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Thermoanalytical investigation of Ni(II), Co(II) and Cu(II) complexes with imidazole-4-acetic acid

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Abstract

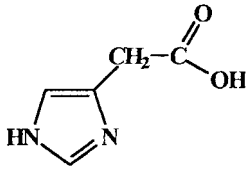
The imidazole ring and its derivatives are very useful models to understand the coordination properties and the reaction mechanisms of the biologically important systems where these molecules are involved. Six different complexes of imidazole-4-acetic acid (IAA) with Co(II), Ni(II) and Cu(II) were precipitated and characterized by elemental analysis, UV–VIS and infrared (IR) spectroscopy. The thermal stability was determined by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA), and the decomposition mechanisms was investigated by coupling on-line thermogravimetry and IR spectroscopy to obtain the evolved gas analysis (EGA by TG–FTIR). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Complexes; Imidazole derivatives; TGA; DSC; Coupled TG–FTIR; EGA; Transition metal ions

1. Introduction

The role of the imidazole ring as metal binding site in metalloproteins is well-known, and, therefore, studies of the coordination properties of this molecule and its derivatives are of interest [1–5].

The aim of this work was to study the coordination properties of the imidazole-4-acetic acid (IAA), to determine the thermal stability of its complexes in the solid state, and to investigate the decomposition mechanisms related to the coordination of the complexes.



Imidazole-4-acetic acid

As demonstrated in two recent papers [6,7], in the monoprotonated and zwitterionic species $H(IAA)^{\pm}$ both nitrogens of the imidazole moiety carry a hydrogen, hence, there are two possibilities for the formation of IAA^- species; it is important to note that a monodentate complex can be formed via N1 as well as via N3. In the IAA molecule, even if the negative charge of the carboxylate group is five atoms away from the N3 site involved in chelation, IAA^- is

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described as less flexible due to the imidazole group, the charge effect being of the same size [7]. 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, like Co(II), Ni(II) and Cu(II) [8–12], six different complexes of IAA were prepared and characterized by elemental analysis, UV–VIS and infrared (IR) spectroscopy.

The thermal stability of the characterized complexes was studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the proposed decomposition mechanisms were investigated by evolved gas analysis by on-line coupling of the TGA analyzer with a FTIR instrument.

2. Experimental

2.1. Materials

IAA and the metal chlorides were purchased from Sigma-Aldrich. Water was purified by passage through a cation–anion exchange column and distillation.

2.2. Syntheses of the complexes

The $M(IAA)_2$ complexes were obtained by adding a 0.01 M MCl_2 solution to a 0.025 M ligand solution (pH = 7.5) until a solid precipitated. The solid was washed with water and dried under vacuum.

The $M(IAA)_2Cl_2$ complexes were obtained by adding a 0.01 M MCl_2 solution to a 0.03 M ligand solution (pH = 2.8) until a solid precipitated. The solid was washed with a diluted aqueous HCl solution and dried under vacuum.

2.3. Instrumental

The UV–VIS spectra were recorded by a Perkin-Elmer Lambda series spectrofotometer.

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 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 and discussion

The results of the elemental analysis are listed in the Table 1, with the values calculated from the proposed molecular formulae.

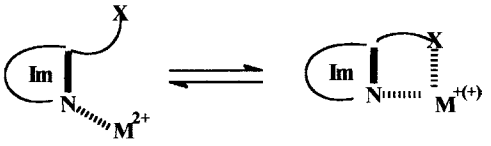
The IR spectra of the complexes (KBr pellets, 20 scans, resolution at 4 cm^{-1}) show the typical bands for the imidazole coordinated molecule, with a clear shift of the COO^- bands to suggest the double coordination via imidazole nitrogen and acetate group, as shown by the literature data cited in the [7].

This behavior was suggested in different papers [13,14] as consequence of an intramolecular equilibrium of the kind indicated in the Scheme 1.

The thermal characterization of the precipitated compounds allows to propose the shift of the equilibrium to the right side, with the double coordination.

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

	C	H	N	O	M (ICP)
$Co(IAA)_2$	38.6 (38.6)	3.0 (3.2)	18.2 (18.0)	20.7 (20.6)	18.6 (18.9)
$Ni(IAA)_2$	38.9 (38.6)	3.3 (3.2)	17.9 (18.0)	20.5 (20.6)	18.7 (18.9)
$Cu(IAA)_2$	38.0 (38.0)	3.1 (3.1)	17.6 (17.7)	19.9 (20.2)	19.9 (20.1)
$Co(IAA)_2Cl_2$	31.6 (31.4)	3.0 (3.1)	14.9 (14.7)	16.7 (16.7)	15.0 (15.4)
$Ni(IAA)_2Cl_2$	31.5 (31.4)	3.2 (3.1)	15.0 (14.7)	16.9 (16.7)	15.6 (15.4)
$Cu(IAA)_2Cl_2$	31.0 (30.8)	3.0 (3.1)	14.7 (14.4)	16.6 (16.4)	16.0 (16.3)



Scheme 1.

