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AN ELECTRICAL CONDUCTIVITY (EC) STUDY OF THE THERMAL DISSOCIATION OF $[Co(NH_3)_6]X_3$ AND $[Co(en)_3]X_3$ COMPLEXES

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ABSTRACT

The thermal dissociation of the $[Co(NH_3)_6]X_3$ ($X = Cl^-$, Br^-, I^-, and NO_3^-), $[Co(en)_3]X_3$ ($X = Cl^-$, Br^-, I^-, NO_3^-, HSO_4^- and 1/2 $C_2O_4^{2-}$), *cis*- $[Co(en)_2Cl_2]Cl$, and *trans*-$[Co(en)_2ClBr]NO_3$ complexes was investigated by an electrical conductivity (EC) technique. During the thermal dissociation reactions, liquid or semi-liquid phases are formed which cause large increases in the EC of the compound. The effect of concentration of the complex in a matrix medium as well as the composition of the matrix material on the EC curves were also determined.

INTRODUCTION

The thermal dissociation of the cobalt(III) ammine complexes has been studied by numerous thermal analysis techniques [1]. These techniques include thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomagnetic analysis (TMA), mass spectrometric analysis (MSA), evolved gas detection (EGD) and analysis (EGA), and many others. A neglected experimental technique, at least for investigating the thermal dissociation process of these complexes, is thermoelectrometry. This technique is defined [2] as "one in which the electrical characteristics of a substance are measured as a function of temperature while the substance is subjected to a controlled temperature program". The most common measurements are of resistance, conductance or capacitance.

In this investigation, the electrical conductivity (EC) of the $[Co(NH_3)_6]X_3$ ($X = Cl^-$, Br^-, I^- and NO_3^-) and $[Co(en)_3]X_3$ ($X = Cl^-$, Br^-, I^-, HSO_4^-, SCN^- and NO_3^-) complexes is recorded as a function of temperature. This experimental parameter was chosen because: (a) it is simple to measure in the laboratory since $C = 1/R = I = E/R$ (or k/R if E is constant); and (b) the compounds undergo a fusion reaction during the thermal dissociation process which has been little investigated by any technique.

EXPERIMENTAL

Apparatus

The EC apparatus is described elsewhere [3]. By a concurrent procedure, it was possible to record the DTA curve of the compound at the same time.

The samples were in the form of a pressed disk, approximately 1 mm thick × 6 mm in diameter, composed of the complex and a matrix material (KBr, KCl, K_2SO_4, etc.). A furnace heating rate of 10°C min^{-1} and a flowing nitrogen (30—40 ml min^{-1}) atmosphere were employed.

The EC measurements were obtained using a 0.1 V applied a.c. potential at 1000 Hz. Under these conditions, the recorded current flow through the sample disk was from 0.2 to 100 μA (R = 100—500 kΩ). The measured current flow appeared to be independent of the frequency over the range 100—5000 Hz.

Sample preparation

The complexes studied had all been prepared for previous investigations.

RESULTS AND DISCUSSION

$[Co(NH_3)_6]X_3$ complexes

The thermal dissociation of the $[Co(NH_3)_6]X_3$ complexes have been the most widely investigated, starting with the work of Biltz in 1913 [4—16]. On the basis of these investigations, the thermal dissociation of $[Co(NH_3)_6]Cl_3$ (and bromide) appears to be

$$6\ [Co(NH_3)_6]Cl_3 \rightarrow 3\ (NH_4)_2CoCl_4 \cdot CoCl_2 + N_2 + 28\ NH_3$$

followed by

$$3\ (NH_4)_2CoCl_4 \cdot CoCl_2 \rightarrow 6\ CoCl_2 + 6\ NH_4Cl$$

so that the overall reaction is (in N_2 or air)

$$6\ [Co(NH_3)_6]Cl_3 \rightarrow 6\ CoCl_2 + 6\ NH_4Cl + N_2 + 28\ NH_3$$

According to the DTA curve, in a nitrogen atmosphere, two endothermic peaks accompany the thermal dissociation reaction; the first narrow peak has a $(T_s—T_r)_{min}$ at 280°C, while the second broader peak is at about 350°C. Physical observation of the compound indicates that a fusion reaction occurs during the first peak while the evolution of a sublimate of NH_4Cl takes place during the second peak. From these data, the EC curve should indicate an increase in conductivity during the initial thermal dissociation reaction due to the presence of a conducting liquid, or at least semi-liquid phase. This is indeed what was observed, although the magnitude of the EC is related to the composition of the matrix substance.

