

THERMAL DECOMPOSITION OF $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Part I. Non-isothermal, quasi-isothermal and scanning electron microscopy studies

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The thermal decomposition reactions of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ were determined in dynamic argon and air atmospheres. The investigations were carried out with simultaneous TG-DTG-DTA measurements under non-isothermal conditions, thermogravimetry under quasi-isothermal conditions, reflectance spectroscopy, absorption spectroscopy, X-ray diffraction and chemical analysis. The data show that the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ occurs in three and four stages in argon and air atmospheres, respectively. The determined sequences are in agreement with that proposed by Simons and Wendlandt [2, 5].

The changes in the morphology of the studied complex crystalline powder in the course of thermal decomposition in air were followed by scanning electron microscopy.

The thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ has been studied by different methods since 1913 [1, 2]. A review of the works published on this subject up to 1966 was given by Wendlandt and Smith [2]. Since then, the thermal decompositions of cobalt(III) ammine complexes, including $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, have continued to be investigated. The overall reaction:



suggested by Clark in 1920 [2, 3] is unanimously accepted. It is also well known that CoCl_2 is a stable intermediate in the solid phase and that the reduction of Co(III) to Co(II) proceeds in the first stage of the complex dissociation [2–12].

However, either ammonia coordinated in the inner sphere of the complex [2–7] or chloride ion [8–11] is recognized as a reductant. Papers [6, 8–11] are mainly concerned with the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in vacuum. Tanaka suggested [9] that chloride was also evolved when an air atmosphere was used, although he did not confirm this experimentally.

Evolved gas analysis by mass-spectrometric [4, 6, 10–12] or gas chromatography methods [7] has not clarified the conflicting nature of the above problem. Certain authors [4, 6, 7, 12] detected NH_3 and N_2 in the gaseous products evolved and indicated that their amounts were fairly consistent with the stoichiometric relation given in Eq. (1).

In the mass spectra of the gases evolved from $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ presented by Boldyreva et al. [10] and Collins and Wendlandt [6], peaks due to ammonia and nitrogen were observed. Additional peaks appeared at m/e 35 and 37 [10], which were interpreted as due to Cl^+ isotopes, while the peak at m/e 36 [6] was ascribed to HCl . Tanaka [9] and Boldyreva [10, 11] suggested that the nitrogen present in the gaseous phase is a product of secondary reactions of ammonia and chlorine. There is as yet no accepted view as to the sequence of the thermal decomposition reactions of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, the nature of the reduction agent, and the identity of the intermediates in the solid and gaseous phases.

The amminecobalt(III) complexes appear interesting as intermediates in cobalt recovery technology [13].

In the present work, the thermal decomposition sequences of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ have been studied in air and argon atmospheres under non-isothermal conditions. Additional investigations under quasi-isothermal conditions have been carried out. The changes in the morphology of crystalline $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ powder were followed in the course of thermal decomposition in air.

Experimental

Materials

All reagents were of AnalaR grade. Hexaamminecobalt(III) chloride was prepared by the method described in [14]. The starting compound was characterized via the methods of elemental analysis. The results of the analysis were: Co, 23.34% found, 22.03% calc.; H, 6.80% found, 6.78% calc.; N, 30.81% found, 31.42% calc.; Cl, 39.05% found, 39.77% calc.

A sieve mesh of ≤ 0.060 mm was used.

Methods

Simultaneous TG–DTG–DTA curves under non-isothermal conditions were obtained with a Paulik–Paulik–Erdey 3427-t derivatograph at 293–1273 K with different linear heating rates ($\beta = 10, 5, 2.5$ and 1.25 deg/min) in flowing air and argon atmospheres. The sample weight was 200 mg. Crucibles of alumina were

used both for the specimen and for the reference material, which was calcined alumina.

