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THE THERMAL DECOMPOSITION REACTIONS OF $[Co(en)_n(phen)_m]Cl_3$ COMPLEXES *

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ABSTRACT

The thermal behaviour of $[Co(en)_n(phen)_m]Cl_3$ complexes has been studied using thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) in air, nitrogen and oxygen atmospheres. The effect of the stoichiometry of the complexes and that of the gas atmosphere in the furnace chamber on the thermal decomposition reaction is evidenced and discussed. The following thermal stability order has been found

$$[Co(en)_3]Cl_3 \cong [Co(en)_2(phen)]Cl_3 > [Co(en)(phen)_2]Cl_3 \gg [Co(phen)_3]Cl_3$$

INTRODUCTION

Several papers have been published on the thermal behaviour of complexes of cobalt ions with ethylenediamine [1–8] or 1,10-phenanthroline [9–13], while few data on mixed complexes of cobalt(III) with the above ligands are reported. In particular the solid–solid thermal reactions between a series of mixed complexes, $[Co(en)_n(phen)_m]Cl_3$ (where en = ethylenediamine, phen = 1,10-phenanthroline, and $m + n = 3$), have been investigated in the presence and absence of ammonium salts under isothermal conditions. The obtained residues after 30 min at 165°C have been analyzed and the thermal stability order established [14].

In this paper the results of thermoanalytical behaviour of the above compounds are reported. The study has been carried out by thermoanalytical techniques in the temperature range 25–800°C in various gas atmospheres (air, nitrogen and oxygen) with the purpose of studying the influence of the stoichiometry of the complexes and that of the gas atmosphere in the furnace chamber on their stability and decomposition trend.

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EXPERIMENTAL

Apparatus

The thermal measurements were carried out by means of a Perkin-Elmer TGS-2 thermal analyzer, equipped also for qualitative magnetic mass change determinations, and DTA 1700. The heating rate was 10°C min^{-1} on samples of 4–6 mg; the furnace atmosphere consisted of static air, dry nitrogen or oxygen at a flow rate of 50–100 ml min^{-1}. The reflectance and UV spectra were recorded using a Beckman DBG spectroreflectometer and a Perkin-Elmer 320 UV–visible spectrophotometer, respectively.

Preparation of the complexes

The complexes were prepared as described previously [15] and their composition checked by spectroscopic and chemical analysis; the diffuse reflectance spectra were in agreement with the six coordinate spin paired diamagnetic complexes of cobalt(III) [16].

RESULTS AND DISCUSSION

The thermoanalytical behaviour of every compound is reported in Figs. 1–4 and described in detail below.

$[Co(en)_3]Cl_3$

Thermogravimetry in air (Fig. 1a) shows that the anhydrous compound is stable up to 220°C and then decomposes through unresolved steps. At 275°C a first inflection in the TG curve occurs and the mass loss (22.4%) corresponds to 1.3 molecules of ethylenediamine. In fact, analysis of the evolved gas does not evidence chlorine or chloride ion. This mass loss, as TG and DTA curves show, is due to two different but almost contemporaneous processes: (a) the loss of undecomposed ethylenediamine (initial endothermic process in DTA curve (Fig. 1d) which leads to the formation of *trans*-$[Co(en)_2Cl_2]Cl$, as it is known in a dynamic nitrogen gas atmosphere [2]; and (b) the partial oxidative decomposition of the intermediate compound thermally unstable at this temperature. This decomposition reaction occurs through the cobalt(III) to cobalt(II) reduction and it is complete at 420°C; at this temperature the residue mass corresponds to a 1 : 1 mixture of $CoCl_2$ and $(NH_4)_2CoCl_4$ (calcd. 53.40%, found 53.0%). In dynamic nitrogen as in oxygen gas atmosphere (Fig. 1b and c) the initial decomposition temperature is delayed (240°C). The decomposition delay in nitrogen is justified by the inhibition of the oxidative decomposition of the second ethylenediamine

