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Synthesis and thermal analysis of tetraethylammonium bromochlorocobaltates(II) $[Et_4N]_2[CoBr_nCl_{4-n}]$

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Abstract

New mixed-ligand tetraethylammonium halogenocobaltates(II) of general formula $[Et_4N]_2[CoBr_nCl_{4-n}]$ have been synthesized. Their thermal properties were characterized on the basis of the TG and DTG curves taken in argon and derivatograms recorded in static air. Some products of successive decomposition steps were identified based on their IR, FIR and VIS spectra as well as the results of elemental analysis. The influence of the nature of the complex anion and oven atmosphere on the progress of thermal decomposition of the compounds has been discussed.

Keywords: Mixed-ligand tetrahalogenocobaltates(II); Thermal characteristics

1. Introduction

Up to the present, our studies have been devoted to a number of compounds of general formula $R[FeBr_nCl_{4-n}]$, where R is an organic cation and $n = 0–4$ [1,2]. This study is an extension of our investigations into analogous compounds with Co(II) as the central ion.

To date, compounds of general formula $[Et_4N]_2[CoX_4]$ (where X = Cl, Br), as well as $[Et_4N]_2[CoBr_2Cl_2]$, have been reported in the literature [3–6]. These complexes have been extensively studied using spectroscopic [3–11] and magnetic [6,8,12] methods. They also aroused our interest and we decided to synthesize mixed-ligand tetrahalogenocobaltates(II) $[Et_4N]_2[CoBrCl_3]$ and $[Et_4N]_2[CoBr_3Cl]$. Another purpose was to explore thermal properties of the new compounds of general formula $[Et_4N]_2[CoBr_nCl_{4-n}]$. To investigate the influence of the atmosphere on thermal decomposition of the compounds, relevant experiments were run in an inert atmosphere (argon) and an oxidative atmosphere (static air).

2. Experimental

The complexes were obtained by using the previously reported procedures [3–6,11,13,14] whereby a cobalt(II) halide was mixed with a solution of an appropriate tetraethylammonium salt.

2.1. Synthesis of $[Et_4N]_2[CoCl_4]$

$CoCl_2{\cdot}6H_2O$ (0.05 mol) was dissolved in a small quantity of hot ethanol and the solution was added to the Et_4NCl (0.1 mol) ethanolic solution. (Found: C, 41.6; N, 6.1; H, 8.8; Cl, 30.0. Calcd. for $[Et_4N]_2[CoCl_4]$, C, 41.6; N, 6.1; H, 8.8; Cl, 30.1%).

2.2. Synthesis of $[Et_4N]_2[CoBrCl_3]$

$CoCl_2{\cdot}6H_2O$ (0.05 mol) was dissolved in a small quantity of hot ethanol and the solution was added to an equimolar mixture (0.05 mol each) of Et_4NCl and Et_4NBr in ethanol. (Found: C, 38.0; N, 5.5; H, 8.1; Br, 15.6; Cl, 22.2. Calcd. for $[Et_4N]_2[CoBrCl_3]$, C, 38.0; N, 5.5; H, 8.0; Br, 15.8; Cl, 21.1%.)

2.3. Synthesis of $[Et_4N]_2[CoBr_2Cl_2]$

$CoBr_2{\cdot}H_2O$ (0.05 mol) was dissolved in a small quantity of ethanol and the solution was added to the Et_4NCl (0.01 mol) ethanolic solution. (Found: C, 34.3; N, 5.0; H, 7.4; Br, 33.7; Cl,

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10.4. Calcd. for $[Et_4N]_2[CoBr_2Cl_2]$, C, 34.9; N, 5.1; H, 7.3; Br, 29.0; Cl, 12.9%.)

2.4. Synthesis of $[Et_4N]_2[CoBr_3Cl]$

$CoBr_2{\cdot}H_2O$ (0.05 mol) was dissolved in a small quantity of ethanol and the solution was added to an equimolar mixture (0.05 mol each) of Et_4NCl and Et_4NBr in ethanol. (Found: C, 32.5; N, 4.7; H, 6.9; Br, 40.1; Cl, 5.5. Calcd. for $[Et_4N]_2[CoBr_3Cl]$, C, 32.3; N, 4.7; H, 6.8; Br, 40.3; Cl, 6.0%.)

