

Two birds with one stone: Self-assembly of metal–organic coordination complexes with discrete metallamacrocycle and 1D zigzag chain based on a flexible dicarboxylate ligand

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ABSTRACT

To assemble metal–organic coordination complexes, a flexible dicarboxylate ligand, 2,2'-(4,6-dimethyl-5-nitro-1,3-phenylene)bis(methylene)-bis-(sulfanediyl)dibenzoic acid (H_2L), has been designed and synthesized. Using the flexible ligand to assemble with copper ions, a mixture of two metal–organic complexes, $Cu_2(L)_2(py)_4 \cdot 4dmsO$ (**1**) and $Cu_2(L)_2(py)_6 \cdot 3dmsO \cdot py$ (**2**), has been generated by solvothermal technology in one glass tube. Through increasing the mole fraction of pyridine, the pure phase of complex **2** was obtained. Both complexes have been characterized by single-crystal X-ray diffraction, elemental analysis, and thermogravimetric analysis. Complex **1** is a discrete rectangular macrocycle. The guest solvents of dimethyl sulfoxide molecules were trapped in the cavity of rectangular metallamacrocycle, resulting in the formation of an infinite supramolecular metal–organic nanotube through van der Waals interactions between the guests and the host molecules. In complex **2**, the flexible ligand adopts a *syn* conformation to assemble with copper ions to form an infinite one-dimensional zigzag chain.

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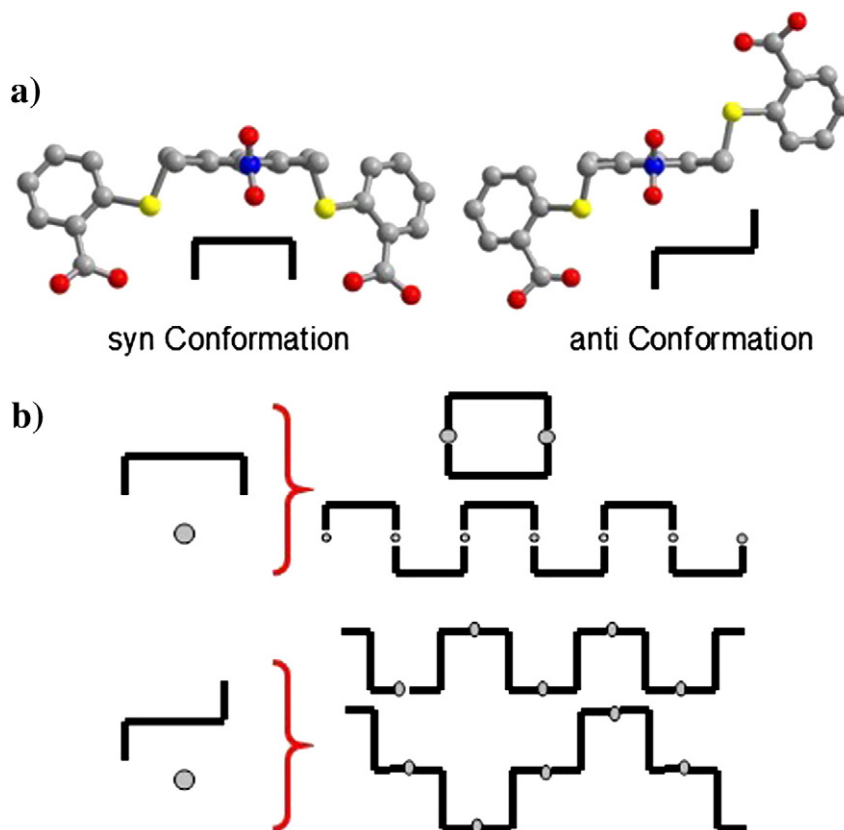
The rational design and synthesis of novel metal–organic coordination complexes are currently of significant interest due to their varied topology and potential applications such as optoelectronic devices and microporous materials for catalysis and shape- and size-selective separations [1–9]. With the development of coordination chemistry and crystal engineering of metal–organic coordination complexes, it is possible to design and synthesize metal–organic complex with desired topologies and special properties [10–13]. However, this predictive ability is primarily limited to metal–organic coordination complexes containing rigid organic ligands and rigid SBUs [14–17]. Compared with the rigid ligands with single conformation, the flexible organic ligands are more complicated when they coordinate to metal ions, because flexible ligands may adopt several kinds of conformations [18–21].