Quasi-isothermal measurements were carried out on a Paulik–Paulik–Erdey Derivatograph Q–1500D in the temperature range 293–1273 K. QTG curves were recorded in air and nitrogen atmospheres at a linear heating rate $\beta = 3$ deg/min, and the rate of transformation was 0.4 mg/min. A 200 mg sample was placed in a covered crucible.

X-ray patterns of the solid final residues were obtained on a DRON–2 (USSR) diffractometer with a CoK_α radiation lamp.

Electron scanning micrographs were made with a Stereoscan 180 Cambridge apparatus.

Reflectance spectra of the solids were recorded in the range 800–200 nm on a Hitachi M 356 spectrophotometer. The reference material was magnesium oxide.

Absorption spectra of investigated solutions were recorded on a SPECORD M40 spectrophotometer.

Results and discussion

The profiles of TG and/or DTA curves obtained in these investigations are generally in agreement with those presented in the literature [2, 4, 12, 15]. The thermoanalytical data obtained show that the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ proceeds in three stages in argon atmosphere, and in four stages in air. The temperature ranges and percentage mass losses of the particular decomposition stages are given in Table 1. The temperatures of greatest rate of decomposition (DTG_{max}), the theoretical percentage mass losses and the DTA data are also given.

Table 1 Thermoanalytical results (TG–DTG–DTA) on $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in air and argon atmospheres. Heating rate 1.25 deg/min

Stage	Temp. range, K	DTG_{max} , K	DTA peak temp., K	Weight loss, %		Composition of residue	Atmosphere
				observ.	theor.		
I	423– 553	533	535	33.0	31.6	$\text{CoCl}_2 + (\text{NH}_4)_2[\text{CoCl}_4]$	air
	423– 553	533	533	33.0	31.6		$(\text{NH}_4)_2[\text{CoCl}_4]$
			545	548			
II	553– 628	618	623	20.0	19.9	CoCl_2	air
	553– 628	620	623	20.0	19.9	CoCl_2	argon
III	673– 913	878	880	18.0	18.5	Co_3O_4	air
	678–1018	1015	1015	21.0	subl.	CoCl_2	argon
IV	1213–1228	1223	1223	2.0	2.2	CoO	air

All the decomposition reactions are endothermic in both air and argon. For the first and second stages of the investigated complex dissociation, all the thermoanalytical parameters (see Table 1) are identical. It may be assumed that the transitions occurring are independent of the gaseous atmosphere. However, for the third stage the observed temperature parameters and weight losses are clearly different in air and argon. The fourth stage of dissociation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ has been observed only in air atmosphere.

These data are generally consistent with those published earlier [2, 4, 5, 15–17]. The temperatures of the DTA peaks (stages I and II) are close to those reported by Wendlandt (553: 648 K—He atm.) and Watt (567: 614— N_2 atm.) [2, 4, 12, 15].

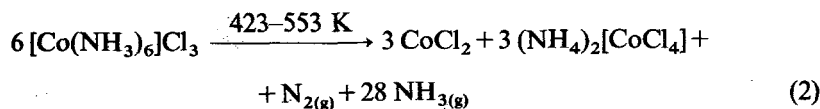
Table 2 Quasi-isothermal analysis data (QTG) on $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in air and nitrogen atmospheres. Heating rate 3 deg/min; rate of transformation 0.4 mg/min

Stage	Temp. range, K	Weight loss, %		Composition of residue	Atmosphere
		observ.	theor.		
I	458–526	31.5	31.6	$\text{CoCl}_2 + (\text{NH}_4)_2[\text{CoCl}_4]$	air
	447–548	30.4	31.6	$\text{CoCl}_2 + (\text{NH}_4)_2[\text{CoCl}_4]$	nitrogen
II	526–600	21.5	19.9	CoCl_2	air
	548–633	20.5	19.9	CoCl_2	nitrogen
III	600–915	18.0	18.5	Co_3O_4	air
	886–1117	26.7	subl.	$\text{CoCl}_2 + \text{Co}_{\text{met}} + \text{CoO}$	nitrogen