2.5. Synthesis of $[Et_4N]_2[CoBr_4]$

$CoBr_2{\cdot}H_2O$ (0.05 mol) was dissolved in ethanol and the solution was added to the Et_4NBr (0.1 mol) ethanolic solution. (Found: C, 30.2; N, 4.4; H, 6.4; Br, 49.8. Calcd. for $[Et_4N]_2[CoBr_4]$, C, 30.1; N, 4.4; H, 6.3; Br, 50%.)

All the compounds precipitated in no time as blue powders.

2.6. Instrumental

Potentiometric titrations were carried out using standard electrodes, SCE (indicator electrode) and silver electrode (the reference one). The FIR spectra were recorded on a BRUKER IFS 66 spectrophotometer in PE over the 650–50 cm^{-1} range. Electronic reflectance spectra (range 5000–50,000 cm^{-1}) were measured on a Cary Scan (Varian) UV–vis–NIR spectrophotometer.

Thermogravimetric measurements (TG–DTG–DTA) were run in static air on a model OD-103 derivatograph of Hungarian origin (range 20–900 °C, Pt crucible, sample mass ca. 500 mg, Al_2O_3 as reference, heating rate 5 K/min). The TG–FTIR analyses in argon (Ar 5.0) were run on a Netzsch TG 209 apparatus coupled with a Bruker FTIR IFS66 spectrophotometer (range 25–800 °C, corundum crucible, sample mass ca. 15 mg, Al_2O_3 as reference, heating rate 15 K/min, flow rate of carrier gas 18 mL/min).

The course of thermal analysis was broken at points corresponding to the main steps of decomposition and the residues in the crucible were quickly cooled in the stream of argon. This enabled to analyze the residues at a strictly pre-determined step of decomposition. The analysis was carried out using the FIR spectroscopic techniques as well as elemental analysis (C, H, N).

3. Results and discussion

The composition of the new compounds $[Et_4N]_2[CoBrCl_3]$ and $[Et_4N]_2[CoBr_3Cl]$, was confirmed by the results of elemental analysis and their IR and FIR spectra. In the IR spectra bands due to $[Et_4N]^+$ are seen, whereas in the FIR spectrum of $[Et_4N]_2[CoBrCl_3]$ the 128 cm^{-1} band can certainly be assigned to the υ(Cl–Co–Cl) vibration, bands at 210 and 228 cm^{-1} to υ(Co–Br) and that at 296 cm^{-1} to υ(Co–Cl). In the FIR spectrum of $[Et_4N]_2[CoBr_3Cl]$, bands due to υ(Br–Co–Br), υ(Co–Br) and υ(Co–Cl) emerge at 76, 228 and 300 cm^{-1}, respectively (Fig. 1) [6].

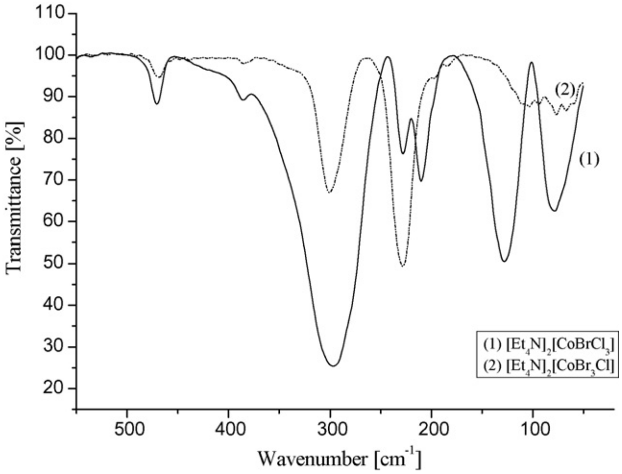

Fig. 1. The FIR spectra of the samples of $[Et_4N]_2[CoBrCl_3]$ (1) and $[Et_4N]_2[CoBr_3Cl]$ (2).

Thermal decomposition of the $[Et_4N]_2[CoBr_nCl_{4-n}]$ compounds occurs in three steps, independent of the oven atmosphere. The first decomposition step of the compounds is accompanied by a large loss in weight in the TG curve. The process is strongly endothermic and manifests itself as a sharp peak both in the DTA and DTG curves. Most probably, the compounds become melted just prior to the onset of decomposition this resulting in overlap of the energetic effect in the DTA curve due to melting with that due to its decomposition. It is also probably that endothermic peak represents the evaporation of the base-HCl product [15]. For this reason, it is difficult at this stage of investigation to precisely determine the melting points of particular compounds and their dependence on the nature of ligands in the coordination sphere of Co(II). At this point, it is interesting to note that the melting of the compound is preceded by a phase transition as highlighted by a small endothermic effect in the DTA curve (Fig. 2).

