

THERMAL DEGRADATION STUDIES ON SOME METAL HYDRAZINIC COMPLEXES

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The paper deals with the characterization of three hydrazinic complexes with Ni, Cu and Cr respectively, by means of non-isothermal thermal methods, TG, DTG and DTA, under nitrogen atmosphere in order to investigate the structure–thermostability–thermal degradation mechanism correlation. The thermal analysis made evident the degradation mechanisms characteristic of every sample in accordance with the chemical structure. The quantitative analysis by TG-DTG afforded the estimation of the metal amount in the complex on the basis of the resulting metallic oxide nature as well as of some aspects of the thermal degradation mechanism supported by mass spectral measurements. The melting points given by DTA and confirmed by the Boetius method and the initial temperatures of thermal degradation from TG-DTG-DTA afforded to ascertain the temperature range proper for using and storing the complexes under study which show potential practical applications as drugs.

Keywords: DTA, DTG, hydrazinic complexes with Ni, Cu, Cr, mass spectrometry, TG

Introduction

The studies on the biologically active products have much been extended in recent years [1, 2]. Among the organic compounds with potential practical applications the hydrazides are particularly important [3, 4]. Significant progresses were noticed since the phenoxyacetic acids synthesized firstly by Baltazzi and Delavegne in 1955 [5] were taken in therapeutical uses.

The condensation of hydrazides with some transitional metals gives metallic complexes showing efficiency against a lot of diseases. Thus, the drugs containing copper hydrazinic complexes are indicated for treating inflammatory processes, ulcer, convulsions, cancer, diabetes, being also beneficial to bone growing and tissue regeneration. The chrome complexes show growing stimulating action on the organism, the iron complexes act as catalysts in some processes in living organism, protect and maintain the functions of the immunity system and the manganese ones activate the destructive processes of the proteins, regulate the glucose level and contribute to the formation of bones and tissues [6].

The hydrazinic complexes with transitional metals show a dual action given by both the hydrazine moiety and the metal in their structure [7].

By taking the practical importance of these compounds into account as well as their easiness of metal releasing the present study is aimed to go on with our previous researches in the field [8, 9] by performing the characterization by thermal methods [10–13] of some new Ni, Cu and Cr complexes starting from the hydrazides of sulphonamidated phenoxyacetic acids

previously synthesized [8, 9] in order to follow the structure–thermostability–thermal degradation mechanism correlation [14–16].

The characterization by thermal methods indicate the temperature range proper for using and storing the compounds under study, the thermostability series being correlated with their structure and the nature of the bound metal.

The quantitative analysis by TG-DTG [17–20] under nitrogen atmosphere afforded a discussion on the thermal degradation mechanism. A similarity between the degradation mechanisms of the Cu and Cr complexes in comparison with the Ni complex is noticed which is indicative of the major influence of the substituents.

The conclusions on the thermal degradation mechanisms drawn by TG-DTG-DTA were confirmed and completed by mass spectra under the conditions of chemical ionization.

The melting points estimated from DTA data under nitrogen atmosphere are in very good agreement with those measured by the Boetius method.

Experimental

Methods

Thermal analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) were performed by using a Perkin-Elmer Pyris Diamond TG/DTA thermo-

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balance which records simultaneously the T , TG and DTA curves. The DTG curves were obtained by numerical differentiation of the TG curves. The working conditions were the following: sample mass 12 mg, heating rate $10^{\circ}\text{C min}^{-1}$, temperature range $30\text{--}900^{\circ}\text{C}$ in nitrogen stream (800 mL min^{-1}).

Mass spectrometry

The mass spectra were recorded on a GCMS Shimadzu QP2010 mass spectrometer with DI (direct inlet) and CI (chemical ionization). Reagent gas was CH_4 .

Results and discussion

The structure of the studied complexes, their chemical formula, IUPAC denominations, molecular masses and melting points measured by the Boetius method are presented in Scheme 1.