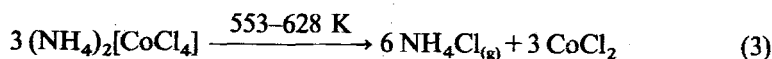
The thermogravimetric results obtained for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition under quasi-isothermal conditions (Table 2) in air and nitrogen atmospheres confirm the non-isothermal experimental data. The inflection points and weight losses observed in TG and QTG measurements during the first and second stages are in accordance with the mechanism of Simons and Wendlandt for the decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ [2, 5]. It is commonly known and has been confirmed that all reactions of thermal decomposition of ammine- and aminocobalt(III) complexes involve the reduction of Co(III) to Co(II) [2, 4, 12, 15–18].

The probable decomposition sequences of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are:

stage I (air, argon):



stage II (air, argon):



The presence of $(\text{NH}_4)_2[\text{CoCl}_4]$ as a component of the solid intermediate near the end of the first dissociation stage was confirmed by spectroscopic measurements. In the course of heating of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ under quasi-isothermal conditions at 493 K (weight loss = 26%), i.e. near the end of the first stage of decomposition deep-blue species were isolated, suggesting the presence of a tetrahedral cobalt(II) compound; in particular a tetrahedral cobaltate(II) anionic complex should be suspected. The reflectance spectrum of the blue products formed during decomposition is shown in Fig. 1. The presence of a tetrahedral cobalt(II) complex is clearly indicated by the strong absorption in the region 750–600 nm, with the asymmetric band at 690 nm [${}^4A_2 \rightarrow {}^4T_1(\text{P})$]. This spectrum is generally in agreement with the data presented by Simons and Wendlandt [5]. The same region of absorption is observed, but the profile of the spectrum differs slightly.

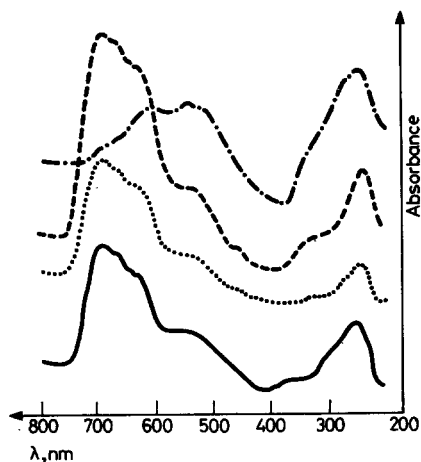


Fig. 1 Reflectance spectra of some cobalt(II) compounds. — · · · · · mechanically mixed $\text{CoCl}_2 + \text{NH}_4\text{Cl}$ mixture, · · · · · $(\text{NH}_4)_2[\text{CoCl}_4]$, — — — — 1 : 1 mixture of $\text{CoCl}_2 + (\text{NH}_4)_2[\text{CoCl}_4]$, — — — — decomposition products of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ at 493 K

It should be noted that the colour of the intermediate is different (a deep-purple was observed by Simons and Wendlandt). The purple colour may have been due to the hydration of $(\text{NH}_4)_2[\text{CoCl}_4]$. The spectra of $(\text{NH}_4)_2[\text{CoCl}_4]$ a 1 : 1 mixture of $\text{CoCl}_2 + (\text{NH}_4)_2[\text{CoCl}_4]$, both prepared as in [5] and a mechanically mixed 1 : 1 mixture of $\text{CoCl}_2 + \text{NH}_4\text{Cl}$ are also presented for comparison. Except for the last one, the spectra of these compounds are almost identical with that observed for the decomposition residue at 493 K. The spectrum of the residue dissolved in dioxane solution (blue colour) was also measured (Fig. 2). The absorption band observed at 685 nm indicates the presence of CoCl_4^{2-} [19], and the second one at 591 nm is characteristic of CoCl_2 solutions [19]. The presence of $(\text{NH}_4)_2\text{CoX}_4$ as a solid

intermediate of the decomposition of cobalt(III) ammine- and amine complexes was confirmed by several investigators [2, 4-6, 16, 20].