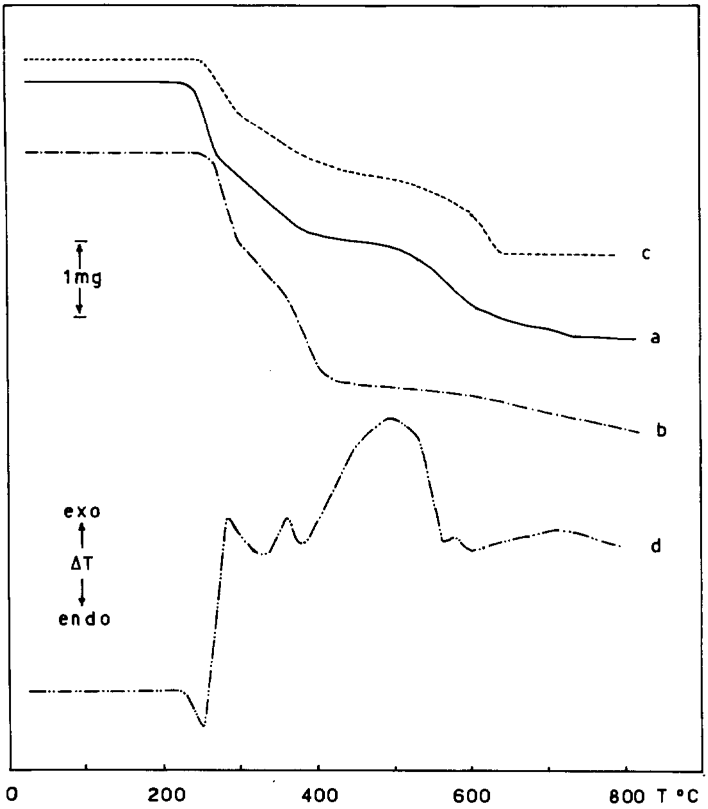

Fig. 1. TG in air(a), nitrogen(b), oxygen(c), and DTA in air(d) curves of $[Co(en)_3]Cl_3$.

molecule, while the decomposition delay in oxygen can be ascribed to the oxidative interaction of this gas with the cobalt(III) → cobalt(II) redox reaction that governs the full process of ethylenediamine elimination, as the exothermic phenomenon corresponding to the oxidation of the second ethylenediamine supplies energy to the first endothermic one.

The last decomposition process in air leads to a residue of cobalt oxide, i.e., Co_3O_4 (calcd. 23.23%, found 22.9%) at 750°C, while in oxygen atmosphere at 640°C the residue results to be Co_2O_3 (calcd. 24.00%, found 23.9%), and in nitrogen atmosphere it does not reach constant weight (800°C).

$[Co(en)_2(phen)]Cl_3$

The anhydrous compound starts to decompose in air at 220°C (Fig. 2a). Up to 310°C, in unresolved steps, the loss of a first ethylenediamine molecule and the decomposition of a second one occur, accompanied by the reduction of cobalt(III) to cobalt(II). The UV spectrum of a methanolic

