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Synthesis, characterization and self-assembly of three dicyanamide bridged polynuclear copper(II) complexes with N$_2$O donor tridentate Schiff bases as blocking ligands

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Abstract: Three copper(II) complexes [Cu(L$^1$)(µ$_{1,5}$-dca)]$_n$ (1), [Cu(L$^2$)(µ$_{1,5}$-dca)]$_n$ (2) and [Cu(L$^3$)(µ$_{1,5}$-dca)]$_n$ (3) [where HL$^1$, HL$^2$ and HL$^3$ are tridentate N$_2$O donor Schiff bases] have been synthesized and characterized by elemental analysis, IR and UV–Vis spectroscopy. The structure of each complex has been confirmed by single-crystal X-ray diffraction studies. In all three complexes, copper(II) centres are bridged by dicyanamide in end to end fashion. Complexes 1 and 2 are zigzag polymers, whereas complex 3 is a helical one. The weak forces like C-H⋯π and π⋯π interactions influence the self-assembly process in all three complexes. Such types of interactions lead to the formation of interesting supra molecular networks in three complexes.

Key words: Copper(II); Polynuclear; Schiff base; Dicyanamide; Crystal structure.
1. Introduction

Coordination polymers with various architectures such as discrete square, linear chain, zigzag chain, square network, honeycomb, square grid, diamondoids etc have been developed in last few decades [1-7]. The importance of the design and synthesis of specific architecture lies mainly in the fact that several properties of coordination polymers are directly linked with their structures and topology [8-9]. The ability of pseudo-halides, especially azide, cyanate and thiocyanate, to bridge metal ions in end-on, end-to-end, a combination of both and many other modes, it is very common to use pseudohalides for the syntheses of such systems [10-15]. Dicyanamide is sometimes called a bent pseudohalide [16] and the coordination polymers based on dicyanamide (dca) have also attracted much attention for their interesting extended architectures [17-20]. Dicyanamide has the unique ability to coordinate to metal ions in terminal monodentate, $\mu^2$, $\mu^3$ as well as unusual $\mu^4$ coordination modes (Scheme 1) [16, 21-24]. This bridging ligand is very popular for the construction of porous organic-inorganic hybrid solids with potential application in gas adsorption and catalysis [25-26]. A small change in the coligands may lead to drastic changes in their supra molecular architecture [27-31].

Focusing to copper(II), dicyanamide bridged polynuclear copper(II) complexes have received considerable attention for their potential applications in bioinorganic modeling chemistry [32], magnetic materials [33] and catalysis [34]. They could also be used to explore interesting supramolecular interactions in them. Several well established non-covalent interactions; e.g. hydrogen bonding, $\pi\cdots\pi$ stacking, C–H⋯$\pi$ forces etc., have widely been used to organize such supramolecular assemblies [35-39].
Our attempts with three different tridentate N$_2$O donor Schiff bases (HL$^1$, HL$^2$ and HL$^3$) afforded three copper(II) chains viz. $[\text{Cu}(L^1)(\mu_{1,5-\text{dca}})]_n$ (1), $[\text{Cu}(L^2)(\mu_{1,5-\text{dca}})]_n$ (2) and $[\text{Cu}(L^3)(\mu_{1,5-\text{dca}})]_n$ (3). In all three complexes, copper(II) centres are bridged by dicyanamide in end-to-end fashion, as established from the single crystal X-ray crystallographic studies. Complexes 1 and 2 are zigzag polymers, whereas complex 3 is a helical one. Herein, we would like to report the synthesis, spectroscopic characterizations, crystal structures and supramolecular assemblies of three new end-to-end dicyanamide bridged polymeric copper(II) complexes.

2. Experimental Section

All chemicals were of reagent grade and used as purchased from Sigma-Aldrich without further purification.

2.1 Preparations
2.1.1 Synthesis of \( [\text{Cu}(L^1)(\mu_1,5\text{-dca})]_n \) \( (1) \) \[ \text{HL}^1 = \text{(1)-(2-((dimethylamino)ethylimino)ethyl)naphthalene-1-ol} \]

A methanol solution (10 mL) of N,N-dimethyl-1,2-diaminoethane (0.10 mL, 1 mmol) and 1-hydroxy-2-acetonaphthone (186 mg, 1 mmol) was refluxed for ca. 1 h to form a tridentate Schiff base, \( \text{HL}^1 \). The ligand was not isolated. A methanol solution (5 mL) of copper(II) acetate monohydrate (200 mg, 1 mmol) was added into the methanol solution of the protonated ligand \( \text{HL}^1 \) with constant stirring. A methanol:water solution (5 mL) of sodium dicyanamide (89 mg, 1 mmol) was added into the reaction mixture to get a dark green solution. The stirring was continued for ca. 2 additional h. Dark green single crystals, suitable for X-ray diffraction, were obtained after few days by slow evaporation of the solution in open atmosphere.

