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A novel 1D chain of azido bridged copper(II) with a salen-type di-Schiff base ligand

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ABSTRACT

One new complex of Cu(II), $[(CuL)_2Cu_3(N_3)_6]_n$ (**1**) has been synthesized by reacting the "ligand complex", [CuL] with copper acetate and sodium azide (NaN_3) in methanol–water where the di-Schiff base ligand H_2L = N,N′-bis(α-methylsalicylidene)-1,3-propanediamine. The X-ray single crystal structural analysis shows that complex **1** consists of an incomplete face-sharing double cube of four Cu(II) ions with the formula of $[(CuL)_2Cu_2(N_3)_2]^{2+}$ which are connected by $[Cu(N_3)_4]^{2-}$ unit to form a novel 1D chain.

1. Introduction

Over the past decades, the rational design and synthesis of polynuclear transition metal complexes have been drawing the attention of coordination chemists not only because of their intriguing variety of architectures and topologies as observed in the metal–organic frameworks or porous coordination polymers, but also for their many possible applications in catalysis [1], magnetism [2–4], electron transport processes [5] and sensing [6]. There are various strategies to synthesize polynuclear complexes; one of them is to use the neutral complexes of divalent transition metal ion with salen type N_2O_2 donor tetradentate di-Schiff base ligands (salen = N,N′-ethylenebis(salicylideneimine)). Among the divalent first transition elements, Cu(II) forms the most stable chelate with these Schiff bases [7–9]. The oxygen atoms of the coordinated Schiff base are capable of bridging another metal ion to form multinuclear complexes in which these chelates act as "ligand complexes". Several homo- and hetero metallic complexes have been synthesized using these "ligand complexes" [10–17]. Among the homonuclear Cu(II) complexes, various species ranging from dinuclear to hexanuclear as well as polymer are reported with several anionic coligands. Interestingly, all the compounds reported so far with azide as coligand are tetranuclear in which two terminal "ligand complexes" are bridged by a central $Cu_2(N_3)_4$ unit and to our knowledge six such tetranuclear complexes are reported [18–22] till now.

We report here the synthesis and crystal structure of one new polynuclear complex of Cu(II) using azide as coligand. The focus of the present study is to synthesize any unusual complex by varying the stoichiometry of reactants and also the reaction conditions. We use ligand complex, [CuL] where H_2L = N,N′-bis(α-methylsalicylidene)-1,3-propanediamine. We succeeded in the synthesis of a novel 1D polymeric chain, $[(CuL)_2Cu_3(N_3)_6]_n$ (**1**). This complex is the first example that exhibits not only a composition and structure different from the tetranuclear [18] one usually formed by the Cu(II)-salen type complexes as precursor, but also an unprecedented chain structure among the plethora of Cu(II)-azide polynuclear complexes.

2. Experimental section

2.1. Starting materials

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

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

2.2. Synthesis of the Schiff base ligand H_2L and ligand complex [CuL]

The di-Schiff-base ligand, H_2L was prepared by standard methods [7]. Briefly, 5 mmol of 1,3-propanediamine (0.42 mL) was mixed with 10 mmol of the 2-hydroxyacetophenone (1.21 mL) in methanol (20 mL). The resulting solution was refluxed for ca. 2 h,

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and allowed to cool. The yellow colored methanolic solution was used directly for complex formation.

To a methanolic solution (10 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.852 g, 5 mmol), was added an methanolic solution of H_2L (5 mmol, 20 mL) to prepare the "ligand complex" [CuL] [7].

2.3. Synthesis of the complex $[(CuL)_2Cu_3(N_3)_6]_n$ (**1**)

The "ligand complex" [CuL] (0.372 g, 1 mmol) was dissolved in methanol (20 mL) and then 5 mL of water solution of sodium azide (0.390 g, 6 mmol) and another 10 mL methanolic solution of $Cu_2(OAc)_4{\cdot}2H_2O$ (0.399 g, 1 mmol) were added to the solution and refluxed for 1 h. The solution was cooled to room temperature and filtered. The filtrate was allowed to stand in open atmosphere for slow evaporation of the solvent. After 2 days, red X-ray quality single crystals appeared at the bottom of the vessel. The crystals were isolated, washed with methanol and dried in vacuum desiccator containing anhydrous $CaCl_2$.

