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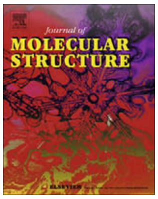

A single-helix copper-containing coordination polymer of dihydroglyoxaline sulfide formed *in situ* through oxidation of 1,3-imidazolidine-2-thione

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ABSTRACT

A novel single-stranded helix coordination polymer [Cu(L)(SO_4)(H_2O)] (L = dihydroglyoxaline sulfide) was synthesized and characterized by single-crystal X-ray diffraction, IR, and TGA analysis. The polymer is an unprecedented 1D helical polymer based on a sulfate bridge and a dihydroglyoxaline sulfide chelating ligand. Both ligands were formed *in situ* through copper-mediated oxidation of 1,3-imidazolidine-2-thione. The helical chain is interlocked with each other through strong hydrogen bonding interactions to form a 2D sheet, which then stacks together to generate a 3D hydrogen bonding network.

1. Introduction

Helical structures have been of considerable interest because the helicity is common in nature and is also important in many applications such as optical devices, enantiomer separation, chiral recognition, and stereoselective synthesis [1]. Their formation often involves noncovalent inter- and intra-molecular interactions [2], such as electrostatic interactions, hydrogen bonding, and π–π stacking. Recently, metal–organic coordination bonding has been shown to be effective in building a series of helical compounds consisting of single- and multi-stranded helices [3,4]. In the formation of 1D helical coordination polymers, the metal ions of certain coordination geometry combine with rigid or flexible organic multidentate ligands, where geometry effect plays an important role. To prevent the formation of 2D and 3D structures, the chelate ligands, *e.g.* 2,2′-bipyridine and 1,10-phenanthroline, are generally used together with bridging organic ligands [5]. Herein we report the preparation and crystal structure characterization of a novel single-stranded helical coordination polymer [Cu(L)(SO_4)(H_2O)] (L = dihydroglyoxaline sulfide), **1**, which is an unprecedented helical polymer based on a dihydroglyoxaline sulfide chelating ligand and a sulfate bridge.

2. Experimental

2.1. General methods

1,3-Imidazolidine-2-thione was prepared according to the literature method [6]. All other chemicals were from commercial source without further purification. Elemental analyses of C, H, S and N were determined with a Perkin-Elmer 2400C elemental analyzer. Infrared spectra were recorded in the range of 400–4000 cm^{-1} on a Vector 22 Bruker spectrophotometer with pressed KBr pellets. Thermal analysis (TG) was carried out in a nitrogen stream using Seiko Extar 6000 TG/DTA equipment with a heating rate of 10 °C/min.

2.2. Synthesis of the compound *1*

A solution of 1,3-imidazolidine-2-thione (0.025 g, 0.25 mmol), CuSCN (0.058 g, 0.48 mmol) in acetonitrile (10 mL) was stirred for 2 h under Ar until the solution became clear. Then a solution of isonicotinonitrile (0.026 g, 0.25 mmol) in DMF (10 ml) was added to the above solution. The mixture was stirred under reflux for 2 h under Ar and then filtered. Blue block crystals were formed on slow evaporation of the filtrate in air at room temperature. Yield: 20% (based on Cu). Anal. Calcd. for $C_6H_{12}CuN_4O_5S_2$: C, 20.71; H, 3.47; N, 16.10; S, 18.43. Found: C, 21.04; H, 3.364; N, 15.23; S, 18.33.

2.3. X-ray crystallographic determinations for the compound *1*

The single-crystal X-ray data collection for the compound was performed on a Bruker SMART CCD diffractometer with graphite-

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monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The relevant crystallographic data are presented in Table 1 and selected bond lengths and angles are given in Table 2 in Supplementary material. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure was solved by direct methods and refined by full matrix least-squares methods on F2 using the SHELXS-97 and SHELXL-97 programs, using atomic scattering factors for neutral atoms. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps.

3. Results and discussion

3.1. Synthesis

It is interesting that both dihydroglyoxaline sulfide and sulfate ligands in **1** were formed *in situ* through oxidation of 1,3-imidazolidine-2-thione. The oxidation of thiourea and its *N*,*N′*-dialkyl derivatives, including 1,3-imidazolidine-2-thione, has been studied because of its relations with metabolism in biological system. These and related compounds, which all contain the thioamide moiety, belong to an interesting class of biologically active ligands [7,8]. 1,3-Imidazolidine-2-thione has been shown to be readily oxidized to dihydroglyoxaline sulfide under mild conditions [9]. Various metal ions such as Ce(IV), Co(III), Mn(III) and Cu(II) are known oxidants in the reaction [7,10,11]. In our synthesis system, we postulated that Cu(I) was oxidized to Cu(II) under aerobic conditions, which then oxidized 1,3-imidazolidine-2-thione to produce dihydroglyoxaline sulfide. It is most likely that the sulfate ion also came from the oxidation of the sulfur in 1,3-imidazolidine-2-thione, which was extruded from the coupling of two 1,3-imidazolidine-2-thione molecules [11]. However, we cannot rule it out that SCN^- was also oxidized to the sulfate ion.

