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The decomposition mechanism of Noradrenaline complexes with transition-metal ions: A coupled TG–FT-IR study

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Abstract

The role of antihistaminic substances is well recognized: exerting action of antiacetylcholines, local anesthetics, antispasmodics, analgesics, etc. Many papers regarding the behavior of Noradrenaline have been published, but only a few studies on the compounds that this molecule can form with transition-metal ions can be found in the literature. In this work, the synthesis and the thermal characterization of Noradrenaline complexes with transition-metal ions, such as Co(II), Ni(II) and Cu(II), are reported; by the IR analysis of the TG evolved gases the proposed decomposition mechanism is confirmed. © 1998 Elsevier Science B.V.

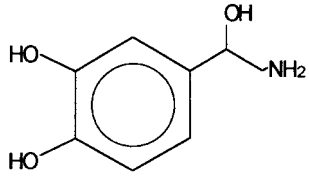
Keywords: Noradrenaline; Complexes; Coupled TG–FT-IR analysis; Decomposition mechanism

1. Introduction

Antihistaminics are a special category of spasmolytic substances with the extraordinarily high specificity in antagonizing histamine-induced physiological effects.

To a varying extent, antihistaminics exert the action of antiacetylcholines, local anesthetics, sympathomimetics, sympatholitics, antispasmodics, analgesics, etc.

Noradrenaline (Nora) belongs to this group of pharmacologically important 'drugs' but, despite the interest around this molecule and the related chemistry, few studies can be found in the literature regarding the solid-state complexes that Noradrenaline forms with transition-metal ions such as Co(II), Ni(II) and Cu(II), and no thermoanalytical characterizations have been reported.



NORADRENALINE

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In this work, the synthesis of complexes of a general formula, $MeNora_4X_2$, where Me can be Co(II), Ni(II) or Cu(II), and X the Cl^- or NO_3^- ion, is described. The compounds were characterized by the coupled TG–FT-IR technique, to determine the thermogravimetric profile and, by the analysis of the IR spectra of the TG evolved gas, to confirm the proposed decomposition mechanism.

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2. Experimental

2.1. Synthesis of the complexes

Noradrenaline was purchased from Aldrich; all the solvents were of the highest purity available.

2.1.1. $MeNora_4(NO_3)_2$

Noradrenaline (0.670 g, 4 mmol) and $Me(NO_3)_2$, in a 4 : 1 molar ratio, were dissolved in 100 ml of absolute ethanol. The mixture was heated to 55°C under constant stirring for 30 min, resulting in the formation of a precipitate. The so-formed compounds were filtered off, washed repeatedly with absolute ethanol and dried under vacuo.

2.1.2. $MeNora_4Cl_2$

Noradrenaline (0.670 g, 4 mmol) and $MeCl_2$, in a 4 : 1 molar ratio, were dissolved in 100 ml of absolute ethanol. The mixture was heated to 45°C under constant stirring for 20 min, resulting in the formation of a precipitate. The so-formed compounds were filtered off, washed repeatedly with absolute ethanol and dried under vacuo.

2.2. Apparatus

The thermoanalytical curves were obtained using a Perkin–Elmer TGA7 thermobalance (20–1000°C range).

The atmosphere was argon, nitrogen or air, at a flow rate of 100 ml min^{-1}.

The heating rate was between 5 and 40°C min^{-1}, with the best results being obtained at a scanning rate of 10°C min^{-1}.

To obtain the IR spectra of the gases evolved during the thermogravimetric analysis, the thermobalance was coupled with a Perkin–Elmer FT-IR spectrometer, model 1760X; the TGA7 is coupled to the heated gas cell of the FT-IR instrument by means of a heated transfer line, and the temperatures of the cell and of the transfer line are independently selected.

The only materials in contact with the sample gases are PTFE of the transfer line, KBr of the cell windows and the glass of the TGA7 furnace.

3. Results

The thermal behaviour of the nitrate complexes, when the operational atmosphere is air, is depicted in Figs. 1–3, respectively for Co(II), Ni(II) and Cu(II).

The decomposition of the $CoNora_4(NO_3)_2$ compound (Fig. 1) is characterized by three main processes: the first being completed in the 150–350°C range, followed by a not so well-defined step and then the last step of decomposition, itself being the overlapping of at least two processes, to give the metal oxide.

