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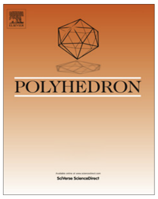

Hydrogen bonding induced lowering of the intra-chain metal–metal distance in single end-on azide bridged one-dimensional copper(II) complexes with tridentate Schiff bases as blocking ligands

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ABSTRACT

Three copper(II) complexes, $[Cu(L^1)(N_3)]_n$ (**1**), $[Cu(L^2)(N_3)]_n.H_2O$ (**2**) and $[Cu(L^3)(N_3)]_n$ (**3**) {where HL^1 = 2-[(2-dimethylamino-ethylimino)-methyl]-4-nitro-phenol, HL^2 = 2-[(2-methylamino-ethylimino)-methyl]-4-nitro-phenol and HL^3 = 2-[(2-ethylamino-ethylimino)-methyl]-4-nitro-phenol are tridentate Schiff-base ligands}, were prepared and characterized. Single crystal X-ray diffraction studies confirm that each complex is an end-on azide bridged one-dimensional polymer. All the complexes exhibit a square pyramidal geometry around the copper(II) centre. Weak forces like hydrogen bonding interactions lead to various supramolecular architectures. The copper(II)···copper(II) distance is minimized by intra chain hydrogen bonding in complex **3**.

1. Introduction

The design and synthesis of transition metal coordination polymers bridged by small conjugated ligands are currently under intense investigation in order to understand the structural and chemical factors that govern the exchange coupling between paramagnetic centers [1–4], with the plan of developing new molecular based magnets [5]. In addition, the variety of their structures, interesting properties and potential applications in the fields of catalysis [6], luminescence [7], gas adsorption [8] and magnetic materials [9,10] have attracted much attention over the past few years. Among them, the synthesis and characterization of coordination polymers of copper(II) have attracted interest due to the relevance of exploring their structures and the function of copper centers in several catalytic systems [11–13]. A variety of bridging groups have been employed for the synthesis of such systems. The pseudo halide azide is one of the most popular bridging ligands [14,15]. The azide ligand usually bridges the metal centers in various modes (Scheme 1), including end-on (EO, μ-1,1), end-to-end (EE, μ-1,3) or a combination of both, to yield dinuclear, tetranuclear, cubane, 1D, 2D and 3D compounds [16–21]. Focusing on copper(II) systems, both types of bridges can be either symmetrical or unsymmetrical due to active Jahn–Teller effects on the metal centre, which make the structures even more versatile [22]. Magnetic exchange via the azide bridge can be ferro- or antiferromagnetic, depending upon the bridging mode and bonding parameters [1,23,24]. On the other hand, Schiff bases have widely been used as blocking ligands in forming several azide bridged polymers [2]. Schiff bases derived from the condensation of N-substituted diamines with salicyldehyde or its derivatives are a group of anionic N_2O donor ligands that react readily with copper(II) to occupy its three equatorial coordination sites, and several anionic or neutral ligands can be coordinated in the fourth coordination site of the square plane to yield different types of complexes [26–28]. Depending upon the proportions and donor properties of these co-ligands, mono-, di- or trinuclear complexes are formed [29–31]. In slightly alkaline medium, trinuclear μ_3-OH bridged complexes are also produced [32]. Incorporation of additional donor groups in the Schiff base moiety has also been found to be useful in forming novel complexes [25]. Keeping this in mind, we have planned to use three N_2O donor Schiff bases, derived from the condensation of N-alkyl ethylenediamine with 5-nitrosalicyaladehyde, to prepare three copper(II) complexes in presence of azide. Among the three Schiff bases, two are capable of forming hydrogen bonding, and the third is not. It has already been shown that hydrogen bonding may tilt the balance in favor of a thiocyanate bridged copper(II) complex over a terminal thiocyanate containing complex when two isomeric Schiff bases are used [33], but in the present study, all the three azide complexes are found

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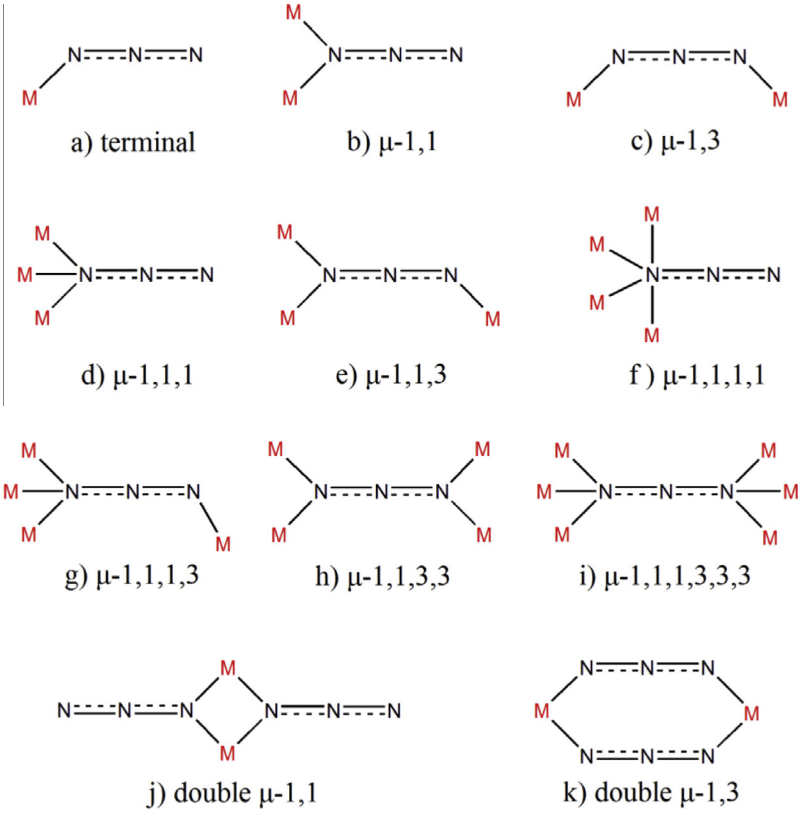


Scheme 1. Different bonding modes of azide ligand.

to form one-dimensional chains, probably due to the greater ability of azide to bridge copper(II) centres compared to thiocyanate. However, intra-chain hydrogen bonding results in shorter copper···copper distances within the chains. In the present paper, we report the synthesis, characterization, X-ray crystal structures and supramolecular assembly of molecular building blocks in three new azide bridged one-dimensional complexes of copper(II). The copper···copper distance is minimized by intra-chain hydrogen bonding.

2. Experimental

2.1. Materials

All reagents were commercially available, reagent grade and were used without further purification.

Caution! The azide complexes are potentially explosive. Although no problem was encountered in the present study, only small amounts of the materials should be prepared and they must be handled with care.

2.2. Synthesis

2.2.1. Synthesis of $[Cu(L^1)(N_3)]_n$ (**1**) [HL^1 = 2-[(2-dimethylamino-ethylimino)-methyl]-4-nitro-phenol]

5-Nitrosalicylaldehyde (170 mg, 1 mmol) and N,N-dimethyl-1,2-diaminoethane (0.1 ml, 1 mmol) were dissolved in methanol (30 ml) and heated to reflux for 1 h. A methanol solution (20 ml) of $Cu(OAc)_2.H_2O$ (200 mg, 1 mmol) and NaN_3 (65 mg, 1 mmol) was added to the reaction mixture, which was heated under reflux for 1 h. On cooling to room temperature, a green precipitate was formed, which was collected by filtration and dried in the open atmosphere (0.43 g, 0.63 mmol, 63%). Single crystals suitable for X-ray diffraction, were formed after a few weeks from a DMSO solution.

Anal. Calc. for $C_{22}H_{28}Cu_2N_{12}O_6$: C, 38.65; H, 4.13; N, 24.59. Found: C, 38.5; H, 4.1; N, 24.4%. IR (KBr, cm^{-1}): 2918 (alkyl CH), 3054 (N-Alkyl), 1643 ($\nu_{C=N}$), 2045 (ν_{N3}), 1310 ($\nu_{N=O}$), UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (acetonitrile): 584 (3.6×10^2), 365 (4.8×10^4), 250 (4.9×10^4).