As we know, the assembly of a metal–organic coordination complex is highly effected by the ligand conformation and the coordination geometry of the metal ion [22–25]. In a general way, the conformation of ligand can determine the structure of the final product [26]. For example, we have designed and synthesized a series of metal–organic complexes based on a series of flexible dicarboxylate ligands, in which the different conformations of the flexible ligands can result in the formation of different topologies [27–30]. Continuing our previous work, we designed a new flexible bended dicarboxylate ligand, namely, 2,2'-(4,6-dimethyl-

5-nitro-1,3-phenylene)bis(methylene)-bis-(sulfanediyl) dibenzoic acid (H_2L). The flexible dicarboxylate ligand shows two possible conformations: *syn*- and *anti*-conformation (Scheme 1a), thus, various structures can be formed when they coordinate to metal ions [31–33]. According to previous reports, when the dicarboxylate ligand adopts a bridging mode, the connection of 2-nodal metal ions by L^{2-} in the *syn* conformation will generate macrometallocycle or 1D zigzag chain subunits, while the connection of 2-nodal metal ions by L^{2-} with the *anti* conformation will form a 1D zigzag chain structure, as shown in Scheme 1b. By one-pot reaction of H_2L and copper ions under solvothermal condition, two metal–organic coordination complexes, $Cu_2(L)_2(py)_4 \cdot 4dmsO$ (**1**) and $Cu_2(L)_2(py)_6 \cdot 3dmsO \cdot py$ (**2**) have been synthesized in one reaction vessel. In this communication, we will focus on the syntheses, structures and characterizations of these two complexes.

The new ligand H_2L was synthesized in three steps starting from *m*-xylene (Scheme 2) [34–37] and the crystallization of complexes **1–2** was obtained in one glass tube at 90 °C by solvothermal technology [38], which has been proven to be an effective and powerful way in the self-assembly of metal–organic frameworks [39,40]. Complex **1** is green rod crystals, while complex **2** is blue rhombus ones (Fig. 1). These two complexes can be easily separated manually. However, pure phase of complex **2** can be obtained when increasing the amount of pyridine, indicating that pyridine plays an important role in the formation of complexes **1** and **2**. When 0.1 mL of pyridine was added in the reaction, a mixture of **1** and **2** can be formed, while pure rhombus-shaped phase of complex **2** was obtained when 0.15 mL of pyridine was added in the reaction. The phase purity can

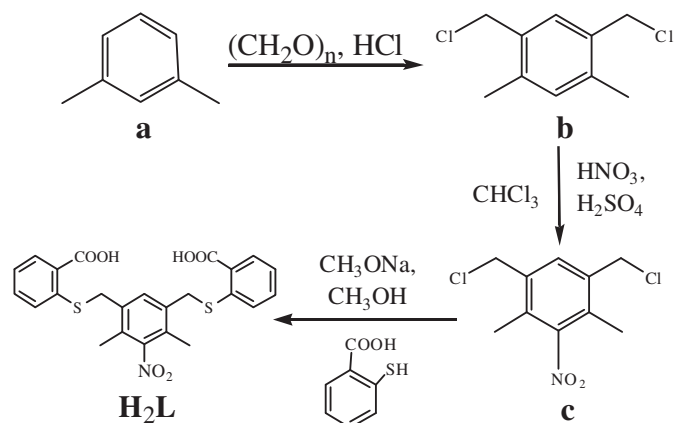
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Scheme 1. (a) The Two conformations of H_2L . (b) The Possible Subunits formed by H_2L with *syn*- or *anti*-conformation.

be determined by powder X-ray diffraction. However, reducing the amount of pyridine to synthesize pure phase of complex **1** failed.

Single-crystal X-ray diffraction reveals [41] that complex **1** is a rectangular macrometallocycle consisted of two L^{2-} ligands, four pyridine ligands and two copper ions in triclinic $P-1$ space group and the asymmetry unit (Fig. 2a) is made of one Cu ion, one L^{2-} ligand, two coordinated pyridine molecules and two guest molecules (dimethyl sulfoxide). As shown in Fig. 2b, the central Cu ion adopts a square geometry and is four-coordinated by two oxygen atoms from two different L^{2-} ligands and two nitrogen atoms from two different pyridine ligands with the average Cu–O and Cu–N distances are 2.007 Å and 2.017 Å, respectively and the average dihedral angle between the side benzene ring and the central benzene ring is 70.82°.