Yield: 296 mg (77%). Anal. Calc. for \( \text{C}_{18}\text{H}_{19}\text{CuN}_5\text{O} \) (384.93): C, 56.17; H, 4.98; N, 18.19%. Found: C, 55.9; H, 4.8; N, 18.3%. FT-IR (KBr, cm\(^{-1}\)): 1577 (C=N); 2175, 2229, 2292 (dca). \( \lambda_{\text{max}} \) (nm) \[ [\varepsilon_{\text{max}}(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})] \) (acetonitrile): 311 (1.46×10\(^4\)), 385 (1.21×10\(^4\)), 603 (2.31×10\(^2\)).

2.1.2 Synthesis of \( [\text{Cu}(L^2)(\mu_1,5\text{-dca})]_n \) \( (2) \) \[ \text{HL}^2 = \text{(1)-(2-((methylamino)ethylimino)ethyl)naphthalene-1-ol} \]

It was prepared in similar method as that of complex 1, except that N-ethyl-1,2-diaminoethane (0.10 ml, 1 mmol) was used instead of N,N-dimethyl-1,2-diaminoethane. Single crystals, suitable for X-ray diffraction, were obtained on slow evaporation of the solution in refrigerator.
Yield: 285 mg (74%). Anal. Calc. for C\textsubscript{18}H\textsubscript{19}CuN\textsubscript{5}O (384.93): C, 56.17; H, 4.98; N, 18.19%. Found: C, 55.9; H, 4.8; N, 18.3%. FT-IR (KBr, cm\textsuperscript{-1}): 1579 (C=N); 2172, 2224, 2295 (dca); 3382 (N-H). \(\lambda_{\text{max}}\) (nm) \([\epsilon_{\text{max}}(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})]\) (acetonitrile): 313 (1.41×10\textsuperscript{4}), 384 (1.19×10\textsuperscript{4}), 598 (2.44×10\textsuperscript{2}).

2.1.3 Synthesis of \([\text{Cu}(L^3)(\mu_{1,5}-\text{dca})])_n\) (3) \([\text{HL}^3 = (1-(2-(ethylamino)ethylimino)ethyl)naphthalene-1-ol]\)

It was also prepared in a similar method as that of complex 1, except that N-methyl-1,2-diaminoethane (0.10 ml, 1 mmol) was used instead of N,N-dimethyl-1,2-diaminoethane. Single crystals, suitable for X-ray diffraction, were obtained on slow evaporation of the solution.

Yield: 301 mg (81%). Anal. Calc. for C\textsubscript{17}H\textsubscript{17}CuN\textsubscript{5}O (370.91): C, 55.05; H, 4.62; N, 18.88%. Found: C, 54.9; H, 4.4; N, 19.1%. FT-IR (KBr, cm\textsuperscript{-1}): 1581 (C=N); 2169, 2231, 2303 (dca); 3387 (N-H). \(\lambda_{\text{max}}\) (nm) \([\epsilon_{\text{max}}(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})]\) (acetonitrile): 307 (1.54×10\textsuperscript{4}), 387 (1.26×10\textsuperscript{4}), 597 (2.49×10\textsuperscript{2}).

2.2 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a PerkinElmer 240C elemental analyzer. IR spectra in KBr (4500-500 cm\textsuperscript{-1}) were recorded with a PerkinElmer Spectrum Two spectrophotometer. Electronic spectra in acetonitrile were recorded on a PerkinElmer Lambda 35 UV-visible spectrophotometer. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu K\alpha radiation.

2.3 X-ray crystallography

The structural analysis of complex 1 was performed on an Agilent SuperNova diffractometer with Atlas detector using mirror monochromatized Mo K\alpha (\(\lambda = 0.71073\) Å)
radiation at 170 K. CrysAlis\textsuperscript{PRO} program was used for data collection and processing [40]. The intensities were corrected for absorption using the built-in absorption correction method [41]. The structure was solved with the program Superflip [42] and refined by full-matrix least squares on $F^2$ using the WinGX [43] software equipped with SHELXL-97 [44-45]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 larger than the respective host atoms.

Suitable single crystals of complexes 2 and 3 were used for data collection using a ‘Bruker SMART APEX II’ diffractometer equipped with graphite-monochromated Mo-K\textsubscript{\alpha} radiation ($\lambda = 0.71073$ Å) at 170 K. The molecular structure was solved by direct method and refined by full-matrix least squares on $F^2$ using the SHELX-97 package [44-45]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to nitrogen atoms were located by difference Fourier maps and were kept at fixed positions. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [46]. Details of crystallographic data and refinements are given in Table 1.