Selected TG curves recorded in argon are shown in Fig. 3. Their shapes indicate similar pathways of decomposition of the

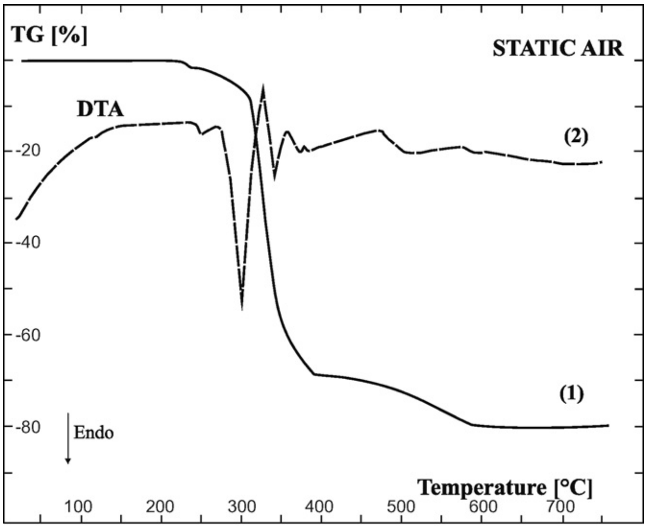

Fig. 2. TG (1) and DTA (2) curves of $[Et_4N]_2[CoBrCl_3]$ recorded in static air.

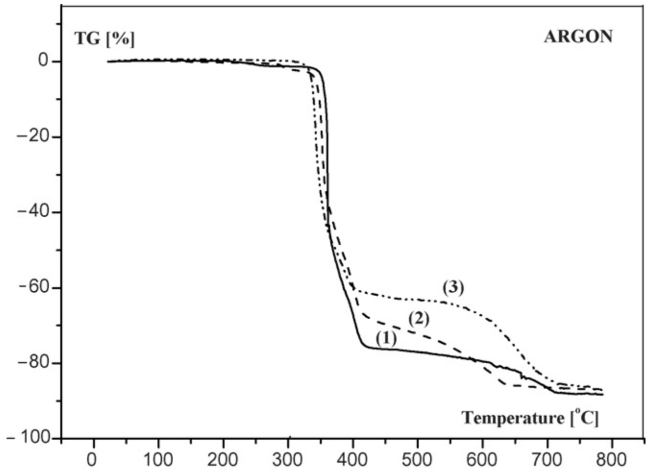

Fig. 3. TG curves of $[Et_4N]_2[CoCl_4]$ (1), $[Et_4N]_2[CoBrCl_3]$ (2) and $[Et_4N]_2[CoBr_4]$ (3) recorded in argon.

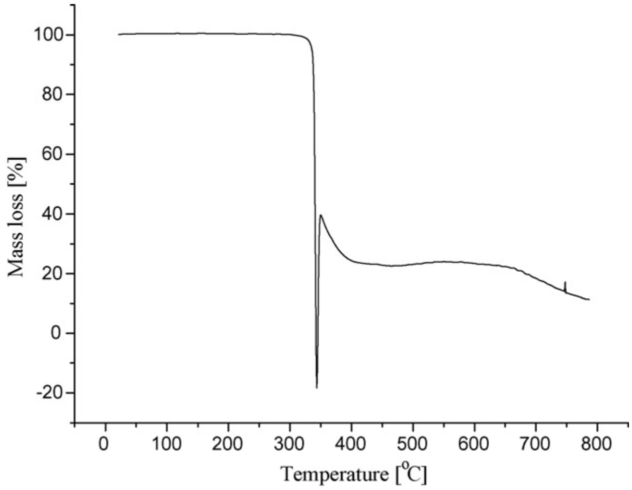

Fig. 4. TG curve of $[Et_4N]_2[CoBr_3Cl]$ in argon illustrating sample explosion.

