

KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. X.

THERMAL DECOMPOSITION OF SOME TRIS-ETHYLENEDIAMINE-COBALT(III) AND CHROMIUM(III) COMPLEXES

J. ZSAKÓ, Cs. VÁRHELYI, G. LIPTAY* and K. SZILÁGYI

Faculty of Chemistry, "Babeş-Bolyai" University, Cluj, Romania; * Department of Applied
Chemistry, Technical University, Budapest

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A study was made of the thermal decompositions of 22 derivatives of $[M(en)_3]X_3$ type complexes. Partial de-amination leading to the formation of $[M(en)_2X_2]X$ type complexes occurs in the case of $M = Cr(III)$ if $X = Cl, Br, I$ or NCS , but in the case of $M = Co(III)$ it is possible only if $X = Cl$. In other cases redox reactions hinder the formation of stable intermediates. Kinetic parameters were derived for the dehydration of 19 compounds.

The validity of a linear kinetic compensation law was observed. The dependence of the kinetic compensation parameters on the nature of the thermal process is discussed.

Of the hexamine complexes of polyvalent metals, those of the type $[M^{(m)}(diamine)_3]^{m+}$, containing aliphatic diamines such as ethylenediamine (en), 1,2- and 1,3-propylenediamine (pn), or their *N*-substituted derivatives, deserve special interest. Complexes of this type have been reported for Ni^{2+} , Cu^{2+} [1], Co^{3+} [2], Cr^{3+} [3], Rh^{3+} [4–5], Ir^{3+} [6] and Pt^{4+} [7]. The derivatives of divalent metals are not too stable, decomposing in aqueous solution even at lower pH values. In contrast, the analogous derivatives of tri- and tetravalent metals are fairly stable, typical second-order chelates, with asymmetrical structure [8].

Pfeiffer and al. [9, 10] observed that some $[Co(en)_3]X_3$ complexes undergo partial de-amination at 150–200°, with the formation of cis- or trans- $[Co(en)_2X_2]X$ type compounds. A similar phenomenon has been observed by O'Brien and Bailar [11] with analogous chromium(III) complexes containing 1,2- and 1,3-propylenediamine. It is worth mentioning that a thermal matrix method has been developed by Wendlandt and al. [12, 13] for this partial de-amination reaction. This method, involving the thermal treatment of mixtures formed from $[Cr(en)_3]X_3$ and ammonium salts, containing mono- and divalent anions, allowed the synthesis of several new diacido-tetramine chromium complexes.

The kinetics of the thermal de-amination were studied earlier for some $[Cr(en)_3]X_3$ complexes on the basis of TG curves recorded under isothermal and dynamic conditions [14]. The formation of relatively stable intermediates $[Cr(en)_2X_2]X$ was observed, and increase of the apparent activation energy in the sequence $X = Cl, Br, J$ was reported. House and Bailar [15] later made similar investigations under "isothermogravimetric" conditions.

George and Wendlandt [16] and Bassett, Grzeskowiak and O'Leary [17] have observed analogous partial de-amination reactions in the case of $[Ni(en)_3]X_2$ and $[Ni(R-en)_3]X_2$ ($R = \text{ethyl, propyl, hydroxyethyl, hydroxypropyl}$), via TG and DTA measurements.

As far as the partial de-amination of the analogous complexes of other tri- and tetravalent metals is concerned, no experimental data have been reported, except for a single paper by Lazerko and al. [18], dealing with the thermal decomposition of $[Co(en)_3]Cl_3 \cdot 3H_2O$. From measurements in various atmospheres, these authors presume partial de-amination to occur, as in the case of the analogous chromium(III) complex, with the formation of $trans-[Co(en)_2Cl_2]Cl$.

All the complex cations of the type studied can form a large number of derivatives with simple and complex anions. Most of the products are well-defined, unitary, crystalline substances, also containing water of crystallization.

In the present paper the thermal decomposition of 22 complexes has been studied by different methods of thermal analysis. These complex salts are listed in Table 1.