Since all of the complexes were studied in the presence of a matrix material, the effect of the composition of the matrix on the EC curve was first investigated. The EC curves of $[Co(NH_3)_6]Cl_3$ in different matrix materials are illustrated in Fig. 1.

As can be seen, there is a wide variation in the EC curve of $[Co(NH_3)_6]Cl_3$ with composition of the matrix material. The EC increase begins at the following temperatures for each matrix: 250°C (KNO_3); 270°C (KBr and

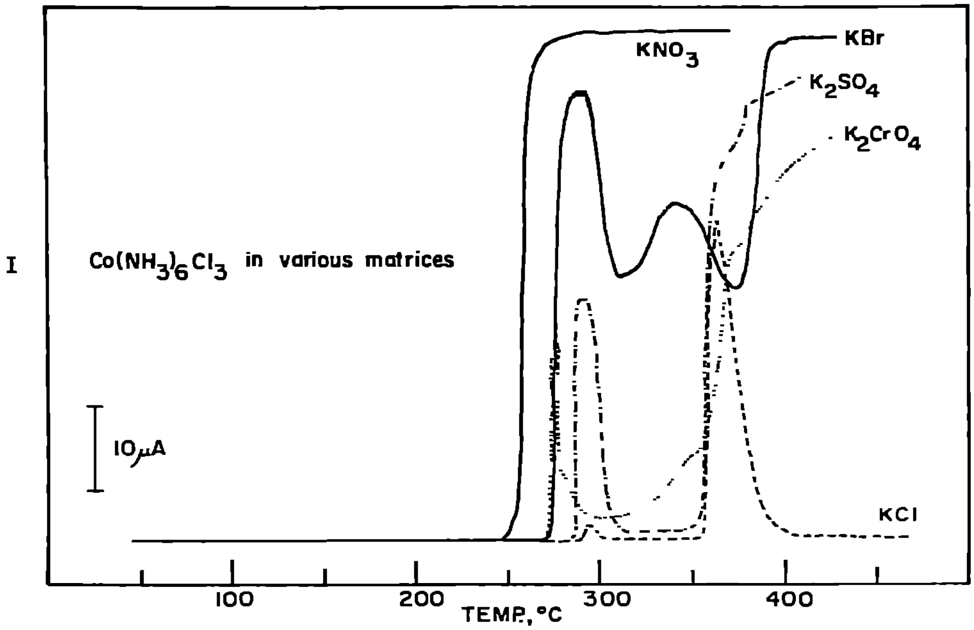

Fig. 1. EC curves of $[Co(NH_3)_6]Cl_3$ in matrices (1 . 1) of KNO_3, KBr, K_2SO_4, K_2CrO_4 and KCl.

K_2CrO_4); 285° C (K_2SO_4) and 290° C (KCl). All of the matrix materials exhibited intermediate peaks in the EC curve except KNO_3, which gave only a pronounced increase in EC to a maximum value of 100 μA. The EC curves all increased with temperature in the 400° C temperature range except that for the KCl matrix. Unfortunately, it is not possible at this time to interpret the reactions responsible for the occurrence of the EC curve peaks in the KCl, KBr, K_2CrO_4 and K_2SO_4 matrices. All of the peaks are related, of course, to the formation of conducting phases formed as intermediates in the thermal dissociation reactions.

The effect of the concentration of $[Co(NH_3)_6]Cl_3$ in a given matrix of KBr is illustrated in Fig. 2.

The minimum temperature for an increase in EC, the peak maximum temperatures and the formation of intermediate curve peaks, are all related to the concentration of $[Co(NH_3)_6]Cl_3$ in the pressed disk samples. The concentration of $[Co(NH_3)_6]Cl_3$ in the disks varied from 6.6 to 50%, all in an identical matrix of KBr. The minimum EC temperature varied from about 270 to 290° C, while the temperatures of the first curve peak maxima ranged from 275 to 315° C. In the 50% composition, a second curve peak was observed at a temperature maximum of about 320° C. The EC curves all increased to a maximum value at about 400° C. The DTA curve for the 50% composition indicates two narrow endothermic peaks at $(T_s - T_r)_{max}$ values of 275 and 390° C, respectively. The first peak is a result of the initial dissociation reaction of the $[Co(NH_3)_6]Cl_3$ while the second is probably a reaction between the KBr matrix and the $CoCl_2$ which is formed during the dissociation reaction. It should be noted that this curve is somewhat differ-