2.4 Hirshfeld surfaces

Hirshfeld surfaces [47-49] and the associated 2D-fingerprint [50-52] plots were calculated using Crystal Explorer [53] which accepted a structure input file in CIF format. Bond lengths to hydrogen atoms were set to standard values. For each point on the Hirshfeld
isosurface, two distances \( d_e \), the distance from the point to the nearest nucleus external to the surface and \( d_i \), the distance to the nearest nucleus internal to the surface, were defined. The normalized contact distance \( (d_{\text{norm}}) \) based on \( d_e \) and \( d_i \) was given by

\[
d_{\text{norm}} = \frac{(d_i - r_i^{\text{vdw}})}{r_i^{\text{vdw}}} + \frac{(d_e - r_e^{\text{vdw}})}{r_e^{\text{vdw}}}
\]

where \( r_i^{\text{vdw}} \) and \( r_e^{\text{vdw}} \) were the van der Waals radii of the atoms. The value of \( d_{\text{norm}} \) was negative or positive depending on intermolecular contacts, being shorter or longer than the van der Waals separations. The parameter \( d_{\text{norm}} \) displayed a surface with a red-white-blue color scheme, where bright red spots highlighted shorter contacts, white areas represented contacts around the van der Waals separation, and blue regions were devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface was unique [54] and it was this property that suggested the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

3. Result and discussion

3.1 Synthesis

Two tridentate \( N_2O \) donor isomeric Schiff bases (\( \text{HL}^1 \) and \( \text{HL}^2 \)) have been produced by the condensation of 1-hydroxy-2-acetonaphtone with \( N,N \)-dimethyl-1,2-diaminoethane and \( N \)-ethyl-1,2-diaminoethane respectively following the literature method [55]. \( \text{HL}^1 \) and \( \text{HL}^2 \) on reaction with copper(II) acetate monohydrate followed by the addition of sodium dicyanamide give zigzag chains of \( [\text{Cu}(L^1)(\mu_{1,5}-\text{dca})]_n \) (1) and \( [\text{Cu}(L^2)(\mu_{1,5}-\text{dca})]_n \) (2) respectively. On the other
hand, HL\textsuperscript{3} is produced in a similar method by the condensation of 1-hydroxy-2-acetonaphthone with N-methyl-1,2-diaminoethane. Copper(II) acetate monohydrate on reaction with HL\textsuperscript{3} in presence of sodium dicyanamide under stirring gives helical chain of \([\text{Cu}(L^3)(\mu_{1,5\text{-dca}})]_n\) (3). In all three complexes, copper(II) centres are bridged by dicyanamide in end to end fashion. Formation of three complexes is shown in Scheme 2.

Scheme 2: Synthetic route to complexes.

3.2 Description of structures

3.2.1 \([\text{Cu}(L^1)(\mu_{1,5\text{-dca}})]_n\) (1) and \([\text{Cu}(L^2)(\mu_{1,5\text{-dca}})]_n\) (2)
The X-ray crystal structure determination reveals that in each complex copper(II) centers are bridged singly by end to end (EE) dicyanamide (dca) with the formation of a copper(II) chain. Perspective views of both complexes with selective atom numbering schemes are shown in Figure 1 and important bond lengths and bond angles are listed in Table 2. In each complex, asymmetric unit consists of a copper(II) centre, one deprotonated Schiff base ligand and a dicyanamide anion. Each copper(II) centre 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 deprotonated Schiff base and a nitrogen atom, N(3), of the EE bridged dicyanamide ligand. The apical position is occupied by one nitrogen atom N(5)\(^{\text{w}}\) (Symmetry transformation; \(\psi = a = 1+x, y, z\) in 1 and \(\psi = b = x, 1/2-y, -1/2+z\) in 2) of another EE bridged dicyanamide from a crystallographically related unit to complete elongated square pyramidal (4 + 1) geometry for each copper(II) center. The Addison parameter (\(\tau\)) for these complexes is 0.28 for 1 and 0.21 for 2. The value of Addison parameter (\(\tau\)) confirms the slightly distorted square pyramidal geometry. In the equatorial plane, the Cu–N\(_{\text{imine}}\) distances [1.958(2) Å for 1 and 1.951(2) Å for 2] is shorter than the Cu–N\(_{\text{amine}}\) [2.043(2) Å for 1 and 2.026(2) Å for 2] distances, as was also observed in similar complexes [56-57]. The deviations of the coordinating atoms N(1), N(2), O(1) and N(3) from the least square mean plane through them are 0.1403(17), -0.1466(16), 0.1482(14), -0.1419(17) Å for 1 and -0.687(3), 1.262(2), -0.6487(19) Å respectively. As usual for a square pyramid structure, the copper(II) is slightly pulled out of this mean square plane towards the apical donor atom at a distance 0.1996(2) Å for 1 and -0.6395(3) Å for 2. The five membered chelate ring, Cu(1)–N(1)–C(14)–C(13)–N(2), in 1 assumes envelope conformation with puckering parameters \(q(2) = 0.438(2)\) Å and \(\phi(2) = 71.9(2)^{\circ}\) [58-60]. In case of 2, the five-
membered chelate ring, \( \text{Cu}(1)\text{-N}(1)\text{-C}(3)\text{-C}(4)\text{-N}(2) \), assumes half-chair conformation twisted on \( \text{C}(3)\text{-C}(4) \) with puckering parameters \( q(2) = 0.426(3) \, \text{Å} \) and \( \phi(2) = 268.3(3)° \) [58-60]. The shortest \( \text{Cu} \cdots \text{Cu} \) distances in the polymeric chains are \( 8.0460(5) \, \text{Å} \) and \( 8.4246(5) \, \text{Å} \) in \( 1 \) and \( 2 \) respectively.

