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# A sulfate-bridged Cu<sup>II</sup> complex with 1-D helical-chain structure: Synthesis, structure and magnetic property

Li-Juan Yang <sup>a</sup>, Tao Lei <sup>b</sup>, Wei Liu <sup>a</sup>, Wen-Qian Chen <sup>a</sup>, Miao-Shui Lin <sup>a</sup>, Lei Li <sup>a</sup>, Wu Li <sup>b</sup>, Yahong Li <sup>a, c,\*</sup>

<sup>a</sup> Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

<sup>b</sup> CAS Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China

<sup>c</sup> State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

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# ABSTRACT

A new 1-D helical chain complex  $[Cu(H_2L)(SO_4)] \cdot CH_3OH$  (1)  $(H_2L=N,N-bis(3,5-dimethyl-2-hydroxybenzyl)-N-(2-pyridylmethyl)amine)$  was synthesized from the reaction of the tripodal tetradentate ligand  $H_2L$  with  $CuSO_4 \cdot 5H_2O$  under solvothermal conditions. Complex 1 was fully characterized by X-ray single crystal diffraction, elemental analysis and IR spectroscopy. X-ray analysis revealed that complex 1 displays a 1-D helical chain structure with the two adjacent metals being bridged by a sulfate ion. Each  $Cu^{II}$  ion is penta-coordinated and exhibits a pseudo square pyramidal geometry. The low-temperature magnetic susceptibility measurement for the solid sample of 1 revealed the ferromagnetic  $Cu^{II}$ ... $Cu^{II}$  interactions.

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Recent years have witnessed an explosion of interest in the design and synthesis of the high-nuclearity paramagnetic complexes [1]. The reasons for this are many, but the most important factors are the search for models of metal-containing sites in biology [2] and the relevance of these complexes to magnetic [3], optical [4], electronic [5] and catalytic [6] materials. A synthetic challenge involves discovering simple and efficient approaches to the incorporation of many metal ions in a small, single molecular entity. It is found that the combination of two ligands will foster the formation of high-nuclearity complexes [7].

We are interested in preparing high-nuclearity coordination complexes by the combination of a tripodal tetradentate amine-bis (phenolate) ligand  $H_2L(H_2L = N,N-bis(3,5-dimethyl-2-hydroxybenzyl)-$ N-(2-pyridylmethyl)amine) with sulfate ions. There is a continuousinterest in the coordination chemistry of tetradentate aminebis(phenolate) ligand. The efforts of several research groups aredriven by a number of considerations. These include the development of the structural models for mimicking the active site ofgalactose oxidase [8], the application of metal ion/tetradentateamine-bis(phenolate) systems as efficient catalysts for the polymerization of olefins and lactide [9], and the employment of the tetradentate amine-bis(phenolate) ligands in the synthesis of coordination complexes with interesting magnetic properties [10]. As a tetrahedral anion, sulfate can bind toward metal cations in various ways [11], and the diverse coordination modes of sulfate anions largely contribute to the formation of the high-nuclearity clusters. The synthesis, structure and properties of a number of transition metal sulfates have been reported in recent years [12]. To the best of our knowledge, the synthesis of the 1-D chain Cu<sup>II</sup> complexes supported by both the tetradentate amine-bis(phenolate) ligands and sulfates has never been reported. Herein, we report the synthesis of a 1-D helical chain polymer [Cu(H<sub>2</sub>L)(SO<sub>4</sub>)]·CH<sub>3</sub>OH (1) via the reaction of the H<sub>2</sub>L ligand with CuSO<sub>4</sub>·5H<sub>2</sub>O. The structural characterizations and the magnetic properties of the complex were also presented.

Complex **1** was prepared under solvothermal conditions in  $CH_3OH$  (Scheme 1). Treatment of  $CuSO_4 \cdot 5H_2O$  with  $H_2L$  in a sealed Pyrex-tube in  $CH_3OH$  led to the formation of **1**. Complex **1** was readily isolated as green crystals with moderate yield.

The presence of -OH groups in **1** is manifested by a broad IR band of medium intensity at 3420 cm<sup>-1</sup>. The band at 2930 cm<sup>-1</sup> has been ascribed to the  $\nu_{as}(C-H)$  vibration. Several bands, which are assigned as the stretching vibrations of the aromatic rings, appear in the 1612–1446 cm<sup>-1</sup> range. The medium intensity band at 1156 cm<sup>-1</sup> has been assigned to the  $\nu(SO)_{sulfate}$  mode.

The single crystal X-ray diffraction [13] determination reveals that compound **1** is monoclinic and crystallizes in space group C2/c. The asymmetric unit contains one  $Cu^{II}$  ion, one  $H_2L$  ligand, one  $SO_4^{2-}$  ion and one solvate methanol molecule (Fig. 1). The  $Cu^{II}$  ion is five-coordinated. The central metal ion displays a slightly distorted square-based

<sup>\*</sup> Corresponding author at: Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. Fax: + 86 512 65880089.