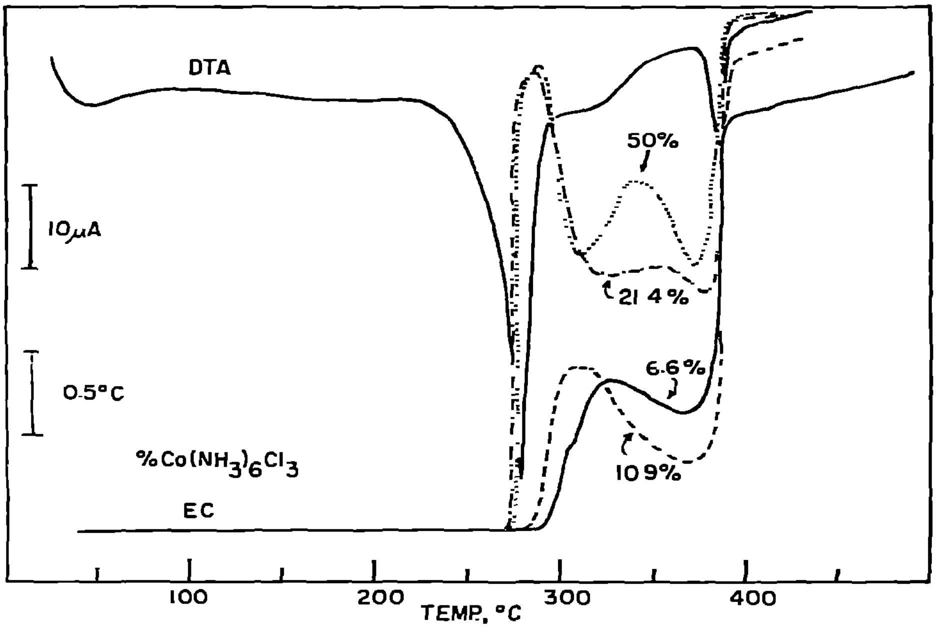

Fig. 2. Effect of concentration of $[Co(NH_3)_6]Cl_3$ in a KBr matrix. Percentage of complex indicated for each curve. DTA curve of 50% complex in KBr.

ent from that obtained for the pure complex, especially the second curve peak.

A comparison of the EC curves for all of the $[Co(NH_3)_6]X_3$ complexes investigated is shown in Fig. 3.

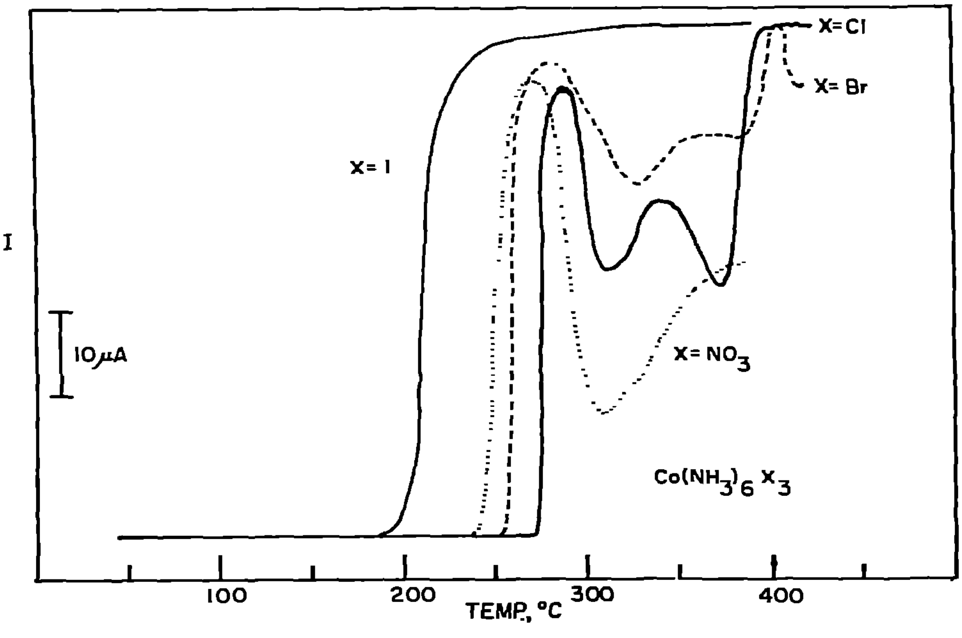

Fig. 3. EC curves for $[Co(NH_3)_6]X_3$ in KBr matrices (1 : 1).

