

## INTERMEDIATE SPECIES IN THERMAL REACTIONS BETWEEN MIXED ETHYLENEDIAMINE-*o*-PHENANTHROLINE COBALT(III) COMPLEXES AND AMMONIUM SALTS IN THE SOLID PHASE \*

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### ABSTRACT

Solid—solid thermal reactions, in the range 140–180°C, between  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$  and some cobalt(III) complexes containing ligands with only nitrogen as donor atoms, are reported. The products are separated by thin layer chromatography and characterized by direct spectrophotometry, scanning the plates after TLC. Only in the case of  $[\text{Co}(\text{o-phen})_2\text{en}]\text{Y}_3$  ( $\text{Y} = \text{Cl}^-$ ,  $\text{NO}_3^-$ ) is an effect of  $\text{NH}_4\text{Cl}$  found. The formation of two intermediate species is evidenced: the first,  $\text{cis-Co}(\text{o-phen})_2\text{Cl}_2^+$ , is obtained by substitution of an ethylenediamine molecule by chloride ions; the other,  $\text{Co}(\text{o-phen})_3^{3+}$ , by subsequent displacement of chloride ions by the free *o*-phenanthroline coming from initial decomposition of the complexes. On heating in the presence of  $\text{NH}_4\text{NO}_3$  the complexes do not undergo any changes. The reactivity order is:  $[\text{Co}(\text{en})_3]\text{Y}_3 \approx [\text{Co}(\text{o-phen})(\text{en})_2]\text{Y}_3 < [\text{Co}(\text{o-phen})_3]\text{Y}_3 < [\text{Co}(\text{o-phen})_2\text{en}]\text{Y}_3$ .

In two previous papers [1,2] we reported the isolation of intermediates formed in the solid phase, on heating  $\text{NH}_4\text{Cl}$  and a compound of the following series of cobalt(III) complexes: *cis*-, *trans*- $[\text{Co}(\text{en})_2(\text{OCOC}_6\text{H}_4\text{R})_2]\text{NO}_3$ ,  $[\text{Co}(\text{en})_2\text{X}]\text{Y}$  (*en* = ethylenediamine; *R* = H, *p*- $\text{CH}_3$ , *p*- $\text{OCH}_3$ , *p*-Cl; *X* =  $\text{CO}_3$ , malonate; *Y* =  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ). In agreement with the observation made by Chang and Wendlandt [3] for aquo—amino complexes, we found that chloride ions preferentially replace ligands having oxygen as donor.

In this study we present results on the thermal stability of some cobalt(III) complexes containing ligands with only nitrogen as donor atoms, in the presence and absence of  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ . The compounds examined are as follows (*o-phen* = *ortho*-phenanthroline)

$[\text{Co}(\text{o-phen})_3]\text{Y}_3$ ,  $[\text{Co}(\text{o-phen})_2(\text{en})]\text{Y}_3$  and  $[\text{Co}(\text{o-phen})(\text{en})_2]\text{Y}_3$ .

In addition the thermal behaviour of *cis*- $[\text{Co}(\text{o-phen})_2\text{Cl}_2]\text{Cl}$ , a species assumed to be an intermediate in reactions involving the first two compounds, was also studied.

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As in our previous studies [1,2], thin layer chromatography (TLC) was used to follow the progress of the reaction. In order to characterize the compounds separated by TLC, we measured the spectra of the unknown species. Elution of the chromatographically separated products and their solution spectra did not give satisfactory results. Good results were achieved by direct spectrophotometry, scanning the plates after TLC.

## EXPERIMENTAL

The complexes were prepared as described in the literature:  $\text{Co}(o\text{-phen})_3^{3+}$  and  $\text{Co}(o\text{-phen})_2(\text{en})^{3+}$ , both as nitrate and chloride [4];  $\text{Co}(o\text{-phen})(\text{en})_2^{3+}$ , as nitrate [4] and as chloride [5]; *cis*- $[\text{Co}(o\text{-phen})_2\text{Cl}_2]\text{Cl}$  [6]; *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  [7];  $[\text{Co}(\text{en})_3]\text{Cl}_3$  [8]. The procedures used for the thermal reactions and detection of *o*-phenanthroline were described in previous papers [1,6]. Both  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$  were used in a fifty-fold molar excess.

