

A STUDY OF THERMAL DECOMPOSITION OF TRIS(ETHYLENEDIAMINE)COBALT(III) CHLORIDE: DILUTION EFFECTS*

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ABSTRACT

Tris(ethylenediamine)cobalt(III) cations were reacted with the clay mineral montmorillonite and were studied by DTA methods. The Co(en)_3^{3+} salt was also mechanically mixed with varying amounts of alumina or silica and DTA patterns obtained. The results of the several DTA runs were compared in order to understand more completely the type of interaction that might be taking place between the Co(en)_3^{3+} ion and the montmorillonite.

INTRODUCTION

In the course of studying a number of transition metal complexes that had been cation exchanged onto a montmorillonite, differential thermal analysis experiments were conducted. The DTA studies were performed in the hope that information concerning the type of interaction between the transition metal complex and the clay surface or clay edges might be determined. DTA patterns were obtained under flowing-air and flowing-nitrogen conditions for these montmorillonite complexes. No correlation was found between the DTA patterns of the complexes on the clay and the DTA patterns of the corresponding pure salts. For this reason it was decided to run the pure complex salts diluted with alumina or silica in order to see if any correlation could be obtained. Silica and alumina were chosen because the montmorillonite structure is an alumina-silicate layer structure consisting of a sandwich of two silica layers containing an alumina layer in the center. Drastic changes in the DTA curves resulted.

Garn¹ and others have reported that dilution of a sample with an "inert" material should be done with care since under some conditions unwanted changes in the DTA patterns take place. Based upon the results obtained in our studies, we felt that it would be well to re-emphasize this problem and to indicate some of the difficulties that one experiences when organic materials or in this case transition metal-organic complexes are diluted with "inert" materials.

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EXPERIMENTAL

The DTA unit used in these experiments was a unit built in these laboratories using a Columbia Scientific Sample Holder utilizing ring thermocouples and a Model I Stone furnace. The programmed heating rate was obtained by means of a West Controller utilizing a motor-driven 10-turn potentiostat as a means of controlling the reference input to the controller. The motor used to drive the potentiostat was a variable speed motor so that the heating rate could be continuously changed depending upon the conditions desired. For the curves reported in this paper all heating rates were 10° per min. A Honeywell potentiometric recorder was used to record the reference temperature while a Brown photopen type recorder and a L and N galvanometer was used to record the differential temperature. A folded light path of approximately 10 feet was used in conjunction with the galvanometer recorder which provided very high sensitivities for the DTA signal.

A number of different transition-metal complexes were used in these experiments but only one is reported herein. This material was the salt, tris(ethylenediamine)cobalt(III) chloride. This was a purified material obtained from Alfa Chemicals. Varying amounts of this salt were added to a centrifuged, sodium ion-exchanged Wyoming montmorillonite obtained from the Bariod Division, NL Industries, Houston, Texas. The montmorillonite used had a cation exchange capacity of approximately 94 milliequivalents (meq) per 100 g of dry clay. The amounts of tris(ethylenediamine)cobalt(III), Co(en)_3^{3+} , used were 100%, 60%, and 20% of the total exchange capacity. In other words the amount of cobalt complex added ranged from 94 meq per 100 g of dry clay to approximately 18 meq per 100 g of dry clay.

The diluents that were used in these studies were a calcined alumina in the form of $\alpha\text{-Al}_2\text{O}_3$ and silica, SiO_2 . No attempt was made to control humidity over samples prior to insertion in DTA cell. Clay samples were kept over H_2SO_4 to keep clay dehydration from obscuring complex peaks.