Scheme 2. The synthesis route of H_2L .

In complex **1**, the L^{2-} is considered as a bridging linker, adopting the *syn* conformation, and connects the neighboring Cu_2 units to generate a rectangular macrocycle with the Cu...Cu separation of 8.379 Å. The central benzene rings of the two ligands are parallel to each other with the dihedral angle of 0°, and the interplanar spacing is 12.040 Å. Herein, the Cu_2 units and the L^{2-} ligands can be considered as the vertices and sides of the macrocycle (Fig. 2c), respectively. In the cavity of one rectangular macrocycle, there are two guest molecules (DMSO) which have a significant effect on the arrangement/packing of the host molecules [41]. Thus, due to the existence of DMSO guest solvents and van der Waals interactions between the guests and the host molecules, all of the **1** molecules extend along the [010] direction, resulting in the formation of an infinite supramolecular metal-organic nanotube (Fig. 3a, b). Compared with the previously reported metal-organic nanotubes, the metal-organic nanotubes formed because of the existence of guest solvents as **1** is relatively rare [42,43]. The existence of weak C–H...O interactions (3.4162 Å) between the two supramolecular metal-organic nanotubes further stabilizes a 3D supramolecular. The 3D packing of the molecules generates 1D channels along the b axis (Fig. 3d).

The asymmetric unit of **2** is shown in Fig. 4a [44], which consists of one five-coordinated Cu ion, three terminal coordinated pyridine ligands, and one fully deprotonated L^{2-} ligand, one uncoordinated pyridine molecule and one dimethyl sulfoxide molecule. The Cu–O (COO⁻) bond distances are located in the typical Cu–O bond range of 1.957 (4)–1.979 (3) Å and the carboxylate groups of L^{2-} ligand show the monodentate coordination mode as compound **1**. The Cu adopts an irregular pentacoordinated mode with distorted square geometry [45], which is coordinated to three nitrogen atoms of three pyridine molecules and two oxygen atoms from two separated L^{2-} (Fig. 4b). The Cu–N distances ranged from 2.026 (4) to 2.276(4) Å and N–Cu–N bond angles ranged from 96.72(17) to 163.49(18)°,

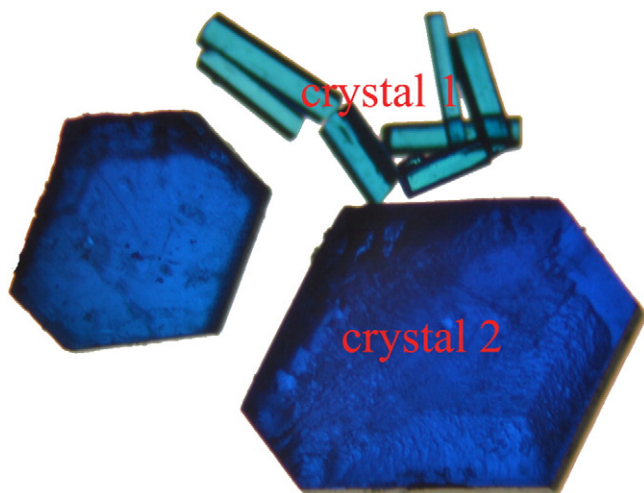


Fig. 1. Photographs of crystals 1 and 2.

which are similar to those of other reported copper(II) complexes [46,47].

As in complex 1, L ligand in 2 also adopts the *syn* conformation, with both functional substituent (2-hydroxybenzoic acid) groups on the same side of the central benzene ring. One side benzene ring is almost perpendicular to the central benzene ring, with an average dihedral angle of 89.66° which is slightly larger than that in 1, while the dihedral angle between the another side benzene ring and the central benzene ring is 66.74°. Different to 1, in which two L²⁻ ligands link two copper ions to generate a 32-membered macrometallocycle, in complex 2, the neighboring copper ions are connected by L²⁻ ligands to form an infinite one-dimensional zigzag chain as shown in Fig. 4c.