Fig. 2 shows the decomposition of the $NiNora_4(NO_3)_2$ complex, with two processes enhanced by the DTG curve, followed by a very broad step over 400°C with at least three different processes overlapped.

Four steps characterize the TG and DTG curves of the $CuNora_4(NO_3)_2$ complex (Fig. 3): the first is completed in the 150–300°C range, while the second step is shifted in a lower temperature range (300°–440°C) with respect to the other nitrate complexes. It follows the final oxidation to give CuO.

The TG curves of the nitrate compounds, when the flow is nitrogen or argon, are shifted to higher temperatures (ca. 20°C in the 150–350°C range) with a final decomposition temperature up to 800°C.

A stacked plot of the IR spectra of the TG evolved gas collected in the 150–350°C range (air flow) for all the nitrate complexes, is shown in Fig. 4.

Figs. 5–7 show the thermal decomposition of the chloride compounds with air flow, respectively for the Co(II), Ni(II) and Cu(II).

A very different thermal stability can be noted when comparing the Co(II) nitrate and chloride compounds (Fig. 5), especially in the 250–450°C range, where the chloride complex is less stable with a marked loss of weight, up to 60%, followed by the final decomposition process to obtain CoO at 620°C.

A similar behaviour is shown by the Ni(II) chloride compound if compared with the respective nitrate one, with four main decomposition processes, the second of them shifted to lower temperature, and the last two being highly overlapped.

A different thermal profile is shown by the Cu(II) complex (Fig. 7), with a broad decomposition step in the 200–640°C range: the DTG curve enhances two main processes resulting from the overlapping

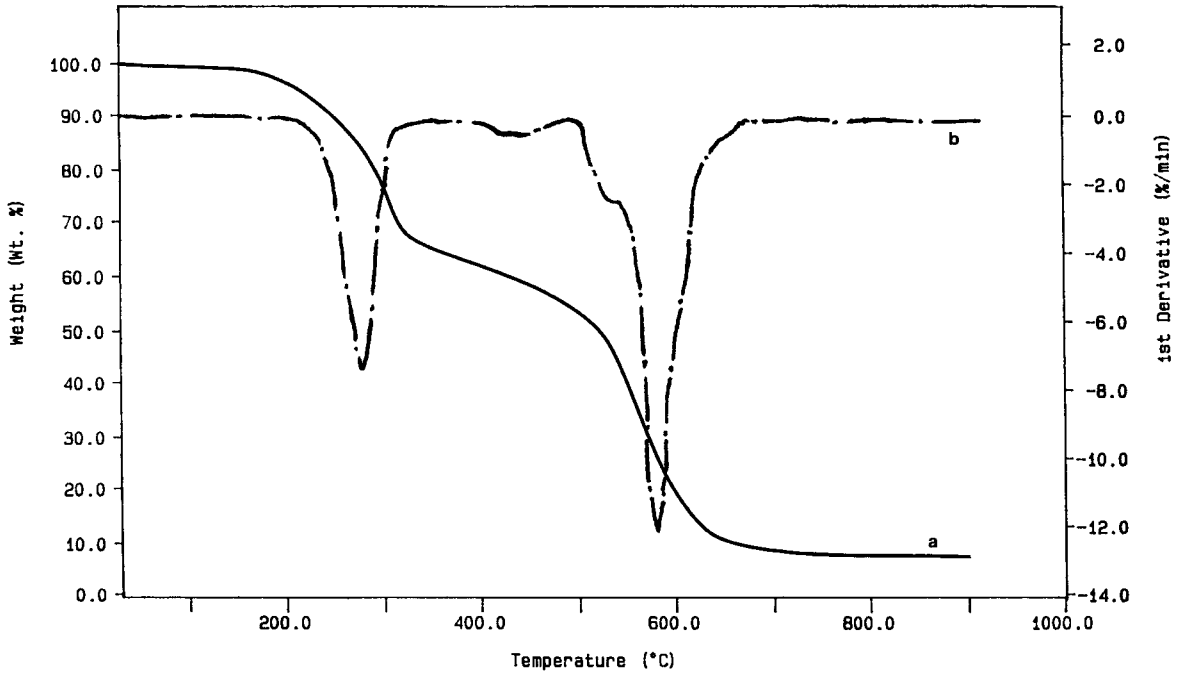

Fig. 1. $CoNora_4(NO_3)_2$ complex: (a) TG curve, and (b) DTG curve. Scanning rate, 10°C min^{-1}; and flow rate, 100 ml min^{-1}.