The synthesis of these complexes and their characterization by elemental analysis and FTIR and NMR spectral measurements were presented in previous papers [8, 9]. The mention has to be made that the

complexes were separated by using a water–ethanol mixture (*b.p.* $\approx 78\text{--}100^{\circ}\text{C}$) as a solvent.

TG and DTG curves of the complexes *a*, *b*, *c* obtained under N_2 (nitrogen) atmosphere within the $30\text{--}900^{\circ}\text{C}$ temperature range are presented in Figs 1a–c.

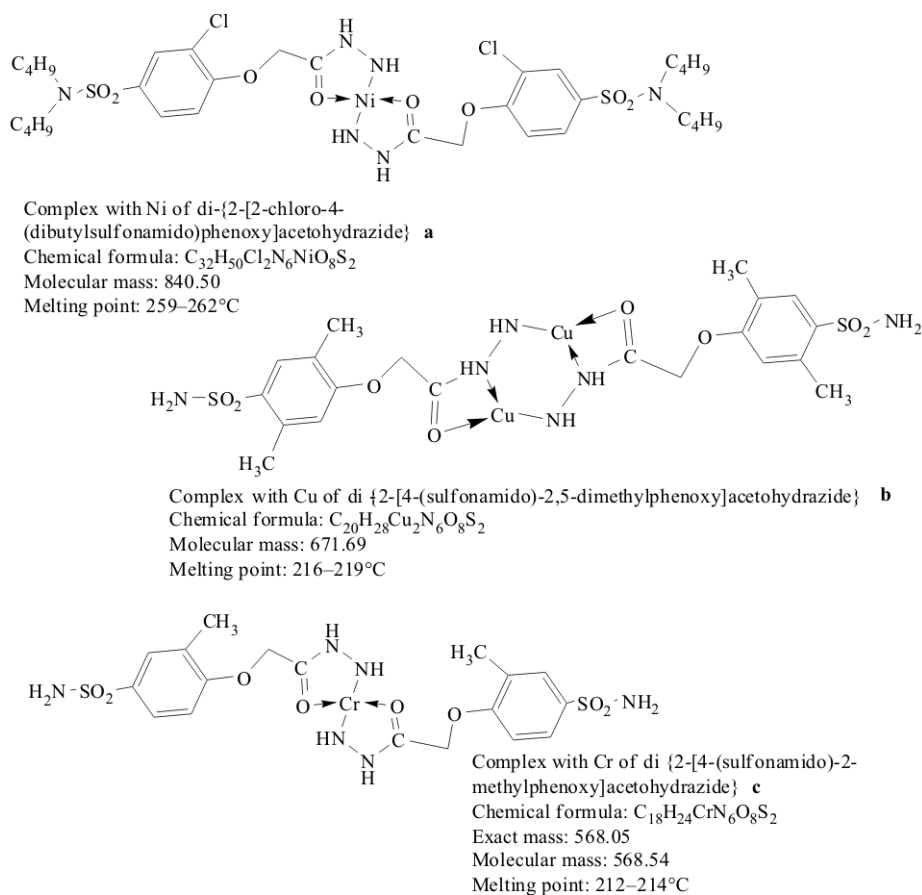
The examination of the TG-DTG curves indicates complex degradation mechanisms specific to the compounds under study [18–21].

The complexes are thermally degraded in one main stage (the IInd stage) within the $218\text{--}900^{\circ}\text{C}$ temperature range, a similarity being noticed between the samples *b* and *c* whose TG and DTG curves show two distinct inflexion points unlike the sample *a* showing a single inflexion point only.

The thermal degradation is preceded by a stage of solvent removal within the $63\text{--}171^{\circ}\text{C}$ range (stage I) where the evaporation points of the solvents lie ($78, 100^{\circ}\text{C}$).

The DTA curves for the thermal degradation of the complexes *a*, *b* and *c* depicted in Fig. 2 also confirm the developing of a complex and specific mechanism with the same stages as resulted from TG-DTG.

