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Thermal stability and decomposition mechanism of 1-allylimidazole coordination compounds: a TG–FTIR study of Co(II), Ni(II) and Cu(II) hexacoordinate complexes

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Abstract

A thermoanalytical study of 1-allylimidazole complexes with divalent transition metal ions, such as Co(II), Ni(II) and Cu(II) is reported. The precipitated $[ML_6](NO_3)_2$ octahedral compounds were characterized by elemental analysis and thermogravimetry (TG)–FTIR spectroscopy.

Studies provided support for the proposed thermal decomposition mechanisms.

Keywords: 1-Allylimidazole; Complexes; TG–FTIR; EGA; TGA

1. Introduction

The imidazole ring is a fundamental unit of many compounds in living organisms. A crucial role is played by the formation of complexes with divalent metal ions, such as Co(II), Ni(II) and Cu(II) in the mechanisms of the majority of the enzymatic reactions [1–8] and in the risk assessment from environmental and occupational exposure, determining the absorbed dose versus the estimated intake [9,10]. Hence, studies on the coordinating properties of ligands containing the imidazole ring are of significant interest.

Several imidazole complexes have been studied by our group. These were characterized by thermoanalytical techniques and evolved gas analysis (EGA) performed by coupling the thermobalance to a FTIR spectrometer (TG–FTIR) [11–16].

The synthesis of solid state 1-allylimidazole complexes and the characterization by X-ray and IR spectroscopy has been reported [17]. Hexacoordinate complexes of general formula $[ML_6](NO_3)_2$, where M = Co(II), Ni(II), and $[CuL_4(NO_3)_2]L_2$ (L = 1-allylimidazole), have been synthesized in the present work and the results of the thermogravimetric characterization are reported. By TG–FTIR evolved gas analysis, the proposed decomposition mechanism of these complexes is proposed.

2. Experimental

2.1. Materials

1-Allylimidazole and the metal salts, from Aldrich, were used without further purification. All the solvents used were RPE grade.

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Table 1
Elemental analysis data

	M	C	H	N	O
$[CoL_6(NO_3)_2]$	7.00 (7.06)	51.70 (51.94)	5.80 (5.77)	23.60 (23.57)	11.75 (11.54)
$[NiL_6(NO_3)_2]$	7.10 (7.06)	52.20 (51.94)	5.90 (5.77)	23.85 (23.57)	11.40 (11.54)
$[CuL4(NO_3)_2]L_2$	7.65 (7.59)	51.50 (51.65)	5.95 (5.74)	23.80 (23.43)	11.75 (11.47)

2.2. Syntheses of the complexes

The complexes were synthesized following the procedure described in the literature [17]. The precipitated solids resulted with molecular formulas $[CoL_6](NO_3)_2$, $[NiL_6](NO_3)_2$ and a new $[CuL_4(NO_3)_2]L_2$ complex also resulted.

2.3. Instrumental

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

Thermogravimetric analysis was performed 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 the 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 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.

