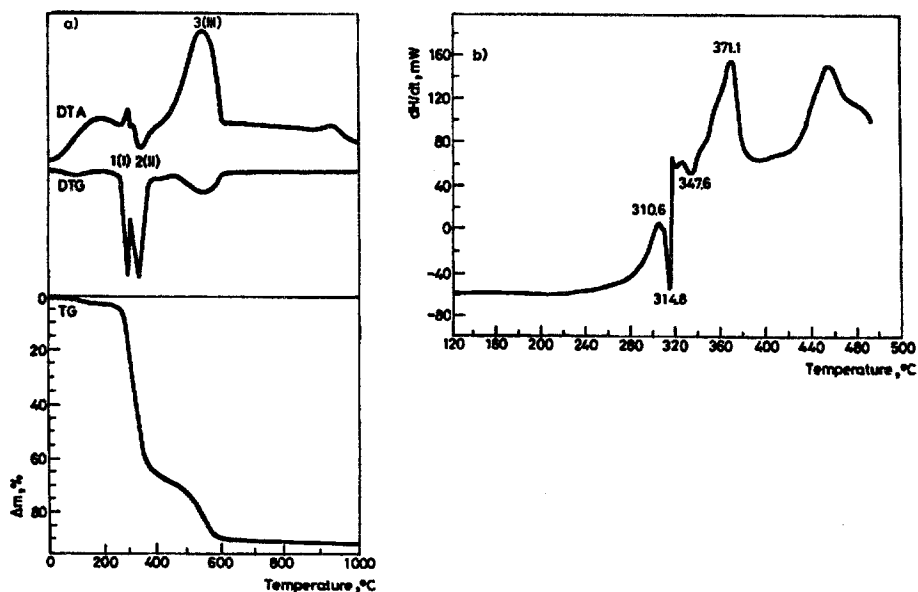


Fig. 2 a) TG, DTA and DTG curves of NiL₂Cl₂ b) DSC curves of NiL₂Cl₂

against an empty aluminium crucible. The mass of the sample was 3-5 mg. The experiments were carried out under atmospheric pressure. The heating rate was 10 deg/min. The enthalpies of the phase transformations were calculated with respect to indium as standard.

Results and discussion

Figure 1 shows a DTA curve for the ligand itself, recorded for the processes in air and in nitrogen atmosphere, while Figs 2-5 were recorded for the particular complexes under the same conditions. It is evident that the decomposition mechanisms of both the ligand and the complex in air differ

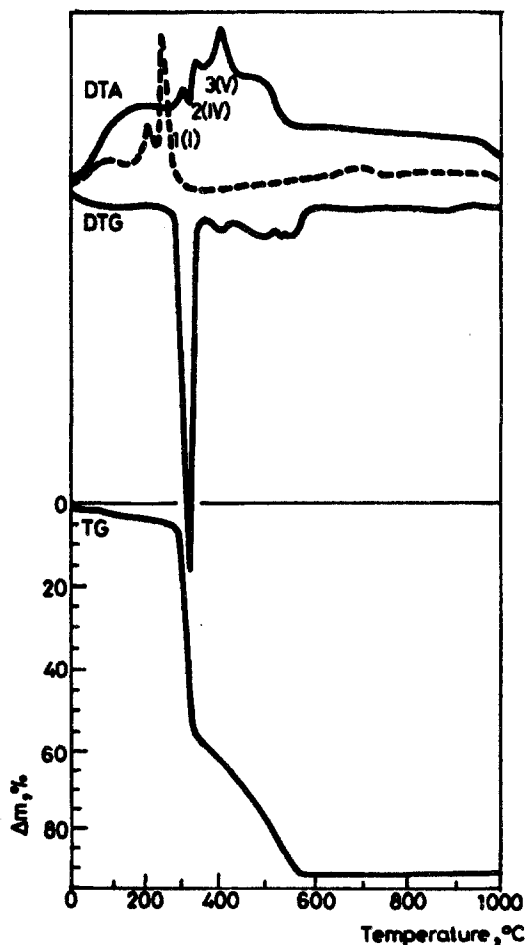


Fig. 3 TG, DTA and DTG curves of NiL_2Br_2 (-----air, nitrogen)

from those in nitrogen atmosphere. For the sake of comparison, Fig. 2b shows a DSC curve for the complex NiL_2Cl_2 in air atmosphere.