Compound **1**: Yield: 0.745 g (63%). $C_{38}H_{40}Cu_5N_{22}O_4$ (1186.67): calcd. C 38.46, H 3.40, N 25.97; found C 38.51, H 3.57, N 25.90. UV/Vis (MeCN): λ_{max} = 272 nm, 347 nm, 532 nm. IR: ν(C=N) = 1597 cm^{-1}, $\nu(N_3^-)$ = 2077 and 2092 cm^{-1}.

2.4. Crystal data collection and refinement

Suitable single crystal of the 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 crystal was positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 10 s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. 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 [23]. All calculations were carried out using SHELXS 97 [24], SHELXL 97 [25], PLATON 99 [26], ORTEP-32 [27] and WinGX system Ver-1.64 [28]. Data collection, structure refinement parameters and crystallographic data for the complex are given in Table 1.

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 (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. The electronic absorption spectra (1000–240 nm) in acetonitrile solution were recorded in a Hitachi U-3501 spectrophotometer.

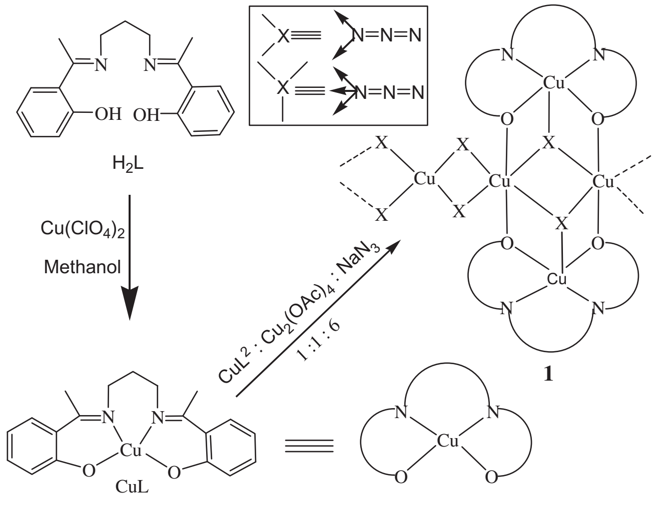
3. Results and discussion

3.1. Synthesis, IR and UV–VIS spectra of the complex

The di-Schiff base ligand (H_2L) and its Cu^{II} complex [CuL] were synthesized using the reported method [7]. The complex $[(CuL)_2Cu_3(N_3)_6]_n$ (**1**) was formed by refluxing the mixture of [CuL] with an excess of copper acetate ($Cu_2(OAc)_4{\cdot}2H_2O$) and sodium azide (1:1:6 M ratios) in MeOH—H_2O medium (see Scheme 1). If the ratios of [CuL]:copper acetate is about 2:1, the tetranuclear complex as reported by Mitra et al. resulted [18]. Therefore, for synthesis of **1**, excess copper acetate must be used. Moreover, among the salts of Cu(II), the use of copper acetate was found to be crucial in the synthesis of **1** as was also found in similar other complexes [29,30]. When we use any copper salt (perchlorate, chloride, etc.) other than acetate, only tetranuclear complex was formed even in the presence of large excess of the salt.

Besides elemental analysis, the complex was initially characterized by IR spectra. The 'ligand complex' [CuL] is neutral and obviously does not have any counter anion, whereas the complex has azide as anion. Therefore, the appearance of the characteristic intense peaks for azide of complex **1** shows a bifurcated peaks ($\upsilon_{N=N}$) in the IR spectra at around 2077 and 2092 cm^{-1}. The splitting of the band is indicative of the presence of two different type coordinated azide ion as is found in the crystal structure. The rest of the spectral pattern and band position of complex and the 'ligand complex' are very similar. A strong and sharp band due to the azomethine $\upsilon_{C=N}$ group of the Schiff base appears at 1597 cm^{-1}.