The minimum EC temperatures increased from about 190°C for the iodide to about 270°C for the chloride complex. Intermediate curve peaks besides the initial peak were observed only for the bromide and chloride complexes. In the case of the former, the narrow EC peak at a maximum temperature of about 405°C is probably due to the formation of $CoBr_n^{(n-2)-}$ type complexes. This type of curve peak was also found in the KCl matrix, as given in Fig. 1. All of the EC peaks are related to the formation of liquid or semi-liquid conducting phases in the sample disks. As the temperature approached 400°C, the EC continued to increase, probably as a result of interactions of the dissociation products with the KBr matrix.

[Co(en)₃]X₃ complexes

The thermal dissociation of the $[Co(en)_3]X_3$ type complexes has not been studied as extensively as the $[Co(NH_3)_6]X_3$ complexes. Collins and Wendlandt [17—19], using conventional thermal analysis techniques, extensively studied the $[Co(en)_3]X_3$ complexes, where $X = Cl^-$, Br^-, NO_3^-, HSO_4^- and SCN^-. In a flowing nitrogen atmosphere, the $[Co(en)_3]Cl_3$ complex dissociates according to the reactions

$$[Co(en)_3]Cl_3 \rightarrow \textit{trans}\text{-}[Co(en)_2Cl_2]Cl + en$$

$$\textit{trans}\text{-}[Co(en)_2Cl_2]Cl \rightarrow CoCl_2 + (NH_4)_2CoCl_4 + \text{organic products}$$

$$(NH_4)_2CoCl_4 \rightarrow CoCl_2 + 2\ NH_4Cl$$

$$CoCl_2 + 2\ H^{\bullet} \rightarrow Co + 2\ HCl$$

Two endothermic peaks were observed in the DTA curve (in nitrogen): the

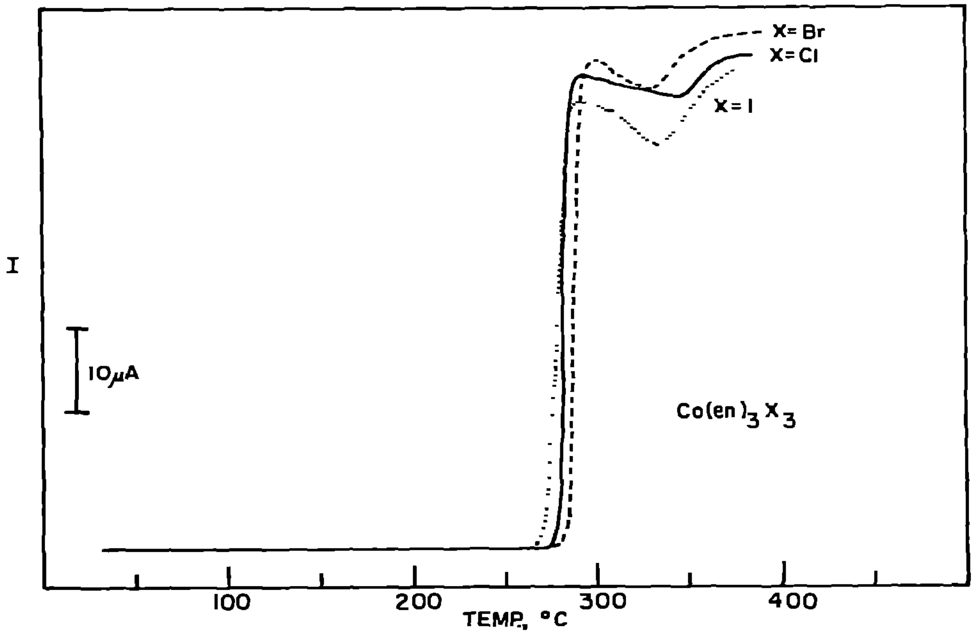

Fig. 4. EC curves of $[Co(en)_3]X_3$ complexes where $X = Cl^-$, Br^- and I^-.