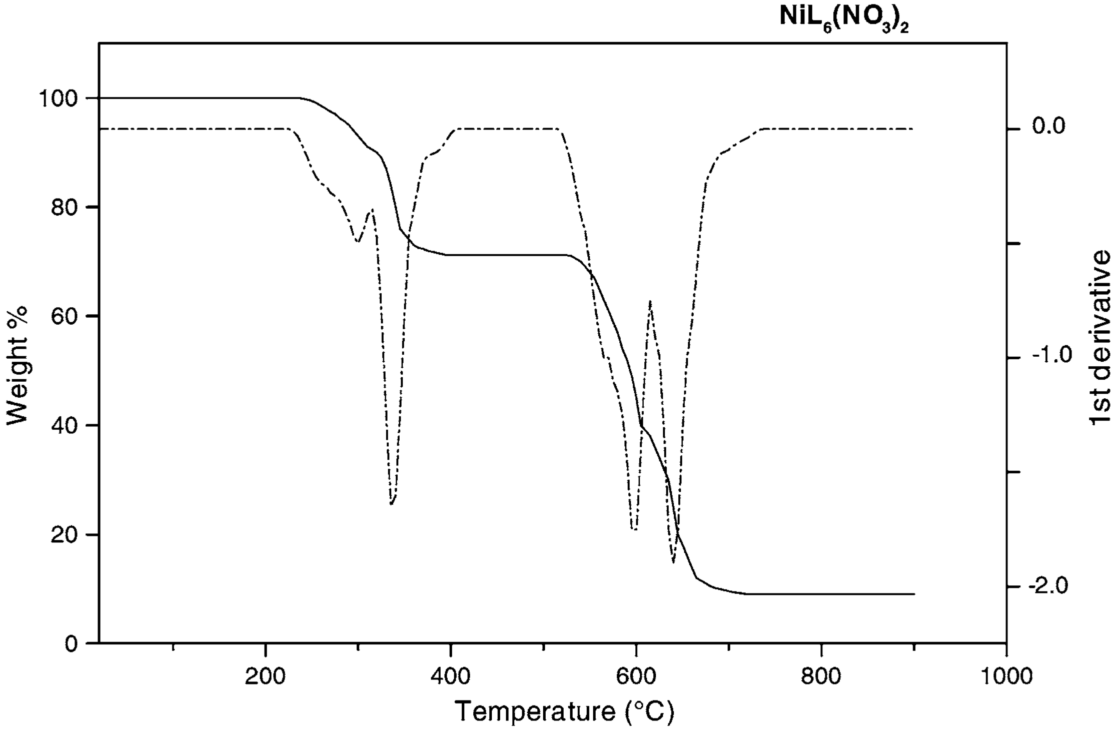

Fig. 1. Thermogravimetric curves of the $[NiL_6(NO_3)_2]$ complex. Mass loss (—); first derivative (-·-·-); scanning rate, 10 °C min^{-1}; air flow at 100 ml min^{-1} rate.

3. Results

3.1. Elemental analysis

Table 1 gives the elemental analysis data.

3.2. Thermal analysis

The thermogravimetric profiles of the three complexes, as reported in Figs. 1–3, show two main decomposition steps for all complexes (air flow).

From the mass loss, the first step is attributed to the release of the six imidazole side chains, while the second step corresponds to overlapping loss of the nitrate groups and of oxidation to give the metal oxide.

From the derivative curve (DTG), it is noted that in the first TG step the side chains are bonded with different energies with two side chains less energetically linked, and consequently lost at a lower temperature.

The infrared spectra of the gases evolved in the temperature range 200–400 °C (air flow) are collected in Fig. 4 and are related to both the Cobalt and the Nickel complexes, since the plots show the same profiles (M = Ni or Co).

4. Discussion

The aim of this study was to relate the structure of nickel and cobalt hexacoordinated complexes of general formula $[ML_6](NO_3)_2$, obtained by X-ray spectroscopy, with their thermal behavior. A new copper complex was also precipitated with the same molecular formula, but with two ligand molecules linked outside the coordination sphere.

The thermogravimetric profiles show very similar decomposition steps for all complexes with air purging flow, with the release of the side chains before complete decomposition to give the metal oxide. The mass loss was recorded in the temperature range 200–400 °C and the infrared spectra collected in the same temperature range support this hypothesis: the weight