The electronic spectra of the complex, (measured in acetonitrile solution) display a single peak at 532 nm (Fig. 1a). The position of these bands is consistent of d–d transitions in copper(II) ions with the observed square-based geometry around the copper centers. Two distinct CT bands appeared in the spectra at 347, 272 nm (Fig. 1b). The band at near 272 nm can be attributed to the n–π^*



Scheme 1. Synthetic route to complex **1**.

Table 1
Crystal data and structure refinement parameters of complex **1**.

Formula	$C_{38}H_{40}Cu_5N_{22}O_4$
Formula wt.	1186.67
Space group	Pbcn
Crystal system	Orthorhombic
a (Å)	12.147(5)
b (Å)	18.899(5)
c (Å)	19.449(5)
$\alpha = \gamma$ (°)	90
β (°)	90
V (Å^3)	4465(2)
Z	4
d_{cal} (g cm^{-3})	1.765
μ (mm^{-1})	2.412
R_{int}	0.0492
No. of unique data	4749
Data with	
$I > 2\sigma(I)$	3828
R1 on $I > 2\sigma(I)$	0.0365
wR2 on $I > 2\sigma(I)$	0.0914
GOF Value	1.036

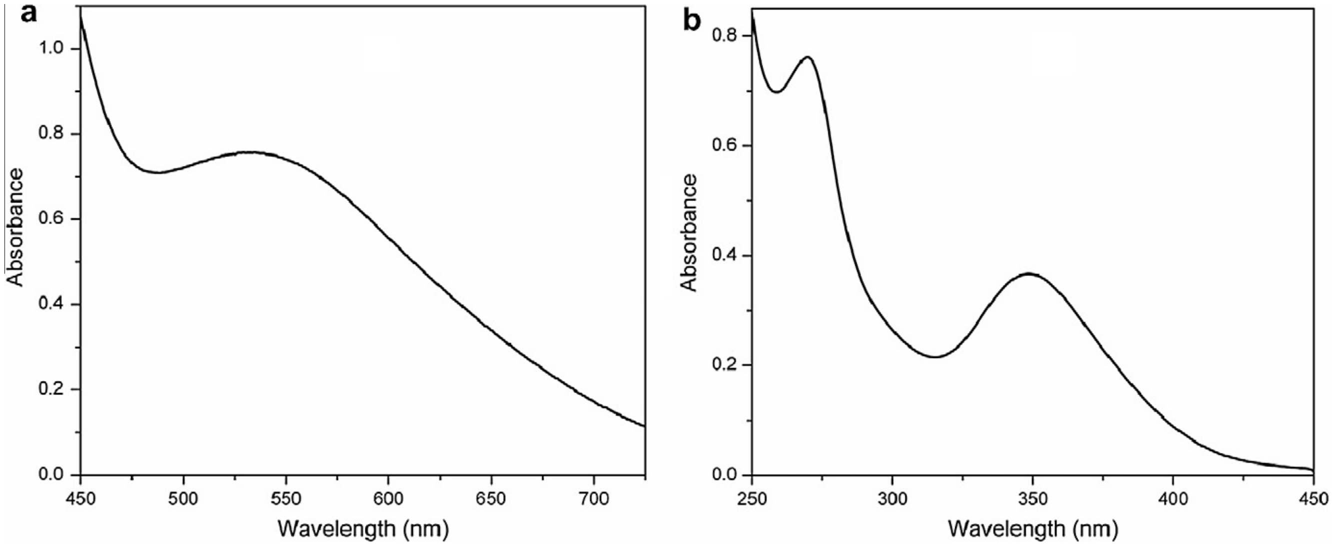


Fig. 1. Electronic spectra of **1** (a) d–d transition band at the concentration of 4×10^{-3} mol/L and (b) charge-transfer bands at the concentration of 2×10^{-5} mol/L.

transition within the ligand [31] and the other band appeared at 347 nm is due to the L → M charge transfer transition.