### Chromatography

Separation of products was by TLC on  $5 \times 5$  silica gel precoated plates (Merck, Darmstadt, West Germany). Development was carried out in small rectangular glass TLC tanks ( $7 \times 3.5 \times 7$  cm). The plates were "washed" in order to concentrate traces of iron, which interfered with the detection of  $\text{Co}^{2+}$ , on the upper edge of the plate. First, ascending development with 1 M  $\text{HCl-EtOH}$  (1 : 5), then with water-EtOH (1 : 5) was used; finally the plates were activated in an oven at  $110^\circ\text{C}$  for 1 h.

A solution (0.1–0.3  $\mu\text{l}$ ) containing 2–3 mg of the sample in 6 M  $\text{HCl-EtOH}$  (1 : 5) was applied as a thin streak. Chromatograms were developed with saturated aqueous  $\text{LiCl-EtOH}$  (1 : 2) as eluent. Under these conditions *cis*- $[\text{Co}(o\text{-phen})_2\text{Cl}_2]\text{Cl}$ , which readily hydrolyses in aqueous solutions, moves as a single narrow band. Ascending development to a height of about 2 cm was normally complete in 15 min. The spots were detected by spraying with ammonium sulphide solution. This reaction may be used to determine whether or not cobalt is still complexed with ethylenediamine and/or phenanthroline: in the presence of ammonium sulphide the spot turns brown in the first case, black in the second.  $R_f$  values found:  $\text{Co}(o\text{-phen})_3^{3+}$ , near starting point;  $\text{Co}(o\text{-phen})_2(\text{en})^{3+}$ , 0.12;  $\text{Co}(o\text{-phen})(\text{en})_2^{3+}$ , 0.58; *cis*- $\text{Co}(o\text{-phen})_2\text{Cl}_2^+$ , 0.21; *cis*- $\text{Co}(\text{en})_2\text{Cl}_2^+$ , 0.94;  $\text{Co}(\text{II})$ , at the liquid front ( $\text{Co}(\text{II})$  denotes cobalt(II) not complexed with *o*-phenanthroline and/or ethylenediamine).

### Spectrophotometry

For these experiments, it is necessary to use 1–2  $\mu\text{l}$  of solution of complexes, prepared as described above, which is applied on the plates as a round spot. After the chromatographic separation, the spots were scanned directly on the plate with the KM-3 Chromatogram-Spectrophotometer (Carl Zeiss, West Germany) in the reflectance mode, in the range from 360 nm to 600 nm. The spectrophotometer parameters were:  $\Delta\lambda$ , 20 nm; slit width, 0.1

mm; slit length, 3.5 mm; scanning speed, 50 mm min<sup>-1</sup>. The plates were scanned in a direction parallel to the direction of solvent flow. The apparatus gives readings at definite wavelengths. We obtained the spectra of each separated species by joining graphically the peaks obtained for each spot at the various wavelengths.

## RESULTS AND DISCUSSION

Preliminary experiments had shown that both the chloride and nitrate forms of the complexes under investigation decompose to a significant extent at temperatures above 200°C only. In order to study their eventual thermal rearrangement, therefore, the complexes or the complex—ammonium salt mixtures were heated at constant temperature for 0.5–24 h. The conditions of the thermal experiments and the main reaction products obtained from the complexes in the chloride form are summarized in Table 1. The reaction products were mainly identified by TLC and spectrophotometry data.

### *[Co(o-phen)<sub>3</sub>]Cl<sub>3</sub>*

The same products were obtained whether this complex was heated in the presence or absence of NH<sub>4</sub>Cl. After a reaction time of about 4 h, free *o*-phenanthroline and Co(II) began to appear on the chromatogram, together with two other spots to be identified. The first of the unknown spots had the same colour and *R<sub>f</sub>* value (0.21) as *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub>, which increased when [Co(*o*-phen)<sub>3</sub>]Cl<sub>3</sub> was heated in the presence of NH<sub>4</sub>Cl. The second unknown species (*R<sub>f</sub>* = 0.6) exhibited a chromatographic behaviour similar to that of the cobalt(II)—phenanthroline intermediate products, which are formed before oxidation in the mixture used for the preparation of Co(*o*-phen)<sub>3</sub><sup>3+</sup> [5]. Considering that the decomposition of some cobalt(III) complexes may also involve reduction to a cobalt(II) species [9], the second product might be a cobalt(II)—phenanthroline complex. It should be noted that both products were present in small quantities only, even after 24 h of heating, and the main species in the samples was always the initial complex.

