SIMULTANEOUS THERMOANALYTICAL INVESTIGATIONS ON THE RAPID DECOMPOSITION OF PENTAMMINECOBALT(III) COMPLEXES

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The thermal decomposition of $[Co(NH_3)_5CO_3]NO_3$, $[Co(NH_3)_5NO_2](NO_3)_2$ and $[Co(NH_3)_5H_2O](NO_3)_3$ complexes was studied by simultaneous TG, DTG, DTA (Derivatograph-C), termogastitrimetry, continuous selective water detection, TG-MS, and XRD methods.

Due to the nearly explosive reaction of these complexes the samples were heated in a labyrinth-type crucible after a 10-fold dilution with alumina.

Through the quantitative determination of NH_3 and H_2O it was possible to reveal the subtleness of decomposition of these complexes.

Based on the qualitative and quantitative results obtained by the different thermoanalytical techniques used the equations of decomposition are given for both stages of the reactions.

Systematic studies on the thermal decomposition of crystalline pentamminecobalt(III) complexes dates back to a relatively early stage of development of thermoanalytical methods [1-4]. It was observed that the peak temperature of the exothermic redox reaction of $[Co(NH_3)_5X]^{2+}$ complexes (where $X = I^-$, Br^-, Cl^-, F^-, and NO_2^-) could be correlated to the ligand field strength of the hetero ligand, X. The remarkable feature of these compounds is that they exhibit a similar trend in their redox reaction induced with electron transfer quenching of the photoexcited $Ru(bpy)_3^{2+}$ complex (bpy = 2,2'-bipyridine) [5-9]. The new aspects of chemistry of these compounds directed our attention to the reinvestigation of their thermal reactions using highly sophisticated thermoanalytical techniques.

Our investigations have been carried out on [Co(NH3)5CO3]NO3, [Co(NH3)5NO2](NO3)2 and [Co(NH3)5H2O](NO3)3 complexes. The results of the thermogravimetric (TG), differential thermal analysis (DTA), evolved gas analysis (EGA), TG-mass spectroscopic (TG-MS), and X-ray diffraction investigations were used to interpret the mechanism of the thermal decomposition of these complexes.

Experimental

Materials used

Carbonatopentamminecobalt(III)nitrate hemihydrate, [Co(NH3)5CO3]3.NO3 0.5 H2O, was prepared from cobalt(III) nitrate according to established procedures [10].

Nitropentamminecobalt(III)nitrate, [Co(NH3)5NO2](NO3)2, and aquopentamminecobalt(III)nitrate, [Co(NH3)5H2O](NO3)3, were obtained from the carbonato-complex.

The stoichiometric composition of the above complexes was checked by thermogravimetry and elemental analysis.

Instrument

Thermoanalytical investigations were carried out by means of a Derivatograph-C type complex thermoanalytical instrument (Hungarian Optical Works Budapest, Hungary). In order to carry out simultaneous EGA measurements continuous selective water detector [11, 12] and thermogastitrimetric equipment [13, 14] were connected to the Derivatograph.

A TG-MS system (a Perkin-Elmer TGS-2 thermobalance connected to a Balzers QMG-511 mass spectrometer) [13] was also used to follow the liberation of gaseous compounds (through the formation of their molecular ions and ionic fragments) in the function of the temperature.

The composition of the solid residues was determined by a Philips PW 1730/10 type X-ray diffractometer.

The chemical composition of the freshly prepared complexes was confirmed by a Perkin-Elmer 240 type elemental analyzer.

Procedure used

Thermoanalytical studies of these types of complexes is rather difficult. Due to their extremely fast decomposition reactions the gases formed upon

heating blow the powdery sample out of the crucible. In order to investigate the thermal behaviour of these complexes 15 to 25 mg samples were diluted with alumina (fired at 1000° for 2 hours) at a ratio of 1 to 10 and heated in a labyrinth-type crucible (used for quasi-isothermal, quasi-isobaric investigations [14]) at a heating rate of 2 deg/min in nitrogen atmosphere. (Crucibles other than the labyrinth one failed to retain the sample even after a 10-fold dilution.)

