



Biomimetic complexes of Co(II), Cu(II) and Ni(II) with 2-aminomethylbenzimidazole. EGA-MS characterization of the thermally induced decomposition



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ABSTRACT

Substituted benzimidazoles are a useful model ligand to simulate specific interactions in biomimetic complexes, since compounds that contain the imidazole ring of the histidine residue are good models of bioinorganic interest. In this study, Co(II), Cu(II) and Ni(II) complexes with 2-aminomethylbenzimidazole ligand, synthesized following the literature, were characterized by mass spectrometry evolved gas analysis (EGA-MS) that allowed one to describe their thermally induced decomposition.

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1. Introduction

Complexes that contain the imidazole ring of the histidine residue are useful model compounds of bioinorganic interest [1–8]. The imidazole ring is an essential metal binding site in metalloproteins (one or more imidazole units are bound to metal ions in almost all copper- and zinc-metalloproteins or e.g., in nickel-containing urease) and thus has profound effects on their biological actions [9,10]. It is also well known that the amino group acts as the primary anchor site for metal ions and, as such, is able to promote the stepwise deprotonation and subsequent coordination of other successive binding sites, leading to the formation of the hydrolytically stable, fused, five-membered chelate rings with M–N bonds. Thus, complexes formed between metal ions and different types of bioligands, namely heteroaromatic nitrogen bases, may be considered as models for substrate–metal ion–enzyme interactions and other metal ion mediated biochemical interactions [11]. Recently, benzimidazole derived drugs have received much attention owing to the fact that benzimidazole residue is a constituent of vitamin B₁₂ which supports their potential use as therapeutics [12,13]. The interest in 2-aminomethylbenzimidazole (2-AMBI) is also due to the fact that compounds containing this heterocycle have been shown

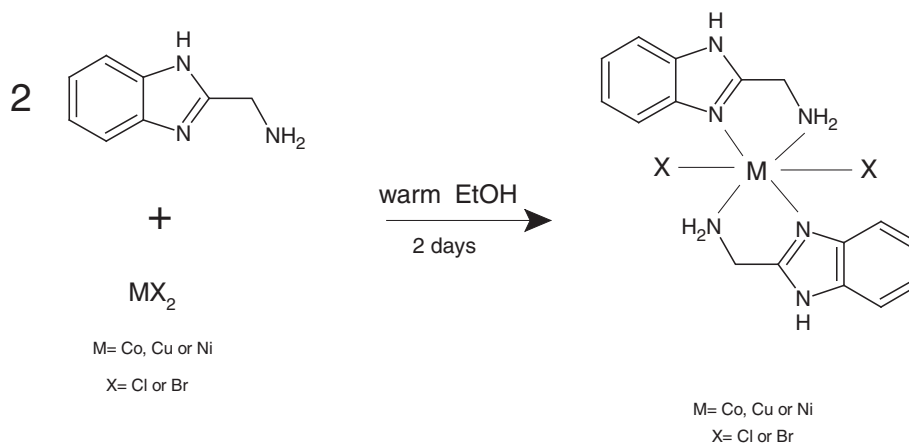
to exhibit a broad spectrum of pharmacological activities [14], including a variety of antifungal [15], antibacterial [16,17], antimicrobial [18,19], antiamoebic [20], antiparasitic [21] and antitumor applications [22,23]. Clinical examples include mebendazole and albendazole (anthelmintics) [24]. The antiviral activity of some 2-substituted benzimidazole derivatives is considered to be related to their ability to chelate trace metal ions in biological systems [25]. Additionally, 2-AMBI possesses two aromatic rings and one of them contains basic nitrogen (imidazole) and possesses π -accepting properties, which are expected to display a stability-enhancement due to the hydrophobic interaction with the substituted group of the amino acids or involved in the aromatic ring π – π stacking effects with purine and pyrimidine bases.

The scientific experience of the authors showed systematic behaviors of coordination compounds [26–30], enhanced by mass spectrometry [31–34] and thermoanalytical techniques [35–42].

To confirm the supposed general characteristic decomposition mechanism, the aim of this work was to study the thermally induced processes on six coordination compounds of general formula ML_2X_2 (where M = Co(II), Cu(II) or Ni(II), and X = Cl or Br). Complexes were precipitated following literature references [43–45] and characterized by elemental analysis and atomic spectroscopy. Evolved Gas Analysis performed by mass spectrometry (EGA-MS) was applied since this hyphenated technique is a very useful tool to solve analytical problems in several different fields [46–51]. Experimental evidences proved the thermally induced decomposition mechanism.