On heating in the presence of NH<sub>4</sub>NO<sub>3</sub> the complex did not undergo any changes according to the chromatographic analysis.

### *[Co(o-phen)<sub>2</sub>(en)]Cl<sub>3</sub>*

In contrast to the previous case, reaction in the presence of NH<sub>4</sub>Cl yielded products different from those obtained from the thermal decomposition of the complex per se, as seen from the results in Table 1. After about 1 h of heating, the mixture complex—NH<sub>4</sub>Cl was coloured green. Our chromatographic results showed that this green colour was not due to the formation of a *trans*-dichloro complex, according to results on the “supposed” *trans*-[Co(bipy)<sub>2</sub>Cl<sub>2</sub>]Cl [10] (bipy = 2,2'-bipyridyl). Together with Co(II) at least four products were found: their relative amounts depended on the reaction time. The *R<sub>f</sub>* values were 0.03, 0.21, 0.6, and 0.7. The first two products appeared after about 30 min, whereas the other two, which in the light of

TABLE I  
Solid-solid reactions of some phenanthroline complexes of cobalt(III) with ammonium salts

Complex	Salt	Reaction temp. (°C)	Heating time (h)	Main species <sup>a</sup>
[Co( <i>o</i> -phen) <sub>3</sub> ]Cl <sub>3</sub>	—	165	1-24	Initial complex; small amount of <i>cis</i> -Cophen <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>
[Co( <i>o</i> -phen) <sub>2</sub> (en)]Cl <sub>3</sub>	—	165	0.5-7	Cobalt(II)—phenanthroline complex ( <i>R</i> <sub>1</sub> 0.7); Co(II); phenanthroline
[Co( <i>o</i> -phen)(en) <sub>2</sub> ]Cl <sub>3</sub>	—	180	1-24	Initial complex
<i>cis</i> -[Co( <i>o</i> -phen) <sub>2</sub> Cl <sub>2</sub> ]Cl	—	165	0.5-7	Initial complex; Cophen <sub>3</sub> <sup>3+</sup>
[Co( <i>o</i> -phen) <sub>3</sub> ]Cl <sub>3</sub>	NH <sub>4</sub> Cl	165	1-24	As in reaction (1)
[Co( <i>o</i> -phen) <sub>2</sub> (en)]Cl <sub>3</sub>	NH <sub>4</sub> Cl	165	0.5-4	<i>cis</i> -Cophen <sub>2</sub> Cl <sub>2</sub> <sup>+</sup> ; Cophen <sub>3</sub> <sup>3+</sup>
[Co( <i>o</i> -phen)(en) <sub>2</sub> ]Cl <sub>3</sub>	NH <sub>4</sub> Cl	180	1-24	Initial complex
<i>cis</i> -[Co( <i>o</i> -phen) <sub>2</sub> Cl <sub>2</sub> ]Cl	NH <sub>4</sub> Cl	165	0.5-7	Initial complex; small amount of Cophen <sub>3</sub> <sup>3+</sup>
[Co( <i>o</i> -phen) <sub>3</sub> ]Cl <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	165	1-24	Initial complex
[Co( <i>o</i> -phen) <sub>2</sub> (en)]Cl <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	165	1-24	Initial complex
[Co( <i>o</i> -phen)(en) <sub>2</sub> ]Cl <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	165	1-24	Initial complex

<sup>a</sup> Cophen<sub>3</sub> = [Co(*o*-phen)<sub>3</sub>]Y<sub>3</sub>. For other abbreviations see text.

the previous consideration are assumed to be complexes of cobalt(II), appeared after about 2 h. The initial complex disappeared after about 4 h.