Table 1
 $[M(en)_3]_r X_s \cdot tH_2O$ type complexes studied

Group	Compound	M	r	X	s	t
1	I	Co	1	Cl	3	3
	II	Co	1	I	3	1
	III	Co	1	CNO	3	3
	IV	Co	1	NO ₃	3	3
2	V	Co	1	Br	3	3
3	VI	Co	2	Cr ₂ O ₇	3	1.5
	VII	Co	1	[Co(NH ₃) ₂ (NO ₂) ₄]	3	1
	VIII	Co	2	[Co(DH) ₂ (SO ₃)(NCS)]	3	22
	IX	Co	2	[Co(DH) ₂ (SO ₃)(NO ₂)]	3	19
	X	Co	1	[Co(DH) ₂ (SO ₃) ₂]	1	8
	XI	Co	1	[Co(DH) ₂ (S ₂ O ₃) ₂]	1	2
4	XII	Cr	1	Cl	3	3
	XIII	Cr	1	I	3	1
	XIV	Cr	1	SbS ₄	1	1.5
5	XV	Cr	1	Br	3	3
	XVI	Cr	1	NCS	3	1
6	XVII	Cr	2	[Co(DH) ₂ (SO ₃)(NCS)]	3	16
	XVIII	Cr	2	[Co(DH) ₂ (SO ₃)(NO ₂)]	3	14
	XIX	Cr	1	[Co(DH) ₂ (SO ₃) ₂]	1	6
7	XX	Co	1	NCS	3	0
	XXI	Co	1	NCS _e	3	0
	XXII	Co	1	ClO ₄	3	0

DH₂ = dimethylglyoxime

The thermal behaviour of the perchlorate XXII is determined by the oxidizing character of the anion. All the other compounds exhibit gradual decomposition, the first stage of which is dehydration in the case of compounds I–XIX. After the water of crystallization is lost, all thermal decomposition reactions involve the transformation of the complex cation. The most interesting of them is the following de-amination reaction:

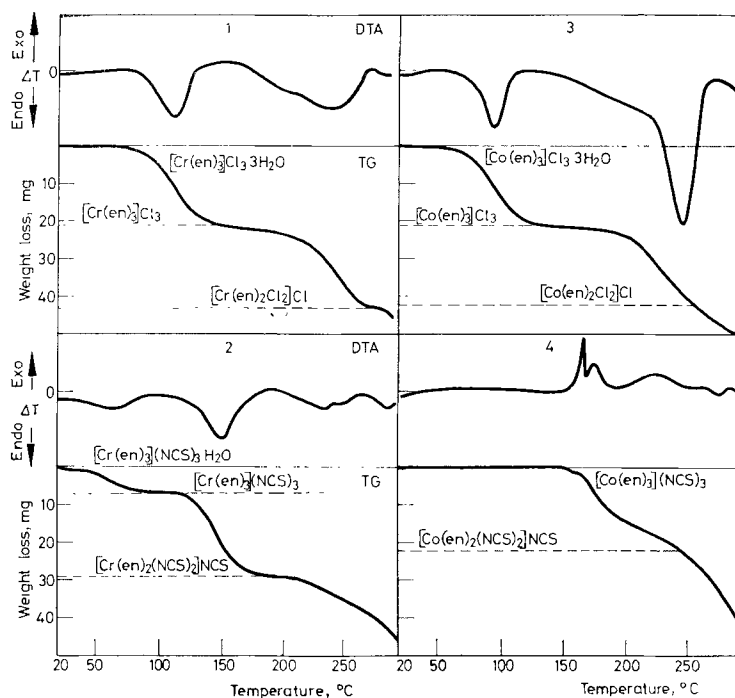
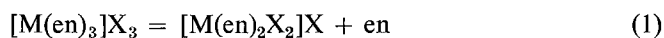


Fig. 1. TG and DTA curves of some tris-ethylenediamine complexes. Sample weight: 150 mg: 1 – Compound XII; 2 – Compound XVI; 3 – Compound I; 4 – Compound XX

Reaction (1) leads to the formation of a relatively stable intermediate, especially in the case of compound XVI, but it can be clearly observed with XII, XIII and XV too. Two typical examples are given in Fig. 1. As seen from the DTA curves of XII and XVI, reaction (1) is endothermic.

