

The decomposition mechanism of new solid-state 4(5)-aminoimidazole-5(4)-carboxamide coordination compounds

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Abstract

Imidazole ring coordination compounds are very useful models to better understand the coordination properties and the reaction mechanisms of biologically important systems. On the basis of previous work, new Co(II)-, Ni(II)- and Cu(II)-4(5)-aminoimidazole-5(4)-carboxamide coordination compounds have been synthesized and characterized by elemental analysis, UV-Vis and IR spectroscopies. Their thermal stability was determined by differential scanning calorimetry and by thermogravimetry, and the decomposition mechanisms were investigated by evolved gas analysis (EGA).

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Keywords: Coordination compounds; Imidazole derivatives; TGA; DSC; Coupled TG-FTIR; EGA; Transition metal ions

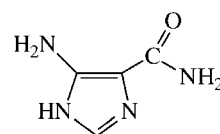
1. Introduction

In living systems, the imidazole ring is an essential metal binding site, since imidazole units are bound to metal ions in almost all copper- and zinc-metalloproteins and in nickel-containing urease [1–5]. Their biological activity is strongly effected by this binding and in this view an extremely wide variety of substituted imidazole ligands have been investigated [6,7].

The aim of the studies on imidazole and imidazole derivatives coordination is to mimic structural features of enzymes. Solid-state structural characterizations and equilibrium studies of several complexes in solution have been reported [8–14], but thermoanalytical studies are also useful to complete the characterization and to relate the coordination properties of imidazole with biologically important transition-metal ions.

As a logical continuation of our studies on the thermoanalytical properties of substituted imidazole solid-state coordination compounds with transition-metal ions [15–21], new Co(II), Ni(II) and Cu(II) coordination compounds of 4(5)-aminoimidazole-5(4)-carboxamide (AIC) have been

synthesized and characterized by elemental analysis and infrared spectroscopy.



4(5)-aminoimidazole-5(4)-carboxamide
(AIC)

The thermal stability of the precipitated complexes was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Evolved gas analysis (EGA), performed by on-line coupling the TG system with an FTIR instrument allowed for an investigation of the decomposition mechanism.

2. Experimental

2.1. Materials

The 4(5)-aminoimidazole-5(4)-carboxamide ligand and the Co(II), Ni(II) and Cu(II) chloride salts were purchased from Sigma-Aldrich.

Acetone was chosen as the synthesis solvent (Sigma-Aldrich-HPLC grade).

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2.2. Syntheses of the complexes

All the complexes were synthesized by following the same procedure:

$M(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Co(II)}$, Ni(II) or Cu(II)). The complex precipitated after the addition of 250 ml of a 0.01 M $\text{MeCl}_2 \cdot n\text{H}_2\text{O}$ solution (acetone) to 250 ml of a 0.025 M ligand solution (acetone), which was continuously stirred because of low solubility. The precipitation was fast and complete and the resulting solid was washed with acetone and dried under vacuum.

2.3. Instrumentation

Infrared spectra of the solid-state complexes were obtained using a Perkin Elmer FTIR spectrometer, model 1760X, from KBr pellets (20 scans, resolution 2 cm^{-1}).

UV-Vis spectra were recorded using a Perkin Elmer Lambda series spectrophotometer.

ICP-OES spectroscopy was performed using a Perkin Elmer ICP Liberty 150 instrument.

The thermoanalytical curves were obtained using a Perkin Elmer TGA7 thermobalance (range $20\text{--}1000^\circ\text{C}$) and a Perkin Elmer DSC7; 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 $40^\circ\text{C min}^{-1}$ with the best resolution achieved at a scanning rate of $10^\circ\text{C min}^{-1}$.