The formation of water was monitored by the continuous selective water detector. The water detector trace was recorded along with the T, TG, DTG, and DTA curves. Quantitation was carried out by calibration. The crystal water liberated from a known amount of heated $Ca(COO)_2.H_2O$ was used for calibration.

The liberation of ammonia from the samples was followed by automatic acid-base titration at pH = 5.0 (pH-static titration) using 0.1 M HCl titrant and potentiometric end-point indication. The thermogastitrimetric (TGT) and derivative thermogastitrimetric (DTGT) curves were recorded simultaneously with the T, TG, DTG, and DTA curves.

TG-MS measurements were carried out in argon atmosphere (140 cm^3/min flow rate) at a heating rate of 10 deg/min with less than 5 mg samples. Volatiles formed upon heating were led to the ion source through a heated capillary tube. The mass spectra were measured from m/z 2 to 60 in intervals of 10 s (1.67°) with an electron impact ionization energy of 70 eV. Data acquisition was controlled by a minicomputer (PDP-11/34). Numerically generated DTG and mass spectrometric intensity curves were plotted by a digital plotter after subtracting the background level.

Results and discussion

The thermoanalytical curves of $[Co(NH_3)_5CO_3]NO_3.0.5 \; H_2O$ are shown in Fig. 1. By comparison of the recorded curves the following conclusions can be drawn. The decomposition of the carbonato-complex takes place in two stages. The first decomposition step at 159° is an endothermic process yielding water vapour (crystal water) and ammonia among the decomposition products. The second decomposition step, however, is rather complicated. At 200° an endothermic process can be identified accompanied with the maximum rate of ammonia formation (see the DTGT curve). Above 200°, however, the decomposition reaction suddenly turns to an exothermic one, resulting in the maxima of the DTG, DTA, and H_2O curves at 207°. Considering the 7° offset of the DTGT and the rest curves (DTG, DTA,

H_2O) it can be concluded that water was formed in the fast exothermic reaction at the expense of ammonia (ammonia was rapidly oxidized by the nitrate ion giving rise to the exothermic peak). The solid residue at 220° was identified as Co_3O_4.
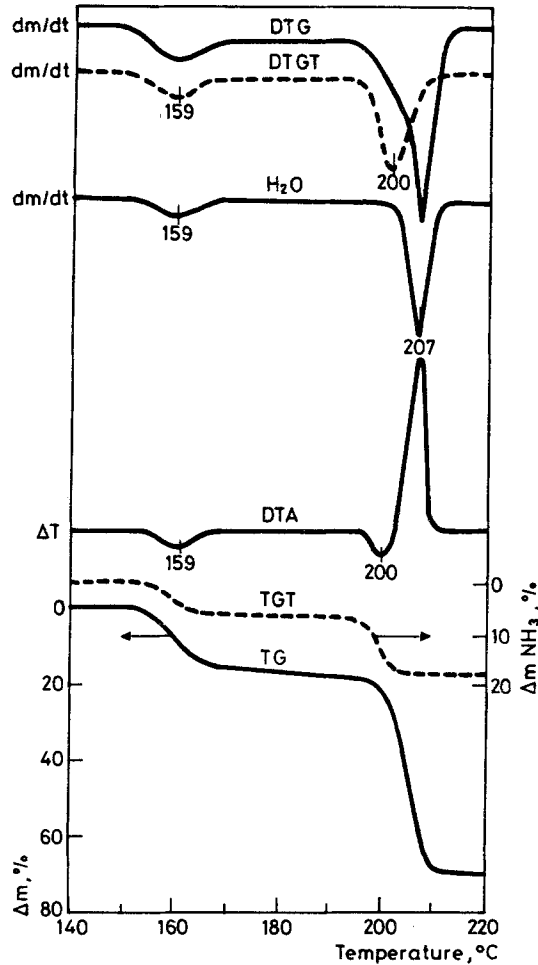

