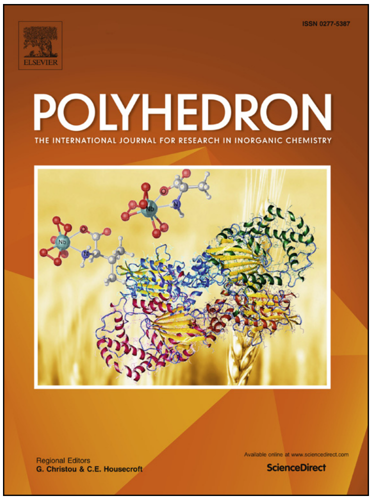

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H-bond assisted coordination bond formation in the 1D chains based on azido and phenoxido bridged tetranuclear Cu(II) complexes with reduced Schiff base ligands

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ABSTRACT

Two new 1D chains $[(CuL^{1R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2]_n$ (**1**) and $[\{(CuL^{2R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2\}\cdot(CH_3)_2CO]_n$ (**2**) based on rare $\mu_{1,1,3}$–N_3 bridged tetranuclear Cu(II) complexes, have been synthesized using $[CuL^{1R}]$ and $[CuL^{2R}]$ as "metalloligands" [where H_2L^{1R} = N,N′-bis(2-hydroxybenzyl)-1,3-propanediamine and H_2L^{2R} = N,N′-bis(2-hydroxybenzyl)-1,2-ethylenediamine]. Both complexes have been characterized by elemental analysis, spectroscopic methods, single crystal XRD, and magnetic study. In case of chain **1**, the basic building block is a centrosymmetric tetranuclear unit whereas for **2**, it is an asymmetric tetranuclear unit containing two types of square pyramidal Cu(II) centres (terminal and central). The $\mu_{1,1}$-N_3 bridged central copper atoms of one tetranuclear unit are connected weakly to the axial position of the terminal copper atoms of neibouring units *via* the azide ions forming a rare $\mu_{1,1,3}$-N_3 bridged novel 1D polymeric chain structure. Variable temperature magnetic susceptibility measurements show the presence of an overall strong antiferromagnetic exchange interactions mediated through the double phenoxido bridges with J values of -123.8 and -144.6 cm^{-1} for **1** and **2**, respectively.

Keywords: Reduced Schiff base; Cu(II); 1D Chain; H-bonding interaction; Antiferromagnetic

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1. Introduction

Since the last few decades, there is a growing interest in the synthesis, structural characterization, and magnetic properties of polynuclear spin-coupled paramagnetic transition metal complexes exhibiting ferro- and antiferromagnetic spin-exchange interactions [1]. There are various strategies to synthesize such polynuclear complexes; one of them is to use the neutral chelate complex of a divalent transition metal ion with different N_2O_2 donor tetradentate di-Schiff base ligands (*e.g.* salen = N,N'-ethylenebis(salicylideneimine), salpn = N,N′-bis(salicylidene)-1,3-propanediamine*etc*...) [2]. The phenoxido oxygen atoms of the coordinated Schiff base are capable of coordinating another transition metal ion to form multinuclear complexes in which these chelates act as ‘‘metalloligand’’. Several homo- and hetero-metallic complexes have been synthesized using this ‘‘metalloligands’’ synthetic approach by different groups including ours [3]. Among the homo-nuclear Cu(II) complexes, various species ranging from discrete dinuclear to hexanuclear as well as polymer are reported with a number of anionic bridges *e.g.* cyanide, thiocyanate, isocyanate, dicyanamide, azide, carboxylate, *etc*...[4]. Most of these bridges can mediate strong magnetic exchange between the metal ions. Recently, we have found that complexes of reduced Schiff bases can also be used as “metalloligands” and in some cases the resulting species showed interesting structural variations compared to their unreduced analogues [5].

A special attention has been paid into the study of azido-bridged metal complexes in the field of molecular magnetism [6]. The motivation in synthesizing new metal-azido complexes comes from the versatility of bonding modes of this triatomic pseudohalide (*e.g.* $\mu_{1,3}$-N_3(end-to-end), $\mu_{1,1}$-N_3(end-on), $\mu_{1,1,3}$-N_3, $\mu_{1,1,1}$-N_3, and also monodentate fashion) [6-7]. If we consider only the Cu(II) systems, there are a total of 822 Cu-complexes with terminal azido ligands. The numbers of end-on ($\mu_{1,1}$-N_3) and end-to-end ($\mu_{1,3}$-N_3) bridged Cu(II) are 351 and 102, respectively. The complexes with other bridging modes are relatively less. For examples, there are only 13 and 6 Cu(II) complexes with $\mu_{1,1,1}$-N_3 and $\mu_{1,1,3}$-N_3 bridges. All these different bridging modes make azido bridge complexes as one of the most fascinating subjects for studying structural variations and super-exchange pathways of magnetic interactions [7]. In fact, more than one of these bonding modes often co-exists in the same complex resulting discrete polynuclear complexes, one-dimensional (1D) chains, two-dimensional (2D) layers and three-dimensional (3D) frameworks [8-10]. The primary ligands which form the complex along with the azide ion are very important in determining the nuclearity and connectivity of the structures. If we consider the N_2O_2 donor salen type Schiff base ligand, there are only nine azido bridged Cu(II) complexes and interestingly all of them possess very similar discrete tetranuclear structure [11-16]. We are interested in synthesizing similar complexes using N_2O_2 donor reduced Schiff base ligands in order to see if there is any variation in the structures and magnetic properties.

Herein, we report the syntheses, structure and magnetic properties of two novel azido bridged Cu(II) 1D chains, $[(CuL^{1R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2]_n$ (**1**) and $[\{(CuL^{2R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2\}\cdot(CH_3)_2CO]_n$ (**2**), where H_2L^{1R} (N,N′-bis(2-hydroxybenzyl)-1,3-propanediamine) and

H_2L^{2R} (N,N′-bis(2-hydroxybenzyl)-1,2-ethylenediamine) are reduced salen-type Schiff bases. In both structures, $\mu_{1,1}$-N_3 and phenoxido bridged tetranuclear units are connected through azide ion ($\mu_{1,1,3}$-N_3) to form polymeric 1D chains. This type of chain is unprecedented with salen type N_2O_2 donor ligands. Both chains exhibit overall antiferromagnetic exchange interactions within the basic structural units.

