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Short communication

# Characterization of thermally induced mechanisms by mass spectrometry-evolved gas analysis (EGA-MS): A study of divalent cobalt and zinc biomimetic complexes with N-heterocyclic dicarboxylic ligands

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ABSTRACT

Mass spectrometry evolved gas analysis (EGA-MS) was applied to characterize cobalt and zinc biomimetic complexes with a polycarboxylate ligand, imidazole-4,5-dicarboxylic acid ($H_2$imdc). The precipitated Co(Himdc)$_2$($H_2O$)$_2$ and Zn(Himdc)$_2$($H_2O$)$_2$ complexes were studied to determine their thermal stability and to prove their decomposition mechanism by evolved gas analysis (EGA-MS). The results confirmed that the decomposition mechanism, already proposed for the analog copper and nickel complexes, can be assumed as representative for these structures, independently from the central coordinating metal.


## 1. Introduction

Studies of "biomimetic complexes", i.e. "*the study of the structure and functions of biological models*...", are important to understand biological pathways. In polycarboxylate ligands, the possibility to form complexes by the carboxyl groups in different orientations makes these molecules very interesting coordination systems. The construction of one-, two- or three-dimensional frameworks is allowed because of the presence of hydrogen bonds, and other weak interactions [1–11]. N-heterocyclic polycarboxylates such as imidazole-, pyrazine- and pyridine-dicarboxylates are excellent building blocks for model coordination compounds with several different bridged or chelated metal centers through carboxyl oxygen atoms and heterocyclic nitrogen donors [12–21]. Among them, imidazole-4,5-dicarboxylic acid ($H_2$imdc) is a useful model for biomimetic complexes. It has been structurally characterized by several authors [8,12] who reported that different starting conditions do not influence the formation of the cobalt complex, but only the final geometry.

The characterizations reported in the literature are however often lacking of studies that relate the thermal stability and the complex thermal behavior (releasing or decomposition steps).

Mass spectrometry coupled to thermoanalytical systems is actually the most accurate evolved gas analysis (EGA) system. EGA-MS has been previously applied by the authors in several different fields [22–30] to solve analytical problems.

To continue previous studies in carboxylate complexes both in solution [31–34] and in the solid state [3–5,11,14,19,35–37], in a very recent article nickel and copper complexes with imidazole-carboxylate ligand were synthesized, characterized and their thermal stability and decomposition mechanism were studied by mass spectrometry evolved gas analysis [5]. The aim of this work was to complete the study and to compare the thermoanalytical behaviors of cobalt and zinc complexes with the (Himdc)$^-$ ligand, synthesized by the same procedure. The precipitated Co(Himdc)$_2$($H_2O$)$_2$ and Zn(Himdc)$_2$($H_2O$)$_2$ complexes were characterized by elemental analysis and studied by thermoanalytical techniques coupled to mass spectrometry, to prove the supposed decomposition mechanism and to compare the results with those previously reported for nickel and copper complexes. The experimental evidences for all the complexes allowed to propose a general decomposition step.

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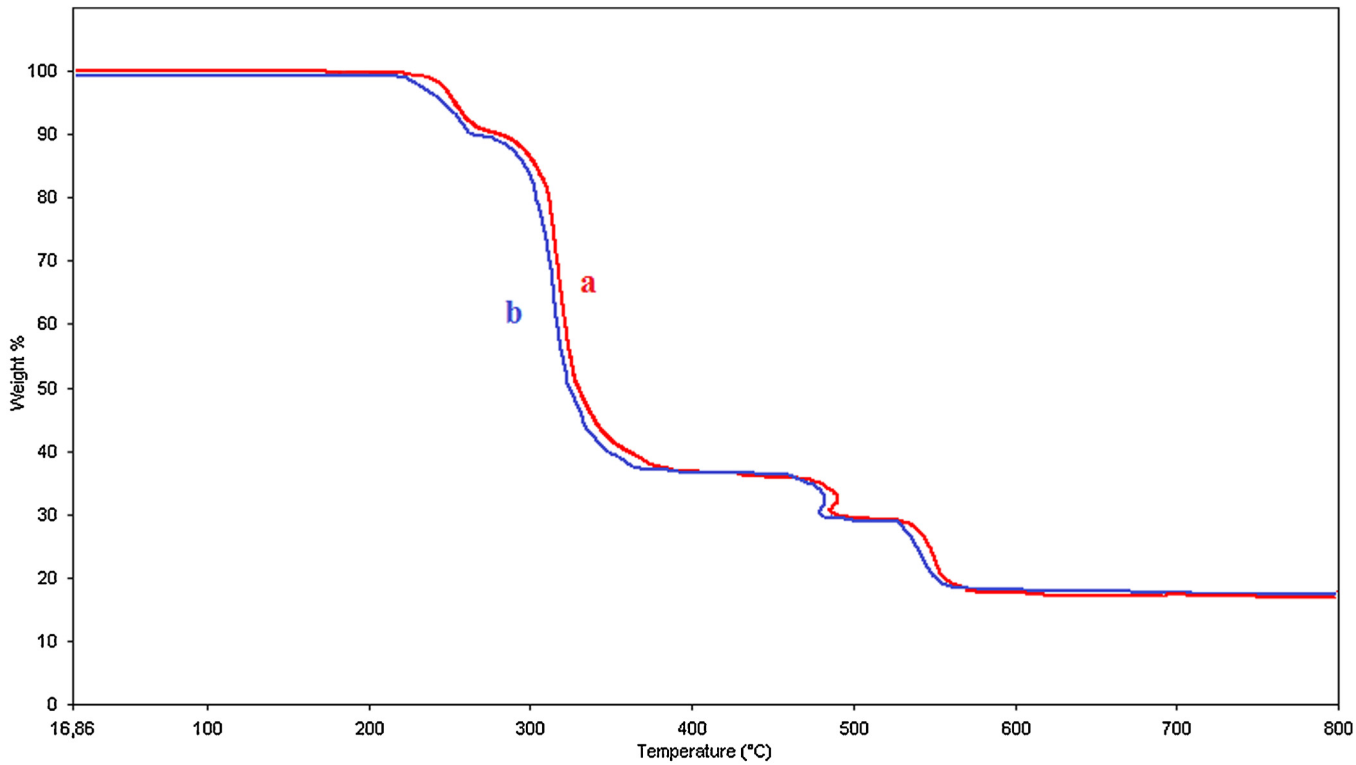
**Table 1**
Elemental analysis results for the precipitated complexes. Co and Zn were determined by ICP-OES.

