

# The first and novel example of a rare 1D–copper(II) complex containing only single end–on azido bridges: crystal structure, electrochemical and magnetic properties

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A novel one–dimensional single azido–bridged coordination polymer of formula  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$ , where NAPPR<sup>–2</sup> is the 1,3–Bis (naphthylideneimino) propane dianion, has been synthesized and characterized by elemental analyses and spectroscopic methods. This compound consists of 1D uniform chains in which the two types of Cu(II) ions, one with a distorted square pyramidal (Cu1) and the other with a distorted trigonal bipyramidal (Cu2) geometry, are interlinked by single end–on azido bridges.

The magnetic properties of the complex have also been studied. Temperature– and field–dependent magnetic analyses reveal that antiferromagnetic interactions between Cu2 centers are mediated by the single EO bridges, while Cu1 moments remain paramagnetic. The cyclic voltammetric study reveals the existence of two structurally different copper(II) centers and the resulting data conform to the crystal structure of this complex determined by single crystal X-ray crystallography.

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## Introduction

The design and magnetic properties of polynuclear molecules and coordination polymers with particular structures are currently the focus of attention for understanding the nature of their magnetic interactions and investigating magneto–structural correlations in molecular systems and for developing new functional molecule–based materials.<sup>[1–2]</sup> In this context, the exceptional abilities of the azide anion as a versatile bridge to link two or more metal centers in different modes and as a good mediator to transmit different magnetic interactions, together with the remarkable diversities of the metal azido systems in polymeric dimensionality, topology, and bulk magnetic property, have evoked considerable interest.<sup>[1–3]</sup> The azido ion can link two or more metal ions in the  $\mu\text{-}1,1$  (end–on, EO),  $\mu\text{-}1,3$  (end–to–end, EE), or a combination of both modes, yielding various polynuclear and one–(1D), two– (2D), or three–dimensional (3D) species of different topologies, depending on the metal ion and the coligand used.<sup>[3–6]</sup> The magnetic exchange mediated via an azido bridge can be ferro–(F) or antiferromagnetic (AF), depending on the bridging mode and bonding parameters. It has been widely stated that the exchange is generally ferromagnetic in nature for the EO mode, and antiferromagnetic for the EE mode,<sup>[3–9]</sup> although an increasing number of exceptions have been reported recently.<sup>[10–11]</sup> For copper(II) systems, the magnetic exchange coupling strongly

depends on the coordination geometries of the metal ion and the coordination mode of the azido bridge. For instance, the azido bridge between two square pyramidal Cu(II) ions may assume a basal–basal or a basal–apical disposition, which affects the magnetic exchange coupling.<sup>[12–18]</sup>

The occurrence of a single EO azido bridge, i.e., the case in which there is no bridge between the two metal ions other than the single EO azido group, is very rare. In all reported compounds with such bridges at least another mode of azide coordination is involved in forming the structure, and to the best of our knowledge, no species containing only single EO bridges have been communicated.<sup>[12,18]</sup>

In the present paper, we report, for the first time, the synthesis, crystal structure, electrochemical and magnetic properties of a 1D compound containing only single EO azido bridges between two copper(II) centers with different donor atoms and coordination geometries. The complex is of the formula  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$  where NAPPR<sup>–2</sup> is a tetradentate N2O2 donor Schiff base obtained from the condensation of 2–hydroxy–1–naphthaldehyde with 1,3–propanediamine.

## Results and Discussion

### Crystal Structure of $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$ (1)

The copper complex build up a 1D chain of Rod–group  $p(1)2_1(1)$ . Each two neighboring Cu(II) centers are linked by a single azido bridge in the EO mode. A *perspective* view of the chain structure is depicted in **Figure 1**, and selected bond lengths and angles are listed in **Table 1**. There are the two structurally different copper(II) centers in each monomeric unit (**Figure 2**) of 1D coordination polymer. Cu1 adopts a distorted square–pyramidal environment containing the two N–atoms and two of the O–atoms of the NAPPR<sup>–2</sup> ligand in the basal plane and an azide anion

apically coordinated and Cu2 a distorted trigonal-bipyramidal geometry consisting of two O-atoms of the NAPPR<sup>2-</sup> ligand and one N-atoms of the azide bridge in the basal plane and two azide anions apically coordinated.