DISCUSSION AND RESULTS

In all of the experiments discussed here the samples were run under conditions of air flow and nitrogen flow. Fig. 1 shows the DTA results for the Co(en)_3^{3+} montmorillonite complexes run under conditions of air flow while Fig. 2 shows the same samples run under conditions of nitrogen flow. The endothermic peak at approximately 100°C on both sets of curves was related to the adsorbed water on the clay complex. Following the water loss peak there appeared an exothermic peak at approximately 250°C which was then followed by a somewhat larger and broader peak at about 325°C with a rather large tailing up to the maximum temperature of 650°C. The difference between the air flow and the nitrogen flow was only slight with the 250°C peak much stronger under air flow conditions than under nitrogen flow conditions. Going from 100% of the exchange capacity to 20% of the exchange capacity with the cobalt complex did not have any great change in the DTA curve, except for

the decreasing 250°C peak. It might be remarked that the particular montmorillonite used in these studies has a very strong dehydroxylation endothermic peak at approximately 600°C. It is interesting to note that the exothermic reaction that was taking place was strong enough so that the dehydroxylation peak was not indicated on these curves except possibly in the 20% exchange capacity curves for both the air flow and nitrogen flow. This was indicated by the slight dip in the broad exothermic curve at approximately 500°C.

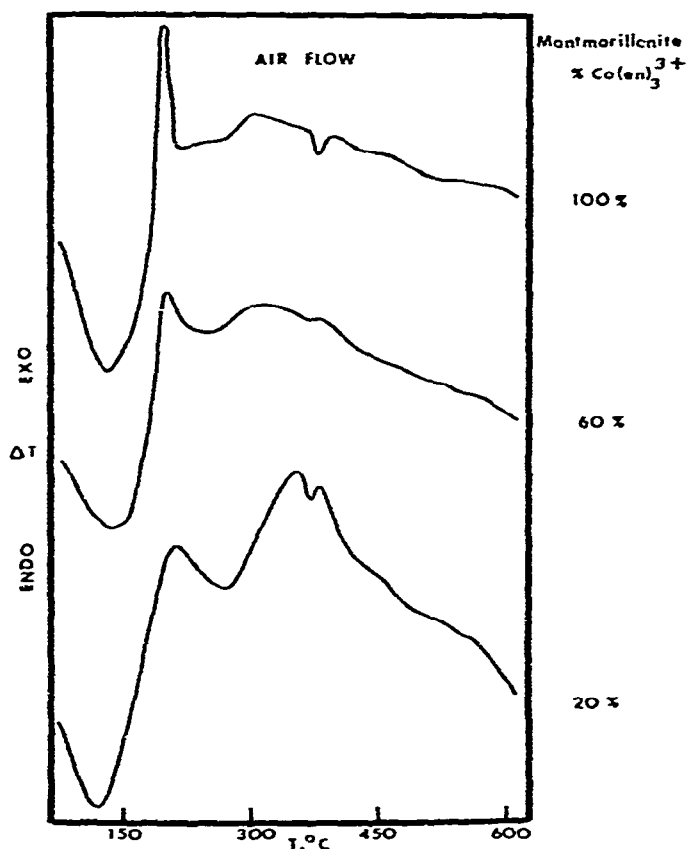


Fig. 1. DTA patterns of the Co(en)_3^{3+} -montmorillonite complexes using air flow; heating rate, $10^\circ\text{C}/\text{min}$.

We were interested in trying to determine what type of interaction the cobalt complex had with the clay montmorillonite. It is known that approximately 20% of the cation exchange capacity of the clay is on the edges of the clay which result from broken alumina and silica bonds². On the other hand the basal surface, or the large flat surface, of the clay montmorillonite is negatively charged due to lattice defects within the montmorillonite structure. For this particular clay most of the defects are in the octahedral alumina layer resulting from substitution of Mg^{2+} ions for the Al^{3+} ions in the idealized structure. This results in a negative charge and this is what leads to the major amount of cation exchange capacity of the clay. The trivalent cobalt

