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Versatile coordination modes of ronidazole towards transition metal ions: five and seven membered chelate rings; supramolecular networks

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ABSTRACT

Coordination compounds with ronidazole (ron) and the transition metals Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} were synthesized and characterized by spectroscopic and analytical techniques. Ronidazole presented monodentate or bidentate coordination modes. A five membered chelate ring was formed by coordination of the carbamate oxygen (C–O–C) and the imidazole nitrogen atoms to the metal center. This coordination mode was observed in the halide compounds of cobalt(II) **1**, **2**, **3**; copper(II) **8**; zinc(II) **11**, **12**, **13**; cadmium(II) **14**, and mercury(II) **15**. On the other hand, the ligand in the nitrate compounds of cobalt(II) **4**, nickel(II) **7** and copper(II) **10**, as the halide compounds of nickel(II) **5**, **6** and copper(II) **9**, formed a seven membered chelate ring through the carbonylic oxygen (C=O) and the imidazolic nitrogen atoms to the metal ion. The coordination compounds presented tetrahedral, trigonal bipyramidal, and octahedral geometries. The X-ray crystal structures of ron and its coordination compounds presented intermolecular hydrogen bonding, oxygen lone pair···π and X···π interactions, giving place to complex 3D supramolecular structures.

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1. Introduction

5-Nitroimidazoles such as metronidazole, tinidazole, and secnidazole are of pharmaceutical significance due to their use as antiprotozoal and antibacterial agents [1–6]. Ronidazole, (1-methyl-5-nitro-1H-imidazol-2-yl)methyl carbamate, is used in the treatment of *Trichomonas foetus* and *Giardia* in cats and dogs respectively [7–9].

Ronidazole undergoes a biotransformation in organisms and its metabolites may bind covalently to proteins [10], which has been proposed as a likely mechanism through which this compound causes mutagenicity in bacteria [11]. Additionally, it may cause neurotoxic effects in cats [12]. The use of low doses reduces its toxicity [13] and is widely used in different veterinary treatments.

Complexes of transition metal ions with biological active ligands have shown that there is a synergistic effect, enhancing or modifying their antimicrobial activity when coordinated to a metal ion [14,15]. We have observed that coordination compounds of Co^{II}, Cu^{II} and Zn^{II} with benzimidazole and imidazole derivatives presented antimicrobial [16] or cytotoxic activity towards different cell lines [17–19].

Carbamate derivatives present diverse pharmacological functions including anticancer, antibacterial, antifungal, and antiviral among others. Studies have shown that incorporating carbamates to pharmacophores increases their biological activity. A relevant example of this is the increased anticancer activity of taxol when substituted with carbamate derivatives in different positions [20]. Coordination compounds with the carbamate derivatives carbendazim and albendazol have been previously studied. Both ligands present two coordination modes, monodentate or bidentate through the imidazolic nitrogen and the carbamate carbonylic oxygen atom, stabilizing a five memebered ring. The chelate copper(II) complexes with both ligands showed good *in vitro* anticancer activity [17,21].

It has been proposed that the bonding mode, structure, and weak interactions are relevant to the antimicrobial activity of coordination compounds with aromatic amines [22]. Intra lone pair S=O···π interactions play an important role in the stabilization of biologically active complexes [23]. Intermolecular hydrogen bonding and lone pair···π interactions, such as O–N–O···π and Cl···π stabilize different supramolecular arrangements [23–26].

Given the relevance of the coordination mode of biological active imidazole derivatives towards transition metal ions, we decided to investigate the interaction of ronidazole with cobalt(II), nickel(II),

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copper(II), zinc(II), cadmium(II) and mercury(II). The obtained compounds are shown in Scheme 1.

2. Materials and methods

2.1. Physical measurements

A FT-IR spectrometer (Perkin-Elmer) was used for obtaining the IR spectrum of solid samples (4000–400 cm^{-1}). The electronic spectra (UV–Vis-NIR) of solid samples were obtained using the diffuse reflectance method on a Cary-5E (Varian) spectrometer, from 40000 to 5000 cm^{-1}. Elemental analysis for carbon, hydrogen and nitrogen were carried out with a Fisons EA 1108 analyzer.

2.2. Materials

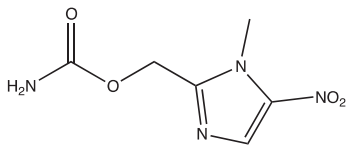
The ligand and the metal salts were used without further purification: ronidazole, $CdCl_2·4H_2O$ (Aldrich, Co); $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$, $ZnCl_2$, $CoBr_2$, $NiBr_2$, $CuBr_2$, $ZnBr_2$, $Ni(NO_3)_2·6H_2O$, $Cu(NO_3)_2·2.5H_2O$, $Zn(NO_3)_2·6H_2O$, $HgCl_2$ (J. T. Baker); $Co(NO_3)_2·6H_2O$ (Mallinckroft).