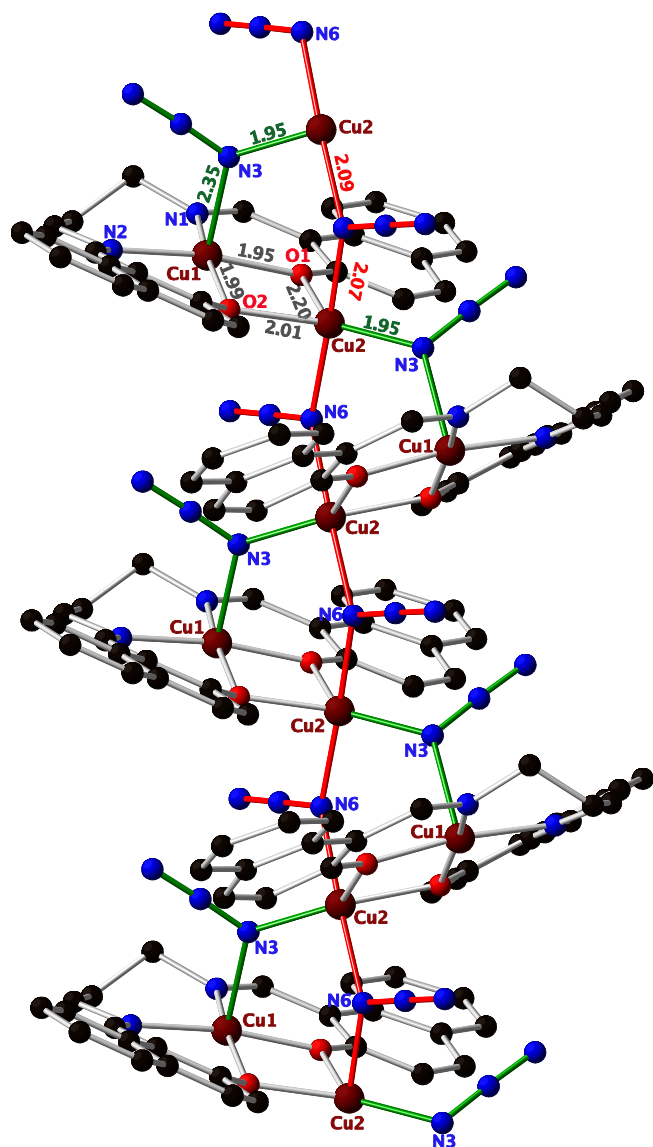


Figure 1. A perspective view of a [010] chain structure of  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$  with the selected bond lengths (Å) and the atom labelling scheme.

The  $\text{Cu1-N3}_{\text{azido}}$ , 2.353(3) Å is the longest bond distance owing to the Jahn-Teller effect reflecting the ability of copper(II) to accommodate long, axial metal-ligand bonds. The bond lengths to the tetradentate Schiff base ligand are:  $\text{Cu1-O1} = 1.945(2)$ ,  $\text{Cu1-N1} = 1.973(3)$ ,  $\text{Cu1-O2} = 1.987(3)$  and  $\text{Cu1-N2} = 1.993(3)$  Å, in agreement with similar compounds.<sup>[19]</sup> The deviations of the four basal donor atoms from the mean basal plane N1, N2, O1, and O2 are -0.0155(0.0014), 0.0153(0.0014), 0.0182(0.0017), and -0.0180(0.0016) Å, respectively, and the Cu1 atom is 0.0984(0.0017) Å out of the plane towards the apex. The trigonality-index (Addison Parameter)<sup>[20]</sup>  $\tau = 0.013$  [=  $(\beta - \alpha)/60^\circ$ , where  $\alpha, \beta$  are the two largest L-M-L angles of the coordination sphere, with  $\tau = 0$  and 1 for perfect square pyramid and trigonal bipyramid geometries, respectively] confirms the square pyramidal environment for Cu1.

Bond lengths for the Cu2 center are  $\text{Cu2-O1} = 2.201(3)$ ,  $\text{Cu2-O2} = 2.014(2)$ ,  $\text{Cu2-N3}^{(i)}(-x, -1/2+y, -z) = 1.954(4)$ ,  $\text{Cu2-N6} = 2.071(4)$  and  $\text{Cu2-N6}^{(i)}(-x, -1/2+y, -z) = 2.095(4)$  Å. The distortion parameter,  $\tau$ , is 0.24 confirming the distorted trigonal bipyramidal environment of the Cu2 ion.

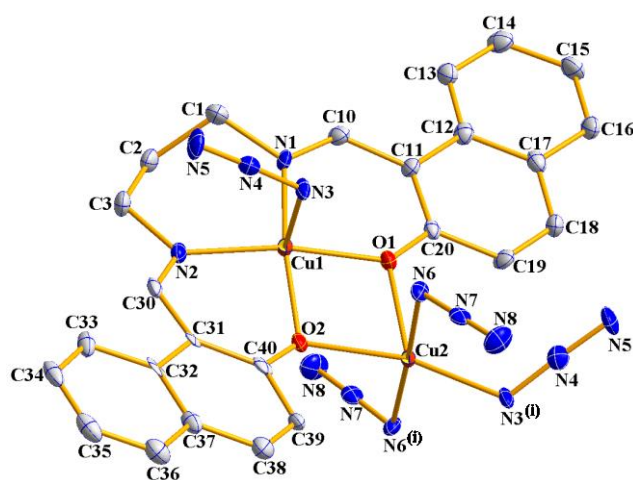


Figure 2. ORTEP-like diagram of the monomeric unit  $[\text{Cu}_2(\text{NAPPR})(\mu\text{-1,1-N}_3)_2]$  and its atom labelling scheme. The displacement ellipsoids are drawn at the 50 % probability level. Symmetry codes: (i)  $-x, -1/2+y, -z$ .

As shown in Figure 1, the structure consists of an assembly of connected copper centers linked via two different types of coordination mode of EO azido bridges, one as a symmetric apical-apical fashion (red) bridge between Cu2 centers [with a  $\text{Cu2}\dots\text{Cu2}$  distance of 3.842 Å] and the other as an asymmetric apical-basal fashion (green) bridge between Cu1 and Cu2 ions [with a  $\text{Cu1}\dots\text{Cu2}$  distance of 3.157 Å] and compares well with those reported for related complexes.<sup>[21-22]</sup> All bridged bond angles between copper (II) centers are:  $\text{Cu1-O1-Cu2} = 98.97(11)^\circ$ ,  $\text{Cu1-O2-Cu2} = 104.18(12)^\circ$ ,  $\text{Cu1-N3-Cu2} = 121.56(16)^\circ$  and  $\text{Cu2-N6-Cu2} = 134.52(14)^\circ$ . The coordinated azide ion is nearly linear with the  $\text{N3-N4-N5}$  and  $\text{N6-N7-N8}$  angles of  $177.7(4)^\circ$  and  $179.2(4)^\circ$ , respectively. According to a branched chain structure model,  $\text{Cu2-Cu2}$  connections through azido bridge continue endlessly as a chain, but  $\text{Cu1-Cu2}$  connections are isolated.

The crystal edifice is three-dimensional and is dominated by endless [010] chains of complexes which are stabilized by two types of intermolecular forces: (i) C-H...N hydrogen bonds between H-naphthyl ring and N-azido bridge, (ii) intermolecular C-H... $\pi$  (C) interactions between naphthyl rings of the neighbouring monomeric units (Figure 3 and Table 2). Laterally, the chains are connected by C-H...N hydrogen bonds.

