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THERMAL DECOMPOSITION KINETICS OF LANTHANUM AND NEODYMIUM BROMIDE COMPLEXES WITH GLYCINE OR ALANINE

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Abstract

Four complexes of rare earth bromides with amino acids, $REBr_3 \cdot 3L \cdot 3H_2O$ (RE =La, Nd; L =glycine or alanine) were prepared and characterized by means of chemical analysis, elemental analysis, molar conductivity, thermogravimetry, IR spectra and X-ray diffraction. Their thermal decomposition kinetics from ambient temperature to 500°C were studied by means of TG-DTG techniques under non-isothermal conditions. The kinetic parameters (activation energy E and pre-exponential constant A) and the most probable mechanisms of thermal decomposition were obtained by using combined differential and integral methods. The thermal decomposition processes of these complexes are distinguished as being of two different types, depending mainly on the nature of the amino acid.

Keywords: alanine, complexes of rare earth bromides, glycine, kinetics, lanthanum, neodymium, thermal decomposition

Introduction

Interest in the study of the coordination chemistry of rare earth ions with amino acids is increasing. Thermal investigations of complexes of rare earth chlorides with amino acids have been carried out by several groups [1–3], but studies of complexes of rare earth bromides with amino acids are comparatively rare [4]. Kinetic parameters and mechanisms for the thermal decompositions of the above complexes have not yet been reported.

In the present work, we have prepared and characterized four complexes, $REBr_3 \cdot 3L \cdot 3H_2O$ (RE=La, Nd; L=glycine or alanine). The kinetics of the thermal decompositions of these complexes were studied under non-isothermal conditions by means of TG-DTG techniques. The most probable mechanism functions and kinetic parameters of the thermal decompositions of $REBr_3 \cdot 3L \cdot 3H_2O$ were determined by means of combined differential and integral methods [5, 6].

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For the kinetic analysis, the differential equation of Achar *et al.* [7] and the modified Coats-Redfern integral equation were used [8]. The differential and integral equations are

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \qquad (1)$$

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \qquad (2)$$

where α is the fraction of material reacted, T is the absolute temperature, β is the linear heating rate, R is the gas constant, E and A are apparent activation energy and pre-exponential constant, respectively, and $f(\alpha)$ and $g(\alpha)$ are the differential and integral mechanism functions, respectively.

Experimental

Reagents and preparation of the complexes

The purities of the La_2O_3 and Nd_2O_3 were better than 99.9 per cent, and the purities of the glycine (Gly) and DL-α-alanine (Ala) were better than 99.0 per cent. All other chemicals were of analytical reagent grade.

$LaBr_3 \cdot 7H_2O$ and $NdBr_3 \cdot 6H_2O$ were prepared as described by Mayer *et al.* [9]. The four complexes were prepared by the following method. Rare earth bromide hydrates and amino acids (in molar ratio 1:3) were dissolved in distilled water, and concentrated at a constant temperature of 50°C. The crystals obtained were filtered off, washed with anhydrous alcohol and dried over 45% H_2SO_4 to constant weight. The resulting complexes were $REBr_3 \cdot 3L \cdot 3H_2O$ (RE=La, Nd; L=Gly or Ala).

Component analysis of the complexes

The rare earth contents of these complexes were determined by EDTA titration, and the Br^- contents were determined by the Volhard method. The contents of C, N and H were determined with a Perkin-Elmer 240C Elemental Analyser.

Physical measurements

The IR spectra of the complexes were recorded with a Nicolet Model FT-IR5DX Spectrophotometer. The samples were mounted as mulls in KBr discs and examined between 4000 and 400 cm^{-1}.

