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The *in situ* formation of a Cu(II) mesoionic complex *via* unexpected ring closure and investigation of its magnetic properties

Yanqing Zhao, Lihong Li*, Rui Yan, Feng Wu, Jianan Zhang, Zhengyi Guo, Yuandong Wu**

The School of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Address No. 222 Longteng Road, Shanghai, China

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ABSTRACT

The reaction of diphenylthiocarbazone, picolinic acid (HL_1) with $Cu(OAc)_2 \cdot H_2O$ under base condition yields a mesoionic complex $[Cu(II)(L_1)_2(L_2)] \cdot MeOH$, where L_2, mesoionic ligand 2,3-diphenyltetrazole-5-thione ligand, derived from an unusual cyclization of diphenylthiocarbazone. Crystallographic studies show that the mesoionic ligand L_2 is weakly interacted with a planar Cu(II) complex *via* S…Cu electrostatic force while S donor atom sits on the top of a pyramidal geometry of five-coordinated Cu complex. π-contacts between two adjacent mesoionic ligands L_2 in the crystal are also observed. The complex is characterized by IR, UV/*vis*, Powder XRD, and SQuID magnetometry studies on magnetic property of the powder sample are also discussed.

1. Introduction

Mesoionic compounds have been known for over 100 years [1,2]. They are typical heterocycles with polar and covalent characters unusually coexisting in one molecule. According to Schőnberg in 1938, to be more precise, the mesoionic compounds should be represented by resonance and charge hybrid structures since their positive and negative charges are delocalized separately in structures and cannot be simply assigned to either covalent or ionic structure [3,4]. The novelty of the mesoionic compounds are also reflected in their intriguingly physical and chemical properties [5–8] that they are able to function as an electrophilic or nucleophilic reagent independently and has been found applications in liquid crystal materials [9–11], biologically activity [8,12,13] as well as catalysis [14,15].

As one of well-known mesoionic compounds, 2,3-diphenyltetrazole-5-thione has attracted much attention recently due to not only the specificity of its electrons distributing in structure, but the simplicity of its geometric structure that it could be used as a fundamental model to understand mesoionic compound [5–8].

The 2,3-diphenyltetrazole-5-thione was firstly synthesized by oxidation of diphenylthiocarbazone in the presence of potassium hexacyanoferrate(III) [5]. As a much known and versatile analytical reagent for qualitative and quantitative determination of metals [16], under different pH environment, various aspects of the reactivity of diphenylthiocarbazone are present. For instance, in an acid condition, the coordination chemistry of diphenylthiocarbazone is well established that either through sulfur donor atom or by chelating bonding metals, diphenylthiocarbazone is expected to form five-membered complexes and most of known complexes are intensively colored [17,18]. However, in a base solution, as far as we concern, the reactions of diphenylthiocarbazone with metals are rarely reported.

Herein, we investigated coordination behavior of the diphenylthiocarbazone by using Cu(II), Co(II) or Ni(II) ions under base condition, in the presence of picolinic acid. Single crystal of $[Cu(II)(L_1)_2(L_2)] \cdot MeOH$ is grown from MeOH, and its crystallographic structure, magnetic and spectroscopic properties are also discussed.

2. Experimental sections

The mixture of diphenylthiocarbazone, $Cu(OAc)_2 \cdot H_2O$, NaOH, and picolinic acid (1:1:2:2) was dissolving in MeOH. The solution was refluxed for 2 h, giving a deep blue solution. After filtration, the filtrate was kept under room temperature for two weeks; blue block crystals were then precipitated. The structural and magnetic properties of the complex are determined by single-crystal X-ray

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* Corresponding author.
** Corresponding author.
E-mail address: 04140007@sues.edu.cn (L. Li).

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diffraction and SQuID magnetometry. The complex was also characterized by IR, UV/*vis*, and Powder XRD (see SI).

3. Results and discussion

Under base condition, diphenylthiocarbazone is inclining to undergo a ring closing reaction in 2 h by refluxing in MeOH (Scheme 1) and readily to convert to a mesoionic compound 2,3-diphenyltetrazole-5-thione, which then weakly interacted with Cu(II) metal ions, giving rise to complex $[Cu(II)(L_1)_2(L_2)]\cdot MeOH$ correspondingly, with a ultimate yield of 67.5%.

However, when the dithizone was treated with transition metal ions in the same condition, depending on metal ions, a complex containing mesoinoic species 2,3-diphenyltetrazole-5-thione could be obtained. We have tried Co(II), Ni(II) and Cu(II) metal ions, for Co(II) and Ni(II) ions, only organic mesoionic 2,3-diphenyltetrazole-5-thione is separated; while for Cu(II) ion, we successfully isolated a uncommon Cu(II) mesoionic complex.

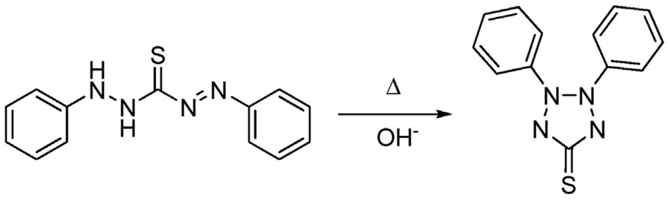
Crystal structure. Single crystal data were collected on a Bruker Smart ApexII CCD diffractometer equipped with Mo Kα radiation at 298 K. Bruker SAINT. SHELXS-97 [19] was used to solve the structure. The final refinement was carried out by full matrix least squares refinement. Non-hydrogen atoms were refined anisotropically.