$[Et_4N]_2[CoBr_nCl_{4-n}]$ compounds, while small differences in mass losses at particular decomposition steps are due to different molecular masses: the higher the bromine content the smaller the loss in mass becomes. At the same time this shows that the volatile product consists of an organic fragment common for all the five compounds.

The data taken from the TG curves recorded in argon and from the derivatograms taken in static air are compiled in Tables 1 and 2, respectively.

It is worthwhile to note a violent first step decomposition of one compound only, namely $[Et_4N][CoBr_3Cl]$. It is accompanied by evolution of large amounts of gases which cause explosion of sample. Consequently, there is a larger loss in mass in the TG curve than that expected due to non-explosive decomposition. This event is seen in the TG curve presented in Fig. 4.

The first process of thermal decomposition of the other compounds is very fast and is accompanied by successive degradation reactions, unambiguous identification of the product is difficult in view of the possibility of co-existence in the analyzed sample of the products of the first and second decomposition steps.

Kandhaswamy and Srinivasan [3] suggested as the product of the first step of thermal decomposition the $[Co(C_2H_5)_4Cl_2]$. Unlike this, our results indicate that in the organic part of the product are the –N–H band and also probably the Co–N band. It is demonstrated by the IR spectrum of the product sampled at 390 °C (Fig. 5) in which the N–H vibrations emerge at 730 cm^{-1} ω(N–H), 1612 cm^{-1} δ(N–H) and 3448 cm^{-1} υ(N–H), as well as by the FIR spectrum (Fig. 6) revealing the Co–N bond (230 cm^{-1} υ(Co–N) [18]) or a Co–Cl bond in a polymerized form. These bands are missing in the spectrum of the undecomposed compound (Fig. 6).

Furthermore, in the spectra of the volatile products of decomposition in argon of a similar compound $[Et_4N]_2[CoBr_2Cl_2]$ (Fig. 7), the C–N bands are missing, thus indicating that the

Table 1
Results of the analysis of decomposition products in argon

Complexes	Stage	Temperature range (°C)	DTG_{max} (°C)	Solid decomposition product	Mass loss (%)		Total mass loss (%)	
					Found	Calcd.	Found	Calcd.
$[Et_4N]_2[CoCl_4]$	1	340–390	360	–	63	–		
	2	390–420	405	$CoCl_2$	15	18	78	75
	3	620–720	–	$CoCl_2 + Co_2C$	10	–		
$[Et_4N]_2[CoBrCl_3]$	1	310–390	350	–	53	–		
	2	390–460	400	$CoCl_2$	15	18	68	74
	3	460–660	624	$CoCl_2 + Co_2C$	16	–		
$[Et_4N]_2[CoBr_2Cl_2]$	1	320–380	350	–	54	–		
	2	380–430	385	$CoBr_2$	10	16	64	60
	3	430–790	663	$CoBr_2 + Co_2C$	16	–		
$[Et_4N]_2[CoBr_3Cl]$	1	310–350	340	–	61	–		
	2	350–410	–	$CoBr_2$	15	15	76	63
	3	600–790	–	$CoBr_2 + Co_2C$	12	–		
$[Et_4N]_2[CoBr_4]$	1	320–370	340	–	49	–		
	2	370–420	390	$CoBr_2$	14	14	63	66
	3	600–720	–	$CoBr_2 + Co_2C$	22	–		

Table 2
Results of the analysis of decomposition products in air

Complexes	Stage	Temperature range (°C)	DTG$_{max}$ (°C)	Solid decomposition product	Mass loss (%)		Total mass loss (%)	
					Found	Calcd.	Found	Calcd.
$[Et_4N]_2[CoCl_4]$	1	300–340	330(+)	–	63	–		
	2	340–400	360(−)	$CoCl_2$	18	18	90	83
	3	400–600	560(−)	Co_3O_4	9	8		
$[Et_4N]_2[CoBrCl_3]$	1	280–320	300(+)	–	58	–		
	2	320–400	–(−)	$CoCl_2$	9	18	78	84
	3	400–600	–(−)	Co_3O_4	11	10		
$[Et_4N]_2[CoBr_2Cl_2]$	1	270–340	300(+)	–	56	–		
	2	340–440	–(−)	$CoBr_2$	24	16	90	85
	3	440–600	520(−)	Co_3O_4	10	25		
$[Et_4N]_2[CoBr_3Cl]$	1	270–320	300(+)	–	40	–		
	2	320–380	–(−)	$CoBr_2$	32	15	72	63
	3	380–800	–(−)	Co_3O_4	–	–		
$[Et_4N]_2[CoBr_4]$	1	280–340	300(+)	–	51	–		
	2	340–400	360(−)	$CoBr_2$	18	14	92	87
	3	400–600	–(−)	Co_3O_4	23	21		

(+)Endothermic; (−) exothermic.