In the third stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ dissociation in air, the reaction of cobalt(II) chloride with oxygen is followed by the evolution of chlorine, and Co_3O_4 is formed as a stable solid residue. In the fourth stage, Co_3O_4 is transformed to CoO , which is in agreement with the literature data [16, 21].

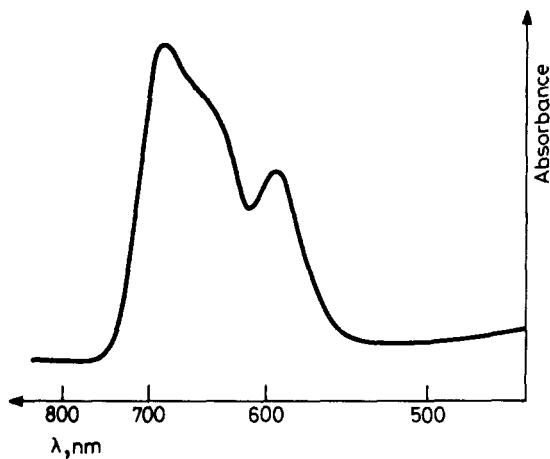
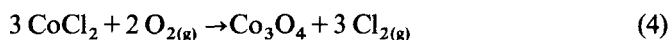


Fig. 2 Absorption spectrum of dioxane solution of the decomposition product of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ at 493 K

The evolution of chlorine was confirmed by a standard method. The complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was decomposed by heating from ambient temperature to 1200 K under dynamic heating conditions. The gaseous products evolved were absorbed in 0.1 M KI solution. The beginning of chlorine evolution was observed above 700 K.

The X-ray pattern confirmed that the final product of the third stage of decomposition is Co_3O_4 (Fig. 3).

The reactions of stages III and IV in air were found to be:



In the course of the third stage in flowing argon atmosphere, CoCl_2 appears to sublime. There is probably some reduction of CoCl_2 to give trace amounts of cobalt metal as residue. Single crystallites of cobalt metal are visible on the walls of the blue-coloured crucible. However, a small quantity of solid blue residue found in the crucible had the X-ray pattern of CoCl_2 (Fig. 3).

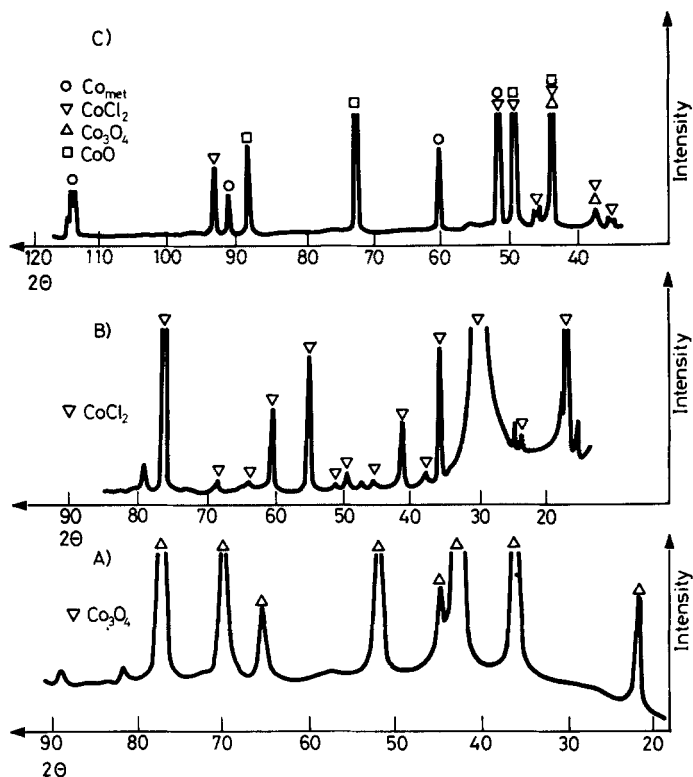


Fig. 3 X-ray patterns of final products of third stage of decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. a) in air — non-isothermal conditions, b) in argon — non-isothermal conditions, c) in nitrogen — quasi-isothermal conditions

The third stage in flowing argon is:



The observed blue tint of the alumina crucible is caused by the formation of Thenard's blue, i.e. CoAl_2O_4 .