In fact, the decomposition of the complexes show similar thermal profiles, with two main TG steps for the $M(IAA)_2$ complexes and three main decomposition processes for the $M(IAA)_2Cl_2$ compounds.

The $M(IAA)_2$ complexes (see Fig. 1) show very similar thermogravimetric profiles: the $Ni(IAA)_2$ is thermally more stable than $Co(IAA)_2$, with the initial decomposition of $Cu(IAA)_2$ taking place about about 20°C lower than that of $Co(IAA)_2$. This thermal

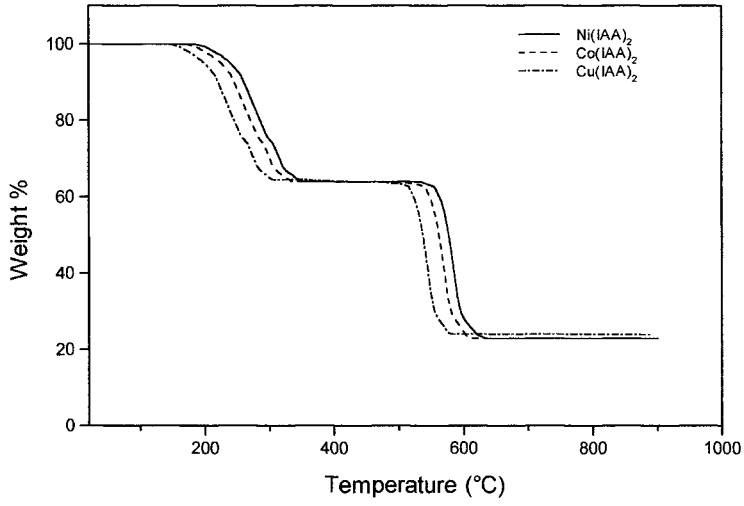


Fig. 1. TG curves of the $M(IAA)_2$ complexes. Scanning rate: 10°C min^{-1}. Air flow at 100 ml min^{-1} rate.

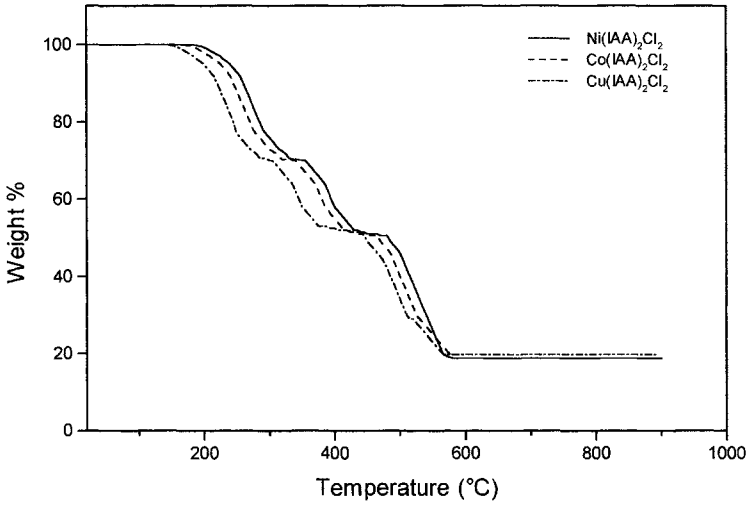


Fig. 2. TG curves of the $M(IAA)_2Cl_2$ complexes. Scanning rate: 10°C min^{-1}. Air flow at 100 ml min^{-1} rate.

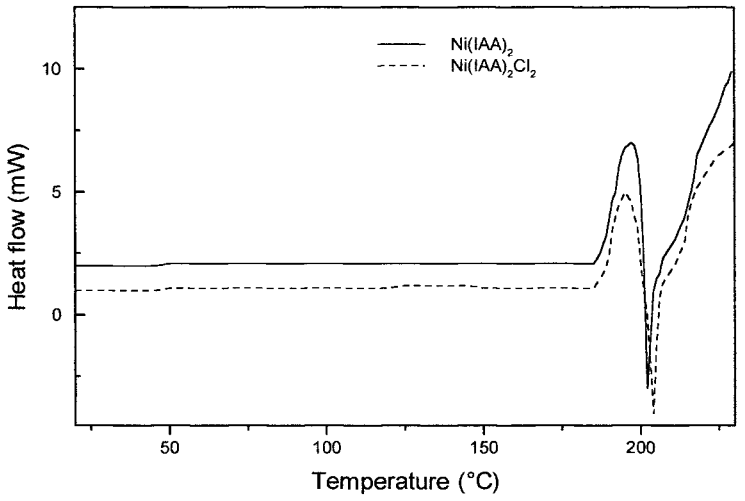


Fig. 3. DSC curves of the Ni(II) precipitated compounds. Scanning rate: 10°C min^{-1}. Air flow at 100 ml min^{-1} rate.

