Thermal Behaviour of Some New Hydrazine Complexes with Potential Biological Importance

ANCA MIHAELA MOCANU*, CONSTANTIN LUCA

"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Organic, Biochemical and Food Engineering, 71 A D.Mangeron Ave, 700050, Iasi, Romania

Three new hydrazine complexes were studied for their thermal behaviour in order to follow the structure-thermal stability-degradation mechanism. The metal amount in the three complexes could be estimated by means of the quantitative analysis by TG-DTG and based on the nature of the resulting metallic oxide as well as on some characteristics of the thermal degradation mechanism. The melting points estimated by DTA and confirmed by the Boetius method as well as the initial temperatures of thermal degradation from TG-DTG-DTA afforded to find the temperature range proper for using and storing the studied complexes showing potential practical applications as drugs.

Keywords: hydrazides, hydrazinic complexes with Mn, Fe, Co, thermal methods (TG, DTG, DTA), thermal stability.

Some metallic complexes showing efficiency against a lot of diseases can be obtained by the condensation of hydrazides with some transitional metals. For example, the drugs containing manganese hydrazine complexes are recommended for treating the diabetes, rheumatoid arthritis, epilepsy, and schizophrenia. The iron complexes are known to act as catalysts in certain processes in living organism, to protect and to maintain the functions of the immunity system while the manganese-containing ones promote the destructive processes of the proteins, regulate the glucose level and contribute to the formation of bones and tissues. The cobalt complexes are involved in the organism self-defence being also important for the integrity of the nervous system and growth processes [1-6].

The transitional metal-containing hydrazine complexes show a dual action due to both the hydrazine moiety and the metal in their structure [7].

Due to the practical importance of these compounds that can release easily the contained metal the present study is aimed to go on with our previous researches in the field [8, 9] by performing the characterization by thermal methods of some new Fe, Mn and Co complexes prepared from the hydrazides of sulphonamidated phenoxyacetic acids previously synthesized [10, 11]. The structure–thermal stability–thermal degradation mechanism correlation was thus followed [12 - 15].

The thermal degradation mechanism could be discussed by performing the quantitative analysis by TG-DTG [16 -19] under nitrogen atmosphere. The similarity noticed between the degradation mechanisms of the Mn and Co complexes compared to the Fe complex is indicative of the major influence of the substituents.

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

Experimental part

Materials and methods

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

Thermal analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) were performed by using a Perkin-Elmer Pyris Diamond TG/DTA thermobalance 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 12mg, heating rate10°C . min^{-1}, temperature range 25-900°C in nitrogen stream (800 mL . min^{-1}).

Results and discussions

The TG and DTG curves of the complexes **a, b, c**, resulting by working under N_2 (nitrogen) atmosphere within the 25°C – 850°C temperature range are depicted in figure 2a, b and c.

The examination of the TG-DTG curves would indicate complex degradation mechanisms specific to the compounds under study [14, 15, 17].

The thermal degradation of the complexes proceeds in one main stage (the II^{nd} stage) within the 217-850°C temperature range. A similarity is noticed between the samples **(a)** and **(b)** whose TG and DTG curves show two distinct inflexion points while the sample **(c)** shows a single inflexion point only.

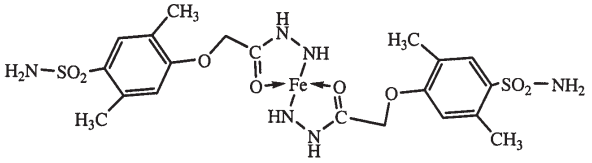
The thermal degradation follows after a stage of solvent removal within the 65-170°C range (stage I) where the evaporation points of the solvents lie (78, 100°C).

In table 1 the characteristic amounts of thermal degradation resulting from the TG – DTG curves as well as the color and residue percentage are presented.

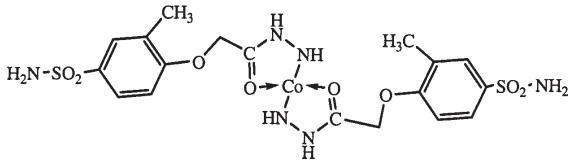
It has to be mentioned that the percentage weight loss by thermal degradation was referred to the complex amount with no solvent included and these compounds were separated with acetone as a solvent.