The X-ray powder diffractions of these complexes were recorded with a X-ray Diffractometer (D/Max-rA, Rigaku, Japan), using Cu radiation. The molar

Table 1 Results of component analysis of the complexes (theoretical values in parentheses)

Complex	RE %	Br %	C %	H %	N %
$LaBr_3{\cdot}3Gly{\cdot}3H_2O$	21.11(21.11)	36.34(36.44)	10.87(10.95)	3.14(3.22)	6.47(6.39)
$NdBr_3{\cdot}3Gly3H_2O$	21.79(21.75)	36.14(36.14)	10.93(10.87)	3.05(3.19)	6.33(6.34)
$LaBr_3{\cdot}3Ala3H_2O$	19.83(19.85)	34.19(34.25)	15.44(15.44)	3.67(3.89)	6.29(6.00)
$NdBr_3{\cdot}3Ala3H_2O$	20.47(20.45)	33.96(33.99)	15.00(15.33)	3.54(3.86)	5.90(5.96)

conductances were determined with a DDS-11A Model Conductometer (made in China) at 26°C.

TG-DTG experimental equipment and conditions

TG-DTG experiments were carried out on a Perkin-Elmer TGA 7 Thermogravimetric Analyzer, in a N_2 atmosphere (60 $ml\cdot min^{-1}$) and a heating rate of 10 $deg\cdot min^{-1}$. The sample sizes were 4–6 mg.

Results and discussion

Component analysis of the complexes

The results of component analysis of the complexes are given in Table 1. The formula weights of all four complexes agree with the general formula $REBr_3\cdot 3L\cdot 3H_2O$, where RE=La or Nd, and L=Gly or Ala.

Physical measurements

The molar conductance values of aqueous solutions (10^{-3} M) of the four complexes were observed in the range 384.4-393.5 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, which indicates that these complexes are electrolytes of 1:3 type and all bromide ions are situated in the outer sphere of the coordination ions. A comparison of the X-ray diffraction data on $REBr_3\cdot 3L\cdot 3H_2O$ (RE=La, Nd; and L=Gly or Ala), $LaBr_3\cdot 7H_2O$, $NdBr_3\cdot 6H_2O$, glycine and alanine reveals that the four complexes and their reactants belong in different phases, and the prepared complexes are new substances.

The IR results indicate that glycine and alanine retain their zwitterionic structure in their rare earth complexes. This excludes the possibility of the coordination of nitrogen to the rare earth ions. There remains the possibility of coordination of the carboxylic group of glycine or alanine to the rare earth ions.

In free glycine, $\Delta\nu(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-) = 202$ cm^{-1}; in complexed glycine, $\Delta\nu(COO^-) = 178$ cm^{-1} (in $LaBr_3\cdot 3Gly\cdot 3H_2O$) and 180 cm^{-1} (in $NdBr_3\cdot 3Gly\cdot 3H_2O$); in free alanine, $\Delta\nu(COO^-) = 184$ cm^{-1}; in complexed alanine, $\Delta\nu(COO^-) = 135$ cm^{-1} (in $LaBr_3\cdot 3Ala\cdot 3H_2O$) and 139 cm^{-1} (in $NdBr_3\cdot 3Ala\cdot 3H_2O$). This indicates that in the complexes the two oxygens of $-COO^-$ have higher symmetry and the two oxygens are coordinated to the rare earth ions.

The O–H stretch of the water molecules in these complexes is observed at 3409–3418 cm^{-1}. This shows that these water molecules are hydrogen-bonded. Lower shifts (55–56 cm^{-1}) of $-NH_3^+$ stretch in complexed glycine may be due to the formation of hydrogen-bonds between glycine and water in the complexes, but this effect is weaker in complexed alanine than in complexed glycine.

Thermal decomposition processes

The TG-DTG curves of the four complexes are shown in Figs 1–4. Their thermal decomposition data are listed in Table 5.