3.2. Description of the structure

The structure of compound **1** consists of three independent copper atoms in the asymmetric unit, two in general positions (one of them, Cu(1), containing the [CuL] unit) and one, namely Cu(3), on a twofold axis. Bond distances and angles are given in Table 2. There is only one independent Schiff base ligand and three independent azide anions (Fig. 2a). The structure consists of an incomplete face-sharing double cube of four Cu(II) ions with the formula of $[(CuL)_2Cu_2(N_3)_2]^{2+}$ (Fig. 2b). These double cubes are connected by $[Cu(N_3)_4]^{2-}$ units to form a 1D chain. Here, three Cu(II) ions in the asymmetric unit have different coordination geometries *viz* Cu(1), Cu(2) and Cu(3) have square pyramidal, octahedral and square planner geometries respectively. Bond angles and bond distances are summarized in Table 3.

Table 2
Bond distances (Å) and angles (°) around the metal centers in complex **1**.

Atoms	Distance (Å)	Atoms	Distance (Å)
Cu1—O1	1.957(2)	Cu2—N9′	2.219(5)
Cu1—O2	1.954(2)	Cu2—O2″	2.034(2)
Cu1—N1	1.982(3)	Cu2—N6″	2.374(4)
Cu1—N2	1.962(3)	Cu3—N3	1.968(4)
Cu1—N6	2.282(3)	Cu3—N9	1.975(5)
Cu2—O1	2.036(2)	Cu3—N3′	1.968(4)
Cu2—N3	2.085(3)	Cu3—N9′	1.975(5)
Cu2—N6	2.152(4)		
	Angle (°)		Angle (°)
O1—Cu1—O2	91.9(1)	N3—Cu2—N6	168.2(1)
O1—Cu1—N1	88.9(1)	N3—Cu2—N9′	72.0(2)
O1—Cu1—N2	159.2(1)	O2″—Cu2—N3	98.1(1)
O1—Cu1—N6	78.0(1)	N6″—Cu2—N3	104.5(1)
O2—Cu1—N1	177.8(1)	N6—Cu2—N9′	101.1(2)
O2—Cu1—N2	86.9(1)	O2″—Cu2—N6	92.9(1)
O2—Cu1—N6	81.6(1)	N6—Cu2—N6″	81.9(1)
N1—Cu1—N2	91.6(1)	O2″—Cu2—N9′	105.4(1)
N6—Cu1—N1	100.6(1)	N6″—Cu2—N9′	175.5(1)
N6—Cu1—N2	122.2(1)	O2″—Cu2—N6″	77.7(1)
O1—Cu2—N3	91.2(1)	N3—Cu3—N9	172.2(2)
O1—Cu2—N6	79.5(1)	N3—Cu3—N3′	103.6(2)
O1—Cu2—N9′	93.4(1)	N3—Cu3—N9′	79.9(2)
O1—Cu2—O2″	160.8(1)	N9—Cu2—N9′	97.5(2)
O1—Cu2—N6″	83.7(1)	N3′—Cu2—N9′	172.2(2)

Symmetry element ′ = 1 − x, y, 1/2 − z; ″ = 1 − x, −y, −z.

