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STUDIES ON THE THERMAL DECOMPOSITION OF THE SODIUM GROUP OF ALKALI METAL NITRITOCOBALTATES(III)

A. CYGAŃSKI

Institute of General Chemistry, Technical University, 90-924 Łódź (Poland)

A. FURMANIAK

Institute of Occupational Medicine, 90-950 Łódź (Poland)

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ABSTRACT

Nitritocobaltates(III) of the sodium group of general formula $M_2Na[Co(NO_2)_6]\cdot H_2O$ ($M = K^+$, NH_4^+, Rb^+), $Na_3[Co(NO_2)_6]$ and $Cs_3[Co(NO_2)_6]$ have been the subject of this investigation. The mechanism of thermal analysis has been determined on the basis of the thermal curves of the compounds investigated, and the chemical, diffractometric and IR spectrophotometric analysis. The compounds investigated have been divided into two groups differing in decomposition products at 300°C (presence or absence of sodium nitrite). Sodium, potassium and rubidium nitritocobaltates are included in the first group, and the other consists of caesium and ammonium nitritocobaltates. In both groups, however, during the thermal decomposition Co_3O_4 is the central ion. The influence of outer-sphere cations on the change in thermal stability of nitritocobaltates(III) of the sodium group has been determined. The sodium and silver group nitritocobaltates have also been compared with respect to their thermal stability.

INTRODUCTION

Nitritocobaltates(III) containing sodium have been investigated. Depending on their composition they can be divided into a single salt, $Na_3[Co(NO_2)_6]$, and double salts of the general formula $M_2Na[Co(NO_2)_6]$ ($M = K^+$, NH_4^+, Rb^+). A single caesium salt, $Cs_3[Co(NO_2)_6]$, which formally does not belong to this group but is isostructural with the sodium salt, has also been included here.

The thermal decomposition of nitritocobaltates of the sodium group has previously been investigated by Duval and Wendlandt. Duval [1] presented the thermogravimetric curve for $(Rb, Na)_3[Co(NO_2)_6]\cdot n\ H_2O$ and discovered the presence of CoO, $RbNO_3$ and $NaNO_3$ at 283–550°C. The course of the decomposition of caesium nitritocobaltate described by this author results in the formation of CoO and $CsNO_3$ at 219–494°C. The description of the thermal decomposition of potassium nitritocobaltate is not explicit.

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While the temperature increases, the compound is decomposed either into a mixture of CoO and KNO_3 or KNO_2 and CoO, depending on the method of obtaining the precipitate, $K_3[Co(NO_2)_6]$ [1]. Duval also described the thermal decomposition of $Na_3[Co(NO_2)_6] \cdot H_2O$ [2]. During heating, the compound loses one molecule of water, and at 123°C, loses three molecules of nitric dioxide. At 300°C the mixture is composed of CoO and $NaNO_2$, and at 560°C Duval identified the presence of CoO and $NaNO_3$. Further increase in temperature results in the decomposition of sodium nitrate into sodium monoxide.

Wendlandt and Southern [2] presented a different course for the decomposition of sodium nitritocobaltate. While $Na_3[Co(NO_2)_6]$ is heated to a temperature of $> 200°C$ it is decomposed into Co_3O_4 and $NaNO_2$, and then at 600–800°C sodium nitrite is decomposed into sodium monoxide.

So far, however, the thermal decomposition of ammonium–sodium nitritocobaltate has not been examined.

Nitritocobaltates forming double salts of formula $M_2Na[Co(NO_2)_6] \cdot H_2O$ ($M = K^+$, NH_4^+, Rb^+) were obtained by Wilcox's method, precipitating potassium, ammonium or rubidium salts by means of sodium nitritocobaltate solution [3]. Caesium nitritocobaltate was obtained by hot-precipitation of caesium salts by means of an agent prepared 24 h before use by mixing water solutions of $Co(NO_3)_2$ and $NaNO_2$ [4]. The nitritocobaltates obtained are salts containing one molecule of water. It was confirmed by an examination of its composition, as carried out by Wilcox [3] and Cygański [5] and by the mass loss determined by TG curves during heating.