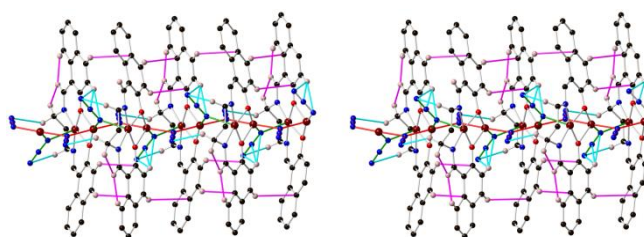


Figure 3. Stereoscopic view of the hydrogen bonds (turquoise tubes) and C-H... $\pi$ (C) interactions (pink tubes) in  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$  along the *b* axis.

Table 1. Selected bond lengths (Å) and angles (°) of (1).

Bond lengths			
Cu1–O1	1.945(2)	Cu2–O1	2.201(3)
Cu1–O2	1.987(3)	Cu2–O2	2.014(2)
Cu1–N1	1.973(3)	Cu2–N3 <sup>(i)</sup>	1.954(4)
Cu1–N2	1.993(3)	Cu2–N6	2.071(4)
Cu1–N3	2.353(3)	Cu2–N6 <sup>(i)</sup>	2.095(4)
N3–N4	1.215(5)	N6–N7	1.242(4)
N4–N5	1.177(5)	N7–N8	1.159(5)
Bond angles			
O1–Cu1–O2	81.27(11)	O1–Cu2–O2	74.68(10)
O1–Cu1–N1	89.74(13)	O1–Cu2–N6	88.69(11)
O1–Cu1–N2	169.77(13)	O1–Cu2–N3 <sup>(i)</sup>	122.03(13)
O2–Cu1–N1	169.01(13)	O1–Cu2–N6 <sup>(i)</sup>	91.31(11)
O1–Cu1–N3	95.47(12)	O2–Cu2–N6	89.38(13)
O2–Cu1–N2	89.41(11)	O2–Cu2–N3 <sup>(i)</sup>	163.29(14)
O2–Cu1–N3	88.69(13)	O2–Cu2–N6 <sup>(i)</sup>	88.60(13)
N1–Cu1–N2	99.02(13)	N3 <sup>(i)</sup> –Cu2–N6	90.96(14)
N2–Cu1–N3	88.48(13)	N6–Cu2–N6 <sup>(i)</sup>	177.91(13)
N3–N4–N5	177.7(4)	N3 <sup>(i)</sup> –Cu2–N6 <sup>(i)</sup>	90.81(13)
Cu1–O1–Cu2	98.97(11)	Cu1–O2–Cu2	104.18(12)
Cu1–N3–Cu2	121.56(16)	Cu2–N6–Cu2	134.52(14)
N6–N7–N8	179.2(4)		

Symmetry codes: (i)  $-x, -1/2+y, -z$ .Table 2. Hydrogen bonds and C–H... $\pi$  interaction: lengths (Å) and angles (°) for (1).

No.	D–H...A	D–H	H...A	D...A	D–H...A
1	C19–H19...N3 <sup>(i)</sup>	0.93	2.736	3.589	153
2	C19–H19...N4 <sup>(i)</sup>	0.93	2.583	3.387	145
3	C19–H19...N5 <sup>(i)</sup>	0.93	2.964	3.617	129
4	C30–H30...N5 <sup>(ii)</sup>	0.93	2.44	3.170	135
5	C38–H38...C12 <sup>(i)</sup>	0.93	2.849	3.607	140
6	C39–H39...C20 <sup>(i)</sup>	0.93	2.823	3.491	130

Symmetry codes: (i)  $-x, -1/2+y, -z$ ; (ii)  $1-x, -1/2+y, -z$ .

### Spectral studies

The infrared spectrum of the free ligand exhibits a broad band characteristic of the OH group at  $3427\text{ cm}^{-1}$ . The absence of this band in the FT-IR spectrum of the copper complex indicates that the ligand is coordinated as a dianion. The  $\nu(\text{C}=\text{N})$  band at  $1626\text{ cm}^{-1}$  in the spectrum of the  $\text{H}_2\text{NAPPR}$  ligand is shifted to lower frequencies by  $8\text{ cm}^{-1}$  in the copper compound ( $1618\text{ cm}^{-1}$ ), due to coordination of the imine nitrogen.<sup>[23]</sup> A strong, sharp stretching band at  $2054\text{ cm}^{-1}$  for copper complex corresponds to stretching vibration of the azide ligand in the end-on coordination mode.<sup>[22]</sup>

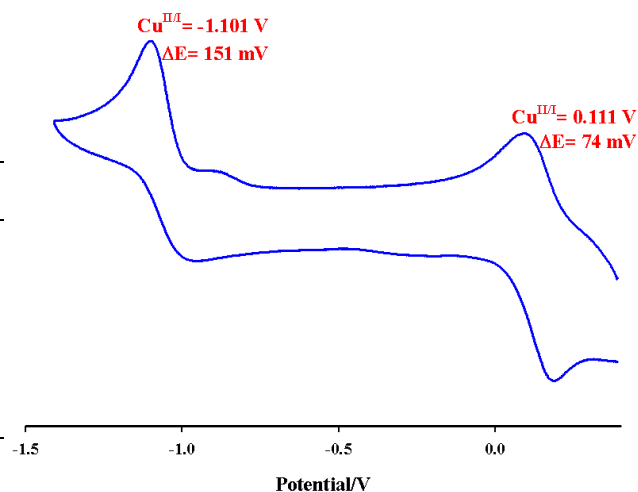
The electronic absorption spectrum of the ligand in DMF consists of one intense band centered at  $307\text{ nm}$ , assigned to  $\pi \rightarrow \pi^*$  transition and two bands at  $403$  and  $423\text{ nm}$ , corresponding to  $n \rightarrow \pi^*$  which, upon coordination of the ligand, disappear from the UV-Vis spectrum of its copper complex. The electronic absorption spectrum of copper complex shows, in

addition to the intraligand transitions in the UV region, charge-transfer bands at  $378$  and  $401\text{ nm}$  and two bands in the visible region at  $598$  and  $686\text{ nm}$  corresponding to a  $d \rightarrow d$  transition for Cu1(square-pyramid) and Cu2(trigonal-bipyramid) centers, respectively.