2. Experimental

2.1. Starting Materials

The salicylaldehyde, 1,2-ethelenediamine, 1,3-propanediamine and sodium borohydride were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! Azide salts and Perchlorate salts of metal complexes with organic ligands is potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

2.2. Synthesis of the reduced Schiff base ligand, N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine (H_2L^{1R}) and "metalloligand" [CuL^{1R}]

The di-Schiff base ligand from 1,3-propanediamine and salicyldehyde was synthesized by a reported method [17]. 5 mmol of 1,3-propanediamine (0.42 mL) was mixed with 10 mmol of the salicylaldehyde (1.04 mL) in methanol (30 mL). The resulting solution was refluxed for *ca.* 2 h and allowed to cool. Then 30mL (5 mmol) of this prepared yellow methanolic ligand solution (H_2L^1) was cooled to 0°C, and solid sodium borohydride (570 mg, 15 mmol) was added to this methanol solution with stirring. After completion of addition, the resulting solution was acidified with concentrated HCl (12 mL) and then evaporated to dryness [18]. The reduced Schiff base ligand H_2L^{1R} was extracted from the solid mass with methanol, and this colourless methanol solution (*ca.* 30 mL) was added to a methanolic solution (10mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.852 g, 5 mmol) to prepare the "metalloligand" [CuL^{1R}] [19].

2.3. Synthesis of the reduced Schiff base ligand, N,N'-bis(2-hydroxybenzyl)-1,2-ethelenediamine (H_2L^{2R}) and "metalloligand" [CuL^{2R}]

The reduced di-Schiff base ligand (H_2L^{2R}) was synthesized by the same procedure as described above for N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine (H_2L^{1R}) using 1,2-ethelenediamine instead of 1,3-propanediamine. The colourless methanol solution (*ca*. 30 mL) of H_2L^{2R} was used for the preparation of a “metalloligand” (CuL^{2R}) following a procedure similar to that for [CuL^{1R}].

*2.4. Syntheses of the complexes $[(CuL^{1R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2]_n$ (**1**) and $[\{(CuL^{2R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2\}\cdot(CH_3)_2CO]_n$ (**2**)*

The precursor complex [CuL^{1R}] (0.348 g, 1 mmol) was dissolved in methanol (20 mL) and then a water solution (2 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.370 g, 1 mmol), followed by an aqueous solution (1 mL) of sodium azide (0.130 g, 2 mmol), was added to this solution. The mixture was stirred for 1 h and then filtered. The filtrate was allowed to stand over night when prism shaped dark red coloured X-ray quality single crystals of **1** appeared at the bottom of the beaker. Similarly, needle shaped single crystals of **2** were obtained by following the same procedure for **1**, but using the “metalloligand” (CuL^{2R}) the instead of [CuL^{1R}]. The crystals (**1** and **2**) were re-crystallised from acetone-water mixture and dried in a desiccator containing anhydrous $CaCl_2$ and then characterized by elemental analysis, spectroscopic methods, and X-ray diffraction.

Complex **1**. Yield: 0.366 g, 74%. Anal. Calc. [$C_{34}H_{40}Cu_4N_{16}O_4$]: C 41.21; H 4.07; N 22.61; found: C 41.32; H 4.25; N 22.85%; UV/vis: [λ_{max} in nm (solid, reflectance)] = 645 and 398. IR (KBr) in cm^{-1}: ν(N-H) 3226, ν(N_3) 2069 and 2039.

Complex **2**. Yield: 0.356 g, 68%. Anal. Calc. [$C_{35}H_{42}Cu_4N_{16}O_5$]: C 47.17; H 4.15; N 21.95; found: C 47.26, H 4.23, N 21.92%; UV/vis: [λ_{max}in nm (solid, reflectance)] = 541 and 399. IR (KBr) in cm^{-1}: ν(N-H) 3239, ν(N_3) 2065 and 2039.

2.5. Physical Measurements

Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–500 cm^{-1}) were recorded using a Perkin- Elmer RXI FT-IR spectrophotometer. Electronic spectra in solid state (1000-300 nm) were recorded in a Hitachi U-3501 spectrophotometer. The magnetic measurements were carried out in the ‘‘Servei de Magnetoquímica (Universitat de Barcelona)” on polycrystalline samples with a

Quantum Design SQUID MPMSXL magnetometer in the temperature range of 2-300 K. The experimental magnetic susceptibility data are correctedfor the diamagnetism estimate from Pascal’s tables.

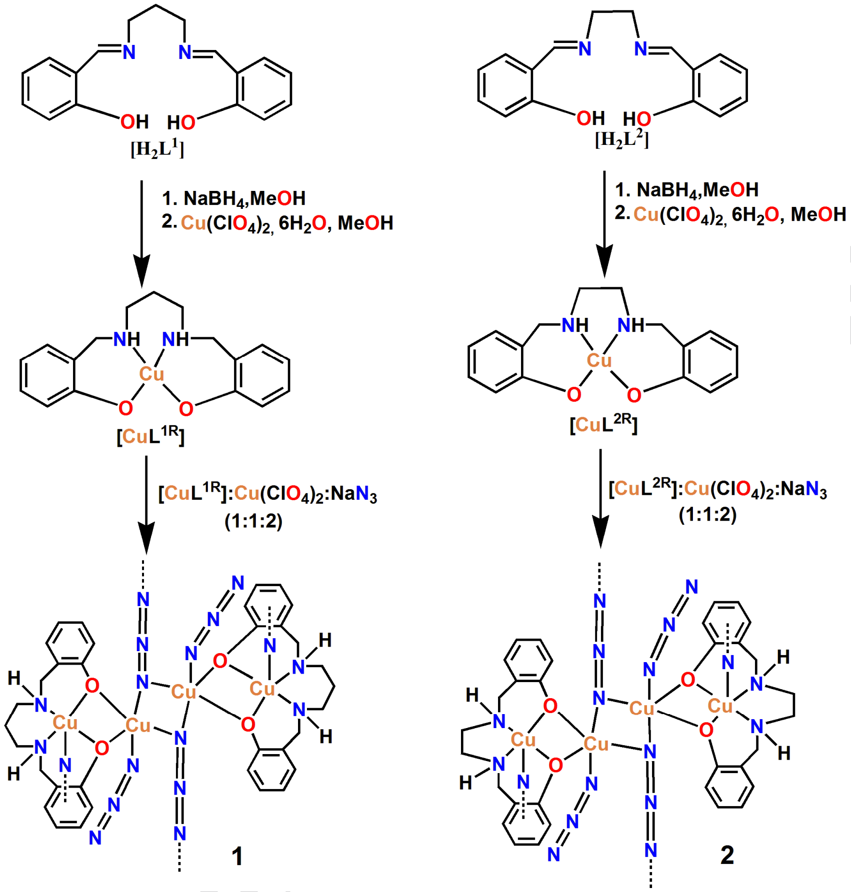
2.6. Crystallographic data collection and refinement