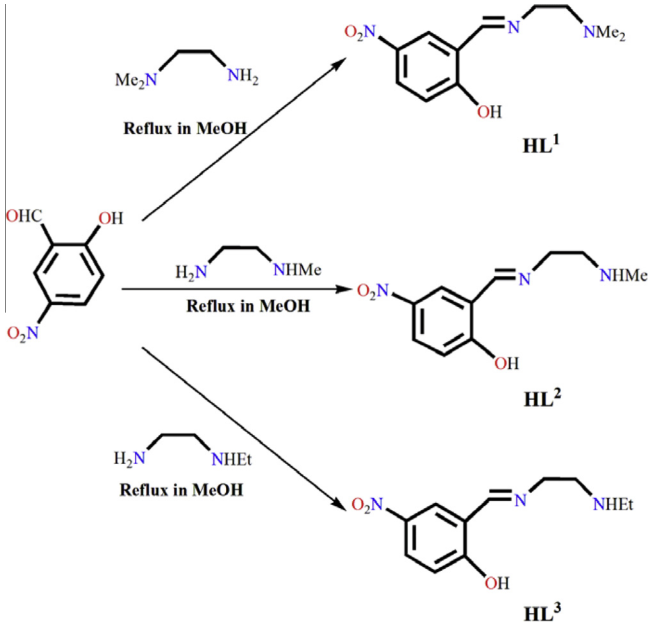
2.2.2. Synthesis of $[Cu(L^2)(N_3)]_n{\cdot}H_2O$ (**2**) [HL^2 = 2-[(2-methylamino-ethylimino)-methyl]-4-nitro-phenol]

5-Nitrosalicylaldehyde (170 mg, 1 mmol) and N-methyl-1,2-diaminoethane (0.1 ml, 1 mmol) were dissolved in methanol (30 ml) and heated to reflux for 1 h. A methanol solution (20 ml) of $Cu(OAc)_2{\cdot}H_2O$ (200 mg, 1 mmol) and NaN_3 (65 mg, 1 mmol) was added to the reaction mixture, which was heated at reflux for 1 h. On cooling to room temperature, a green precipitate was formed, which was collected by filtration and dried in the open atmosphere (0.44 g, 0.65 mmol, 65%). Single crystals suitable for X-ray diffraction, were formed after few weeks from a DMSO solution.

Anal. Calc. for $C_{20}H_{26}Cu_2N_{12}O_7$: C, 35.66; H, 3.89; N, 24.95. Found: C, 35.5; H, 3.7; N, 24.8%. IR (KBr, cm^{-1}): 2922 (alkyl CH), 3245 (NH), 1641 ($\nu_{C=N}$), 2048 (ν_{N3}), 1313 ($\nu_{N=O}$), UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (acetonitrile): 582 (1.9×10^2), 365 (3.0×10^4), 250 (3.1×10^4).

2.2.3. Synthesis of $[Cu(L^3)(N_3)]_n$ (**3**) [HL^3 = 2-[(2-ethylamino-ethylimino)-methyl]-4-nitro-phenol]

5-Nitrosalicylaldehyde (170 mg, 1 mmol) and N-ethyl-1,2-diaminoethane (0.1 ml, 1 mmol) were dissolved in methanol (30 ml) and heated to reflux for 1 h. A methanol solution (20 ml) of $Cu(OAc)_2{\cdot}H_2O$ (200 mg, 1 mmol) and NaN_3 (65 mg, 1 mmol) was added to the reaction mixture, which was heated to reflux



Scheme 2. Formation of the tridentate N_2O donor Schiff base ligands HL^1, HL^2 and HL^3.

for 1 h. On cooling to room temperature, a green precipitate was formed, which was collected by filtration and dried in the open atmosphere (0.22 g, 0.64 mmol, 64%). Single crystals suitable for X-ray diffraction, were formed after few weeks from a DMF solution.

Anal. Calc. for $C_{11}H_{14}CuN_6O_3$: C, 38.65; H, 4.13; N, 24.59. Found: C, 38.5; H, 4.0; N, 24.4%. IR (KBr, cm^{-1}): 2925 (alkyl CH), 3225 (NH), 1650 ($\nu_{C=N}$), 2053 (ν_{N3}), 1311 ($\nu_{N=O}$), UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (acetonitrile): 580 (1.8×10^2), 366 (2.3×10^4), 250 (2.4×10^4).

Table 1
Crystal data and refinement details of complexes **1**–**3**.

	1	**2**	**3**
Formula	$C_{22}H_{28}Cu_2N_{12}O_6$	$C_{20}H_{26}Cu_2N_{12}O_7$	$C_{11}H_{14}CuN_6O_3$
Formula weight	683.64	673.61	341.82
T (K)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$Pca2_1$
a (Å)	6.6135(3)	6.5392(3)	21.7550(13)
b (Å)	19.2197(6)	18.7111(6)	10.0835(4)
c (Å)	21.1949(9)	21.0104(9)	6.2678(3)
α (°)	90	90	90
β (°)	95.388(4)	97.060(3)	90
γ (°)	90	90	90
Z	4	4	4
d_{calc} ($g\ cm^{-3}$)	1.693	1.754	1.651
μ (mm^{-1})	1.650	1.735	1.609
F(000)	1400	1376	700
Total reflections	20240	28868	12847
Unique reflections	5686	5403	2894
Observed data [$I > 2\sigma(I)$]	4421	4089	2425
No. of parameters	383	454	192
R_{int}	0.041	0.0450	0.051
R_1, wR_2 (all data)	0.0400, 0.0493	0.0431, 0.0738	0.0518, 0.1028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0244, 0.0469	0.0290, 0.0712	0.0441, 0.1006

2.3. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) of complexes **1** to **3** were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer Spectrum Two FT-IR Spectrometer. Electronic spectra in acetonitrile (900–200 nm) were recorded in a Hitachi U-3501 spectrophotometer. Fluorescence spectra were obtained on a HORIBA Jobin Yvon FluoroMax-P spectrophotometer at room temperature. The thermal behavior of the complexes were studied in a dynamic nitrogen atmosphere (150 mL min^{-1}) at a heating rate of 10 °C min^{-1} using a thermo-gravimetric (TG) technique in a Perkin Elmer (Singapore) Pyris Diamond TG/DTA instrument. The powder XRD data were collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The powder XRD spectra were recorded in a 2θ range of 2–50° using a 1D Lynxeye detector under ambient conditions.

2.4. X-ray crystallography

Single crystals of the three complexes of suitable dimensions were mounted in inert oil and transferred to the cold gas stream of the cooling device. Data were collected at 100 K on a STOE IPDS 2T diffractometer using graphite monochromated MoKα radiation and were corrected for absorption effects using multiscanned reflections. Non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The programs used were SHELXL-97 [34,35], PLATON [36], XAREA [37], SIR92 [38], DIAMOND [39], ORTEP [40] and MERCURY [41]. The crystallographic and refinement data are summarized in Table 1.

The chains N(1)(C10)–C(1)–C(2) and N(101)(C110)–C(101)–C(102) of the ligands show two fold positional disorder with ratios 50:50 and 55:45, respectively, and have been refined using restraints. This conformational disorder leads to an inversion of the N–H bond direction in both cases. The water molecule that is involved in the hydrogen bond with N(101) as a donor atom also was refined using two positions with an occupation ratio of 50:50.