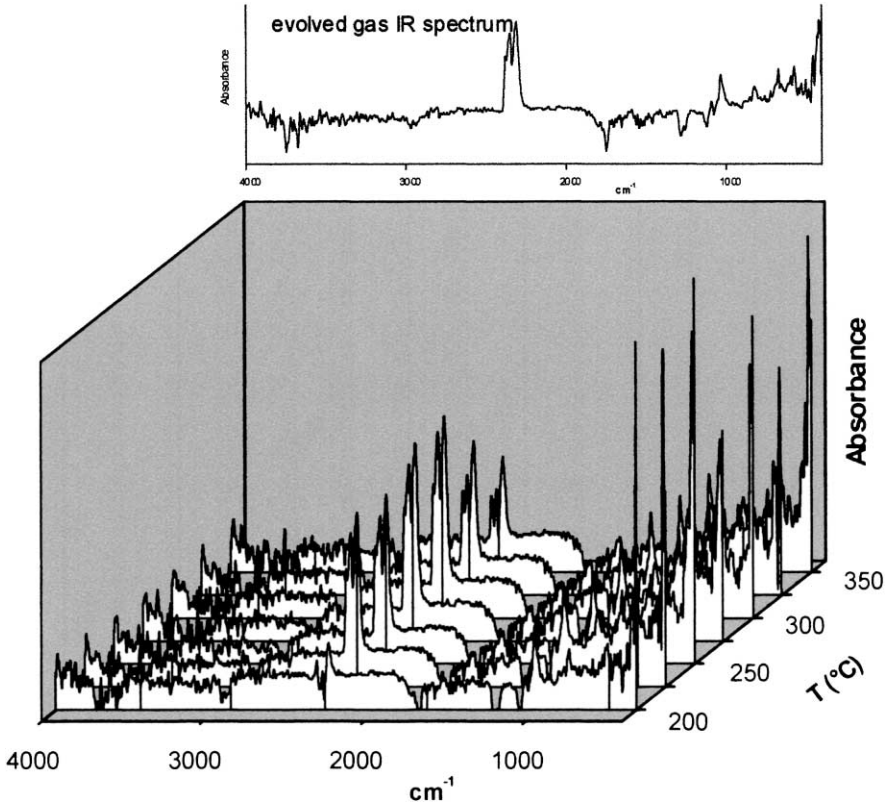


Fig. 4. Infrared spectra of the TG evolved gases in the temperature range 200–350°C. Resolution: 8 cm^{-1} — 10 scans per spectrum.

stability scale is in inverse order to the stability range in solution reported in [6].

For the $M(IAA)_2Cl_2$ complexes (Fig. 2) the thermal stability scale is again $Ni(II) > Co(II) > Cu(II)$ for all the three TG releasing steps.

The thermal behavior of all the complexes under inert flow is characterized by the shift of the final temperature of the TG releasing steps to higher temperatures, with both the Ni(II) TG curves not reaching a plateau at 900°C.

Evidence of the coordination described in the Scheme 1 is given by the UV–VIS spectra: the spectroscopic parameters suggest coordination via $2N_{im}$ and $2COO^-$ forming six-membered chelate rings; the $Cu(IAA)_2$ complex, for example, shows a d–d transition band at 640 nm, with strong CT transition (shoulder) at 350 nm.

The TG decomposition steps propose the first releasing process for all the six complexes as the loss of the two side chains; the DSC curves, reported as examples in the Fig. 3, show an endo-exothermic peak; this behavior is typical of the energy absorption and the consequent energy release due to the structural rearrangement of a complex structure undergoing the loss of a chain involved in the coordination (see again the Scheme 1).

This hypothesis is confirmed by the IR spectra of the released gases, on-line recorded by the coupled TG–FTIR technique: the IR spectra in the temperature range 200–350°C, as clearly shown in the stacked plot of the Fig. 4, confirm the bands related to water and carbon dioxide for the thermal decomposition with air flow, and the thermogravimetric step height in the same temperature range is corresponding to the molecular weight loss of two CH_2COO^- groups.

4. Conclusions

The solid state precipitated complexes of IAA with Co(II), Ni(II) and Cu(II), characterized in this study, confirm the data reported in the literature for the complexes in solution; by elemental analysis, UV–VIS and IR spectroscopies, DSC analysis and by the coupling of thermogravimetry and IR spectroscopy (TG–FTIR) to obtain the qualitative characterization of the gases evolved during the thermal decomposition, the supposed double coordination via imidazole nitrogen and acetate group was shown and the thermal stability scale among the different complexes was proposed.

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