

Thermoanalytical characterization of solid-state Co(II)-, Ni(II)- and Cu(II)-4(5)-aminoimidazole-5(4)-carboxamide complexes

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Abstract

Derivatives of the imidazole ring are very useful models to better understand the coordination properties and the reaction mechanisms of biologically important systems. Six different complexes of 4(5)-aminoimidazole-5(4)-carboxamide (AIC) with Co(II), Ni(II) and Cu(II) have been synthesized and characterized by elemental analysis, UV–VIS and IR spectroscopies. The thermal stability was determined by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA), and the decomposition mechanisms were investigated by evolved gas analysis (EGA).

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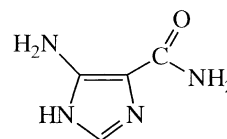
Keywords: Complexes; Imidazole derivatives; TGA; DSC; Coupled TG–FT-IR; EGA; Transition metal ions

1. Introduction

The imidazole ring is an essential metal binding site in many metalloproteins. One or more imidazole units are bound to metal ions in almost all copper- and zinc-metalloproteins and in nickel-containing urease and this binding has important effects on their biological activity. Hence, an extremely wide variety of imidazole-containing ligands have been investigated to mimic structural features of these enzymes. In addition to equilibrium and structural studies of these complexes in solution [1–7], thermoanalytical studies are also useful to complete the characterization and to relate the coordination properties of these ligands with biologically important transition metal ions.

On the basis of the data reported in the literature, and following our studies on the thermoanalytical

properties of substituted imidazole solid-state coordination compounds with transition metal ions [8–13], six different complexes of 4(5)-aminoimidazole-5(4)-carboxamide (AIC) have been synthesized and characterized by elemental analysis, UV–VIS and infrared spectroscopies.



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

The thermal stability of the characterized complexes was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Evolved gas analysis (EGA), performed by on-line coupling the TGA system with an FT-IR instrument, allowed the investigation of the decomposition mechanisms.

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2. Experimental

2.1. Materials

The ligand AIC and the metal chlorides were purchased from Sigma–Aldrich. Water was purified by passage through a cation–anion exchange column and bidistillation.

2.2. Syntheses of the complexes

$\{M(AIC) \cdot 2.5H_2O\}_n$: The polymeric complexes were obtained by adding 250 ml of a 0.01 M MCl_2 solution ($M = Co(II)$, $Ni(II)$ and $Cu(II)$) to 250 ml of a 0.01 M ligand solution ($pH = 5$). The precipitation was fast and complete, and the resulting solid was washed with water and dried under vacuum.

$M(AIC)_2 \cdot 2H_2O$: The complexes were obtained by adding 250 ml of a 0.01 M MCl_2 solution ($M = Co(II)$, $Ni(II)$ and $Cu(II)$) to 250 ml of a 0.025 M ligand solution (constant pH value = 1.5). The precipitation was fast and complete, and the resulting solid was washed with water and dried under vacuum.

2.3. Instrumental

Infrared spectra of the solid-state complexes were obtained using a Perkin-Elmer FT-IR spectrometer, model 1760X, from KBr pellets (20 scans, resolution 4 cm^{-1}).

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

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

The thermoanalytical curves were obtained using a Perkin-Elmer TGA7 thermobalance (range 20–1000 °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 °C min^{-1} , with the best resolution achieved at a scanning rate of 10 °C min^{-1} .

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

3. Results and discussion

Both the imidazole-4-acetic acid and the AIC are suitable models for studying the coordination behaviour of the imidazole ring in the presence of oxygen donors [13]. Due to the varying substituents on the imidazole ring, a comparative study of basicity and metal binding properties is possible. The coordination of the more basic nitrogens and the amide oxygens is consequently the most plausible in $M(AIC)$ and in $M(AIC)_2$ complexes, as previously reported [4].

The results of the elemental analysis of the AIC complexes are listed in the Table 1.

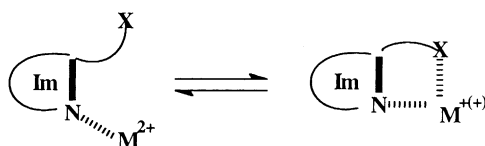
The infrared spectra of the solid-state complexes show the typical bands of coordinated imidazole, with a clear shift of the $C=O$ bands which suggests double coordination via imidazole nitrogen and amide oxygen, as also shown by previously reported [5,13–15] which is a consequence of an intramolecular equilibrium of the type indicated in Scheme 1.