3. Results and discussion

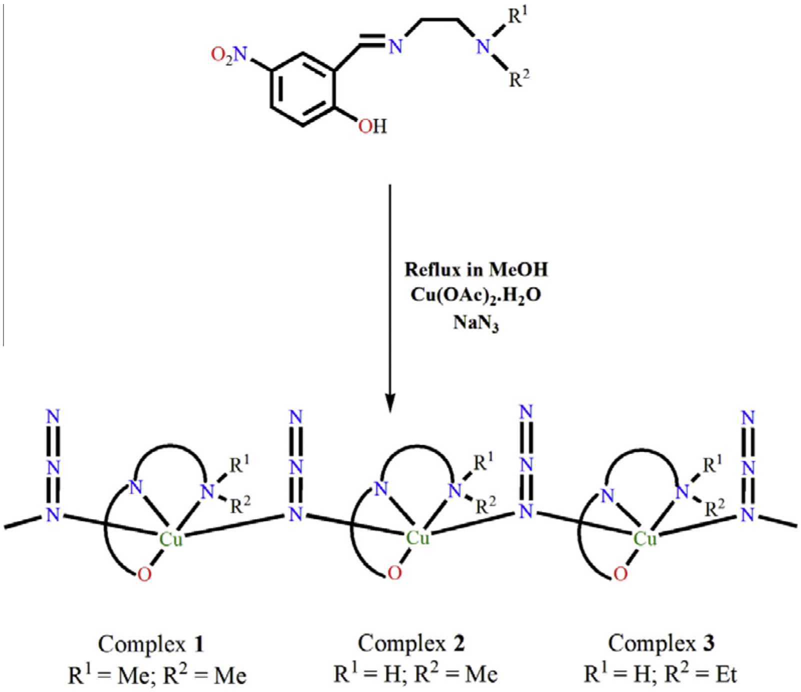
3.1. Synthesis of the ligands and copper(II) complexes

The preparation of the tridentate Schiff-base ligands (Scheme 2) were routinely achieved by the condensation of N,N-dimethyl-1,2-diaminoethane, N-methyl-1,2-diaminoethane and N-ethyl-1,2-diaminoethane with 5-nitrosalicylaldehyde separately in a 1:1 M ratio following the literature method [25]. The reactions were quantitative and no purification of the resulting ligands was required. The Schiff base ligands HL^1, HL^2, and HL^3 on reaction with copper(II) acetate and sodium azide resulted in the formation of complexes **1**, **2** and **3**, respectively (Scheme 3).

3.2. Description of the structures

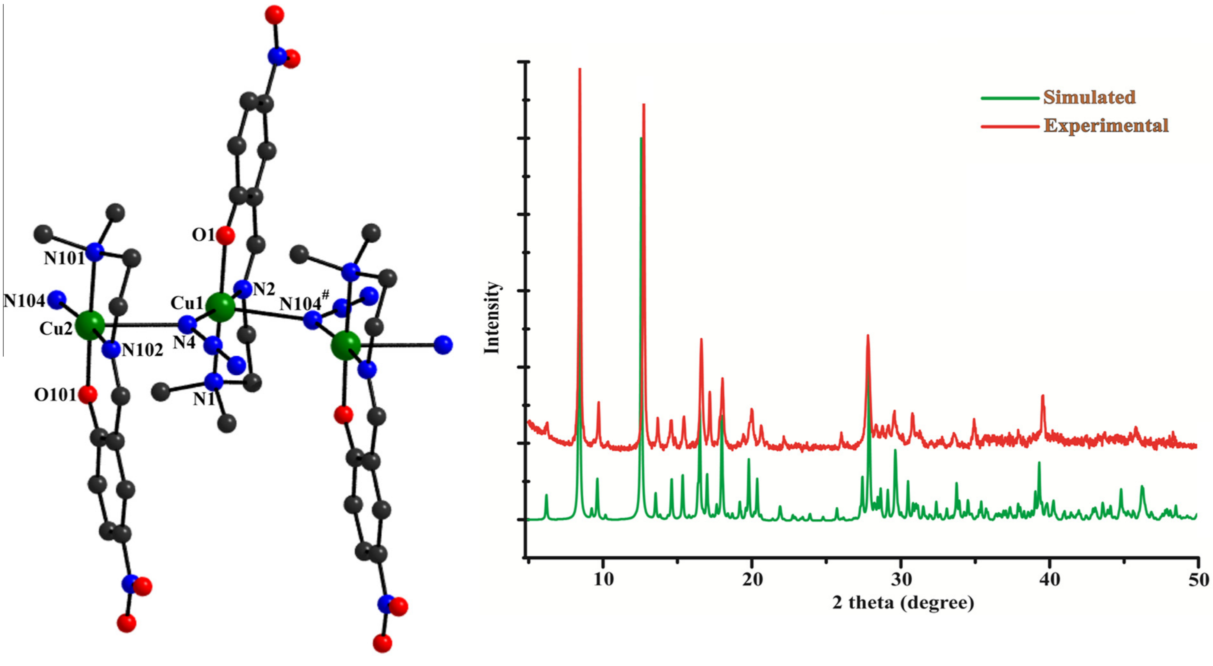
3.2.1. $[Cu(L^1)(N_3)]_n$ (**1**)

Complex **1** crystallized as green blocks in the monoclinic space group $P2_1/n$. A perspective view of the complex with selective atom labeling scheme is shown in Fig. 1(i). Selected bond lengths and angles are given in Table 2. The X-ray crystal structure analysis reveals that the copper(II) centres are connected singly by end-on (EO) bridged azide ligands, with the occurrence of a zigzag chain. The asymmetric unit contains two independent copper(II) centers, Cu(1) and Cu(2), having different environments. Both the copper(II) centers possess distorted square-pyramidal geometries, as



Scheme 3. Synthesis of complexes **1**, **2** and **3**.

indicated by the Addison parameter (τ) (the Addison parameter is defined as the difference between the two largest donor–metal–donor angles divided by 60, a value that is zero for an ideal square pyramid and one for a trigonal bipyramid) [42]; $\tau = 0.07$ for Cu(1) and 0.12 for Cu(2). Each copper(II) center is linked to two neighboring copper(II) centers by two azide ligands in end-on fashions to form the zigzag chain. Cu(1) is coordinated equatorially by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one oxygen atom, O(1), of the tridentate Schiff base ligand HL^1 and a nitrogen atom, N(4), of the EO bridged azide ligand; this defines the basal plane. The apical position is occupied by one nitrogen atom N(104)$^{\#}$ {symmetry code $^{\#}$ = 1 + x, y, z} of another end-on bridged azide from a crystallographically related unit. Similarly, one amine nitrogen atom, N(101), one imine nitrogen atom, N(102), and one oxygen atom, O(101), of the tridentate Schiff base and one nitrogen atom, N(104), of the end-on bridged azide ligand



(i) (ii)

Fig. 1. (i) One-dimensional polymeric structure of complex **1**. Hydrogen atoms are omitted for clarity. Symmetry element: $^{\#} = 1 + x, y, z$. (ii) Experimental and simulated powder XRD patterns of complex **1** confirming the purity of the bulk material.

Table 2
Selected bond lengths (Å) and bond angles (°) of complexes **1**, **2** and **3**.