The Cu(1) ion has a distorted square pyramidal geometry where the equatorial plane is formed by the two imine N atoms N(1) and N(2) at distances 1.982(3) and 1.962(3) Å, and the two phenoxido O atoms, O(1) and O(2) at 1.957(2) and 1.954(2) Å, respectively, of the Schiff base and an axially coordinated nitrogen N(6) atom of azide coligand at 2.282(2) Å (Fig. 2b). The r.m.s. deviation of the four equatorial donor atoms from their mean coordination plane is 0.161 Å. The metal atom is 0.193(1) Å from this plane towards the axially coordinated nitrogen atom (N6). The Addison parameter of the Cu(1) atom is 0.310, indicating that it has moderate distortion towards trigonal bipyramid geometry [32]. The basal positions of octahedral Cu(2) atom is occupied by two phenoxido oxygen atoms (O1 and O2″) (symmetry operation ″ = 1 − *x*, −*y*, −*z*) at the distances 2.036(2) and 2.034(2) Å respectively and two nitrogen atoms N3 and N6 of azido coligands at 2.085(3) and 2.132(4) Å respectively. Here, one pair of nitrogen atoms (N9′ and N6″) of azido coligands are coordinated to the apical positions with the distances of 2.219(5) and 2.374(4) Å respectively (symmetry operation ′ = 1 − *x*, *y*, 1/2 − *z*) to complete the octahedral geometry around Cu(2). The r.m.s. deviation of four basally coordinated donor atoms from their mean plane is 0.204 Å. The Cu(3) atom is in a square planar environment with four coordinated azido coligands. The bond distances of azido nitrogen atoms N3 and N9 to Cu(3) are 1.968(4) and 1.975(5) Å respectively. The r.m.s. deviation of four donor atoms from their mean coordination plane is 0.123 Å with the metal atom in the plane indicating small tetrahedral distortion. This tetrahedral geometry is also verified by the so-called τ_4 index that measures the distortion between a perfect tetrahedron ($\tau_4 = 1$) and a perfect square planar geometry ($\tau_4 = 0$) with the formula: $\tau_4 = [360° - (\alpha + \beta)]/141°$, being α and β (in °) the two largest angles around the central metal in the complex [33]. The τ_4 value for Cu(3) is 0.111, confirming a slightly distorted square planar geometry for this metal center. The various kind of bridges in the compound lead to different Cu···Cu distances. The distances between Cu(1)···Cu(2) and Cu(1)···Cu(2)″ which are bridged by phenoxido and $\mu_{1,1,1}$-azido groups are at 3.236(1) and 3.286(1) Å respectively whereas the distance between Cu(2)···Cu(2) which are linked by two $\mu_{1,1,1}$-azido at 3.422(2) Å is longer than the double $\mu_{1,1}$-azido bridged Cu(3)···Cu(2) at 3.206(1) Å.

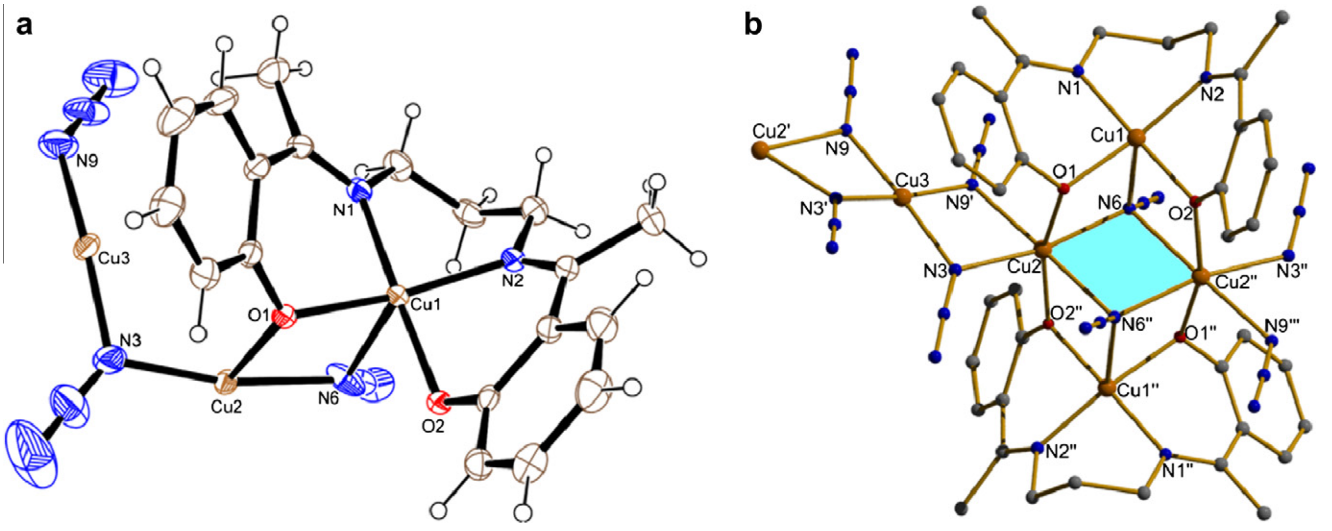


Fig. 2. (a) The asymmetric unit of complex **1** with ellipsoids at 30% probability. (b) Molecular propagation of complex **1**, symmetry element $' = 1 - x, y, 1/2 - z$; $'' = 1 - x, -y, -z$; $''' = 1 - x, y, -1/2 + z$.