To achieve complete thermal decomposition of the ligand, the sample was heated to 1000° . It was observed that the ligand was stable up to 200° , when its melting occurred (Table 1). On the basis of a comparison with the decomposition of pure naphthalene [4], it can be presumed that in the range $240\text{--}380^\circ$ the naphthalene rings decompose, yielding ethylene and carbon monoxide, the formation of the latter product being accompanied by the ab-

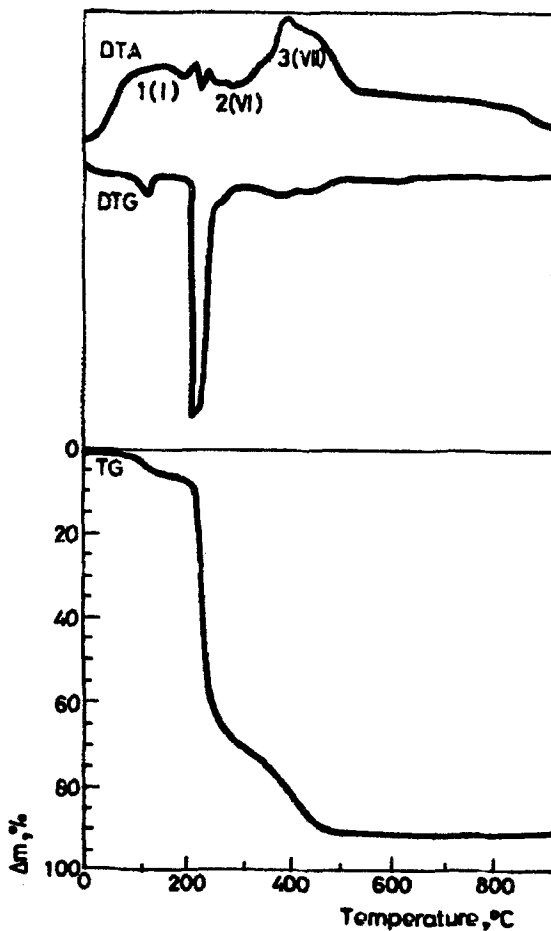


Fig. 4 TG, DTA and DTG curves of $\text{NiL}_2(\text{NCS})_2$

sorption of oxygen from the air. The broad exothermic peak in the DTA curve in the range $400\text{--}680^\circ$ is accompanied by a small loss in mass of the sample. From a comparison with the ligand decomposition in nitrogen atmosphere, where the corresponding peak is an endothermic one, it can be assumed that the ligand decomposed in an endothermic process, followed by combustion of the ligand fragments.

For the complex NiL_2X_2 , the exothermic peak observed at 295 , 310 and 190° in the DTA curves correspond to the removal of two ethylene