### Electrochemistry

The electrochemical behavior of (1) was studied, at  $25\text{ }^\circ\text{C}$ , in  $N,N$ -dimethylformamide with  $0.1\text{ M}$  TBAH as the supporting electrolyte at a glassy carbon working electrode under argon atmosphere with an approximate concentration of  $4 \times 10^{-3}\text{ M}$  of the complex.

The ligand is electro-inactive from  $+0.8$  to  $-1.8\text{ V}$ . The cyclic voltammogram of  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$  is shown in Figure 4. Due to the existence of two types of copper(II) centers in this complex, the voltammogram shows two cathodic peaks ( $E_{pc}$ ) at  $+0.11$  and  $-1.10\text{ V}$  with a peak-to-peak separation ( $\Delta E$ )  $74$  and  $151\text{ mV}$  corresponding to the electrochemically reversible and quasi-reversible reduction process of  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  for Cu2(salt-like complex) and Cu1(Schiff-base complex) centers, respectively. The electrochemical behavior and the data are in agreement with those reported for the complexes closely related to each copper center in this compound.<sup>[24–25]</sup> To the best of our knowledge, the large difference between the redox potentials of the two copper centers ( $1.21\text{ V}$ ) with different coordination geometries in a polymeric complex is an interesting case reported for the first time.

Figure 4. Cyclic voltammogram corresponding to  $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I})$  for  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$  in DMF at  $298\text{ K}$ . Scan rate,  $100\text{ mV/s}$ .  $c=4 \times 10^{-3}$ .

### Magnetic studies

The molar magnetic susceptibility for (1) was measured on a Quantum Design MPMS-5 SQUID magnetometer at temperatures ranging from  $5$  to  $300\text{ K}$  at a magnetic field of  $1\text{ T}$ . Figure 5 and Figure 6 show plot of  $1/\chi_M$  vs.  $T$  (based on Curie-Weiss law) and plot of  $\chi_M$  vs.  $T$  (based on the chain+paramagnetic structural model), respectively. The  $1/\chi_M$  vs.  $T$  plot shows that the magnetic susceptibility above  $60\text{ K}$  obeys the Curie-Weiss law (Weiss constant  $\theta = -47.5\text{ K}$ , Curie constant  $C = 0.45\text{ emu mol}^{-1}\text{K}$ ). The  $C$  value is consistent with magnetic moments belonging to  $\text{Cu}(\text{II})$  ions ( $S = 1/2$ ) with  $g = 2.19$ . The  $\chi_M$  and  $\chi_M T$  vs  $T$  plots (Figure 7) reveal that, upon cooling the value of  $\chi_M T$  gradually decrease from

0.62 emu mol<sup>-1</sup>K at room temperature to 0.2 emu mol<sup>-1</sup>K at 5 K. This magnetic behaviour is indicative of an antiferromagnetic interaction.

The antiferromagnetism of the compound is further sustained by the field-dependent magnetization measured at 5 K (Figure 8). As the field is increased from 0 to 5 T, the magnetization increases much slower than that predicted by the Brillouin function for non-interacting Cu(II) systems.

For a more detailed discussion let us consider this copper compound as a branched chain model of Cu(II) ions with three exchange interactions: 1) the connections of Cu1–O1–Cu2 and Cu1–O2–Cu2 are approximately orthogonal, so one would not expect any magnetic exchange coupling via these two bridges. 2) the coupling through EO azido-bridges (Cu1–N3–Cu2) showing very small interaction, so magnetic moments remain paramagnetic on Cu1 centers, and 3) the coupling through EO azido-bridged (Cu2–N6–Cu2) indicating the possibility of antiferromagnetic coupling between Cu(II) centers through EO azido-bridge. Considering that the Cu–N–Cu angle is larger than 104°, these results are in agreement with those observed for the binuclear complexes reported by Thompson et al. based on experimental data.<sup>[26]</sup>

In case 2, the singly occupied orbital around the square pyramidal Cu1 is mainly of  $d_{x^2-y^2}$  lying in the basal plane, with a small contribution from  $d_{z^2}$  due to the distortion of the coordination geometry. Consequently, the spin density of Cu2 is effectively delocalized toward the azido nitrogen (N3) atom that resides in the basal plane of the Cu2(TBP geometry). However the delocalization of the spin density of Cu1 ion toward the same nitrogen atom is poor because the nitrogen atom occupies the apical position of Cu1 with a longer distance. Therefore, the overlap between the magnetic orbitals of the two Cu(II) ions is rather small, and the resulting magnetic exchange is predicted to be rather weak.

According to the structural data, the antiferromagnetic interactions should be attributed to intrachain super exchange mediated *via* the EO bridges. To simulate the experimental magnetic behavior, we use the following numerical expression for uniform antiferromagnetic chains of  $S = 1/2$ .<sup>[27]</sup>

$$\chi_M = Ng^2\beta^2/kT \times (0.25 + 0.074975x + 0.075235x^2)/(1 + 0.9931x + 0.172135x^2 + 0.757825x^3) \quad (1)$$

and

$$\chi_M = \chi_{\text{paramagnetic}} + \chi_{\text{chain}} + \chi_0$$

$x = |J|/kT$ , and  $J$  is the coupling parameter based on the isotropic spin Hamiltonian  $H = -J\sum S_i S_{i+1}$ . In agreement with the crystal structure, we keep the number of moments participating in the chain equal to the number of paramagnetic ones. The least-squares fits of the experimental data to the above expression led to  $J = 25$  K with  $g = 2.19$  for (1). The  $J$  parameter confirms that antiferromagnetic interactions are mediated by the single EO azido bridges in (1).