Table 3
Hydrogen bond dimensions of complex **1**.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	∠D—H···A (°)	Symmetry
C2—H2···N8	0.9300	2.5900	3.455(5)	154.00	$1 - x, -y, -z$
C11—H11B···N8	0.9700	2.5000	3.109(5)	121.00	$1/2 + x, 1/2 - y, -z$

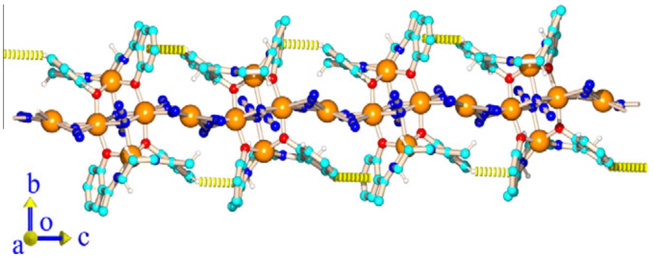


Fig. 3. 1D chain formation facilitated by C—H···π interactions. (Color codes: Cu, orange; C, light blue; N, blue; O, red; H, white.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The packing of the complex **1** was controlled by mainly two types of interactions. The C—H···π interaction with the one phenyl ring of [CuL] unit with hydrogen atom H(5) at the distance 2.92 Å along the *c*-direction to facilitate the 1D chain formation (Fig. 3). Each 1D chains are connected by C2—H2···N8 and C11—H11B···N8 hydrogen bonding interactions to produce 3D supramolecular structure (Fig. 4 and Table 3) with the distances 3.455(5) and 3.109(5) Å respectively.

It is to be noted that tetranuclear type of compounds is usually formed when salen type Schiff bases are allowed to react with excess Cu(II)-azide [18–22]. Our different synthetic approach, allowing the neutral "ligand complex" to react with copper acetate, afforded a novel 1D complex, **1** by using [CuL] as ligand complex precursor.

4. Conclusions

The synthesis of complex **1** shows that the Cu(II)-chelate, [CuL] can conveniently be used to synthesize polynuclear Cu(II) complex through bridging of the phenoxido oxygen of the Schiff base. As we mentioned earlier, the effects of various anionic coligands on structure for this type of complexes are already known. However, synthesis of compound **1** indicates that for azido coligands a compound with very unusual stoichiometry can be obtained by varying the reaction conditions, starting copper salts and stoichiometric ratios of the components.

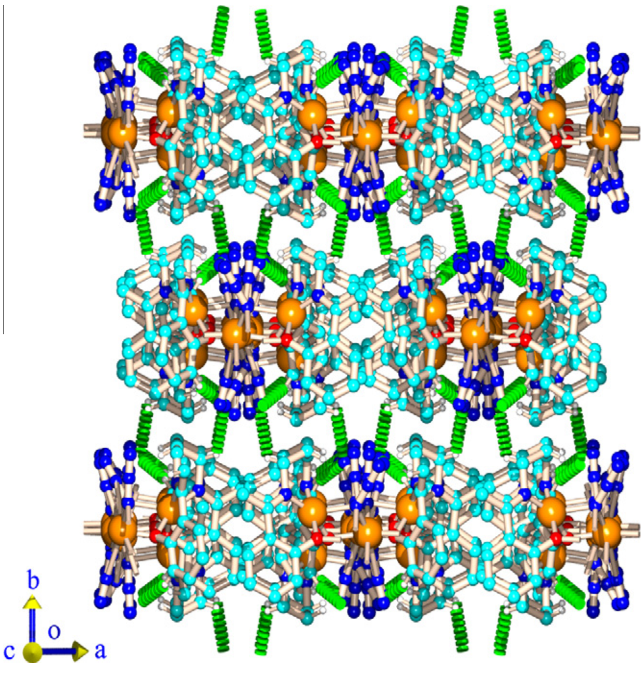


Fig. 4. 3D supramolecular structure formed by C–H···N hydrogen bonding interactions in complex **1**. (Color codes: Cu, orange; C, light blue; N, blue; O, red; H, white.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Acknowledgments

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Appendix A. Supplementary material

CCDC 842852 contains the supplementary crystallographic data in CIF format for **1**. This 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.03.030.

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