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A thermoanalytical study of unusual adrenaline complexes

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Abstract

A thermoanalytical study of unusual adrenaline coordination compounds with the divalent transition-metal ions Co(II), Ni(II) and Cu(II) is reported. The precipitated compounds were characterized by elemental analysis and by thermogravimetric (TG) analysis coupled to FTIR spectroscopy to analyze the evolved gases and make consistent the proposed decomposition steps. The complexes were obtained with metal/ligand molar ratios of 1:1 (base unit, only for the copper), 1:3 and 1:5. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Epinephrine, commonly called adrenaline (adr), forms coordination compounds with the divalent transition metal-ions, Co(II), Ni(II) and Cu(II), that are useful models for the complexing behaviour of catecholamines and discover correlations of the properties of these compounds in solution with their properties in the solid state.

Several studies of this kind of complex can be found in the literature [1–8], but few thermoanalytical data are reported and there is little information about the decomposition steps that can be directly related with the coordination energies of each complex [9].

The aim of this work is to compare the thermoanalytical properties of the solid complexes obtained after precipitation from aqueous or ethanolic solutions using several metal(II) nitrate/adrenaline (M/L) molar ratios. Unusually, the obtained compounds showed M/L molar ratios of 1:3 and 1:5, with successive ligand molecules being coordinated to a 1:1 base-unit $[M(L)]^{2+}$, precipitated only with Cu(II) and resulting in the molecular formula $[Cu(adr)](NO_3)_2$. As previously reported [9], the solvent makes the difference, especially in the complexes with higher number of coordinated ligand molecules.

Characterization of the solid complexes was performed by elemental analysis and thermogravimetric (TG) analysis and coupled to TG–FTIR evolved gas analysis.

2. Experimental

2.1. Materials

Adrenaline and the metal(II) salts were from Aldrich Chemical Co. and were used without further purification. All the solvents used were of RPE grade.

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2.2. Syntheses of the complexes

All the complexes were precipitated either from aqueous solutions at pH 4 or from ethanolic solutions, with the same starting Me/adr ratios. The conditions are described for the synthesis in absolute EtOH.

2.2.1. $[Co(adr)_5](NO_3)_2$

To a solution of adrenaline (5 mmol) in 250 ml of absolute ethanol, was added a solution of $Co(NO_3)_2 \cdot 3H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.2. $[Co(adr)_3](NO_3)_2$

To a solution of adrenaline (2.7 mmol) in 250 ml of absolute ethanol, was added a solution of $Co(NO_3)_2 \cdot 3H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.3. $[Ni(adr)_5](NO_3)_2$

To a solution of adrenaline (5 mmol) in 250 ml of absolute ethanol, was added a solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.4. $[Ni(adr)_3](NO_3)_2$

To a solution of adrenaline (2.7 mmol) in 250 ml of absolute ethanol, was added a solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.5. $[Cu(adr)_5](NO_3)_2$

To a solution of adrenaline (5 mmol) in 250 ml of absolute ethanol, was added a solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.6. $[Cu(adr)_3](NO_3)_2$

To a solution of adrenaline (3 mmol) in 250 ml of absolute ethanol, was added a solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.7. $[Cu(adr)](NO_3)_2$

To a solution of adrenaline (0.8 mmol) in 250 ml of absolute ethanol, was added a solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol, with heating (50 °C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo. The yield of this complex was extremely low (<15%).

2.3. Instrumental

Elemental analysis was performed by a Perkin-Elmer CHN analyzer and by a Perkin-Elmer ICP Liberty 150 instrument.

The thermoanalytical curves were obtained using a Perkin-Elmer TGA7 thermobalance (range 20–1000 °C); the atmosphere was either pure nitrogen or air, at a flow rate of 100 ml min^{-1}; the heating rate was varied between 5 and 40 °C min^{-1}, with the best resolution achieved at a rate of 10 °C min^{-1}.

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

3. Results

3.1. Elemental analysis

Table 1 gives the results from the elemental analyses.

3.2. Thermal analysis

Figs. 1–3 show the TG profiles of the complexes.

All the precipitated solids show a strong tendency to bind hygroscopic water that is lost in the temperature range 20–95 °C.