	1	**2**	**3**
Cu(1)–O(1)	1.9341(13)	1.9402(15)	1.939(3)
Cu(1)–N(1)	2.0687(15)	2.034(6)	2.031(4)
Cu(1)–N(2)	1.9574(17)	1.9591(17)	1.952(3)
Cu(1)–N(4)	1.9879(17)	1.9979(19)	1.985(3)
Cu(1)–N(4)$^{\$}$	–	–	2.390(4)
Cu(1)–N(104)$^{\#}$	2.4843(14)	2.497(2)	–
Cu(2)–O(101)	1.9211(11)	1.9183(19)	–
Cu(2)–N(4)	2.5964(14)	2.709(2)	–
Cu(2)–N(101)	2.0527(15)	1.992(11)	–
Cu(2)–N(102)	1.9451(15)	1.9369(17)	–
Cu(2)–N(104)	1.9775(15)	1.976(2)	–
O(1)–Cu(1)–N(1)	176.06(6)	169.3(3)	176.12(14)
O(1)–Cu(1)–N(2)	91.88(6)	91.86(7)	93.18(13)
O(1)–Cu(1)–N(4)	89.09(6)	89.35(8)	88.75(15)
O(1)–Cu(1)–N(4)$^{\$}$	–	–	96.23(14)
O(1)–Cu(1)–N(104)$^{\#}$	89.24(5)	92.18(7)	–
N(1)–Cu(1)–N(2)	84.78(6)	86.0(2)	84.53(13)
N(1)–Cu(1)–N(4)	93.91(6)	91.5(3)	92.53(15)
N(1)–Cu(1)–N(4)$^{\$}$	–	–	86.88(15)
N(1)–Cu(1)–N(104)$^{\#}$	92.82(5)	98.3(4)	–
N(2)–Cu(1)–N(4)	171.57(6)	172.68(8)	162.89(15)
N(2)–Cu(1)–N(4)$^{\$}$	–	–	89.28(12)
N(2)–Cu(1)–N(104)$^{\#}$	89.55(5)	89.63(7)	–
N(4)–Cu(1)–N(104)$^{\#}$	98.84(5)	97.54(7)	–
N(4)–Cu(1)–N(4)$^{\$}$	–	–	107.43(13)
O(101)–Cu(2)–N(4)	86.40(5)	89.65(8)	–
O(101)–Cu(2)–N(101)	177.77(6)	177.0(6)	–
O(101)–Cu(2)–N(102)	92.79(6)	93.76(7)	–
O(101)–Cu(2)–N(104)	89.04(6)	89.01(9)	–
N(4)–Cu(2)–N(101)	92.23(5)	93.3(6)	–
N(4)–Cu(2)–N(102)	88.30(6)	87.22(7)	–
N(4)–Cu(2)–N(104)	101.21(6)	95.11(7)	–
N(101)–Cu(2)–N(102)	85.41(6)	86.8(4)	–
N(101)–Cu(2)–N(104)	92.95(6)	90.3(4)	–
N(102)–Cu(2)–N(104)	170.41(6)	176.40(9)	–
Cu(1)–N(4)–Cu(2)	130.33(7)	130.17(9)	–
Cu(1)–N(4)–Cu(1)$^{!}$	–	–	118.37(15)
Cu(1)–N(4)–N(5)	118.68(11)	117.72(16)	126.7(3)
Cu(1)$^{!}$–N(4)–N(5)	–	–	114.8(3)
Cu(2)–N(4)–N(5)	110.07(12)	109.03(14)	–
Cu(2)–N(104)–N(105)	115.38(11)	113.43(16)	–
Cu(1)$^{\#}$–N(104)–Cu(2)	132.60(7)	128.39(10)	

Symmetry elements $^{\#}$ = 1 + *x*, *y*, *z*; $^{\$}$ = 1 – *x*, 2 – *y*, –1/2 + *z*; $^{!}$ = 1 – *x*, 2 – *y*, 1/2 + *z*.

comprises the basal plane for Cu(2); and the apical position is occupied by a nitrogen atom, N(4), of the end-on bridged azide. Thus, the azide bridges assume an asymmetric apical-basal disposition between neighboring copper(II) ions; i.e., the same end-on azide bridge resides in the apical position of one copper but in the basal plane of the neighboring copper, with the apical Cu–N distance {2.484(1)–2.596(1) Å} being significantly longer than the basal one {1.945(2)–2.069(1) Å}, as an obvious result of the Jahn Teller effect in a d^9 copper(II) system. In the equatorial plane, the Cu–N_{imine} distances {1.945(2)–1.957(2) Å} are shorter than the Cu–N_{amine} {2.053(1)–2.069(1) Å} distances, as was also observed in similar systems [33]. Deviation of the Cu(1) and Cu(2) atoms from the mean plane towards the apical donor atom is about 0.0918 and 0.0705 Å respectively. The closest conformation of the five-membered chelate ring, Cu(1)–N(1)–C(1)–C(2)–N(2), is twisted on N(1)–C(1) with puckering parameters [43] q(2) = 0.4437(19) Å and ϕ(2) = 254.8(9)°, whereas the closest conformation of the similar type of five-membered chelate ring, Cu(2)–N(101)–C(101)–C(102)–N(102), adopts an envelope conformation with puckering parameters q(2) = 0.4287(18) Å and ϕ(2) = 247.0(2)° [43].

There are some C–H···O and C–H···N interactions in complex **1** that form a two-dimensional network (Fig. 2). The hydrogen atoms H(10E), attached to C(10), and H(11D), attached to C(111), form intra-molecular hydrogen bonds with O(101) and O(1), respectively. On the other hand, H(1A), attached to C(1), forms an inter-molecular hydrogen bond with the symmetry-related O(3)$^{\alpha}$ {$^{\alpha}$ = 1/2 + *x*, 1/2 – *y*, 1/2 + *z*}. Similarly, H(3), attached to C(3), is hydrogen bonded to N(6)$^{\beta}$ {$^{\beta}$ = 3/2 – *x*, –1/2 + *y*, 1/2 – *z*}, H(10D), attached to C(102), is hydrogen bonded to O(103)$^{\gamma}$ {$^{\gamma}$ = –1/2 + *x*, 3/2 – *y*, –1/2 + *z*} and H(11G), attached to C(11), is hydrogen bonded to O(101)$^{\delta}$ [$^{\delta}$ = 1 + *x*, *y*, *z*}. H(103), attached to C(103), and H(109), attached to C(109), form bi-furcated hydrogen bonds with N(106)$^{\eta}$ [$^{\eta}$ = 1/2 – *x*, 1/2 + *y*, 1/2 – *z*}. Details of the hydrogen bonding are given in Table 3.

3.2.2. [Cu(L^2)(N_3)]$_n$·H_2O (**2**)

Complex **2** crystallized as blue blocks in the monoclinic space group $P2_1/n$. A perspective view of complex **2** with the atom labeling scheme is shown in Fig. 3(i). Selected bond lengths and angles are given in Table 2. The X-ray crystal structure analysis reveals

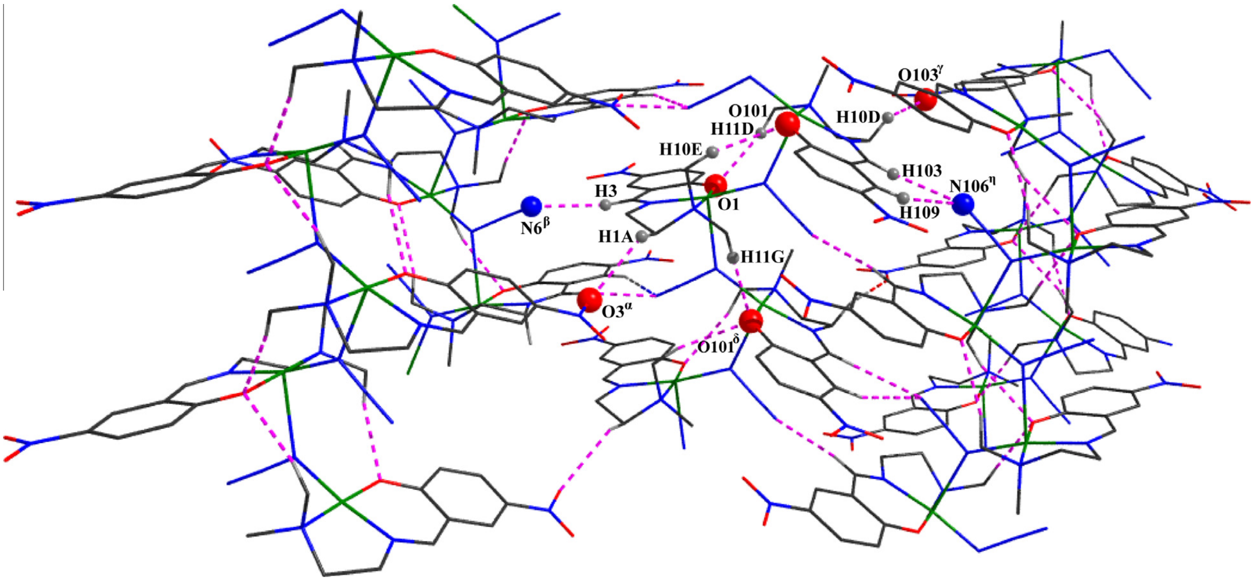


Fig. 2. The hydrogen bonded supramolecular network in complex **1**. Symmetry elements: $^{\alpha}$ = 1/2 + *x*, 1/2 – *y*, 1/2 + *z*; $^{\beta}$ = 3/2 – *x*, –1/2 + *y*, 1/2 – *z*; $^{\gamma}$ = –1/2 + *x*, 3/2 – *y*, –1/2 + *z*; $^{\delta}$ = 1 + *x*, *y*, *z*; $^{\eta}$ = 1/2 – *x*, 1/2 + *y*, 1/2 – *z*.