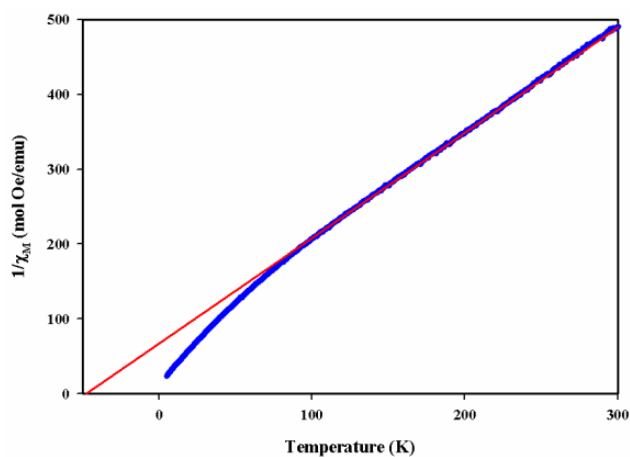


Figure 5. Plot of  $1/\chi_M$  vs.  $T$  for (1). The red line shows the best fit theoretical curve of Curie-Weiss law.

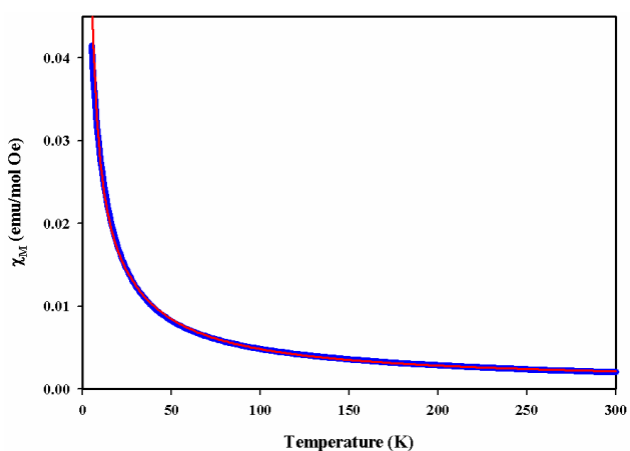


Figure 6. Plot of  $\chi_M$  vs.  $T$  for (1). The red line shows the best fit theoretical curve of the chain+paramagnetic model.

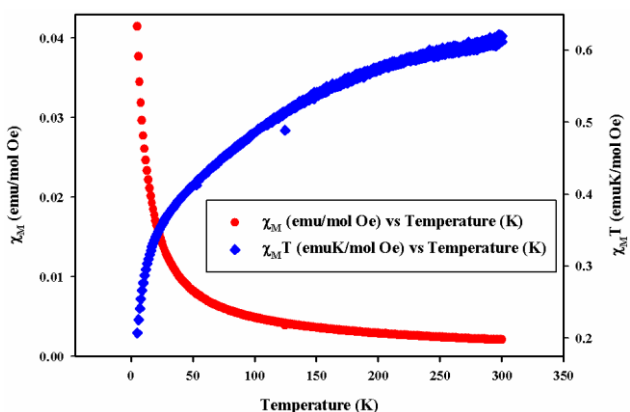


Figure 7. Plot of  $\chi_M$  vs.  $T$  (red) and  $\chi_M T$  vs.  $T$  (blue) for (1).



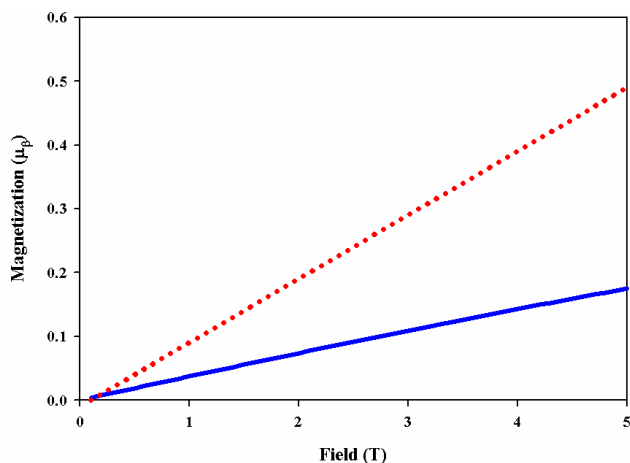


Figure 8. Magnetization curve for (I) at 5 K. The dotted line represents the curve predicted by the Brillouin function with  $S = 1/2$  and  $g = 2.19$ .

## Conclusions

The present work shows that the NAPPR<sup>-2</sup> as a tetradentate N<sub>2</sub>O<sub>2</sub> donor Schiff base forms a really novel one-dimensional copper(II) coordination polymer with single end-on azido bridges. In addition to considering that the occurrence of a single EO azido bridge is very rare, what is reporting for the first time is the existence of two structurally different copper(II) centers, one with a distorted square pyramidal (Cu1) and the other with a distorted trigonal bipyramidal (Cu2) geometry, are interlinked by single end-on azido bridges. According to completely different donor atoms, Cu1 adopts a distorted square-pyramidal environment containing the two N-atoms and two of the O-atoms of the NAPPR<sup>-2</sup> ligand in the basal plane and an azide anion apically coordinated and Cu2 a distorted trigonal-bipyramidal geometry consisting of two O-atoms of the NAPPR<sup>-2</sup> ligand and one N-atoms of the azide bridge in the basal plane and two azide anions apically coordinated.

In the electronic absorption spectrum of this compound, appearance of two bands in the visible region at 598 and 686 nm corresponding to a  $d \rightarrow d$  transition for Cu1(square-pyramid) and Cu2(trigonal-bipyramid) centers, respectively confirms the existence of two copper(II) ions with different donor atoms and coordination geometries.