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Scheme 1. Synthesis of the complexes (generic reaction).

2. Experimental and methods

2.1. Materials

2-Aminomethylbenzimidazole and the cobalt, copper and nickel chlorides and bromides were purchased from Aldrich and Merck. All the reagents were of A.R. grade and used without further purification. Several different procedures can be found in the literature to precipitate the complexes of general formula ML_2X_2 , where $M = \text{Co(II), Cu(II) or Ni(II)}$, and $X = \text{Cl or Br}$ [43–45].

The generic reaction is shown in Scheme 1.

Several different attempts, following those reported in the literature, gave yield of the reactions always sensibly lower than the expected, even if the conditions were strictly followed in all the approaches. Probably due to a high solubility, an average of 60% yield of precipitated complex was usually found.

2.2. Instrumental

Elemental analysis was performed by a VarioEl III CHN Analyzer; FTIR measurements were carried out by a Perkin Elmer 1760X instrument. Metal concentration was determined by ICP-OES (Varian ICP/VISTA MPX) equipped with an ultrasonic nebulizer (U 5000 AT+, Cetac Technologies Inc.). Analytical blanks were performed. A subtraction of blanks (calculated as the mean value of six replicated measurements) was in any case applied to all results. To control nebulizer efficiency, an internal standard (yttrium 100 $\mu\text{g/L}$ at a wavelength of 371.030 nm) was used.

Thermoanalytical curves were recorded using a Perkin-Elmer TGA7 equipment. The samples investigated (approximately 7–8 mg) were heated in platinum crucibles in the temperature range of 20–850 $^\circ\text{C}$, in atmosphere of pure nitrogen or air (gaseous mixture of nitrogen and oxygen with 80 and 20%, v/v, respectively) by a flow rate of 100 $\text{mL} \cdot \text{min}^{-1}$ and a scanning rate of 5 $^\circ\text{C} \cdot \text{min}^{-1}$ (best resolution rate).

Mass spectra of the gases evolved during the experiments were recorded by a STD 2960 simultaneous DTA–TGA apparatus (TA Instruments Inc., USA) using sealed crucibles with a pinhole on the top. The gaseous species were analyzed by a ThermoStar GDS 200 (Balzers Instrument) quadrupole mass spectrometer equipped with Chaneltron detector (EI, 70 eV), through a heated 100% methyl deactivated fused silica capillary tubing.

3. Results and discussion

The results from the elemental analysis of the six precipitated complexes are reported in Table 1. Calculated and found element percent are in good agreement.

The thermally induced decomposition steps of the precipitated complexes were comparatively studied by mass spectrometry evolved gas analysis (EGA-MS). In Fig. 1, the thermoanalytical profiles of the chloride complexes are overlapped to compare the releasing steps when the purging flow is air.

The thermal decomposition is based on three main steps. The calculated percent weight loss allows one to suggest a first release of the chloride ion, followed by the rupture of the ligand molecules with the consequent loss of benzimidazole and the final decomposition to the oxide of the metal involved. This hypothesis is supported by a typical sublimation of the benzimidazole in the temperature range of 180–220 $^\circ\text{C}$ when the purging flow was nitrogen, that was neglected by changing to air the furnace atmosphere. No differences were however noted in the thermoanalytical profile related to the first and the second step when changing the purging flow (nitrogen/air).

The oxygen present in the air flow made the difference only on the third process, with a clear oxidation and a more defined step if compared to the curve recorded under nitrogen atmosphere.

A similar behavior characterized the bromide complexes. As shown in Fig. 2, the thermal profiles are very similar, with again three main steps. The experimental evidences were confirmed,

Table 1
Elemental analysis results for the precipitated complexes. Co, Cu and Ni (M%) were determined by ICP-OES.

Complex	C/%		H/%		N/%		M/%	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
Co(2-AMBI) ₂ Cl ₂	45.0	45.3	4.3	4.2	19.6	19.8	13.6	13.9
Cu(2-AMBI) ₂ Cl ₂	44.9	44.8	4.2	4.2	19.6	19.6	15.1	14.8
Ni(2-AMBI) ₂ Cl ₂	45.2	45.3	4.3	4.2	19.9	19.8	14.1	13.9
Co(2-AMBI) ₂ Br ₂	37.1	37.4	3.4	3.5	16.6	16.4	11.6	11.5
Cu(2-AMBI) ₂ Br ₂	37.0	37.1	3.4	3.5	16.5	16.2	12.1	12.3
Ni(2-AMBI) ₂ Br ₂	37.6	37.4	3.5	3.5	16.6	16.4	11.4	11.5

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