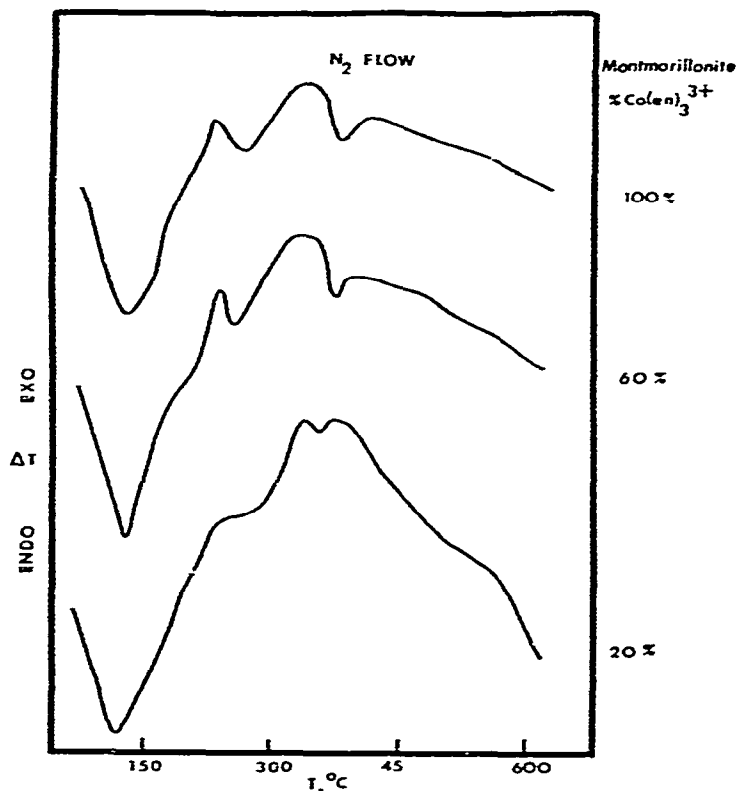


Fig. 2. DTA patterns of the Co(en)_3^{3+} -montmorillonite complexes using N_2 flow; heating rate, $10^\circ\text{C}/\text{min}$.

complex was therefore associated with the clay surface through the electrostatic forces involved between the negatively charged clay and positively charged cation. We were interested to determine if the structure of the cobalt complex might be changed in some manner so that the positive charge could be more closely associated and aligned with the negative charges of the basal surface, or possibly the edges, or whether it was predominantly an interaction of the ethylenediamine molecules with the surface or edges of the clay. If it was the former, one would expect the interaction to be both through the electrostatic forces and through possible hydrogen bonding of the ethylenediamine portion of the molecule to the oxygen surfaces or the oxygen edges of the clay. X-ray diffraction studies of the 100% complex-clay indicated a d -spacing of approximately 14.2 \AA . Utilizing a model of the Co(en)_3^{3+} ion and the fact that the clay particle thickness is approximately 9.4 \AA it can be deduced that the Co(en)_3^{3+} molecule was oriented along its long axis between subsequent clay platelets. This also indicated that there was no deformation of the Co(en)_3^{3+} ion as it interacted with the clay surface.

The Co(en)_3^{3+} salt was added in varying ratios to both silica and to alumina to determine if any correlation with the complex-clay results could be obtained as a result of possible interaction between the cobalt complex and these diluents. Figs. 3-6

illustrate the DTA results obtained when the Co(en)_3^{3+} was diluted to varying ratios with alumina and silica under conditions of air flow and nitrogen flow.

Fig. 3 shows the DTA curves obtained for a series of the cobalt complexes diluted with varying amounts of alumina. The uppermost curve was that obtained for the pure Co(en)_3^{3+} . Going down the set of curves the amount of alumina was increased with respect to the amount of cobalt complex salt. These curves were obtained under conditions of air flow. It will be noted in the pure cobalt complex that a small endothermic peak was obtained which was probably due to adsorbed water. This was followed by a peak at approximately 275°C which corresponded to the melting point