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

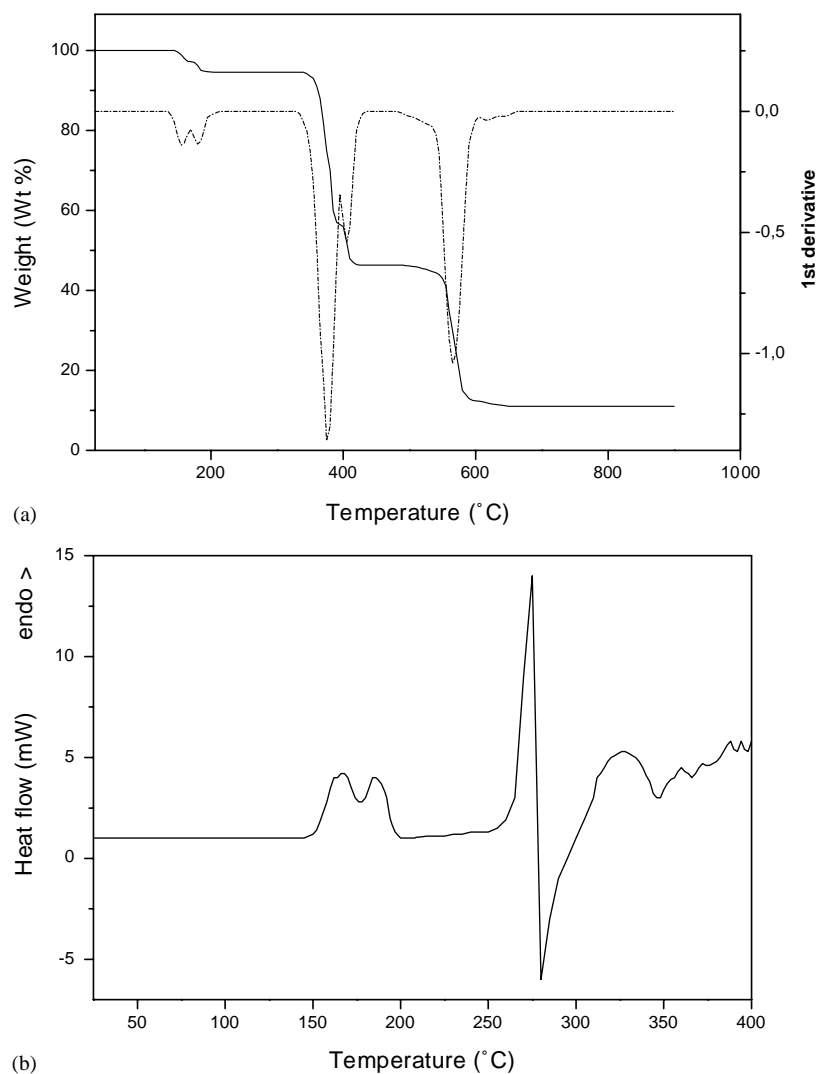


Fig. 1. Thermoanalytical curves of the $\text{Co}(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complexes: (a) TG (—), DTG (---), scanning rate: $10^\circ\text{C min}^{-1}$; (b) DSC, air flow at 100 ml min^{-1} rate.

Table 1
Elemental analysis and ICP-OES resulting (and calculated) % data

	C	H	N	O	M (ICP)
Co(AIC) ₄ Cl ₂ ·2H ₂ O	28.9 (28.90)	4.5 (4.18)	33.6 (33.48)	14.5 (14.35)	8.7 (8.67)
Ni(AIC) ₄ Cl ₂ ·2H ₂ O	28.8 (28.90)	4.2 (4.18)	33.7 (33.48)	14.4 (14.35)	8.6 (8.67)
Cu(AIC) ₄ Cl ₂ ·2H ₂ O	28.7 (28.48)	4.5 (4.15)	33.1 (33.23)	14.5 (14.24)	9.4 (9.34)

3. Results and discussion

Previous work from our group [20,21] demonstrated that both imidazole-4-acetic acid and 4(5)-aminoimidazole-5(4)-carboxamide are suitable models for studying the coordination behavior of the imidazole ring in the presence of oxygen donors. A variation of the coordination of the AIC complexes and a comparative study of the thermoanalytical behavior, due to the different binding properties, will provide new useful information to better understand the ligand substitution effects and the decomposition mechanism.