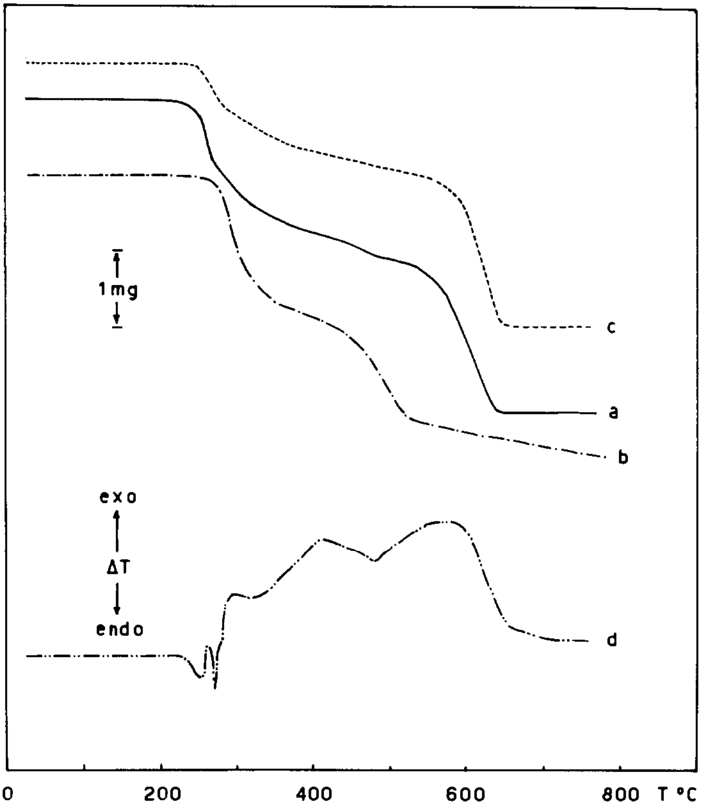

Fig. 2. TG in air(a), nitrogen(b), oxygen(c), and DTA in air(d) curves of $[Co(en)_2(phen)]Cl_3$.

solution of the residue at 260°C shows the characteristic absorption maxima of the cobalt(II)–1,10-phenanthroline complexes (λ_{max} = 270 and 227 nm) [17]. The residue still continues to lose mass at a slow rate until about 500°C where the rate increases and a rapid decomposition process takes place leading mainly to CoO (calcd. 16.11%, found 16.3%). The DTA analysis (Fig. 2d) shows a first endothermic peak connected to the loss of ethylenediamine while an exothermic process corresponds to the decomposition of the second ethylenediamine molecule. An endothermic peak occurs between these two processes and it is connected to the melting of the first intermediate decomposition product. A series of exothermic reactions characterizes the last oxidative decomposition of the complex. The gas atmosphere in the furnace chamber influences this decomposition mechanism as seen for the $[Co(en)_3]Cl_3$ complex. In fact in a dynamic nitrogen atmosphere the initial decomposition temperature is delayed (240°C) as in oxygen (Fig. 2b and c); the residue does not reach constant weight (800°C) in nitrogen, while the decomposition trend in oxygen atmosphere leads to the oxide Co_2O_3 at 650°C.

[Co(en)(phen)$_2$]Cl$_3$

The complex decomposes in air between 210 and 630°C through successive unresolved steps (Fig. 3a). The initial weight loss corresponds to the partial sublimation of phenanthroline and the decomposition of the ethylenediamine molecule; no chlorine or chloride ion are present in the evolved gas. At 300°C the residue analyzed for ammonia, chloride and cobalt(II) agrees with a $Co(phen)_{1.7}Cl_2NH_4Cl$ intermediate. The successive decomposition steps lead to a residue which is mainly CoO (calcd. 12.81%, found 11.5%) but also contains small amounts of metallic cobalt. DTA analysis (Fig. 3d) confirms the thermal decomposition trend of the complex. As for $[Co(en)_3]Cl_3$ and $[Co(en)_2(phen)]Cl_3$, the initial decomposition temperature is delayed in dynamic nitrogen atmosphere (Fig. 3b) as well as in oxygen (Fig. 3c), and in the latter, the residue reaches a constant weight at 640°C (calcd. for Co_2O_3 14.16%, found 14.3%).

