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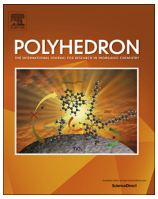

Synthesis and crystal structures of mononuclear Cu^{II}/Co^{II} coordination complexes from pyrazole-dicarboxylate acid derivatives

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ABSTRACT

Three novel pyrazole-dicarboxylate acid derivatives namely 1-(carboxymethyl)-5-methyl-1H-pyrazole-3-carboxylic acid [**L1**], 1-[(3-carboxy-5-methyl-1H-pyrazol-1-yl) methyl]-5-methyl-1H-pyrazole-3-carboxylic acid [**L2**] and 1-[3-(3-carboxy-5-methyl-1H-pyrazol-1-yl) propyl]-5-methyl-1H-pyrazole-3-carboxylic acid [**L3**] were synthesized and characterized by ^{1}H NMR and ESI-MS. The coordination/chelation and crystallization property of these organic molecules with $Cu^{II}/Co^{II}/Zn^{II}$ were studied and single crystals were obtained with **L1** and **L3** on reaction with $Cu(NO_3)_2$ and $Co(NO_3)_2$, respectively. Single crystal X-ray diffraction experiments revealed that both resulted in mononuclear chelate complexes of formula $[Cu(\mathbf{L1})_2(H_2O)]\cdot 2H_2O$ (**A**) and $[Co(\mathbf{L3})(H_2O)_2]$ (**B**). **A** and **B** consist of 2D hydrogen bonded networks with and without lattice included water molecules, respectively. The crystal structure of the free derivative **L2** is also presented.

1. Introduction

Pyrazole derivatives are important biologically active heterocyclic compounds. These derivatives are the subject of many studies due to their widespread biological activities such as anti-inflammatory [1], anti-anxiety [2], antipyretic [3], antimicrobial [4], antiviral [5], antitumor [6], anticonvulsant [7], antihistaminic [8], antidepressant [9], insecticides and fungicides [10]. Nitrogenous systems have attracted more attention in these last years due to their interesting properties in coordination chemistry [11–17]. Particularly the ability of pyrazole and its derivatives to act as ligands has been the research subject of many studies [18,19], in particular the synthesis of iron complexes due to their spin crossover [20–22] and molecular magnet properties [23]. This aptitude is mainly owed to the presence of sp^2 hybrid nitrogen donors [24–27] with the involvement in some cases, of other sites donors as oxygen and sulfur atoms [28,29]. Moreover, polydentate pyrazolic receptors are well known for their ability to complex not only alkali cations [30–34] but also to form stable complexes with transition metal ions [35–38].

With the aim of searching new candidate ligands for metal complex assemblies, we have considered the case of pyrazole carboxylic ligands with O and N donor atoms. Such molecules are particularly interesting as ligands for the building of polynuclear complexes as models for bioinorganic systems [39] as well as for the discovery of new catalyst precursors [40]. They could also be interesting for metal organic framework constructions [41]. In this work, we disclose the synthesis of new derivatives of pyrazole molecules functionalized with dicarboxylic acids as well as the crystal structure of two coordination complexes derived from these ligands.

2. Experimental

2.1. Synthesis

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification. ^{1}H NMR spectra were obtained with a Bruker AC 300 spectrometer. Molecular weights were determined on a JEOL JMS DX-300 Mass Spectrometer. IR spectra were taken with potassium bromide discs on a Perkin Elmer 1310 spectrometer. Melting points were determined on a micro hot stage apparatus and are uncorrected.

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2.1.1. Synthesis of methyl 1-((ethoxycarbonyl)methyl)-5-methyl-1H-pyrazole-3-carboxylate (*2*)

A mixture of **1** (5.68 mmol) and potassium tert-butoxide (7.59 mmol) in 80 ml of anhydrous THF was heated under reflux for 1 h. After cooling to 0 °C, a solution of ethylbromoacetate (7.78 mmol) in 20 ml of THF was slowly added. The reaction mixture was then stirred for 5 h at room temperature. The resulting mixture was filtered and the solvent was evaporated to dryness. The obtained residue was purified on alumina using dichloromethane as eluant.