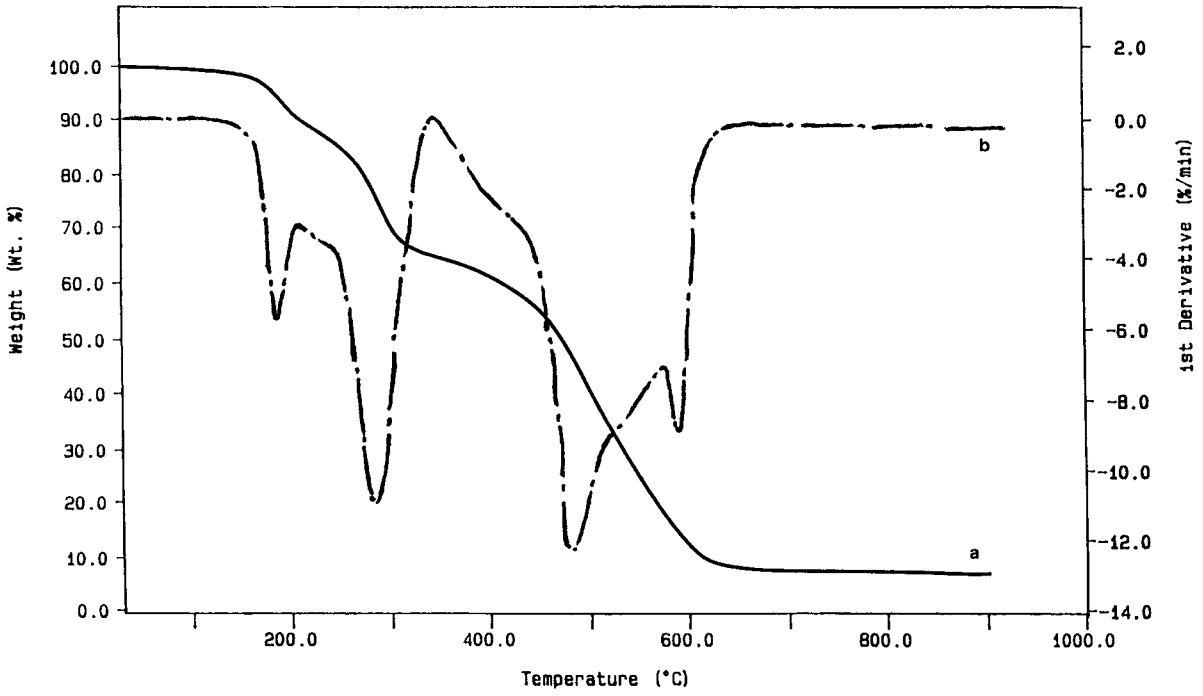

Fig. 2. $NiNora_4(NO_3)_2$ complex: (a) TG curve; and (b) DTG curve. Scanning rate, 10°C min^{-1}; and flow rate, 100 ml min^{-1}.