However, for the polymeric complexes an extensive discussion is not possible due to difficulties in interpreting the recorded spectra.

The thermal characterization of the precipitated AIC compounds supports the shift of the equilibrium

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

	C	H	N	O	M (ICP)
$\{Co(AIC) \cdot 2.5H_2O\}_n$	21.1 (21.0)	3.0 (2.9)	24.7 (24.5)	24.5 (24.5)	25.7 (25.9)
$\{Ni(AIC) \cdot 2.5H_2O\}_n$	21.2 (21.0)	2.8 (2.9)	24.6 (24.5)	24.7 (24.5)	25.9 (25.9)
$\{M(AIC) \cdot 2.5H_2O\}_n$	20.8 (20.6)	3.0 (2.8)	24.0 (24.0)	24.3 (24.0)	27.5 (27.5)
$Co(AIC)_2 \cdot 2H_2O$	27.9 (27.8)	2.5 (2.3)	32.6 (32.5)	18.5 (18.5)	17.1 (17.1)
$Ni(AIC)_2 \cdot 2H_2O$	27.8 (27.8)	2.2 (2.3)	32.7 (32.5)	18.4 (18.5)	17.1 (17.1)
$Cu(AIC)_2 \cdot 2H_2O$	27.7 (27.4)	2.5 (2.3)	32.1 (32.0)	18.5 (18.3)	18.1 (17.3)



Scheme 1.

(Scheme 1) to the right, with the double coordination previously found in the imidazole-4-acetic acid complexes [13].

In Fig. 1, the thermogravimetric curves of the polymeric $\{M(AIC) \cdot 2.5H_2O\}_n$ show very similar profiles, with three main steps related to the loss of water (temperature range 80–150 °C), followed by overlapping of the release of the side chain and the decomposition of the imidazole ring, to obtain the metal oxide as the final residue. The loss of 1 + 1.5 water molecules is more clearly demonstrated in the corresponding DSC curves, shown in Fig. 2.

The temperature range 250–300 °C corresponds to a thermogravimetric plateau, all the complexes undergo an endo–exothermic sharp process, typical of the polymeric-to-monomeric rearrangement. The shift of 15 cm^{-1} in the IR bands (spectra recorded from KBr

disks of the complexes heated up to 300 °C) confirms the structural modification.

In Fig. 3, the thermogravimetric curves of the $M(AIC)_2 \cdot 2H_2O$ show very similar profiles, with three main steps, similar to the polymeric complexes and relate to the loss of water (temperature range 80–130 °C), followed by release of the side chains and the decomposition of the imidazole rings, to obtain the metal oxide as the final residue.

In Fig. 4, the corresponding DSC curves clearly define the release of 1 + 1 water molecules. In these curves, no other thermal processes are observed until the decomposition of the complexes which commences at 285 °C (Ni and Co), and at 270 °C (Cu).

The thermal stability scale is the same for both the monomeric and polymeric complexes (Ni \approx Co > Cu), and the monomeric species are more stable than the corresponding polymeric complexes.

The chelate formation via amide oxygen and imidazole nitrogen, also shown by Torok et al. [4] and by Sigel et al. [5], are confirmed by EGA data. The stacked plot of Fig. 5 shows that, when the anhydrous complex starts to decompose, the bands of CO_2 (air flow: 2370 and 670 cm^{-1}) and NH_3 (air flow: 966 and 931 cm^{-1}) appear in the IR spectra simultaneously.