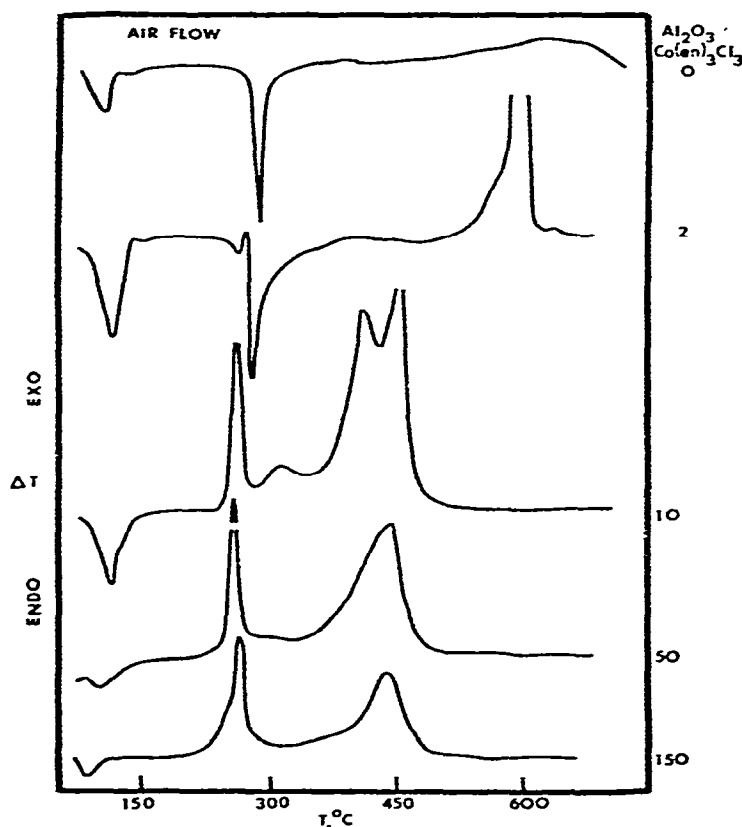


Fig. 3. DTA patterns of $\text{Co(en)}_3\text{Cl}_3$ diluted with alumina using air flow; heating rate, $10^\circ\text{C}/\text{min}$.

of the Co(en)_3^{3+} . The curve did not seem to indicate any pyrolysis or decomposition until a temperature of about 450°C was reached at which time a very broad exothermic reaction commenced. This broad exothermic peak was probably due to the pyrolysis of the organic portion of the Co(en)_3^{3+} . When two moles of aluminum oxide per 1 mole of the cobalt complex were placed in the DTA furnace curve number 2 was obtained. It will be noted from this curve that the main difference from curve 1 is a very small exothermic peak just preceding the melting of the cobalt complex at approximately 275°C . This is followed by a very strong, sharp exothermic peak which appears at

about 550°C. The presence of the small amount of alumina seemed to cause the pyrolysis or decomposition of the organic portion of the complex to occur over a much narrower range of temperature and to change what was formerly a very broad peak to a very narrow, strong exothermic peak.