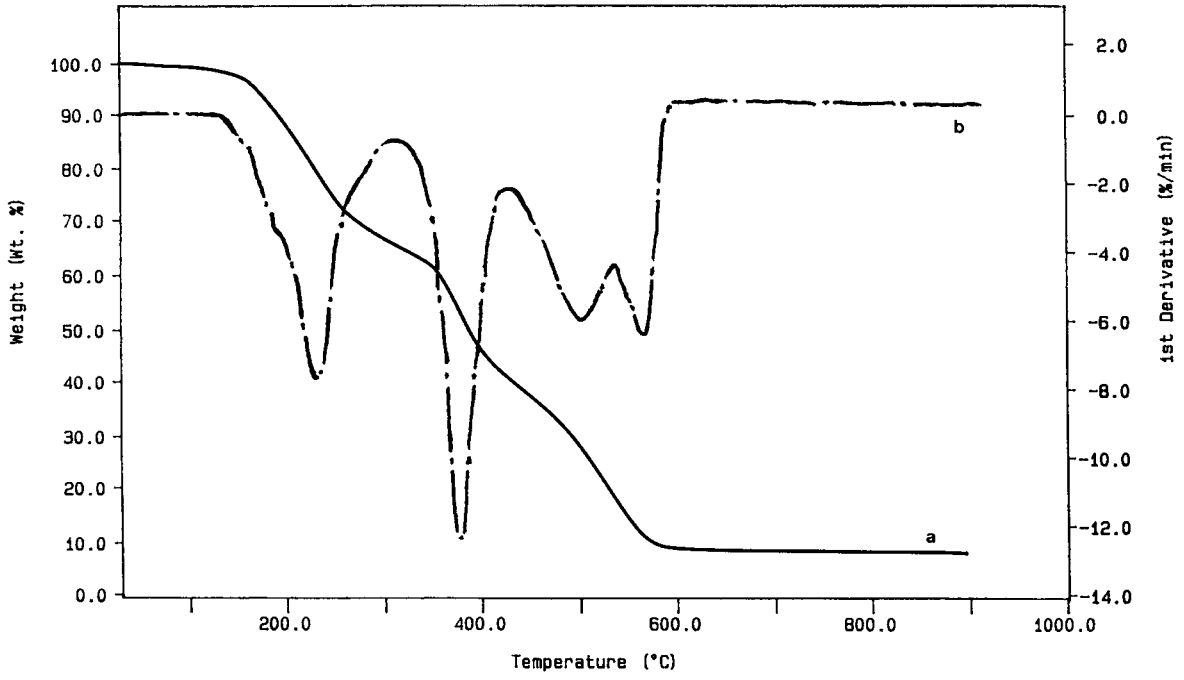

Fig. 3. $CuNora_4(NO_3)_2$ complex: (a) TG curve; and (b) DTG curve. Scanning rate, 10°C min^{-1}; and flow rate, 100 ml min^{-1}.