The powder X-ray diffraction (PXRD) pattern of 1 and 2 was also investigated at room temperature. As shown in the Fig. S2, all the XRPD patterns measured for the as-synthesized samples were in good agreement with the XRPD patterns simulated from the respective single-crystal X-ray data using the Mercury 1.4 program, demonstrating the phase purity of the product. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples [48]. The TGA analyses of the title compounds 1

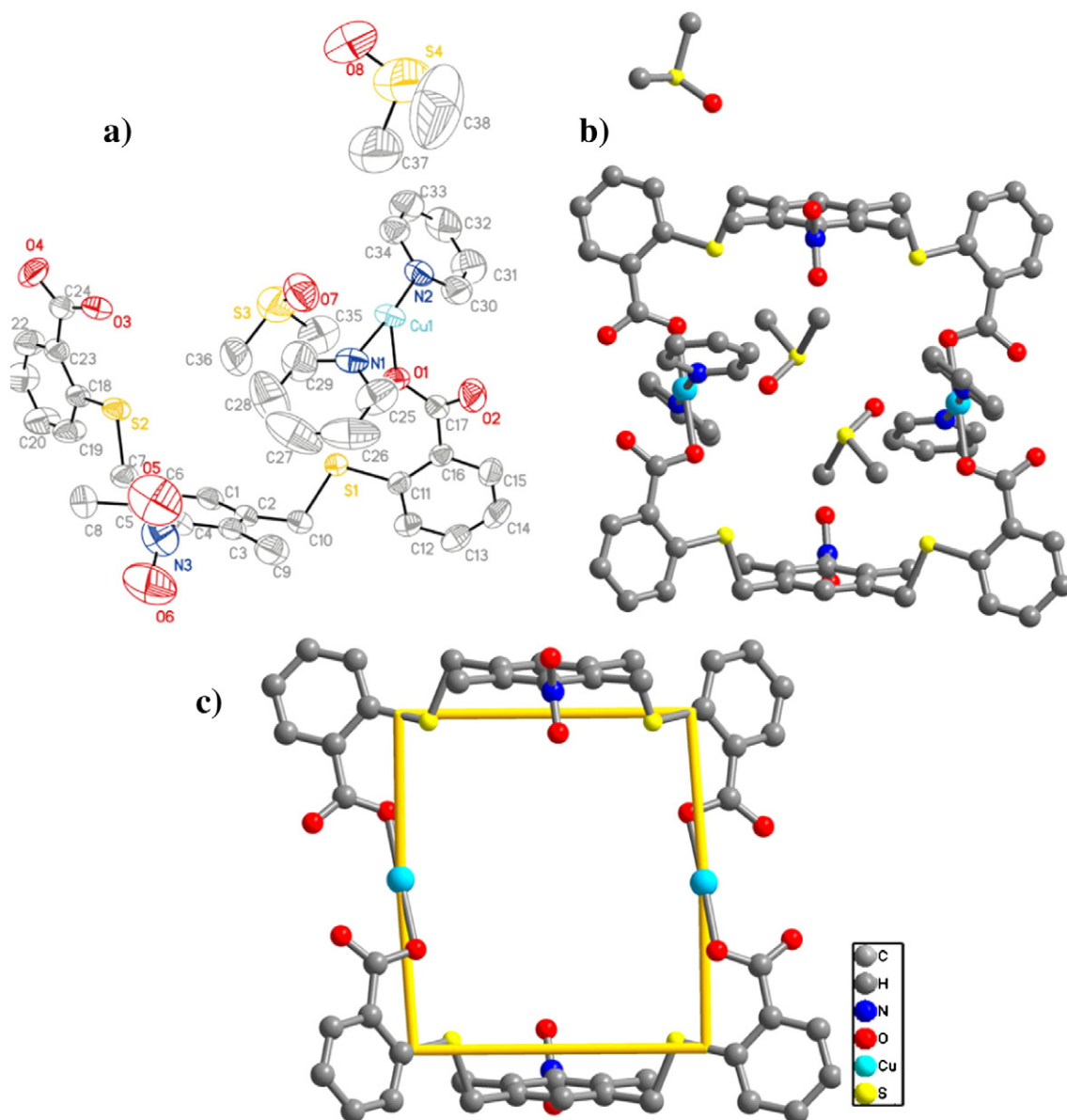


Fig. 2. (a) The asymmetry unit of complex 1. (b) The coordination environment of the Cu(II) ions in complex 1. Hydrogen atoms have been omitted for clarity. (c) Schematic representation of the rectangular macrocycle.