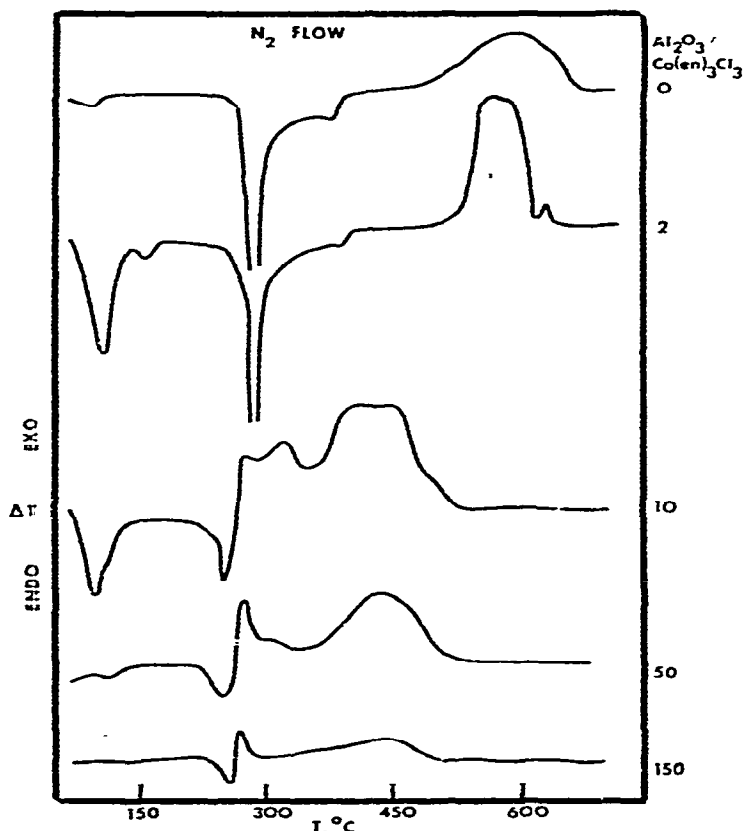


Fig. 4. DTA patterns of $\text{Co(en)}_3\text{Cl}_3$ diluted with alumina using N_2 flow; heating rate, $10^\circ\text{C}/\text{min}$.

Further increase in the amount of alumina caused a very drastic change in the character of the DTA curve. What had formerly been an endothermic peak associated with the melting point of the Co(en)_3^{3+} was now, at a slightly lower temperature, a very strong, sharp exothermic peak. This was then followed by another weaker exothermic peak at about 350°C which was then followed by a pair of very strong exothermic peaks starting at about 400°C and ending a little above 450°C . It appeared that the alumina was interacting with the cobalt complex in such a way that the entire character of the DTA curve was changed. It is proposed that the first exothermic peak at about 260°C may be associated with the adsorption of the melted Co(en)_3^{3+} salt onto the surface of the alumina. With the cobalt complex now adsorbed on the surface of the alumina, the interaction between the salt and its surroundings can be enhanced, and thus the breakdown and pyrolysis of the organic portion of the complex takes place at a considerably lower temperature than it did when the salt was in its pure state.

or even when only a small amount of alumina was present. The other two curves in Fig. 3 obtained with increasing amounts of alumina were essentially the same, with the exception that the intensity of the peaks were decreased. This of course would be expected since the amount of the cobalt complex was decreasing from a mole ratio of 10:1 to 150:1. It can be seen, however, that even at a ratio of 150 moles of alumina to 1 mole of cobalt complex salt, the distinguishing features of the DTA curve were quite apparent.

Fig. 4. shows the same set of curves for the alumina-cobalt complex but under conditions of nitrogen flow. Essentially the curves behaved in the same manner as in air. There was one feature that appears on the nitrogen flow curves that did not appear in the air flow. This was a small endothermic peak at a temperature of about 380°C. The endothermic peak that appeared on the pure sample, the 2-mole-ratio sample and the 10-mole-ratio sample at a somewhat lower temperature, may be associated with some physical change that was taking place. It will be noted that the presence of the alumina caused a sharpening of the high temperature exothermic peak and then as the amount of alumina is increased it caused a lowering of the temperature at which the decomposition of the organic material occurred. It will also be noted that the change from an endothermic peak to an exothermic peak took place under nitrogen flow although the exothermic peak was not as pronounced as it was in air flow.

