



# A novel 2-D coordination polymer with mixed azido and alkoxido bridges: Synthesis, structure and magnetic properties



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## ABSTRACT

A novel 2-D coordination polymer  $[\text{Cu}_2(\text{L})(\text{N}_3)_3]_n$  **1** (HL: 1,5-diaminopentan-3-ol) has been synthesized and its crystal structure and magnetic properties have been studied. The crystal structure of the compound **1** consists of binuclear moieties  $[\text{Cu}_2(\text{L})(\text{N}_3)_3]$  with mixed alkoxido/end-on azido bridges, which are linked by double asymmetric end-on and single asymmetric end-to-end azido bridges, resulting in a 2-D layer extended within the *ab* crystallographic plane. Variable-temperature magnetic susceptibility data evidence strong antiferromagnetic interaction between the  $\text{Cu}^{\text{II}}$  ions within the binuclear units, which are mediated by the two types of bridges ( $J = -123(2) \text{ cm}^{-1}$ ,  $H = -2J\text{S}_1\text{S}_2$ ). The experimental value of the exchange coupling constant is confirmed by DFT calculations.

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## 1. Introduction

The azide ion is extensively used as a ligand to generate a wide variety of transition metal complexes and coordination polymers with a rich structural diversity and interesting magnetic properties. The azide ion is recognized as a versatile ligand that can bridge two or more metal ions in different modes, such as  $\mu_{1,1}$  (end-on, EO),  $\mu_{1,3}$  (end-to-end, EE),  $\mu_{1,1,3}$ ,  $\mu_{1,1,1}$ ,  $\mu_{1,1,1,1}$ ,  $\mu_{1,1,3,3}$ , and  $\mu_{1,1,1,3,3,3}$  [1]. The aggregation of various azido complexes, ranging from oligonuclear complexes to 1-D, 2-D, and 3-D coordination polymers, can be influenced by using bridging or terminal co-ligands [1,2]. The neutral organic co-ligands are usual, while the bridging anionic co-ligands have been more rarely used [2]. Among the bridging anionic co-ligands, those having a potentially bridging alkoxido group can be employed to obtain compounds with mixed azido and alkoxido bridges. So far, several structurally characterized oligonuclear complexes [3] and 1-D coordination polymers [4] incorporating  $\mu$ -alkoxido- $\mu_{1,1}$ -azido or  $\mu$ -alkoxido- $\mu_{1,3}$ -azido hetero-bridges have been reported. In this study we

describe the synthesis, crystal structure and magnetic properties of a 2-D coordination polymer with mixed azido and alkoxido bridges  $[\text{Cu}_2(\text{L})(\text{N}_3)_3]_n$  **1** (HL: 1,5-diaminopentan-3-ol).

## 2. Experimental

### 2.1. Materials and methods

All reagents and solvents used in this study are commercially available (Aldrich, Fluka or Merck) and were used without further purification. All syntheses were carried out in aerobic conditions. **Caution!** Azide compounds are potentially explosive. Only small quantities of compound should be prepared, and it should be handled with care!

### 2.2. Physical measurements

The IR spectrum of the compound **1** (KBr pellet) was recorded with a Bruker Tensor 37 spectrometer in the 4000–400  $\text{cm}^{-1}$  range. The magnetic susceptibility measurements were obtained with the use of MPMS-XL Quantum Design SQUID magnetometer that works between 1.8 and 400 K for *dc* applied fields ranging from –7 to 7 T. Measurements were performed on a polycrystalline

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sample of 13.53 mg for **1**, introduced in a polyethylene sample holder ( $3 \times 0.5 \times 0.02$  cm; 26.54 mg). *M* versus *H* measurements have been performed at 100 K to check for the presence of ferromagnetic impurities that have been found absent. The magnetic data were corrected for the sample holder and the diamagnetic contribution [5].

### 2.3. Synthesis

1,5-Diaminopentan-3-ol dihydrochloride (0.019 g, 0.1 mmol), synthesized according to a reported method [6], was deprotonated with sodium methoxide (0.016 g, 0.3 mmol) in methanol (5 mL). The NaCl precipitate was filtered and to the filtrate  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.04 g, 0.2 mmol) was added. The reaction mixture was stirred for one hour at room temperature. Then, the resulted blue solution was carefully layered on a methanolic solution (25 mL) of  $\text{NaN}_3$  (0.019 g, 0.3 mmol) in a test tube. The test tube was sealed and kept in a refrigerator for crystallization. After 3 days, greenish-brown crystals of **1** formed; they were filtered and washed with cold methanol. Yield 0.022 g (59.5%). IR data ( $\bar{\nu} \text{ cm}^{-1}$ ): 3319 (w), 3269 (w), 2068 (s), 2034 (s), 1343 (w), 1292 (w), 1088 (w). Elemental analysis: *Anal. Calc.* for  $\text{C}_5\text{H}_{13}\text{Cu}_2\text{N}_{11}\text{O}$  (370.32): C, 16.2; H, 3.5; N, 41.6. Found: C, 16.7; H, 3.9; N, 41.0%.

### 2.4. X-ray data collection and crystal structure refinement

X-ray diffraction measurements for compound **1** were performed at 293 K on a STOE IPDS II diffractometer using a graphite-monochromated Mo  $K\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods and refined by full-matrix least-squares techniques based on  $F^2$ . All non-H atoms were refined anisotropically, and hydrogen atoms were introduced at calculated positions. Calculations were performed using SHELXL-97 [7] and PLATON [8]. The figures were drawn with Diamond Version 3.0 [9]. A summary of the crystallographic data and the structure refinement is given in Table 1.