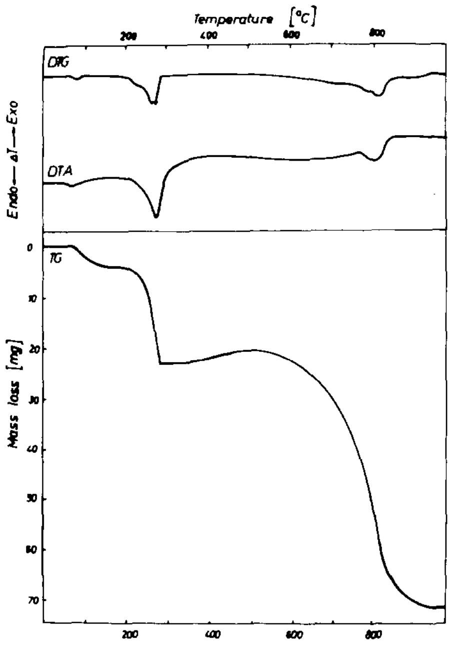
EXPERIMENTAL

Thermal analysis

Thermal investigations on caesium, sodium, potassium–sodium, rubidium–sodium and ammonium–sodium nitritocobaltates were carried out using a thermal analyser (MOM, Budapest, type OD-102/1500°C). The measurements were made in air in the temperature range 20–1000°C, at a heating rate of 5°C min^{-1}. The sensitivity of the galvanometer for the DTA curve was 1/15, for the DTG curve, 1/20, and TG curve, 200 mg. α-Al_2O_3 was used as a reference material in all cases. The weight of the samples used for investigation was 250 mg.

The thermal curves of potassium–sodium, caesium and ammonium–sodium nitritocobaltates are presented in Figs. 1–3. From the thermal curves of potassium–sodium nitritocobaltate (Fig. 1) it is evident that, during the heating of the compound, three thermal processes take place. The first one corresponds to the release of one molecule of water. This is an endothermic process. The second process is also endothermic (a sharp peak on the DTA curve) and is connected with a decrease in the mass of the sample. It starts at 210°C, reaches a maximum rate at 280°C, and ends at 310°C. From 360 to 500°C an increase in the mass of the heated sample takes place (from TG), and then from 570°C a mass decrease begins, slight at first, becoming faster from 700°C. At 880°C the process reaches a maximum rate. The thermal curves of $Na_3[Co(NO_2)_6]$ and $Rb_2Na[Co(NO_2)_6]$ are similar. As they are heated, three endothermic processes take place, and at about 400°C an increase in the mass of the heated sample occurs. No increase in the mass of the sample was observed when caesium and ammonium–sodium nitritocobaltates were heated.

From the thermal curves presented for the caesium nitritocobaltate it follows that as the compound is heated four endothermic processes take place (Fig. 2). The first process corresponds to the release of one molecule of water. The second endothermic process (a sharp peak on the DTA curve), which is connected with a decrease in the mass of the sample, reaches a maximum rate at 300°C. The third endothermic conversion which takes place at 410°C is not connected with a mass loss. It corresponds to the process of melting of $Cs_3[Co(NO_2)_6]$ [6]. The fourth conversion begins at 550°C and reaches a maximum rate at 800°C. It is accompanied by a considerable decrease in mass (from TG).



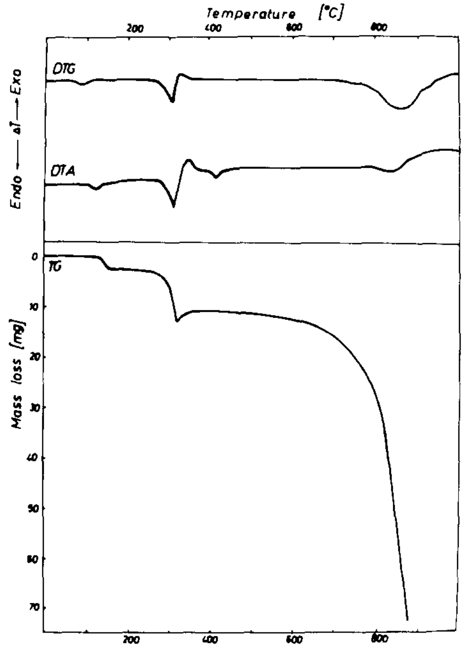


Fig. 1. Thermal analysis curves of potassium–sodium nitritocobaltate(III).