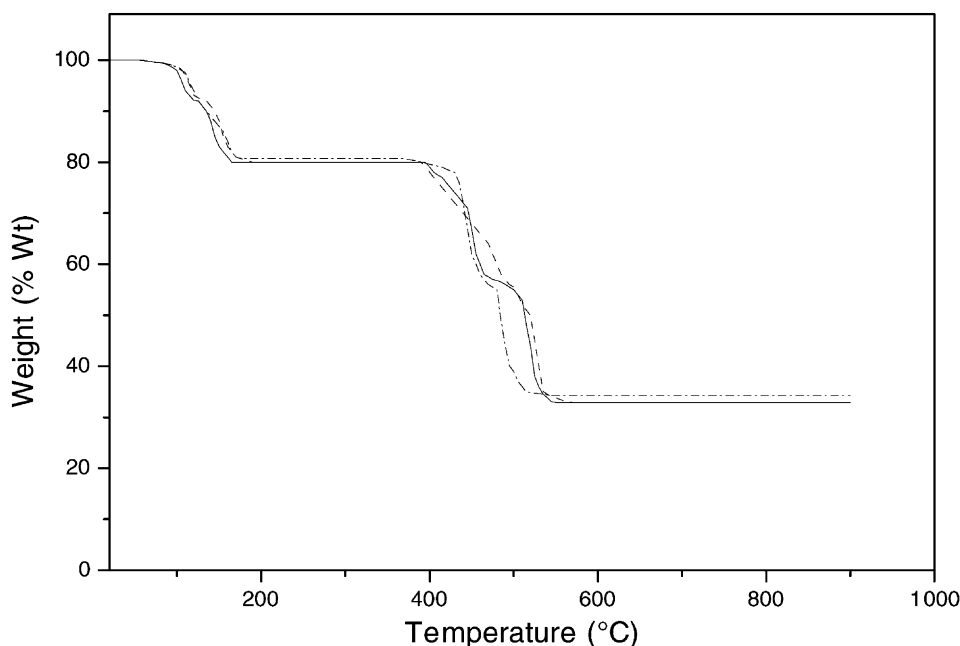


Fig. 1. TGA curves of the $M_n(AIC)_n$ complexes. Scanning rate: 10 °C min^{-1} ; air flow at 100 ml min^{-1} rate; (—) Co; (---) Ni; (- - - -) Cu.

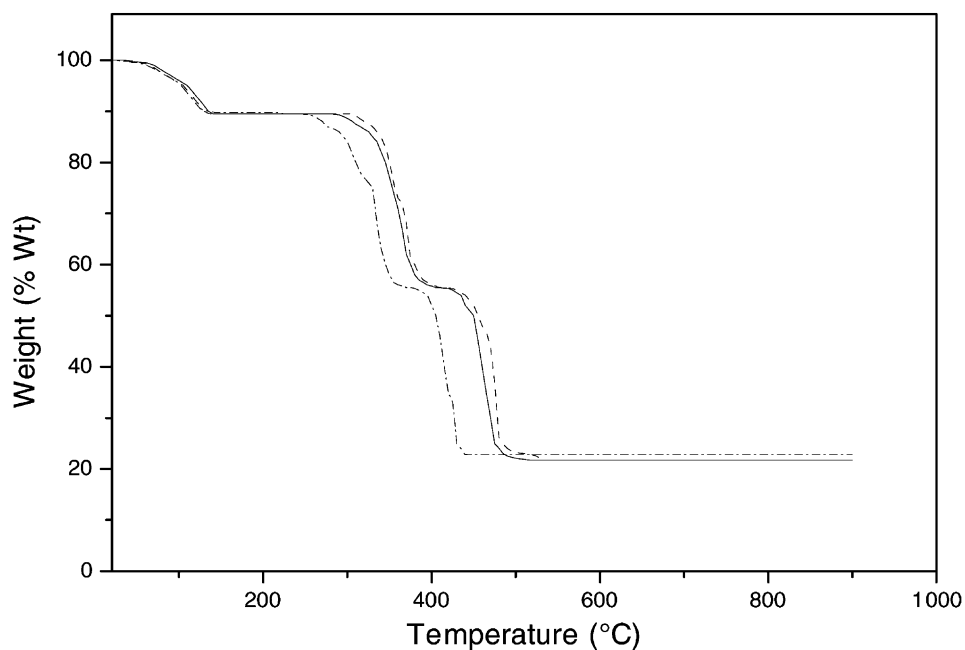


Fig. 2. DSC curves of the $M_n(AIC)_n$ complexes. Scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} rate; (—) Co; (---) Ni; (- - - -) Cu.