Fig. 1 Thermoanalytical curves of $[Co(NH_3)_5CO_3]NO_3.0.5H_2O$

Figure 2 illustrates the results of the TG-MS measurements. Since it is very confusing to show all the recorded curves in a single diagram, the NH_3, H_2O, and CO_2 curves were selected in addition to the TG and DTG curves

(solid lines). In order to easily observe differences between the recorded curves, the ion intensity curves are shown with equal heights in the same diagram. The ordinate values of the DTG and MS intensity curves are arbitrary and not displayed. Quantitative estimations ragarding the ratio of the gaseous components were made based on the maximum intensity values which are thought to be more reliable especially when background level is high or changing [15]. The shapes of the TG and DTG curves somewhat differ from those of Fig. 1 which can be due to the completely different experimental conditions. These investigations, however, are very important to confirm and identify various decomposition products formed in the reaction. In the TG-MS experiment ammonia is released in three steps. The third step (resulting in a very sharp peak in the ion intensity curve) cannot be found in the TGT and DTGT curves of Fig. 1. This, however, is quite understandable upon considering the much longer residence time of ammonia in the labyrinth crucible, resulting in a much higher rate of conversion for ammonia.
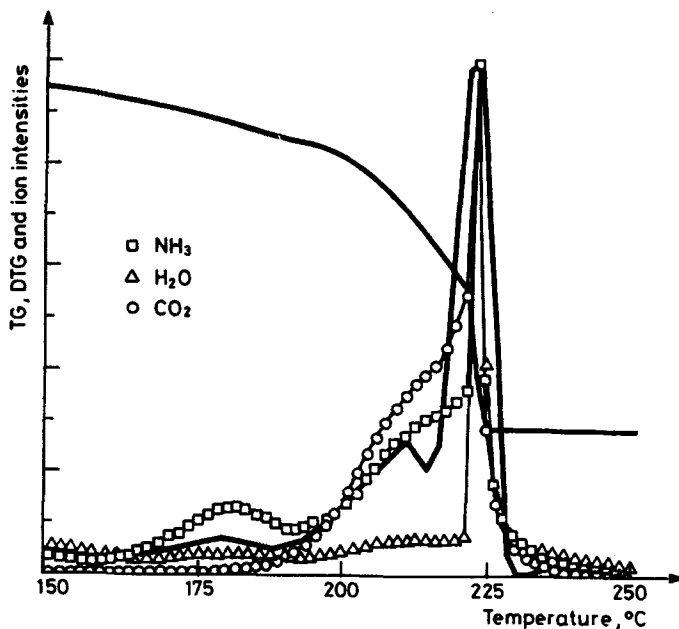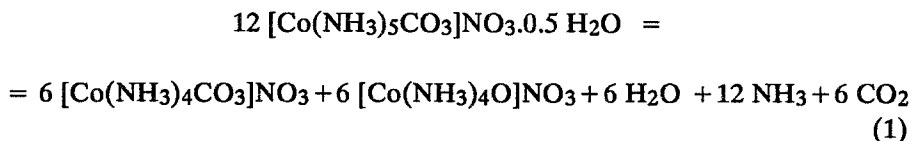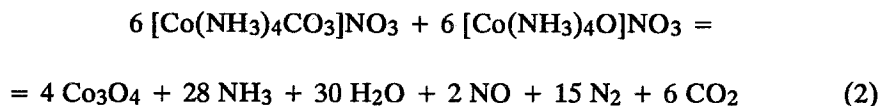