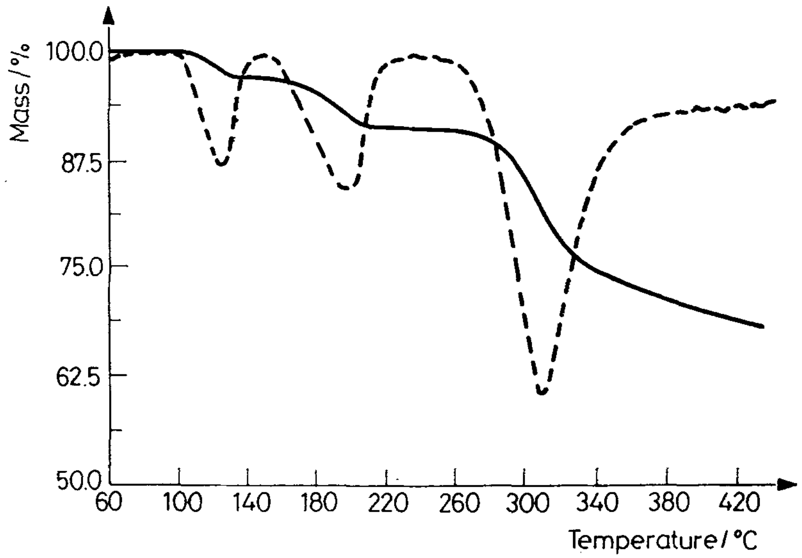

Fig. 1 TG-DTG curves of $LaBr_3 \cdot 3Gly \cdot 3H_2O$ (— TG; - - - DTG)

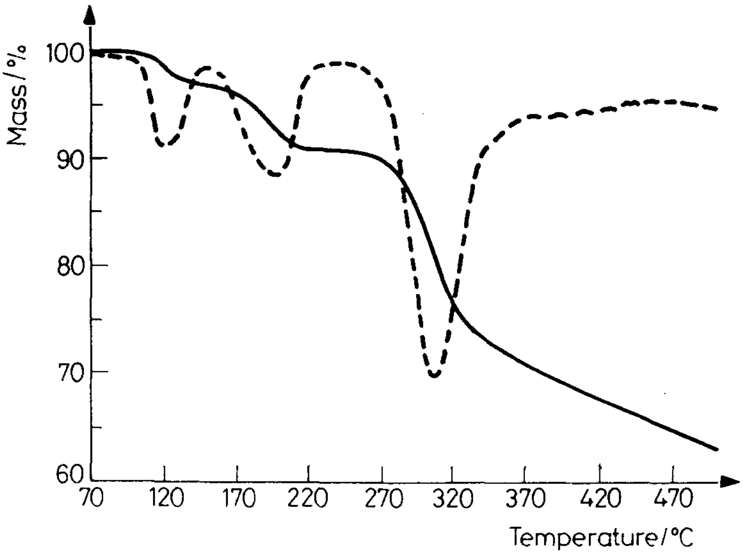

Fig. 2 TG-DTG curves of $NdBr_3 \cdot 3Gly \cdot 3H_2O$ (— TG; - - - DTG)

The TG-DTG curves suggest that the thermal decomposition processes of the four complexes in the given range of experimental temperature may be described by the following sequences:

$$\mathrm{REBr_3{\cdot}3Gly{\cdot}3H_2O} \xrightarrow[-\mathrm{H_2O}]{\mathrm{I}} \mathrm{REBr_3{\cdot}3Gly{\cdot}2H_2O} \xrightarrow[-2\mathrm{H_2O}]{\mathrm{II}} \mathrm{REBr_3{\cdot}3Gly} \xrightarrow[-2\mathrm{Gly}]{\mathrm{III}} \mathrm{REBr_3{\cdot}Gly} \quad (3)$$

$$\mathrm{REBr_3{\cdot}3Ala{\cdot}3H_2O} \xrightarrow[-3\mathrm{H_2O}]{\mathrm{I}} \mathrm{REBr_3{\cdot}3Ala} \xrightarrow[-2\mathrm{Ala}]{\mathrm{II}} \mathrm{REBr_3{\cdot}Ala} \quad (4)$$

(*Re*=La, Nd)

It is obvious that the thermal decomposition processes of the complexes with a given amino acid are similar.