Figs. 5 and 6 show the DTA curves for mixtures of silica and cobalt complex salt with increasing amounts of silica under conditions of air flow and nitrogen flow, respectively. Under conditions of air flow it will be noted that, as in the case of the alumina-cobalt complex salt mixtures, as the amount of silica is increased, there occurred a lowering of temperature and sharpening of the strong high-temperature exothermic peak, which is associated with the decomposition of the organic portion of the molecule. It will be also noted that as with the alumina samples the endothermic reaction associated with the melting of the cobalt salt reversed to an exothermic reaction at a slightly higher temperature. In Fig. 5 the curve for the 3 moles of silica per 1 mole of cobalt complex salt, there also appeared a relatively strong and sharp exothermic reaction at a temperature of about 325°C. Since this particular peak does not appear on either of the other two curves it was not known what its significance might be. It will be noted on this same sample that there did appear an indication of an exothermic peak following the endothermic peak associated with the melting. Fig. 6 shows these same curves under nitrogen flow and again essentially the same results were obtained. However, it will be noted that in the 20 mole-ratio sample that the 325°C endothermic peak still appeared and furthermore, as was the case with the alumina samples, the exothermic reaction following the endothermic peak associated with melting was not nearly so pronounced under conditions of nitrogen flow.

Comparing Figs. 3, 4, 5, and 6 with Figs. 1 and 2 for the Co(en)_3^{3+} montmorillonite complex showed little, if any, correlation between the various curves. One possible conclusion was that the broad exothermic reaction associated with the montmorillonite-cobalt complex was the same type of pyrolysis and decomposition that took place when the cobalt complex was mixed with either alumina or silica. This may

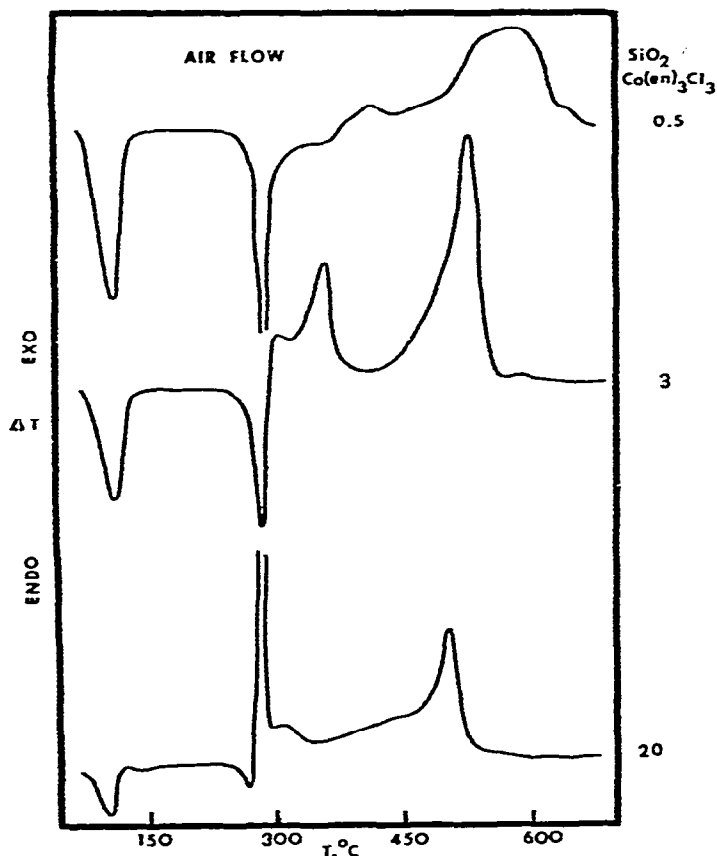


Fig. 5. DTA patterns of $\text{Co}(\text{en})_3\text{Cl}_3$ diluted with silica using air flow; heating rate, $10^\circ\text{C}/\text{min}$.

indicate that as a thin layer of the cobalt complex was spread out on an essentially inert surface such as alumina, silica or clay, that the transfer of heat energy to the material took place more efficiently or more rapidly, thus allowing the decomposition to occur at a much lower temperature than it can for the pure cobalt complex salt. A further consideration must also be made with regard to the possible catalytic effects that may be occurring. It may be that the lowering of the temperature of decomposition and/or pyrolysis may be due to a catalytic effect of the alumina, silica or montmorillonite surfaces. If this was the case, the indications would be that the alumina catalyzed the decomposition at a temperature of about 375°C and allowed the reaction to take place over a very narrow range. On the other hand, the silica catalyzed this reaction at a temperature of about $475\text{--}500^\circ\text{C}$ and the reaction occurred over a much wider temperature range as indicated by the broader exothermic peak that occurred. The montmorillonite on the other hand appears to have catalyzed this decomposition at even a lower temperature than occurred with the alumina. The sample containing the largest amount of $\text{Co}(\text{en})_3^{3+}$ ion had its exothermic peak starting at a temperature as low as $200\text{--}225^\circ\text{C}$. There were several broad peaks which lasted up to approximately 600°C . As the amount of cobalt complex on the montmorillonite surface was