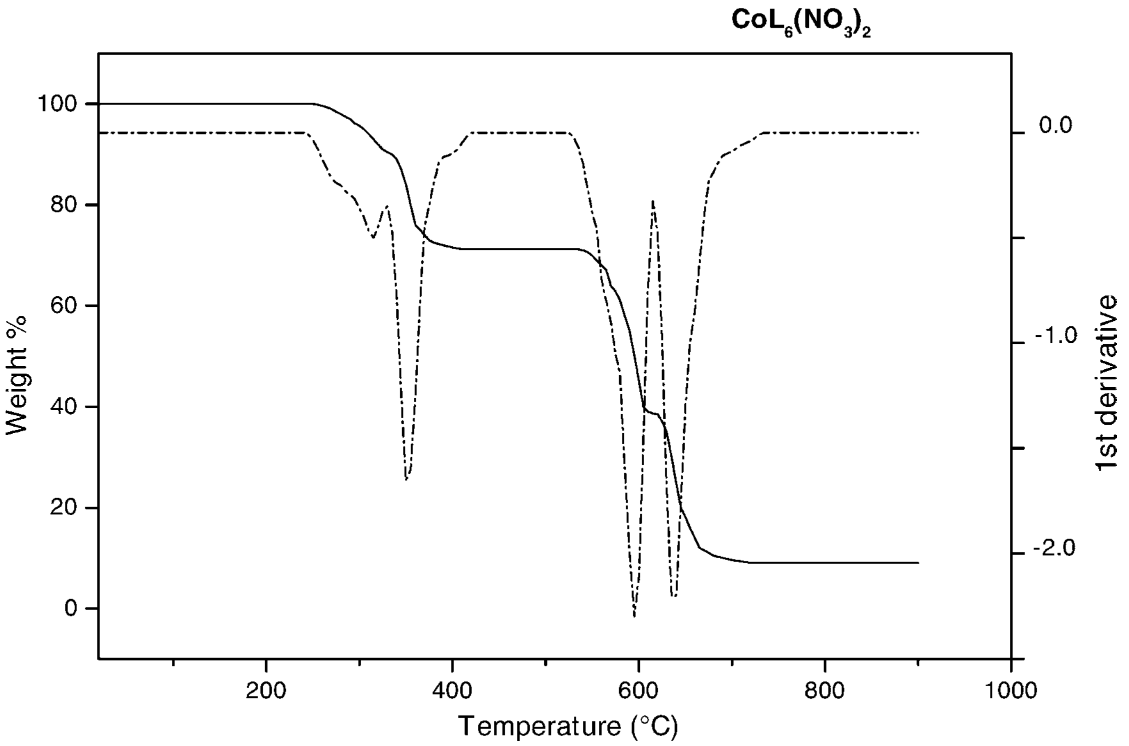

Fig. 2. Thermogravimetric curves of the $[CoL_6(NO_3)_2]$ complex. Mass loss (—); first derivative (-·-·-); scanning rate, 10 °C min^{-1}; air flow at 100 ml min^{-1} rate.

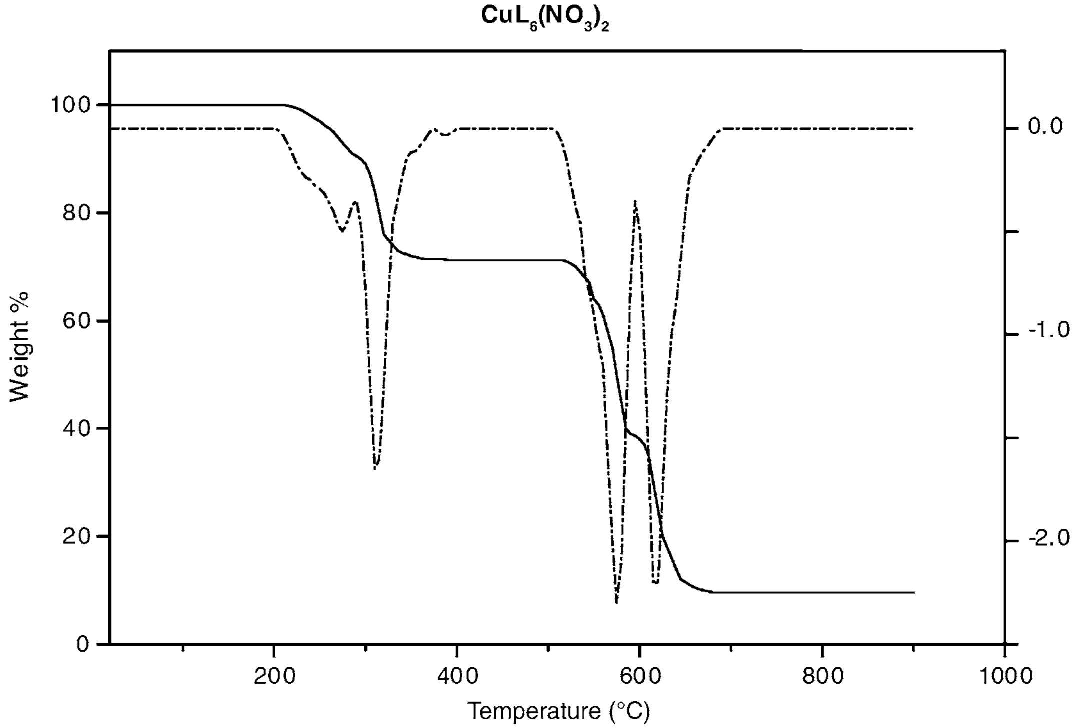

Fig. 3. Thermogravimetric curves of the $[CuL_4(NO_3)_2]L_2$ complex. Mass loss (—); first derivative (-·-·-); scanning rate, 10 °C min^{-1}; air flow at 100 ml min^{-1} rate.

loss corresponds to 28.3% for Co and Ni complexes (calculated 28.8%) and to 28.0% for Cu complex (calculated 28.1%); the bands of water and CO_2 (2352 and 670 cm^{-1}) appear in the stacked plot, as a consequence of the release under air flow.