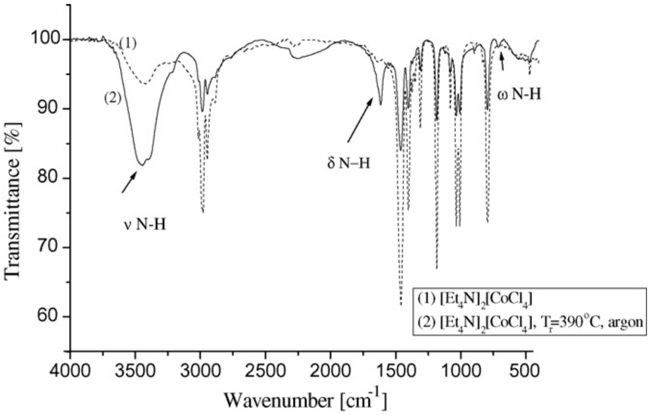

Fig. 5. The IR spectra of the samples of $[Et_4N]_2[CoCl_4]$ (1) and $[Et_4N]_2[CoCl_4]$ taken at 390 °C in argon (2).

nitrogen atom present in the undecomposed compound still remains in the solid product sampled after the first step. This band emerges at higher temperatures, thus, suggesting the reaction leading to $CoCl_2$.

The presence of $CoCl_2$ is confirmed by the 575, 630 and 674 nm bands in the FIR and VIS spectra [7,19], by the reflectance spectrum (Fig. 8) as well as by the results of elemental analysis of a sample taken at ca. 600 °C (Found: C, 0; N, 0; H 0%). In addition, in the IR spectra of the volatile products sampled above 420 °C in argon, bands due to the C–H, $-CH_2-$ and $-CH_3$ groups were missing (Fig. 7).

Peaks in the reflectance spectrum (Fig. 8(2)) at 6200, 14,200, 18,000 and 18,800 cm^{-1} can be assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions [20] and reveal the presence of an octahedral $CoCl_2$.

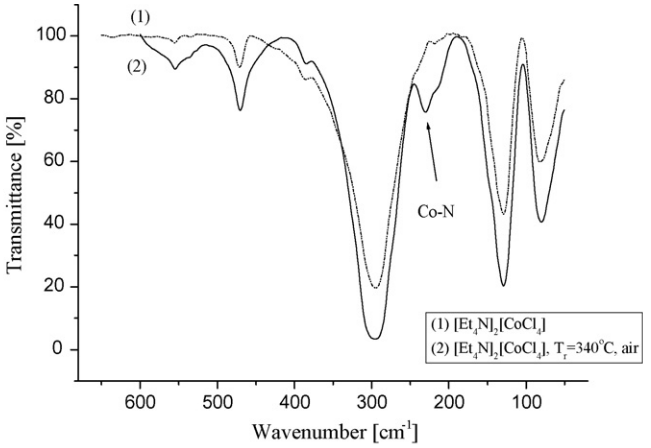

Fig. 6. The FIR spectra of the samples of $[Et_4N]_2[CoCl_4]$ (1) and $[Et_4N]_2[CoCl_4]$ taken at 340 °C in air (2).

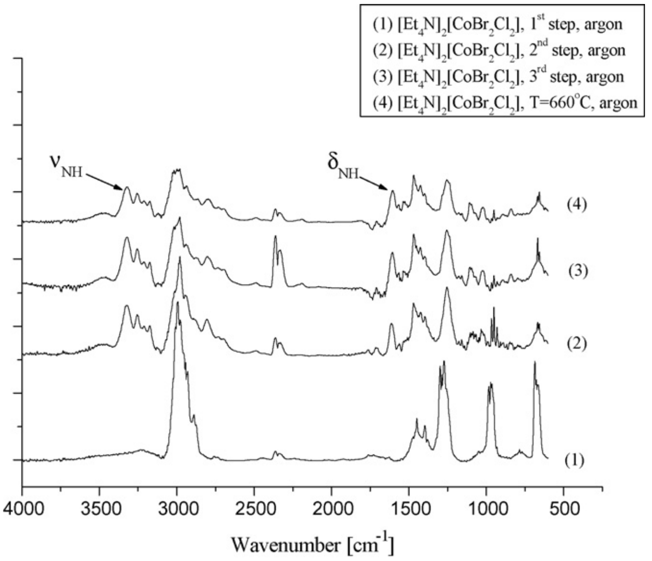

Fig. 7. IR spectra of the volatile products of thermal decomposition of $[Et_4N]_2[CoBr_2Cl_2]$ in argon.