There is no significant hydrogen bonding interaction in complex \( 1 \). Complex \( 1 \) shows only one inter chain \( \text{C} \cdots \text{H} \cdots \pi \) interaction. The hydrogen atom, \( \text{H}(16\text{C}) \), attached with \( \text{C}(16) \), is involved in inter chain \( \text{C} \cdots \text{H} \cdots \pi \) interaction with a symmetry related \( (-1/2+x,3/2-y,-1/2+z) \) phenyl ring \( [\text{C}(1)\text{-C}(2)\text{-C}(3)\text{-C}(4)\text{-C}(5)\text{-C}(10)] \) to form a supra molecular sheet structure.

The hydrogen atom, \( \text{H}(1) \), attached to the amine nitrogen atom, \( \text{N}(1) \), of complex \( 2 \) forms inter chain hydrogen bond with a symmetry related (Symmetry transformation; \( \text{d} = -x,-y,1-z \)) phenoxy oxygen atom, \( \text{O}(1)\text{d} \). As a result of this hydrogen bonding a supra molecular sheet structure is formed as shown in Figure 2. The details of hydrogen bonding interactions are gathered in Table 3.

Complex \( 2 \) also shows two \( \text{C} \cdots \text{H} \cdots \pi \) interactions. The hydrogen atom, \( \text{H}(1\text{B}) \), attached with \( \text{C}(1) \), is involved in inter chain \( \text{C} \cdots \text{H} \cdots \pi \) interaction with a symmetry related \( (1-x,-1/2+y,3/2-z) \) phenyl ring \( [\text{C}(10)\text{-C}(11)\text{-C}(12)\text{-C}(13)\text{-C}(14)\text{-C}(15)] \). Similarly the hydrogen atom, \( \text{H}(3\text{A}) \), attached with \( \text{C}(3) \), is involved in another inter chain \( \text{C} \cdots \text{H} \cdots \pi \) interaction with a symmetry related \( (1-x,-1/2+y,3/2-z) \) phenyl ring \( [\text{C}(7)\text{-C}(8)\text{-C}(9)\text{-C}(10)\text{-C}(15)\text{-C}(16)] \). Again as a result of these \( \text{C} \cdots \text{H} \cdots \pi \) interactions a supra molecular sheet structure is formed. The details of geometric features of \( \text{C} \cdots \text{H} \cdots \pi \) interactions of both complexes are given in Table 4.

\[ 3.2.2 \quad \text{[Cu}(L^3)\!(\mu_1,5\text{-dca})]_n \quad (3) \]
The X-ray crystal structure determination reveals that copper(II) centers are bridged singly by end to end dicyanamide with the formation of both P and M helical chains (Figure 3). Important bond lengths and bond angles are listed in Table 2. The asymmetric unit consists of a copper(II) centre, one deprotonated Schiff base ligand and a dicyanamide anion. Each copper(II) centre 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 deprotonated Schiff base and a nitrogen atom, N(3), of the EE bridged dicyanamide ligand. The apical position is occupied by one nitrogen atom N(5)^(c) (Symmetry transformation; ^c = 3/2-x,-1/2+y,3/2-z) of another EE bridged dicyanamide from a crystallographically related unit to complete elongated square pyramidal (4 + 1) geometry for each copper(II) center, as confirmed by the value of the Addison parameter (τ = 0.25). In the equatorial plane, the Cu–N_imine distances [1.933(13) Å] is shorter than the Cu–N_amine [2.032(13) Å] distance, as was also observed in similar complexes [56-57]. The deviations of the coordinating atoms N(1), N(2), O(1) and N(3) from the least square mean plane through them 0.130(3), -0.134(2), 0.133(2) and -0.129(3) Å respectively. As usual for a square pyramid structure, the copper(II) is slightly pulled out of this mean square plane towards the apical donor atom at a distance 0.2432(3) Å. The closest conformation of the five-membered chelate ring, Cu(1)-N(1)-C(2)-C(3)-N(2), is envelope with puckering parameters q(2) = 0.376(3) Å, φ(2) = 247.7(4)° [58-60]. The shortest Cu···Cu distances in the polymeric chain is 8.1036(5) Å.