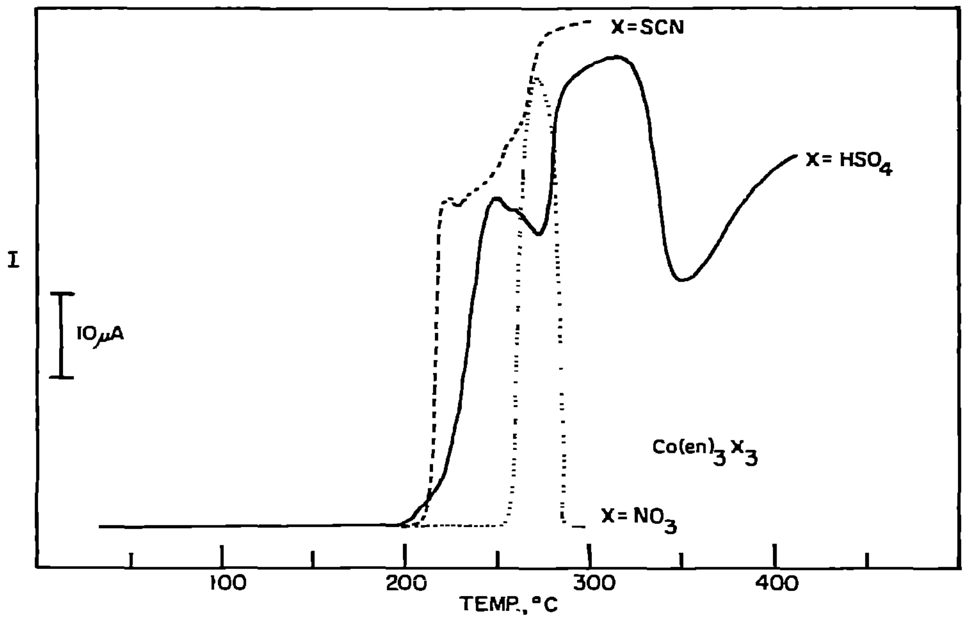

Fig. 5. EC curves of $[Co(en)_3]X_3$ complexes where $X = NO_3^-$, SCN^- and HSO_4^-.

first, a large peak, which was due to the initial fusion and dissociation of the complex, was followed by a smaller peak caused by the dissociation of the compound, $(NH_4)_2CoCl_4$. As in the case of $[Co(NH_3)_6]Cl_3$, the initial dissociation reaction involves fusion of the compound which should cause a large increase in the EC of the sample.

The EC curves of six of the $[Co(en)_3]X_3$ complexes are illustrated in Figs. 4 and 5.

All of the EC curves for the complexes in Fig. 4 reveal a lack of intermediate species that could be resolved by changes in electrical conductivity. The minimum EC temperatures of the complexes ranged from 260 to 270°C with small mimima observed in the 315—325°C range. The EC curves continued at their maximum values up to a maximum temperature of about 400°C.

The EC curve of $[Co(en)_3](HSO_4)_3$ was somewhat more complex (Fig. 5) than the curves for the previous three compounds. Two prominent peaks are displayed with maxima at about 240 and 310°C, respectively. According to the DTA curve of the pure compound [19], a small endothermic peak at 210°C coincided with the initiation of the dissociation process. As the reaction progressed, the rate increased rapidly to a small explosion which appears as a small exothermic peak at about 300°C. These two peaks are presumed to be due to the reaction

$$[Co(en)_3](HSO_4)_3 \rightarrow [Coen(HSO_4)_2] + \text{sulfur oxides} + \text{organic products}$$

The narrow endothermic peak that follows the small exothermic peak is due to the fusion of the product, $[Coen(HSO_4)_2]$. This is then followed by a larger endothermic peak between 300 and 360°C which is due to the dissociation of $[Coen(HSO_4)_2]$ to $Co(HSO_4)_2$. The thermal behavior of

$[Co(en)_3](HSO_4)_3$ in a KBr matrix gave a similar DTA curve (not shown here). Thus, the first peak in the EC curve is caused by the initial dissociation of the complex, while the second one is probably due to the dissociation of the product, $[Coen(HSO_4)_2]$.

