

In Situ Self-Assembly of 1D Copper(II) Coordination Polymer Containing EO Azide and Phenolate Bridges: Crystal Structure and Magnetic Properties

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A novel one-dimensional copper(II) coordination polymer with formula $[\text{Cu}^{\text{II}}(\text{L}_1)(\text{N}_3)]_n$ (**1**), has been prepared via in situ self-assembly. Compound **1** consists of 1D uniform chains in which the copper(II) ions are bridged by end-on azide and an oxygen of salicylideneamine (L_1). Magnetic susceptibility measurement reveals the existence of relatively strong ferromagnetic interactions in the 1D chain.

The design and construction of coordination polymers have been a field of rapid growth in materials chemistry because of their fascinating structures and applications as new materials. For studies of the molecule-based magnets, coordination polymers have aroused wide interests of the experimental and theoretical chemists.¹ The growing interest in this field is motivated by the ability of metalloligand coordination to provide a simple route to the controlled assembly of 1D, 2D, and 3D coordination polymers.^{2,3} One of the points to be seriously considered for the preparation of these materials is the selection of the appropriate paramagnetic metal ions, bridging ligands, and suitable synthesis methods.^{4,5}

The pseudohalide azide has been demonstrated to be not only an extremely versatile ligand but also an excellent magnetic coupler. Thus, a large number of azide-bridged coordination polymers have been synthesized and magneto-structurally characterized.⁶ In general, the very common bridging modes observed for the azido linker are end-to-end (EE) and end-on (EO). The former one is mainly known as an antiferromagnetic coupler (AF) with a few exceptions where some systems have been shown the formation of EE azido bridged ferromagnetic materials.⁷ EO mode can mediate both ferro- and antiferromagnetic interactions depending on the M–N–M bond angle.⁸

On the other hand, one-dimensional metal–azido systems are important because of the possibility of enhancement of the bulk magnetic interactions. The introduction of a second hybrid ligand to a metal–azido system is important to control the

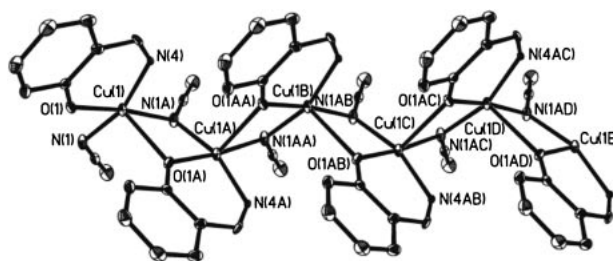
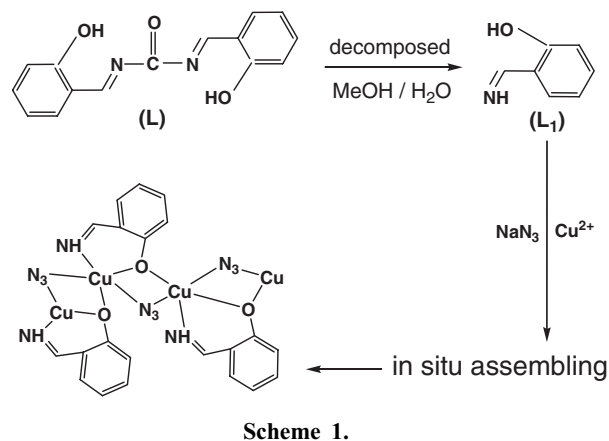


Figure 1. Perspective view showing the atomic labeling scheme, metal coordination environment and the topology of the chain.

assembly of coordination polymers. In the majority of the cases, different chelated organic ligands have been used for this purpose.^{9,10}

In this paper, we report the syntheses, structure, and magnetic properties of a novel 1D mixed bridges (EO-azide and oxygen of salicylideneamine) copper(II) compound **1**. Compound **1**, of formula $[\text{Cu}^{\text{II}}(\text{L}_1)(\text{N}_3)]_n$, consists of 1D uniform chains. Ferromagnetic interactions are existed in the 1D compound.