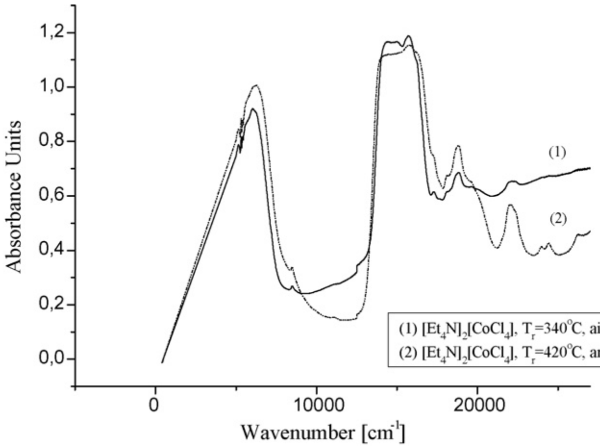

Fig. 8. Reflectance spectrum of $[Et_4N]_2[CoCl_4]$ sampled at 340°C in static air (1) and that of the compound sampled at 420 °C in argon (2).

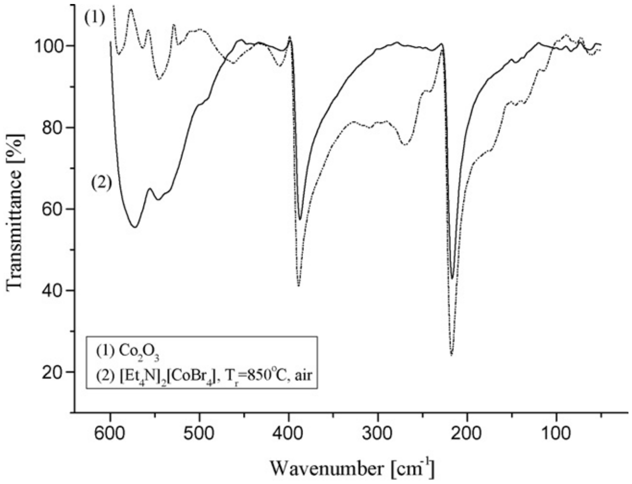

Fig. 9. FIR spectra of the final decomposition products of $[Et_4N]_2[CoBr_4]$ in static air (2) and of Co_2O_3 (1).

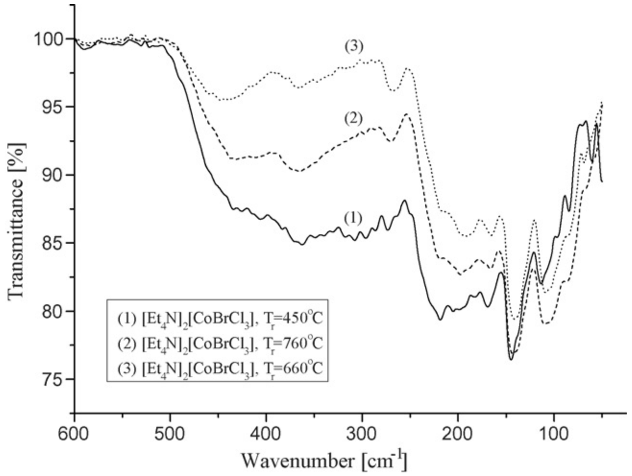

Fig. 10. FIR spectra of the decomposition products of $[Et_4N]_2[CoBrCl_3]$ in argon at 450, 660 and 760 °C.

In comparison to this spectrum, that of the decomposition of $[Et_4N]_2[CoCl_4]$ at 340 °C in static air shows only small displacements in relation to the spectrum of the octahedral $CoCl_2$ which are likely to indicate an octahedral (polymeric) structure of the first decomposition product, whereas small shifts relative to the spectrum of $CoCl_2$ may be due to the presence of axial nitrogen atoms in the molecule of the complex. This structure could be similar to that of $CoCl_2{\cdot}2NC_5H_5$ [21].