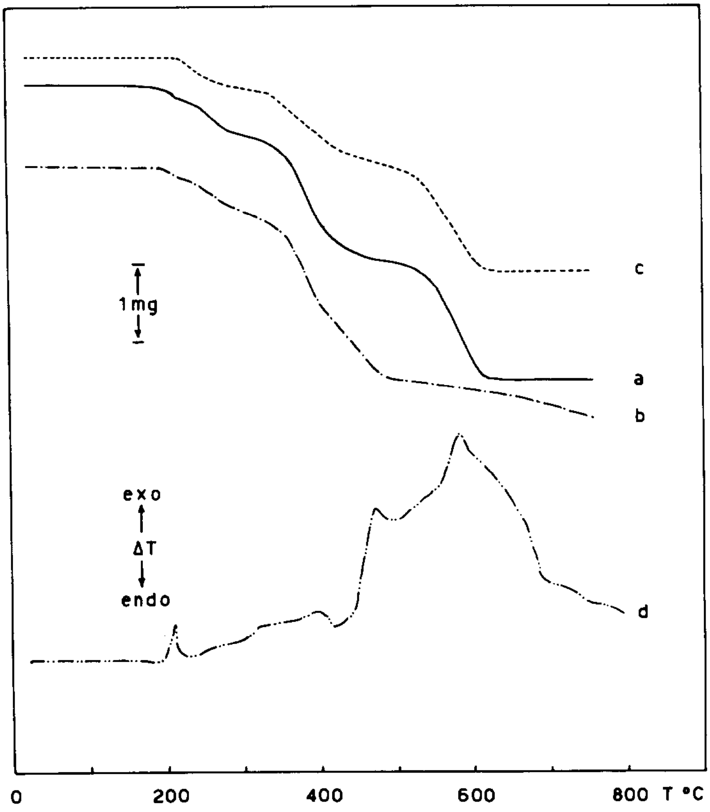

Fig. 3. TG in air(a), nitrogen(b), oxygen(c), and DTA in air(d) curves of $[Co(en)(phen)_2]Cl_3$.

[Co(phen)$_3$]Cl$_3$

In air the anhydrous compound starts to decompose slowly at 150°C and reaches a mass loss of about 30% in two decomposition steps up to 280°C (Fig. 4a). This corresponds to the formation of an intermediate of composition [Co(phen)$_2$Cl$_2$]. The UV spectrum of a methanolic solution of this residue confirms the redox reaction of cobalt(III) to cobalt(II) and analysis of the evolved gas shows the loss of chloride ion and partially undecomposed phenanthroline. The decomposition process is complete at 700°C and leads to a residue of metallic cobalt (calcd. 8.36%, found 8.3%). The inert gas atmosphere in the furnace chamber (Fig. 4b) does not influence the first slow mass loss, because this process, due to the steric hindrance of the phenanthroline molecule, occurs at a rather low temperature. On the contrary, the second process corresponding to the redox reaction of cobalt and the partial oxidative decomposition of phenanthroline is delayed; the TG curve then shows a continuous decomposition trend and the residue does not reach constant weight (800°C). The same decomposition trend has been

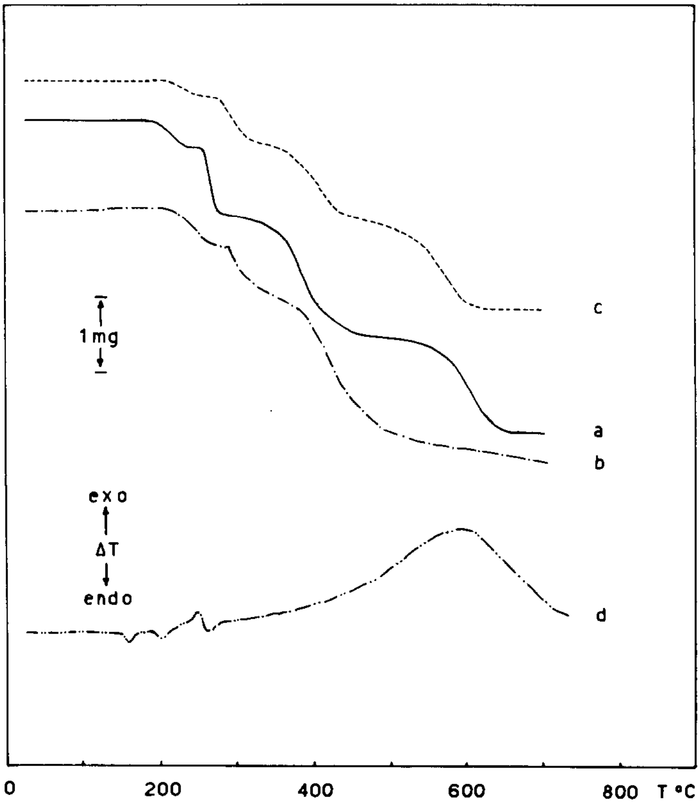

Fig. 4. TG in air(a), nitrogen(b), oxygen(c), and DTA in air(d) curves of [Co(phen)$_3$]Cl$_3$.