If the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is carried out under quasi-isothermal conditions (covered crucible, N_2 atm.), the solid residue at the end of stage III is a mixture of CoCl_2 , CoO and Co metal, as revealed by an X-ray diffractogram (Fig. 3). On the blue walls of the crucible, numerous, glossy-grey, single grains were observed. This is illustrated in the micrograph (Fig. 4). Electron probe microanalysis of the individual grains on the walls of the crucibles in both cases (Ar , N_2 atm.) indicated the presence of cobalt only. The presence of cobalt metal in the final solid residue of the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in an

inert gas atmosphere may be caused by secondary reactions of CoCl_2 with reducing agents remaining in the system, i.e. NH_3 or HCl . It may be assumed that cobalt metal forms as a result of reaction [7], for which $\Delta G^\circ = -60.92 \text{ kJ}$ at 800 K. ΔG° was calculated from the data in [22].

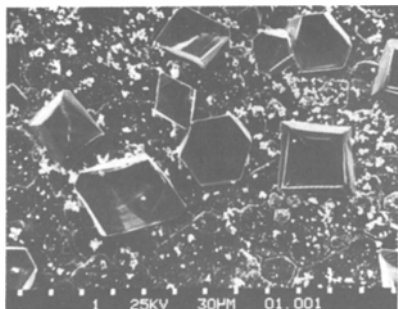
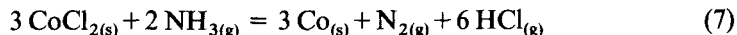


Fig. 4 Scanning electron micrograph of single Co metal grains formed at end of third stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in nitrogen and argon atmospheres

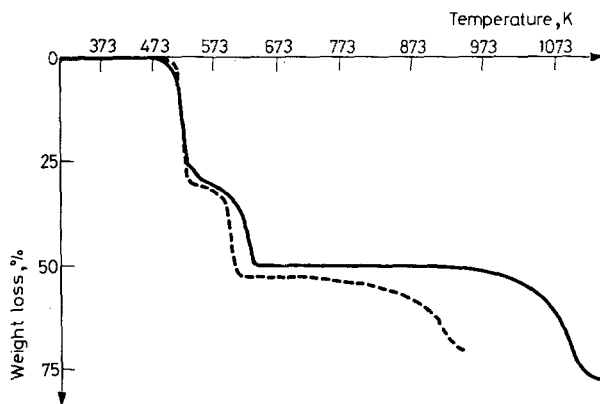


Fig. 5 QTG curves of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ - - - - in air, ——— in nitrogen

One purpose of a scanning microscopy investigation was to recognize the changes in the morphology of crystalline $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ powder in the course of its thermal decomposition in air at 298–953 K. On the basis of the QTG curve (Fig. 5), the solid intermediates which were the final residues after the particular stages of substrate decomposition (stages I–III) were isolated from the system investigated. Samples of the hexaammine complex were heated under quasi-isothermal conditions up to the temperatures listed in Table 3. The process was then

Table 3 Samples for scanning electron microscopy analysis

Stage	Weight loss, %	Temp., K	Colour	Intermediate
I	26.0	523	blue-green	<i>A</i>
	30.8	548	deep-blue	<i>B</i>
II	51.2	608	blue	<i>C</i>
III	70.0	953	black	<i>D</i>

interrupted, and after quenching an intermediate was prepared for microscopic measurements.