P helices are interconnected to adjacent M helices to generate a two dimensional (2D) supramolecular sheet structure by hydrogen bonding interactions as shown in Figure 4. The hydrogen atom, H(1), of P helix is involved in hydrogen bonding interactions with a symmetry
related (Symmetry transformation; \( e = 2-x,-y,2-z \)) dicyanamide nitrogen atom, \( N(4)^{e} \), from adjacent \( M \) helix. The details of hydrogen bonding interactions are gathered in Table 3.

Complex 3 shows significant C–H⋯π interactions. The hydrogen atoms, H(2A) and H(2B), attached with C(2), are involved in inter helix C–H⋯π interactions with symmetry related \((1/2+x,1/2-y,1/2+z)\) phenyl rings \([C(5)–C(6)–C(7)–C(8)–C(13)–C(14)]\) and \([C(8)–C(9)–C(10)–C(11)–C(12)–C(13)]\) respectively. On the other hand, the hydrogen atom, H(3B), attached with C(3), is involved in another inter helix C–H⋯π interaction with a symmetry related \((2-x,-y,1-z)\) phenyl ring \([C(8)–C(9)–C(10)–C(11)–C(12)–C(13)]\). As a result of these C–H⋯π interactions a supra molecular sheet structure is formed. The details of geometric features of C–H⋯π interactions are given in Table 4.

Complex 3 also shows significant π⋯π stacking interactions among the chelate ring \([Cu(1)–O(1)–C(14)–C(5)–C(4)–N(2)]\), another symmetry related \((2-x,-y,1-z)\) chelate ring \([Cu(1)–O(1)–C(14)–C(5)–C(4)–N(2)]\) and a symmetry related \((2-x,-y,1-z)\) phenyl ring \([C(5)–C(6)–C(7)–C(8)–C(13)–C(14)]\). The details of geometric features of π⋯π stacking interactions are given in Table 5.

3.4 IR and electronic spectra and X-ray powder diffraction pattern

In the IR spectra of complexes 1-3 strong and sharp bands at 1577, 1579 and 1581 cm\(^{-1}\) respectively are routinely noticed due to azomethine (C=N) groups of Schiff bases [55]. Two bands at 3382 and 3387 cm\(^{-1}\) respectively in the IR spectra of complexes 2 and 3 are observed due to N–H stretching vibrations [61]. For all complexes 1-3 three bands in the region 2170-2300 cm\(^{-1}\) indicate the presence of dicyanamides [62].
The electronic spectra of each complex in acetonitrile display a single broad absorption band due to d-d transitions around 600 nm [63]. Copper(II), in square pyramidal environment, usually have three transitions in between of $^2A_{1g} \leftarrow ^2B_{1g}$, $^2B_{2g} \leftarrow ^2B_{1g}$, and $^2E_g \leftarrow ^2B_{1g}$ states. The broad absorption band is due to two overlapping bands corresponding to $^2B_{2g} \leftarrow ^2B_{1g}$, and $^2E_g \leftarrow ^2B_{1g}$ states [64]. The UV absorption bands around 310 nm may be assigned to intra ligand n - $\pi^*$ transitions of azomethine (C=N) function of Schiff base [65-66]. The band around 385 nm may be attributed to LMCT transition from the N donor centres of Schiff base to copper(II).

The experimental PXRD patterns of the bulk products are in good agreement with the simulated XRD patterns from single-crystal X-ray diffraction, indicating consistency of the bulk sample. The simulated patterns of the complexes are calculated from the single crystal structural data (Cif files) using the CCDC Mercury software.

