

## THE THERMAL DISSOCIATION OF THE $[\text{Co}(\text{en})_3](\text{SCN})_3$ AND $[\text{Co}(\text{en})_3]\text{I}_3$ COMPLEXES

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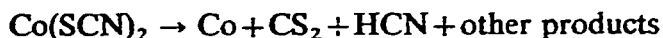
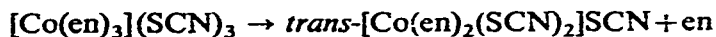
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### ABSTRACT

The thermal dissociation of the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  and  $[\text{Co}(\text{en})_3]\text{I}_3$  complexes was studied by thermogravimetry, differential thermal analysis, thermomagnetic analysis, pyrolytic techniques, evolved gas analysis, and mass spectrometry, *in vacuo* and nitrogen atmospheres. It was found that the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  complex dissociated in four steps:



It was not possible to elucidate the intermediate compounds formed in the thermal dissociation of the  $[\text{Co}(\text{en})_3]\text{I}_3$  complex.

### INTRODUCTION

Recent investigations of the thermal decomposition reactions of some tris(ethylenediamine)cobalt(III) complexes have shown that the anionic species exerts considerable influence on the mode of dissociation of the  $[\text{Co}(\text{en})_3]^+$  cation<sup>1,2</sup>. The  $[\text{Co}(\text{en})_3]\text{Cl}_3$  and  $[\text{Co}(\text{en})_3]\text{Br}_3$  complexes were found to dissociate in a similar manner but the  $[\text{Co}(\text{en})_3](\text{NO}_3)_3$  and  $[\text{Co}(\text{en})_3](\text{HSO}_4)_3$  complexes dissociated by an entirely different set of reactions.

In this study, the dissociation of two additional tris(ethylenediamine)cobalt(III) complexes,  $[\text{Co}(\text{en})_3](\text{SCN})_3$  and  $[\text{Co}(\text{en})_3]\text{I}_3$ , are investigated using several thermo-analytical techniques. The data which are obtained indicated dissociation reactions

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and intermediate compounds which are entirely different from those reported for the  $[\text{Co}(\text{en})_3]$  chloride, bromide, nitrate, and bisulfate complexes.

## EXPERIMENTAL PART

### *Compounds*

The starting material for both  $[\text{Co}(\text{en})_3](\text{SCN})_3$  and  $[\text{Co}(\text{en})_3]\text{I}_3$  was  $[\text{Co}(\text{en})_3]\text{-Cl}_3$ , which was prepared according to the method of Work<sup>3</sup>. The  $[\text{Co}(\text{en})_3](\text{SCN})_3$  complex was prepared by adding potassium thiocyanate to a solution of the chloride complex, precipitating the crystals with ethanol, filtering and drying at 110°C. The  $[\text{Co}(\text{en})_3]\text{I}_3$  complex was recovered from a solution of the chloride complex and hydroiodic acid by precipitation with ethanol. The cobalt content of the complexes was determined gravimetrically by ignition to the oxide,  $\text{Co}_3\text{O}_4$ . The thiocyanate and iodide content was determined by gravimetric analysis with silver nitrate.

### *Thermobalance*

The thermobalance used in this study has been previously described<sup>2</sup>. Sample masses of 5 to 10 mg were used with heating rates of 5° and 10°C/min. The thermal dissociation reactions were carried out in a dynamic nitrogen gas atmosphere at a flow rate of 50 ml/min.

### *DTA apparatus*

DTA studies were performed on a Deltatherm instrument. The DTA runs were made in a dynamic nitrogen atmosphere at a flow rate of about 30 ml/min. Sample sizes used were from 5 to 10 mg with heating rates of 5 to 10°C/min. Runs were made with the reference pan empty and with an alumina reference. The maximum temperature was 500°C.

### *Thermomagnetic analysis*

Simultaneous magnetic-mass change curves were obtained for the complexes by the method previously described<sup>4</sup>. However, the measurements were qualitative and indicated only whether the complex was diamagnetic or paramagnetic. A heating rate of 10°C/min was used with a nitrogen flow rate of 100 ml/min.