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 – FeO, CoO, MnO –

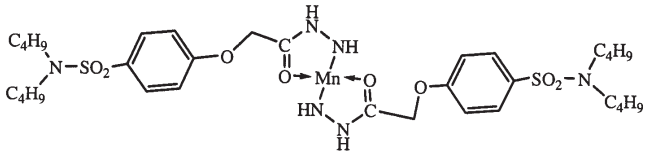
* email: ancamocanu2004@yahoo.com



Complex with Fe of di {2-[4-(sulfonamido)-2,5-dimethylphenoxy]acetohydrazide} (**a**)
Chemical Formula: $C_{20}H_{28}FeN_6O_8S_2$
Molecular Weight: 600
Melting Point: 219-221°C

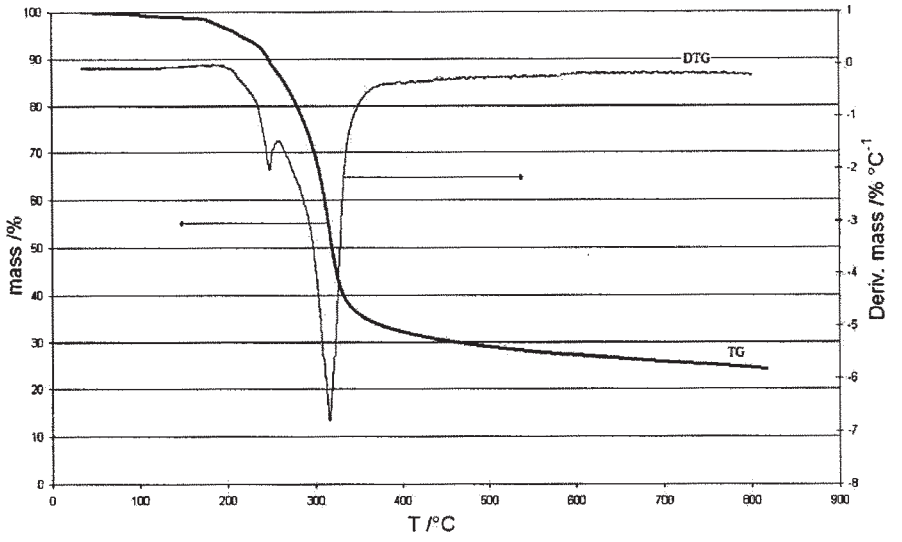


Complex with Co of di {2-[4-(sulfonamido)-2-methylphenoxy]acetohydrazide} (**b**)
Chemical Formula: $C_{18}H_{24}CoN_6O_8S_2$
Molecular Weight: 575
Melting Point : 204- 206°C



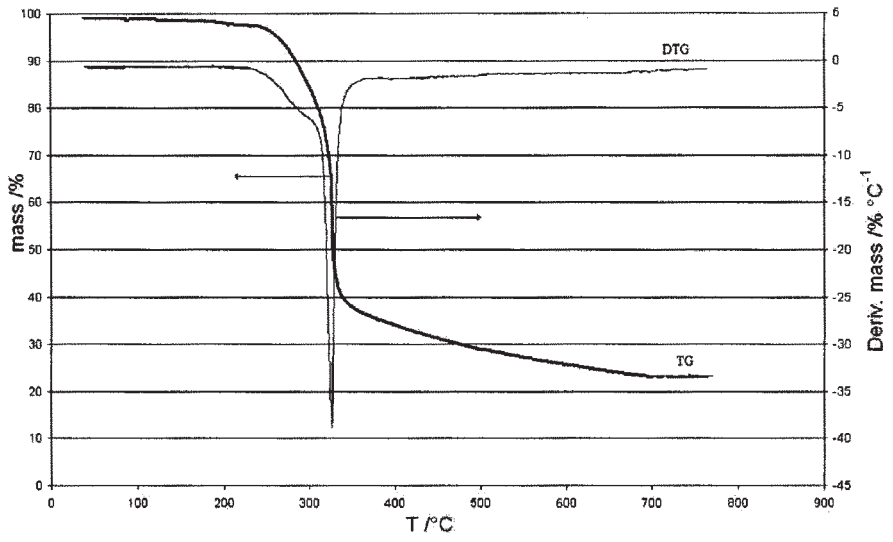
Complex with Mn of di{2-[4(dibuthylsulfonamido) phenoxy]acetohydrazide} (**c**)
Chemical Formula: $C_{32}H_{52}N_6MnO_8S_2$
Molecular Weight: 767
Melting Point: 265-267°C

Fig. 1. Samples under study (structure, molecular weight and melting points)