As shown in Fig. 2, the unit cell of Cu(II) complex contains two crystallographically independent species, one is organic mesoionic species 2,3-diphenyltetrazole-5-thione derived from cyclization of diphenylthiocarbazone, another one is a four-coordinated planar complex where two picolinate ligands coordinated with a Cu(II) ion to keep the molecule charge balance, and there is one methanol molecule as well randomly distributed in the crystal.

For molecule 2,3-diphenyltetrazole-5-thione, the thiocarbonyl of tetrazole lie on a twofold axis, the bond lengths of N3—N0AA, N3—N8, N4—N8 are 1.3244(1) Å, 1.3380(3) Å and 1.3194(1) Å respectively, which are longer than a typical double bond for N=N (1.25 Å) and shorter than 1.45 Å for a N—N single bond [20]. Apparently, there are no strict single bonds or double bond in the tetrazole ring, adding that the thiocarbonyl group and tetrazole ring are almost exactly planar, indicating a considerable electron delocalization in such area.

The copper ion is located on a center of inversion and the unit at Cu1 has the conventional all-trans structure, with two bidentate pyridine-2-carboxylate ligands occupying the meridional plane, and the angles subtended by two O or N Donor atoms are all close to 180°. The bond distances of N1—Cu1, O1—Cu1 are observed to be 1.9809(5) Å and 1.9739(2) Å, which is well agree with reported literatures [21].

The Compound 2,3-diphenyltetrazole-5-thione was known as one of classical mesoionic compounds in literatures for a very long time [7]. Jian [22] recently describe the compound 2,3-diphenyltetrazole-5-thione as that two positive electrons delocalize on the two benzene rings while thetetrazole and thiocarbonyl group accordingly are electron rich and therefore nucleophilic (Fig. 1). In order to see how strong the interactions are between the Cu(II) ion and the compound 2,3-diphenyltetrazole-5-thione, we investigated the bond length changing of thiocarbonyl group in crystal structures. We have therefore collected crystallographic data of pure compound 2,3-diphenyltetrazole-5-thione(See SI). In comparison with the bond length of thiocarbonyl group for pure compound 2,3-diphenyltetrazole-5-thione(*ca.* 1.69 Å), the bond length of thiocarbonyl group has elongated to *ca.*1.71 Å in the complex, which means that electrons of the thiocarbonyl group have further delocalized in the Cu(II) complex. Although the distance of S1···Cu1 is measured to be 3.11 Å, comparatively longer than 2.28 Å for a typical bond length of S—Cu, but the strong nuclearphilicity of thiocarbonyl group interacts *via* Van der Waals' force or electrostatic force with Cu1 center is noticeable and is vital for the formation of the complex $[Cu(II)(L_1)_2(L_2)]\cdot MeOH$. Also, sulfur donor atom just occupied a special position and prohibit Cu1 unit from the formation of a more conventional 5 or 6 coordinated trigonal or bipyramidal structure. The angle between tetrazole plane and Cu1 unit is 16.1° (Fig. 3).



Scheme 1. The formation of 2,3-diphenyltetrazole-5-thione.

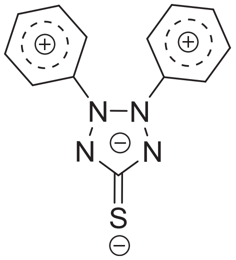


Fig. 1. Suggested resonance structure of mesoionic compound 2,3-diphenyltetrazole-5-thione.

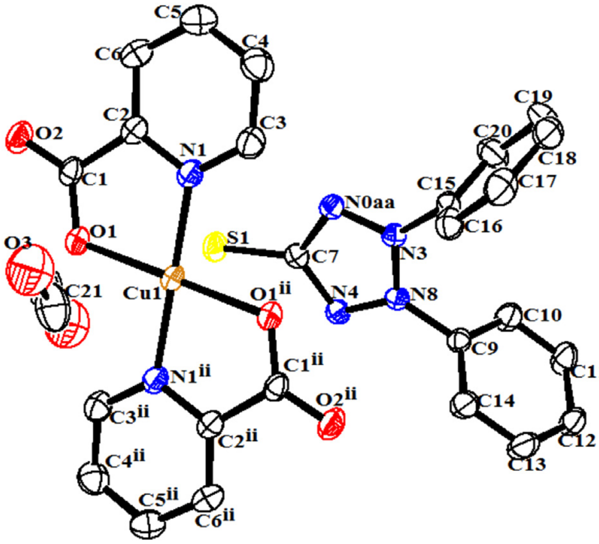


Fig. 2. ORTEP diagram for complex $[Cu(II)(L_1)_2(L_2)]\cdot MeOH$ showing isolated mesoionic molecule and a Cu(II) planar complex, hydrogen atoms and solvent were removed for clarity.

Regarding the crystal packing, Cu(II) ions are seemly embed into a pore composed of six 2,3-diphenyltetrazole-5-thione which are head to tail connected. π-π stacking are clearly observed between two benzene rings from neighbouring 2,3-diphenyltetrazole-5-thione molecules, with a distance of 3.63 Å for the π-π stacking as shown in Fig. 4.

Magnetic measurement. The magnetic property of the present compound was investigated on polycrystalline samples using