Thus, during the endothermic processes proceeding between $60\text{--}160^{\circ}\text{C}$ the solvent mixtures retained in the samples are eliminated, their evaporation temperatures being situated within this range ($78, 100^{\circ}\text{C}$).



Scheme 1 Samples under study (structure, molecular mass and melting points)

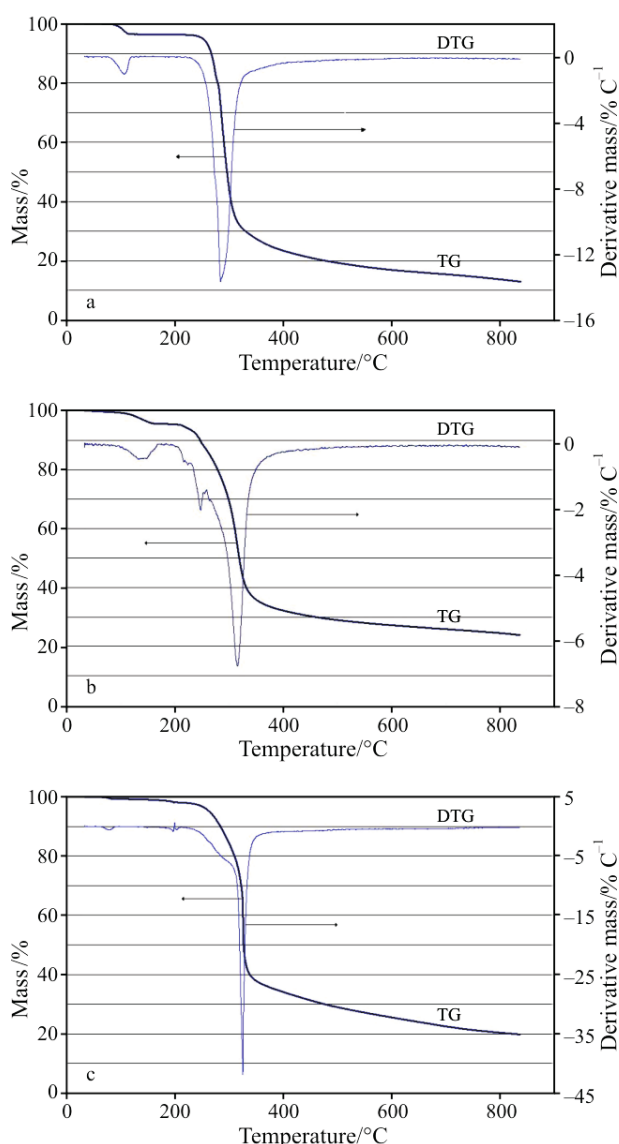


Fig. 1 TG and DTG curves of the a – complex a, b – complex b, c – complex c

The complexes remaining after the solvent removal show an endothermic process within the 180–260°C range where the masses of the samples **b** and **c** in TG-DTG remain constant corresponding to the melting peak.

The sample melting points were estimated from the temperatures corresponding to the DTA-melting peak maximum [22] excepting for the sample **a** where the degradation process is overlapped with the melting and the T_1 °C was estimated from the inflexion point temperature of the melting–degradation peak.

The melting points obtained by the DTA and Boetius methods are in very good agreement (Scheme 1).

Within the 260–900°C temperature range the DTA curves show endothermic processes correspond-

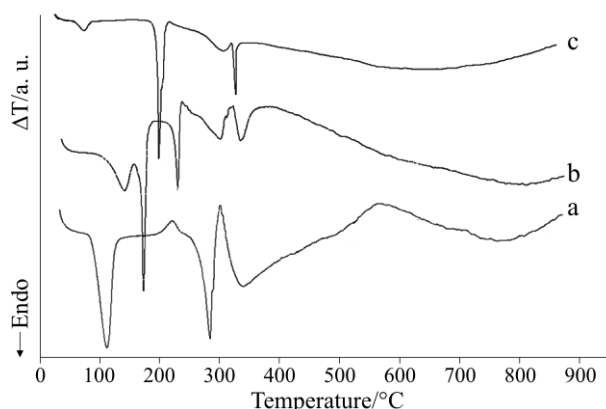


Fig. 2 DTA curves of samples a, b, c

ing to the sample thermal degradation which are also to be found in TG-DTG.