Table 3
Hydrogen bond distances (Å) and angles (°) of complexes **1**, **2** and **3**.

Complexes	D–H···A	D–H	D···A	H···A	∠D–H···A
1	C(1)–H(1A)···O(3)$^{\alpha}$	0.990(2)	3.068(2)	2.599(1)	109.1(1)
	C(3)–H(3)···N(6)$^{\beta}$	0.950(2)	3.453(3)	2.516(2)	169.1(1)
	C(102)–H(10D)···O(103)$^{\gamma}$	0.990(2)	3.120(2)	2.411(1)	128.0(1)
	C(10)–H(10E)···O(101)	0.979(2)	3.511(3)	2.547(1)	168.3(1)
	C(111)–H(11D)···O(1)	0.980(2)	3.361(2)	2.406(1)	164.7(1)
	C(11)–H(11G)···O(101)$^{\delta}$	0.980(2)	3.314(2)	2.345(1)	169.9(1)
	C(103)–H(103)···N(106)$^{\eta}$	0.949(2)	3.373(3)	2.505(2)	151.9(1)
	C(109)–H(109)···N(106)$^{\eta}$	0.950(2)	3.332(3)	2.454(2)	153.5(1)
2	O(100)–H(10K)···O(1)	0.870(6)	2.900(6)	2.067(1)	160.1(4)
	N(101)–H(101)···O(100)	0.93(2)	3.10(2)	2.270(7)	148.3(9)
	C(3)–H(3)···N(6)$^{\theta}$	0.951(2)	3.478(3)	2.566(2)	160.8(1)
	C(103)–H(103)···N(106)$^{\varphi}$	0.950(2)	3.311(3)	2.434(2)	153.4(1)
	C(109)–H(109)···N(106)$^{\varphi}$	0.950(2)	3.454(3)	2.611(2)	148.0(1)
3	N(1)–H(1)···O(1)$^{\$}$	0.910(3)	3.139(5)	2.298(3)	153.5(2)
	C(3)–H(3)···N(6)$^{\psi}$	0.930(4)	3.387(6)	2.522(4)	154.7(3)
	C(10)–H(10A)···O(3)$^{\omega}$	0.970(5)	3.388(6)	2.494(3)	153.3(3)
	C(10)–H(10B)···N(4)	0.970(6)	3.166(8)	2.568(4)	120.0(3)

D, donor; H, hydrogen; A, acceptor, symmetry elements $^{\alpha}$ = 1/2 + x, 1/2 − y, 1/2 + z; $^{\beta}$ = 3/2 − x, −1/2 + y, 1/2 − z; $^{\gamma}$ = −1/2 + x, 3/2 − y, −1/2 + z; $^{\delta}$ = 1 + x, y, z; $^{\eta}$ = 1/2 − x, 1/2 + y, 1/2 − z; $^{\theta}$ = 3/2 − x, 1/2 + y, 3/2 − z; $^{\varphi}$ = 1/2 − x, −1/2 + y, 3/2 − z; $^{\$}$ = 1 − x, 2 − y, −1/2 + z; $^{\psi}$ = x, −1 + y, z; $^{\omega}$ = 1 − x, 1 − y, 1/2 + z.

that the copper(II) centers are bridged singly by end-on bridged azide ligands to form a one-dimensional zigzag polymer. The asymmetric unit contains two independent copper(II) centres, Cu(1) and Cu(2), having different environments, as in complex **1**. Both the copper(II) centers possess distorted square-pyramidal geometries, as indicated by the Addison parameter [42], τ = 0.06 for Cu(1) and 0.01 for Cu(2). Each copper(II) center is linked to two neighboring copper(II) centers by two azide ligands in end-on fashions to form the zigzag chain. Cu(1) is coordinated equatorially by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one oxygen atom, O(1), of the tridentate Schiff base ligand HL^{2} and a nitrogen atom, N(4), of the EO bridged azide ligand; this defines the basal plane. The apical position is occupied by one nitrogen atom N(104)$^{\#}$ {symmetry code, $^{\#}$ = 1 + x, y, z} of another end-on bridged azide ligand from a crystallographically related unit. Similarly, one amine nitrogen atom, N(101), one imine nitrogen atom, N(102), and one oxygen atom, O(101), of the tridentate Schiff base and one nitrogen atom, N(104), of the end-on bridged azide ligand comprises the basal plane of Cu(2), and the apical position is occupied by the nitrogen atom N(4) of the end-on bridged azide ligand. Thus, the azide bridges assume an asymmetric apical-basal disposition between neighboring copper(II) ions; with the apical Cu–N distance {2.709(2)–2.497(2) Å} being significantly longer than the basal one {1.937(2)–2.034(7) Å}, as an obvious

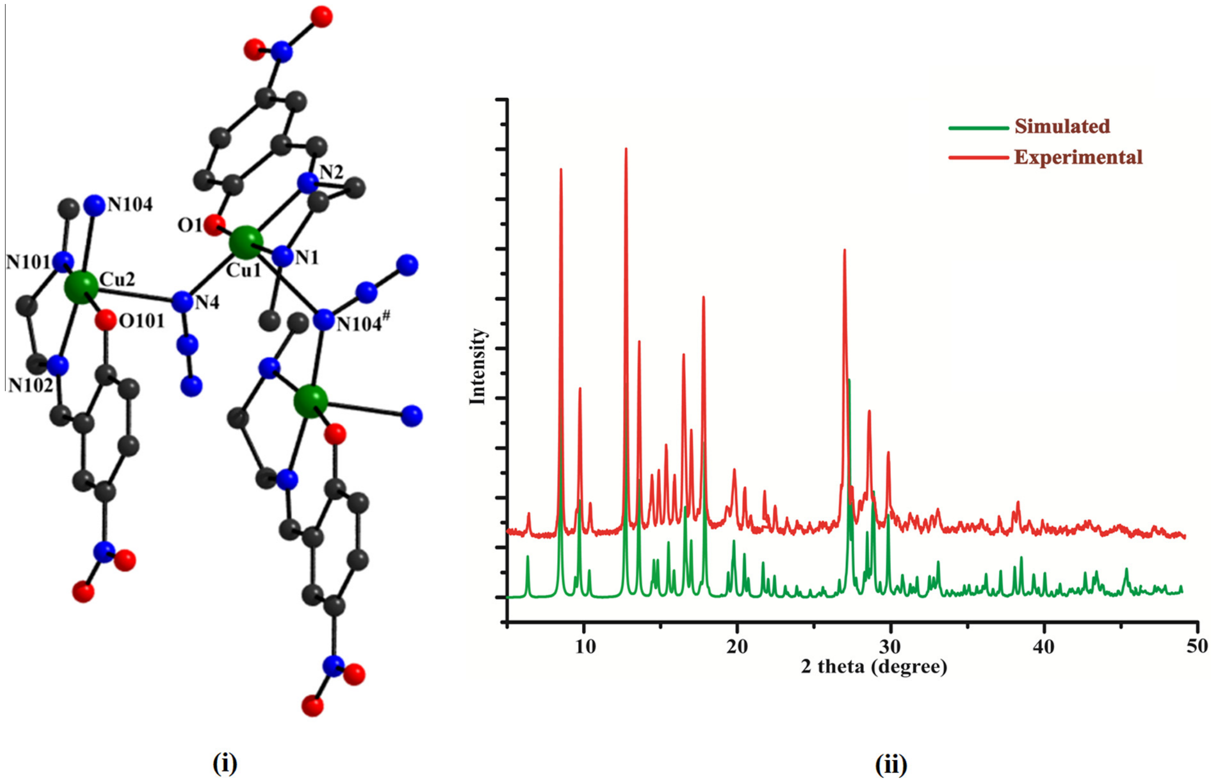


Fig. 3. (i) Perspective view of the one-dimensional polymeric structure of complex **2**. Hydrogen atoms are not shown for clarity. Symmetry element: $^{\#}$ = 1 + x, y, z. (ii) Experimental and simulated powder XRD patterns of complex **2**.