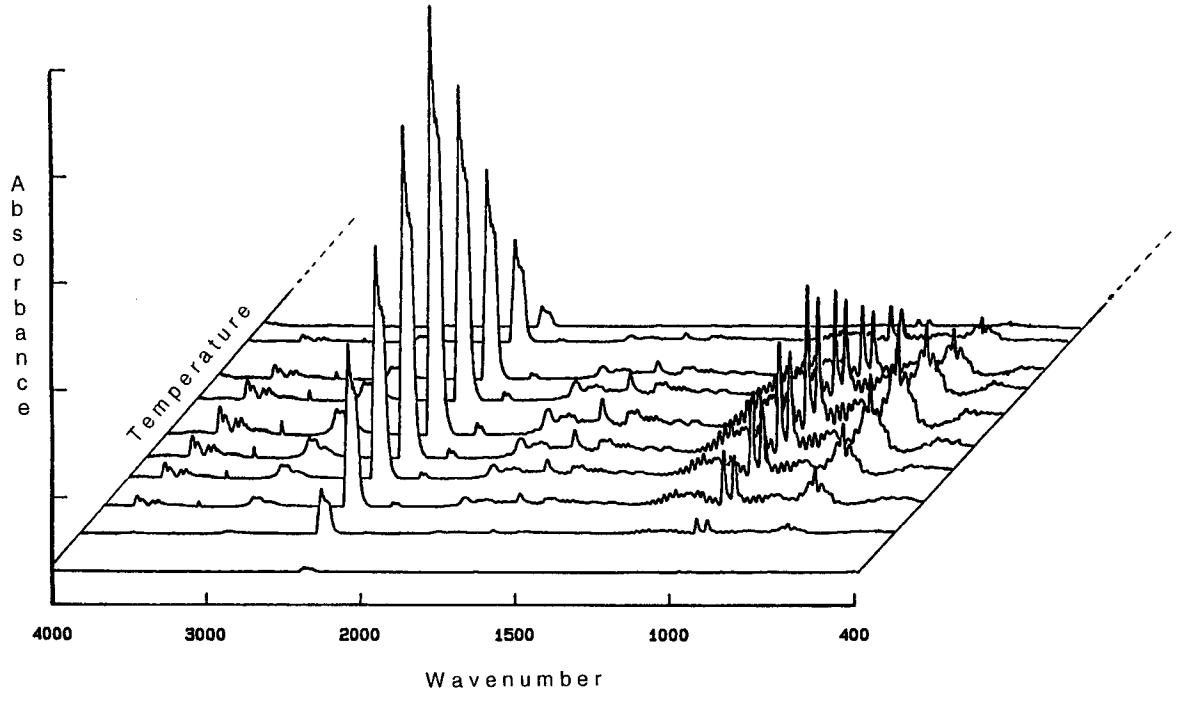

Fig. 4. Stacked plot of the infrared spectra of the evolved gas for the $MeNora_4(NO_3)_2$ complexes. Resolution: 8 cm^{-1}.

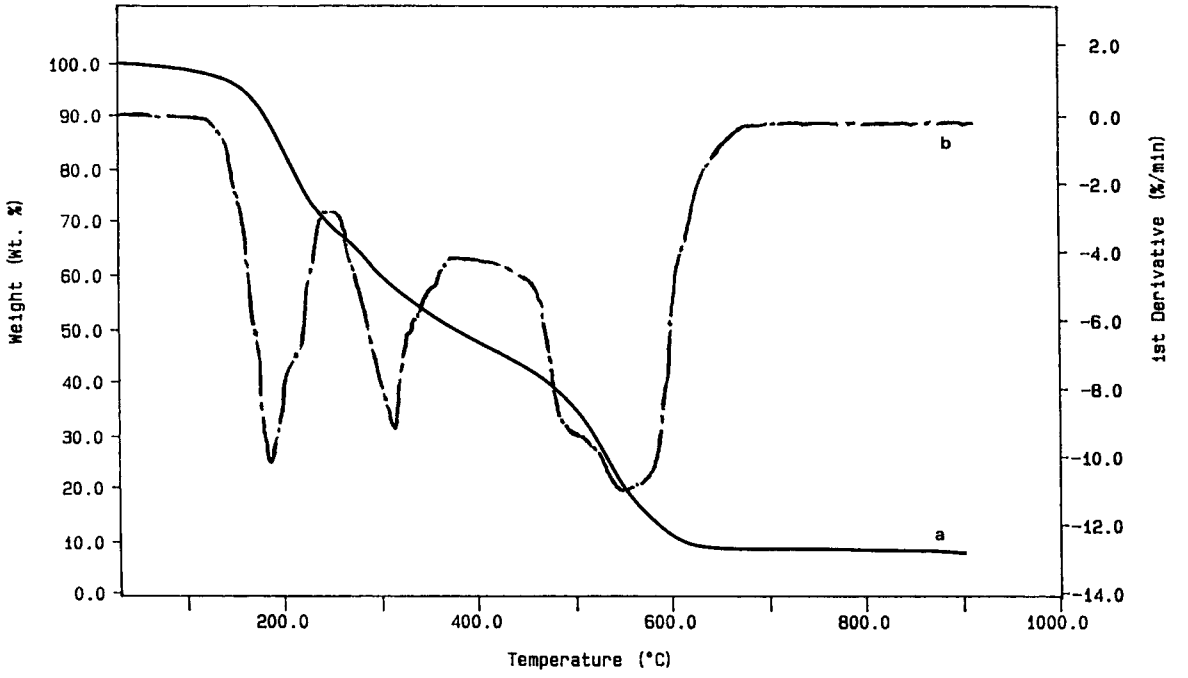

Fig. 5. $CoNora_4Cl_2$ complex: (a) TG curve; and (b) DTG curve. Scanning rate, 10°C min^{-1}; and flow rate, 100 ml min^{-1}.