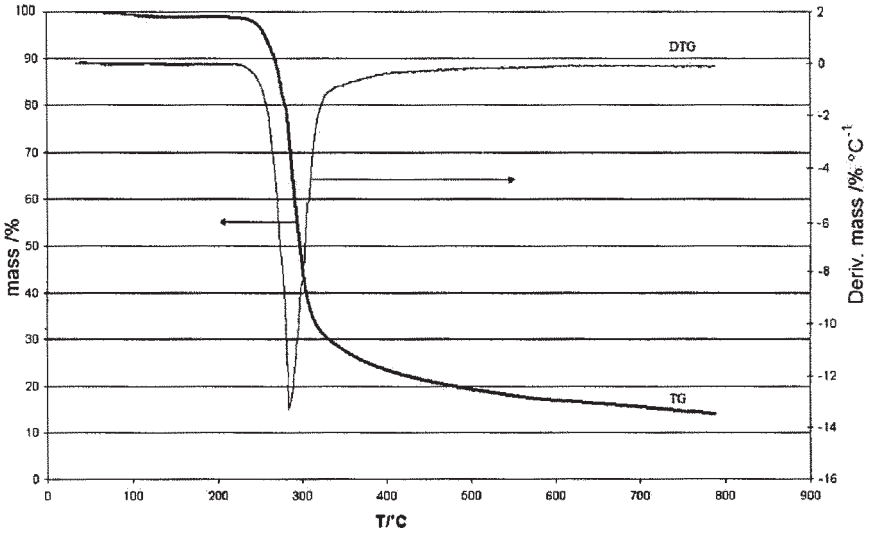


a

Fig. 2. TG and DTG curves of the complexes: (a)– complex **a**, (b) – complex **b**



b



c

Fig. 2. TG and DTG curves of the complexes: (c) - complex **c**

Sample / Stage		a	b	c
Stage I	T_i°C	89.40	65.22	77.90
	T_m°C	137.22	77.89	110.60
	T_f °C	170.10	91.45	120.24
	W_∞%	4.18	1.66	3.35
Stage II	T_i°C	217.80	242.20	262.10
	T'_{inf}°C	258.80	252.10	-
	$W'_{\infty in}$%	4.70	5.58	-
	T_{inf}°C	300.50	310.20	282.50
	$W'_{\infty in}$%	19.50	16.87	11.68
	Tm' °C	325.45	338.50	295.44
	T_f °C	375.55	358.50	340.50
	W_∞%	57.16	42.84	73.34
Residue	%	20.18	18.50	9.65
	Nature Colour	FeO black	CoO green	MnO black

T_i °C – initial degradation temperature;

T'_{inf} °C, T_{inf} °C – temperatures corresponding to the inflexion points;

T_m°C – temperature corresponding to the maximum degradation rate;

T_f °C – final degradation temperature;

W'_{inf}%, W_{inf}% and W_∞% - weight losses at the inflexion point temperatures and the subsequent weight loss, respectively.

Table 1
CHARACTERISTIC AMOUNTS FROM TG-DTG CURVES.

Sample	Residue nature	Experimental residue%	Theoretical residue %	Retained metal experimental (g)	Retained metal theoretical (g)
a	FeO	18.50	18.26	$1.182 \cdot 10^{-3}$	$1.176 \cdot 10^{-3}$
b	CoO	9.65	9.12	$9.984 \cdot 10^{-4}$	$9.754 \cdot 10^{-4}$
c	MnO	20.18	20.00	$2.35 \cdot 10^{-3}$	$2.27 \cdot 10^{-3}$

Table 2
EXPERIMENTAL AND THEORETICAL VALUES FOR THE RESIDUE AND METAL CONTENT

resulted by the thermal degradation in N_2 atmosphere which was also confirmed by the residue colour [20].

The experimental and theoretical values for the residue and the metal retained in the sample under study listed in table 2 are in agreement with the formation of these complexes.

The DTA curves for the thermal degradation of the complexes **(a), (b)** and **(c)** illustrated in figure 3 also confirm a complex and specific mechanism developing in the same stages as resulted from TG-DTG curves.

Thus, during the endothermic processes proceeding between 65 -170°C the solvent mixtures retained in the samples are removed, their evaporation temperatures being within this range (78, 100°C).

The complexes remaining after the solvent removal show an endothermic process within the 180 - 262°C range where the weights of the samples **(a)** and **(b)** in TG-DTG remain constant according to their melting peak.

The sample melting points were estimated from the temperatures corresponding to the DTA-melting peak maximum [21] excepting for the sample **(c)** where the degradation process is overlapped with the melting and the T_i°C was estimated from the inflexion point temperature of the melting–degradation peak.

In table 3 the melting points estimated by the Boetius method and the initial temperatures of the complex thermal degradation from DTA curves are given. The melting points obtained by the DTA curves and Boetius methods are in very good agreement.

Within the 250-850°C temperature range the DTA curves show developing of endothermic processes corresponding to the sample thermal degradation which are also to be found in TG-DTG curves.