Fig. 2 TG, DTG and ion intensity curves of $[Co(NH_3)_5CO_3]NO_3.0.5H_2O$

The quantitative results of the complex thermoanalytical investigations (thermogastitrimeter and water detector connected to the Derivatograph) are summarized in Table 1. As a conclusion, the following decomposition mechanism can be given for the carbonato-complex:
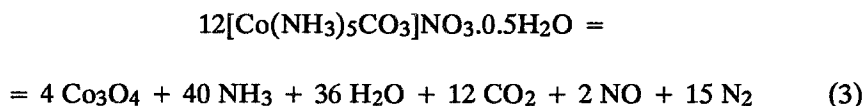
1st step:

$$12 \, [Co(NH_3)_5CO_3]NO_3.0.5 \, H_2O \ =$$

$$= 6 \, [Co(NH_3)_4CO_3]NO_3 + 6 \, [Co(NH_3)_4O]NO_3 + 6 \, H_2O \ + 12 \, NH_3 + 6 \, CO_2 \tag{1}$$

2nd step:

$$6 \, [Co(NH_3)_4CO_3]NO_3 \ + \ 6 \, [Co(NH_3)_4O]NO_3 \ =$$

$$= 4 \, Co_3O_4 \ + \ 28 \, NH_3 \ + \ 30 \, H_2O \ + \ 2 \, NO \ + \ 15 \, N_2 \ + \ 6 \, CO_2 \tag{2}$$

The overall reaction:

$$12[Co(NH_3)_5CO_3]NO_3.0.5H_2O \ =$$

$$= 4 \, Co_3O_4 \ + \ 40 \, NH_3 \ + \ 36 \, H_2O \ + \ 12 \, CO_2 \ + \ 2 \, NO \ + \ 15 \, N_2 \tag{3}$$

The theoretical amount of ammonia released in the reaction (20.64%) is very close to the figure determined by thermogastitrimetry (19.24 % in average). The amount of water obtained by the water detector (16.47%) is lower than the theoretical value (19.64 %) but it is quite acceptable as a confirmatory evidence considering the semi-quantitative nature of the device. The presence of NO was clearly identified by the TG-MS method, showing a profile similar to that of N_2. Traces of NO_2 were also observed. In principle, N_2O can also be formed at the expense of NO. In this case, however, oxygen should be formed, which was observed in a negligible amount, only.

The thermoanalytical curves of the nitro-complex are shown in Fig. 3, and some of the intensity curves obtained in the TG-MS run are given in Fig. 4. The quantitative results of the thermoanalytical investigations are summarized in Table 2. Based on the comparison of the simultaneously recorded thermoanalytical curves of Fig. 3 the following can be concluded. The decomposition reaction takes place in two stages. As to the first step at 156° NH_3 was released but no water formation was observed. The second step shows an overall exothermic reaction at 205°. However, an offset of 6°

Table 1 The amount of ammonia and water released from $[Co(NH_3)_5CO_3]NO_3 \cdot 0.5 H_2O$

No	Sample mass	1st step				2nd step				Total			
		NH₃		H₂O		NH₃		H₂O		NH₃		H₂O	
	mg	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%
1	17.30	1.14	6.59	-	-	2.23	12.89	-	-	3.37	19.48	-	-
2	21.35	1.32	6.18	-	-	2.70	12.65	-	-	4.02	18.83	-	-
3	23.04	1.43	6.21	-	-	3.04	13.19	-	-	4.47	19.40	-	-
4	13.95	-	-	0.39	2.80	-	-	1.78	12.76	-	-	2.17	15.56
5	15.19	-	-	0.50	3.29	-	-	2.03	13.36	-	-	2.53	16.65
6	16.11	-	-	0.53	3.30	-	-	2.24	13.90	-	-	2.77	17.20

