1D μ-glycine-briged copper (II) chain in complex [Cu(μ-Gly)Im(ClO4)]n and ferromagnetic interactions among copper (II)

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ABSTRACT

Complex $[Cu(\mu\text{-}Gly)Im(ClO_4)]_n$ (Im = imidazole, and Gly = glycine) with μ-glycine-briged copper (II) chain, containing six-coordination distorted elongated octahedron, was synthesized and characterized. The complex belongs to space group $P\ 21/c$ measured by X-ray single crystal diffraction. In the cluster, each Cu^{2+} ion are six-coordination by one nitrogen atom and two oxygen atoms of glycine, one nitrogen atoms of imidazole, and two of oxygen atoms of two perchlorate. Each Cu^{2+} ion has an N_2O_4 donor set, which forms the distorted elongated octahedron due to the Jahn−Teller (JT) effect. The magnetic and thermodynamic properties were researched. Magnetic susceptibilities of the complex showed that ferromagnetic interactions occurred between the Cu (II) atoms. The Curie−Weiss constant $C = 0.565$ cm³ K·mol⁻¹ and the Weiss constant $\theta = 1.0585$ K were given by the Curie-Weiss law The ferromagnetic nature of the interaction could be deduced as the exchange pathway of Cu−O−C−O−Cu, which involved an equatorial position at one copper (II) ion and an axial position of the nearest copper (II). The complex decomposed from 511 to 538 K as two steps.

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1. Introduction

It is well known that Cu (II) ions will distort its coordination sphere to minimize its electronic energy, which is called Jahn−−Teller (JT) effect. As a result, Cu (II) ions exhibit good coordination ability to different kinds of ligands [1] and played certain role in the human body as biological trace elements [2]. Glycine is the structurally simplest amino acid, which has two types of coordination atoms and can act as various kinds of bridging ligands by using a carboxylate [3−9]. Imidazole is an important nitrogen-rich heterocycle ligand, which provides a potential binding site for metal ions [10].

In the biomolecules such as histidine, some relevant structures of Cu (II) ions bonding to the nitrogen of the imidazole rings of several histidine residues have been researched as an important functional group [11−15], which play a key role in the mechanism of several metalloenzymes [16−18]. On the other hand, Cu (II) −nitrogen complexes [19−25], especially some copper imidazole complexes have been synthesized and characterized as energetic materials [26−28].

Up to now, some works about the different properties of complexes of transition metal (like copper [29]) imidazole or glycine have been reported [30−33]. For instance, an article researched a series of complex $[LnCu_6(m_3\text{-}OH)_3(Gly)_6im_6](ClO_4)_6$ involving precisely chelaitng glycine and imidazole coordinated to Cu (II) ions [34]. For another example, complex copper (II) − gadolinium (III) 15-metallacrown-5 were also reported [35]. However, in the present work, a single crystal complex of copper perchlorate coordinated with glycine and imidazole, $[Cu(\mu\text{-}Gly)Im(ClO_4)]_n$, was synthesized, which structure was quite different from the complexes reported in the above articles. The structure was determined using X-ray single diffraction. The thermodynamic and magnetic properties of the complex were studied in particular.

2. Experimental section

2.1. Synthesis and characterization of the complex [Cu(μ-Gly)Im(ClO4)]n

The title complex $[Cu(\mu\text{-}Gly)Im(ClO_4)]_n$ was synthesized from water solution under room temperature. The starting reagents bought from Beijing Chemical Reagent Co. were the analytical. Solution of the copper perchlorate was prepared by the reaction of

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perchloric acid (1:1) with the copper oxide (30 mL, 16 mmol). Then, 16 mmol imidazole and 16 mmol glycine were added and the mixture was magnetically stirred at 338 K for 5 h. The mixture was cooled to room temperature naturally. A month later, the blue crystals were found, filtrated, washed with ethanol and dried.

The C, H, N of the complex were measured by an elemental analysis apparatus (Model PE-2400 II, USA). And found: C (19.60%), N (13.68%) and H (2.60%), which were near to the theoretical values: C (19.68%), N (13.77%) and H (2.64%).

2.2. X-RAY structure determinations

The structure determinations of the single crystals were performed by using the X-ray single diffractometer. A CCD area-detector diffractometer was used to collect the data with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω-scan mode. The structures were analysed with SHELXS-97. Program package SHELXL-97 [36] was used to merge data and model refinement against structure factors through least-square method. Software OLEX2 was also used in the treatments of the data. The structure was analysed by direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares method. The hydrogen atoms were generated geometrically, located from the difference Fourier syntheses and introduced with isotropic displacement parameters on F^2 by full-matrix least squares methods.

2.3. Magnetic properties

Magnetic susceptibilities of the complex were collected on a Quantum Design SQUID-VSM magnetometer. The magnetic susceptibility was corrected for the contribution of the gel capsule and for the core diamagnetism (using Pascal's constants).