Reaction (1) may also be expected to occur in the case of *Co*(III) complexes, if the anion *X* is a simple one. However, in the case of complexes II–V, XX and XXI, the DTA curves show an exothermic peak, which can hardly be assigned to reaction (1). On the other hand, the TG curves are not consistent with the formation of $[Co(en)_2X_2]X$ type intermediates either (see Fig. 1). Only in the case of a

single compound, viz. I, can reaction (1) be presumed to occur. As seen from Fig. 1, a slow endothermic reaction begins after the completion of the dehydration, similarly as for the analogous chromium(III) complex, but it does not lead to the formation of a stable intermediate. Presumably, at higher temperature another reaction is superposed, involving the further decomposition of the complex ion. The shape of the TG curve, Lazerko's observations concerning the decomposition of $\text{trans-[Co(en)}_2\text{Cl}_2\text{]Cl}$ (the presumable intermediate), and especially the appearance of a sharp endothermic peak on the DTA curve (see Fig. 1), are consistent with this.

Thus, reaction (1) seems to be real in the case of Co(III) complexes only if $X = \text{Cl}$. The exothermic character of the decomposition in the case of complexes II–V, XX and XXI suggests that the thermal decomposition also involves redox reactions, viz. the oxidation of the ligands by the central Co^{3+} ion. Taking into

Table 2
Kinetic parameters of the dehydration

Compound	q , °C/min	n	E_a , kcal/mole	$\log Z$
I	10	1/3	14.2	5.9
	3	1/3	16.1	6.4
II	10	1/3	22.3	11.0
	3	1/3	23.8	11.1
III	10	2/3	18.3	8.3
	3	2/3	9.6	2.5
IV	10	2/3	19.4	8.4
	3	2/3	18.7	8.3
V	10	2/3	19.5	8.1
	3	2/3	17.9	8.7
VI	10	1	18.3	8.6
	3	1	26.2	14.8
VII	10	1	13.7	6.4
VIII	10	1	13.7	6.2
IX	10	1	27.5	15.4
	3	1	10.3	3.9
X	10	1	22.3	11.9
	3	1	10.1	3.8
XI	10	2	22.3	12.3
XII	10	1	15.4	6.4
	3	1	21.3	9.6
XIII	10	1	23.3	11.6
XIV	10	1	22.3	10.4
XV	10	1	16.7	8.1
XVI	10	2/3	12.6	5.4
	3	2/3	11.5	4.6
XVII	10	1	14.3	6.8
XVIII	10	1	18.3	9.3
XIX	10	1	21.7	11.6

account the much higher oxidizing character of Co^{3+} as compared to Cr^{3+} , the different thermal behaviours of $Co(III)$ and $Cr(III)$ complexes appear easily explainable. In these redox processes the outer sphere anion can play an important part as electron-donor [19], which might explain the special behaviour of the chloro derivative.

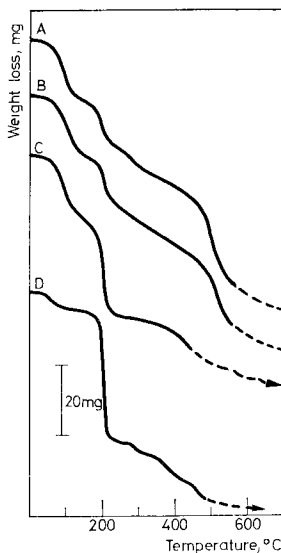


Fig. 2. TG curves of some $[Cr(en)_3]^{3+}$ derivatives

- | | | |
|---|---|---|
| A | $[Cr(en)_3]_2[Co(DH)_2SO_3NCS]_3 \cdot 16H_2O$, | end-product $Cr_2O_3 + Co_3O_4$ |
| B | $[Cr(en)_3][Co(DH)_2(SO_3)_2] \cdot 6H_2O$, | end-product $1/2 Cr_2O_3 + 1/3 Co_3O_4$ |
| C | $[Cr(en)_3]_2[Co_2(DH)_2SO_3NO_2]_3 \cdot 14H_2O$, | end-product $Cr_2O_3 + Co_3O_4$ |
| D | $[Cr(en)_3]SbS_4 \cdot 1.5H_2O$, | end-product $1/2 Cr_2O_3 + 1/2 Sb_2O_3$ |

Since clear de-amination reactions have been observed with only a few chromium complexes, the kinetic analysis of the TG curves has been limited to the first stage of the thermal decomposition, involving the loss of the water of crystallization and observed with the majority of the complexes studied (see Figs 2, 3).