Table 2 The amount of ammonia and water released from $[Co(NH_3)_5NO_2](NO_3)_2$

No	Sample mass	1st step NH$_3$		2nd step NH$_3$		2nd step H$_2$O		Total NH$_3$		Total H$_2$O	
	mg	mg	%	mg	%	mg	%	mg	%	mg	%
1	20.45	1.21	5.92	1.94	9.47	-	-	3.15	15.39	-	-
2	20.58	1.02	4.96	2.06	10.00	-	-	3.08	14.96	-	-
3	21.20	1.19	5.61	2.14	10.12	-	-	3.33	15.73	-	-
4	23.05	-	-	-	-	3.01	13.07	-	-	3.01	13.07
5	23.26	-	-	-	-	2.96	12.73	-	-	2.96	12.73
6	23.15	-	-	-	-	3.14	13.57	-	-	3.14	13.57
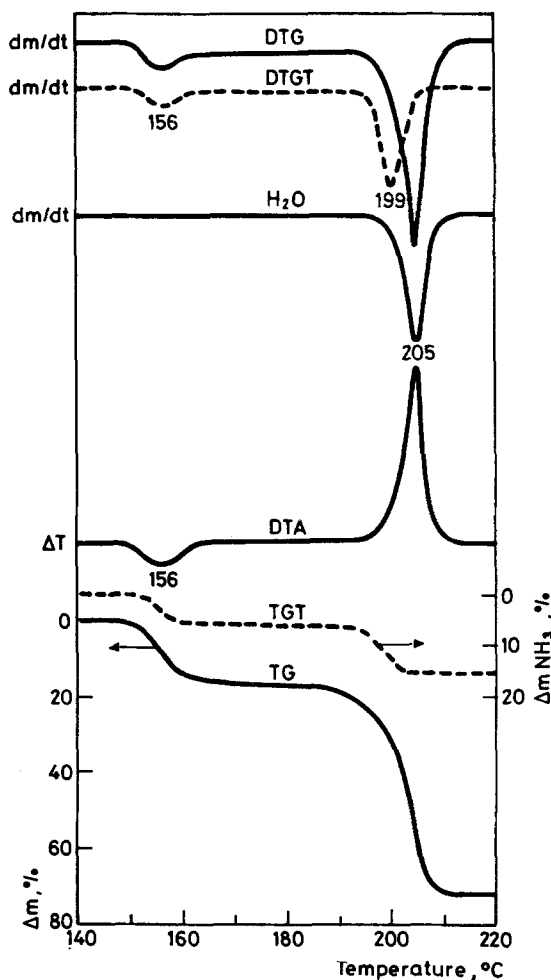
Fig. 3 Thermoanalytical curves of [Co(NH₃)NO₂](NO₃)₂

can be observed between the peak of the DTGT curve (at 199°) and those of the rest curves (DTG, DTA, and H_2O). Again, water was formed in the redox reaction via the oxidation of NH_3 by the nitrate ion. The amount of NH_3 formed during the first step is about one third of the observed mass loss. The TG-MS experiment, however, revealed that at the early stage of decomposition N_2O and O_2 was also formed, along with the release of NH_3 (Fig. 4). The amount of NO was negligible in this phase. At higher tempera-
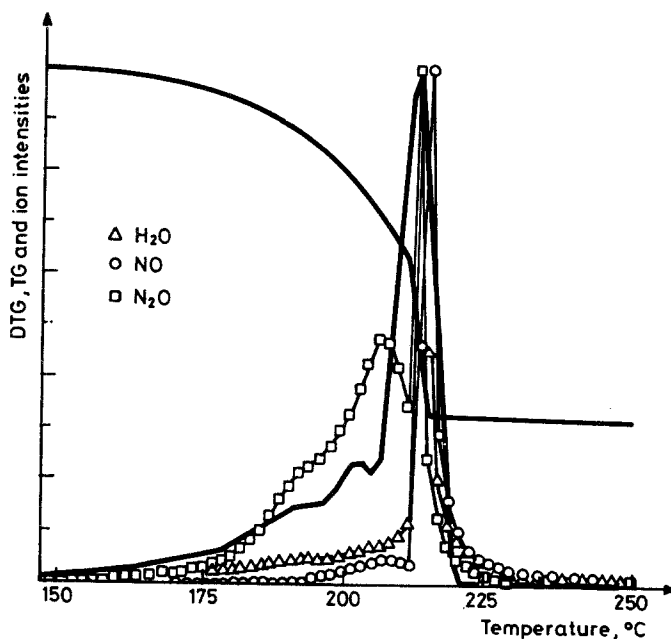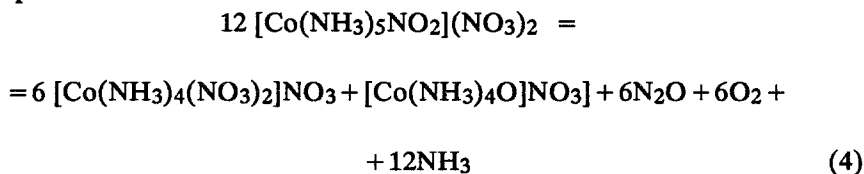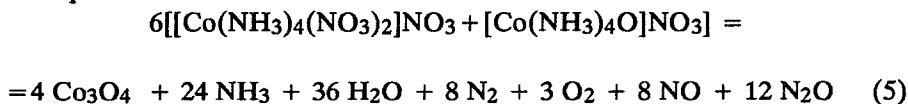
Fig. 4 TG, DTG and ion intensity curves of $[Co(NH_3)_5NO_2](NO_3)_2$

