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Short Communication

THERMAL DECOMPOSITION OF COMPLEXES OF Co(II), Ni(II) AND Zn(II) IONS WITH THIOSALICYLIC ACID OR ETHYLENEDIAMINE

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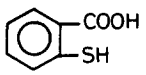
The thermal decompositions of crystalline Co(II), Ni(II) and Zn(II) complexes with thiosalicylic acid or ethylenediamine were investigated via the respective thermal curves. On the basis of the decomposition temperatures, the following sequences of stabilities of the studied compounds have been proposed: 1. $[Co(SR)] \leq [Ni(SR)] < [Zn(SR)]$; 2. $[Zn(en)_2](NO_3)_2 \cdot 2H_2O < [Co(en)_2](NO_3)_2 < [Ni(en)_3](NO_3)_2$.

During our studies on ternary complexes of transition metals with thiosalicylic acid (H_2SR) and polyethylenepolyamines [1, 2] we succeeded in obtaining crystalline compounds of type $[M(SR)]^0$ (where: M = Co(II), Ni(II) or Zn(II) ions, and thiosalicylate) and ethylenediamine (en) complexes: $[Co(en)_2](NO_3)_2$, $[Ni(en)_3](NO_3)_2$ and $[Zn(en)_2](NO_3)_2 \cdot 2H_2O$ [3].



(H_2SR)

$H_2N - CH_2 - CH_2 - NH_2$

(en)

The chemical formulae of these complexes have been established on the basis of analytical data (Table 1).

The present paper includes the results of studies on the decomposition of the solid crystalline complexes.

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Table 1 Analytical data of the complexes

Complex	C, %		H, %		N, %		S, %		Metal, %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
[Co(SR)]	39.82	37.90	1.91	1.88	-	-	15.19	14.74	27.91	28.54
[Ni(SR)]	39.87	39.15	1.92	2.02	-	-	15.20	14.92	27.84	28.13
[Zn(SR)]	38.65	38.10	1.82	1.93	-	-	14.47	14.52	30.05	30.87
$[Co(en)_2](NO_3)_2$	15.85	17.84	5.33	5.53	27.72	27.16	-	-	19.44	18.50
$[Ni(en)_3](NO_3)_2$	19.85	20.42	6.68	6.84	30.87	30.79	-	-	16.17	15.95
$[Zn(en)_2](NO_3)_2 \cdot 2H_2O$	15.79	13.42	3.51	3.40	24.32	23.50	-	-	18.91	19.75

Experimental

The thermal curves of these compounds were taken with a 1000/1500 Paulik-Paulik-Erdey derivatograph (MOM, Budapest), in static air atmosphere, using weighed portions of 100 mg. Other conditions were as follows: temperature range 293-1273 K, heating rate 5 deg/min. α-Al_2O_3 was the reference material.

Results and discussion

The TG, DTG and DTA curves of Co(II), Ni(II) and Zn(II) thiosalicylates and the ethylenediamine complexes are shown in Figs 1 and 2, respectively. The characteristic data and stages of pyrolysis are given in Tables 2 and 3, respectively. In every case the corresponding metal oxide is present at the end of pyrolysis. The stages of decomposition of the investigated thiosalicylates are not precisely defined. The thermal stability sequence

$$\text{Co(II)} \leq \text{Ni(II)} < \text{Zn(II)}$$

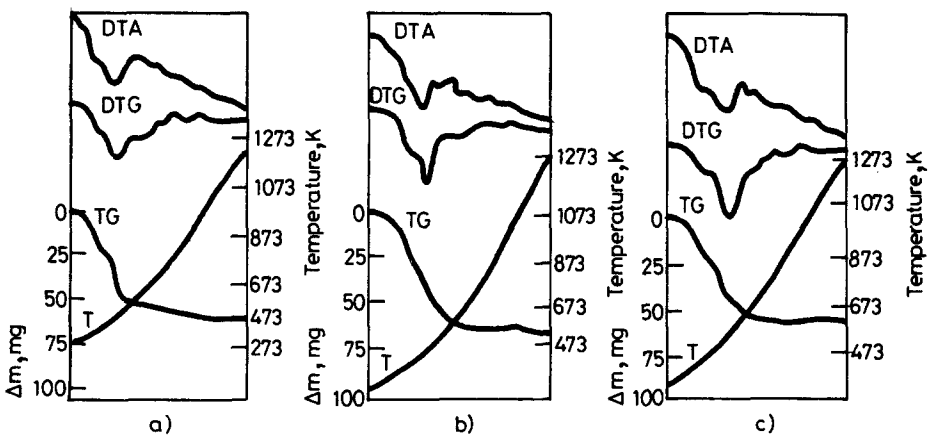

Fig. 1 Simultaneous TG, DTG and DTA curves of thiosalicylates in static air atmosphere: a) [Co(SR)], b) [Ni(SR)], c) [Zn(SR)]