Well formed single crystals of each complex was mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.71073 Å) radiation. The crystals were positioned 60 mm from the CCD, and frames (360) were measured with a counting time of 5 s. The structures were solved using the Patterson method through the SHELXS 97 program. Non hydrogen atoms were refined with independent anisotropic displacement parameters, while difference Fourier synthesis and least-squares refinement showed the positions of any remaining non-hydrogenatoms. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 (or 1.5 for methyl groups) times those of the atom to which they were attached. Hydrogen atoms that bonded to N or O were located in a difference Fourier map and refined with distance constraints. We squeezed the disorder solvent molecule acetone present in complex **2**. Hope, this revised cif is now of publication standard.Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least-squares refinement. Absorption corrections were carried out using the SADABS program [20], while all calculations were made *via* SHELXS 97 [21], SHELXL 97 [22], PLATON 99 [23], ORTEP-32 [24], WINGX system ver-1.64 [25] and refined using SHELXL-2014 [26]. Data collection, structure refinement parameters, and crystallographic data for the two complexes are given in Table 1.

3. Results and Discussion

3.1. Syntheses of the Complexes

The Cu(II) complexes, [CuL^{1R}] and [CuL^{2R}] of the reduced Schiff-base ligands (H_2L^{1R} and H_2L^{2R}) were synthesized using the reported procedures. Both the “metalloligands”, [CuL^{1R}] and [CuL^{2R}], on reaction with copper perchlorate hexahydrate and sodium azide in 1 : 1 : 2 molar ratio in a MeOH-H_2O medium (10 : 1, v/v) resulted in two new 1D Cu-azide chain complexes, $[(CuL^{1R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2]_n$ (**1**) and $[\{(CuL^{2R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2\}\cdot(CH_3)_2CO]_n$ (**2**) (Scheme 1)



Scheme 1. Syntheses of complexes **1** and **2**.

3.2. IR and UV−Vis Spectra

Besides elemental analysis, two complexes were initially characterized by the IR spectra. A moderately strong and sharp peak at 3226 and 3239 cm^{-1} (due to a N−H stretching vibration) for complexes **1** and **2**, respectively and absence of any peak at around 1620 cm^{-1}, (Figs. S1 and S2) indicate that the imine group of the Schiff base is reduced. In addition, the presence of azido ligands in both complexes is confirmed by the appearance of strong and sharp peaks at 2069 and 2065 cm^{-1} along with shoulders at 2039 cm^{-1} in the spectra of **1** and **2** respectively (Figs. S1 and S2). The splitting of the band is indicative of the presence of two different coordinated azido ions in agreement with their crystal structures.

The electronic spectra of these two compounds were recorded in the solid state (Fig. S3). Compounds **1** and **2** show broad absorption bands at 645 and 541 nm, respectively, while the band maxima for “metalloligands” [CuL^{1R}] and [CuL^{2R}] appear at 697 and 593 nm, respectively. These bands are attributed to d–d transitions of Cu(II) ions. In addition, the these two compounds show a sharp single absorption maximum near 398 and 399 nm for **1** and **2**, respectively, and the two “metalloligands” [CuL^{1R}] and [CuL^{2R}] show absorption maxima at 401 and 394 nm, respectively, attributed to ligand-to-metal charge transfer transitions.

3.3. Description of the Structures

*3.3.1. Complex **1***

The X-ray crystal structure shows that complex **1** is a rare $\mu_{1,1,3}$-N_3 bridged 1D polymeric chain (Fig. 1) based on centrosymmetric tetranuclear [$(CuL^{1R})_2Cu_2(N_3)_2(\mu_{1,1,3}$-$N_3)_2$] unit. The basic tetranuclear unit is depicted in Fig. 2.

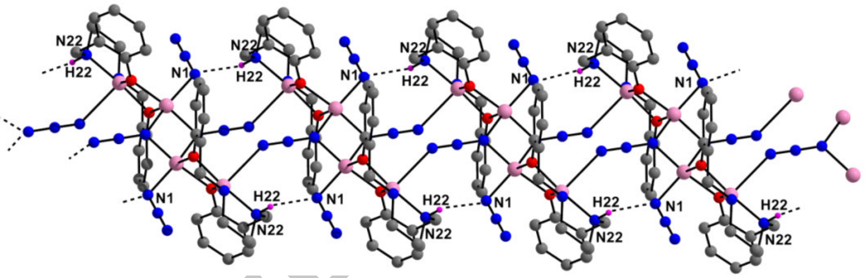


Fig. 1. 1D supramolecular chain structure of complex **1**. Chain formation of **1** is facilitated by N22–H22---N1, H-bonding interactions. Other H-atoms are removed for clarity.

Selected bond lengths and angles of the repeating tetranuclear basic unit of the chain are listed in Table 2. In this basic unit, the terminal copper centre [Cu(1)] has a distorted square pyramidal geometry. The equatorial plane is formed by the two imine N-atoms and two phenoxido O-atoms. The basal Cu−N bond distances are greater than the basal Cu−O distances (Table 2). The axial position is weakly occupied by a nitrogen atom of a triply bridging azido-anion ($\mu_{1,1,3}$-N_3) from a neighboring unit at a distance of 2.592(7) Å. The range of *cis* [81.7(2)−106.0(2)°] and *trans* angles [162.8(2)−171.5(2)°] (Table 2) around this Cu center are indicative of the deviation from the ideal square pyramidal geometry. The deviation of this geometry from square pyramid to trigonal bipyramid has been calculated by the Addison parameter (τ) [27]. The value of τ is defined as the difference between the two largest donor-metal-donor angles divided by 60, τ is 0 for the ideal square pyramid and 1 for the trigonal bipyramid. The τ value of Cu(1) is 0.145, indicating that the geometry is slightly distorted from its ideal square pyramidal geometry. The distortion around Cu(1) is also apparent from the dihedral angle (17.1(1)°) between the two N–Cu–O planes and the r.m.s. deviation (0.187Å) of the four equatorial donor atoms from their mean coordination plane.