In this work, the syntheses of the coordination compounds were driven by the starting concentration ratios and by the temperature (adjusted to 70 °C). Despite the fast precipitation and the relatively low solubility of the ligand in the acetone solvent, the experimental conditions allowed for an easy procedure; the compounds always resulted in a good stoichiometric ratio and no mixtures were precipitated.

The results of the elemental analysis of the precipitated 4(5)-aminoimidazole-5(4)-carboxamide coordination compounds are listed in Table 1 and support the proposed molecular formulas.

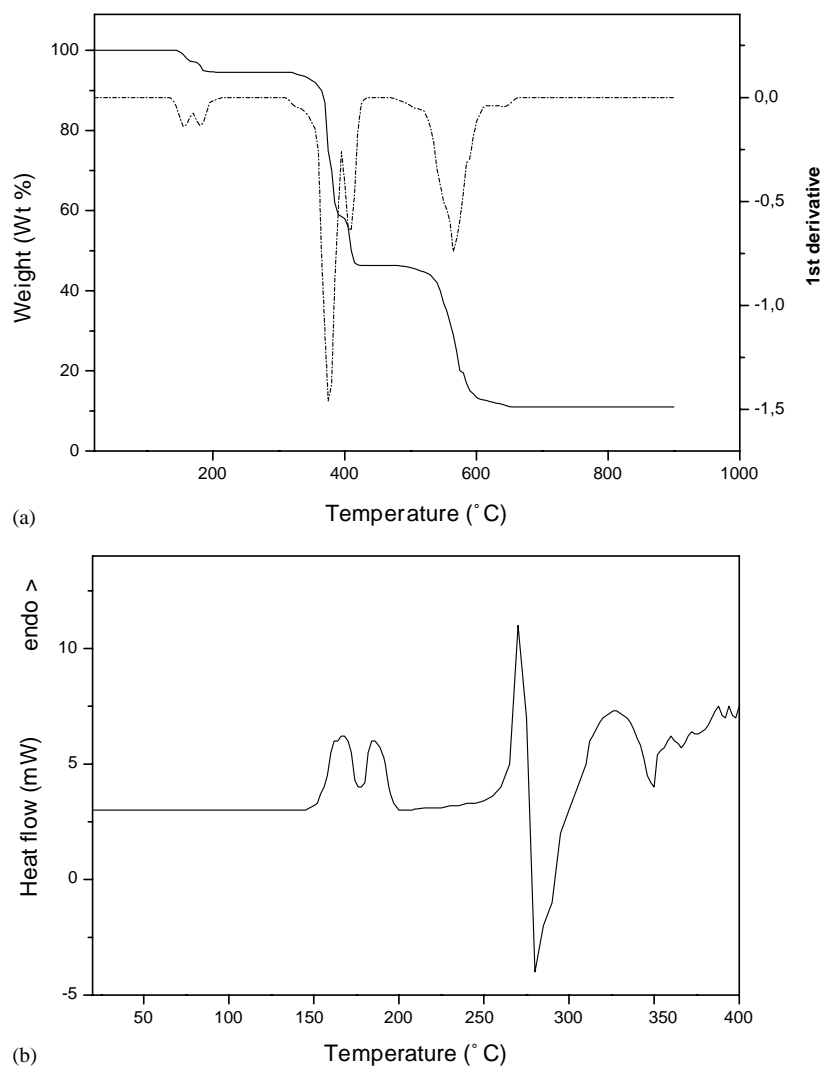


Fig. 2. Thermoanalytical curves of the Ni(AIC)₄Cl₂·2H₂O complexes: (a) TG (—), DTG (---), scanning rate: 10 °C min⁻¹; (b) DSC, air flow at 100 ml min⁻¹ rate.

The infrared spectra of the solid-state complexes show typical bands of coordinated imidazole; there is a clear shift of the C=O bands which suggests double coordination via imidazole nitrogen and amide oxygen, as was also shown in previous papers [12,20–23].