| Complex | C/% | | H/% | | N/% | | M/% | |
|---|---|---|---|---|---|---|---|---|
| | Found | Calculated | Found | Calculated | Found | Calculated | Found | Calculated |
| $Co(Himdc)_2(H_2O)_2$ | 30.0 | 29.6 | 2.5 | 2.5 | 13.6 | 13.8 | 14.8 | 14.5 |
| $Zn(Himdc)_2(H_2O)_2$ | 29.0 | 29.2 | 2.4 | 2.4 | 13.6 | 13.6 | 16.1 | 15.9 |



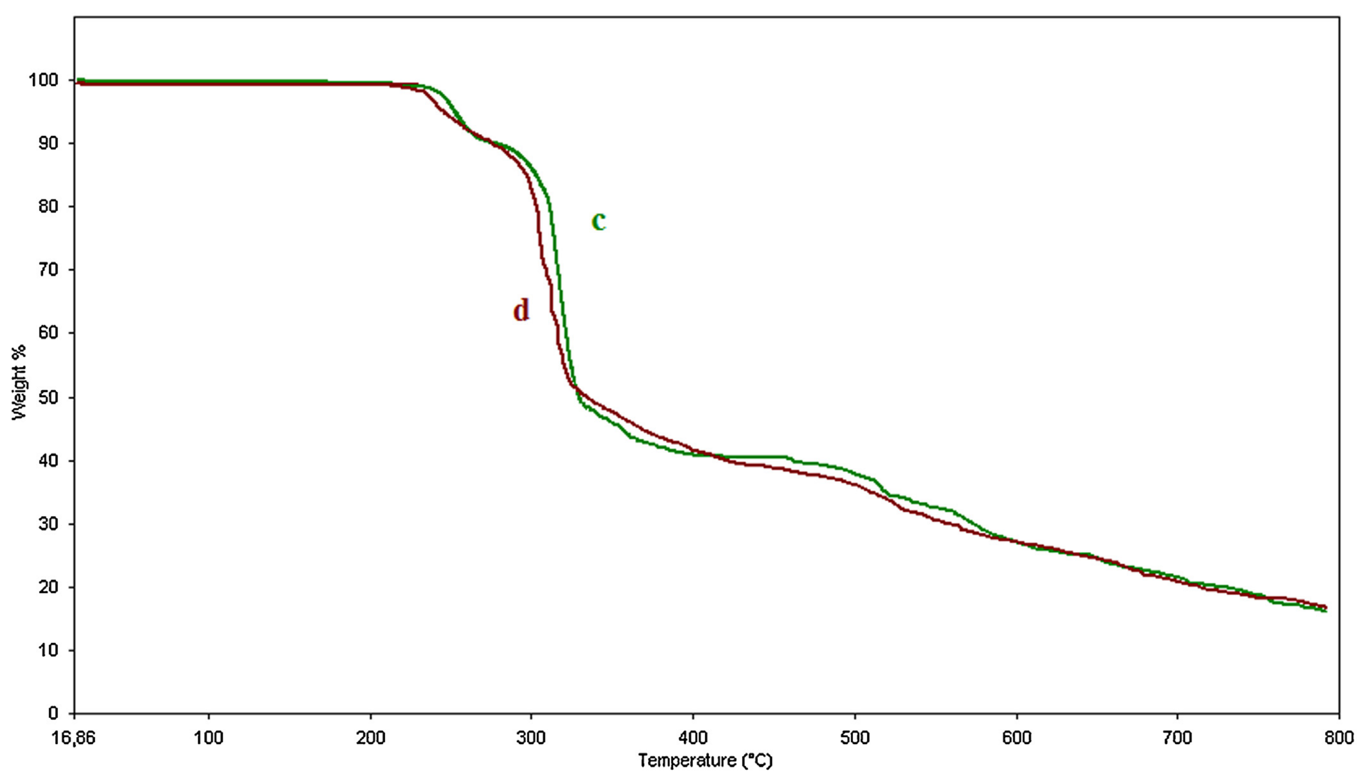




**Fig. 1.** Thermogravimetric curves of the $Co(Himdc)_2(H_2O)_2$ and $Zn(Himdc)_2(H_2O)_2$: (a and b) air flow – (c and d) nitrogen flow at 100 ml min$^{-1}$; heating rate 5 °C min$^{-1}$.