The cobalt(II), nickel(II) and copper(II) complexes in the M/L ratio of 1:5 (Fig. 1) show a different thermal stability, the Ni(II) complex being slightly more stable than those of Co(II), and Cu(II) having the lowest thermal stability. The decomposition steps of the three complexes (air flow) show the release of two adrenaline molecules, followed by the release of another

Table 1
Elemental analysis of the precipitated complexes found, expressed in percentage[a]

Complex	M	C	H	O	N
$[Co(adr)_5](NO_3)_2$	5.4 (5.34)	49.2 (49.15)	4.6 (4.55)	30.5 (30.58)	9.0 (8.92)
$[Co(adr)_3](NO_3)_2$	8.1 (8.01)	44.3 (44.24)	4.1 (4.10)	32.6 (32.77)	9.3 (9.56)
$[Ni(adr)_5](NO_3)_2$	5.4 (5.34)	49.0 (49.16)	4.6 (4.55)	30.3 (30.58)	9.1 (8.92)
$[Ni(adr)_3](NO_3)_2$	8.0 (8.02)	44.2 (44.25)	4.2 (4.10)	32.5 (32.77)	9.3 (9.56)
$[Cu(adr)_5](NO_3)_2$	5.8 (5.74)	48.5 (48.94)	4.6 (4.53)	30.1 (30.45)	8.7 (8.88)
$[Cu(adr)_3](NO_3)_2$	8.6 (8.60)	43.7 (43.96)	4.5 (4.07)	32.1 (32.56)	9.3 (9.50)
$[Cu(adr)](NO_3)_2$	17.1 (17.11)	29.0 (29.14)	2.8 (2.70)	38.6 (38.85)	11.3 (11.33)

[a] The calculated values are shown in parenthesis.

adrenaline molecule, and the final decomposition to give the metal oxide (MO).

Fig. 2 presents the TG profiles of the complexes with the M/L ratio of 1:3; they show a very different thermal stability with air flow, with the Cu(II) complex less stable than the Co(II) complex, both significantly less stable than the Ni(II) complex. The thermal decomposition is characterized by three main decomposition steps, the first being the release of one adrenaline molecule, the second being the loss of the nitrate ions, followed by the final step of oxidation to obtain the MO.

The thermal profile of the copper complex with a M/L ratio of 1:1 (base-unit), shown in the Fig. 3, is characterized by two main steps after the water release when heated in air flow; the first one is the release of