tures the reaction is finished rapidly. Water, O, N_2, NO, O_2, and N_2 are found among the decomposition products. Based on the qualitative information regarding the nature of the decomposition products (together with the quantitative figures of Table 2) as well as the intensity ratios of the recorded MS-curves the following decomposition mechanism can be proposed for the two-staged reaction of the nitro-complex:
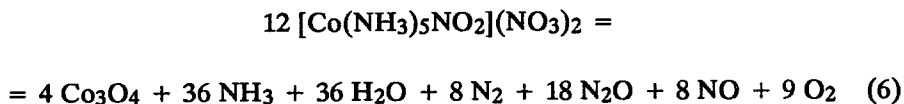
1st step:
$$12\,[Co(NH_3)_5NO_2](NO_3)_2 =$$

$$= 6\,[Co(NH_3)_4(NO_3)_2]NO_3 + [Co(NH_3)_4O]NO_3] + 6N_2O + 6O_2 +$$

$$+ 12NH_3 \tag{4}$$

2nd step:
$$6[[Co(NH_3)_4(NO_3)_2]NO_3 + [Co(NH_3)_4O]NO_3] =$$

$$= 4\,Co_3O_4 + 24\,NH_3 + 36\,H_2O + 8\,N_2 + 3\,O_2 + 8\,NO + 12\,N_2O \tag{5}$$

the overall reaction:

$$12 \ [Co(NH_3)_5NO_2](NO_3)_2 \ =$$

$$= \ 4 \ Co_3O_4 \ + \ 36 \ NH_3 \ + \ 36 \ H_2O \ + \ 8 \ N_2 \ + \ 18 \ N_2O \ + \ 8 \ NO \ + \ 9 \ O_2 \quad (6)$$

Depending on the experimental conditions, the N_2O/NO ratio can vary which is taken into account in Eq. 7:

$$6 \ [Co(NH_3)_5NO_2](NO_3)_2 \ =$$

$$2 \ Co_3O_4 \ + 18 \ NH_3 + 18 \ H_2O + 4 \ N_2 + XN_2O + 2 \ (22\text{-}X)NO + 0.5 \ X \ O_2 \quad (7)$$