The first stage of pyrolysis of $[Zn(en)_2](NO_3)_2 \cdot 2H_2O$ is dehydration. Next, deamination takes place. Deamination is the first stage of $[Co(en)_2](NO_3)_2$

Table 2 Observed stages of thermal decomposition of Co(II), Ni(II) and Zn(II) thiosalicylates in static air atmosphere

Complex	Temperature range, K	Thermal effect	Mass loss, %	The observed process
[Co(SR)]	403-513	endo	19	I stage of decompn.
	513-673	endo	45	II stage of decompn.
	673-973	exo	59	oxidation of decompn. products
	1073-1153	endo	63	the change: $Co_2O_3 \rightarrow 2CoO + 1/2O_2$
[Ni(SR)]	423-548	endo	21	I stage of decompn.
	548-688	endo	55	II stage of decompn.
	688-1073	exo	66	oxidation of decompn. products
[Zn(SR)]	458-573	endo	21	I stage of decompn.
	573-753	endo	55	II stage of decompn.
	773-1073	exo	60	oxidation of decompn. products

Table 3 Observed stages of thermal decomposition of Co(II), Ni(II) and Zn(II) ethylenediamine complexes in air static atmosphere

Complex	Temperature range, K	Thermal effect	Mass loss, %	The observed process
$[Co(en)_2](NO_3)_2$	453- 548	endo	33	deamination
	533- 673	endo	74	decompn. of cobalt nitrate
	1073-1173	endo	77	the change: $Co_2O_3 \rightarrow 2CoO + 1/2O_2$
$[Ni(en)_3](NO_3)_2$	448-603	endo	24	I stage of deamination
	603-673	endo	50	II stage of deamination, decompn. of nickel nitrate
	673-873	endo	79	the end of decompn. of nickel nitrate
$[Zn(en)_2](NO_3)_2 \cdot 2H_2O$	383-423	endo	21	dehydration
	423-523	endo	45	deamination
	523-723	endo	77	decompn. of zinc nitrate

and $[Ni(en)_3(NO_3)_2$ decomposition. In the latter case, the deamination consists of two part-stages. After the liberation of ethylenediamine, the decomposition of the metal nitrates occurs.

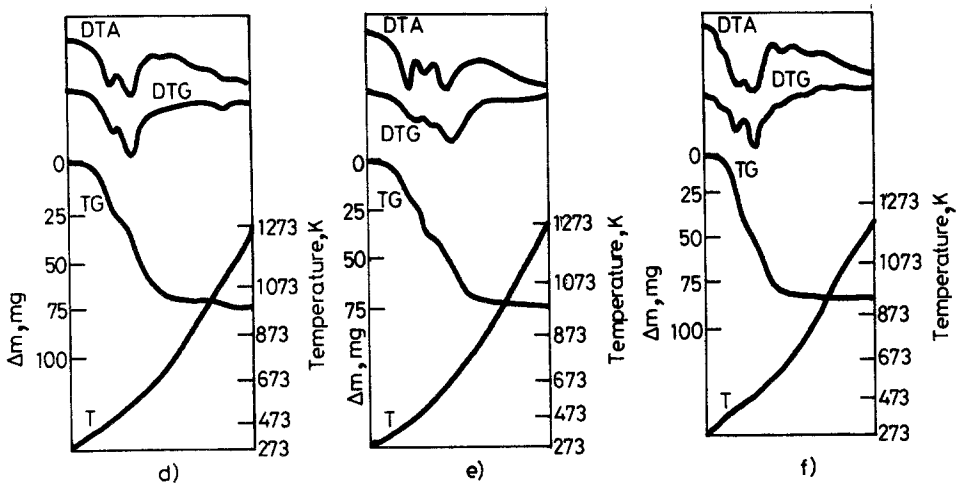

Fig. 2 Simultaneous TG, DTG and DTA curves of ethylenediaminecomplexes in static air atmosphere: d) $[Co(en)_2](NO_3)_2$, e) $[Ni(en)_3](NO_3)_2$, f) $[Zn(en)_2](NO_3)_2 \cdot 2H_2O$

The thermal stability sequence for the ethylenediamine complexes is different:

$$Zn(II) < Co(II) < Ni(II)$$

The investigated amine complexes are markedly less stable than the corresponding thiosalicylates.

References

1 J. Maslowska and J. Szmich, Proc 11th Conf. Coord. Chem., Smolenice (Czech.), 1987, p. 221.
2 J. Maslowska and J. Szmich, Acta Univ. Lodziensis, Folia Chim., 1989, (in print).
3 J. Szmich, Doctoral Thesis, Technical Univ., Lódz (1989).