### *Thermal analyzer-mass spectrometer-computer system*

This system has been previously described<sup>5</sup>. A heating rate of 6°C/min was used with a mass spectrometer scan rate of  $1.2 \text{ min}^{-1}$ .

## RESULTS AND DISCUSSION

### *Thermogravimetry*

Thermogravimetric curves for the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  and  $[\text{Co}(\text{en})_3]\text{I}_3$  complexes in a dynamic nitrogen atmosphere and *in vacuo* are presented in Fig. 1.

The dissociation of the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  complex begins at about  $215^\circ\text{C}$  in nitrogen and  $150^\circ\text{C}$  *in vacuo*. The complex loses mass at a steady rate until about 17 per cent mass loss where a change in the decomposition rate produces an inflection point in the TG curve. This inflection point corresponds to the formation and subsequent dissociation of  $[\text{Co}(\text{en})_2(\text{SCN})_2](\text{SCN})$ . The greenish appearance of this intermediate suggests that it exists predominately as the *trans* rather than the *cis* isomeric form.

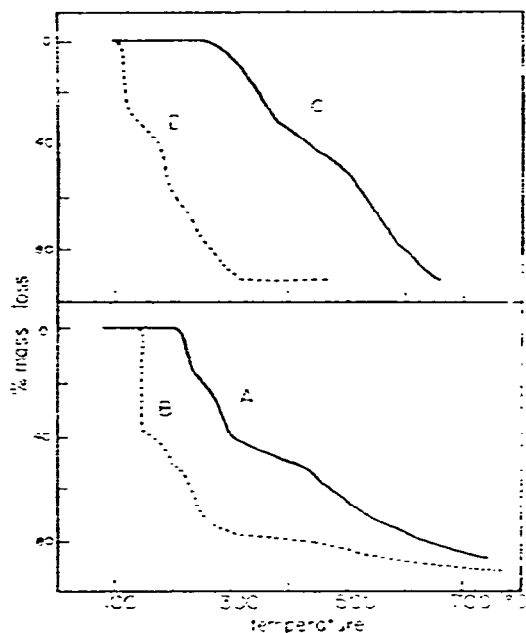


Fig. 1. Thermogravimetric curves of: (A)  $[\text{Co}(\text{en})_3](\text{SCN})_3$  in a nitrogen atmosphere; (B)  $[\text{Co}(\text{en})_3](\text{SCN})_3$  *in vacuo*; (C)  $[\text{Co}(\text{en})_3]\text{I}_3$  in a nitrogen atmosphere; and (D)  $[\text{Co}(\text{en})_3]\text{I}_3$  *in vacuo*.

The intermediate compound produced by the dissociation of the  $[\text{Co}(\text{en})_2(\text{SCN})_2](\text{SCN})$  complex appears as an inflection point in the TG curve at about 40 per cent mass loss. *In vacuo*, the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  complex dissociates directly to this mass level in one reaction step. The compound which is formed corresponds to a substance which seems to have an empirical formula of  $\text{NH}_4\text{Co}(\text{SCN})_3$ ; however, there is some doubt as to whether this intermediate is an ammonium or an ammine complex. Infrared spectra of the intermediate compound show no evidence for an ammonium complex of the type formed in the dissociation of the  $[\text{Co}(\text{en})_3\text{C}]\text{I}_3$  and  $[\text{Co}(\text{en})_3]\text{Br}_3$  complexes. Also, mass spectrometric data suggest that the intermediate may contain ammonia rather than ammonium. Since the intermediate compound could not be isolated in a pure form, no structure determination could be performed.

If the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  complex is heated to  $300^\circ\text{C}$  and held isothermal at this temperature for a day, the complex decomposes to  $\text{Co}(\text{SCN})_2$ . The  $\text{Co}(\text{SCN})_2$  appears in the TG curve as a slight break in the curve at a mass loss of about 55 per cent. This

inflection point appears only at fast heating rates, i.e., 10°C/min or higher, and is a slow change in the slope of the curve rather than a sharp break. The  $\text{Co(SCN)}_2$  decomposes to the cobalt metal which give a stable mass level at about 85 per cent mass loss, in a nitrogen atmosphere. The final mass level was slightly lower under *in vacuo* conditions which could be due to either sublimation of the  $\text{Co(SCN)}_2$  or slight losses of cobalt containing products in the explosive first reaction step.