With the first two decomposition steps of the compounds affording cobalt(II) halide, the same course of the process is observed both in the inert atmosphere (argon) and in the oxidative atmosphere (static air). It can thus be concluded that the oven atmosphere does not affect the course of thermal decomposition of the $[Et_4N]_2[CoBr_nCl_{4-n}]$ compounds. However, above 400 °C there is a distinct difference both in the course of decomposition and identity of the residues. Thus, in the static air, Co_3O_4 is formed during the third step owing to the presence of oxygen in the atmosphere [17], where certainly the following reaction takes place:

$$CoX_2 + O_2 \rightarrow CoO \rightarrow \tfrac{1}{3}Co_3O_4 \quad (X = Cl, Br)$$

Most probably the halogen is released in a gaseous form as HX as is the case with decomposition in argon at higher temperatures. There is also the probability that the halogen ligands are released in small amounts as Cl_2 and Br_2, respectively. These products were released during decomposition of similar compounds $[Bu_4N][FeCl_4]$ [1]. This conclusion is supported by the mass loss taken from the derivatogram and the FIR spectrum of the residue (Fig. 9).

The intermediate oxide, CoO, could not be isolated due to its instantaneous oxidation to Co_3O_4. This process is so rapid that cannot be recorded in the DTA and TG curves [16].

The same step has also been noticed during decomposition of cobalt(II) complexes with pyridine and its derivatives [22,23].

When the decomposition was carried out in the argon atmosphere, no significant changes were observed in the TG curves over the range 400–600 °C. A plot of the total amount of the volatiles shows that their amount is negligible, this indicating that the product of the second step of decomposition is stable. At 720 °C, some changes in the TG curve of $[Et_4N]_2[CoCl_4]$ are seen (the mass loss of 10%), and in the IR spectra bands due to HCl appear, this indicating that a part of $CoCl_2$ is probably converted to Co_2C. Analogous products were observed during thermal decomposition of similar compounds with iron [2,24].

To sum up, the final decomposition product of the $[Et_4N]_2[CoBr_nCl_{4-n}]$ compounds in argon consists of a mixture of $CoCl_2$ and Co_2C, $CoCl_2$ being still present in the FIR spectrum of the decomposition product of $[Et_4N]_2[CoBrCl_3]$ at 750 °C (Fig. 10).

4. Conclusions

Cobalt(II) complexes of general formula R_2CoX_4 (X = Cl, Br) have been reported in the literature. Also a mixed-ligand complex $[Et_4N]_2[CoBr_2Cl_2]$, has been described [6]. We have demonstrated that other mixed-ligand complexes with the $[CoBrCl_3]^{2-}$ and $[CoBr_3Cl]^{2-}$ anions could be obtained. Both their FIR spectra and their clear-cut melting points confirm the identity of the complexed anions, and rule out the existence of mixtures of simple complexes $[CoX_4]^{2-}$.

The synthesized $[Et_4N]_2[CoBr_nCl_{4-n}]$ complexes undergo thermal decomposition over the range 270–720 °C in three steps. Both in the inert atmosphere (argon) and in the oxidative atmosphere (static air), $CoCl_2$ is the product of the second step. This indicates that during this step the oven atmosphere does not affect significantly the decomposition process. The atmosphere affects, however, the final decomposition product, because at high temperatures (around 700 °C), $CoCl_2$ is either oxidized to the oxide in the presence of air, or is converted to Co_2C in argon. Also cobalt(II) carbide may be one of the final decomposition products in both atmospheres. However, it could not be identified by available methods among the products of decomposition in static air. It could also not be isolated during the process, because at high temperatures it is instantaneously oxidized to Co_3O_4, the ultimate product of decomposition of the $R_2[CoBr_nCl_{4-n}]$ compounds in the oxidative atmosphere.

The results of this study lead to conclusions that the pathway of decomposition of the bromochlorocobaltates(II) $[CoBr_nCl_{4-n}]^{2-}$, is not affected by the kind of the anion, the temperatures of particular steps are comparable, and the decomposition products are similar. The influence of the kind of the cation on thermal characteristics of the compounds will be investigated.

Acknowledgements

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