In Fig. 1a, the TG and DTG curves of the $\text{Co}(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex show three main steps. These are related to the loss of two water molecules (temperature range 150–200 °C), followed by the release of two ligand molecules and two chloride ions, and this is followed by decomposition to obtain the metal oxide as the final residue.

The experimental data from the TG curve are in a good agreement with the theoretical mass percent loss: –5.4% for loss of water (calculated –5.4%), –37.5% for the loss of two ligands (calculated –37.7%), –10.8% for the releasing step of two chlorides (calculated –10.6%) and –35.1% for the final oxidation (calculated –35.24%).

The loss of 1 + 1 water molecules is more clearly shown by the DSC curve (Fig. 1b). In the temperature range

200–350 °C, corresponding to a TG plateau, the complex undergoes an endo-exothermic sharp process that is due to the break-down of the complex coordination, with the consequent loss of two ligand molecules and two Cl^- ions.

When the TG atmosphere is inert (argon or nitrogen flow), the thermogravimetric profile shows a difference only in the final decomposition step, which is not complete even at 900 °C. Moreover, argon flow enhances sublimation of the two ligand molecules that are lost in the second main TG step (temperature range 350–380 °C).

In Fig. 2a, the TG and DTG curves of $\text{Ni}(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ show a profile that is very similar to the cobalt complex. The DSC curve, shown in Fig. 2b, suggests the same behavior as the cobalt complex, but the loss of 1 + 1 water molecules is not well resolved as for the cobalt coordination compound. The endo-exothermic peak related to the structure breakdown and the consequent loss of two ligand molecules and two anions are shifted to a lower temperature of about 15 °C.