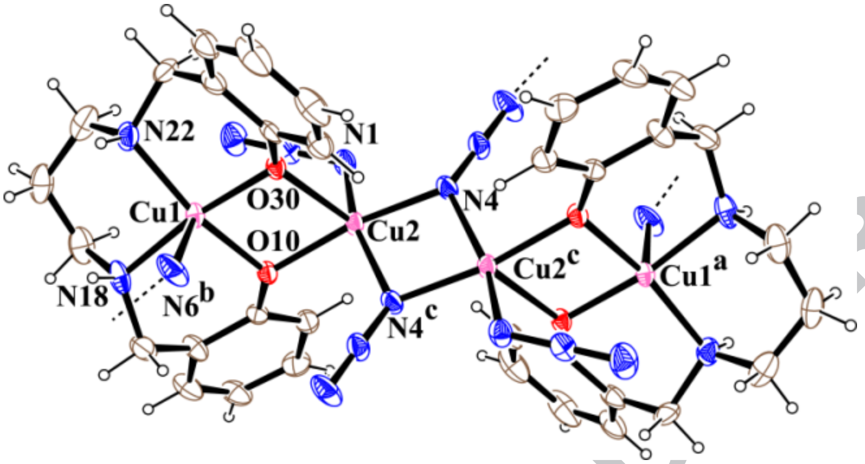


Fig. 2. Ortep structure of the tetranuclear basic unit of chain complex **1** with ellipsoids at 30% probability. Symmetry element ^{a} = x,-1+y,z; ^{b} = x,1+y,z; ^{c} = 1-x,-y,1-z.

The central copper atom [Cu(2)] also presents a distorted square pyramidal geometry like the terminal one. Here, the equatorial plane is formed by the two N atoms from $\mu_{-1,1,3}$ bridging azides, one N-atom of terminally coordinated azido ligand and one μ_2–phenoxido O-atom; the axial position is occupied by another μ_2-phenoxido O–atom of tetradentate reduced Schiff-base ligand. The equatorial Cu−N/O bond distances are smaller than the axial Cu−O bond distance (Table 2). The range of *cis* [75.1(2)−108.9(2)°] and *trans* angles [158.2(2)−170.3(2)°] around central Cu atoms indicates that it suffers a distortion from the ideal square pyramidal geometry like the terminal ones. The distortion from the ideal square pyramidal geometry of Cu(2) is also apparent from the Addison parameter (τ = 0.202), the r.m.s. deviation (0.152 Å) of the four equatorial donor atoms from their mean coordination plane and the dihedral angle between O30−Cu2−N4 and N1−Cu2−N4^c planes (20.8(1)°).
Along with the $\mu_{-1,1,3}$ azido bridge, the tetranuclear units are also connected by the strong intermolecular H-bonding interaction (see Table 3) between one of the H-atom of reduced imine moiety of one unit and the coordinated N-atom of the terminal azido ligand of another unit (Fig. 1) reinforcing the formation of the 1D chain.

*3.3.2. Complex **2***

Complex **2** having molecular formula $[\{(CuL^{2R})_2Cu_2(N_3)_2(\mu_{1,1,3}\text{-}N_3)_2\}\cdot(CH_3)_2CO]_n$, also possesses a polymeric chain structure (Fig. 3) in which the central copper atoms of one tetranuclear unit (Fig. 4) are connected weakly to the terminal copper atom of another unit by $\mu_{1,1,3}$-N_3 bridge like **1**. However, unlike **1** the tetranuclear unit is asymmetric in **2**.

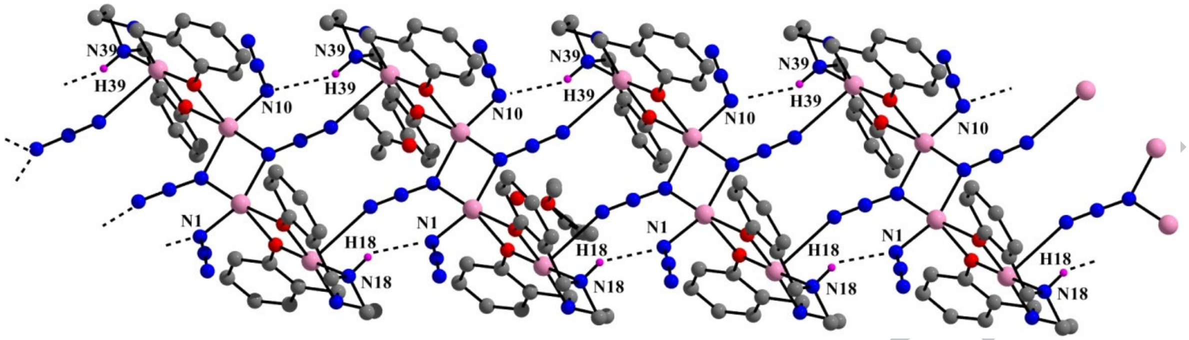


Fig. 3. 1D supramolcular chain structure of complex **2**. H-bondings interactions (N1---H18–N18 and N10---H39–N39) reinforce in the formation of 1D chain. Other H-atoms are removed for clarity.