Due to the existence of two types of copper(II) centers in this complex, the cyclic voltammogram shows two cathodic peaks ( $E_{pc}$ ) at +0.11 and -1.10 V with a peak-to-peak separation ( $\Delta E$ ) 74 and 151 mV corresponding to the electrochemically reversible and quasi-reversible reduction process of Cu<sup>II</sup>/Cu<sup>I</sup> for Cu2(salt-like complex) and Cu1(Schiff-base complex) centers, respectively and this large difference between the redox potentials of the two copper centers (1.21 V) with different coordination geometries, is an interesting case reported for the first time.

Study of the magnetic properties of the copper(II) coordination polymer and the temperature- and field-dependent magnetic analyses reveal that antiferromagnetic interactions between Cu2 centers are mediated by the single EO bridges, while Cu1 moments remain paramagnetic. This result is reasonable, according to a branched chain structure model that Cu2-Cu2 connections through azido bridge continue endlessly as a chain, but Cu1-Cu2 connections with magnetically very small interaction are isolated.

## Experimental Section

### Materials and general methods

All solvents and chemicals were purchased from commercial sources and used as received. Elemental analyses were performed on a Perkin-Elmer 2400II CHNS-O elemental analyzer. Infrared spectra (KBr pellets) were obtained on an FT-IR JASCO 680 plus spectrophotometer. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer. Proton NMR spectra were measured on a Bruker AVANCE DR X500 spectrometer (500 MHz). <sup>1</sup>H chemical shifts are reported in ppm relative to Me<sub>4</sub>Si as internal standard. The magnetic susceptibility of the complex was measured in the 5–300 K temperature range with a Quantum Design MPMS-5 SQUID susceptometer in a 1T magnetic field. The measured susceptibility was corrected for diamagnetism using Pascal's constants ( $-60 \times 10^{-6}$  cgs unit). The redox properties of the complexes were studied by cyclic voltammetry. Cyclic voltammograms were recorded on a SAMA 500 Research Analyzer using three electrodes: a glassy carbon working electrode, a platinum disk auxiliary electrode and a silver wire as reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with  $2.0 \pm 0.1$  mm diameter was manually cleaned with 1  $\mu$ m alumina polish prior to each scan. Tetrabutylammoniumhexafluorophosphate (TBAH) was used as supporting electrolyte. Cyclic voltammetric measurements were performed in N,N-dimethylformamide. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus an internal Fc<sup>+/0</sup> ( $E^0 = 0.45$  V versus SCE) couple under the same conditions.<sup>[28]</sup>

**Synthesis:** Caution! Although our samples never exploded during handling, azide metal complexes are potentially explosive: only a small amount of material should be prepared and it should be handled with care.

**Synthesis of the ligand, H<sub>2</sub>NAPPR:** Typical procedures for tetradentate Schiff base synthesis are as follows: a solution of 0.1 mol diamine in 50 ml methanol was slowly added to 0.2 mol 2-hydroxy-1-naphthaldehyde in 50 ml methanol. After slow stirring for 2 h, the yellow precipitate was collected by filtration.<sup>[29]</sup> Yield 97%. Anal. Calc. for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.51; H, 5.80; N, 7.32; Found: C, 78.50; H, 5.94; N, 7.34%. FT-IR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 3427 (O-H), 1626 (C=N), 1542 (C=C), 1207 (C-O). UV-Vis:  $\lambda_{max}$  (nm) ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>) (DMF): 423 (13400), 403 (13000), 307 (17300).

**Synthesis of [Cu<sub>2</sub>( $\mu$ -NAPPR)( $\mu_{1,1}$ -N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (I):** To 10 mL of a methanolic solution of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.399 g, 2 mmol) was added 0.38 g (1 mmol) of H<sub>2</sub>NAPPR dissolved in 5 mL methanol, and the resulting green solution was stirred for 30 min. A solution of NaN<sub>3</sub> (0.65 g, 10 mmol) in 5 mL of MeOH was then added slowly to the above mixture. The brown solution was left undisturbed at room temperature, and red-brown crystals appeared after one day. The crystals were collected by filtration and washed with methanol. Yield 84%. Anal. Calc. for C<sub>25</sub>H<sub>20</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>2</sub>: C, 50.75; H, 3.41; N, 18.94. Found: C, 49.47; H, 3.24; N, 18.82%. FT-IR (KBr, cm<sup>-1</sup>)  $\nu_{max}$ : 2054 (s, bridging N3), 1618 (s, C=N), 1547 (C=C), 1191 (C-O). UV-Vis:  $\lambda_{max}$  (nm) ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>) (DMF): 686 (69), 598 (141), 401 (14700), 378 (19900), 315 (41100).

### X-ray crystallography

Crystals of (I) suitable for X-ray crystallography were grown by slow evaporation of methanolic solutions at room temperature. Diffraction data for this complex were collected at SNBL-ESRFT = 100 K on a MAR345 image plate system, using a wavelength of 0.69711 Å prepared by means of Si(111) mirrors. Cell refinement, data reduction and a numerical absorption correction were performed with the help of the program CrysAlis (Version 1.171.35).<sup>[30]</sup> The structure was solved with direct methods using the program SHELXS-97 and structure refinement on  $F^2$  was carried out with the program SHELXL-97.<sup>[31]</sup> The crystallographic and refinement data are summarized in Table 3 for [Cu<sub>2</sub>( $\mu$ -NAPPR)( $\mu_{1,1}$ -N<sub>3</sub>)<sub>2</sub>]<sub>n</sub>. Crystallographic

data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, [CCDC No. ?](https://www.ccdc.cam.ac.uk/data_request/cif). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](https://www.ccdc.cam.ac.uk/data_request/cif).