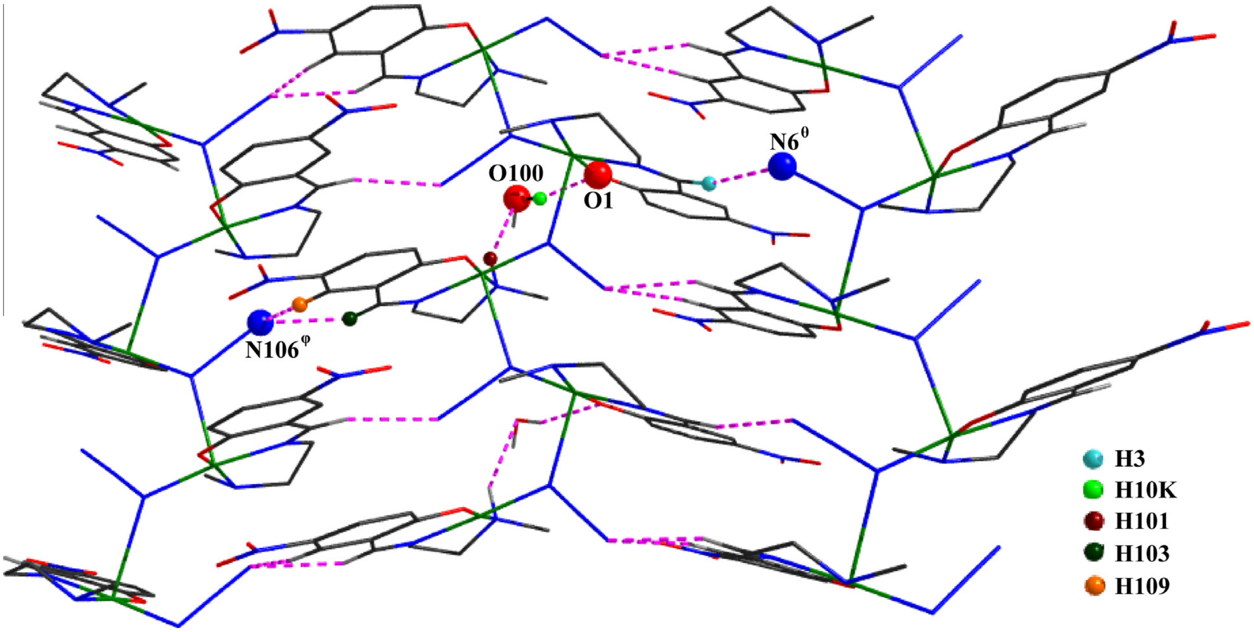
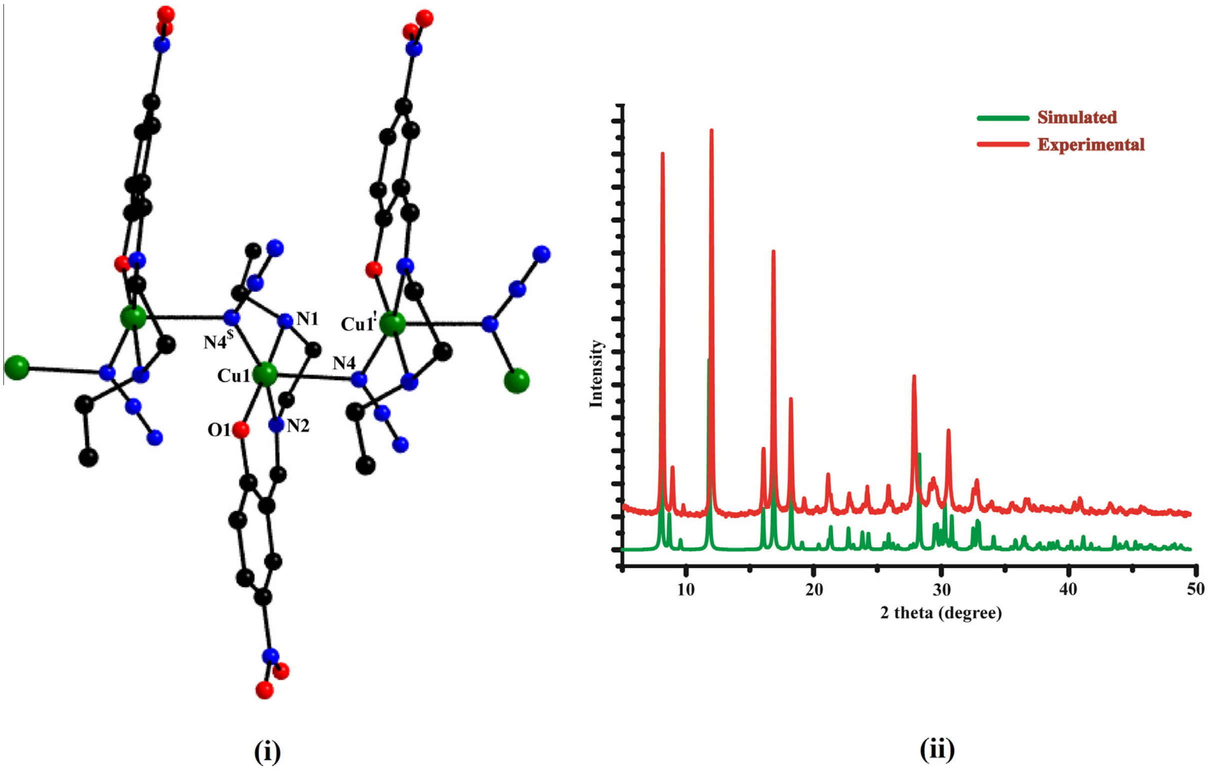


Fig. 4. The hydrogen bonded supramolecular network in complex **2**. The disordered atoms are omitted for clarity. Symmetry elements: $^{\theta}$ = 3/2 − *x*, 1/2 + *y*, 3/2 − *z*; $^{\varphi}$ = 1/2 − *x*, −1/2 + *y*, 3/2 − *z*.

result of the Jahn Teller effect in a d^9 copper(II) system. In the equatorial plane, the Cu–N$_{\text{imine}}$ distances {1.937(2)–1.959(2) Å} are shorter than the Cu–N$_{\text{amine}}$ {1.99(1)–2.034(7) Å} distances, as was also observed in similar systems [33]. The deviation of the Cu(1) and Cu(2) atoms from the mean plane towards the apical donor atom is about 0.1532(3) and 0.0438(3) Å respectively.

Hydrogen H(101), which is attached to N(101), of the Schiff base forms a strong hydrogen bond with O(100) of the water of crystallization. H(10 K) of the same water molecule forms another hydrogen bond with the phenolate oxygen atom, O(1). There are also some C-H· · ·O and C-H· · ·N interactions in complex **2**. The hydrogen atom H(3), attached to C(3), is hydrogen bonded to the symmetry-related N(6)$^{\theta}$ {$^{\theta}$ = 3/2 − *x*, 1/2 + *y*, 3/2 − *z*}. On the other hand, H(103), attached to C(103), and H(109), attached to C(109), form bi-furcated hydrogen bonds with N(106)$^{\varphi}$ {$^{\varphi}$ = 1/2 − *x*, −1/2 + *y*, 3/2 − *z*}. Details of the hydrogen bonding are given in Table 3.