The selected bond parameters of the basic tetranuclear unit are summarized in Table 2. The terminal copper centres have the distorted square pyramidal geometry like **1**. The basal plane of each copper atom is formed by the two imine N-atoms and two phenoxido O-atoms from dianionic tetradentate reduced Schiff-base ligand $[(L^{2R})^{2-}]$ and the axial position is weakly coordinated by a nitrogen atom of a bridged azido-anion ($\mu_{1,1,3}$-N_3) at a distance, Cu(1)/Cu(4)−N(9)/N(6) 2.779(9) Å / 2.782(9) Å which is slightly greater than that in complex **1**. The basal Cu−N bonds are larger than the Cu-O ones like **1** (Table 2). The range of *cis* [84.9(2)–94.8(4)° for Cu(1) and 84.1(2)–95.3(3)° for Cu(4)] and *trans* angles [174.6(4)–176.3(4)° for Cu(1) and 173.4(3)–177.3(3)° for Cu(4)] around these Cu centers, the Addison parameters (τ = 0.028 and 0.065 for Cu(1) and C(4) respectively), the dihedral angles between the two N–Cu–O planes (6.8(3) and 6.6(2)° for Cu(1) and Cu(4), respectively) and r.m.s. deviation of the four equatorial donor atoms from their mean coordination plane (0.015 and 0.052 Å for Cu(1) and Cu(4), respectively) of **2** show that here the terminal metal centres are less distorted than that in **1**.

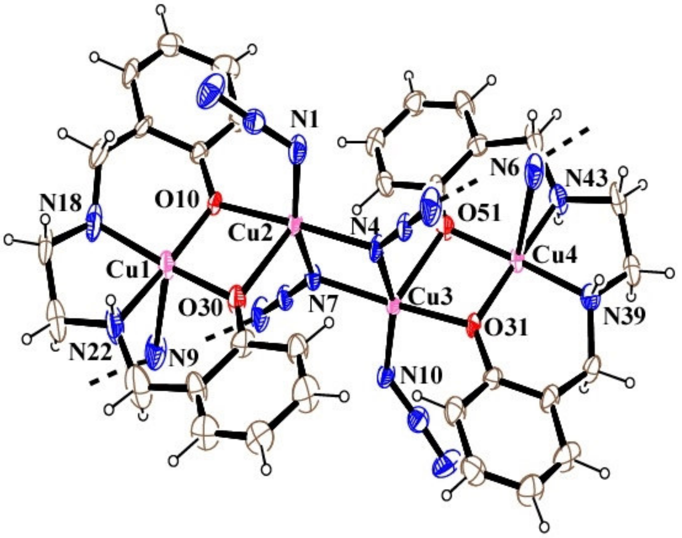


Fig. 4. Ortep picture of the basic tetrameric building unit of chain **2** with ellipsoids at 30% probability. Acetone solvent molecules are removed for clarity.

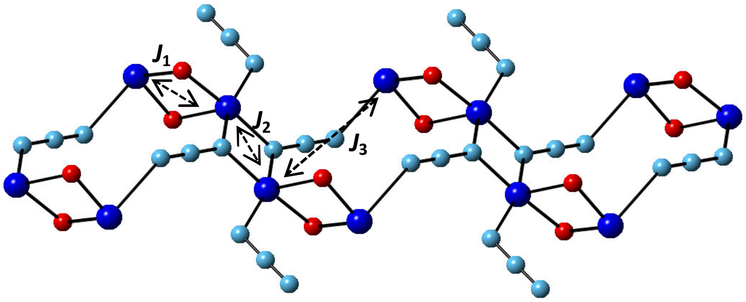
Both the central copper atoms [Cu(2) and Cu(3)] present a distorted square pyramidal geometry like **1**, where the equatorial plane is formed by the two N atoms from $\mu_{-1,1,3}$ azides, one N-atom of terminally coordinated azido ligand and one μ_2-phenoxido O-atom; the axial position is occupied by another μ_2-phenoxido O-atom of tetradentate reduced Schiff-base ligand. The axial Cu–O bond distances of each of the central Cu-atoms are considerably longer than the equatorial Cu–O/N distances as in **1** (Table 2). The range of *cis* [72.7(2)–108.6(3)° for Cu(2) and 75.1(2)–106.1(3)° for Cu(3)] and *trans* angles [160.1(3)–172.9(3)° for Cu(2); 157.6(4)–173.8(3)° for Cu(3)], the Addison parameters, τ (0.2116 and 0.2733 for Cu(2) and Cu(3) respectively), the r.m.s. deviations (0.130 and 0.155 Å for Cu(2) and Cu(3), respectively) of the four equatorial donor atoms from their respective mean coordination plane and the dihedral angles between two N–Cu–N and N–Cu–O planes (17.8(4) and 19.1(4)° for Cu(2) and Cu(3) respectively) indicate that these two copper centres have slightly less distortion from the ideal square pyramidal geometry than that in **1**.

Like **1**, here also intermolecular H-bonding interactions (see Table 3) are observed (Fig. 3) between one of the H-atom of reduced nitrogen of one unit and N-atom of a terminal azido ligand of another unit which facilitate the formation of the 1D chain.

Literature shows that nine tetranuclear Cu(II) complexes similar to the basic tetranuclear units of the present complexes have been reported till date. It is interesting to note that all these tetranuclear species are discrete and have been synthesized using unreduced N_2O_2 donor Schiff base ligands. The bridging patterns in all these nine complexes are the same: two central Cu(II) are connected with each other by double $\mu_{1,1}$-N_3 bridge and with terminal Cu(II) by double phenoxido bridge. For the synthesis of the present complexes, we used reduced N_2O_2 donor Schiff base ligands. The H atom which is added to the N-atom on reduction of C=N moiety has the strong potential for H-bond formation. There are several O and N atoms in the molecule which can act as acceptor for H-bond. However, the crystal structures clearly show that H-bond is formed by the coordinated N-atom of the terminal monodentate azide ion presumably because such orientation of the molecules facilitates the coordination bond formation by the other terminal N-atom of the $\mu_{1,1}$-N_3 to the axial position of the Cu(II). Thus, the $\mu_{1,1}$-N_3 bridging mode of azide which remained unchanged in all nine complexes of Schiff base ligands changes to $\mu_{1,1,3}$-N_3 bridging mode in the present complexes with the assistance of H-bond formation. This synergy between H-bond and coordinate bond links the neighboring tetranuclear units by four bridges (two azido bridges and two H-bonded) to stabilize the 1D structures of **1** and **2** (Figs. 1 and 3) .

3.4. Magnetic properties

From structural point of view complexes, **1** and **2** are 1D coordination polymer consisting of centrosymmetric tetranuclear units for **1** and asymmetric tetranuclear unit for **2**. The tetranuclear entities are linked through weakly coordinated asymmetric $\mu_{1,1,3}$-azido bridges. In the tetranuclear units, the copper (II) ions are connected by pairs through a double phenoxo bridge given dinuclear entities which are further connected by two $\mu_{1,1}$-azido bridge. Two possible exchange pathways are present in the tetranuclear entity (Scheme 2): i) the double phenoxo bridge in axial-axial position (J_1), and ii) the double $\mu_{1,1}$-azido bridge in axial-axial position (J_2).