Table 3. Crystal and refinement data of  $[\text{Cu}_2(\mu\text{-NAPPR})(\mu_{1,1}\text{-N}_3)_2]_n$

Empirical Formula	$\text{C}_{25}\text{H}_{20}\text{Cu}_2\text{N}_8\text{O}_2$
Formula weight	591.57
Temperature (K)	100(2)
Crystal system	Monoclinic
Space group	$P2_1$
$a$ (Å)	11.41500
$b$ (Å)	7.68300
$c$ (Å)	13.49300
$\beta$ (°)	95.60
$V$ (Å <sup>3</sup> )	1177.71
$Z$	2
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.668
$\mu$ (mm <sup>-1</sup> )	1.848
Crystal size (mm)	0.15 × 0.03 × 0.01
$F(000)$	600
$\theta$ Range (°)	2.5–26.0
Index range	$-14 \leq h \leq 14$ , $-9 \leq k \leq 9$ , $-16 \leq l \leq 16$
Absorption correction	empirical
Reflections collected	16665
Independent reflections ( $R_{\text{int}}$ )	4606 (0.061)
Maximum and minimum transmission	0.98, 0.76
Data/restraints/parameters	4606 / 1 / 334
Goodness-of-fit on $F^2$	1.025
Final $R$ indices [ $> 2\sigma(I)$ ]	$R_1 = 0.0404$ , $wR_2 = 0.0951$
$R$ indices (all data)	$R_1 = 0.0444$ , $wR_2 = 0.1005$
Largest difference peak and hole (e.Å <sup>-3</sup> )	0.91 and -0.98

## Acknowledgments

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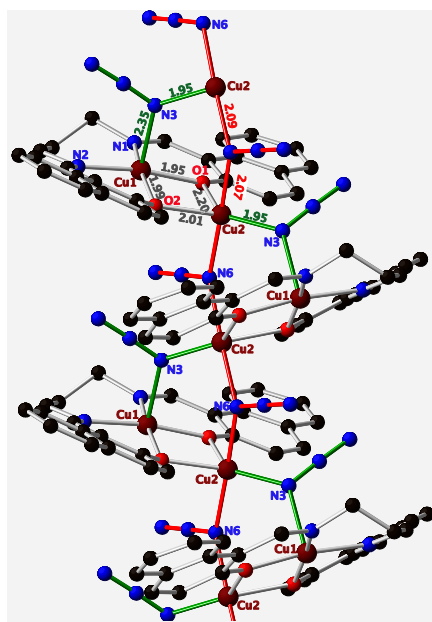
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## Entry for the Table of Contents

### Layout 1:

Interesting crystal structure, electrochemical and magnetic properties of a novel one-dimensional copper(II) coordination polymer with single end-on azido bridges. In addition to considering that the occurrence of a single EO azido bridge is very rare, what is reporting for the first time is the existence of two structurally different copper(II) centers.



Farzaneh Fadaee,<sup>[a,c]</sup> Mehdi Amirnasr,<sup>\*[a]</sup> Krunoslav Prša,<sup>[b]</sup> Philip Pattison,<sup>[c]</sup> Henrik Rønnow,<sup>[b]</sup> Kurt Schenk-Joß<sup>[c]</sup>

The first and novel example of a rare 1D-copper(II) complex containing only single end-on azido bridges: crystal structure, electrochemical and magnetic properties

**Keywords:** Copper(II) / Crystal structure / Single end-on azido bridge / Magnetic properties / Cyclic voltammetry



## Supporting Information

### Supplementary Figures (just for the reviewers' kind consideration):

- Fig. 1-S-1. IR spectrum of H<sub>2</sub>NAPPR (KBr pellet) ..... 9  
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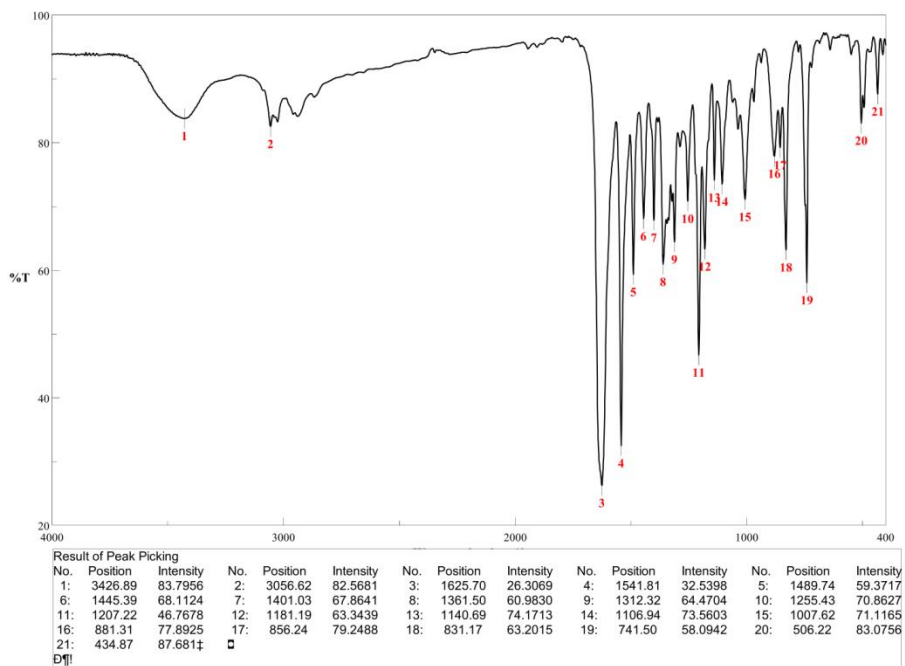


Fig. 1-S-1. IR spectrum of H<sub>2</sub>NAPPR (KBr pellet).