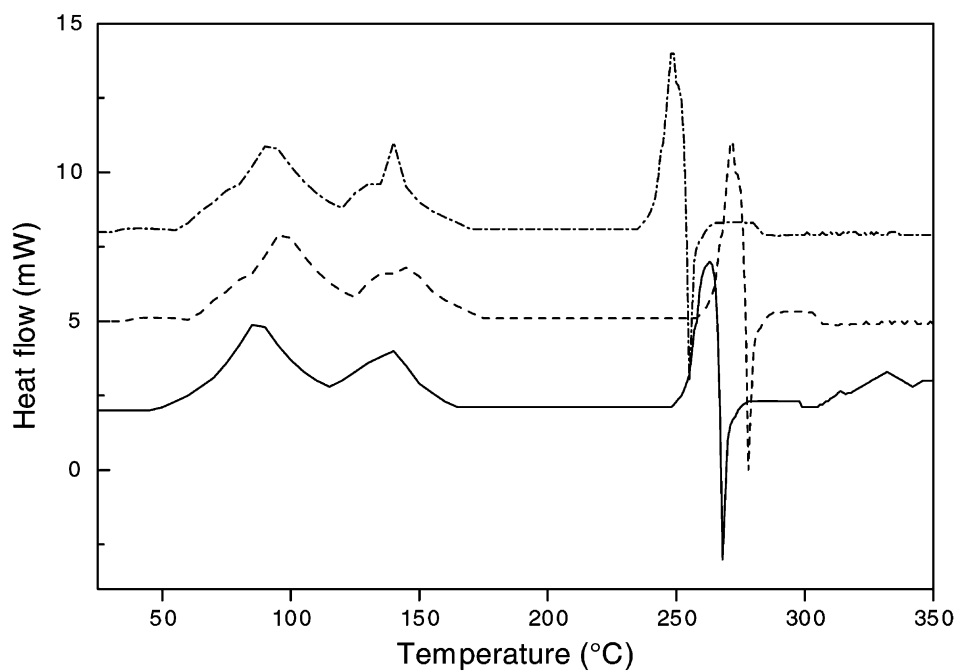


Fig. 3. TGA curves of the $M(AIC)_2$ complexes. Scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} rate (—) Co; (---) Ni; (- - - -) Cu.

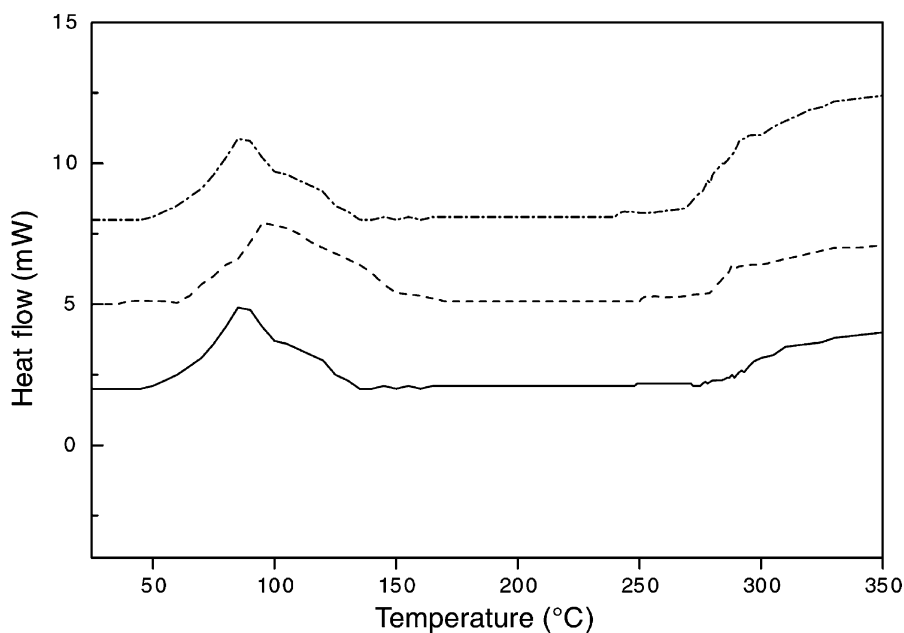


Fig. 4. DSC curves of the $M(\text{AIC})_2$ complexes. Scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} rate (—) Co; (---) Ni; (- - - -) Cu.