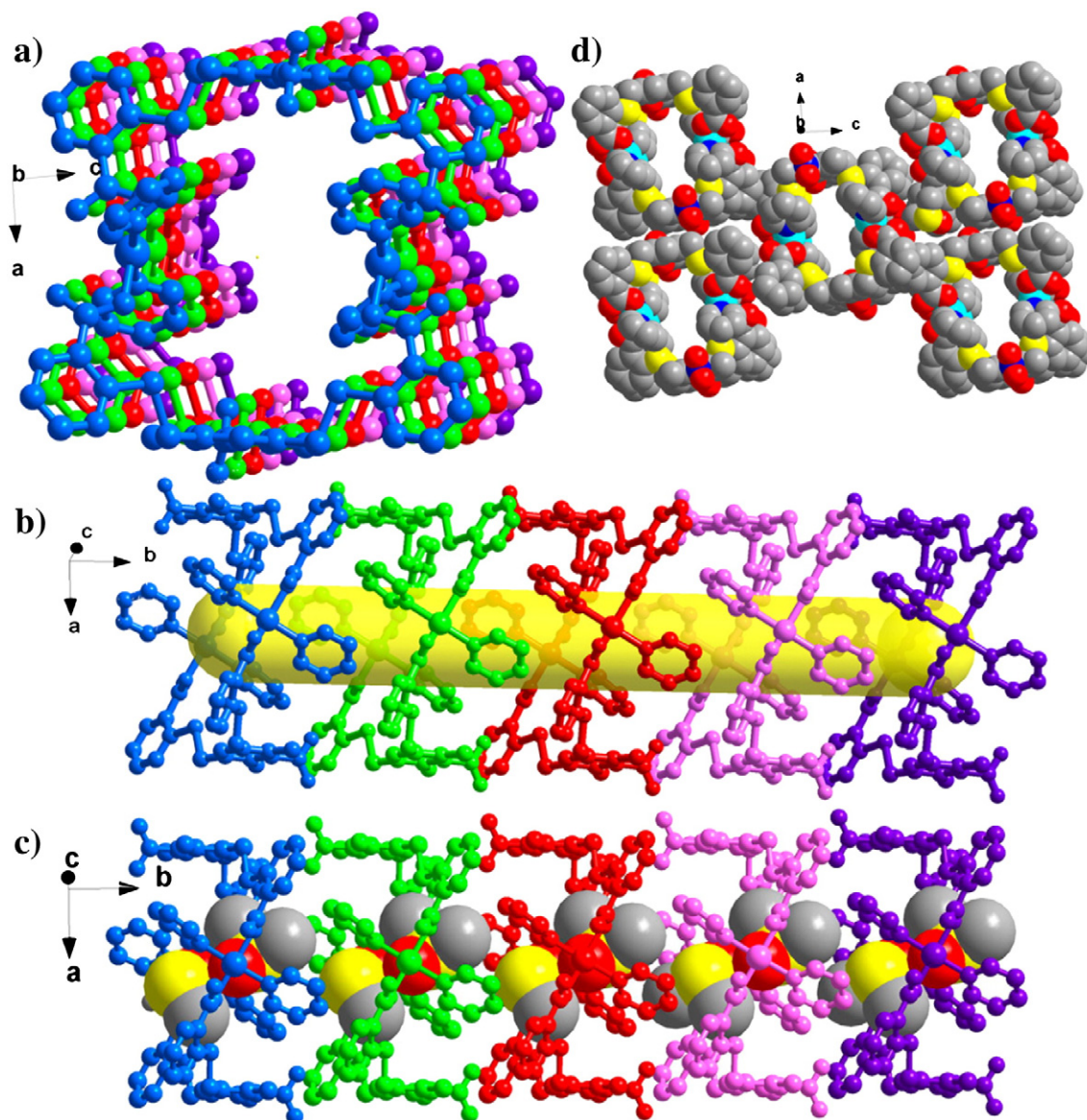


Fig. 3. (a) and (b) the 1D supramolecular MONT of **1** along different directions. (c) The arrangement of **1** along one direction under the effect of guest solvents. The guests in the 1D supramolecular MONT of **1** are shown in a space-filling mode. (d) A space-filling representation of the 3D packing of **1** showing the 1D channels.