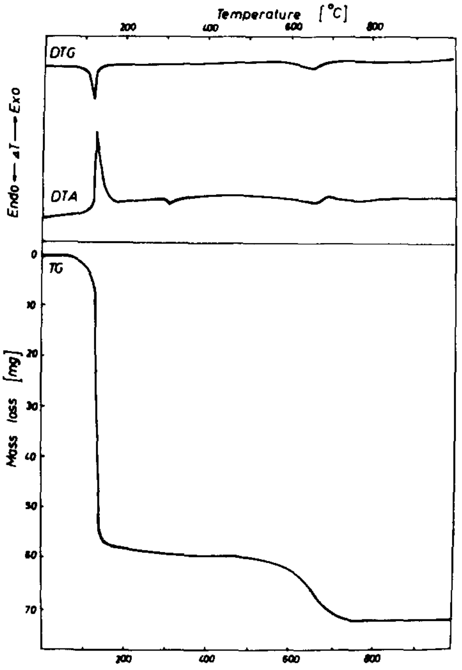
Fig. 2. Thermal analysis curves of caesium nitritocobaltate(III).

The thermal decomposition of ammonium–sodium nitritocobaltate takes a slightly different course (Fig. 3). As the temperature increases to 1000°C three thermal processes take place. The first is exothermic (sharp peak on the DTA curve) and is connected with a considerable decrease in mass. It begins at 110°C and reaches a maximum rate at 140°C. The second conversion, at 200°C, is an endothermic process not connected with any mass loss. The third process is also endothermic which begins at 520°C and ends at 800°C. It is accompanied by a decrease in mass.

After the decomposition temperature of a given compound had been attained, we tried to define the products of the process. In order to achieve this, sinters of the investigated compounds were prepared by heating them in an electric silite furnace at a heating rate of 5°C min^{-1}. To control the sinter preparation, the mass loss was determined and compared with that found from the TG curve.

Chemical analysis

The prepared sinters were divided into fractions: soluble and insoluble in water. In order to achieve this the sinters were treated with hot water for



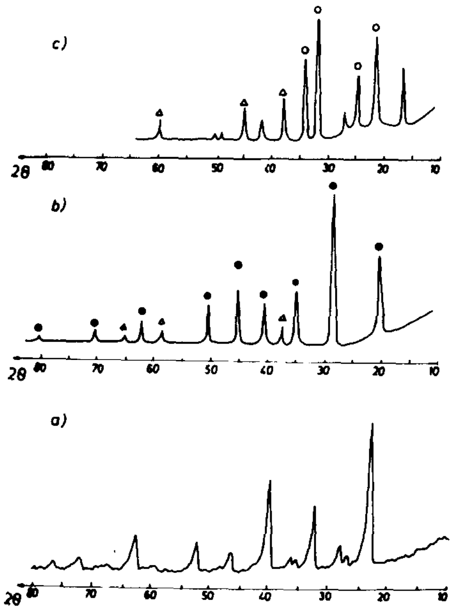


Fig. 3. Thermal analysis curves of ammonium–sodium nitritocobaltate(III).

Fig. 4. X-ray diffraction patterns of caesium nitritocobaltate(III): (a) before sintering; (b) after sintering to 300°C; (c) after sintering to 950°C; (●) $CsNO_3$; (○) Cs_2O; (△) Co_3O_4.

TABLE 1

Results of the chemical analysis of sinters of the sodium-group alkali metal nitritocobaltates(III) prepared at 300°C

Compound	Determined (%)			Calculated (%)		
	Soluble fraction	Insoluble fraction	Percentage in the sinter	Soluble fraction	Insoluble fraction	Percentage in the sinter
$Na_3[Co(NO_2)_6]\cdot H_2O$ [a]	73.69	26.31	Co = 18.4 Na = 21.5 NO_2^- = 20.01	74.42	25.58	Co = 18.79 Na = 21.97 NO_2^- = 19.53
$(NH_4)_2Na[Co(NO_2)_6]\cdot H_2O$ [b]	52.2	47.8	Co = 34.8 Na = 14.2 NO_2^- = —	51.41	48.59	Co = 35.69 Na = 13.9 NO_2^- = —
$K_2Na[Co(NO_2)_6]\cdot H_2O$ [c]	76.72	23.28	Co = 16.06 K = 21.2 NO_2^- = 12.4	77.13	28.87	Co = 16.0 K = 22.2 NO_2^- = 13.09
$Rb_2Na[Co(NO_2)_6]\cdot H_2O$ [c]	80.74	19.26	Co = 13.46 Rb = 39.8 NO_2^- = 10.9	81.92	18.08	Co = 13.28 Rb = 38.5 NO_2^- = 10.35
$Cs_3[Co(NO_2)_6]\cdot H_2O$ [d]	87.08	19.92	Co = 8.71 Cs = 57.58 NO_2^- = —	87.92	12.08	Co = 8.87 Cs = 59.95 NO_2^- = —