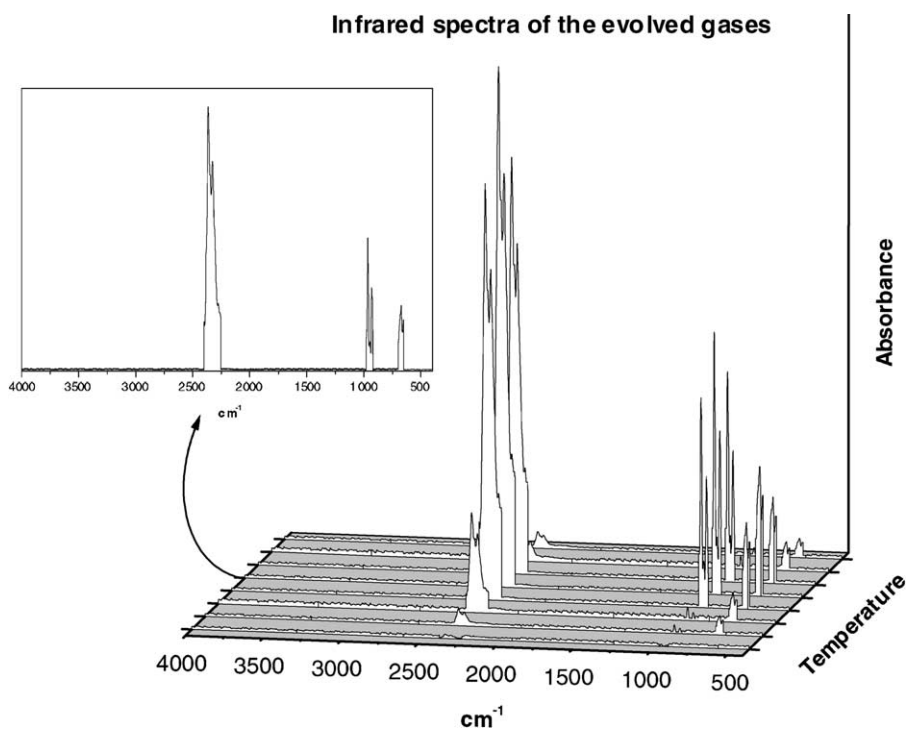


Fig. 5. Infrared spectra of the TG evolved gases for the decomposition of $M(\text{AIC})_2$ complexes in the temperature range $300\text{--}400^\circ\text{C}$. Resolution: 8 cm^{-1} (10 scans per spectrum).

This behaviour, which is observed for both the $M(\text{AIC})$ and the $M(\text{AIC})_2$ complexes, is the consequence of the breakdown of both the coordination sites, followed by complete oxidation to the metal oxide as the final product. The loss of the side chains in a well defined TG step verifies the proposed double complexation. Differently, the side chains would be lost in at least two different processes. Moreover, once the breakdown is started, all the complexes decompose in a sharp temperature range as shown in the Fig. 3.

Evidence of the coordination shown in the Scheme 1 is also supported by the UV–VIS spectra. The spectroscopic parameters suggest coordination via two imidazole nitrogens and two amide oxygens forming six membered chelate rings. The $\text{Cu}(\text{AIC})_2$ complex, for example, shows a d–d transition band at 644 nm, with strong CT transition (shoulder) at 400 nm (dark green solution).

From previous studies [5,6], EPR parameters in a frozen solution of the $\text{Cu}(\text{AIC})_2$ complex support the double 2N,2O coordination, with distorted octahedral structure.

It is interesting to compare the thermal behaviour of the $M(\text{AIC})_2$ with the $M(\text{IAA})_2$ complexes [13]. Both are realistic models for studying the coordination behaviour of the imidazole ring in presence of oxygen donors. Due to the very different substituents on the imidazole ring, comparative data between basicity and metal binding properties can be achieved. The different coordinations of IAA and AIC complexes are reflected in the thermal profiles. The AIC complexes decompose in a well defined temperature range, losing both ligand molecules in two steps separated by 30 °C. The IAA complexes show two separate well defined thermogravimetric steps, separated by 150 °C. The first ligand molecule is lost at 50 °C lower than AIC complexes and the second molecule is lost 100 °C greater than AIC complexes.

This new compound, resulting from the loss of one ligand molecule, can be described as $M(\text{IAA})$. It was not described previously [13], but is more stable of the $M(\text{IAC})$ compound previously described. The high stability can be again explained by the possibility of the IAA ligand to rearrange a mono-chelate complex via imidazole nitrogen and carboxyl group, being thermally more stable than the corresponding bis-chelate complex.

4. Conclusions

The solid-state complexes of AIC with $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$, synthesized and characterized in this study, confirmed the coordination reported in the literature for the complexes in solution, and showed a thermal stability in inverse order to the stability range in solution reported in the literature. The supposed coordination via imidazole nitrogen and acetate group was investigated by DSC and coupled TG–FT-IR. The polymeric structure of the $\{M(\text{AIC}) \cdot 2.5\text{H}_2\text{O}\}_n$ complexes is suggested by the DSC analysis, and the coupling of thermogravimetry and infrared spectroscopy (TG–FT-IR) gives the qualitative characterization of the gases evolved during the thermal decomposition.

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