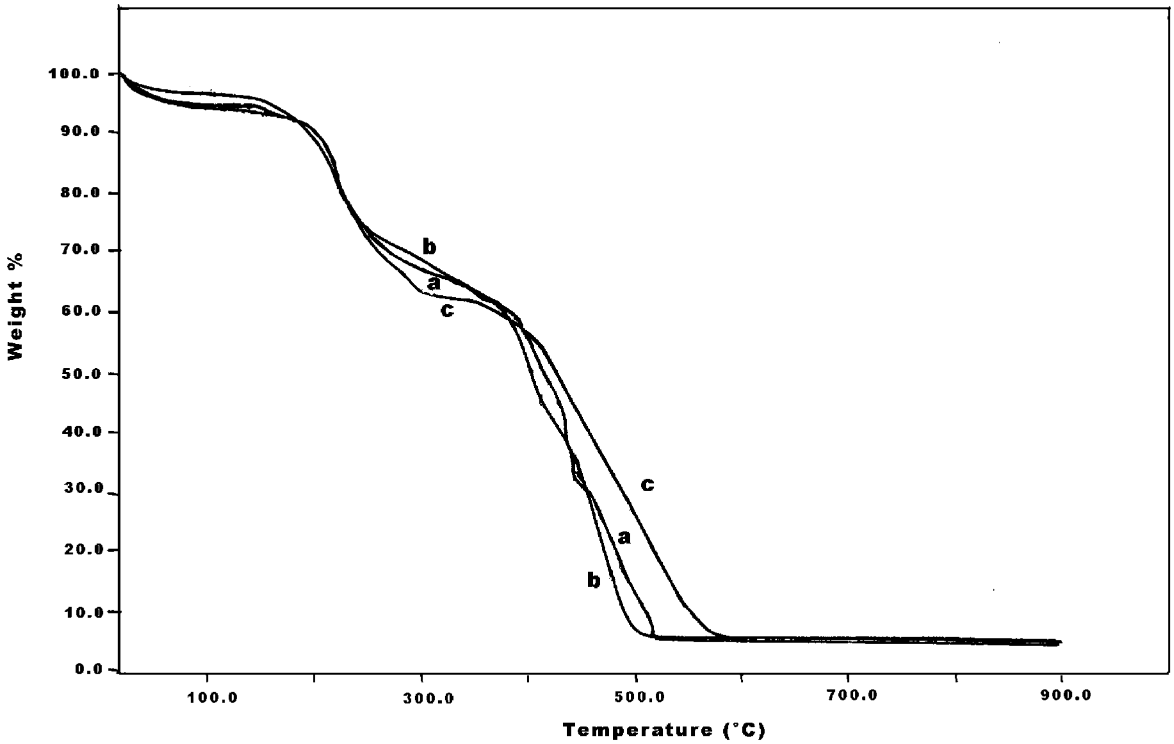

Fig. 1. TG profiles of the $[Me(adr)_5](NO_3)_2$ complexes precipitated from EtOH solution: (a) Co(II); (b) Cu(II); (c) Ni(II). Scanning rate: 10 °C min^{-1}; air flow rate: 100 ml min^{-1}.

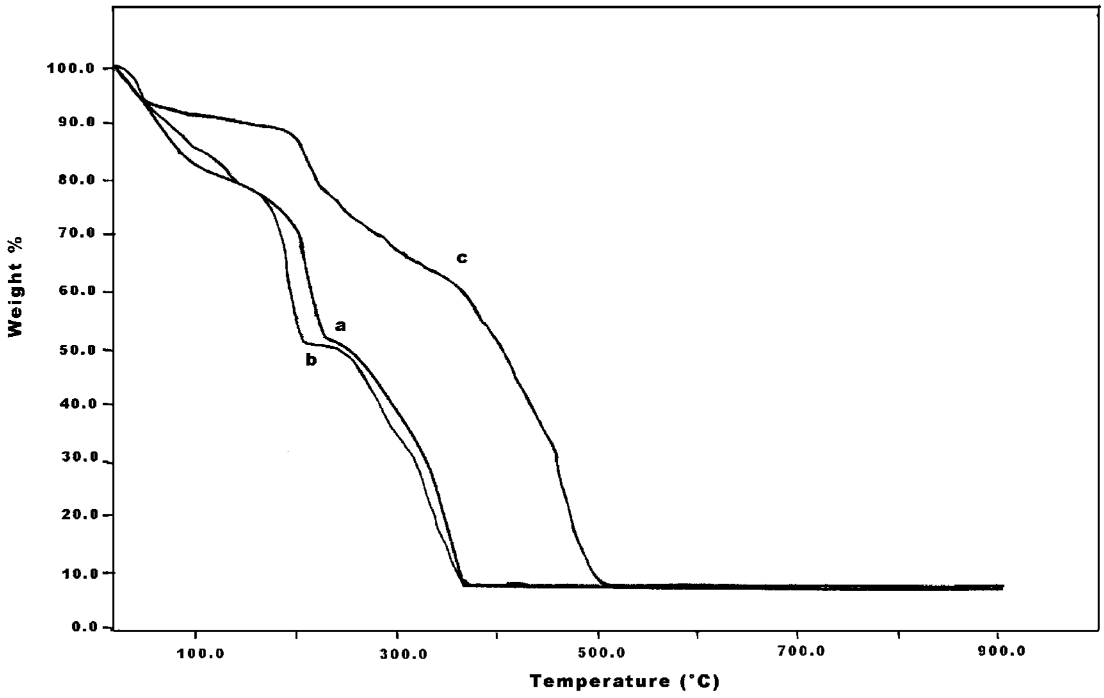

Fig. 2. TG profiles of the $[Me(adr)_3](NO_3)_2$ complexes precipitated from EtOH solution: (a) Co(II); (b) Cu(II); (c) Ni(II). Scanning rate: 10 °C min^{-1}; air flow rate: 100 ml min^{-1}.