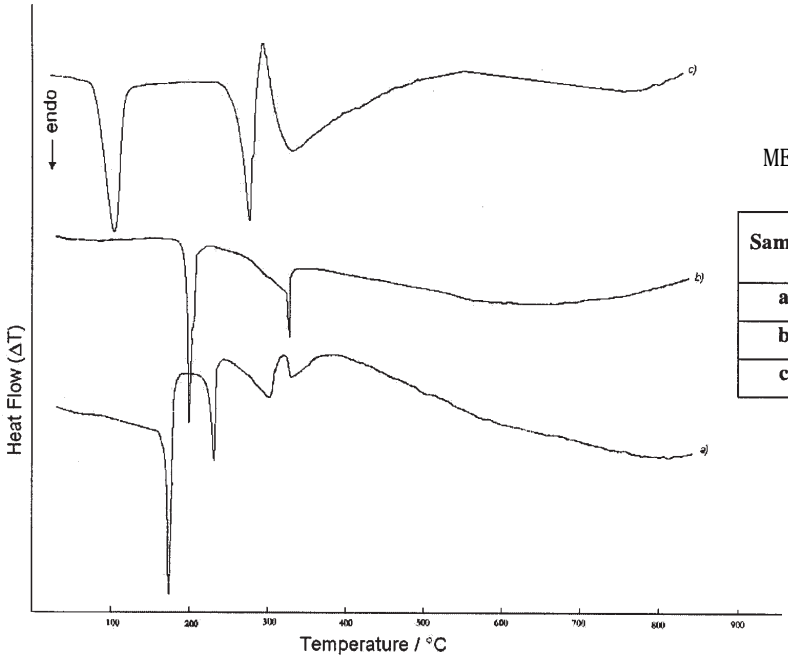


Fig. 3. DTA curves of the samples

TABLE 3
MELTING TEMPERATURES AND INITIAL DEGRADATION TEMPERATURES FROM DTA

Sample	T_i°C (DTA)	T_t°C (Boetius Method)	T_i°C (DTA)
a	215.0	219-220	224.0
b	206.0	204-206	225.0
c	261.0	265-267	261.0

Sample	Molecular weight	NH_2			SO_2		
		W'_{inf} %	$W_{theoretical}$ % ($2NH_2$)	Temperature range °C	W_{inf} %	$W_{theoretical}$ % ($2SO_2$)	Temperature range °C
a	600.00	4.66	4.76	218-255.5	15.74	19.04	255.5-294.06
b	575.00	5.28	5.63	241-258	19.88	22.53	258-311.04
c	767.00	-	-	-	16.66	15.24	258-280,3

Table 4
EXPERIMENTAL AND THEORETICAL WEIGHT LOSSES (%) FOR $2NH_2$ AND $2SO_2$ IN COMPLEXES UNDER STUDY

The initial temperatures of the thermal degradation resulting from both TG-DTG (table 1) and DTA (table 3) curves are indicative of the following series of thermal stability: **(c)>(b)>(a).**

The fact is known [22] that the stronger metal-ligand bond the lower the stability is. The peripheral bonds are influenced by the substitutes in their proximity being thus weakened. Consequently, the end functional groups would be detached firstly and removed, the thermal degradation taking then place from the external to the internal parts of the complex molecule.

The fact is also made evident by the data in table 1 that in case of the complexes **(a)** and **(b)** 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 would also result by taking into account the presence of the same end functional group, $-NH_2-SO_2-$ in the structures of the samples **(a)** and **(b)** unlike the sample **(c)** where the $(C_4H_9)_2N-SO_2-$ group is the end functional group and the initial degradation temperature is different from that of the samples **(a)** and **(b).**

The weight losses corresponding to the inflexion point in TG (%), the residue content (%) as well as the consideration of the complex structures afford a discussion on the thermal degradation mechanism. Thus, the fact is noticeable that with the complexes **(a)** and **(b)** the weight loss (%) corresponding to the first inflexion point at T_{inf} corresponds to the elimination of 2 NH_2 followed by the elimination of 2 SO_2 between T'_{inf}-T_{inf}.

For the complex **(c)**, the weight loss (%) till T_{inf} corresponds to the elimination of 2 SO_2 from the $(C_4H_9)_2N-SO_2-$ end functional group which is different from that of the complexes **(a)** and **(b)**. The results are presented in table 4.

Conclusions

The TG-DTG-DTA curves obtained with the complexes under study are indicative of complex and specific degradation mechanisms and consequently of the structure influence.

The complex thermal stabilities estimated by means of the initial degradation temperatures from DTG and DTA curves are situated in the following order: **(c)>(b)>(a).**

The thermal stability depends on the chemical structure and the metal ligand bond nature making possible to ascertain the temperature range proper for using and storing these complexes.

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

The melting points of the complexes resulting from DTA curves and from measurements by the Boetius method are in good agreement.

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