For this purpose Coats and Redfern's integral method [20] was used. The following apparent reaction orders were tried: $n = 0, 1/3, 1/2, 2/3, 1$ and 2 .

The apparent reaction order ensuring the best linearity of the Coats–Redfern plot is given in Table 2. One can see that if two different heating rates were used, the same n value was obtained. Table 2 also contains the apparent activation energy values derived from the slopes of the straight lines obtained. The $\log Z$ values given in Table 2 were calculated by means of the formula [22]

$$\log Z = \log g(x) - \log p(x) + \log Rq - \log E_a \quad (2)$$

where $g(x)$ is the integrated conversion function, $p(x)$ is the exponential integral tabulated in [22], $x = E_a/RT$, and E_a is the apparent activation energy. The heating rate q is given in units of $^{\circ}/\text{min}$.

As seen from Table 2, the activation energy values increase with decreasing heating rate in the case of all substances studied under two different conditions,

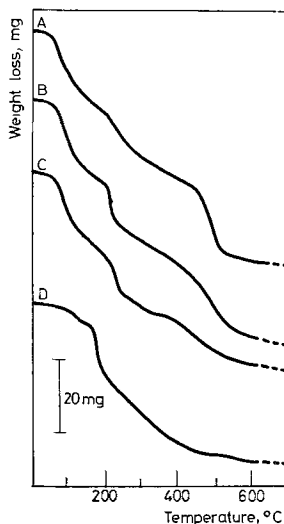


Fig. 3. TG curves of some $[\text{Co}(\text{en})_3]^{3+}$ derivatives

- A $[\text{Co}(\text{en})_3]_2[\text{Co}(\text{DH})_2\text{SO}_3\text{NCS}]_3 \cdot 22\text{H}_2\text{O}$, end-product $5/3 \text{Co}_3\text{O}_4$
 B $[\text{Co}(\text{en})_3][\text{Co}(\text{DH})_2(\text{SO}_3)_2] \cdot 8\text{H}_2\text{O}$, end-product $2/3 \text{Co}_3\text{O}_4$
 C $[\text{Co}(\text{en})_3]_2[\text{Co}(\text{DH})_2\text{SO}_3\text{NO}_2]_3 \cdot 19\text{H}_2\text{O}$, end-product $5/3 \text{Co}_3\text{O}_4$
 D $[\text{Co}(\text{en})_3][\text{Co}(\text{DH})_2(\text{S}_2\text{O}_3)_2] \cdot 2\text{H}_2\text{O}$, end-product $2/3 \text{Co}_3\text{O}_4$

excepting only XVI, although different apparatuses were used with the two different heating rates.

This result is in good agreement with our earlier observations [23, 24].

The Coats – Redfern plot sometimes indicated two distinct kinetic stages in the dehydration process, i.e. two linear portions with differing slopes, although both DTA and DTG curves showed a single process. In the case of III the first kinetic stage corresponds to a lower activation energy. A similar phenomenon was observed previously [24, 25], the first stage being presumed to consist of the decomposition of a surface layer of the crystals. In the case of complexes IX and X, as seen from Table 2, the first kinetic stage needs a higher activation energy, than the second. This effect is presumably due, to the hindered diffusion of the water vapour in the second kinetic stage, which makes the TG curves flatter. In terms of the kinetic parameters derived from the TG curves this means smaller Z values [26] and owing to the kinetic compensation effect smaller E_a values too [27].

As far as the dependence of the E_a values on the nature of the anion is concerned, the following sequences have been observed:

Co(III) complexes: $Cl < Br < CNO < NO_3 < I$,

Cr(III) complexes: $NSC < Cl < Br < SbS_4 < I$.