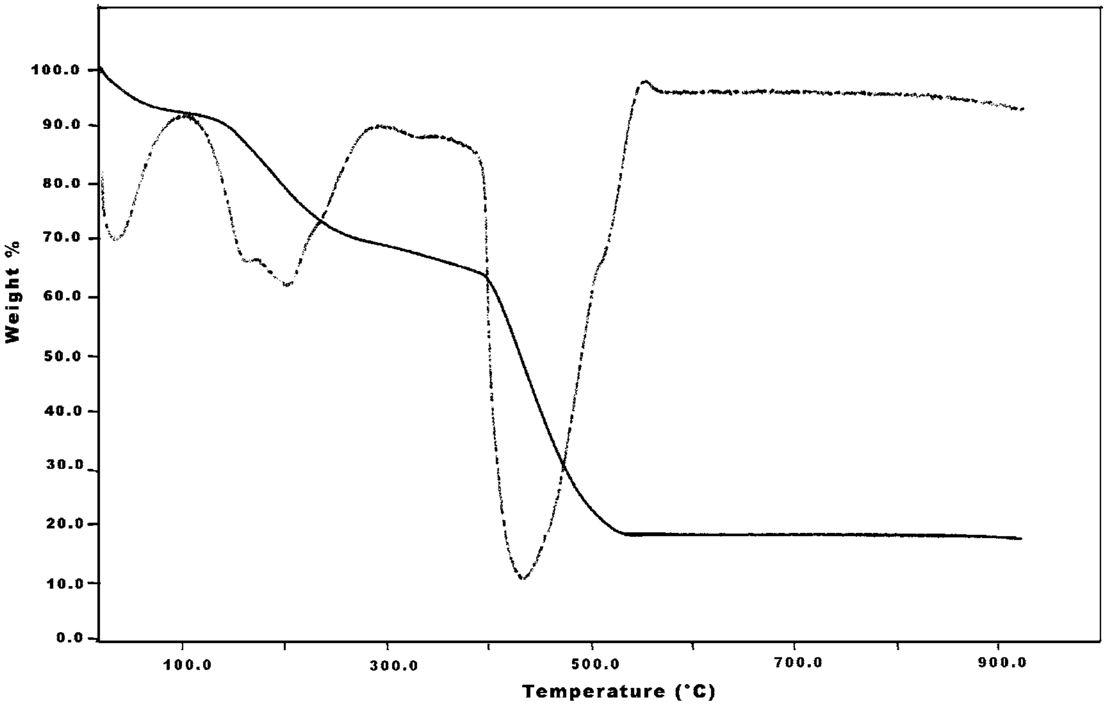

Fig. 3. TG profile of the $[Cu(adr)](NO_3)_2$ complex precipitated from EtOH solution. (a) TG curve (—); (b) first derivative (DTG) curve (- · · -). Scanning rate: 10 °C min^{-1}; air flow rate: 100 ml min^{-1}.