Yield 70%; M.p. = 54–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.21 (s, 3H, $–CH_3$); 1.31 (t, 3H, $CH_3–CH_2–$); 3.70 (s, 1H, OCH_3); 4.21 (q, 2H, $CH_3–CH_2–$); 4.75 (s, 2H, $CH_2–N$); 6.40 (s, 1H, Py); *m/z* $(M+H)^+$: 226.2; IR: $\nu(C{=}O) = 1720\ cm^{-1}$, $\nu(C–O) = 1150\ cm^{-1}$.

2.1.2. Synthesis of 1-(carboxymethyl)-5-methyl-1H-pyrazole-3-carboxylic acid (*L1*)

A mixture of **2** (0.025 mol) and NaOH (0.025 mol) in 150 ml of water was stirred for 24 h. After cooling to 0 °C, the mixture was neutralized by diluted HCl. The precipitated product was filtered off, washed with water and dried in a desiccator. The product was then purified by recrystallization from water.

Yield 98%; M.p. = 260–262 °C (recrystallized in water); ^{1}H NMR (300 MHz, DMSO d_6) δ ppm: 2.16 (s, 3H, $–CH_3$); 4.94 (s, 2H, $CH_2–N$); 6.43 (s, 1H, Py); *m/z* $(M)^+$: 184; $\nu(OH) = 3100\ cm^{-1}$, $\nu(C{=}O) = 1690\ cm^{-1}$.

2.1.3. Synthesis of 1-[(3-carboxy-5-methyl-1H-pyrazol-1-yl) methyl]-5-methyl-1H-pyrazole-3-carboxylic acid (*L2*)

Under a similar procedure as for **2** and **L1** but using 1,3-dibromopropane instead of ethylbromoacetate: a mixture of **4** (0.025 mol) and NaOH (0.025 mol) in 150 ml of water was stirred for 24 h. After cooling to 0 °C, the mixture was neutralized by diluted HCl. The residue was filtered, washed with water and dried in desiccators. The product was purified by recrystallization from water. Yield 98%; M.p. = 290–292 °C (crystallized in water); ^{1}H NMR (300 MHz, DMSO d_6) δ ppm: 2.18 (s, 3H, $–CH_3$); 5.96 (s, 2H, $CH_2–N$); 6.45 (s, 1H, Py); *m/z* $(M)^+$: 264.2; $\nu(OH) = 3150\ cm^{-1}$, $\nu(C{=}O) = 1695\ cm^{-1}$. Single crystals were obtained after two weeks from the mother solution by reacting $Zn(NO_3)_2\ 6H_2O$ with **L2** in a 1:2 ratio dissolved in H_2O/EtOH (1:4) with **L2** dissolved in DMF (4 ml).

2.1.4. Synthesis of 1-[3-(3-carboxy-5-methyl-1H-pyrazol-1-yl) propyl]-5-methyl-1H-pyrazole-3-carboxylic acid (*L3*)

L3 was obtained under a similar procedure as for **2** and **L1** but using dibromomethane instead of ethylbromoacetate. The product was purified by recrystallization from water.

Yield 98%; M.p. = 285–286 °C (crystallized in water); ^{1}H NMR (300 MHz, DMSO d_6) δ ppm: 2.19 (s, 3H, $–CH_3$); 2.33 (m, 2H, $–CH_2–$); 4.03 (t, 2H, CH_2-N); 6.42 (s, 1H, Py); *m/z* $(M)^+$: 292.2; $\nu(OH) = 3150\ cm^{-1}$, $\nu(C{=}O) = 1695\ cm^{-1}$.

2.1.5. Synthesis of $[Cu(\mathbf{L1})_2(H_2O)]\cdot 2H_2O$

L1 (40 mg, 0.21 mmol, 2 equiv.) was dissolved in water (8 mL). $Cu(NO_3)_2\cdot 6H_2O$ (26.2 mg, 0.1 mmol, 1 equiv.) was dissolved in water (8 mL) and added to the above solution of L1. The resulting dark blue solution was left at r.t. and allowed to stand. Blue block shaped single crystals were obtained by slow evaporation of a clear dark blue solution of the reaction mixture over a period of 3–4 days. Yield: 0.109 g (50%).