Table 1 presents characteristic amounts resulting from TG-DTG-DTA and the colour and residue percentage.

The mention has to be made that the percentage mass loss by thermal degradation was referred to the complex amount with no solvent included.

The quantitative analysis from TG gives a good agreement of the theoretical and experimental values for the resulting residue and the retained metal under the assumption that the metal oxides – NiO, Cu₂O, CrO₃ – resulted by the thermal degradation in N₂ atmosphere which was also confirmed by the residue colour [23].

The experimental and theoretical values for the residue and the metal retained in the sample under study given in Table 2 support the formation of these complexes.

The initial temperatures of the thermal degradation resulting from both TG-DTG-DTA (Table 1) are indicative of the following thermostability series: **a**>**c**>**b**.

Since the metal–ligand bond strength obeys the order: **b**>**c**>**a** [23, 24] it follows that the stronger metal–ligand bond the lower the stability is [23]. It is known [25, 26] that the peripheral bonds which can be influenced by the substituents in their proximity are thus weakened.

Consequently, the end functional groups are expected to be the first detached and removed being then followed by the thermal degradation proceeding from the external to the internal parts of the complex molecule.

The fact can also be noticed in Table 1 that with the complexes **b** and **c** the initial degradation temperatures as well as those corresponding to the first inflection are very close which would suggest the splitting of the same bond type. This conclusion is also confirmed by the presence of the same end functional group, –NH₂–SO₂– in the structures of the samples **b** and **c** unlike the sample **a** where the (C₄H₉)₂N–SO₂–

group is the end functional group and the initial degradation temperature is different from that of the samples **b** and **c**.

The mass losses corresponding to the inflexion point in TG (%) as well as the residue content (%) in correlation with the complex structures afford a discussion on their thermal degradation mechanism.

Table 1 Characteristic amounts from TG-DTG-DTA curves

Thermal method	Stage	Sample			
		a	b	c	
TG-DTG	Stage I	$T_i/^\circ\text{C}$	78.70	90.50	63.40
		$T_m/^\circ\text{C}$	109.44	139.49	78.72
		$T_f/^\circ\text{C}$	121.00	171.50	90.20
		$W_\infty/\%$	3.44	4.08	1.36
	Stage II	$T_i/^\circ\text{C}$	258.00	218.00	241.00
		$T'_{inf}/^\circ\text{C}$	-	255.50	258
		$W'_{inf}/\%$	-	4.66	5.28
		$T_{inf}/^\circ\text{C}$	280.30	294.06	311.04
		$W_{inf}/\%$	11.56	19.38	17.00
		$T'_m/^\circ\text{C}$	289.92	318.56	330.24
		$T_f/^\circ\text{C}$	900	900	900
		$W_\infty/\%$	73.34	57.16	42.84
		$\%$	10.00	22.44	17.68
		Residue	nature	NiO	Cu ₂ O
colour	green		red	green	
DTA	$T_i/^\circ\text{C}$	257.50	219.90	201.40	
	$T_f/^\circ\text{C}$	257.50	224.00	225.00	

T_i – melting point, T_i – initial degradation temperature, T'_{inf} , T_{inf} – temperatures corresponding to the inflexion points, T_m – temperature corresponding to the maximum degradation rate, T_f – final degradation temperature, W'_{inf} , W_{inf} and W_∞ – mass losses at the inflexion point temperatures and the subsequent mass loss, respectively

Thus, the fact is noticed that with the complexes **b** and **c** the mass loss (%) corresponding to the first inflexion point at T_{inf} corresponds to the elimination of 2NH₂ followed by the elimination of 2SO₂ between $T'_{inf} - T_{inf}$.