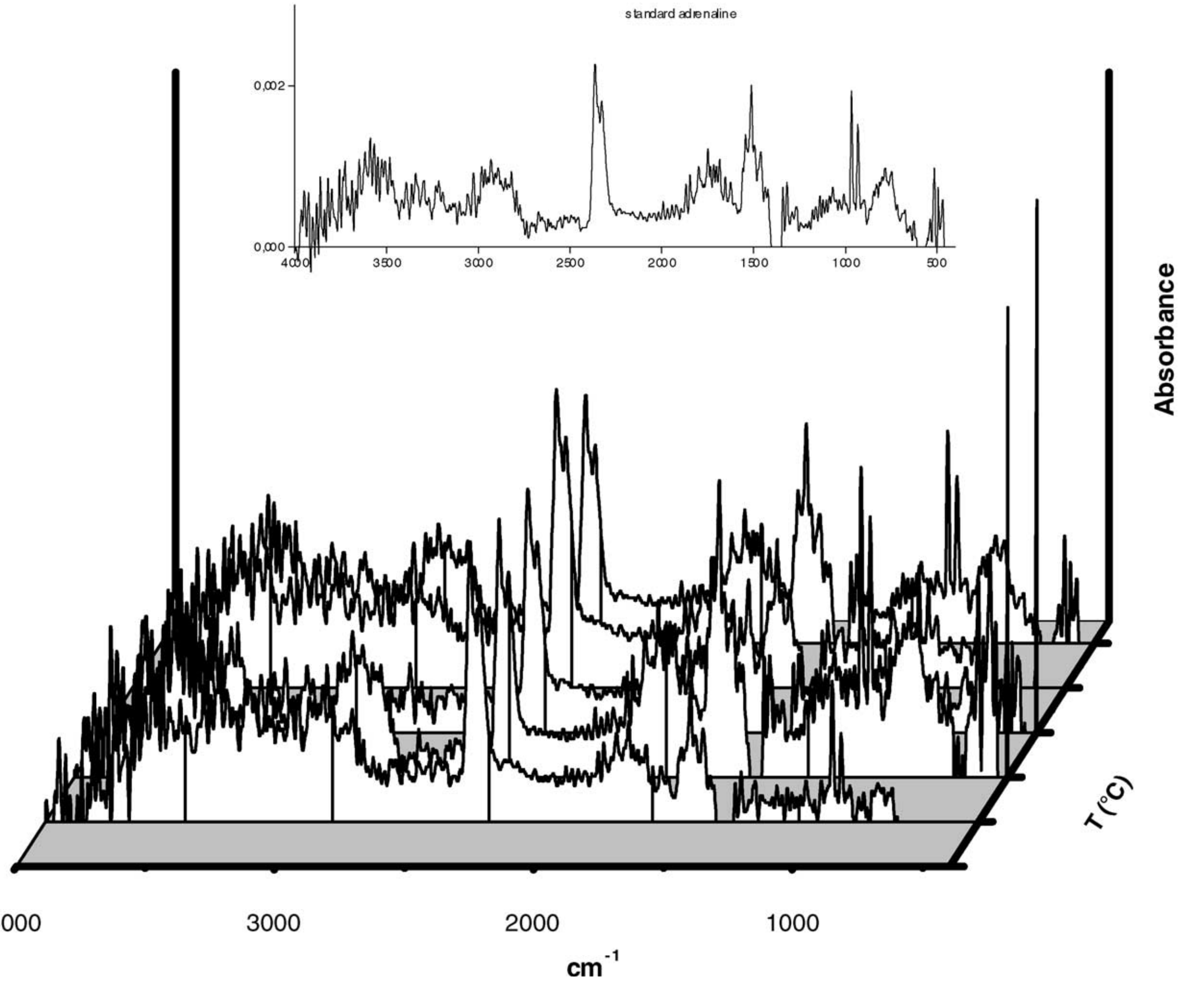

Fig. 4. IR spectra of the TG evolved gases for the release of adrenaline molecules. Resolution: 8 cm^{-1}.

the nitrate ions, the second one corresponds to the oxidation to give MO.

The evolved gas analysis, performed by coupling the TG analyzer to an IR spectrophotometer and with the consequent characterization of the IR bands related to the gases evolved in the range 20–350 °C, supports the proposed decomposition processes. One representative IR spectrum is shown in Fig. 4.

The TG curves of the decomposition under nitrogen flow (not reported) show a similar profile in the temperature range 20–300 °C, with the final decomposition step very broad and often not reaching a constant weight at 900 °C.

4. Discussion

The TG profiles of the solid complexes show an interesting property commonly observed for other coordination compounds prepared in our laboratory: the TG curves let us suppose the presence of a fundamental 1:1 base-unit for all the 1:3 and 1:5 complexes, as previously observed for the 1:4 and 1:6 complexes [9] having a 1:2 base-unit. This can be again deduced from the releasing temperature and because the step height is always equivalent to two ligand molecules before the final decomposition process to obtain the MO. Thus, we propose the same coordinating behaviour observed for the 1:4 and 1:6 adrenaline complexes, with the formation of a 1:1 base unit, followed by the coordination of two more molecules of adrenaline at a second or at a third stage, to form, respectively, the 1:3 and the 1:5 complexes. This base-unit complex was reported to exist for the Cu(II) with adrenaline and noradrenaline complexes in solution by Grgas-Kuznar et al. [2]. The experimental evidence is that the number of coordinated molecules increases with the increasing starting M/L molar ratio.

The analysis of the IR spectra recorded on the TG effluent gases clearly shows that the processes related to the loss of two or four adrenaline molecules are eliminations and not decompositions. The characteristic IR bands of the TG evolved gases are typical of adrenaline and can be attributed to the stretching and bending vibrations of the –OH, $-CH_3$ and $-NH_2$ groups.

The possibility of driving the reaction to obtain solids of different thermal stability, supposed for the 1:2, 1:4 and 1:6 complexes, was again observed in the syntheses of the 1:1, 1:3 and 1:5 complexes precipitated, by using different solvents (water and absolute ethanol). The different solvent used for the syntheses neither changed the final stoichiometry, nor the characteristic TG decomposition in three main steps; however, the solids precipitated from water solutions systematically resulted in thermally less stable solids with respect to those precipitated from ethanolic solutions, sometimes even 150 °C less stable. This behaviour could be attributed to the different polarity of the solvents used in the syntheses, with a higher stability of the complexes in water solution than in the ethanolic solution. This means an opposite trend in the solid state, with the solids obtained from ethanolic solutions being thermally more stable than those obtained from aqueous solutions, thus confirming the studies previously reported.

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