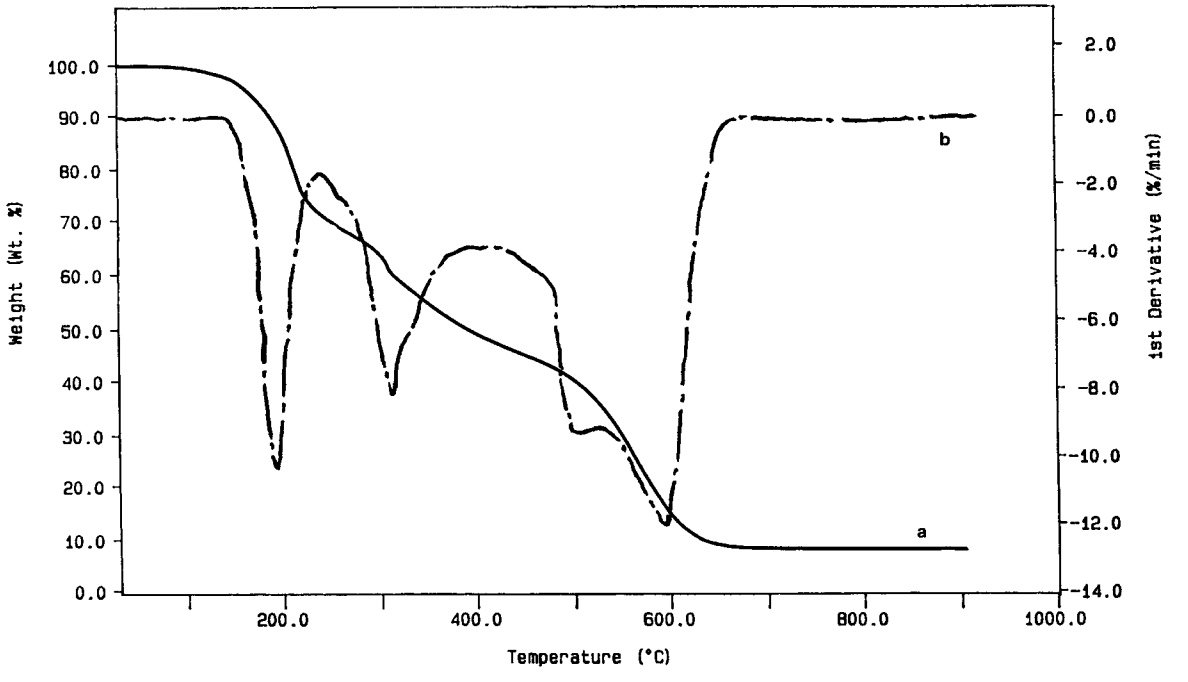

Fig. 6. $NiNora_4Cl_2$ complex: (a) TG curve; and (b) DTG curve. Scanning rate, 10°C min^{-1}; and flow rate, 100 ml min^{-1}.