3.5 Hirshfeld surface analysis

The Hirshfeld surfaces of the complex, mapped over $d_{\text{norm}}$ (range of -0.1 to 1.5 Å), shape index and curvedness, are illustrated in Figure 5. The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The dominant interaction between O⋯H atoms can be seen in the Hirshfeld surfaces as red spots on the $d_{\text{norm}}$ surface in Figure 5. Other visible spots in the Hirshfeld surfaces correspond to H⋯H contacts. The small extent of area and light color on the surface indicates weaker and longer contact other than hydrogen bonds. The intermolecular interactions appear as distinct spikes in the 2D fingerprint plot (Figure 6). Complementary regions are visible in the fingerprint plots where one molecule acts as donor ($d_{e} > d_{i}$) and the other as an acceptor ($d_{e} < d_{i}$). The fingerprint plots can
be decomposed to highlight particular atoms pair close contacts [67]. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The proportions of N⋯H/H⋯N interactions comprise 19.6% of the total Hirshfeld surfaces for each molecule of 1. This N⋯H/H⋯N interaction appears as two distinct spikes in the 2D fingerprint plots (Figure 6). The lower spike corresponding to the acceptor spike represents the N⋯H interactions (d_e = 1.42, d_i = 1.1 Å) and the upper spike being a donor spike represents the H⋯N interactions (d_e = 1.1, d_i = 1.42 Å) in the fingerprint plots. In case of 2 proportions of N⋯H/H⋯N interactions comprise 17% of the total Hirshfeld surfaces for each molecule. This N⋯H/H⋯N interaction also appears as two distinct spikes in the 2D fingerprint plots. The lower spike corresponding to the acceptor spike represents the O⋯H interactions (d_i = 1.6, d_e = 1.2 Å) and the upper spike being a donor spike represents the H⋯O interactions (d_e = 1.6, d_i = 1.2 Å) in the fingerprint plots. The proportions of N⋯H/H⋯N interactions comprise 15.1% of the total Hirshfeld surfaces for each molecule of 3. The lower spike corresponding to the acceptor spike represents the N⋯H interactions (d_i = 1.4, d_e = 1.08 Å) and the upper spike being a donor spike represents the H⋯N interactions (d_e = 1.4, d_i = 1.08 Å) in the fingerprint plots.

4. Concluding Remarks

In conclusion, we report here the synthesis and characterization of three end to end dicyanamide bridged polynuclear copper(II) complexes (1-3) with three very similar tridentate Schiff bases as blocking ligands. In each complex, one tridentate Schiff base ligand and dicyanamide anion occupy the equatorial positions of copper(II) in similar fashion. A nitrogen atom from a symmetry related bridging dca coordinates axially at a rather long distance
furnishing an elongated square–pyramidal (4 + 1) geometry for each copper(II) center. Complexes 1 and 2 form zigzag chains, whereas complex 3 forms both P (right handed) and M (left handed) helical ones. There is no significant hydrogen bonding interactions in complex 1, but complex 2 forms a 2D sheet by interchain hydrogen bonding interactions. The adjacent P and M helices of complex 3 are interconnected by hydrogen bonding interactions to generate a 2D supramolecular sheet structure. All three complexes show significant C-H⋯π interactions. Hirshfeld surface analysis was used for visually analyzing intermolecular interactions in the crystal structures. Surfaces mapped with \( d_{\text{norm}} \) help to envisage hydrogen bonding interactions. Fingerprint plots reveal the percentage of intermolecular contacts (O⋯H and N⋯H) in the complexes.

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**Appendix A. Supplementary data**

CCDC 1409356, 1412636 and 1409357 contain the supplementary crystallographic data for 1, 2 and 3 respectively. These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/conts/retrieving.html](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.
References


Table 1: Crystal data and refinement details of complexes 1-3.