### 2.5. Computational details

The DFT calculations were performed using the GAUSSIAN 09 suit of programs [10] considering the UB3LYP [11] functional and two basis sets, Lanl2dz [12] and TZVP [13]. The calculations were

carried out on a simplified model, which consists in the binuclear alkoxido/azido bridged moiety, the apical azido ligands being removed. According to literature data [14,15], for calculating the magnetic coupling constant, *J*, the geometry was not optimized, employing the crystal geometry already described and displayed in Fig. 1. The energies of the Broken Symmetry ( $E_{\text{BS}}$ ) and the High Spin ( $E_{\text{HS}}$ ,  $S = 1$ ) states were obtained using the methodology of the fragments as implemented in the GAUSSIAN09 program and checked for the stability.

## 3. Results and discussion

### 3.1. Synthesis and IR spectroscopy

1,5-Diaminopentan-3-ol is a potential mono-anionic, tridentate ligand that includes alkoxido and amino donor groups. Murase et al. [6] have previously reported that by the reactions of methanolic solutions of  $\text{Cu}^{\text{II}}$  salts (chloride, bromide, perchlorate, tetrafluoroborate, and nitrate) with HL in the presence of triethylamine, binuclear complexes  $[\text{Cu}_2\text{L}_2\text{X}_2] \cdot n\text{H}_2\text{O}$  ( $\text{X}: \text{Cl}, \text{Br}, n = 1$ ;  $\text{X}: \text{ClO}_4, \text{BF}_4, \text{NO}_3, n = 0$ ) are obtained. We supposed that by replacing the  $\text{X}^-$  anion with another anion, able to acts as a bridging ligand, a coordination polymer can be assembled. Indeed, the slow diffusion of diluted methanolic solutions of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , HL, and  $\text{NaN}_3$ , in the presence of sodium methoxide (2:1:3:1 molar ratio) affords greenish-brown crystals of the 2-D coordination polymer **1**. These crystals are insoluble in common solvents and appear to be air and moisture stable. The IR spectrum of the compound **1** displays the characteristic bands of the azido bridges, as well as of the alkoxido and amino groups. The two strong absorptions bands at 2068 and  $2034 \text{ cm}^{-1}$ , corresponding to  $\nu_{\text{as}}(\text{N}_3)$  stretching vibrations, suggest the presence of different types of azido bridges. The  $\nu_{\text{s}}(\text{N}_3)$  stretching vibrations appear at  $1343$  and  $1292 \text{ cm}^{-1}$ . The characteristic IR band for the alkoxido C–O stretching vibration is observed at  $1088 \text{ cm}^{-1}$ , whereas absorption bands corresponding to  $\nu_{\text{as}}(\text{NH}_2)$  and  $\nu_{\text{s}}(\text{NH}_2)$  appear at  $3319$  and  $3269 \text{ cm}^{-1}$  [16].

### 3.2. Description of the structure

The crystallographic asymmetric unit of **1** consists of two  $\text{Cu}^{\text{II}}$  ions, one mono-anionic tridentate ligand  $[\text{L}]^-$ , and three azido

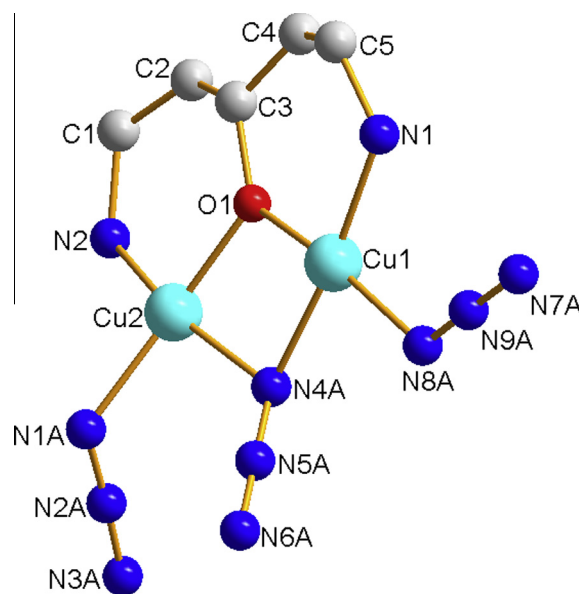
**Table 1**  
X-ray crystallographic data for compound **1**.

Chemical formula	$\text{C}_5\text{H}_9\text{Cu}_2\text{N}_{11}\text{O}$
<i>M</i> ( $\text{g mol}^{-1}$ )	366.31
<i>T</i> (K)	293
$\lambda$ ( $\text{\AA}$ )	0.71073
Crystal system	monoclinic
Space group	$P2_1/a$
<i>a</i> ( $\text{\AA}$ )	8.6012(11)
<i>b</i> ( $\text{\AA}$ )	14.6516(14)
<i>c</i> ( $\text{\AA}$ )	10.2809(13)
$\beta$ ( $^\circ$ )	99.325(10)
<i>V</i> ( $\text{\AA}^3$ )	1278.5(3)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> ( $\text{g cm}^{-3}$ )	1.903
$\mu$ ( $\text{mm}^{-1}$ )	3.339
<i>F</i> (000)	728
Goodness-of-fit on $F^2$	1.062
Final $R_1^a$ , $wR_2^b$ [ $I > 2\sigma(I)$ ]	0.0430; 0.0981
$R_1^a$ , $wR_2^b$ (all data)	0.0754; 0.1089
Largest difference peak and hole ( $\text{e \AA}^{-3}$ )	0.487 and $-0.483$

$$w = 1/[\sigma^2(F_0^2) + (0.0536P)^2] \text{ where } P = [(F_0^2) + 2F_c^2]/3.$$

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$



**Fig. 1.** View of the asymmetric unit of **1**. Hydrogen atoms are omitted for clarity.

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