With the complex **a**, the mass loss (%) till T_{inf} corresponds to the elimination of 2SO₂ in the (C₄H₉)₂N–SO₂– end functional group which is different from that of the complexes **b** and **c**.

The results are given in Table 3.

These findings from TG-DTG are confirmed by the mass spectra obtained under the conditions of chemical ionization with CH₄ as ionization gas.

The mass spectra of the three complexes indicate the occurrence of fragments of the mass value 64 corresponding to the SO₂ group, detached probably by the splitting of the S–N and S–C end bonds. Thus, in the spectra of the complexes **a**, **b**, **c** this fragment occurs corresponding to the intensities: 3.5% **a**, 5.73% **b** and 1.74% **c**.

Since the mass spectra were recorded within the m/z domain situated between 40–800 the fragment $m/z=16$ corresponding to the NH₂ group resulting probably from the complexes **b** and **c** by the N–S bond splitting could not be made evident. However, this breaking up is made evident by the signal $m/z=64$ previously mentioned as well as by the absence of the signal at $m/z=80$ corresponding to the NH₂–SO₂ group which would have been released by the splitting of the S–C bond only with no involvement of the N–S bond. The fact that the N–S bond is firstly broken is better revealed with the complex **a** whose spectrum shows both the fragment $m/z=64$ of the 3.5% intensity corresponding to the SO₂ group and the fragment $m/z=128$ of the 20.41% intensity corresponding to the –N(C₄H₉)₂ group.

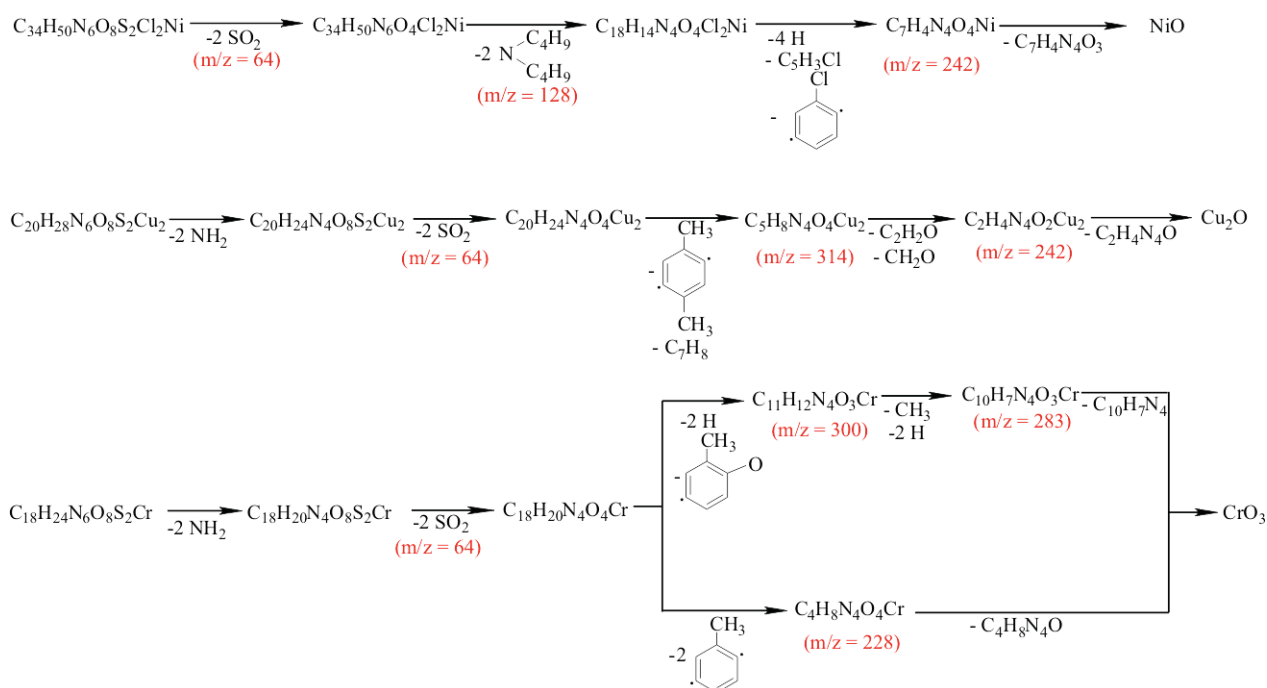
The advanced degradation mechanism proceeding from the external to the internal part of the mole-