[a] Calculated values based on reaction (1).
[b] Calculated values based on reaction (6).
[c] Calculated values based on reaction (2).
[d] Calculated values based on reaction (5).

several hours. In the insoluble fraction the amount of cobalt was determined by the complexometric method [4]. In the soluble fraction the amount of a given alkali metal was determined [3,4]. The results of the analyses of sinters of the sodium group nitritocobaltates(III) prepared at 300°C are presented in Table 1.

X-ray analysis

The X-ray analysis of the sinters of the compounds investigated was carried out on a DRON-2 diffractometer using CuK_α radiation with a nickel

TABLE 2

X-ray identification of the sodium nitritocobaltate(III) sinter prepared at 300°C

Data from X-ray pattern		Literature data	
2θ	d/n (Å)	d/n (Å)	Compound
29.5	3.03	3.03	$NaNO_3$
30.1	2.969	2.97	$NaNO_2$
32.2	2.78	2.78	$NaNO_2$
37.0	2.43	2.43	Co_3O_4
39.1	2.304	2.31	$NaNO_3$
45.3	2.00	2.00	$NaNO_2$
55.8	1.647	1.65	$NaNO_3$
59.4	1.556	1.56	Co_3O_4
61.8	1.5	1.497	$NaNO_2$
65.0	1.435	1.432	Co_3O_4

TABLE 3

X-ray identification of the rubidium–sodium nitritocobaltate(III) sinter prepared at 300°C

Data from X-ray pattern		Literature data	
2θ	d/n (Å)	d/n (Å)	Compound
20.8	4.27	4.28	$RbNO_3$
29.5	3.02	3.02	$RbNO_3$
30.1	2.969	2.97	$NaNO_2$
31.3	2.858	2.86	Co_3O_4
32.2	2.78	2.78	$NaNO_2$
36.6	2.455	2.46	$RbNO_3$
37.0	2.43	2.43	Co_3O_4
40.2	2.238	2.23	$RbNO_3$
45.1	2.01	2.02	$NaNO_2$
47.8	1.903	1.89	$RbNO_3$
52.5	1.74	1.74	$RbNO_3$
59.6	1.55	1.56	Co_3O_4
65.5	1.425	1.432	Co_3O_4
69.6	1.35	1.351	Co_3O_4

TABLE 4

X-ray identification of the ammonium–sodium nitritocobaltate(III) sinter prepared at 300°C

Data from X-ray pattern		Literature data	
2θ	d/n (Å)	d/n (Å)	Compound
29.5	3.03	3.03	$NaNO_3$
31.3	2.858	2.86	Co_3O_4
32.0	2.797	2.8	$NaNO_3$
37.0	2.43	2.43	Co_3O_4
39.1	2.3	2.31	$NaNO_3$
45.0	2.01	2.02	Co_3O_4
48.2	1.888	1.89	$NaNO_3$
59.5	1.554	1.56	Co_3O_4
65.2	1.431	1.432	Co_3O_4

filter. The diffraction curves were recorded over the range of 2θ angles from 10 to 90°.

Figure 4 presents an X-ray diffraction pattern for caesium nitritocobaltate(III). In the sinter at 300°C the presence of $CsNO_3$ and Co_3O_4 was noted, whereas at 950°C Cs_2O and Co_3O_4 were identified. Tables 2–4 present the reflexes occurring in the diffractogram of the sinter at 300° for $Na_3[Co(NO_2)_6]$, $Rb_2Na[Co(NO_2)_6]$ and $(NH_4)_2Na[Co(NO_2)_6]$, and Fig. 5 presents the diffractogram of potassium–sodium nitritocobaltate.