3.2. Crystal structure

Compound **1** crystallizes in the space group *P*2(1)/c and adopts a single-stranded helical polymer structure with a chelating dihydroglyoxaline sulfide, a bridging sulfate and one terminal water molecule. As shown in Fig. 1, the Cu atom exhibits a distorted square pyramidal coordination geometry through bonding to two nitrogen atoms from one dihydroglyoxaline sulfide, two oxygen atoms from two sulfates and one from an aqua ligand. The bond lengths of the Cu–O in the base plane (*i.e.* from one sulfate and an aquo ligand) are 1.986(4) and 2.000(4) Å, respectively, which are much shorter than the apical Cu–O distance of 2.317(4) Å from another sulfate. The Cu–N bond lengths are 1.933(5) and 1.975(5) Å, which are slightly shorter than those in related compounds (1.990–2.013 Å) [11,12]. The bond angles around the Cu center vary from 86.9(2)° to 101.7(2)°, satisfying its square pyramidal coordination geometry. The bond valence sum calculations [13] for Cu (1.78) suggest Cu is divalent.

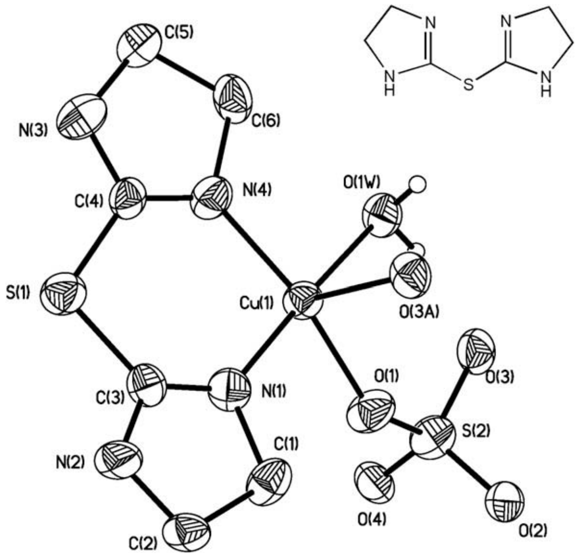

Fig. 1. The coordination environment of Cu in compound **1**. The H atoms of dihydroglyoxaline sulfide (see inset) are omitted for clarity.

It is interesting that each sulfate in **1** acts as a bridge ligand to neighboring Cu(II) center, generating a single-stranded helix along the *b* axis (Fig. 2). The rest of the coordination sites in Cu are saturated by the chelate ligand dihydroglyoxaline sulfide and one water molecule. The helix is stabilized by strong intrachain hydrogen bonding between water molecules and sulfates (*cf.* the O–H. . .O distance of 2.674 Å). These helical chains are further interlocked with each other through interchain N–H. . .O hydrogen bonds, creating a 2D sheet in the *bc* plane (Fig. 3a). Each dihydroglyoxaline sulfide molecule is sandwiched by its two counterparts in neighboring chains. This arrangement results in an extended alternating arrangement of the single-stranded helices along the *c* axis, as seen in Fig. 3a. The 2D layers are held together via C–H. . .O interactions to create a 3D hydrogen bonding network (Fig. 3b).

3.3. Infrared spectrum studies

Infrared spectrum of **1** (Fig. S1 in Supplementary material) shows that the bands at 3420, 3280 and 1600 cm^{-1} are attributed to the vibrational modes of water [14]. The peaks around 3100,

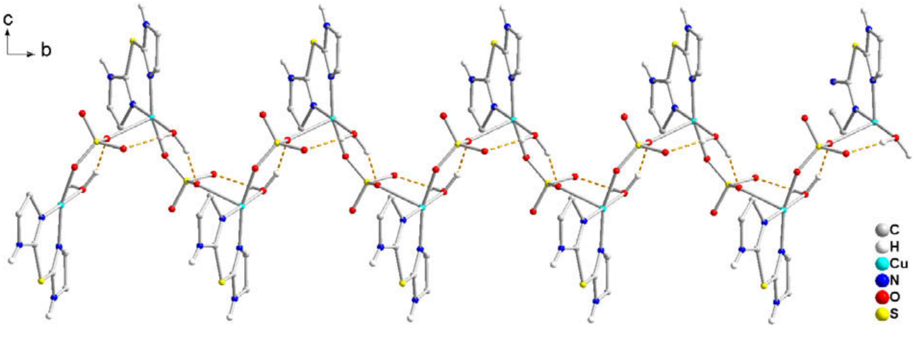

Fig. 2. View of the single-stranded helix in **1**, showing the O–H. . .O hydrogen bonding interactions. The H atoms on C are omitted for clarity.