2.1.6. Synthesis of $[Co(\mathbf{L3})(H_2O)_2]$

L3 (50 mg, 0.17 mmol, 2 equiv.) was dissolved in DMF (2 mL) and EtOH (8 mL). $Co(NO_3)_2\cdot 6H_2O$ (24.8 mg, 85.52 mmol, 1 equiv.) was dissolved in water (8 mL) and added to the above solution of L3. The resulting solution was left at r.t. and allowed to stand. Pink triangle shaped single crystals were obtained by slow evaporation of the reaction mixture over a period of 15 days. Yield: 0.102 g (44%).

2.2. X-ray analysis

Crystals were mounted on a nylon loop with paratone or grease and measured at room temperature except for the crystals of **L2** which were flash-cooled in a 150 K N_2 gas steam. The data were collected using Mo Kα ($\lambda = 0.71073$ Å) radiation on a MAR345 image plate. The structures were solved by direct methods SHELXS97 [13] and refined by full least-squares on $|F^2|$ using SHELXL97 (free Ligand) and SHELXL2014 (complexes) [13]. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed at calculated positions in riding mode with isotropic temperature factors fixed at 1.2 U_{eq} of the parent atoms (1.5 for methyl groups). The water molecules located in the structures of the complexes were treated as follows: all hydrogen atoms were located in the Fourier density maps, the water molecules were then idealized (distance/angle restraints) and treated as a rigid group in subsequent refinement cycles, where the water molecule as a whole was allowed to rotate around the oxygen atom. For compound B, a total of 36 restraints were introduced to properly treat the disorder, 18 restraints to make the two disordered parts similar in terms of geometry (sd 0.02), and 18 restraints to approximate the anisotropically refined disordered atoms to isotropic behavior (sd 0.01). One additional restraint was automatically introduced to fix the origin along the twofold axis. The crystallographic and refinement data are summarized in Table 1.

3. Result and discussion

3.1. Synthesis of pyrazole-dicarboxylic ligands *L1*–*L3*

Our strategy was to develop a simple and high yielding synthetic procedure, in few steps, to prepare the desired dicarboxylic acid derivatives. The development of these structures was given in Scheme 1: The preparation in good yield of one isolated major product **2** [42], from 3(5)-carboxymethyl-5(3)-methylpyrazole **1** [11], was carried out using potassium *tert*-butoxide as base and by heating under reflux with THF for 3 h. The second step was to hydrolyse product **2** under reflux conditions [43] of NaOH followed by neutralization with HCl to give the pyrazolic acid ligand **L1** in good yield.

Molecules **3** and **4** were already prepared in our laboratory [44] and were quantitatively converted by neutralization to newly carboxylic acid derivatives **L2** and **L3**, respectively.

3.2. Synthesis of coordination complexes *A* and *B*

The trials for crystallization of coordination compounds obtained from the pyrazole-dicarboxylic ligands and Cu^{II}/Co^{II} in aqueous methanolic solutions (both in 1:1 and 1:2 metal:ligand ratio) resulted in the single crystals of two coordination complexes $[Cu(\mathbf{L1})_2(H_2O)]\cdot 2H_2O$ **A** and $[Co(\mathbf{L3})(H_2O)_2]$ **B**. The trials with **L2** for the crystallization of Zn coordination complexes under similar conditions failed as it resulted in the crystallization of the ligand **L2** (Scheme 2). Nevertheless, the crystal structure proved informative (*vide infra*).

3.3. Description of the crystal structures of the complexes $[Cu(\mathbf{L1})_2(H_2O)]\cdot 2H_2O$ (*A*) and $[Co(\mathbf{L3})(H_2O)_2]$(*B*) and of *L2*

3.3.1. $[Cu(\mathbf{L1})_2(H_2O)]\cdot 2H_2O$ (*A*)

When **L1** and $Cu(NO_3)_2\cdot 4H_2O$ were reacted in aqueous medium (see Experimental) in a 1:2 metal:ligand ratio, blue colored block