Analysis of kinetic data

Several selected kinetic functions used in the present analysis are tabulated in Table 2.

As an example, analysis of the kinetic data is carried out on the first step of the thermal decomposition process of $LaBr_3{\cdot}3Gly{\cdot}3H_2O$. The original data for this step from the TG-DTG curves are listed in Table 3.

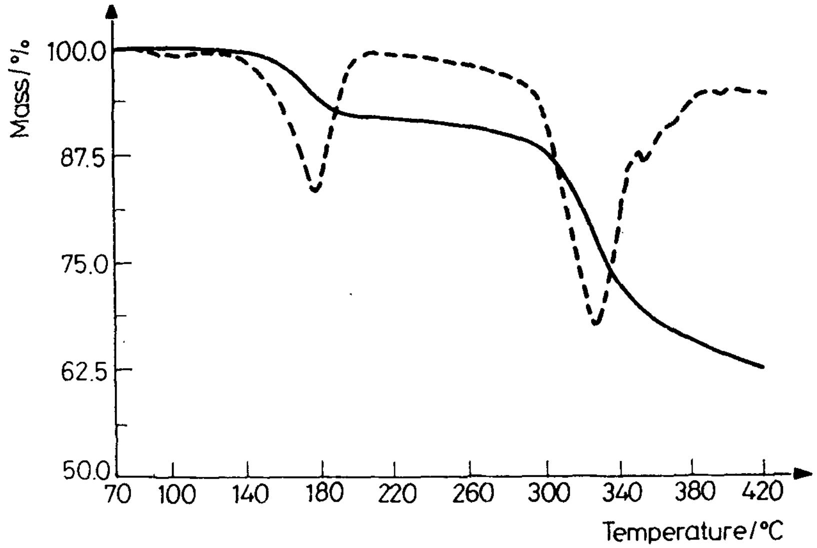

Fig. 3 TG-DTG curves of $LaBr_3{\cdot}3Ala3H_2O$ (— TG; - - - DTG)

Table 2 The selected several kinetic functions used in the present analysis

Function no.	Function form: Integral form $g(\alpha)$	Function form: Differential form $f(\alpha)$
1	α^2	$1/(2\alpha)$
2	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
3	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
4	$[1-(1-\alpha)^{1/3}]^2$	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
5	$[(1+\alpha)^{1/3}-1]^2$	$1.5(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$
6	$[\{1/(1-\alpha)\}^{1/3}-1]^2$	$1.5(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$
7	$-\ln(1-\alpha)$	$1-\alpha$
8	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
9	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
10	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
11	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
12	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
13	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
14	α	1
15	$\alpha^{1/2}$	$2\alpha^{1/2}$
16	$\alpha^{1/3}$	$3\alpha^{2/3}$
17	$\alpha^{1/4}$	$4\alpha^{3/4}$
18	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$
19	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$

Table 3 Data on $LaBr_3{\cdot}3Gly{\cdot}3H_2O$ determined by TG-DTG (step I)

Data point	T/K	α	$[d\alpha/dt](s^{-1})$
1	380.52	0.0798	0.42
2	382.49	0.1342	0.58
3	384.73	0.2153	0.88
4	386.61	0.2982	1.05
5	388.85	0.3869	1.14
6	390.55	0.4584	1.23
7	392.88	0.5642	1.33
8	394.66	0.6484	1.42
9	396.81	0.7429	1.45
10	398.69	0.8251	1.44
11	400.67	0.9045	1.33