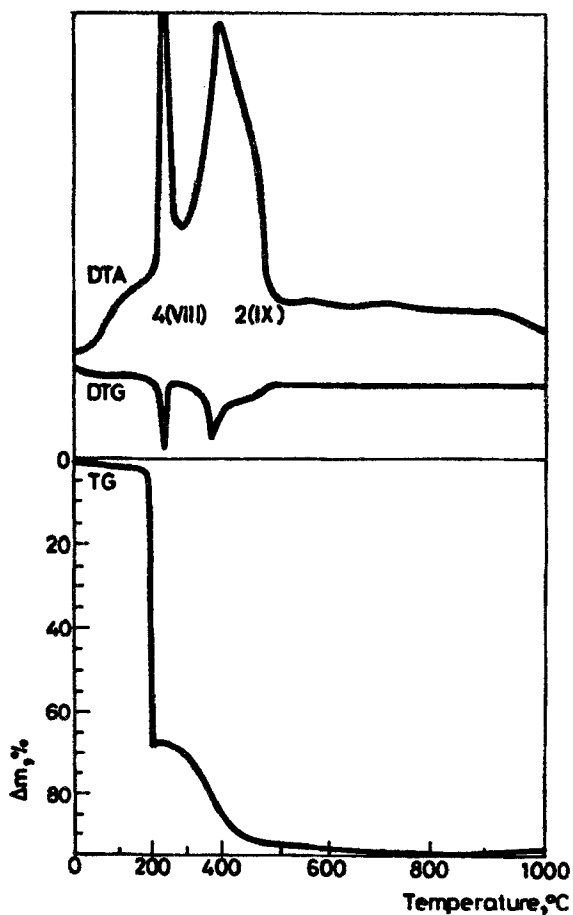


Fig. 5 TG, DTA and DTG curves of $\text{NiL}_2(\text{NO}_3)_2$

molecules from the complexes containing Cl, Br or NCS. The exothermic peaks at 315, 340 and 320° correspond to decomposition of the HCl, HBr or NCS group, which is accompanied by partial decomposition of the organic ligand (Table 1) [4-6]. The DSC curves of these complexes exhibit several exothermic effect; this is illustrated in Fig. 2b which gives a DSC curve of the complex NiL_2Cl_2 . In nitrogen atmosphere, these exothermic peaks appear as endothermic ones, i.e. the exothermic processes are due to oxidation involving atmospheric oxygen.

The exothermic peaks in the range 320-640° correspond to decomposition of the organic ligand moiety.

The decomposition process of the nitrate complex is accompanied by two very strong exothermic effects (Fig. 5, Table 1). One exothermic peak, in the range 200-270°, corresponds to decomposition of both the organic ligand and the nitrate group [7]. The other exothermic process corresponds to decomposition of the remaining part of the ligand, accompanied by an oxidation process involving oxygen.

An X-ray analysis of the powdered residue sample showed that the final decomposition product of all complexes was NiO.

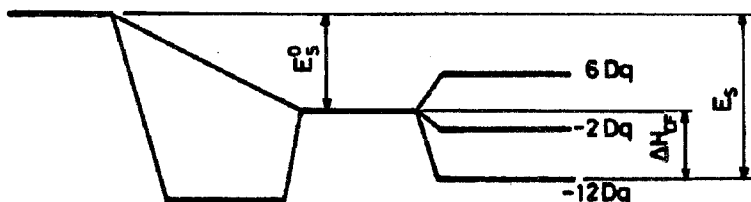


Fig. 6 Stabilization energies of Ni(II) complexes

The understanding of the processes of thermal decomposition of the octahedral Ni(II) complexes and of the ligand itself permitted calculation of the stabilization energies of the complexes (E_s^0) (Fig. 6). The enthalpies of all the endothermic and exothermic effects were first calculated, for both the ligand and the complexes. It was then assumed that the difference in the enthalpies of the processes (ΔH_s) is approximately composed of the metal oxidation energy (E^0) and the energy of binding the ligand and the metal ion (E_s) [9]. The bases for the E^0 values were the literature oxidation energies [7, 8], which were corrected for the percentage metal oxide content in the total mass of the sample.

The data on the crystal field splitting parameters, obtained from the electronic spectra of the complexes [2], served as the basis for the calculation of the crystal field stabilization energies (Table 2).