It is noted the addition of the bands related to the NH_3 (966 and 931 cm^{-1}) starting around 320 °C, when the air purging flow allows the oxidation (Fig. 4).

From the TG curves, the release of the side chains is also characterized by two overlapped steps and from the corresponding mass loss, a difference of binding energy is suggested, two side chains being less energetically linked. This behavior can be explained from the structures obtained by X-ray analysis, where two M–L bonds are shorter, precisely the bonds M–N(51) and M–N(61) [17]: the shorter is the metal–ligand bond, the weaker can be linked the side-chain of each imidazole unit.

The final decomposition step represents overlapping of two processes, as enhanced by the first derivative curves. However, the infrared bands do not allow a clear interpretation of the decomposition mechanism. By the mass loss, the release of three imidazole rings and of the two nitrate groups is proposed followed by oxidation to give the metal oxide. The release of the nitrate groups together with the imidazole rings also verifies the same decomposition behavior in this temperature range even when the purging gas is changed from air to argon or nitrogen. The related TG curves (not reported) give no useful information, but this behavior can be expected because the NO_3^- ions enhance the oxidation, the shift of the TG curves to higher temperatures being not so marked.

As observed for other coordination compounds, the thermal stability is exactly the opposite of the stability in solution, as reported by Kurdziel and Glowiak [17]. From the TG curves it is proposed that the thermal stability scale results, $[CoL_6](NO_3)_2 > [NiL_6](NO_3)_2$, as already observed in our previous studies of substituted imidazole ligand complexes [11–16].

The $[CuL_4(NO_3)_2]L_2$ complex is less stable than the nickel and cobalt complexes but exhibits a similar thermal decomposition mechanism.

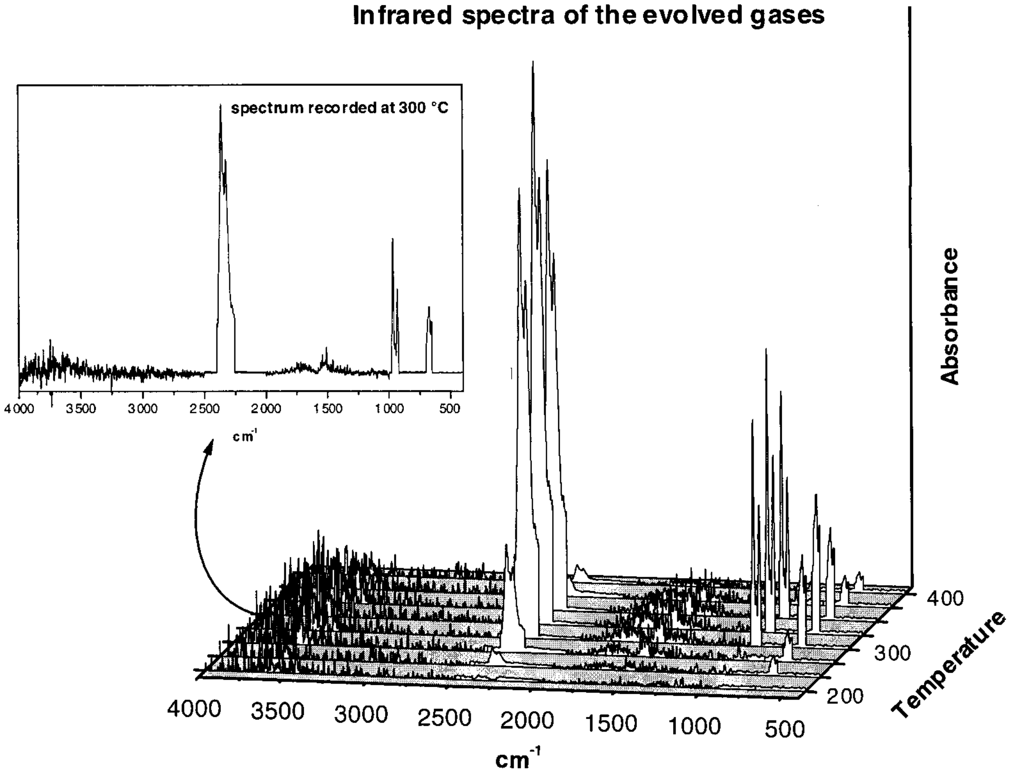

Fig. 4. Infrared spectra of the TG evolved gases for the decomposition of $[ML_6(NO_3)_2]$ complexes in the temperature range 200–400 °C (air flow). Resolution: 8 cm^{-1} to 10 scans per spectrum.

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