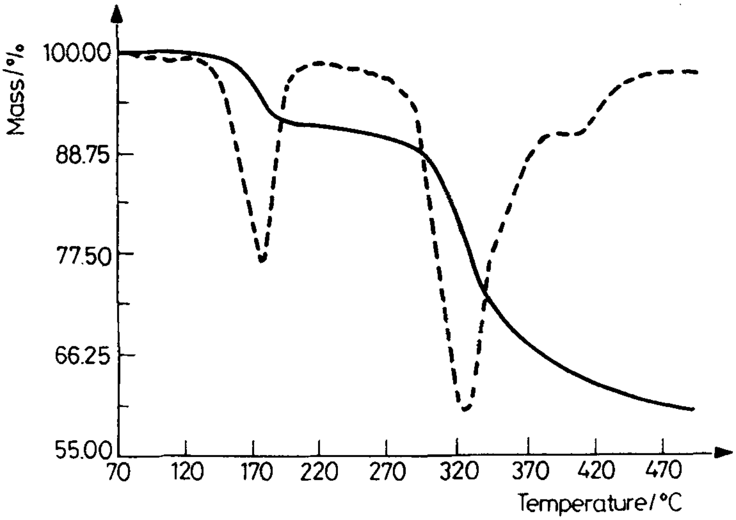

Fig. 4 TG-DTG curves of $NdBr_3 \cdot 3Ala \cdot 3H_2O$ (— TG; - - - DTG)

Table 4 Results of analysis of the thermal decomposition data of $LaBr_3 3Gly \cdot 3H_2O$ in Table 3 by differential [Eq.(1) and integral [Eq.(2)] methods

Function	Differential method			Integral method		
no.	E /kJ·mol^{-1}	ln A/s^{-1}	r	E /kJ·mol^{-1}	ln A/s^{-1}	r
1	211.59	63.14	0.9415	281.47	81.45	0.9653
2	265.46	79.41	0.9734	311.01	90.18	0.9753
3	288.24	85.07	0.9816	323.36	92.60	0.9790
4	331.32	98.62	0.9905	348.60	100.62	0.9850
5	173.90	48.96	0.9176	255.02	70.75	0.9582
6	460.57	139.26	0.9959	434.77	127.94	0.9954
7	196.86	59.72	0.9935	191.37	54.66	0.9912
8	130.91	39.20	0.9860	125.41	34.12	0.9909
9	97.93	28.86	0.9731	92.44	23.76	0.9905
10	64.96	18.40	0.9337	59.46	13.26	0.9898
11	48.47	13.08	0.8814	42.97	7.91	0.9890
12	132.23	38.70	0.9872	161.81	44.50	0.9800
13	153.78	45.07	0.9925	171.05	47.06	0.9844
14	67.61	19.07	0.8726	137.49	37.36	0.9637
15	–4.38	–3.31	0.2228	65.50	14.93	0.9601
16	–28.38	–10.94	0.9069	41.50	7.25	0.9560
17	–40.38	–14.84	0.9686	29.50	3.29	0.9513
18	326.11	100.37	0.9831	266.74	78.67	0.9961
19	261.49	79.35	0.9886	58.13	13.45	0.9319

Table 5 Thermal decomposition data and kinetic parameters for the decomposition of $REBr_3 3L \cdot 3H_2O$ (*RE* = La; Nd, *L* = Gly or Ala)

Complex	Decomp. step	Temp. range/ °C	Weight loss (%)		Range of α	E/kJ mol^{-1}			ln A/s^{-1}			Mecha- nism*
			Calcd.	Found		Diff. method	Integral method	Average	Diff. method	Integral method	Average	
$LaBr_3 \cdot 3Gly \cdot 3H_2O$	I	94–150	2.74	2.92	0.080-0.905	196.86	191.37	194.12	59.72	54.66	57.19	F1
	II	150–240	5.48	5.67	0.073–0.977	255.41	258.63	257.02	63.87	60.24	62.04	D3
	III	240–400	22.82	21.17	0.072–0.777	161.94	185.92	173.93	32.86	33.44	33.15	F2
$NdBr_3 \cdot 3Gly \cdot 3H_2O$	I	98–150	2.72	2.92	0.054–0.954	158.87	162.12	160.50	48.86	45.37	47.12	F1
	II	150–242	5.43	5.93	0.058–0.957	219.87	225.53	222.70	54.58	51.49	53.04	D3
	III	242–470	22.64	20.23	0.058–0.797	199.04	198.44	198.74	40.86	36.40	38.43	F2
$LaBr_3 \cdot 3Ala \cdot 3H_2O$	I	122–230	7.72	7.89	0.051–0.969	239.70	246.64	243.17	61.87	59.72	60.80	D3
	II	230–410	25.46	25.31	0.065–0.812	201.25	211.12	206.19	39.11	37.57	38.34	F2
$NdBr_3 \cdot 3Ala \cdot 3H_2O$	I	126–245	7.66	7.90	0.052–0.890	259.33	255.13	257.23	67.22	62.08	64.65	D3
	II	245–475	25.28	25.38	0.059–0.761	134.87	144.86	139.87	25.99	23.65	24.82	F2