decreased its decomposition appeared to occur over a somewhat narrower range, but in all cases the very strong exothermic peak starting at about 200°C continued to indicate that the montmorillonite surface interaction with the cobalt complex allowed the decomposition to start at a substantially lower temperature than it did with either the alumina or the silica.

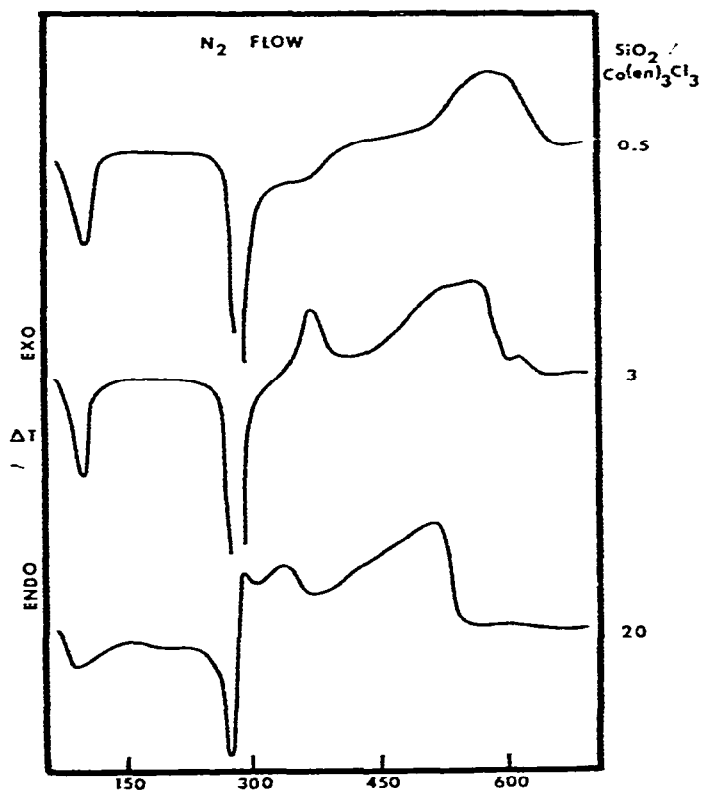


Fig. 6. DTA patterns of $\text{Co(en)}_3\text{Cl}_3$ diluted with silica using N_2 flow; heating rate, $10^\circ\text{C}/\text{min}$.

The one big difference, of course, was the fact that the montmorillonite has a negative charge on its basal surfaces and this is where most of the Co(en)_3^{3+} ion was associated. As indicated earlier, according to the X-ray diffraction results, the cobalt complex was oriented along its long axis and there was apparently electrostatic interaction between the lower and the upper particles of montmorillonite. This electrostatic pull associated with the silica surfaces of the clay might be sufficient to decrease the energy of association of the ethylenediamine molecules with the cobalt to a point where they decompose at the lower temperature.

These results show the need to be cautious in the use of "inert" diluents in DTA experiments. Figs. 3, 4, 5 and 6 all show that quite different DTA patterns were obtained for the same complex simply diluted with increasing amounts of the "inert" diluents. Therefore, attempts to qualitatively or semi-quantitatively analyze for a given compound in mixtures by DTA must be done with great caution. Checks for

dilution effects over a large range of compositions should be checked for each new type of mixture.

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