The thermal dissociation of $[Co(en)_3](NO_3)_3$ results in a single, narrow EC peak (Fig. 5). This complex dissociates in a rapid exothermic manner, as indicated by its DTA curve [19]. However, the dissociation reaction results in the formation of a conducting species, probably fused NH_4NO_3, if it proceeds according to the stoichiometry [19]

$$[Co(en)_3](NO_3)_3 \rightarrow Co(NO_3)_2 + NH_4NO_3 + en + \text{organic products}$$

For $[Co(en)_3](SCN)_3$, the EC curve indicates a shoulder peak at about 210°C followed by a general increase in conductivity up to about 300°C (Fig. 5). According to the DTA curve for pure $[Co(en)_3](SCN)_3$ [18], there is a large endothermic peak beginning at 215°C which is due to the fusion and initial dissociation of the complex to $[Co(en)_2(SCN)_2]SCN$.

The EC curves $[Co(en)_3]_2(C_2O_4)_3$ and two bis(ethylenediamine) complexes are illustrated in Fig. 6.

The EC curve for $[Co(en)_3]_2(C_2O_4)_3$ contained a very small peak with a peak maximum temperature of about 290°C. This peak occurs during the main dissociation reaction of the complex, as indicated by the DTA curve (not shown). There is then a gradual increase in conductivity starting at about 340°C; however, the DTA curve reveals no dissociation reactions in this temperature range.

The EC curve for *cis*-$[Co(en)_2Cl_2]Cl$ is very similar to that for $[Co(en)_3]Cl_3$.

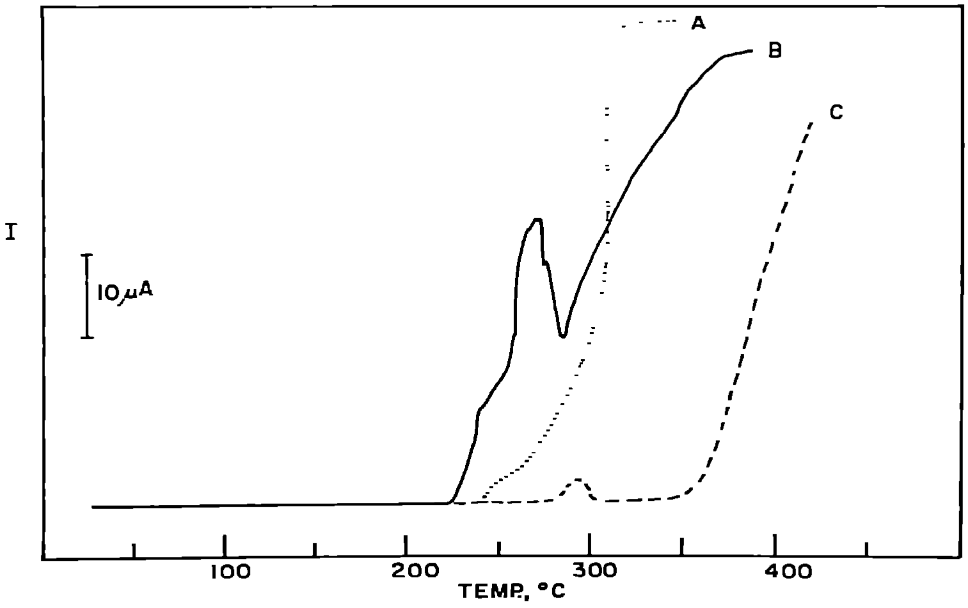

Fig. 6. EC curves of some miscellaneous complexes. (A) *cis*-$[Co(en)_2Cl_2]Cl$; (B) *trans*-$[Co(en)_2ClBr]NO_3$; (C) $[Co(en)_3]_2(C_2O_4)_3$.

The conductivity increases rapidly, starting at about 240° C, and attains a maximum value at 260° C.

The EC curve for *trans*-[Co(en)$_2$ClBr]NO$_3$ reveals the presence of the nitrate ion in the curve by the peak at 270° C. This peak is in the same temperature range as the exothermic peak in the DTA curve (not shown).

CONCLUSIONS

The electrical conductivity (EC) curves of the cobalt(III) ammine complexes reveal temperature ranges in the thermal dissociation reactions where liquid or semi-liquid conducting phases occur. It is difficult, with the data available at the present time, to interpret the origin of some of the curve peaks. Additional studies are needed to elucidate the composition of the intermediate species that are formed during the thermal dissociation reaction, especially for the [Co(en)$_3$]X$_3$ complexes. All that can be concluded from this investigation is that conducting phases are formed, either by the complex itself or by interaction with the matrix material.

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