IR spectrophotometric analysis

IR spectrophotometric studies were carried out by means of a spectrophotometer (IR-10 Zeiss) in the 670–3800 cm^{-1} range. Measurements in the

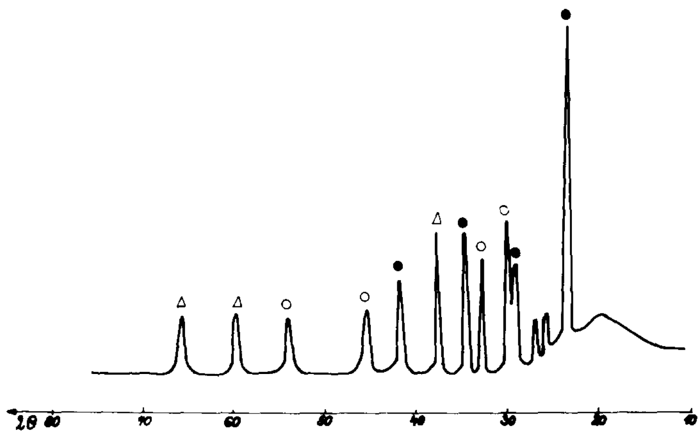


Fig. 5. X-ray diffraction patterns of potassium–sodium nitritocobaltate(III) after sintering to 300°C: (●) KNO_3; (○) $NaNO_2$; (△) Co_3O_4.

range 670–2000 cm^{-1} were made using a prism of NaCl whereas in the range 2000–3800 cm^{-1}, LiF was used. The substance was investigated in the solid state, using KBr tablets. The placing of spectral bands was determined to 5 cm^{-1}. Figure 6 presents an absorption spectrum of the sinter of sodium nitritocobaltate prepared at 300°C. Vibrations occurring in the spectrum at 830, 1265 and 2555 cm^{-1} were attributed to the presence of sodium nitrite, while those occurring at 840, 1375 and 2425 cm^{-1}, to sodium nitrate. For comparison, Fig. 7 presents IR absorption spectra of pure $NaNO_2$ and $NaNO_3$. Sodium nitrite is characterized by the vibrations $\delta ONO = 828.5$,

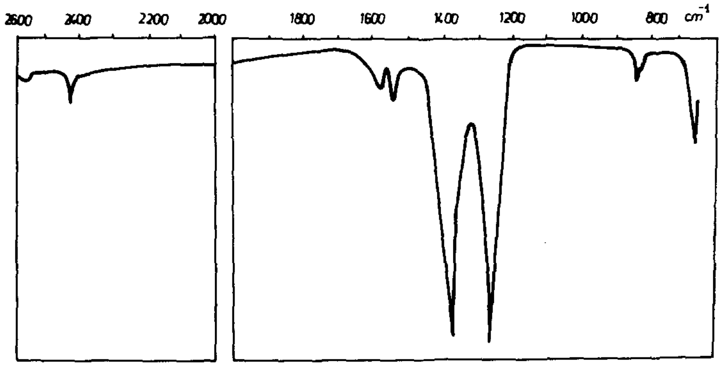


Fig. 6. IR absorption curves for sodium nitritocobaltate(III) sinter prepared at 300°C.

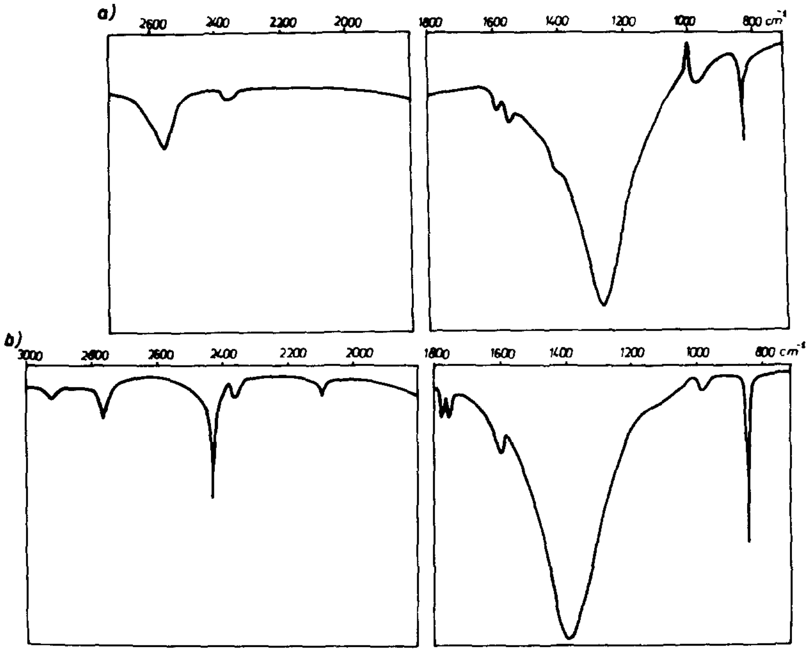


Fig. 7. IR absorption curves for sodium nitrite (a) and sodium nitrate (b).