and **2** under N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ were investigated and the TGA curves are shown in Fig. S3. The TGA curve of **1** displays a weight loss of 37.33% at $177\text{--}223\text{ }^\circ\text{C}$, which corresponds to the loss of coordinated pyridine molecules and lattice DMSO molecules. Then, the metallamacrocycle began to decompose as the temperature was further increased. The TGA curve of complex **2** shows a first weight loss of 28.12% at $110\text{--}149\text{ }^\circ\text{C}$, corresponding to the loss of coordinated pyridine molecules and lattice pyridine molecules, and the compound began to decompose as the temperature was further increased.

In summary, two metal–organic coordination complexes based on a new flexible dicarboxylate ligand were synthesized and characterized. The flexible dicarboxylate ligand adopts a *syn* conformation connected with copper ions to form two different topologies: discrete macrometallocycle and 1D zigzag chain. More interestingly, the two complexes were synthesized in the same reaction, and through increasing the mole fraction of pyridine we obtained the pure phase of complex **2**. Meanwhile, the guest molecules in the cavity and the van der Waals interactions between the guest and the host molecules have a significant effect on the packing of the metal–organic

supramolecular nanotubes. Our results further indicate that slight change of the reaction condition can result in the formation of different structures.

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Appendix A. Supplementary data

CCDC 902368 and 902369 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be

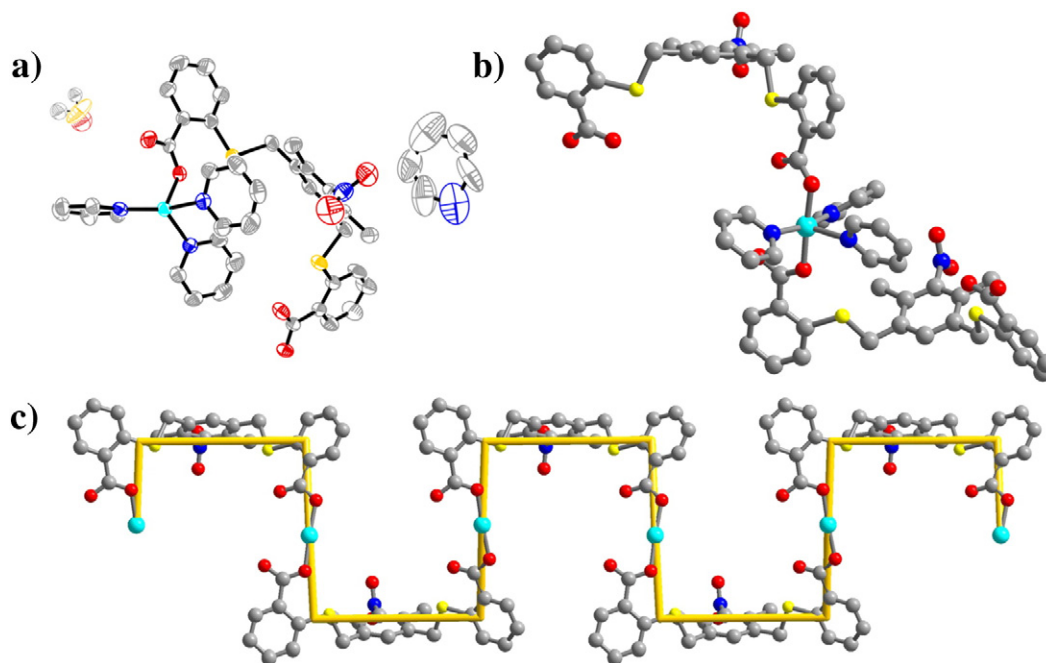


Fig. 4. (a) The asymmetry unit of complex **2**. (b) The coordination environment of the Cu(II) ions in complex **2**. Hydrogen atoms have been omitted for clarity. (c) Schematic representation showing the 1D zigzag chain.

found, in the online version <http://dx.doi.org/10.1016/j.inoche.2012.11.019>.

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