The thermogravimetric curves in Fig. 1 for the  $[\text{Co(en)}_3]\text{I}_3$  complex *in vacuo* and in a nitrogen atmosphere are very similar to each other in shape but exhibit a large difference in the temperatures at which the dissociation processes occur. Dissociation begins at 255°C in nitrogen and 120°C *in vacuo* with the first inflection point in both curves occurring at about 30 per cent mass loss. The major portion of this mass loss was determined to be due to the loss of ethylenediamine with very little of the iodine being lost. However, the exact stoichiometric composition of this intermediate compound was not determined in this study due to the difficulty in obtaining a pure product.

A slight inflection in the  $[\text{Co(en)}_3]\text{I}_3$  TG curves occurs at about 50 per cent mass loss and corresponds to the composition,  $\text{CoI}_2$ ; this compound can also be obtained by heating the complex isothermally at 300°C for a day. The  $\text{CoI}_2$  dissociates to cobalt metal with the evolution of iodine vapor, which can be detected visually.

#### DTA studies

The DTA curves for the  $[\text{Co(en)}_3](\text{SCN})_3$  and  $[\text{Co(en)}_3]\text{I}_3$  complexes in a dynamic nitrogen atmosphere are presented in Fig. 2.

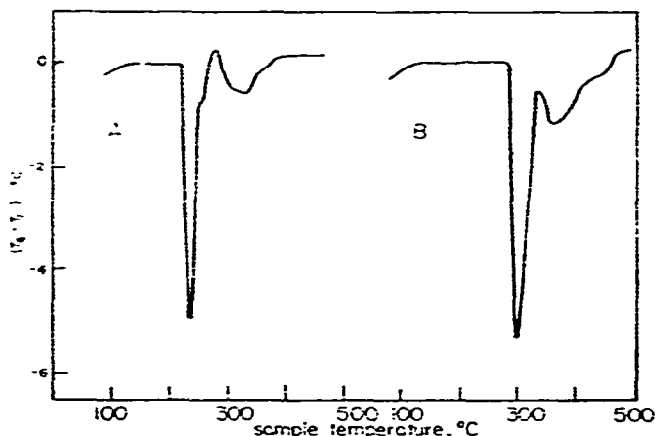


Fig. 2. DTA curves of: (A)  $[\text{Co(en)}_3](\text{SCN})_3$ ; (B)  $[\text{Co(en)}_3]\text{I}_3$ ; (dynamic nitrogen atmosphere at a heating rate of 10°C/min).

The DTA curve for the  $[\text{Co(en)}_3](\text{SCN})_3$  complex shows a large endothermic peak beginning at 215°C and returning to the base line at about 250°C. This peak is due to the melting of the complex and the initial dissociation of the complex to  $[\text{Co(en)}_2(\text{SCN})_2](\text{SCN})$ . The total heat of reaction for the dissociation of  $[\text{Co(en)}_2-$

$(\text{SCN})_2](\text{SCN})$  to  $\text{NH}_4\text{Co}(\text{SCN})_3$  appears to be very near zero or possibly slightly exothermic, as indicated by the 250 to 280 °C region in the curve. Decomposition of the  $\text{NH}_4\text{Co}(\text{SCN})_3$  and  $\text{Co}(\text{SCN})_2$  intermediates produces the final endothermic peak which extends to slightly over 400 °C.

The first large endothermic peak in the DTA curve of  $[\text{Co}(\text{en})_3]\text{I}_3$  corresponds to the loss of ethylenediamine with formation of an intermediate compound of undetermined composition. The other broad, endothermic peak is due to the decomposition of the intermediate compound and  $\text{CoI}_2$ , with the evolution of iodine.