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<td>Formula</td>
<td>C$<em>{18}$H$</em>{19}$CuN$_{5}$O</td>
<td>C$<em>{18}$H$</em>{19}$CuN$_{5}$O</td>
<td>C$<em>{17}$H$</em>{17}$CuN$_{5}$O</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>384.92</td>
<td>384.93</td>
<td>370.91</td>
</tr>
<tr>
<td>Temperature(K)</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/n</td>
<td>P2$_1$/c</td>
<td>P2$_1$/n</td>
</tr>
<tr>
<td>a(Å)</td>
<td>8.0460(3)</td>
<td>10.2698(2)</td>
<td>10.7877(3)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>13.7795(4)</td>
<td>12.1204(3)</td>
<td>14.1330(4)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>15.2279(5)</td>
<td>14.0994(3)</td>
<td>11.1638(3)</td>
</tr>
<tr>
<td>β(deg)</td>
<td>97.112(3)</td>
<td>92.772(1)</td>
<td>103.010(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>d$_{calc}$(g cm$^{-3}$)</td>
<td>1.526</td>
<td>1.459</td>
<td>1.486</td>
</tr>
<tr>
<td>μ(mm$^{-1}$)</td>
<td>1.320</td>
<td>1.262</td>
<td>1.331</td>
</tr>
<tr>
<td>F(000)</td>
<td>796</td>
<td>796</td>
<td>764</td>
</tr>
<tr>
<td>Total Reflections</td>
<td>6950</td>
<td>25212</td>
<td>24293</td>
</tr>
<tr>
<td>Unique Reflections</td>
<td>3842</td>
<td>3284</td>
<td>3183</td>
</tr>
<tr>
<td>Observed data [I &gt; 2 σ (I)]</td>
<td>3325</td>
<td>2663</td>
<td>2510</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>229</td>
<td>230</td>
<td>217</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.024</td>
<td>0.040</td>
<td>0.042</td>
</tr>
</tbody>
</table>
Table 2: Selected bond lengths (Å) and bond angles (°) around copper(II) for complexes 1-3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond lengths</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(1)-O(1)</td>
<td>1.8824(14)</td>
<td>1.893(2)</td>
<td>1.883(2)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.0426(17)</td>
<td>2.026(2)</td>
<td>2.017(2)</td>
</tr>
<tr>
<td>Cu(1)-N(2)</td>
<td>1.9584(16)</td>
<td>1.951(2)</td>
<td>1.961(2)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.0062(18)</td>
<td>2.474(3)</td>
<td>2.007(2)</td>
</tr>
<tr>
<td>Cu(1)-N(5)$^\psi$</td>
<td>2.5409(17)</td>
<td>1.981(3)</td>
<td>2.281(3)</td>
</tr>
<tr>
<td><strong>Bond angels</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(1)</td>
<td>176.76(6)</td>
<td>164.44(9)</td>
<td>173.41(10)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(2)</td>
<td>93.03(6)</td>
<td>92.31(9)</td>
<td>92.74(9)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(3)</td>
<td>87.93(7)</td>
<td>97.96(10)</td>
<td>88.77(9)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(5)$^\psi$</td>
<td>93.44(6)</td>
<td>89.97(10)</td>
<td>95.46(10)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(2)</td>
<td>86.05(7)</td>
<td>85.96(10)</td>
<td>85.67(9)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>91.88(7)</td>
<td>97.32(11)</td>
<td>90.33(10)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(5)$^\psi$</td>
<td>89.68(6)</td>
<td>91.49(11)</td>
<td>91.11(11)</td>
</tr>
<tr>
<td>N(2)-Cu(1)-N(3)</td>
<td>159.96(7)</td>
<td>85.61(10)</td>
<td>158.05(10)</td>
</tr>
<tr>
<td>N(2)-Cu(1)-N(5)$^\psi$</td>
<td>90.69(6)</td>
<td>177.36(10)</td>
<td>99.46(11)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(5)$^\psi$</td>
<td>109.25(7)</td>
<td>95.39(11)</td>
<td>102.19(11)</td>
</tr>
</tbody>
</table>
\( \psi = \text{Symmetry transformation; } \psi^a = 1+x,y,z \text{ in 1, } \psi^b = x,1/2-y,-1/2+z \text{ in 2 and } \psi^c = 3/2-x,-1/2+y,3/2-z \text{ in 3.} \)

**Table 3:** Hydrogen bonding details of complexes 2 and 3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>D–H⋯A</th>
<th>D–H(Å)</th>
<th>D⋯A(Å)</th>
<th>H⋯A(Å)</th>
<th>( \angle ) D–H⋯A(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>N(1)-H(1)⋯O(1)(^d)</td>
<td>0.87</td>
<td>3.230</td>
<td>2.51</td>
<td>140</td>
</tr>
<tr>
<td>3</td>
<td>N(1)-H(1)⋯N(4)(^e)</td>
<td>0.91</td>
<td>3.311</td>
<td>2.53</td>
<td>144</td>
</tr>
</tbody>
</table>

Symmetry transformations: \(^d = 1-x,-y,1-z\); \(^e = 2-x,-y,2-z\). D = donor; H = hydrogen; A = acceptor.

**Table 4:** Geometric features (distances in Å and angles in °) of the C–H⋯π interactions obtained for complexes 1–3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>X–H⋯Cg(Ring)</th>
<th>H⋯Cg (Å)</th>
<th>C–H⋯Cg (°)</th>
<th>C⋯Cg (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C(16)–H(16C)⋯Cg(3)(^f)</td>
<td>2.85</td>
<td>128</td>
<td>3.535(3)</td>
</tr>
<tr>
<td></td>
<td>C(1)–H(1B)⋯Cg(4)(^d)</td>
<td>2.95</td>
<td>131</td>
<td>3.659(4)</td>
</tr>
<tr>
<td></td>
<td>C(3)–H(3A)⋯Cg(3)(^g)</td>
<td>2.76</td>
<td>140</td>
<td>3.557(3)</td>
</tr>
<tr>
<td></td>
<td>C(2)–H(2A)⋯Cg(3)(^h)</td>
<td>2.84</td>
<td>119</td>
<td>3.428(4)</td>
</tr>
<tr>
<td>2</td>
<td>C(2)–H(2B)⋯Cg(4)(^h)</td>
<td>2.98</td>
<td>136</td>
<td>3.747(4)</td>
</tr>
<tr>
<td></td>
<td>C(3)–H(3B)⋯Cg(4)(^i)</td>
<td>2.75</td>
<td>166</td>
<td>3.695(3)</td>
</tr>
</tbody>
</table>
Symmetry transformations: $^d = 1-x,-y,1-z; \quad ^f = -1/2+x,3/2-y,-1/2+z; \quad ^g = 1-x,-1/2+y,3/2-z; \quad ^h = 1/2+x,1/2-y,1/2+z; \quad ^i = 2-x,-y,1-z. Cg(3) = \text{Centre of gravity of the ring } [C(1)–C(2)–C(3)–C(4)–C(5)–C(10)] \text{ for complex 1}; Cg(3) = \text{Centre of gravity of the ring } [C(7)–C(8)–C(9)–C(10)–C(15)–C(16)] \text{ and } Cg(4) = \text{Centre of gravity of the ring } [C(10)–C(11)–C(12)–C(13)–C(14)–C(15)] \text{ for complex 2}; Cg(3) = \text{Centre of gravity of the ring } [C(5)–C(6)–C(7)–C(8)–C(13)–C(14)] \text{ and } Cg(4) = \text{Centre of gravity of the ring } [C(8)–C(9)–C(10)–C(11)–C(12)–C(13)] \text{ for complex 3}.