The scanning electron micrographs of the substrate and investigated intermediates are presented in Figs 6–10. The results showed that, even in the first stage of the thermal decomposition, the morphological orientation of the substrate was clearly distorted. Cracking of the crystallites and the formation of numerous pores of different sizes were observed (intermediate *A*—Fig. 7). These changes in morphology were probably caused by the intensive evolution of the gaseous products of decomposition, i.e. NH_3 and N_2 . The changes observed in the morphology of the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ crystallites are similar to those presented by Boldyreva et al. [10, 11] for the isothermal decomposition of monocrystals of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in vacuum at 493 K.

At the end of the first stage of decomposition, two morphological forms of intermediate *B* may be distinguished. They are both strongly porous, and one of them shows parallel stratification and a more compact structure (Fig. 8).

The changes observed in the morphology of the intermediates (*A*, *B*) with regard to the substrate are in agreement with the chemical process occurring in the first stage of the decomposition. The complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ yields to decomposition gradually. Reduction of the central ion $\text{Co}(\text{III})$ to $\text{Co}(\text{II})$ and the elimination of NH_3 disturb the octahedral structure and change both the shape and the size of the


Fig. 6 Scanning electron micrographs of crystalline $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ powder (magnification $3000\times$)

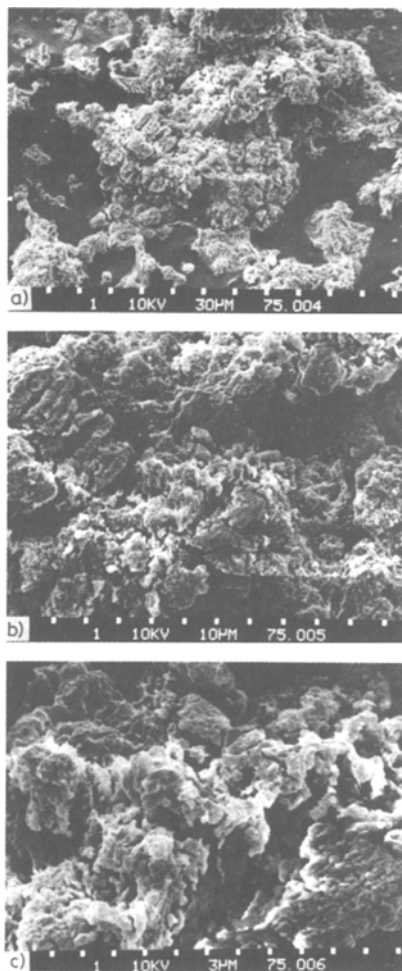


Fig. 7 Scanning electron micrographs of intermediate *A* – first stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in air. a) Magnification $300\times$, b) magnification $1000\times$, c) magnification $3000\times$

$[\text{Co}(\text{NH}_3)_6]^{3+}$ ion. This can create local stress in the crystallite and its cracking, which was in fact observed (see Figs 6–8). The final product of the first stage of decomposition is a mixture of CoCl_2 (octahedral structure) and $(\text{NH}_4)_2[\text{CoCl}_4]$ (tetrahedral structure). Two forms of intermediate *B* were observed.

Intermediate *C*, the final product of the second stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition, appears to have a more compact structure and smaller crystallites relative to intermediates *A* and *B*. However, numerous crevices and pores or even cavities are still observed (Fig. 9). At this stage, the gaseous products continue to be