* F1: $f(\alpha) = 1-\alpha$; $g(\alpha) = -\ln(1-\alpha)$; D3: $f(\alpha) = 1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$; $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$; F2: $f(\alpha) = (1-\alpha)^2$; $g(\alpha) = (1-\alpha)^{-1}-1$

With the possible forms of $g(\alpha)$ and $f(\alpha)$ from Table 2, the data in Table 3 were analysed by means of Eqs (1) and (2). The kinetic analyses were completed with the linear least-squares method on a computer. The results are shown in Table 4.

The results in Table 4 clearly show that the values of E and $\ln A$ from the two methods are approximately the same, and that the linear correlation coefficients are best ($r \approx 1$), when the most probable mechanism function is function no. 7 (F1: $f(\alpha) = 1 - \alpha$; $g(\alpha) = -\ln(1 - \alpha)$).

The other thermal decomposition processes for these complexes may be inferred by analogy. The results for the kinetic parameters and the most probable mechanisms for the four complexes are listed in Table 5.

Conclusions

It can be concluded from the above results (see Eqs (3)–(4) and Table 5) that the thermal decomposition processes for the complexes of rare earth bromides with amino acids depend mainly on the nature of the amino acid. The thermal decomposition processes of the complexes with glycine take place in three steps, whereas those of the complexes with alanine do so in two steps only.

The most probable mechanisms for the thermal decomposition of $REBr_3 \cdot 3L \cdot 3H_2O$ (RE=La, or Nd; L=Gly or Ala) are F1 ($f(\alpha)=1-\alpha$; $g(\alpha) = -\ln(1-\alpha)$) with the loss of one water molecule, D3 ($f(\alpha)= 1{,}5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$; $g(\alpha)=[1-(1-\alpha)^{1/3}]^2$) with the loss of two or three water molecules, and F2 ($f(\alpha)=(1-\alpha)^2$; $g(\alpha)=(1-\alpha)^{-1}-1$) with the loss of two glycine or two alanine molecules.

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Zusammenfassung — Vier Komplexe von Seltenerdenbromiden mit Aminosäuren, $REBr_3 \cdot 3L \cdot 3H_2O$= ($RE$=La, Nd; L=Glycin oder Alanin) wurden hergestellt und mittels chemischer Analyse, Elementaranalyse, molarer Leitfähigkeit, Thermogravimetrie, IR-Spektren und Röntgendiffraktion charakterisiert. Mittels TG-DTG wurde unter nichtisothermen

Bedingungen im Temperaturbereich Raumtemperatur bis 500°C die Kinetik ihrer thermischen Zersetzung untersucht. Unter Einsatz kombinierter Integrations- und Differentialmethoden erhielt man die kinetischen Parameter, namentlich die Aktivierungsenergie E, den präexponentiellen Faktor A sowie den wahrscheinlichsten Mechanismus der thermischen Zersetzung. Die Untersuchungen zeigen, daß die thermischen Zersetzungsprozesse dieser Komplexe – je nach Art der Aminosäure – zwei Typen angehören.