Scheme 2. Possible exchange pathways present in the tetranuclear unit.

A search in the CCDC data base shows that there exist nine Cu^{II} tetramers presenting similar double μ-phenoxo and $\mu_{1,1}$-azido bridges [11-16]. Only four of them has been magnetically characterized [11(a)-13].

Magnetostructural correlations in dinuclear copper(II) complexes bridged equatorially by pairs of hydroxide or alkoxide [28,31] groups show that the major factor controlling spin coupling between the S = 1/2 metal centres is the Cu-O(R)-Cu angle. Hatfield and Hodgson found a linear correlation between the experimental exchange coupling constant and the Cu−O−Cu bond angle, larger Cu−O−Cu angle than 97.6º favours large antiferromagnetic J values [28]. Thompson *et. al.* found differences in μ-hydroxo, μ-alkoxo and μ-phenoxo [32], the slope of the J vs Cu−O−Cu angle plots for the three cases are comparable, but the absolute value of $-J$ are larger for phenoxo than for alkoxo and this is larger than for hydroxo. The main conclusion for phenoxo systems is that, generally, strong antiferromagnetic exchange will dominate in these complexes. For complexes **1** and **2**, the coupling through the phenoxo groups should be antiferromagnetic having a Cu1-O-Cu2 average angle of 101.13º and 101.12° for **1** and **2**, respectively.

Density functional calculations (DFT) show that the nature of coupling between two copper ions with $\mu_{1,1}$-azido bridges depends on two parameters, the Cu-N-Cu angles and the Cu-N distances [33,34]. If the Cu-N-Cu is in the 96º-104º range, the interaction is ferromagnetic; otherwise is antiferromagnetic. The ferromagnetic coupling decreases as the Cu-N distance increases, at distances larges than 2.05 Å the coupling becomes antiferromagnetic. In complexes **1** and **2**, the coupling through the double $\mu_{1,1}$-azido bridge should be ferromagnetic having a Cu-N-Cu angles of 101.24º and of 102.38°, and Cu-N average distances of 1.98 and 2.01 Å, for **1** and **2**, respectively.

An additional exchange pathways exist between the tetranuclear entities (J_3) through a weakly coordinated asymmetric $\mu_{1,3}$-azido bridge in axial-equatorial fashion, that involved two copper(II) ions of two neighbouring tetranuclear entities (Scheme 2), with Cu-N distance equal to 2.592 Å for **1** and 2.779(9) Å / 2.782(9) for **2**. According to the literature data [35,36], we can assumed, in a first approach, that the antiferromagnetic coupling through the $\mu_{1,3}$-azido bridges are negligible as compared with the expected strong antiferromagnetic coupling through the double phenoxo bridges, thus, the coupling scheme is reduced to the two different coupling constants (J_1, J_2) into the tetranuclear unit.

Considering the structural parameter in the tetranuclear units, a strong antiferromagnetic coupling (J_1) through the double phenoxo bridge and a moderate ferromagnetic coupling (J_2) through the double $\mu_{1,1}$-azido bridge were expected. To study the correlation between both exchange coupling a simulation of $\chi_M T$ vs T, using the PHI program [37], was performed, fixing the J_1 value at 120 cm^{-1} and the g value as 2.2 and varying the J_2 value between 0 and +40 cm^{-1} (Fig. 5).

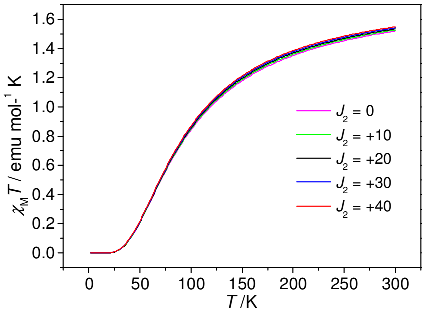


Fig. 5. Theoretical curves obtained by PHI program (see text) for different J_2 values considering J_1 = 120 cm^{-1}, and g = 2.2.

The simulation was performed according to the following Hamiltonian:

$$H = -J_1 (S_1S_2+S_3S_4) - J_2(S_2S_3)$$

As expected, the variation of $\chi_M T$ *vs T* with these ferromagnetic J_2 values is not noticeable. Therefore the global exchange interaction in complexes **1** and **2** will be expected to depend predominantly on the double μ-phenoxo bridge.

The temperature dependence of $\chi_M T$ *vs* T for complexes **1** and **2** (referred to the two copper ions) in an applied field of 10000 and 500 G in the temperature range of 2-300 K and 2-30 K, respectively, is shown in Figs. 6 and 7, respectively.

For complex **1**, the $\chi_M T$ value at 300 K, 0.76 cm^3 mol^{-1} K, which is slightly more than that expected for two uncoupled Cu^{II} ion with g = 2 (0.74 cm^3 mol^{-1} K). Upon cooling, the $\chi_M T$ value decreases continuously, reaching a value of 0.023 cm^3 mol^{-1} K at 2 K. The χ_M *versus T* plot exhibits a maximum at 100 K (Fig. 6 inset), indicating an overall antiferromagnetic interaction and the presence of paramagnetic impurities. Considering all the above discussions, the experimental data were fitted to the Bleaney-Bowers expression for an isotropically coupled pair of S = 1/2 ions [38], assuming the isotropic Hamiltonian H = -$J_1S_1S_2$ and introducing a ρ term to evaluate the paramagnetic impurity. The best-fit parameters for reproducing satisfactorily the experimental data, as shown in fig. 6, are: J_1 = -123.8 cm^{-1}, g =2.20, ρ= 2.6% and R = 3x10^{-5}, $R = \Sigma_i(\chi T_{icalc} - \chi T_{iexp})^2/\Sigma_i\ (\chi T_{iexp})^2$.