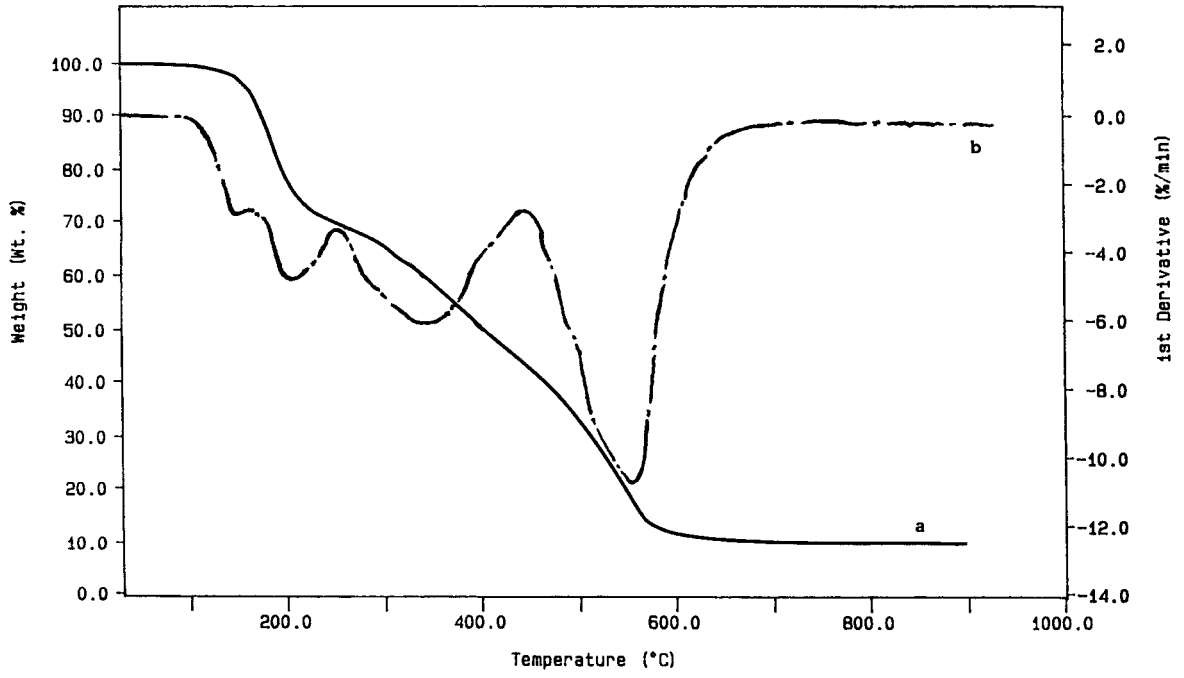

Fig. 7. $CuNora_4Cl_2$ complex: (a) TG curve; and (b) DTG curve. Scanning rate, 10°C min^{-1}; and flow rate, 100 ml min^{-1}.

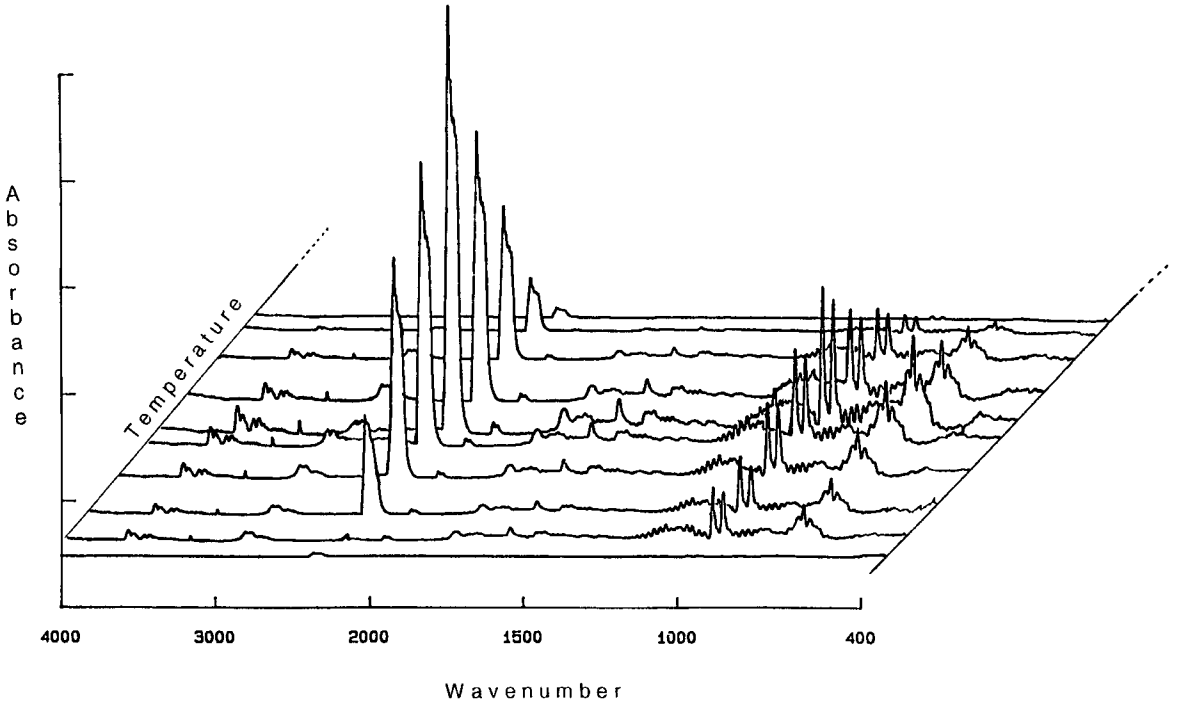

Fig. 8. Stacked plot of the infrared spectra of the evolved gas for the $MeNora_4Cl_2$ complexes. Resolution: 8 cm^{-1}.

of many decomposition steps to obtain the copper oxide.

The stacked plot of the IR spectra of the TG evolved gas in the 150–250°C range (air flow) for all the chloride complexes, is shown in Fig. 8.