Table 1a TG analysis data for octahedral Ni(II) complexes with L

Effect	Fragment eliminated	L		NiL ₂ Cl ₂		NiL ₂ Br ₂				
		T, °C	Δm_{exp} %	Δm_{calc} %	T, °C	Δm_{exp} %	Δm_{calc} %	T, °C	Δm_{exp} %	Δm_{calc} %
endo	melting	200								
endo	naphthalene ring + (2CO-O) + CH ₂ =CH ₂	240- -380	86.0	86.3						
exo	2(CH ₂ =CH ₂)				295	10.0	9.9	310	8.5	8.3
exo	2HCl + naphthalene ring				315	55.0	55.3			
exo	2HBr + 2(CO + NH ₃ + NO)							340	29.5	29.4
exo	2(2CO + NH + NO)				390- -600	25.0	25.3			
exo	naphthalene ring							360- -580	38.0	37.5
exo	NH ₃ + NO	380- -680	14.0	13.7						
Residue	NiO					10.0	9.9		8.5	8.6

In the treatment of data on the enthalpic contributions, it was established that the energy contribution of the intermediates (HCl, HBr, etc.) was less than 30 kJ/mol, i.e. the contribution to the corresponding stabilization energy was below 3%, which confirmed the validity of the above approximation.

Table 1b TG analysis data for octahedral Ni(II) complexes with L

Effect	Fragment eliminated	NiL ₂ (NCS) ₂			NiL ₂ (NO ₃) ₂		
		T, °C	Δm_{exp} , %	Δm_{calc} , %	T, °C	Δm_{exp} , %	Δm_{calc} , %
exo	2(CH ₂ =CH ₂)	190	9.0	8.9			
exo	CH ₂ =CH ₂ +8NO ₃ + + naphthalene ring				200- -270	68.5	68.3
exo	2(CO+NH ₃ +NO)				270- -500	23.0	23.3
exo	2(NCS+2CO+ +NO+NH ₃)	320	41.0	41.2			
exo	naphthalene ring	320- -640	40.0	40.5			
Residue	NiO		9.4	9.4		8.5	8.4

Table 2 Energies of ligand field stabilization for octahedral Ni(II) complexes

Complex	ΔH_C , Jg ⁻¹	E^o , Jg ⁻¹	$E_s = \Delta H_C - E^o$, Jg ⁻¹	ΔH_{CF} , Jg ⁻¹	$E_s^o = E_b - \Delta H_{CF}$, Jg ⁻¹
NiL ₂ Cl ₂	1510.4	3200.2	-1698.3	-283.8	-850.0
NiL ₂ Br ₂	1161.4	3008.3	-1846.9	-261.0	-994.8
NiL ₂ (NCS ₂)	854.4	2560.2	-1705.8	-248.3	-997.9

$$\Delta H_{CF} = 119.7 \cdot 10^{-6} \cdot \tilde{\nu}, \text{ kJ mol}^{-1} (\tilde{\nu} \text{ in cm}^{-1})$$

The process of thermal decomposition of NiL₂(NO₃)₂ was accompanied by a significant enthalpic contribution of the nitrate group, and thus the above approach could not be applied.

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Zusammenfassung - In Luft- und Stickstoffatmosphäre wurde die thermische Zersetzung von Azeton-1-naphthoylhydrazon (L) und seinen oktaedrischen Komplexen mit Ni(II) mit der allgemeinen Formel NiL_2X_2 (mit $X = Cl, Br, NO_3$ und NCS) untersucht. Es wurde festgestellt, daß der organische Ligand in einem exothermen Prozeß einer Zersetzung und einer anschließenden Oxydation der Zersetzungsprodukte durch Luftsauerstoff unterliegt. Unterhalb 640° zerfallen alle Komplexe vollständig und liefern NiO als Endprodukt, welches mittels Röntgendiffraktionsanalyse identifiziert wurde. Aus dem Unterschied zwischen Enthalpieänderungen für die Zersetzung der Komplexe und des Liganden selbst, aus der Art der erhaltenen Oxide und aus den Parametern der durch optische Messungen bestimmten Kristallfeldaufspaltung wurden die entsprechenden Stabilisierungsenergien bestimmt.