The species with  $R_f = 0.21$  is an intermediate product which merits particular discussion. Owing to the violet colour of the spot, it is expected to be a dichloro complex in the *cis*-form, probably *cis*-[Co(*o*-phen)(en)Cl<sub>2</sub>]Cl or *cis*-[Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub>]Cl. Since the preparation of *cis*-[Co(*o*-phen)(en)Cl<sub>2</sub>]Cl has not been reported in the literature according to our knowledge, we attempted to estimate the chromatographic behaviour of this compound from the relation between the ligand and the chromatographic or electrophoretic mobility reported recently [5,11,12] for some cobalt(III) complexes. We found that mixed complexes have intermediate  $R_f$  values and that in our chromatographic system adsorption to silica decreases in the order: Co(*o*-phen)<sub>3</sub><sup>3+</sup> > Co(*o*-phen)<sub>2</sub>(en)<sup>3+</sup> > Co(*o*-phen)(en)<sub>2</sub><sup>3+</sup> > Co(en)<sub>3</sub><sup>3+</sup> and *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> > *cis*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. In both cases there is an increase in the  $R_f$  values with decreasing number of phenanthroline ligands in the complex. Consequently, the results suggest that the  $R_f$  value of the mixed Co(*o*-phen)(en)Cl<sub>2</sub><sup>+</sup> complex is between those of the corresponding bis-*o*-phenanthroline and bis-ethylenediamine dichloro complexes. Therefore the chromatographic behaviour of the unknown dichloro species was compared to that of the standards *cis*-[Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub>]Cl and *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl. The unknown intermediate species had the same  $R_f$  value as *cis*-[Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub>]Cl.

The other intermediate ( $R_f = 0.03$ ) gave a yellow spot, thus showing the same colour and chromatographic behaviour as Co(*o*-phen)<sub>3</sub><sup>3+</sup>.

The TLC experiments showed that by heating at 165°C a mixture of [Co(*o*-phen)<sub>2</sub>(en)]Cl<sub>3</sub> and NH<sub>4</sub>Cl three main species are present after 1 h, the colour and chromatographic behaviour of which correspond to those of *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, the initial complex, and Co(phen)<sub>3</sub><sup>3+</sup>. In order to characterize these compounds, the spectra of the corresponding chromatographic spots were obtained as described earlier. For these experiments, the following were chromatographed on the same plate and then scanned: (1) a standard mixture of the initial complex, Co(*o*-phen)<sub>2</sub>(en)<sup>3+</sup>, and of the two probable reaction products, *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and Co(*o*-phen)<sub>3</sub><sup>3+</sup>; (2) a sample of [Co(*o*-phen)<sub>2</sub>(en)]Cl<sub>3</sub> + NH<sub>4</sub>Cl heated for 1 h at 165°C. The spectra obtained from the standard mixture corresponded well to those obtained from the sample. In Fig. 1 the visible spectra of the two products ( $R_f = 0.03$  and 0.21) formed after heating the sample are reported. For comparison, in Fig. 2 the visible absorption spectra of [Co(*o*-phen)<sub>3</sub>]Cl<sub>3</sub>, [Co(*o*-phen)<sub>2</sub>(en)]Cl<sub>3</sub> and *cis*-[Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub>]Cl are reported [13,14]. As seen in Fig. 2, the spectrum of the initial complex, [Co(*o*-phen)<sub>2</sub>(en)]Cl<sub>3</sub>, is substantially different from the spectra of the two supposed reaction products, *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and Co(*o*-phen)<sub>3</sub><sup>3+</sup>. Comparison of Figs. 1 and 2 strongly support our assignment of Co(*o*-phen)<sub>3</sub><sup>3+</sup> to the species with  $R_f = 0.03$  and *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> to the species with  $R_f = 0.21$ . Thus the spectrophotometric results confirm that in the reaction between [Co(*o*-phen)<sub>2</sub>(en)]Cl<sub>3</sub> and NH<sub>4</sub>Cl, substitution of an ethylenediamine ligand by chloride has occurred with the formation of *cis*-Co(*o*-phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. In addition the presence of Co(*o*-phen)<sub>3</sub><sup>3+</sup> in the reaction products is confirmed.