Single crystals of compound **1** were obtained by slow diffusion in an H-shaped tube.^{11–13} During the reaction, *N,N'*-disalicylideneurea (**L**) decomposed into salicylideneamine (L_1) and compound **1** was obtained via in situ self-assembly (Scheme 1).

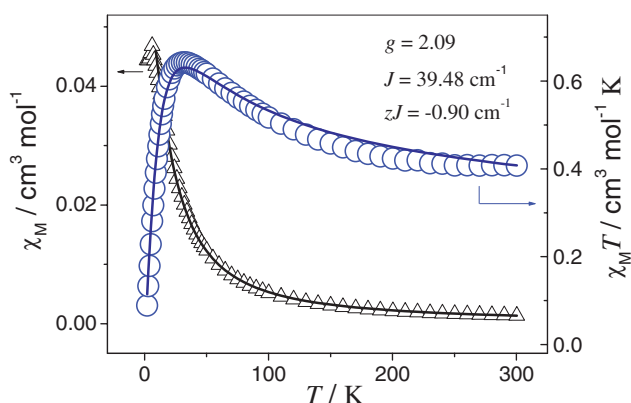
The crystal structure of compound **1** was determined by X-ray diffraction analysis.¹⁴ Figure 1 shows the building unit drawing of the 1D chain. Table 1 shows the selected bond lengths/Å and angles/°.

The coordination geometry around copper(II) ion is the distorted square pyramidal: CuN_3O_2 . The basal plane for copper(II) ion consists of the nitrogen atom of EO-azide N(1) and N(1A), oxygen atom of salicylideneamine O(1), and the nitrogen atom of the imine N(4). The axial coordination site of copper(II) is occupied by the oxygen atom of salicylideneamine O(1A) [Symmetry transformations used to generate equivalent atoms: $-x + 3/2, y, z + 1/2$], and the bond length of apical bond: Cu(1)–O(1A) is 2.416(2) Å, which is much longer than the equatorial bond distances 1.918(2) Å for Cu(1)–O(1). All the O–Cu–O, O–Cu–N, or N–Cu–N angles are deviation from a few degrees of 90 or 180°. The copper(II) ion and the four equatorially bound atoms are coplanar. The equatorially

Table 1. Selected Bond Lengths/Å and Bond Angles/° for Compound **1**^{a)}

Cu(1)–O(1)	1.918(2)	Cu(1)–N(4)	1.934(3)
Cu(1)–N(1A)	1.968(3)	Cu(1)–N(1)	1.983(3)
Cu(1)–O(1A)	2.416(2)		
O(1)–Cu(1)–N(4)	92.31(11)	O(1)–Cu(1)–N(1A)	171.93(12)
N(4)–Cu(1)–N(1A)	90.84(12)	O(1)–Cu(1)–N(1)	82.77(11)
N(4)–Cu(1)–N(1)	160.11(12)	N(1)–Cu(1)–N(1A)	96.66(12)
O(1)–Cu(1)–O(1A)	101.17(11)	N(4)–Cu(1)–O(1A)	92.35(10)
N(1)–Cu(1)–O(1A)	71.27(11)	N(1)–Cu(1)–O(1A)	107.50(11)
Cu(1)–O(1A)–Cu(1A)	95.15(2)	Cu(1)–N(1A)–Cu(1A)	109.02(71)

a) Symmetry transformations used to generate equivalent atoms: $-x + 3/2, y, z + 1/2$.

**Figure 2.** Plots of $\chi_M T$ and χ_M vs. T for compound **1**; the solid line represents the best fitting with eqs 1 and 2.

coordination plane suffers a small tetrahedral distortion as indicated by deviations of the relevant atoms (the deviations from the average planes are 0.2264 Å) and the deviation of Cu(1) from the least-square plane is 0.0937 Å. The neighboring copper(II) ions are connected by nitrogen atoms of EO-azide and oxygen atoms of salicylideneamine and the 1D uniform chain is formed. The separation between the neighboring copper(II) ions through the mixed bridges is 3.2168(8) Å. It is interesting to note that the phenoxo-oxygen atom assumes an asymmetric apical-basal disposition between neighboring copper(II) ions, i.e., the same oxygen bridge resides on the apical position of one copper but in the basal plane of the neighboring copper, with the apical Cu–O distance (Cu(1)–O(1A) = 2.416(2) Å) being significantly longer than the basal one (Cu(1)–O(1) = 1.918(2) Å). In the lattice, the chains run along the c direction and there is no evident indication of interchain π – π interactions.