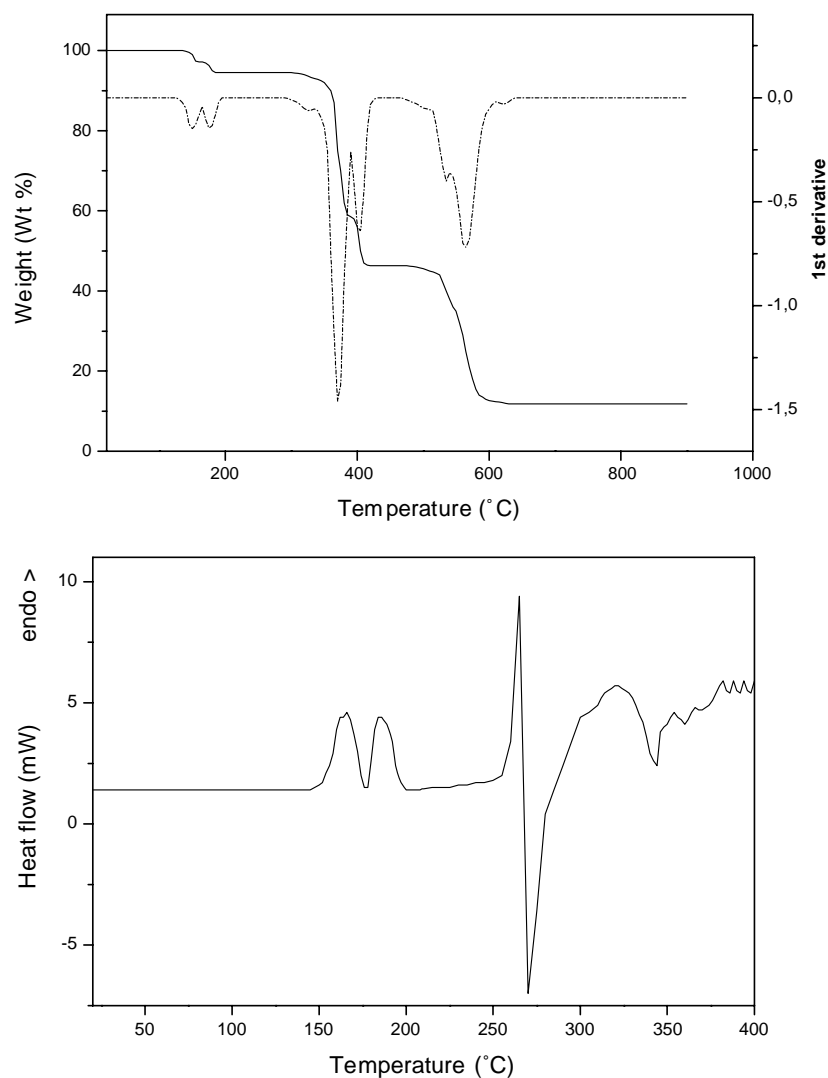


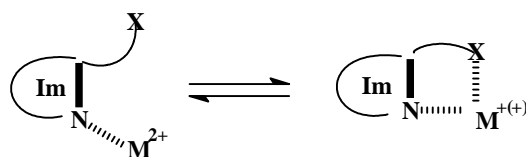
Fig. 3. Thermoanalytical curves of the $\text{Cu}(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complexes: (a) TG (—), DTG (---), scanning rate: $10\text{ }^\circ\text{C min}^{-1}$; (b) DSC, air flow at 100 ml min^{-1} rate.

In Fig. 3, the decomposition traces of $\text{Cu}(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex show again a very similar profile with a well defined release of 1 + 1 water molecules, either in the DTG or in the DSC curves. As for the cobalt and the nickel compounds, a sharp endo-exothermic process is observed in the DSC curve. The final oxidation occurs about 10°C lower than the cobalt and nickel complexes.

The thermal stability scale is similar to that of previously reported complexes [21], with the nickel and cobalt compounds being more stable than the copper one.

The release of two ligand molecules and two chloride ions in the second main TG step is confirmed by evolved gas analysis (EGA). The infrared spectra collected in the stacked plot of Fig. 4 clearly show that the FTIR bands are the same as those observed in the decomposition step of the standard ligand molecule when the anhydrous complex starts to decompose (see extracted spectra 4a and b). This behavior, observed for all the $\text{M}(\text{AIC})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complexes, is a consequence of the breakdown of the coordination shown by the endo-exothermic peak in the DSC curves.

Although the TG and DTG processes are well-defined, the absence of IR bands in the spectra over the temperature range $385\text{--}410^\circ\text{C}$ (see extracted spectrum 4c) can be explained by a gas-phase reaction in which the two released chloride



Scheme 1.

ions react to give a Cl_2 molecule which is not active in the IR spectrum.

After this loss, the $\text{M}(\text{AIC})_2$ complex is formed, as a consequence of the well-known [20,21] intramolecular equilibrium of the type indicated in Scheme 1.

The thermal process shifts the equilibrium in Scheme 1 to the right, with the double coordination previously found in the imidazole-4-acetic acid and 4(5)-aminoimidazole-5(4)-carboxamide complexes [20,21].

All of the imidazole-derivative complexes are realistic models for studying the coordination behavior of the imidazole ring in the presence of oxygen donors. Due to the very different substituents on the imidazole ring, comparative data between basicity and metal binding properties are achieved and compared, and the different coordination energies of IAA and AIC complexes are reflected in the thermal profiles.