We were interested to find out whether this latter product was generated

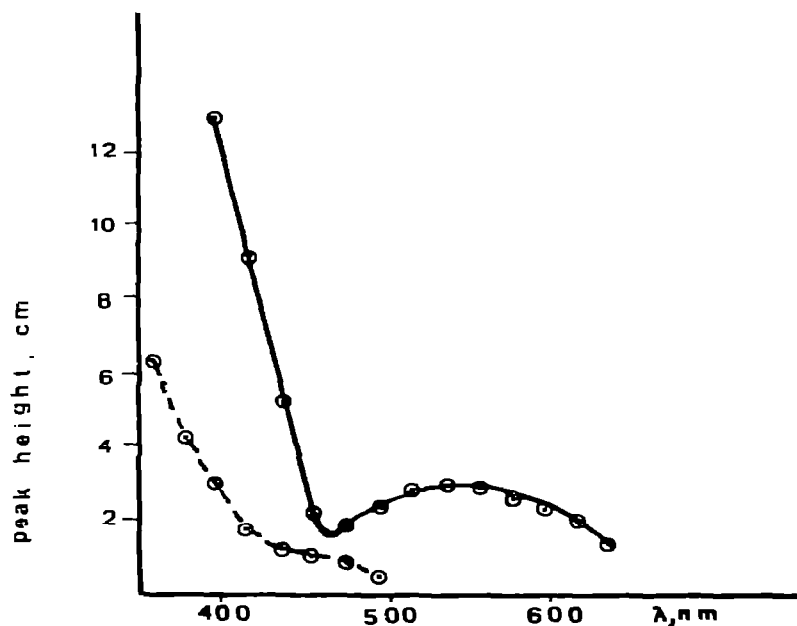


Fig. 1. Visible absorption spectra of the reaction products of  $[\text{Co}(\text{o-phen})_2(\text{en})]\text{Cl}_3$  and  $\text{NH}_4\text{Cl}$  after 1 h of isothermal heating at  $165^\circ\text{C}$ . determined by scanning a TLC plate in the reflectance mode. (—) Product with  $R_f = 0.21$ ; (-----) product with  $R_f = 0.03$ .

directly by rearrangement of the initial complex,  $[\text{Co}(\text{o-phen})_2(\text{en})]\text{Cl}_3$ , or from the first intermediate, which was identified as  $\text{cis-Co}(\text{o-phen})_2\text{Cl}_2^+$ . Therefore a standard of  $\text{cis-}[\text{Co}(\text{o-phen})_2\text{Cl}_2]\text{Cl}$  as well as a mixture of this complex and  $\text{NH}_4\text{Cl}$  were heated as described previously. After about 1 h the sample without  $\text{NH}_4\text{Cl}$  turned gray-green, whereas the mixture remained

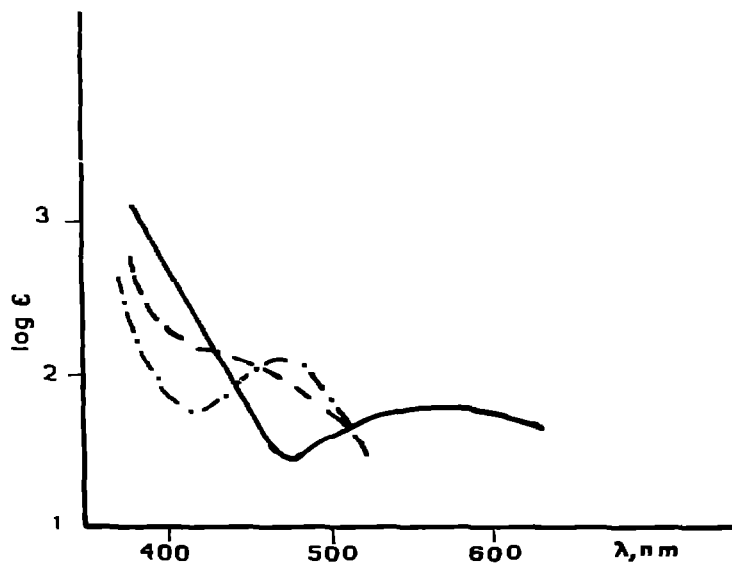


Fig. 2. Visible absorption spectra of: (—)  $\text{cis-}[\text{Co}(\text{o-phen})_2\text{Cl}_2]\text{Cl}$  [13]; (-----)  $[\text{Co}(\text{o-phen})_3]\text{Cl}_3$  [14]; (- · - · -)  $[\text{Co}(\text{o-phen})_2(\text{en})]\text{Cl}_3$  [14].