found in oxygen atmosphere (Fig. 4c) but the decomposition is complete at 620°C (calcd. for Co_2O_3 11.75%, found 12.0%). The DTA curve shows an endothermic peak (160°C) with no appreciable weight variation and it should be associated with a partial internal ligand substitution. Other endothermic and exothermic peaks are connected to the sublimation of 1,10-phenanthroline and to oxidative decomposition processes of the complex, respectively.

CONCLUSION

Analysis of the data obtained produces some information concerning the influence of the number of 1,10-phenanthroline molecules contained in the complex species and that of the gas atmosphere on their decomposition behaviour. All the complexes studied were observed to be diamagnetic at room temperature but become paramagnetic during the heating process. In fact, in the temperature range 200–300°C the reduction reaction of the central metal ion occurs, as UV spectra of the residue at 260–300°C confirm. This redox reaction also occurs in a dynamic oxygen atmosphere.

The initial decomposition temperature, the thermoanalytical behaviour and the final residue are influenced by the number of 1,10-phenanthroline molecules contained in the complex species. In fact, the thermal stability order in air is

$$[Co(en)_3]Cl_3 \cong [Co(en)_2(phen)]Cl_3 > [Co(en)(phen)_2]Cl_3$$
$$\gg [Co(phen)_3]Cl_3$$

This order partially differs from that determined under isothermal conditions where $[Co(en)(phen)_2]Cl_3$ was found to be less stable than $[Co(phen)_3]Cl_3$ [14]. This fact could be justified taking into account the different technique employed. In fact it is reasonable to suppose that $[Co(phen)_3]Cl_3$, because of steric hindrance, starts to decompose at a temperature lower than $[Co(en)(phen)_2]Cl_3$ so that it becomes less stable under dynamic heating, but the reduction of cobalt(III) to cobalt(II), which influences the quantitative thermal decomposition of the studied complexes, occurs at a higher temperature than that of the $[Co(en)(phen)_2]Cl_3$ and this compound becomes very reactive under isothermal conditions.

The ethylenediamine molecules in the complexes influence the decomposition mechanism. The NH_4^+ ions formed through the ethylenediamine decomposition balance the total charge of the residue after the reduction of the central metal ion. In the case of $[Co(phen)_3]Cl_3$ this decomposition trend does not occur and a mole of chloride ion is eliminated during the redox reaction of cobalt up to 280°C.

The oxidative decomposition of phenanthroline molecules probably produces a local reducing atmosphere and, in static air, the composition of the final residue corresponds to that predicted for Co_3O_4, (Co_3O_4 + CoO) mixture, (CoO + Co) mixture and Co, respectively, for $[Co(en)_3]Cl_3$, $[Co(en)_2(phen)]Cl_3$, $[Co(en)(phen)_2]Cl_3$ and $[Co(phen)_3]Cl_3$ complexes.

In a dynamic oxygen atmosphere, as in nitrogen atmosphere, the first decomposition step is delayed. The TG curves in oxygen show the influence of the redox reaction of cobalt(III) in the thermal decomposition of the complexes. In fact, a delay of this reaction produces a delay in the initial decomposition process. In nitrogen the decomposition delay is justified by the inhibition of the first oxidative decomposition of the ligand molecule. Moreover, in a dynamic oxygen atmosphere the final decomposition temperature is anticipated (600–650°C) and a Co_2O_3 residue for all the complexes is observed, while in nitrogen atmosphere the residue does not reach constant weight (800°C).

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