These sequences are very close to the sequence of increasing polarizability. Since the water of crystallization can be presumed to be bonded to the anion in these complexes, this activation energy sequence suggests that, to some extent, this kinetic parameter is determined by the water-anion bond strength.

Our earlier experiments showed the kinetic parameters E_a and Z not to be independent of each other. For a given thermal decomposition and in a series of compounds of analogous structure, both kinetic parameters depend on the working conditions and on the nature of the different substituents. This dependence frequently takes the form of the following linear compensation law:

$$\log Z = aE_a + b \quad (3)$$

As seen from Table 2, the higher the activation energy, the higher also the $\log Z$ value in general. Thus, the validity of a compensation law type [3] can be expected. The graphical plot of $\log Z$ vs. E_a shows approximate linearity, as seen from Fig. 4.

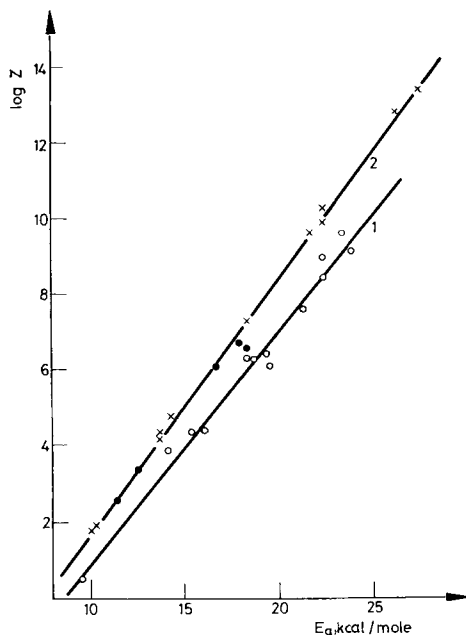


Fig. 4. Kinetic compensation effect on the dehydration of the complexes studied. 1 — calculated for groups 1 + 4; 2 — calculated for groups 2+3+5+6. \circ — groups 1+4; \times — groups 3+6; \bullet — groups 2+5

The experimental points can be seen to be disposed in two distinct straight lines; the compounds of groups 1 and 4 (see Table 1) give straight line 1 and these of groups 2, 3, 5 and 6 straight line 2.

In order to test the legitimacy of this division of the compounds into two classes, the kinetic parameter data were subjected to statistical analysis. To this end the kinetic compensation parameters a and b were calculated for different groups and group combinations of the compounds studied, by using the least squares method. In each case errors were calculated in the normal statistical way, by using tabulated $t_{0.95}$ factor values. Results of these calculations are given in Table 3.

Table 3

Kinetic compensation parameters calculated for different groups and group combinations of the complexes studied

Group combination	Number of experimental points	a	b
1+2+3+4+5+6	29	0.638 ± 0.057	-2.99 ± 1.06
1+2+3	19	0.659 ± 0.072	-3.42 ± 1.36
4+5+6	10	0.573 ± 0.110	-1.78 ± 0.63
3	8	0.675 ± 0.021	-2.98 ± 0.49
6	3	0.648 ± 0.187	-2.49 ± 3.43
3+6	11	0.673 ± 0.016	-2.95 ± 0.23
1	9	0.612 ± 0.081	-3.23 ± 1.49
4	4	0.620 ± 0.285	-3.26 ± 5.93
1+4	13	0.619 ± 0.054	-3.31 ± 1.04
1+2	11	0.613 ± 0.095	-3.10 ± 1.74
4+5	7	0.550 ± 0.097	-1.66 ± 1.40
1+2+4+5	18	0.580 ± 0.077	-2.39 ± 1.41
3+2	10	0.675 ± 0.035	-3.10 ± 0.65
6+5	6	0.679 ± 0.042	-3.12 ± 0.68
3+6+2+5	16	0.675 ± 0.025	-3.08 ± 0.45

Table 3 indicates that there is no reason to divide the compounds studied into cobalt and chromium complexes. On the other hand, the compounds containing complex anions (groups 3 + 6) give excellent linearity. Of the salts containing simple anions, the best linearity is obtained for the group combination 1 + 4. As far as the compounds of groups 2 and 5 are concerned, it is clear that they belong more to the group combination 3 + 6, than to 1 + 4. Their inclusion in the former increases the error of the a value by 0.009 kcal⁻¹, and in the latter by 0.023. Thus, the most legitimate division into 2 classes of the compounds studied, is that given in italics in Table 3. In Fig. 4 the straight lines 1 and 2 correspond to these parameters.