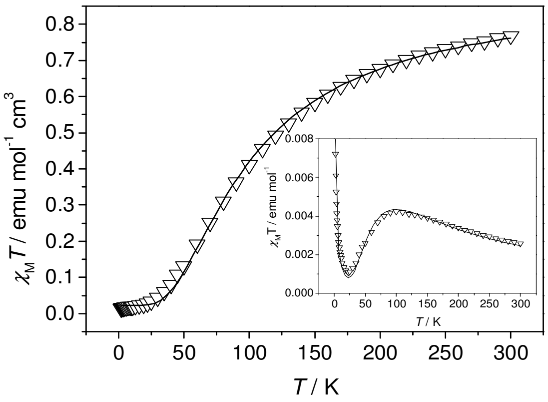


Fig. 6. Temperature dependence of $\chi_M T$ for complex **1**. The solid lines represent the best-fit results with the parameters described in the text. Inset: Temperature dependence of χ_M for complex **1**.

For complex **2**, the $\chi_M T$ value at 300 K, 0.72 cm^3 mol^{-1} K, which is than that expected for two uncoupled Cu^{II} ion with g = 2 (0.74 cm^3 mol^{-1} K). Upon cooling, the $\chi_M T$ value decreases continuously, reaching a value of 0.012 cm^3 mol^{-1} K at 2 K. The χ_M *versus* T plot exhibits a maximum at 130 K (Fig. 7 inset),

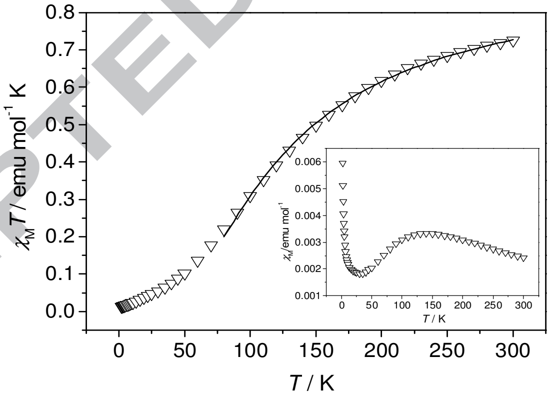


Fig. 7. Temperature dependence of $\chi_M T$ for complex **2**. The solid lines represent the best-fit results, in the 80 K-300 K range, with the parameters described in the text. Inset: Temperature dependence of χ_M for complex **2**.

indicating an overall antiferromagnetic interaction and the presence of paramagnetic impurities. The X-ray experimental diffraction patterns of **2** and the calculate diffraction patterns from the CIF file show the presence of some impurities, so the fit in the overall range of $\chi_M T$ *vs* T values using the Bleaney-Bowers expression for an isotropically coupled pair of S = 1/2 ions [38], do not fit well in the low temperature range. In order to evaluate the J_1

value, the fit was made in the 300-80 K range. The best-fit parameters for reproducing satisfactorily the experimental data, as shown in fig. 7, are: J_1 = -144.6 cm^{-1}, g = 2.18, and R = 4 x 10^{-5}, $R = \Sigma_i(\chi T_{icalc} - \chi T_{iexp})^2/\Sigma_i (\chi T_{iexp})^2$. The J values of complexes **1** and **2** are according with their analogous structural data.

4. Conclusions

We have synthesized and characterized two new Cu(II) azide complexes with reduced salen type Schiff base ligands in order to see if the reduction of the C=N bond has any effect on the structures and magnetic properties of the resulting complexes. The structures of these species are found to be unusual 1D chains based on phenoxido and azido bridged ($\mu_{1,1,3}$-N_3) tetranuclear units in contrast to the discrete phenoxido and azido bridged ($\mu_{1,1}$-N_3) tetranuclear units found in all the reported complexes of unreduced Schiff base ligands. The H atom which is added on the N-atom of reduced Schiff base not only forms strong intermolecular H-bonds between the tetranuclear units but also facilitates the change of most common $\mu_{1,1}$-N_3 bridging mode of azide to the very rare $\mu_{1,1,3}$-N_3 in Cu(II). Hence, in the present complexes, linking of the tetranuclear units takes place with the synergic formation of H-bond and coordination bond to result in the 1D chain which is unprecedented in similar complexes of unreduced Schiff base ligands. The overall magnetic coupling is dominated by strong antiferromagnetic interaction between the double phenoxo bridged Cu(II) ions for both the complexes (**1** and **2**) like the complexes of unreduced ligands, in agreement with their phenoxido bridging angles, Addison parameters and the dihedral angle in the Cu_2O_2 core.

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Appendix A. Supplementary data

CCDC 1565581-1565582 contains the supplementary crystallographic data for **1**–**2**. These data can be obtained free of charge via http://dx.doi.org..., or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-

336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org...

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Table 1

Crystal data and structure refinement of complexes **1** and **2**.

	1	**2**
Formula	$C_{34}H_{40}Cu_4N_{16}O_4$	$C_{35}H_{42}Cu_4N_{16}O_5$
M	990.97	1020.99
Crystal System	Monoclinic	Monoclinic
Space Group	P21/n	Pn
a/Å	13.863(5)	7.970(5)
b/Å	8.001(5)	13.722(5)
c/Å	18.718(5)	20.223(5)
α/°	90	90
β/°	104.877(5)	91.350(5)
γ/°	90	90
V/Å^3	2006.6(15)	2211.1(17)
Z	2	2
D_c/g cm^{-3}	1.640	1.545
μ/mm^{-1}	2.151	1.958
F (000)	1008	1041
R(int)	0.057	0.055
Total Reflections	8719	15415
Unique reflections	3204	6660

$I>2\sigma(I)$	2160	4322
R1^a, wR2^b	0.0475, 0.1285	0.0521, 0.1157
GOF^{c}on F^2	1.05	0.98
R (all)	0.0822	0.0865
Temp (K)	293	293

^{a}R1 = $\sum||F_o|-|F_c||/\sum|F_o|$, ^{b}$w$R2 $(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2/\sum w F_o^4]^{1/2}$ and ^{c}GOF = $[\sum[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{params})]^{1/2}$

Table 2

Bond distances (Å) and angles (°) for complexes **1** and **2**.