(i)

(ii)

Fig. 5. (i) One-dimensional polymeric structure of complex **3**. Hydrogen atoms are not shown for clarity. Symmetry elements: $^{\$}$ = 1 − *x*, 2 − *y*, −1/2 + *z*; $^{!}$ = 1 − *x*, 2 − *y*, 1/2 + *z*. (ii) Experimental and simulated powder XRD patterns of complex **3**.

All these hydrogen bonds lead to the formation of a two-dimensional supramolecular network in complex **2** (Fig. 4).

3.2.3. [Cu(L^3)(N_3)]$_n$ (**3**)

The structure determination reveals that complex **3** consists of a chain in which two neighboring [Cu(L^3)]$^+$ units are linked by end-on bridging azide ligand. Selected bond lengths and angles are summarized in Table 2. A perspective view of complex **3** is shown in Fig. 5(i). Each copper(II) centre in the chain has a distorted square pyramidal environment {with trigonality index, τ (Addison parameter) = 0.22}, in which one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one phenolic oxygen atom, O(1), of the tridentate Schiff base ligand HL^3 and a nitrogen atom, N(4), of the azide coordinate to define an equatorial plane. The apical fifth coordination site of the square pyramid is occupied by a nitrogen atom, N(4)$^{\$}$, of a symmetry related {$^{\$}$ = 1 – x, 2 – y, –1/2 + z} azide. Deviations of the coordinating atoms N(1), N(2), N(4) and O(1) from the least-square basal plane are –0.115(4), 0.118(3), 0.112(4) and –0.115(3) Å respectively. The copper(II) centre shows a displacement of –0.1746(6) Å from this basal plane towards the axially coordinated azide nitrogen, N(5)$^{\$}$. The apical Cu–N distance (2.390 Å) is significantly longer than the basal ones {1.952(3)–2.031(4) Å}, which is in good agreement with those previously reported in the literature [26]. In the basal plane, the Cu–N$_{\text{imine}}$ distance {1.952(3) Å} is shorter than the Cu–N$_{\text{amine}}$ distance {2.031(4) Å}, as has been observed in similar systems [33]. The saturated five membered Cu(1)–N(1)–C(1)–C(2)–N(2) ring adopts an envelope conformation [44] with puckering parameters q(2) = 0.416(4) Å and ϕ(2) = 75.5(4)°.

Intra-chain N–H···O hydrogen bonding is observed between H(1) (attached to N(1) of the Schiff base) and the symmetry related O(1)$^{\$}$ ($^{\$}$ = 1 – x, 2 – y, –1/2 + z) of a crystallographically related unit, leading to the formation of an R_1^1(6) ring [45]. There are also some C–H···O and C–H···N interactions in complex **3**. The hydrogen atom H(10B), attached to C(10), forms an intra-molecular hydrogen bond with N(4). On the other hand, the hydrogen atom H(3), attached to C(3), is hydrogen bonded to the symmetry-related N(6)$^{\psi}$ {$^{\psi}$ = x, –1 + y, z}. Similarly, H(10A), attached to C(10), is hydrogen bonded to the symmetry-related O(3)$^{\omega}$ {$^{\omega}$ = 1 – x, 1 – y, 1/2 + z}. Details of the hydrogen bonding are given in Table 3. Formation of all these hydrogen bonds leads to the formation of a two-dimensional supramolecular network in complex **3** (Fig. 6).

3.3. IR, electronic spectra, magnetic moments and and luminescence studies

The IR bands corresponding to the C = N stretching vibrations for complexes **1**–**3** appear in the range 1641–1650 cm^{-1} [46]. An intense band within the range 1310–1313 cm^{-1} may be attributed to the $\nu_{N=O}$ vibration [47]. In the IR spectrum of complex **2**, a broad band at 3430 cm^{-1} was observed, which may be assigned to the OH stretching vibration of the lattice water molecule. The IR spectra of these complexes exhibit characteristic $\nu(N_3)$ bands in the 2045–2053 cm^{-1} region [48]. The bands in the range of 2918–2925 cm^{-1} in the IR spectra of all the complexes are due to alkyl C–H bond stretching vibrations [46]. The sharp bands due to the amino NH group appear at 3216 and 3246 cm^{-1} in the spectra of complexes **1** and **2** [28].

The electronic spectra of all the complexes were recorded in acetonitrile solution in the range 200–1000 nm. The intense absorption bands at short wavelengths, around 360 nm, may be assigned to ligand-to-metal ion charge transfer bands (LMCT). The absorptions around 580 nm may be assigned to d–d transitions. Complexes **1**–**3** exhibit luminescence in acetonitrile medium. The luminescence data are listed in Table 4 (without solvent corrections). These are assigned to intra-ligand $^1(\pi-\pi^*)$ fluorescence [49].

Table 4
Photophysical data for complexes **1**–**3**.

Complex	Excitation (nm)	Emission (nm)
1	350	423.5
2	350	430.5
3	350	423.5

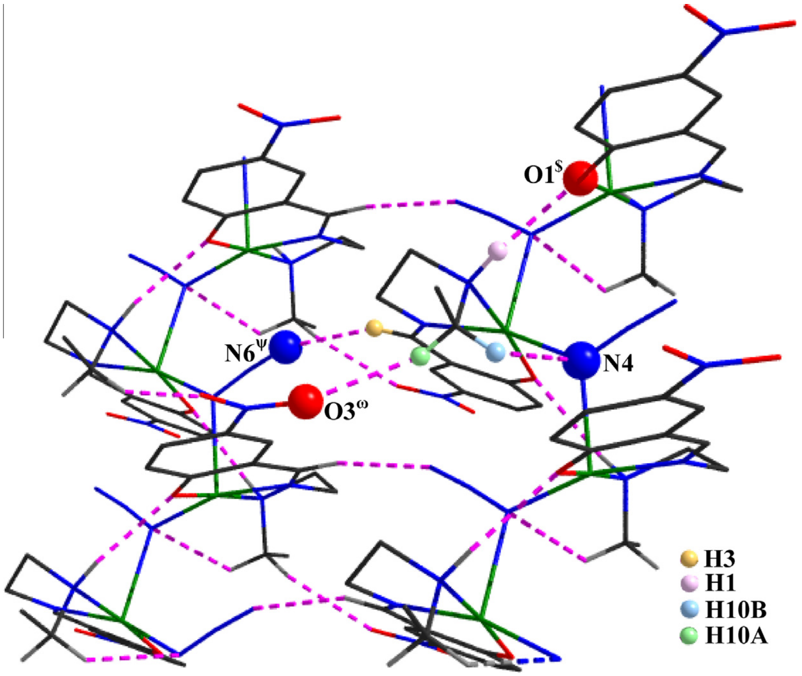
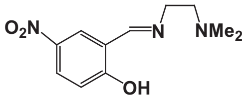
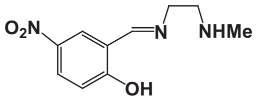
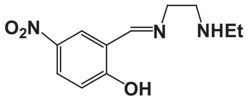
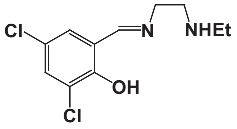
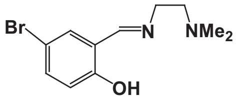
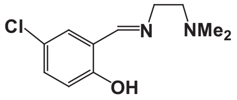
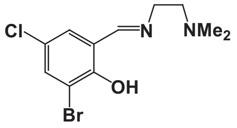
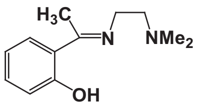
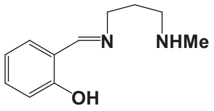
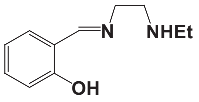
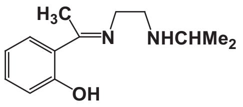
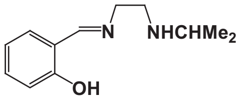
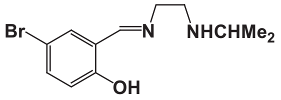
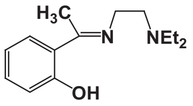
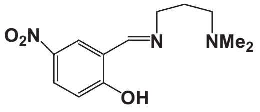


Fig. 6. The hydrogen bonded supramolecular network in complex **3**. Symmetry elements: $^{\$}$ = 1 – x, 2 – y, –1/2 + z; $^{\psi}$ = x, –1 + y, z; $^{\omega}$ = 1 – x, 1 – y, 1/2 + z.