Table 2 Experimental and theoretical values for the residue and metal content

Sample	Residue nature	Experimental residue/%	Theoretical residue/%	Retained metal experimental/g	Retained metal theoretical/g
a	NiO	10.00	9.00	$11.6 \cdot 10^{-4}$	$8.204 \cdot 10^{-4}$
b	Cu ₂ O	22.44	21.29	$2.29 \cdot 10^{-3}$	$2.17 \cdot 10^{-3}$
c	CrO ₃	17.68	17.606	$1.087 \cdot 10^{-3}$	$1.082 \cdot 10^{-3}$

Table 3 Experimental and theoretical mass losses (%) for 2NH₂ and 2SO₂ in complexes under study

Sample	Molecular mass	NH ₂			SO ₂		
		$W'_{inf}/\%$	$W_{theoretical}/\%$ (2NH ₂)	Temperature range/ $^\circ\text{C}$	$W_{inf}/\%$	$W_{theoretical}/\%$ (2SO ₂)	Temperature range/ $^\circ\text{C}$
a	840.00	–	–	–	16.66	15.24	258–280.3
b	671.53	4.66	4.76	218–255.5	15.74	19.04	255.5–294.06
c	567.99	5.28	5.63	241–258	19.88	22.53	258–311.04



Scheme 2 Thermal degradation mechanism of the complexes

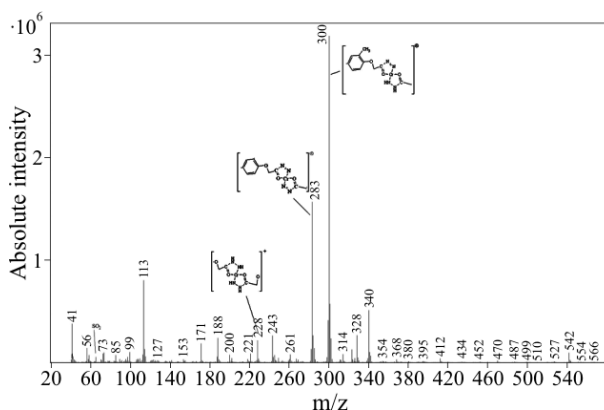


Fig. 3 Mass-spectrum of the complex c

cule is also supported by the high or very high signals corresponding to some groups including the metallic ion and the chelatic ring in the three complexes.

Thus, the following main signals are to be found in the spectra of the three complexes along with other fragments discussed above: $m/z=242$ ($I=33.93$) – complex **a**; $m/z=314$ ($I=100\%$) – complex **b**; $m/z=300$ ($I=100\%$) – complex **c**. Figure 3 presents as an example the mass spectrum of complex **c**.

The most probable thermal degradation mechanism of the three complexes advanced on the basis of thermal analysis data correlated to the mass spectral measurements is depicted in Scheme 2.

Conclusions

The examination of the TG-DTG-DTA curves of the complexes under study indicates complex and specific degradation mechanisms which confirm the structure influence. The complex thermostabilities estimated by means of the initial degradation temperatures respect the following order: $\mathbf{a} > \mathbf{c} > \mathbf{b}$. The thermostability is correlated with the chemical structure and the metal ligand bond nature affording the temperature range proper for using and storing these complexes to be ascertained.

The theoretical and experimental values of the amounts of resulting residue and bound metal are in very good agreement which confirms the formation of the complexes.

The thermal analysis and the mass spectral measurements afforded the most probable degradation mechanism to be advanced, namely the degradation development from the external to the internal part of the complex molecule.

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