apparently unchanged. The products of the two reactions, as evidenced by TLC, were almost the same, but different in quantity. In both cases a yellow spot appeared at the point of application, as in the previous experiments. In addition, phenanthroline, Co(II) and an unknown substance yielding an elongated spot with  $R_f = 0.7$  were present. The spot of the initial complex did not disappear even after 24 h of heating. The above results suggest that in the reaction between  $[\text{Co}(o\text{-phen})_2(\text{en})]\text{Cl}_3$  and  $\text{NH}_4\text{Cl}$  two consecutive reactions occur: first an ethylenediamine molecule is displaced by  $\text{Cl}^-$  ions to give  $\text{cis-phen}_2\text{Cl}_2$  ( $\text{cis-phen}_2\text{Cl}_2 = \text{cis-}[\text{Co}(o\text{-phen})_2\text{Cl}_2]\text{Y}$ ); then the free  $o$ -phenanthroline from initial decomposition of the complexes present in the mixture displaces the  $\text{Cl}^-$  ions to give  $\text{Co}(o\text{-phen})_3^{3+}$ . This finding agrees with the reported preparation of  $[\text{Co}(o\text{-phen})_3]\text{Cl}_3$  from  $\text{cis-}[\text{Co}(o\text{-phen})_2\text{Cl}_2]\text{Cl}$  and phenanthroline [4]. Comparison of the products resulting from thermal rearrangement of  $[\text{Co}(o\text{-phen})_2(\text{en})]\text{Cl}_3$  in both the presence and absence of  $\text{NH}_4\text{Cl}$  suggests that the substitution of the ligand ethylenediamine by chloride ions dominates the process when  $\text{NH}_4\text{Cl}$  is present.

Upon heating  $[\text{Co}(o\text{-phen})_2(\text{en})]\text{Cl}_3$  with  $\text{NH}_4\text{NO}_3$  the sample turned yellow-brown and the initial complex was always the main species present, even after 24 h.

#### $[\text{Co}(o\text{-phen})(\text{en})_2]\text{Cl}_3$

Chromatograms of the samples obtained before and after heating were almost the same, even in the presence of  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ . It appears, therefore, that under our experimental conditions this complex has the highest thermal stability.

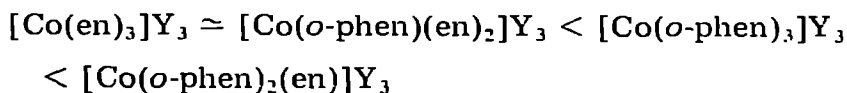
#### Complexes in the nitrate form

In order to investigate how the nature of counter ion affects the thermal stability of the complexes, a series of experiments were performed with complexes in the nitrate form. With  $[\text{Co}(o\text{-phen})_3](\text{NO}_3)_3$  and  $[\text{Co}(o\text{-phen})(\text{en})_2](\text{NO}_3)_3$  the results were almost the same as those found with the corresponding chlorides. On the other hand  $[\text{Co}(o\text{-phen})_2(\text{en})]\text{Cl}$  showed a thermal stability lower than that of  $[\text{Co}(o\text{-phen})_2(\text{en})](\text{NO}_3)_3$ . However the last complex and  $\text{NH}_4\text{Cl}$  also formed small quantities of  $\text{cis-}[\text{Co}(o\text{-phen})_2\text{Cl}_2]\text{Y}$ .

#### Other remarks

Further insight into the behaviour of such complexes has been obtained from investigating the thermal stability of  $[\text{Co}(\text{en})_3]\text{Cl}_3$ . This complex reacts above  $200^\circ\text{C}$  [15,16] and remains unchanged when heated under the same conditions as the other complexes reported above.

If the loss of initial complex from the reaction mixture after 4 h of isothermal heating at  $165^\circ\text{C}$  is taken arbitrarily as a measure of reactivity, the order is:



The greater reactivity of the last complex with respect to the others proves that the order of stability is not strongly dependent on the gradual substitu-

tion of a molecule of ethylenediamine by a molecule of *o*-phenanthroline. Rather, the complexes react by a more complicated process, probably dependent upon two different effects of the ligands, the first being the rate of the substitution reaction and the second the reduction rate. From the above results it is possible to deduce that these two effects do not seem to act in the same direction. Support for this hypothesis is found by the presence of reduction products in the species evidenced by TLC.

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