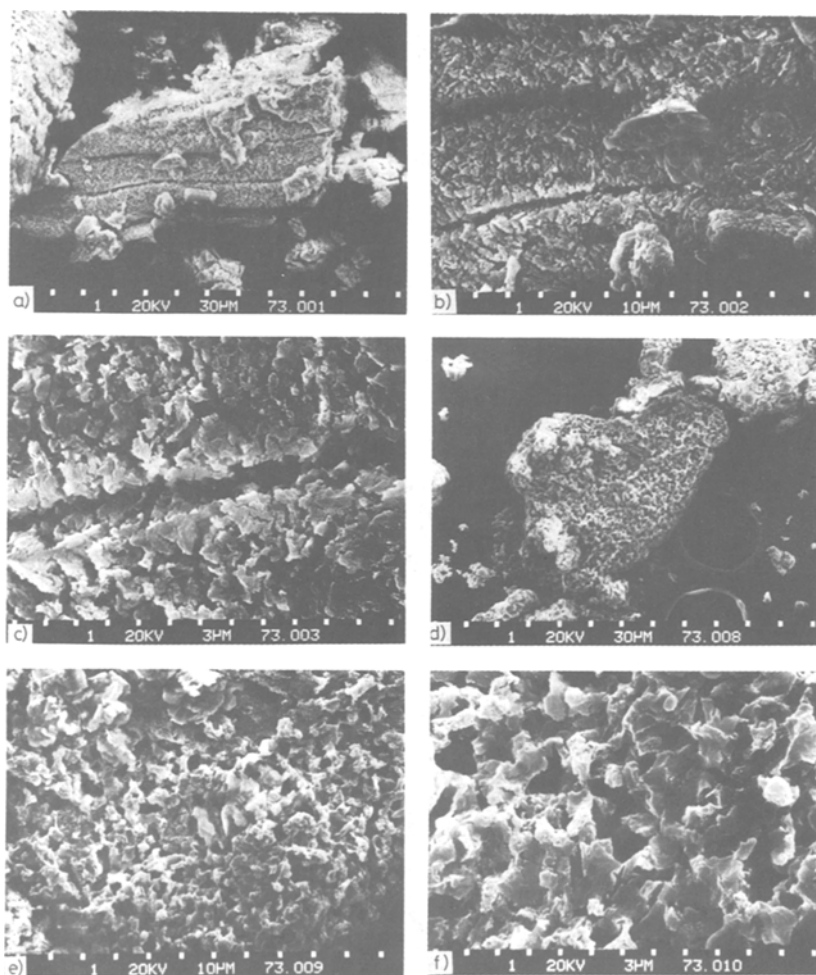


Fig. 8 Scanning electron micrographs of intermediate *B* – final residue of first stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in air; form I: a) magnification $300\times$, b) magnification $1000\times$, c) magnification $3000\times$; form II: d) magnification $300\times$, e) magnification $1000\times$, f) magnification $3000\times$

evolved, i.e. NH_4Cl . The compacting of the intermediate *C* structure may be a result of the sintering process (with the share of a liquid phase). These results conform with the data of Watt [4], who observed a blue liquid as an intermediate at 562–573 K.

The end-product of the third stage of decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Co_3O_4 as confirmed by the x-ray pattern) clearly has a crystal structure (Fig. 10). There is an octahedron of different size, this being one of the regular system shapes [23]. The

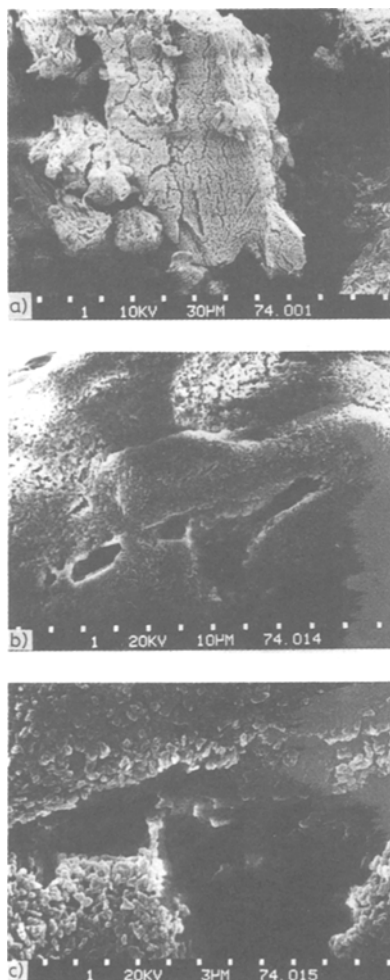


Fig. 9 Scanning electron micrographs of intermediate *C* – final residue of second stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in air. a) Magnification $300\times$, b) magnification $1000\times$, c) magnification $3000\times$