Figure 2 shows the temperature dependence of the magnetic susceptibility of compound **1**, where the plots of χ_M and $\chi_M T$ vs. T are displayed. The value of $\chi_M T$ at room temperature is 0.41 cm³ K mol⁻¹, which is larger than the expected value for the one spin system with $S = 1/2$. With lowering the temperature, $\chi_M T$ increases gradually and reaches the maximum value (0.64 cm³ K mol⁻¹) at 23 K, indicating the intra-chain ferromagnetic spin–spin interaction. When decreasing the temperature further, $\chi_M T$ decreases sharply, likely due to the inter-chain antiferromagnetic interaction.

Crystal structural analysis shows that 1D magnetic chain is formed in the crystal lattice of compound **1**. The magnetic data of compound **1** can be well fitted with a 1D magnetic chain model.¹⁵ The inter-chain spin–spin interaction is treated simply with mean-field theory. Accordingly, the temperature dependence of the magnetic susceptibility of compound **1** was fitted to eqs 1 and 2,

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{4kT} \left[\frac{N}{D} \right]^{\frac{1}{2}} \quad (1)$$

$$N = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5$$

$$D = 1.0 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4$$

$$y = J/2kT$$

$$\chi_M = \frac{\chi_{\text{chain}}}{1 - (2zJ/Ng^2\beta^2)\chi_{\text{chain}}} \quad (2)$$

where J is referred to as the magnetic exchange constant within the 1D chain and zJ represents the inter-chain spin–spin interaction. The best fitting leads to $g = 2.09$, $J = 39.48 \text{ cm}^{-1}$, and $zJ = -0.90 \text{ cm}^{-1}$, showing that the intra-chain spin–spin interaction is relatively strongly ferromagnetic, while the inter-chain spin–spin interaction is weakly antiferromagnetic.

It has been widely cited that the interaction through an EO azido bridge is ferromagnetic for lower Cu–N–Cu angles and antiferromagnetic for higher angles. The critical angle is 104° according to empirical analyses¹⁶ and 108° according to a density functional study.¹⁷ It appears that the ferromagnetic coupling in **1**, with a Cu–N–Cu angle of 109.02°, disagrees with the above trends. Furthermore, comparing to double EO azido bridging mode in the literatures,¹⁸ the mixed bridges containing an EO azide and phenoxo-oxygen in **1**, mediate relatively strong ferromagnetic interaction. The ferromagnetic interaction may work through the phenoxo-oxygen because of orthogonality of magnetic orbitals among neighboring copper(II) ions.

In summary, we report for the synthesis, crystal structure, and magnetic properties of a novel 1D copper(II) coordination polymer of formula $[\text{Cu}^{\text{II}}(\text{L}_1)(\text{N}_3)]_n$ (**1**). Compound **1** consists of 1D uniform chain and there exists relatively strong ferromagnetic interaction in the chain. It should be pointed out that compound **1** is interesting for the studies of molecular-based magnets in terms of the following two points: (1) formation of new complexes with paramagnetic metal ions via in situ self-assembly; (2) mixed bridging mode containing μ -phenoxo-oxygen and EO azide can transmit ferromagnetic interaction. Relatively strong ferromagnetic interaction may work through the phenoxo-oxygen because of orthogonality of magnetic orbitals among neighboring copper(II) ions. This result opens up a route to the synthesis of a new family of mixed EO azide bridging compounds, and the work is already underway to establish the series.

