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Crystal structure, solid state and solution characterisation of copper(II) coordination compounds of ethyl 5-methyl-4-imidazolecarboxylate (emizco)

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Abstract

The synthesis and characterisation of the following compounds derived from the biological relevant compound ethyl 5-methyl-4-imidazolecarboxylate (emizco) (**1**): [Cu(emizco)Cl_2] (**2**), [Cu(emizco)$_2Cl_2$] (**3**), [Cu(emizco)$_2Br_2$] (**4**), [Cu(emizco)$_2(H_2O)_2$]$(NO_3)_2$ (**5**) and [Cu(emizco)$_4$]$(NO_3)_2$ (**6**), is presented. These compounds were characterised by IR and UV spectroscopic techniques, in addition the crystal structures of compounds **1**–**5** were determined. For complexes **2**–**5**, emizco is coordinated as a bidentate ligand, through the oxygen atom of the carboxylate moiety and the nitrogen atom of the imidazolic ring. Different geometries are stabilised: compound **2** includes a pentacoordinated square pyramidal metal centre, while **3**–**5** are derived from octahedral geometry. Halide compounds **3** and **4** show a *cis*-octahedral arrangement, which is not very common on [$CuN_2O_2X_2$] systems, while **5** stabilises the *trans*-octahedral isomer. Compound **6** displays a square planar geometry. Finally, hydrolysis of emizco to its corresponding carboxylic acid (mizco), allowed the preparation of another square planar complex **7**, identified as [Cu(mizco)$_2$] $0.5H_2O$. Solution studies of these compounds indicate that emizco is not substituted from the coordination sphere, remaining as a bidentate ligand. Halides are substituted by water molecules, changing from *cis* octahedral to the *trans*-[Cu(emizco)$_2(H_2O)_2$]$^{2+}$ isomer.

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1. Introduction

The interaction of imidazole derivatives with metal ions is a subject of continuous interest. It is well known that a number of imidazole derivatives have biological activity, e.g. presenting pharmaceutical, biocidal or fungicidal properties [1], among others. Within this class of compounds, nitroimidazoles have been used in the treatment of tropical diseases, in protozoal and anaerobic microbial infections [2–5] and as radiosensitisers [6]. Furthermore, these molecules may easily coordinate to transition metal ions, giving stable coordination compounds, and their biological activity as radiosensitisers or as hypoxic cytotoxins has been studied [7–15]. The nitro group adjacent to an imidazolic nitrogen may occupy a coordination site, stabilising chelate metal complexes, while the hydroxyethyl and nitro groups act as supramolecular synthons, with the option to gen-

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erate hydrogen-bonded networks of different dimensions. The number, orientation and type of hydrogen bonding drives the formation of mono and two-dimensional networks. The contribution of metal ions in metronidazol coordination compounds is shown in the stabilisation of different aggregate structures, as we have informed [16]. Ethyl 5-methyl-4-imidazolecarboxylate (hereafter abbreviated emizco) **1,** is used as an intermediate in the synthesis of a variety of imidazolic compounds with pharmacological properties [17]. Previously, we have investigated the coordination ability of emizco towards nickel(II) and cobalt(II), and the biological activity of their complexes on photosynthesis. They showed to be inhibitors of the photosynthetic electron flow and ATP-synthesis [18,19]. In these complexes, the imidazole nitrogen atom and its neighbouring ester group are active sites for binding the Co^{2+} and Ni^{2+} atoms, giving place to mono- or bi-dentate coordination modes, therefore stabilising tetrahedral or octahedral geometries. In this paper, we present the synthesis and the structural characterisation of coordination compounds of emizco with copper(II) salts. This work was undertaken to contribute to a better understanding of the coordination behaviour of this biological relevant compound towards metal ions.