micrographs (Fig. 10) illustrate nucleation and liberation of the nucleus from the face of the crystals. The above results show no topotactic decomposition behaviour of the complex under investigation. This is in contrast with the data presented by Boldyreva et al. [10, 11], who found a topotactic transformation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ monocrystals decomposed in air atmosphere at 443 K. On the other hand, Oswald and Gunter [23] observed no topotactic decomposition behaviour for the octahedral complex $\text{Ni}(\text{SCN})_2(\text{NH}_3)_4$.

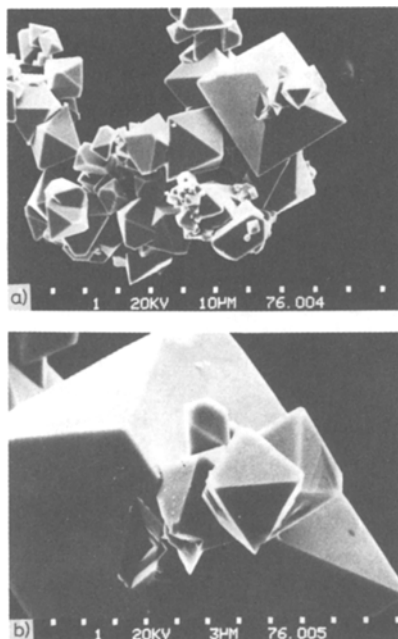


Fig. 10 Scanning electron micrographs of intermediate *D* – final residue of third stage of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ decomposition in air. a) Magnification $1000\times$, b) magnification $3000\times$

Conclusions

1. The thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ occurs in three and four stages in argon and air atmospheres, respectively.
2. The courses of the first and second stages of decomposition are the same in the two atmospheres. The sequences determined are in agreement with that proposed by Simons and Wendlandt [2, 5].
3. The third stage of the decomposition differs in air and argon atmospheres.
4. The thermal decomposition of the polycrystalline $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in air atmosphere is not a topotactic process.

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Zusammenfassung — In bewegter Argon- und Luftatmosphäre wurden die Zersetzungsreaktionen für $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ bestimmt. Zu den Untersuchungen wurden folgende Methoden zu Hilfe gezogen: simultane TG-DTG-DTA-Messungen unter nichtisothermen Bedingungen, Thermogravimetrie unter quasi-isothermen Bedingungen, Remissionsspektroskopie, Absorptionsspektroskopie, Röntgendiffraktion und chemische Analyse. Die Ergebnisse zeigen, daß sich $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in Argon in drei und in Luft in vier Schritten thermisch zersetzt. Die festgestellten Sequenzen stehen in Übereinstimmung mit den von Simon und Wendlandt [2, 5] vorgeschlagenen. Veränderungen in der Morphologie des untersuchten Komplexkristallpulvers wurden über die thermische Zersetzung in Luft mittels Scanning-Elektronen-Mikroskopie beobachtet.

Резюме — В динамической атмосфере аргона и воздуха определены реакции термического разложения комплекса $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. Исследования были проведены с помощью совмещенного ТГ, ДТГ и ДТА метода в неизотермических условиях, метода термогравиметрии в квази-изотермических условиях, спектроскопии отражения, абсорбционной спектроскопии, рентгеноструктурного и химического анализа. Полученные результаты показали, что термическое разложение комплекса в атмосфере аргона и воздуха протекает, соответственно, в три и четыре стадии, последовательность которых согласуется с таковой, предложенной Симонсом и Вепдландом. Используя сканирующую электронную микроскопию прослежено морфологическое изменение порошкообразного комплекса в ходе его термического разложения в атмосфере воздуха.