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References

- 1 D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, 36, 770, and references therein.
- 2 G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, 100, 3483.
- 3 A. M. Kirillov, Y. Y. Karabach, M. Haukka, M. F. C. G. da Silva, J. Sanchiz, M. N. Kopylovich, A. J. L. Pombeiro, *Inorg. Chem.* **2008**, 47, 162.
- 4 S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, 35, 972.
- 5 S. C. Manna, J. Ribas, E. Zangrando, N. Ray Chaudhuri, *Inorg. Chim. Acta* **2007**, 360, 2589.
- 6 A. Escuer, G. Aromí, *Eur. J. Inorg. Chem.* **2006**, 4721.
- 7 F.-C. Liu, Y.-F. Zeng, J.-P. Zhao, B.-W. Hu, X.-H. Bu, J. Ribas, J. Cano, *Inorg. Chem.* **2007**, 46, 1520.
- 8 P. S. Mukherjee, T. K. Maji, A. Escuer, R. Vicente, J. Ribas, G. Rosair, F. A. Mautner, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* **2002**, 943.
- 9 S. Konar, E. Zangrando, M. G. B. Drew, T. Mallah, J. Ribas, N. Ray Chaudhuri, *Inorg. Chem.* **2003**, 42, 5966.
- 10 J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, 193–195, 1027, and references therein.
- 11 L. F. Capitán-Vallvey, F. Salinas, C. Jiménez, L. Cuadros, *Can. J. Chem.* **1982**, 60, 1706.
- 12 D. Hakan, S. Serap, S. Yasemin, H. Tuncer, Z. Kılıç, *J. Mol. Struct.* **2005**, 753, 84.
- 13 Single crystals suitable for X-ray diffraction were obtained by slow diffusion in an H-shaped tube (total volume ca. 40 mL) of two methanol/aqueous (1:1) solutions. A methanol/aqueous (1:1) solution 10 mL containing L (0.44 g, 2 mmol) and NaN₃ (0.13 g, 2 mmol) were in one arm and the solution of Cu(ClO₄)₂·6H₂O (0.74 g, 2 mmol, 10 mL) was in the other arm. And then 20 mL of methanol/aqueous solvent was carefully added so that the bridge of the tube was filled. The tube was sealed and left to stand at room temperature. Two weeks later, the dark-green crystals were collected and air-dried (0.124 g, 27%). IR (cm⁻¹): 3441, 3347, 2098, 1639, 1616, 1528, 1433, 1317, 1285, 1191, 770. Anal. Calcd for C₇H₆CuN₄O: C, 37.22; H, 2.66; N, 24.81%. Found: C, 37.37; H, 2.95; N, 24.59%.
- 14 Crystal data: C₇H₆CuN₄O, *M_r* = 225.70, Orthorhombic, *Pccn*, *a* = 14.319(3) Å, *b* = 19.465(4) Å, *c* = 5.7610(10) Å, *V* = 1605.7(5) Å³, *Z* = 8, *D_{calcd}* = 1.867 g cm⁻³; *F*(000) = 904, *μ*(Mo Kα) = 2.678 mm⁻¹. 3358 reflections of which 1828 are unique (*R_{int}* = 0.0197) were collected to a *θ* limit of 2.85–27.43° on a Rigaku RAXIS RAPID IP instrument at 293(2) K. The structure was solved by direct methods and refined by a least-squares matrix method. The final cycle of full-matrix least-square refinement was based on 1828 observed reflections [*I* > 2σ(*I*)] and 118 variable parameters and converged to *R* = 0.0390, *wR*₂ = 0.0625 (*R* indices for all data: *R*₁ = 0.0710, *wR*₂ = 0.0929), GOF = 0.868, Largest diffraction peak and hole of 0.659 and –0.655 e Å⁻³. CCDC reference number 697911.
- 15 G. A. Baker, Jr., G. S. Rushbrooke, H. E. Gilbert, *Phys. Rev.* **1964**, 135, A1272.
- 16 S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.* **1994**, 33, 5555.
- 17 E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, 120, 11122.
- 18 E.-Q. Gao, S.-Q. Bai, C.-F. Wang, Y.-F. Yue, C.-H. Yan, *Inorg. Chem.* **2003**, 42, 8456, and references therein.