Table 4

Kinetic compensation parameters for different type thermal decomposition reaction

Reaction	a	b	Reference
$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$	0.195	-1.86	28
de-amination of $[\text{CoX}_2(\text{amine})_2]$, second stage	0.416	-3.47	25
de-amination of $[\text{Co}(\text{Diph.H})_2(\text{amine})_2]\text{X}$	0.446	-2.55	27
de-amination of $[\text{Co}(\text{Niox.H})_2(\text{amine})_2]\text{X}$	0.501	-2.09	27
de-amination of $[\text{Co}(\text{DH})_2(\text{amine})_2]\text{X}$	0.517	-2.75	27
de-amination of $[\text{CoX}_2(\text{amine})_2]$, first stage	0.534	-3.75	25
dehydration of $[\text{M}(\text{en})_3]_r\text{X}_s \cdot t\text{H}_2\text{O}$ type salts with simple anions	0.619	-3.31	this paper
dehydration of $[\text{M}(\text{en})_3]_r\text{X}_s \cdot t\text{H}_2\text{O}$ type salts with complex anions	0.675	-3.08	this paper

Diph.H₂ = diphenylglyoximeNiox.(H)₂ = 1,2-cyclohexanedioxime (nioxime)

In Table 4 the compensation parameters obtained are compared to the analogous parameters derived for other thermal decompositions. The parameter a characterizes the sensitivity of Z towards changes in F_a . If the reactions studied are arranged in the order of increasing a values, some interesting conclusions can be drawn. Thus, results presented in this Table suggest that the stronger the leaving group is bonded, the smaller the compensation parameter a . The smallest a value has been reported for the thermal decomposition of CaCO_3 , which involves the complete decomposition of CO_3^{2-} ions the major part of this ion leaving the crystalline lattice [28]. In the case of the de-aminations, the leaving amine is coordinated to a transition metal ion. The sequence of the a values is consistent with Co-amine bond strengths expected on the basis of the structure. In the case of the dioximine complexes the Co-amine bond must be stronger in the diphenylglyoxime derivatives, owing to the electron-withdrawing effect of the aromatic rings, and weaker in the dimethylglyoxime derivatives, in good agreement with our experimental results.

In the complexes $[\text{CoX}_2(\text{amine})_2]$ the presence of the seventh d electron of the central ion diminishes the Co-amine bond strength [25], but after the loss of some of the amine molecules, the remainder can be bonded even more strongly than in the dioximine complexes. This is why the lower a value derived for the second stage of this de-amination is not surprising.

It is obvious that water of crystallization must be bonded more weakly to the anions, than the amine molecules in the inner co-ordination sphere of transition metal complexes. Thus, the high a values obtained are consistent with our above assumption. As regards the existence of two distinct classes, this too seems to be understandable, taking into account that simple anions create a stronger electrostatic field than do complex ones. In this respect, only the behaviours of the bromides and the thiocyanates (compounds of groups 2 and 5) seem to remain an

open question, but it must not be forgotten that the compensation parameters obtained are affected by considerable errors, and it would be unjustified to draw too categorical conclusions.

The compensation parameters b are affected by even larger probable errors than the parameters a . Thus, there is no possibility of correlating their values with the characteristics of the reactions studied.