$\nu_{as}NO_2 = 1270$. $\nu_sNO_2 = 1326$ and 2551 cm^{-1}, whereas sodium nitrate is characterized by the following vibration frequencies: 836, 1358, 1790 and 2428 cm^{-1}.

Analysis of the gaseous products

An analysis of the gaseous products released during the thermal decomposition of nitritocobaltates(III) at 300°C was also carried out. A precipitate of potassium–sodium nitritocobaltate was placed in a silica vessel and heated to 300°C. The vessel was equipped with a thermometer and two outlets with cocks. One of them served to convey air to the system, the other was to remove released nitric oxides to three bubblers connected in series. The last of the bubblers was connected through a rotameter with a membrane pump which allowed the air to flow through the system at a rate of 10 $l\ h^{-1}$. The silica vessel and the sample investigated were placed in an electric furnace and heated at a rate of 5°C min^{-1}. The oxides evolved were absorbed in three bubblers filled with: (a) 20 ml 0.2 M NaOH; (b) 20 ml 0.02 M $KMnO_4$ and (c) 1 ml 0.5 M NaOH. After the decomposition had been completed, the composition of the absorbed nitrogen oxides was determined by acidimetry (a) and oxidimetric titration (b).

DISCUSSION

On the basis of the results of the thermal, chemical and diffractometric analyses, equations for the thermal decomposition of the sodium-group alkali metal nitritocobaltates(III) were arrived at. These compounds were divided into two groups. The first includes sodium, potassium–sodium, and rubidium–sodium nitritocobaltates. The second consists of caesium and ammonium–sodium nitritocobaltates. Both groups differ in the presence or absence of sodium nitrite in the sinter prepared at 300°C.

Mechanism of the decomposition of potassium–sodium, sodium and rubidium–sodium nitritocobaltates

The thermal curves for sodium, potassium–sodium and rubidium–sodium nitritocobaltates indicate that during the heating of the above mentioned compounds three endothermic processes involving a mass loss take place.

Stages I and II

The first stage of the thermal decomposition of nitritocobaltates consists of the expulsion of the one molecule of water. For instance, Fig. 1 presents an endothermic peak on the DTA curve corresponding to this process. It is confirmed by the mass loss visible on the TG curve for potassium–sodium nitritocobaltate, which at 100–140°C amounts to 3.6% (the calculated content of water in $K_2Na[Co(NO_2)_6] \cdot H_2O$ is 3.96%).

The second stage of thermal decomposition starts at about 250°C and is accompanied by a mass loss. The mass losses determined from the TG curve for $Na_3[Co(NO_2)_6]$, $K_2Na[Co(NO_2)_6]$ and $Rb_2Na[Co(NO_2)_6]$ for stages I and II are 25.6, 23.2 and 19.2%, respectively. The diffractometric analysis of the sinter of sodium nitritocobaltate showed the presence of $NaNO_3$, $NaNO_2$ and Co_3O_4 in the sinter. The chemical analysis of the sinter of $Na_3[Co(NO_2)_6]$ prepared at 300°C indicates that the ratio $Co : Na : NO_2$ is 1.00 : 2.98 : 1.35. The presence of nitrites in the sinter at 300°C was confirmed by the analysis of the IR absorption spectrum and by a manganometric determination of the quantity of nitrites. In Fig. 6 the presence of $NaNO_2$ in the sinter is supported by the vibrations found at 1265 and 2555 cm^{-1}. The vibrations at 830 cm^{-1} agree with the frequency of vibrations of the nitrates (836 cm^{-1}). In the spectrum of the sinter of sodium nitritocobaltate at 300°C, the two characteristic adjacent sharp peaks are caused by the presence of both nitrites (1265 cm^{-1}) and nitrates (1358 cm^{-1}).

On the basis of the investigation on gaseous products it was assumed that during the thermal decomposition of nitritocobaltates(III) at 300°C an equimolar mixture of nitrogen oxide and dioxide is formed. The mixture results from the reaction of evolved nitrogen oxides and oxygen from the air. The analyses made indicate that the thermal decomposition of the sodium nitritocobaltate has the following course

$$6\ Na_3[Co(NO_2)_6] \cdot H_2O + \tfrac{9}{2} O_2 = 10\ NaNO_3 + 8\ NaNO_2 + 2\ Co_3O_4 + 9\ NO + 9\ NO_2 + 6\ H_2O \qquad (1)$$

The discovery of the formation of sodium nitrite and cobaltous-cobaltic oxide as a result of the decomposition of sodium nitritocobaltate is in agreement with the results of the investigation carried out by Wendlandt and Southern [2].