E-mail address: liyahong@suda.edu.cn (Y. Li).

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Scheme 1. Synthesis of complex 1.

pyramidal geometry with  $\tau = 0.013$  [14], composed of two nitrogen atoms (N1, N2), one oxygen atom (O2) from one H<sub>2</sub>L ligand (Cu-N1=2.015(3)Å, Cu-N2=1.976(3)Å and Cu-O2=2.001(3)Å) and one oxygen atom (O6) from the SO<sub>4</sub><sup>2-</sup> ion (Cu-O6=1.949(2)Å) in the equatorial plane, the other one oxygen atom of another SO<sub>4</sub><sup>2-</sup> ion is at the axial position (Cu-O3=2.302(3)Å).

The most remarkable structural feature of **1** is that it exhibits a 1-D single helical chain structure (Fig. 2a–d). The helical chain is made up of metal centers,  $SO_4^{2-}$  ions and the H<sub>2</sub>L ligands. The adjacent Cu<sup>II</sup> ions are linked by two oxygen atoms of a  $SO_4^{2-}$  ion ( $\eta^1:\eta^1:\mu_2$  or 2.1100 coordination mode [15]), giving rise to an infinite helical chain  $[-Cu(H_2L)-O-S(O_2)-O]_n$  along the *b* axis.

Complex 1 joins a small family of coordination complexes employing sulfates as ligands [12]. To the best of our knowledge, 1 is also the first  $Cu^{II}$  coordination polymer in which  $SO_4^{2-}$  ions and the



Fig. 1. Coordination environment of  $\text{Cu}^{\text{II}}$  atom in 1. All the H atoms and the solvate molecule are omitted for clarity.

tripodal tetradentate amine-bis(phenolate) ligands are combined to give a 1-D helical chain structure.

Magnetic property studies on polynuclear metal complexes are of continuing interest for coordination chemists since they can provide understanding of fundamental factors governing their magnetic properties. The dc magnetic property for **1** was measured in the temperature range of 2–300 K at the applied magnetic field of 1000 Oe. The obtained data are shown in Fig. 3 in the  $\chi_{\rm M}T$  vs. *T* and  $\chi_{\rm M}$  vs. *T* forms.

The  $\chi_{\rm M}T$  value is 0.343 cm<sup>3</sup> mol<sup>-1</sup> K per Cu<sup>II</sup> ion at 300 K, which is close to the expected value for one magnetically isolated Cu<sup>II</sup> ion (0.375 cm<sup>3</sup> mol<sup>-1</sup> K for g = 2.0, S = 1/2). The  $\chi_{\rm M}T$  product increases continuously to a maximum of 0.47 cm<sup>3</sup> mol<sup>-1</sup> K at 4 K before dropping to 0.45 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K, suggesting dominating ferromagnetic interactions. The temperature dependence of the reciprocal susceptibility ( $\chi_{\rm M}^{-1}$ ) above 2 K obeys the Curie–Weiss law  $\chi_{\rm M} = C/(T - \theta)$  with Curie constant C = 0.34 cm<sup>3</sup> mol<sup>-1</sup> K and Weiss constant  $\theta = +5.79$  K, thus indicating a ferromagnetic behavior in complex **1**.

In summary, under solvothermal conditions one 1-D helical chain  $Cu^{II}$  complex  $[Cu(H_2L)(SO_4)]_n \cdot CH_3OH$  (1) was synthesized and characterized by X-ray single crystal diffraction, IR spectroscopy, and elemental analysis. The weak ferromagnetic  $Cu^{II}$ ... $Cu^{II}$  interactions were determined. As a tripodal tetradentate amine-bis(phenolate) ligand supported 1-D helical chain, complex 1 has potential utility in biologic systems, nonlinear optical materials and catalysis. The indepth researches to produce more interesting coordination polymers by adding alternative tripodal amine-bis(phenolate) ligands and other transition metal ions are under investigation in our lab. Our studies, already well advanced, will be reported in due course.

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#### Appendix A. Supplementary data

CCDC 821012 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac. uk/data\_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.inoche.2012.03.035.



Fig. 2. (A) The 1-D helical chain of 1 viewed down the *c*-axis. (B) The 1-D sulfate-bridged chain of 1 viewed down the *c*-axis. (C) Space filling view of the 1-D helical chain of 1. (D) Polyhedron view of the 1-D helical chain of 1.



**Fig. 3.** Temperature dependence of magnetic susceptibilities in the form of  $\chi_M T$  vs. *T* and  $\chi_M$  vs. *T* for **1** (per Cu<sub>2</sub> unit) at 1 kOe. Inset: temperature dependence of magnetic susceptibilities in the form of  $\chi_M^{-1}$  vs. *T* for **1** (per Cu<sub>2</sub> unit) at 1 kOe. The solid line corresponds to the best fit from 300 K to 2 K.

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