	1	**2**		**1**	**2**
Cu(1)–O(10)	1.902(4)	1.890(7)	N(1)–Cu(2)–O(10)	95.1(2)	93.7(3)
Cu(1)–O(30)	1.969(4)	1.877(6)	N(4)–Cu(2)–O(30)	170.3(2)	100.0(3)
Cu(1)–N(18)	2.011(6)	1.954(10)	N(4)^c–Cu(2)–O(30)	91.6(2)	…
Cu(1)–N(22)	1.987(6)	1.970(11)	N(4)–Cu(2)–O(10)	108.9(2)	95.1(3)
Cu(1)–N(6)^b/ N(9)	2.592(7)	2.779(9)	N(4)–Cu(2)–N(7)	…	77.7(3)
Cu(2)–O(10)	1.985(6)	2.244(13)	O(30)–Cu(2)–O(10)	75.1(2)	72.7(2)
Cu(2)–O(30)	1.965(4)	2.285(6)	N(7)–Cu(2)–O(30)	…	108.6(3)
Cu(2)–N(1)	1.997(5)	1.972(9))	N(1)–Cu(2)–N(4)	93.4(2)	160.1(3)
Cu(2)–N(4)	1.961(5)	2.018(7)	N(7)–Cu(2)–O(10)	…	172.9(3)
Cu(2)–N(4)^C	2.007(5)	**…**	N(1)–Cu(2)–N(4)^c	158.2(2)	…
Cu(3)–O(31)	**…**	1.971(6)	N(4)–Cu(2)–N(4)^c	78.8(2)	…
Cu(3)–O(51)	**…**	2.247(7)	O(10)–Cu(2)–N(4)^c	106.7(2)	…
Cu(3)–N(4)	**…**	2.009(7)	N(7)–Cu(3)–N(4)	**…**	77.5(3)
Cu(3)–N(7)	**…**	2.018(8)	N(7)–Cu(3)–O(51)	**…**	97.5(3)
Cu(3)–N(10)	**…**	1.922(9)	N(7)–Cu(3)–O(31)	**…**	96.4(3)
Cu(4)–O(51)	**…**	1.894(6)	N(10)–Cu(3)–O(51)	**…**	103.9(3)
Cu(4)–O(31)	**…**	1.957(7)	N(10)–Cu(3)–N(4)	**…**	90.3(3)
Cu(4)–N(39)	**…**	1.970(7)	N(10)–Cu(3)–O(31)	**…**	95.3(3)
Cu(4)–N(43)	**...**	2.004(9)	O(51)–Cu(3)–O(31)	**…**	75.1(2)
O(10)–Cu(1)–O(30)	81.7(2)	84.9(2)	N(4)–Cu(3)–O(31)	**…**	173.8(3)
N(18)–Cu(1)–N(22)	92.7(3)	85.8(4)	N(7)–Cu(3)–N(10)	**…**	157.6(4)
N(22)–Cu(1)–O(30)	92.4(2)	94.1(3)	N(4)–Cu(3)–O(51)	**…**	106.1(3)
N(18)–Cu(1)–O(10)	94.7(2)	94.8(4)	O(31)–Cu(4)–O(51)	**…**	84.1(2)
N(18)–Cu(1)–O(30)	162.8(2)	174.6(4)	N(39)–Cu(4)–N(43)	**…**	87.3(3)
N(22)–Cu(1)–O(10)	171.5(2)	176.3(4)	N(39)–Cu(4)–O(31)	**…**	93.2(3)
O(30)–Cu(1)–N(6)^b	106.0(2)	**…**	N(43)–Cu(4)–O(51)	**…**	95.3(3)
N(18)–Cu(1)–N(6)^b	90.6(2)	**…**	N(39)–Cu(4)–O(51)	**…**	177.3(3)
N(22)–Cu(1)–N(6)^b	86.6(2)	**…**	N(43)–Cu(4)–O(31)	**…**	173.4(3)
N(1)–Cu(2)–O(30)	95.2(2)	99.7(3)			
N(1)–Cu(2)–N(7)	**…**	92.9(3)			

Symmetry element ^{b} = x,1+y,z and ^{c} = 1-x,-y,1-z for **1**

Table 3

Hydrogen Bond parameters in Complexes **1** and **2**.

Complex **1**				
D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	∠D–H···A(°)
N(22)–H(22)···N(1)	0.88(7)	2.23(6)	3.04(8)	154.51(6)
Complex **2**				
D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	∠D–H···A(°)
N(39)–H(39)···N(10)	0.91(8)	2.30(2)	3.12(4)	149.50(6)
N(18)–H(18)···N(1)	0.92(7)	2.45(6)	3.28(1)	151.88(3)

Highlights:

(i) Intermolecular H-bonds facilitates the change of common $\mu_{1,1}$-N_3 bridging mode to rare $\mu_{1,1,3}$-N_3.

(ii) Synergic formation of H-bond and coordination bond ($\mu_{1,1,3}$-N_3) to result in the 1D chains (**1** and **2**).

(iii) Strong antiferromagnetic exchange interactions between two Cu(II) centers are observed for both **1** and **2**.

Graphical Abstract (Pictogram)

H-bond assisted coordination bond formation in the 1D chains based on azido and phenoxido bridged tetranuclear Cu(II) complexes with reduced Schiff base ligands

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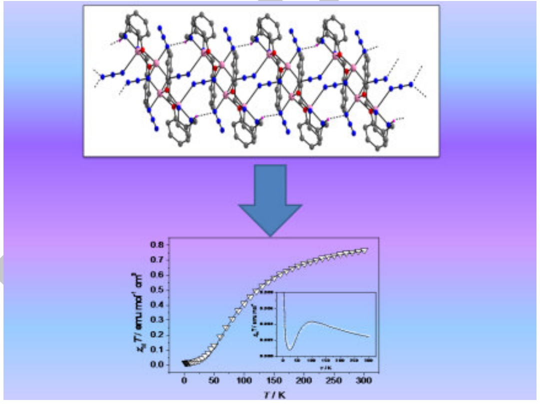

Graphical Abstract (Synopsis)

H-bond assisted coordination bond formation in the 1D chains based on azido and phenoxido bridged tetranuclear Cu(II) complexes with reduced Schiff base ligands

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Structural analysis reveals that the synergic formation of H-bond and a very rare $\mu_{1,1,3}$-N_3 bridging bond in Cu(II) tetramers resulting in two unusual 1D chains. Magnetic study shows an overall antiferromagnetic exchange interaction in both the chains.