The diffractometric analysis confirmed the presence in the sinters of potassium–sodium and rubidium–sodium nitritocobaltates, of KNO_3, $NaNO_2$ and Co_3O_4 and of $RbNO_3$, $NaNO_2$ and Co_3O_4, respectively, prepared at 300°C. On the basis of the results of chemical, IR spectrophotometric and diffractometric analyses the following decomposition reaction was suggested

$$6\ M_2Na[Co(NO_2)_6] \cdot H_2O + \tfrac{11}{2} O_2 = 12\ MNO_3 + 6\ NaNO_2 + 2\ Co_3O_4 + 9\ NO + 9\ NO_2 + 6\ H_2O \qquad (2)$$

where $M = K^+, Rb^+$.

Stage III

The third stage begins at about 600°C and is accompanied by a considerable decrease in mass. It consists of the decomposition of nitrates and nitrites to alkali metal oxides according to the equations

$$10\ NaNO_3 + 8\ NaNO_2 + 2\ Co_3O_4 = 9\ Na_2O + 2\ Co_3O_4 + N_{18}O_{37} \qquad (3)$$

$$10\ MNO_3 + 6\ NaNO_2 + 2\ Co_3O_4 = 6\ M_2O + 3\ Na_2O + 2\ Co_3O_4 + N_{18}O_{39} \qquad (4)$$

(These reactions contain a summary formula of the gaseous products due to the mass loss.) The presence of an alkali metal oxide and cobaltous-cobaltic oxide was confirmed by diffractometric investigations on a sinter of the compounds obtained at 950°C. Also, Wendlandt and Southern [2], on examining the decomposition of $Na_3[Co(NO_2)_6]$ suggested that at 600–900°C the decomposition of sodium nitrite to sodium oxide takes place.

Mechanism of the decomposition of caesium and ammonium–sodium nitritocobaltates

The thermal decompositions of $Cs_3[Co(NO_2)_6]$ and $(NH_4)_2Na[Co(NO_2)_6]$ differ from that of other alkali metal nitritocobaltates in that there is no sodium nitrite in the sinter prepared at 300°C.

Stages I and II

The first stage of decomposition of the above mentioned compounds consists of the release of one molecule of water. While in the case of $Cs_3[Co(NO_2)_6]$ the process is illustrated as a separate peak on the TG curve (Fig. 2), for $(NH_4)_2Na[Co(NO_2)_6]$ it is connected with the further decomposition of the compound (Fig. 3). The diffractometric analysis of the sinter of caesium nitritocobaltate allowed the identification of $CsNO_3$ and Co_3O_4 at 300°C. The mass loss determined from the TG curve is 11.6% and that lost while the sinter is being obtained is 11.7%. The following course for the thermal decomposition reaction at 300°C was suggested

$$6\ Cs_3[Co(NO_2)_6] \cdot H_2O + \tfrac{17}{2}O_2 = 18\ CsNO_3 + 2\ Co_3O_4 + 9\ NO + 9\ NO_2 + 6\ H_2O \qquad (5)$$

The composition of the solid products presented in reaction (5) is in agreement with that of the substances determined in the sinter by means of quantitative analysis.

The diffractometric analysis of the sinter of ammonium–sodium nitritocobaltate at 300°C revealed the presence of $NaNO_3$ and Co_3O_4. The mass loss determined from the TG curve is 59.2%. On the basis of the results obtained, the following decomposition reaction was suggested

$$6\ (NH_4)_2Na[Co(NO_2)_6] \cdot H_2O + \tfrac{23}{2}O_2 = 6\ NaNO_3 + 2\ Co_3O_4 + 6\ N_2 + 15\ NO + 15\ NO_2 + 30\ H_2O \qquad (6)$$

The mass loss while the sinter is being obtained is 58.9% and that calculated according to reaction (6) is 59.87%.