Table 5: Geometric features (distances in Å and angles in °) of the π⋯π stacking interactions obtained for complex 3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Cg(Ring I)⋯Cg(Ring J)</th>
<th>Cg⋯Cg (Å)</th>
<th>α (°)</th>
<th>Cg(I)⋯Perp (Å)</th>
<th>Cg(J)⋯Perp (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Cg(2)⋯Cg(2)(^i)</td>
<td>3.7581(14)</td>
<td>0</td>
<td>3.4395(10)</td>
<td>3.4395(10)</td>
</tr>
<tr>
<td></td>
<td>Cg(2)⋯Cg(3)(^i)</td>
<td>3.7978(16)</td>
<td>5.24(12)</td>
<td>3.4912(10)</td>
<td>3.5926(12)</td>
</tr>
</tbody>
</table>

Symmetry transformation: \(^i = 2-x,-y,1-z.

$\alpha = \text{Dihedral Angle between ring I and ring J}; \ Cg(I)⋯\text{Perp} = \text{Perpendicular distance of } Cg(I) \text{ on ring J}; \ Cg(J)⋯\text{Perp} = \text{Perpendicular distance of } Cg(J) \text{ on ring I}. \ Cg(2) = \text{Centre of gravity of the ring } [\text{Cu}(1)–\text{O}(1)–C(14)–C(5)–C(4)–\text{N}(2)] \text{ and } Cg(3) = \text{Centre of gravity of the ring } [C(5)–C(6)–C(7)–C(8)–C(13)–C(14)] \text{ for complex 3}.
Figure 1: Perspective views of complexes 1 and 2 with selective atom numbering scheme.

Symmetry transformations: $^a = 1+x,y,z$ in 1 and $^b = x,1/2-y,1/2+z$ in 2.
**Figure 2:** Sheet structure formed by inter chain hydrogen bonding interactions in complex 2.

Hydrogen atoms of ethyl groups attached to amine nitrogen atoms is not shown for clarity.
Figure 3: Perspective views of P and M helical chains of complex 3 with selective atom numbering scheme. Symmetry transformation: \[ c^\prime = 3/2-x, 1/2+y, 3/2-z. \]
Figure 4: Sheet structure formed by inter helix hydrogen bonding interactions in complex 3.
Figure 5: Hirshfeld surfaces mapped with $d_{\text{norm}}$ (top), shape index (middle) and curvedness (bottom) for complexes 1-3.
Figure 6: Fingerprint plot: Full (top); resolved into N⋯H/H⋯N (middle) and O⋯H/H⋯O (bottom) contacts contributed to the total Hirshfeld Surface area of complexes 1-3.
Synthesis, characterization and self-assembly of three dicyanamide bridged polynuclear copper(II) complexes with N₂O donor tridentate Schiff bases as blocking ligands

Anik Bhattacharyya¹, Biswa Nath Ghosh², Kari Rissanen², Shouvik Chattopadhyay¹,*

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Three polynuclear copper(II) complexes \([Cu(L^1)(\mu_{1,5}\text{-dca})]_n\) (1), \([Cu(L^2)(\mu_{1,5}\text{-dca})]_n\) (2) and \([Cu(L^3)(\mu_{1,5}\text{-dca})]_n\) (3) have been synthesized and characterized by elemental analysis, IR and UV–Vis spectroscopy. The structure of each complex has been confirmed by single-crystal X-ray diffraction studies. In all three complexes, copper(II) centres are bridged by dicyanamide in end to end fashion. The weak forces like C-H⋯π and π⋯π interactions influence the self-assembly process in all three complexes.
Synthesis, characterization and self-assembly of three dicyanamide bridged polynuclear copper(II) complexes with N$_2$O donor tridentate Schiff bases as blocking ligands

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$^b$ Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 Jyväskylä, Finland.

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