Experimental

Synthesis of $[Co(en)_3]X_3$ and $[Cr(en)_3]X_3$ type complexes

$[Co(en)_3]Cl_3 \cdot 3H_2O$: 0.3 moles of ethylenediamine and about 2 g of active carbon were added to a solution of 0.1 mole of $CoCl_2$ in 300 ml water. A strong air stream was bubbled through this solution for 4–5 hours. After this the solution was heated up to the boiling point, filtered and after cooling treated with the same volume of cc. HCl and the same volume of ethanol. The yellow, powdery, crystalline product was filtered off and washed with ethanol.

$[Cr(en)_3]_2(SO_4)_3$ was synthesized as described by Pfeiffer [10].

The complex salts studied were obtained by double decomposition reactions, using 5–10% solutions of $[Co(en)_3]Cl_3$ or $[Cr(en)_3]_2(SO_4)_3$, depending on the solubility of the product.

In order to perform the double exchange reactions, besides the easily available anions, some mixed bis-dimethylglyoximatocobalt(III) complexes were used, viz. $Na_2Co(DH)_2(NCS)SO_3$, $Na_2Co(DH)_2(NO_2)(SO_3)$, $Na_3Co(DH)_2(SO_3)_2$ and $Na_3Co(DH)_2(S_2O_3)_2$.

These sodium salts were obtained from the $Co(DH)_2(H_2O)NO_2$ and $Co(DH)_2(H_2O)(NCS)$ aquo-non-electrolyte type chelates by means of anation and substitution reactions as described by Ablov and Syrzova [29].

TG measurements were performed with a thermobalance constructed on the basis of literature data [30]. Sample weight: 100 mg. Heating rate: 10°/min. Atmosphere: static air. Platinum crucible. Some measurements were performed with a MOM Derivatograph [31]. Sample weight: 150 mg. Heating rate: 3°/min. Atmosphere: static air. Reference material: $\alpha-Al_2O_3$. Platinum crucible.

References

1. H. GROSSMANN and B. S. SCHÜCK, Ber. dtsch. chem. Ges., 39 (1906) 1899.
2. S. M. JÖRGENSEN, J. prakt. Chem. 39 (1889) 8.
3. P. PFEIFFER, Z. anorg. Chem. 36 (1903) 349; 55 (1907) 97.
4. A. WERNER, Ber. dtsch. chem. Ges., 45 (1912) 1228.
5. F. M. JAEGER, Rec. Trav. chim. 38 (1919) 171.
6. I. LEBEDINSKII and M. FEDOROV, Izvest. Sektora Platiny, Akad. Nauk S.S.S.R., 15 (1938) 13.
7. F. M. JAEGER, Z. Kryst., 58 (1923) 172.
8. H. MATHIEU, Bull. soc. chim. France, 6 (1939) 1258.
9. P. PFEIFFER and H. HAIMANN, Liebigs. Ann. Chem., 346 (1906) 72.
10. P. PFEIFFER, Ber. dtsch. chem. Ges., 37 (1907) 4255.