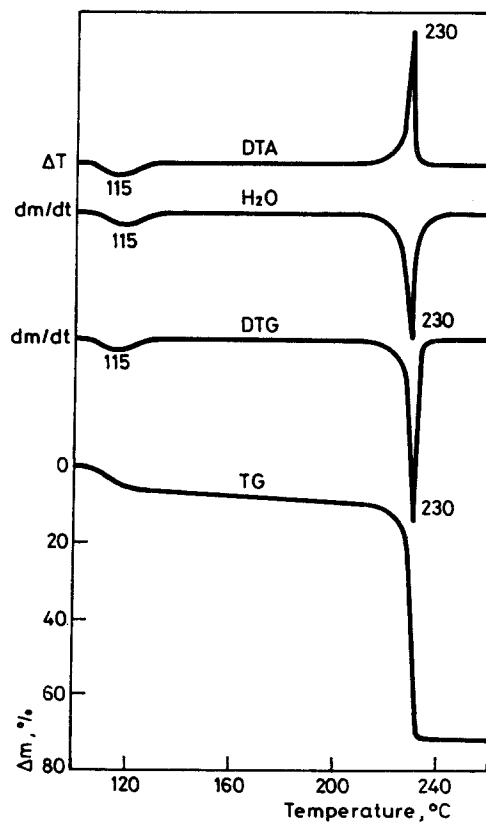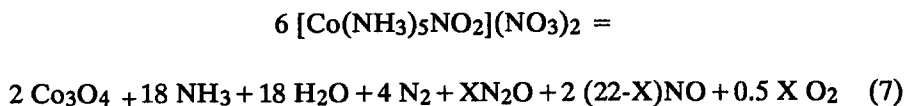Fig. 5 Thermoanalytical curves of $[Co(NH_3)_5H_2O](NO_3)_3$

where $0 \leq X \leq 22$

The terminal solid residue was identified as Co_3O_4. The amount of ammonia formed (15.36 % in average) is close to the theoretical value (16.27 %). The difference between the observed and theoretical values of water (13.12 % average and 17.21 %, respectively) is considerable, which can be due to the semi-quantitative nature of the water detector.
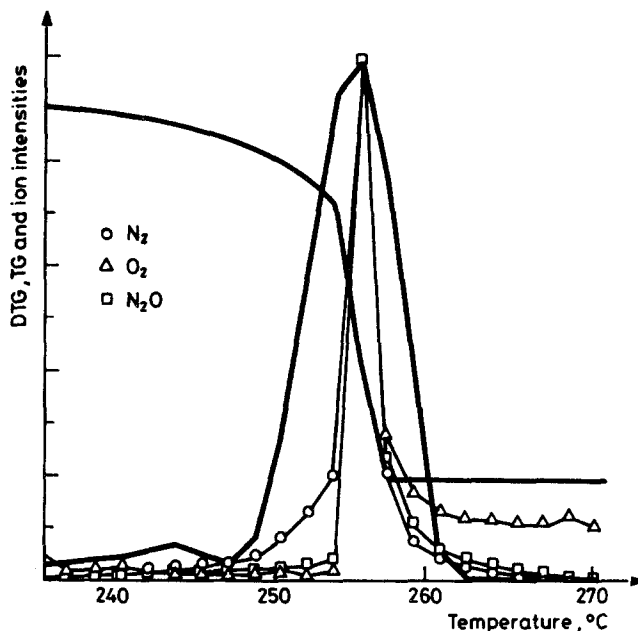

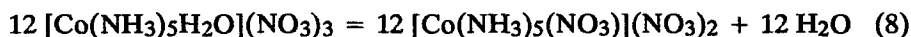Fig. 6 TG, DTG and ion intensity curves of [Co(NH3)5H2O](NO3)3

The thermal decomposition curves of the aquo-complex are shown in Fig. 5. The TG, DTG as well as the ion intensity curves of N_2O, O_2, and N_2 obtained during the TG-MS run are given in Fig. 6. The quantitative results are summarized in Table 3.

The first decomposition step at 115° belongs to the deaquation of the complex [1]. This relatively slow process was followed by a very rapid mass loss at 230°. Similarly to the decomposition of the nitro-complex NH_3, H_2O, N_2O, NO, N_2, and O_2 were present among the decomposition products. A precise determination of NH_3 was possible by the titrimetric method, but quantitative results of the water determination were ignored (due to the
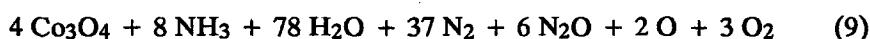
high concentration of water vapour in the carrier gas a tailing was observed in the H_2O - curve causing a positive error during integration).