2.4. Thermal analysis

Thermal analysis was performed by a Differential Scanning Calorimeter (DSC -141, SETARAM, France) and a thermogravimetric analyzer (Model: setsys 16/18 from Setaram Company, France). In DSC measurement, liquid nitrogen was used as cryogen from 200 to 300 K, and nitrogen gas was taken as protective gas with flow rate of 50 cm^3 min^{-1} from T 300–700 K with the heating rate of 10 K min^{-1}. The TG measurement was carried out by at the heating rate of 10 K min^{-1} under nitrogen atmosphere (99.999%), with flow rate of 65 cm^3 min^{-1}. The calibration of TG analyzer was performed by the SRM in thermal analysis, CaC$_2$O$_4$·H$_2$O(s).

3. Results and discussion

3.1. Description of structure

The coordination geometry of center Cu (II) ion and the molecule structure of the complex are shown in Figs. 1 and 2. The connection of the μ-glycine-briged copper (II) chain by ClO$_4^-$ ion in the complex is shown in Fig. 3. The summary of crystal data and structure refinement are listed in Table 1. The selected bond lengths and angles are listed in Table 2. Further information of the crystal structure determinations is available in the Supporting information section in CIF format.

Fig. 1 shows that each Cu (II) ion is six-coordinated forming a distorted elongated octahedron. It consists of one nitrogen atom (N1) of a glycine molecule, one nitrogen atom (N2) of an imidazole ringe, two carboxyloxygen atoms (O1 and O2) from two glycine molecules and two oxygen atoms (OA3 and O5) from one ClO$_4^-$ ion. These six coordinated atoms forms a N$_2$O$_4$ donor set. To the Cu (II)

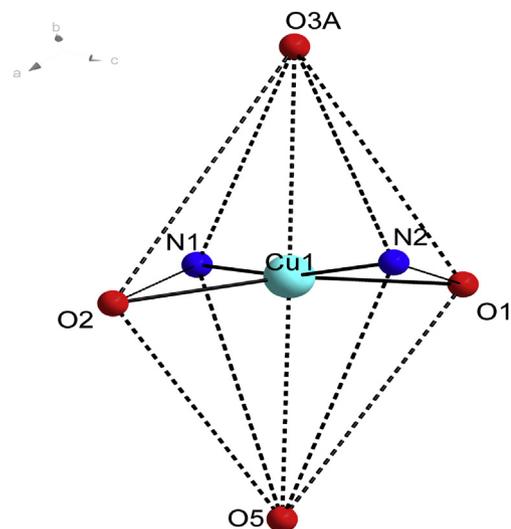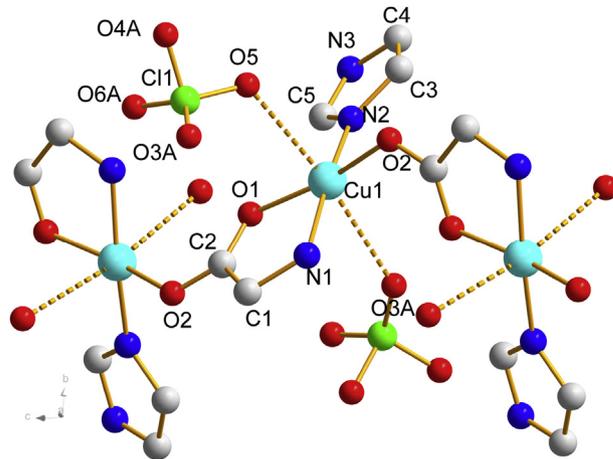**Fig. 1.** Coordination geometry of Cu (II) ion.

Fig. 2. The 1D μ-glycine-briged copper (II) chain in the complex [Cu(μ-Gly)Im(ClO$_4$)]$_n$. Hydrogen atoms have been omitted for clarity.

ion, small deviations of bond angles from the idealized octahedral geometry were found for angles N(2)–Cu(1)–O(2) (92.5(2)°), N(2)–Cu(1)–O(1) (92.0(2)°), O(2)–Cu(1)–N(1) (93.3(2)°), O(1)–Cu(1)–N(1) (84.0(2)°), O(2)–Cu(1)–O(1) (167.8(2)°), N(2)–Cu(1)–N(1) (170.1(3)°). It can be seen that each Cu (II) ion has two distorted pyramidal configuration in a distorted octahedron. In one of the distorted pyramidal configuration, the Cu^{2+} ion is 0.3608 Å above the average plane defined by N1, N2, O1 and O2, which deviate from such average plane 0.2029 Å above (N1), 0.0986 Å above (N2), 0.1950 Å above (O1) and 0.1890 Å above (O2). Longer bonding distance may imply weaker force.

Jahn−Teller (JT) effect existed in crystals containing transitional metal ions [37,38], which is caused by the ground orbital state. It would lead to the reduction of symmetry of crystal field and the minimization of system energy. The forming of distorted elongated octahedron is the typical result of Jahn-Teller effect [39]. To the central Cu (II) ($3d^9$) ions, octahedral environment is that the d-orbit splits to two section of orbits (t_{2g} and e_g) and the configuration is $[t_{2g}^6 e_g^3]$. Two electrons occupy t_{2g} orbit, and one electron occupies e_g orbit. Then, the shielding effect, which is the d-electron on the equatorial plane (orbit) to nuclear charge of the central ion, is less. As a result, the attraction, which is the central copper ions to the