11. T. D. O'BRIEN and J. C. BAILAR jr., *J. Amer. Chem. Soc.*, **67** (1945), 1856.
12. W. W. WENDLANDT and L. K. SVEUM, *J. Inorg. Nucl. Chem.* **28** (1966), 393.
13. W. W. WENDLANDT and C. H. STEMBRIDGE, *J. Inorg. Nucl. Chem.*, **27** (1965) 575.
14. J. ZSAKÓ, Cs. VÁRHELYI and M. SZÉCSI, *Rev. Roumaine Chim.*, **13** (1968) 1335.
15. J. E. HOUSE and J. C. BAILAR, *J. Amer. Chem. Soc.* **91** (1969) 67.
16. T. D. GEORGE and W. W. WENDLANDT, *J. Inorg. Nucl. Chem.* **25** (1963) 395.
17. J. BASSETT, R., GRZESKOWIAK and B. L. O'LEARY, *J. Inorg. Nucl. Chem.*, **32** (1970) 3861; *J. Thermal Anal.* **3** (1971) 143.
18. G. A. LAZERKO. E. C. KOSINSKAIA and L. N. NEOKLADNOVA, *Zhur. neorg. Khim.*, **3** (1972) 720.
19. P. KRÖBL, Doctor Thesis, Babeş-Bolyai University, Cluj, Romania, 1968.
20. H. W. COATS and J. P. REDFERN, *Nature*, **201** (1964) 68.
21. J. ZSAKÓ, *J. Thermal Anal.*, in press.
22. J. ZSAKÓ, *J. Phys. Chem.*, **72** (1968) 2406.
23. J. ZSAKÓ, E. KÉKEDY and Cs. VÁRHELYI, *J. Thermal Anal.*, **1** (1969) 339; *Rev. Roumaine Chim.*, **15** (1970) 865.
24. J. ZSAKÓ, E. KÉKEDY and Cs. VÁRHELYI, *Prcc. 3rd Int. Conf. Therm. Anal. Davos, Switzerland*, 1971, 487.
25. Cs. VÁRHELYI, J. ZSAKÓ and M. BOÁRIU-FARKAS, *Rev. Roumaine Chim.* **1973**, in press.
26. J. ZSAKÓ, *J. Chim. Phys.*, **66** (1969) 1041.
27. J. ZSAKÓ and M. LUNGU, *J. Thermal Anal.*, **5** (1973) 77.
28. J. ZSAKÓ and H. E. ARZ, *J. Thermal Anal.*, **6** (1974) 651.
29. A. V. ABLOV and G. P. SYRZOVA, *Zhur. neorg. Khim.* **5** (1960) 1221.
30. L. ERDEY and F. PAULIK, *Magy. Tud. Akad. Kém. Oszt. Közl.* **5** (1955) 461; L. KÉKEDY, P. KRÖBL, Á. SZURKOS and E. KÉKEDY, *Studia Univ. Babeş-Bolyai, Chem.* **3** (1958) 99.
31. F. PAULIK, J. PAULIK, L. ERDEY, *Z. anal. Chem.* **160** (1958) 291.

RÉSUMÉ — On a étudié la décomposition thermique de 22 dérivés des complexes du type $[M(en)_3]X_3$. La réaction de désamination partielle qui amène la formation des complexes du type $[M(en)_2X_2]X$ se produit dans le cas de $Cr(III)$, si $X = Cl, Br, I$ ou NCS , mais dans le cas de $Co(III)$ elle n'est possible que si $X = Cl$. Dans les autres cas, la formation d'intermédiaires stables est empêchée par des réactions d'oxydo-réduction. On a calculé les paramètres cinétiques pour la déshydratation de 19 composés.

On a constaté la validité d'une loi de compensation cinétique linéaire. On discute la manière dont les paramètres de compensation cinétique dépendent de la nature du processus thermique.

ZUSAMMENFASSUNG — Die thermische Zersetzung von 22 Derivaten des Komplextyps $[M(en)_3]X_3$ wurde untersucht. Die partielle Deaminierungsreaktion, welche zur Bildung von Komplexen des Typs $[M(en)_2X_2]X$ führt, tritt bei $Cr(III)$ -Komplexen in dem Falle $X = Cl, Br, I$ oder NCS auf, ist aber bei $Co(III)$ -Komplexen nur bei $X = Cl$ möglich. In anderen Fällen wird die Bildung von stabilen Zwischenprodukten durch Redoxreaktionen verhindert. Für die Dehydratation von 19 Verbindungen wurden kinetische Parameter abgeleitet.

Die Gültigkeit eines linearen kinetischen Kompensationsgesetzes wurde beobachtet. Die Abhängigkeit kinetischer Kompensationsparameter von der Beschaffenheit des thermischen Vorganges wird erörtert.

Резюме — Исследован термораспад 22 производных комплексов типа $[M(en)_3]X_3$. Реакция, приводящая к образованию комплексов типа $[M(en)_2X_2]X$, имеет место в случае $Cr(III)$ комплексов, в которых $X = Cl, Br, I$ или NCS , в случае же производных $Co(III)$ эта реакция возможна только при $X = Cl$. В других случаях окислительно-восстановительные реакции мешают образованию стабильных промежуточных соединений. Рассчитаны кинетические параметры дегидратации 19 соединений.

Обнаружена справедливость закона линейной кинетической компенсации. Обсуждается зависимость параметров кинетической компенсации от характера термического процесса.