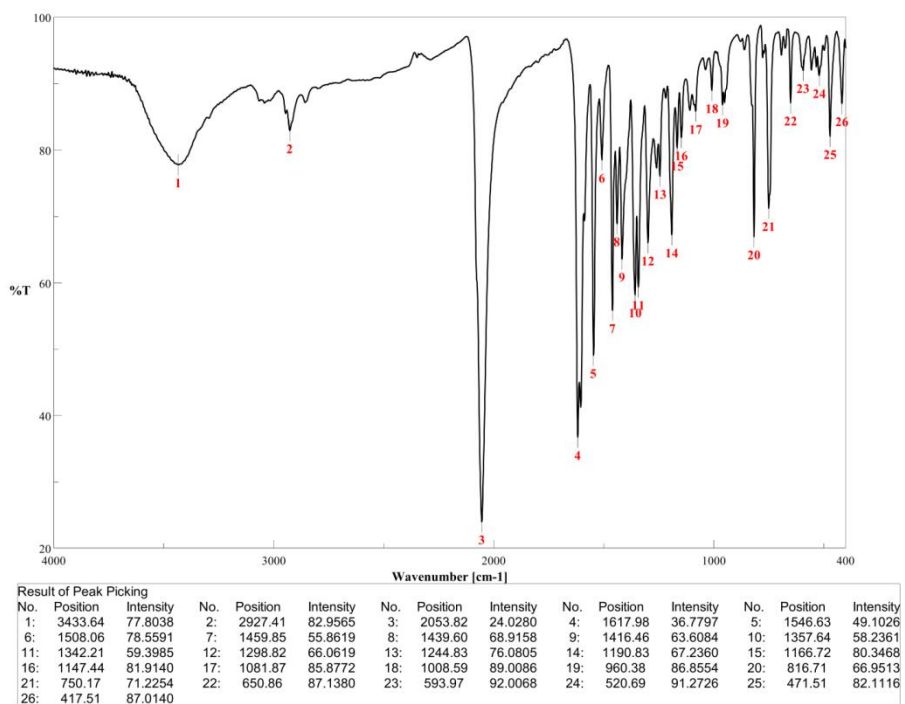
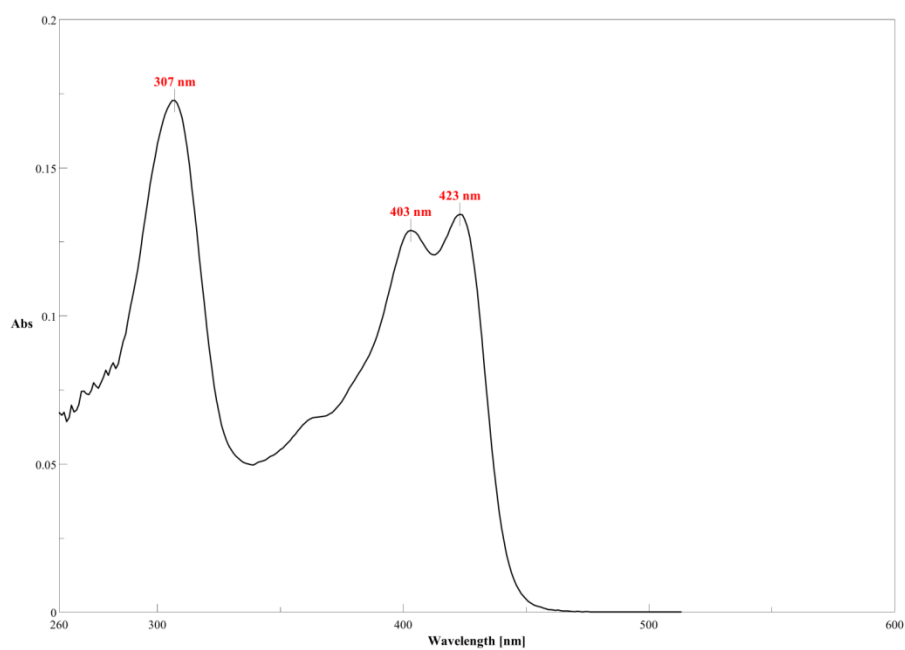
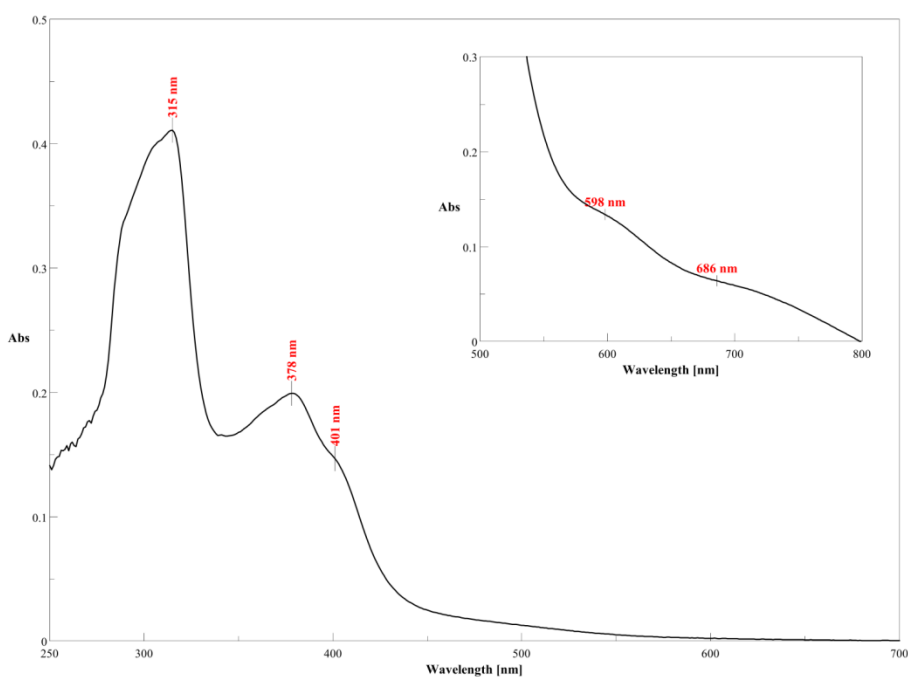


Fig. 1-S-2. IR spectrum of [Cu<sub>2</sub>(μ-NAPPR)(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (KBr pellet).



**Fig. 2-S-1.** UV-Vis spectrum of H<sub>2</sub>NAPPR in DMF solution.



**Fig. 2-S-2.** UV-Vis spectrum of [Cu<sub>2</sub>(μ-NAPPR)(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> in DMF solution.