Table 5

Cu···Cu distances (Å) of some reported copper(II) complexes with single μ-1,1-azide/ double μ-1,1-azide bridges. The dimers have been indicated in parenthesis.

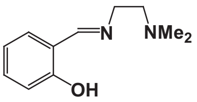
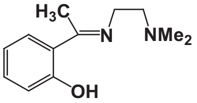
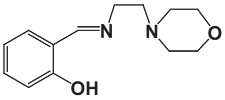
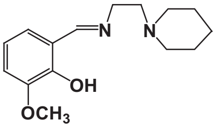
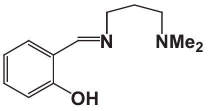
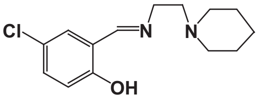
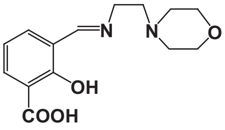
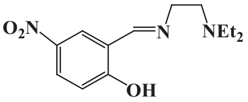
Ligand used	μ-1,1-bridged azide (single) Cu···Cu distance (Å)	Intra-chain hydrogen bonding	Refs.
	4.1682(3)	no	this work
	4.0336(4)	no	this work
	3.7632(7)	yes	this work
	3.6656(8)	yes	[51]
	4.1964(9)	no	[52]
	4.1674(7)	no	[53]
	4.292(1)	no	[54]
	3.866(2) (dimer)	no	[23]
	3.555(2), 3.599(1), 3.168(1), 3.3232(5), 3.306(1) (dimer)	yes	[55–56]
	3.104(2) (dimer)	yes	[57]
	3.2365(3) (dimer)	yes	[58]
	3.2568(9) (dimer)	yes	[59]
	3.308(1) (dimer)	yes	[60]
	3.605(1) (dimer)	no	[61]
	3.3273(7) (dimer)	no	[62]

3.4. Intra-chain hydrogen bonding and the intra-chain copper(II)-copper(II) distance: A literature survey

Azide bridged di- or polynuclear complexes of copper(II) have been well-known for decades [50–71]. Several groups have already used different N_2O donor tridentate Schiff bases as blocking ligands. We have searched the CSD to gather all the double μ-1,3-azide bridged, double μ-1,1-azide bridged, single μ-1,3-azide bridged and single μ-1,1-azide bridged dimers and one-dimensional chains of copper(II) with N_2O donor Schiff bases. The results are given in Tables 5 and 6. One can examine the data represented in Tables 5 and 6 to conclude that (i) the copper(II)···copper(II) distances in single μ-1,3-azide bridged complexes are longer than those in single μ-1,1-azide bridged ones, (ii) copper(II)···copper(II) distances in double μ-1,1-azide bridged complexes are shorter than those in single μ-1,1-azide bridged complexes and (iii) intra-chain hydrogen bonding can lower the intra-chain copper(II)···copper(II) distances. Thus with a tactful choice of Schiff base, one can modulate the intra-chain copper(II)···copper(II) distance. However, no systematic study of the modulation of intra-chain copper(II)···copper(II) distances by the formation of intra-chain hydrogen bonds has been reported in the literature to date. We are interested to study this phenomenon for the first time.

Among the three single μ-1,1-azide bridged one-dimensional chains of copper(II) prepared by us, only one contains intra-chain hydrogen bonding. The copper(II)···copper(II) distance {3.7632(7) Å} is much less in it compared to that {4.1682(3) and 4.0336(4) Å} found in the other two complexes, as was also observed for other complexes. The N···O (donor···acceptor) distance in this complex is 3.139(5) Å. We found in the literature only one one-dimensional copper(II) complex with a Schiff base [51]. In that complex, the donor–acceptor distance is 2.989(3) Å, which is smaller than that found in our complex. The donor–H and acceptor···hydrogen distances in this complex are 0.898(13) and 2.122(18) Å, which are also smaller than the respective distances in our complex.

Table 6
Cu···Cu distances (Å) of some of reported copper(II) complexes with μ-1,3-azide bridges.

Ligand used	μ-1,3-bridged azide (single) Cu···Cu distance (Å)	Refs.
	5.5304(9), 5.393(2), 5.3185(6)	[63–64]
	5.708(1), 5.251(2)	[23,65]
	5.5935(9), 5.638(1), 5.867(1)	[66–68]
	6.0145(4), 6.0818(7)	[66,68]
	5.7461(7)	[67]
	6.085(3)	[69]
	5.129(2) (dimer)	[70]
	5.205(2) (dimer)	[71]

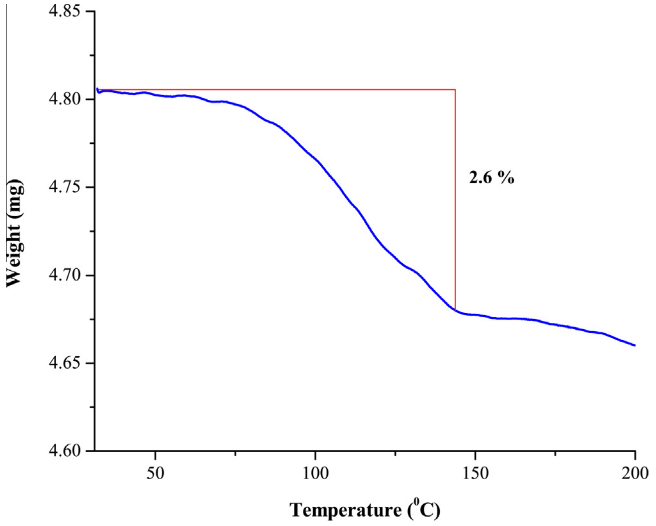


Fig. 7. TGA plot for complex **2**.

3.5. Thermogravimetric study

In the thermogravimetric analysis of complex **2**, a weight loss of 2.5% took place in the temperature range 100–150 °C (Fig. 7), corresponding to the loss of one water molecule (calc. 2.6%). The dehydrated species does not absorb any water molecule on exposure to the open atmosphere. There was a broad band at ca. 3432 cm^{-1} in the IR spectrum of complex **2** due to OH stretching vibrations. In the IR spectrum of the dehydrated species, this band was absent, confirming the elimination of the water molecule on heating.

3.6. Powder X-ray diffraction

The experimental powder XRD patterns of the bulk products are in good agreement with the simulated XRD patterns from single-crystal X-ray diffraction, indicating purity of the bulk samples (Figs. 1(ii), 3(ii) and 5(ii)). The simulated patterns of the complexes were calculated from the single crystal structural data (cif files) using the CCDC Mercury software.

4. Concluding remarks

Three new one-dimensional copper(II) complexes have been isolated and characterized. We have used two isomeric Schiff bases and a related Schiff base to prepare these complexes. In all the three complexes, the copper(II) centers are bridged by single end-on azides. Intra-chain N–H···O hydrogen bonding is present in only one complex. The copper(II)···copper(II) distance is minimum in that complex. The literature also shows that intra-chain hydrogen bonding interactions in related complexes lower the intra-chain copper(II)···copper(II) distances. Thus we may conclude that the intra-chain N–H···O hydrogen bonding lowers the copper(II)···copper(II) distance within the chain.

Acknowledgment

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Appendix A. Supplementary data

CCDC 956478, 956479 and 956480 contain the supplementary crystallographic data for complexes **1**, **2** and **3** respectively. 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

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