4. Discussion

There is almost general agreement that catecholamines form rather stable complexes with transition-metal ions, the two oxygens of the phenolic groups acting as donor atoms [1–3].

The Noradrenaline molecule contains two separate chelate-forming groups: hence, the *ortho*-phenolic hydroxy groups can form catechol-like O,O-coordinated, and the side chain donor atoms can form ethanolammine-like O,N-coordinated complexes with metal ions.

It was established that, when there is an excess of ligand, only the *ortho*-phenolic hydroxy groups take part in the coordination and that the participation of the side chain in the complex formation is subordinated [4].

The 1 : 4 precipitated complexes show different thermal stabilities by changing either the central metal ion or the anionic group.

By the TG and DTG curves already described, the following thermal stability scale for the nitrate complexes can be proposed: Cu(II)<Ni(II)<Co(II), while for the chloride complexes the stability scale is as follows: Cu(II)<Ni(II)≅Co(II); all the nitrate complexes are slightly more stable than the respective chloride complexes.

By comparing the thermal stability scale with the solution stability constants reported in literature [5], the expected opposite behaviour can be noted, the stability constant of the Cu(II) complex being decidedly greater than those of the Co(II) and Ni(II) complexes.

The coupled TG–FT-IR analysis is a broad-based joint technique that enables confirmation of the hypothesized decomposition mechanisms by the characterization of the TG evolved gases.

Fig. 4 shows a stacked plot of the IR spectra of the evolved gas released in the first decomposition step (temperature range: 150–350°C; air flow) of the nitrate complexes as a function of increasing temperature; the bands at 966 and 931 cm^{-1} can be attributed to the loss of $–NH_2$ groups as NH_3, and the bands at 2350 and 670 cm^{-1} can be attributed to the oxidation of the side chains to CO_2. From the related thermogravimetric curves, the molecular weight loss calculated for the first process is ca. 240. By comparing the characteristic IR bands in the spectra of the evolved gas and the calculated molecular weight loss, the hypothesis that the process is the release of the four side chains of the ligand, not involved in the complexation, can be confirmed: only for the Ni(II) complex, this process is divided in two steps, as clearly shown by the DTG curve, but no differences in the related IR spectra have been detected.

The second final process is a convolution of the nitrate loss and the decomposition of the ligand molecules to give the metal oxides for all the complexes.

A very similar behaviour is shown by the chloride complexes: the IR bands of the evolved gas related to the loss of the side chains, as in the case for nitrate complexes (Fig. 8), and a calculated molecular weight loss of ca. 240 for the first TG step, confirm our hypothesis.

Regarding the second main TG process, a molecular weight loss of ca. 70 can be calculated from the TG curve, suggesting the release of the chloride ions, immediately overlapped by the final decomposition reaction: it would be expected that the presence of the IR bands in the evolved gas is related to the H–Cl bond. Conversely, no bands appear in the IR spectra related to this temperature range; this can be explained by a gas-phase oxidation reaction of two Cl^- ions to give Cl_2, with obviously no characteristic IR bands on the evolved gas spectra.

The last main process involves the oxidative decomposition reactions with the formation of the metal oxides.

A parallel IR study of the solid-state complexes has been carried out, and two significant bands can be considered to evaluate the coordination of Noradrenaline to the metal ions, as also reported in literature by El-Hendavy et al. [6].

These bands are assigned to the catecholamine bonds that are known to be sensitive to the coordination: the band at 1485 cm^{-1} is associated with a ring stretch [7,8], while the band at 1260 cm^{-1} is associated with a C–O stretch. Such bands have been observed in other complexes involving Noradrenaline as a ligand molecule [9].

5. Conclusions

The coupled TG–FT-IR analysis is a broad-based technique that allows a thermal characterization of the complexes and confirms, by the analysis of the bands in the IR spectra of the TG evolved vapours or gases, the proposed decomposition mechanisms.

By this coupled analysis it is confirmed that, in the Noradrenaline nitrate and chloride complexes, the side chain does not take part to the coordination, and that the nitrate complexes are thermally more stable than the corresponding chloride compounds, with the release of the side chains as first decomposition process for all the synthetized complexes.

Acknowledgements

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