#### *Thermomagnetic analysis*

The magnetic state of the cobalt ion in  $[\text{Co}(\text{en})_3](\text{SCN})_3$  was monitored to temperatures up to 500 °C. The complex, which was originally diamagnetic, remained diamagnetic to a temperature of almost 300 °C. As the mass level of the  $\text{NH}_4\text{Co}(\text{SCN})_3$  intermediate was approached, the remaining product became slightly paramagnetic. This indicates that the cobalt(III) ion was not reduced until  $[\text{Co}(\text{en})_2(\text{SCN})_2](\text{SCN})$  dissociated to  $\text{NH}_4\text{Co}(\text{SCN})_3$ . The residue was becoming increasingly ferromagnetic as the temperature of the system increased (upper limit was 500 °C).

The  $[\text{Co}(\text{en})_3]\text{I}_3$  complex remained diamagnetic until about 30 per cent of the mass was lost. At this point, the remaining residue became paramagnetic. The paramagnetic substance was probably  $\text{CoI}_2$  formed by the dissociation of the unstable intermediate compound. If a significant amount of the iodide had been lost during the first 30 per cent mass loss, the residue would have appeared to be paramagnetic at a much smaller mass loss.

#### *Pyrolysis*

The  $[\text{Co}(\text{en})_3]\text{I}_3$  complex was heated to 275 °C and held at this temperature until about 30 per cent of the mass was lost. At this point, the remaining residue was rapidly cooled and the contents analyzed for iodine content. The experimentally determined amount of iodine was within 5 per cent of the calculated value. This indicates that the initial mass loss was primarily ethylenediamine or fragments of this molecule.

#### *Mass spectroscopy*

The gas evolution curves for the thermal dissociation of the  $[\text{Co}(\text{en})_3](\text{SCN})_3$  shows that gas is evolved in three phases. The first large peak arises from the initial dissociation of the complex to the  $\text{NH}_4\text{Co}(\text{SCN})_3$  intermediate. The second smaller peak is due to the dissociation of this compound while dissociation of the compound,  $\text{Co}(\text{SCN})_2$ , is responsible for the gaseous products released between 300 and 800 °C.

The first step in the dissociation process involves the release of the most of the ethylenediamine, as shown in Fig. 3. This was anticipated since this first step is thought to be the conversion of  $[\text{Co}(\text{en})_3](\text{SCN})_3$  to  $\text{NH}_4\text{Co}(\text{SCN})_3$  with the evolution of ethylenediamine. However, small quantities of ethylenediamine remain in the system to temperatures in excess of 500 °C.

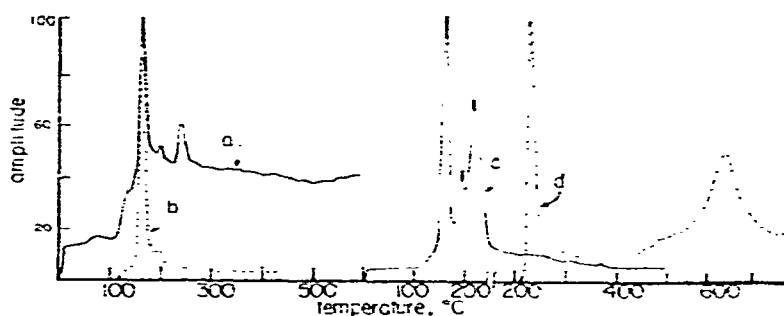


Fig. 3. Mass spectrometric data of: (a) total gas evolution; (b) ethylenediamine evolution; (c) ammonia evolution; (d) carbon disulfide evolution resulting from the thermal decomposition of  $[\text{Co}(\text{en})_3](\text{SCN})_3$  *in vacuo*.

The evolution of ammonia as a function of temperature occurs in essentially two steps. The first large peak in the ammonia gas evolution curve superimposes exactly over the first peak in the ethylenediamine gas evolution curve. Therefore, most of the ammonia is probably due to the fragmentation of the evolved ethylenediamine. The second peak, which extends from about  $175^\circ$  to  $250^\circ\text{C}$ , is due to the dissociation of  $\text{NH}_4\text{Co}(\text{SCN})_3$ . This compound dissociates by first releasing ammonia followed by thiocyanate or thiocyanate-dissociation products. This can be seen in Fig. 3 by comparing the ammonia evolution curve with the gas evolution curve for carbon disulfide, a product from the decomposition of the thiocyanate ion. These two curves will not superimpose on each other since the ammonia peak occurs about  $15^\circ\text{C}$  below the first carbon disulfide peak. If these two products were the result of the dissociation of an ammonium complex or of  $\text{NH}_4\text{SCN}$ , the two peaks would be superimposable, as in the case of the chloride and bromide complexes<sup>1</sup>. This is another indication that the intermediate is an ammine complex.