2.3. Synthesis

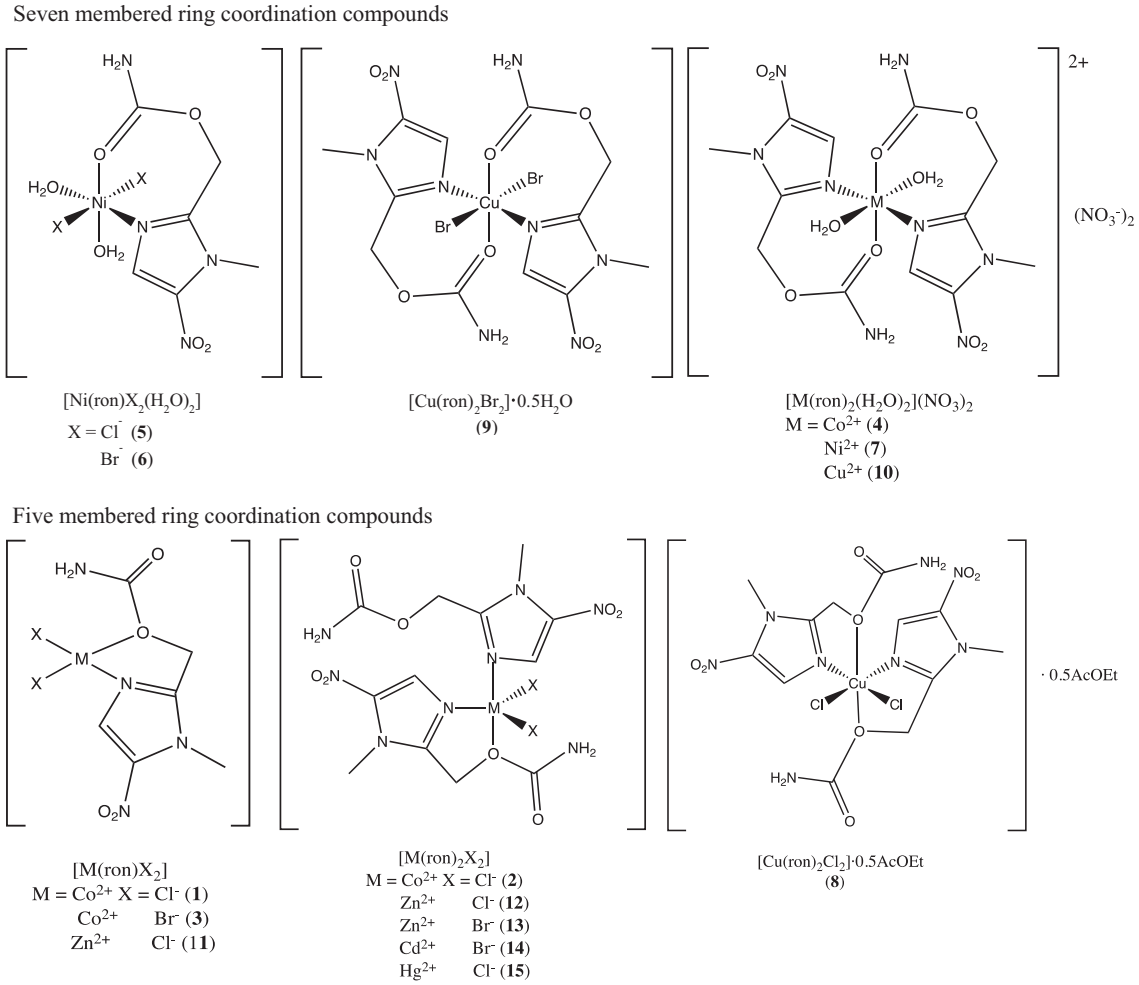
Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} coordination compounds were synthesized using an ethanol: acetone solution. The metal salts were dissolved in ethanol to which the ligand was added in solid form and then acetone was added. The solution was stirred under reflux. The products obtained were washed with ethanol and acetone. Details of the reaction conditions are addressed below.

2.3.1. Synthesis of compound $[Co(ron)Cl_2]·H_2O$ (*1*). General procedure

A solution of $CoCl_2·6H_2O$ (0.119 g, 0.5 mmol) in ethanol (15 mL) was added to a solution of ronidazole (0.100 g, 0.5 mmol) in acetone (30 mL). The solution was heated under reflux for 2.5 h and left to stand at room temperature. A blue solid was obtained and



(1-methyl-5-nitro-1H-imidazol-2-yl)methyl carbamate



Scheme 1. Structures of ronidazole compounds.

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