Stage III

The third stage consists of the decomposition of caesium and sodium nitrates into the respective oxides

$$18\ \mathrm{CsNO_3} + 2\ \mathrm{Co_3O_4} = 9\ \mathrm{Cs_2O} + 2\ \mathrm{Co_3O_4} + \mathrm{N_{18}O_{45}} \tag{7}$$

$$6\ \mathrm{NaNO_3} + 2\ \mathrm{Co_3O_4} = 3\ \mathrm{Na_2O} + 2\ \mathrm{Co_3O_4} + \mathrm{N_6O_{15}} \tag{8}$$

(These reactions contain a summary formula of the gaseous products due to the mass loss.) Figure 4 presents a diffractogram of the sinter of caesium nitritocobaltate at 950°C which proves the presence of Cs_2O and Co_3O_4.

When the mass loss in stage III, determined from the TG curves, and that found during the preparation of the sinters was compared with that calculated according to the reactions suggested, the greatest consistency was observed for the ammonium and sodium salts. There is a greater difference between the mass loss calculated according to the equation and that determined from the TG curve for $Cs_3[Co(NO_2)_6]$. This results from a partial conversion of Cs_2O into a peroxide and a metal which evaporates [7].

The sodium-group alkali metal nitritocobaltates were divided into two groups which differed with respect to their decomposition products at 300°C. However, in all cases Co_3O_4 forms the central ion. Similarly, when the compounds $M_2Ag[Co(NO_2)_6]$ ($M = K^+$, NH_4^+, Rb^+, Cs^+) were thermally decomposed, the central ion was also found to be Co_3O_4 [8]. The ammonium–sodium nitritocobaltate proved to be the least stable of all the compounds examined (decomposition temperature, 110°C). This is connected with the properties of the ammonium group. The ammonium–silver nitritocobaltate also has a comparatively low decomposition temperature (~ 140°C) [8]. A comparison of the thermal stability of sodium and silver group nitritocobaltates is presented in Table 5. From the data presented it follows that the sodium group nitritocobaltates(III) exhibit more thermal stability than the nitritocobaltates(III) of the silver group (except for the ammonium salts). The difference in thermal stability of nitritocobaltates of the above mentioned groups results from the polarizing properties of outer-sphere cations. The outer-sphere cations with a strong polarizing effect depolarize the complex anion by weakening the bond between the central ion and the ligands in a far higher degree than the cations of weaker

TABLE 5

Thermal decomposition temperatures of sodium- and silver-group alkali metal nitritocobaltates(III)

Compound	*T*(°C)	Compound	*T*(°C)
$Na_3[Co(NO_2)_6]\cdot H_2O$	240		
$K_2Na[Co(NO_2)_6]\cdot H_2O$	280	$K_2Ag[Co(NO_2)_6]$	230
$(NH_4)_2Na[Co(NO_2)_6]\cdot H_2O$	110	$(NH_4)_2Ag[Co(NO_2)_6]$	140
$Rb_2Na[Co(NO_2)_6]\cdot H_2O$	250	$Rb_2Ag[Co(NO_2)_6]$	240
$Cs_3[Co(NO_2)_6]\cdot H_2O$	300	$Cs_2Ag[Co(NO_2)_6]$	200

polarizing effect. A silver ion exerts a stronger polarizing effect than a sodium ion, which is caused by the additional polarizing effect which takes place when a strongly polarizable complex anion is affected by a strongly polarizing cation, which at the same time has a considerable deformation capability.

When caesium and sodium nitritocobaltates are compared with respect to their thermal stability, it is evident that the caesium compound is more stable than the sodium compound (the decomposition temperatures are 300 and 240°C, respectively). The greater stability of caesium nitritocobaltate may be explained by the fact that an ion of caesium has a far weaker polarizing effect than an ion of sodium. In the case of double salts, $M_2M'[Co(NO_2)_6]$, the effect of two different outer-sphere cations must be taken into consideration. It has been observed that, generally, a compound exhibits less stability when cation M has a greater deformation capability and cation M′ has a stronger polarizing effect. Therefore, the rubidium–sodium salt is less stable than the potassium–sodium one. The higher thermal stability of $Cs_3[Co(NO_2)_6]$ (decomposition temperature, 300°C) when compared with $Cs_2Ag[Co(NO_2)_6]$ (decomposition temperature, 200°C) [8] indicates the considerable influence of the polarizing properties of outer-sphere cations on the stability of nitritocobaltates.

The thermal decomposition of potassium–sodium and ammonium–sodium nitritocobaltates was utilized to evaluate a new, direct method for determining potassium and ammonium [9]. The main advantage of this method is the possibility of its application for determining K^+ and NH_4^+ ions without the need for their separation.

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