2. Experimental

2.1. Reagents

Emizco, metal salts: $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(O_2CMe)_2 \cdot H_2O$, and solvents were purchased from Aldrich Chem., Merck and J.T. Baker and were used as received. Emizco (**1**) was recrystallised from hot methanol (0.617 g, in 20 cm^3). The solution was allowed to stand for 3 weeks. The colourless crystals were washed with methanol and dried in vacuo. Anal. Found: C, 54.0; H, 6.8; N, 18.6%. Calcd. for $C_7H_{10}N_20_2$: C, 54.5; H, 6.5; N, 18.2%.

2.2. Spectroscopic measurements

IR spectra in the range 4000–600 cm^{-1} were recorded in KBr pellets (Perkin–Elmer 599 B) and in the range 700–70 $cm^{-1}$with polyethylene pellets (Nicolet FTIR 740). Electronic spectra of powdered crystalline samples were measured by the diffuse reflectance method on a Cary-5E Varian spectrometer, over the range 250–2000 nm (40,000–5000 cm^{-1}). For solution studies, a diode array Hewlett Packard HP 8452A spectrometer was used, 300–800 nm (33,000–12,500 cm^{-1}). Elemental analyses were carried out with a Fisons EA 1108 analyser. Magnetic susceptibility measurements at room temperature of powdered samples were recorded on a Johnson-Matthey DG8 5HJ balance, using the Gouy method.

2.3. Crystallography

Diffraction data for single crystals were obtained at room temperature for **1**–**5**, using standard procedures, on a Enraf-Nonius CAD4 diffractometer (**1**) or a Bruker P4 diffractometer (**2**–**5**). Structures were solved and refined using the SHELX-97 package [20]. H atoms were placed on idealised positions, with the exception of H atoms of water molecules in **5**, which were found on difference maps. Non-H atoms were refined anisotropically, while H atoms were treated with a riding model. Table 2 gives a selection of crystal data while Table 3 includes main bond distances and angles.

2.4. Synthesis of complexes: general procedure

Copper coordination compounds were prepared using methanol as solvent and 1:1, 2:1, 4:1 and 1:4 ligand:Cu(II) molar ratios. Different products were obtained when varying the ligand:Cu(II) ratio.

2.4.1. $[Cu(emizco)Cl_2]$ (**2**)

Copper(II) chloride dihydrate (0.171 g, 1 mmol) was dissolved in hot methanol (15 cm^3) and added to a solution of emizco (0.154 g, 1 mmol) in hot methanol (15 cm^3). The green solution was refluxed for 5 h and then allowed to stand for 4 weeks. The resulting emerald green crystals were filtered off, washed with methanol and dried in vacuo. Yield: 35.0%. Anal. Found: C, 28.5; H, 3.6; N, 9.6%. Calcd. for $C_7H_{10}CuCl_2N_2O_2$: C, 29.1; H, 3.5; N, 9.7%.

2.4.2. $[Cu(emizco)_2Cl_2]$ (**3**)

Copper(II) chloride dihydrate (0.085 g, 0.5 mmol) was dissolved in hot methanol (15 cm^3) and added to a solution of emizco (0.154 g, 1 mmol) in hot methanol (15 cm^3). The blue solution was refluxed for 5 h and then allowed to stand for 2 weeks. The resulting green crystals were filtered off, washed with methanol and dried in vacuo. Yield: 71.5%. Anal. Found: C, 37.2; H, 4.5; N, 12.7%. Calcd. for $C_{14}H_{20}CuN_4O_4Cl_2Cu$: C, 37.9; H, 4.6; N, 12.7%.

2.4.3. $[Cu(emizco)_2Br_2]$ (**4**)

The previous procedure was repeated using copper(II) bromide (0.112 g, 0.5 mmol), giving olive green crystals. Yield: 71.0%. Anal. Found: C, 31.3; H, 3.8; N, 10.5%. Calcd. for $C_{14}H_{20}CuN_4O_4Br_2Cu$: C, 31.6; H, 3.8; N, 10.5%.

2.4.4. $[Cu(emizco)_2(H_2O)_2]$ $(NO_3)_2$ (**5**)

Copper(II) nitrate trihydrate (0.121 g, 0.5 mmol) was dissolved in hot methanol (15 cm^3) and added to a

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