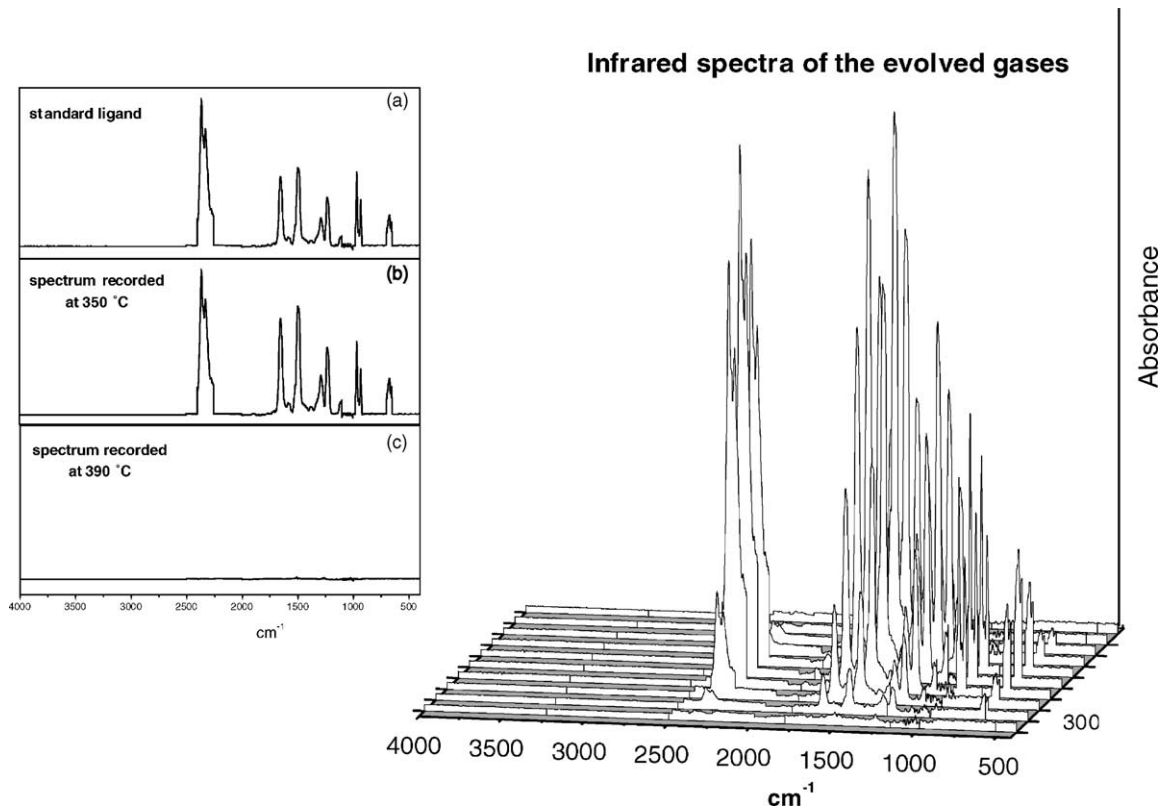


Fig. 4. Infrared spectra of the TG evolved gases for the decomposition of the complexes in the temperature range $300\text{--}400^\circ\text{C}$: (a) EGA-FTIR spectrum of the standard ligand release; (b) EGA-FTIR extracted spectrum for the analyzed complexes recorded at 350°C ; (c) EGA-FTIR extracted spectrum for the analyzed complexes recorded at 390°C . Resolution: 8 cm^{-1} –10 scans per spectrum.

All of the studied complexes show rearrangements to obtain the complex shown on the right side of the equilibrium in Scheme 1.

The thermal stability of this “base” unit is not only dependent on the R group characteristics of the imidazole ring, but also on the coordination of the parent compounds. The decomposition step for the $M(AIC)_2$ compound [21], obtained after water release from $M(AIC)_2 \cdot 2H_2O$, is split into two different processes over a 200 °C temperature range, with a final plateau around 500 °C. When the $M(AIC)_2$ complex is obtained after a thermally induced releasing process and the following rearrangement described in this work, the process is shifted to a higher temperature, with only one decomposition step that is much sharper and shifted almost 100 °C to a higher temperature.

4. Conclusions

New solid-state coordination compounds of 4(5)-aminoimidazole-5(4)-carboxamide with Co(II), Ni(II) and Cu(II), not previously described in the literature and synthesized in this work, were characterized by elemental analysis, IR spectroscopy and thermoanalytical techniques.

The results allowed to compare the different thermal behavior as a consequence of the different starting complex coordination. The thermal properties and the decomposition mechanisms were investigated by TG/DTG, DSC and coupled TG-FTIR analysis.

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