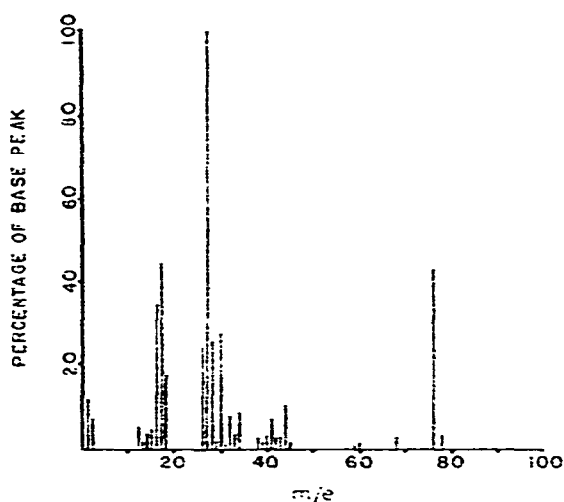


Fig. 4. Mass spectrum of gases evolved from  $[\text{Co}(\text{en})_3](\text{SCN})_3$  at  $230^\circ\text{C}$  *in vacuo*.

The carbon disulfide gas evolution curve gives several additional items of information. This curve shows that no carbon disulfide was evolved until  $\text{NH}_4\text{Co}(\text{SCN})_3$  dissociated to  $\text{Co}(\text{SCN})_2$  while the broad peak which extends to over  $800^\circ\text{C}$  corresponds to the dissociation of  $\text{Co}(\text{SCN})_2$  to cobalt metal.

The mass spectrum of gases evolved from the thiocyanate complex at  $230^\circ\text{C}$  is given in Fig. 4. At this temperature,  $\text{NH}_4\text{Co}(\text{SCN})_3$  is dissociating with the evolution of ammonia and the products from the thiocyanate ion. Dissociation of the thiocyanate ion produces carbon disulfide which is responsible for the peak at  $m/e = 76$ . The base peak in this spectrum occurs at  $m/e = 27$  and is probably due to HCN, which is also a possible dissociation product of the thiocyanate ion. Most of the remaining peaks are probably due to traces of organic compounds which remain in the system from the decomposition of the ethylenediamine.

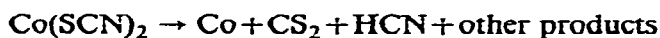
Mass spectroscopy was of limited use in the study of the thermal dissociation of the  $[\text{Co}(\text{en})_3]\text{I}_3$  complex since data were obtained only for  $m/e$  of 110 or less. Therefore, no compounds containing iodine could be observed. However, all spectra obtained at temperatures of less than about  $150^\circ\text{C}$  were identical to the spectrum obtained for ethylenediamine.

#### CONCLUSIONS

The  $[\text{Co}(\text{en})_3](\text{SCN})_3$  complex was found to dissociate in a series of four steps. The initial two steps are:



where  $\text{NH}_4\text{Co}(\text{SCN})_3$  is only the empirical formula of the intermediate compound. Although the actual structure was not determined, there is some evidence which suggests that this intermediate is actually an ammine rather than an ammonium complex. Dissociation of the intermediate compound gives the final two reactions:



The  $[\text{Co}(\text{en})_3]\text{I}_3$  complex initially dissociates with a 30 per cent mass loss, most of which is ethylenediamine, to an undetermined intermediate compound. These data suggest that this intermediate is a cobalt(III) complex containing all or most of the iodide from the original complex. The intermediate compound is thermally unstable and dissociates to  $\text{CoI}_2$  which evolves iodine to yield cobalt metal.

#### ACKNOWLEDGEMENTS

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