Based on the experimental results obtained the thermal decomposition of the aquopentammine-complex can be described as follows:
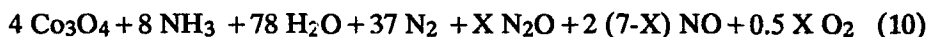
1st step:

$$12 \, [Co(NH_3)_5H_2O](NO_3)_3 = 12 \, [Co(NH_3)_5(NO_3)](NO_3)_2 + 12 \, H_2O \quad (8)$$

2nd step:
$$12 \, [Co(NH_3)_5NO_3](NO_3)_2 =$$

$$4 \, Co_3O_4 + 8 \, NH_3 + 78 \, H_2O + 37 \, N_2 + 6 \, N_2O + 2 \, O + 3 \, O_2 \quad (9)$$

Considering the possible changes of the N_2O/NO ratio, the overall reaction in a more general form is

$$12 \, [Co(NH_3)_5NO_3](NO_3)_2 =$$

$$4 \, Co_3O_4 + 8 \, NH_3 + 78 \, H_2O + 37 \, N_2 + X \, N_2O + 2 \, (7\text{-}X) \, NO + 0.5 \, X \, O_2 \quad (10)$$

where $0 \le X \le 7$

The amount of ammonia obtained by titration (2.96 % in average) is in a good agreement with the theoretical value (3.26 %). Since Co_3O_4 was obtained as the solid residue, the amounts of H_2O and N_2 are determined by the stoichiometry of the reaction.

Table 3 The amount of ammonia released from $[Co(NH_3)_5H_2O](NO_3)_3$

No	Sample mass	Ammonia		Average
	mg	mg	%	%
1	20.70	0.664	3.21	
2	20.97	0.527	2.52	2.96
3	22.16	0.749	3.38	
4	20.54	0.561	2.73	

The above equations describe the decomposition of these complexes at a given set of experimental conditions. If these conditions (e.g. crucible type, sample amount, heating rate, etc.) are changed, the decomposition products will probably be the same, but their amounts will be different.

Conclusions

With the use of simultaneous TG, DTG, DTA measurements (Derivatograph), termogastitrimetry, continuous selective water detector, and TG-MS equipment it is possible to reveal the subtle decomposition mechanism of crystalline cobaltpentammine(III) complexes in spite of the rapid processes.

Although the nature of the decomposition products was determined long ago by mass spectrometric measurements [1], the second step of the reaction was not known with any degree of certainty. It is the quantitative termogastitrimetric determination of ammonia - along with EGA results obtained by various methods - which led to the description of the decomposition mechanism.

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Zusammenfassung — Mittels simultaner TG, DTG, DTA (Derivatograph-C), weiterhin mittels Thermogastitrimetrie, kontinuierlicher selektiver Wasserdetektierung, TG-MS und XRD-Verfahren wurde die thermische Zersetzung der Komplexe [Co(NH3)5CO3]NO3, [Co(NH3)5NO3](NO3)2 und [Co(NH3)5H2O](NO3)3 untersucht.

Wegen dem beinahe explosiven Verlaufes der Reaktion dieser Komplexe wurden die Proben in einem Labyrinth-Tiegel in zehnfacher Verdünnung mit Aluminiumoxid erhitzt.

Mittels der quantitativen Bestimmung von NH3 und H2O war es möglich, die komplizierte Zersetzungsreaktion dieser Komplexe aufzuklären.

Ausgehend von den mit Hilfe der verschiedenen thermoanalytischen Verfahren erhaltenen qualitativen und quantitativen Ergebnissen wurden die Zersetzungsgleichungen für beide Reaktionsschritte gegeben.