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Synthesis and characterization of four dicyanamide bridged copper(II) complexes with N_2O donor tridentate Schiff bases as blocking ligands

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- **1** Synthesis and characterization of four dicyanamide bridged
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- 3 as blocking ligands
- 4
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10 Abstract

Four copper(II) complexes $[Cu(L^1)(dca)]_n$ (1), $[Cu(L^2)(dca)(H_2O)]_2$ (2), $[Cu(L^3)(dca)]_n$ 11 (3) and $[Cu(L^4)(dca)]_n$ (4), where $HL^1 = 2 - [(2-aminoethylimino)methyl] - 4-nitrophenol, <math>HL^2 = 2 - \frac{1}{2} - \frac{1}{2}$ 12 HL^3 [(2-(methylamino)ethylimino)methyl]-4-nitrophenol, 2-[(2-13 HL^4 (dimethylamino)ethylimino)methyl]-4-nitrophenol, 14 2-[(2-= (diethylamino)ethylimino)methyl]-4-nitrophenol are tridentate Schiff-base ligands, were 15 synthesized and characterized by elemental analysis, IR and Uv-Vis spectroscopy and single-16 17 crystal X-ray diffraction studies. Complex 1 is 1-D helical, complex 2 is dimeric, complex 3 is 1-D linear chain and complex 4 is helical. X-ray single crystal structure analyses reveal that in 18 19 complexes 1, 2 and 4, dicyanamide (dca) anions act as a purely μ -1,5-bridging ligand whereas in case of complex 3, two consecutive dca units serves as 1,3-bridging ligand while the third one 20 exhibits end-to-end 1,5-bridging mode. Copper(II) centers in case of two complexes (1 and 3) 21

exhibit square pyramidal geometry as depicted by Addison parameter (τ) values whereas metal centers of complex 2 and 4 depict distorted octahedral and inverse square pyramidal geometry respectively. The role of weak forces like lone pair $\cdots \pi/\pi \cdots \pi$ interactions in influencing the selfassembly process appears to be of importance. Such types of interactions leading to supramolecular network in the four complexes are described here.

27 Keywords: Crystal Structures; Copper(II); Polynuclear; Schiff bases; Dicyanamide.

28 **1. Introduction**

Coordination polymers with diverse architectures such as the 1-D linear chain, zigzag 29 chain, 2-D square network, interwoven honeycomb, 3-D square grid, interpenetrated square 30 grids, railroad-like networks, interwoven diamondoids and even discrete squares have been 31 extensively developed [1-9]. Many important properties of coordination polymers arise from 32 these structures and topologies, and thus the rational design and construction of specific 33 architecture are particularly important. As the network topologies based on molecular building 34 35 blocks are usually controlled and modified by the coordination geometry of the central metal and 36 the structural chemistry of the organic ligands, a careful selection of the proper organic spacer and metal ion can offer some degree of control over the resultant architecture and properties [10]. 37 38 The dicyanamide (dca) in conjugation with other co-ligands has already been used extensively 39 for the synthesis of polymetallic complexes with interesting supra-molecular architectures [11-12]. Moreover, dca can also act as a linear spacer between metal centers, thus allowing the 40 investigation of the intra-molecular magnetic interaction between magnetic centers [13-16]. A 41 large variety of topologies and magnetic properties are seen in dicyanamide based complexes 42 due to their different bridging modes [17-18]. Dca based coordination polymers have also 43

44 attracted much attention because of their ability to facilitate the synthesis of metal–organic
45 frameworks containing channels and cavities with various sizes and shapes [19].

The ease of synthesis, stability under a variety of oxidative and reductive conditions and 46 their structural versatility associated with diverse applications are some of the various reasons 47 which made Schiff bases to be used as interesting chelating ligands [20-21]. They are widely 48 used in designing molecular ferromagnets, in catalysis, in biological modeling applications and 49 in preparing liquid crystals [22-25]. Tetradentate ligands of salen-type Schiff bases with N_2O_2 50 donor sets were a long standing choice of coordination chemists as they provided suitable 51 coordination environments to form mono- and poly-nuclear complexes with fascinating 52 structures [26-28]. Now-a-days, N₂O donor terdentate Schiff bases, prepared by refluxing N-53 substituted diamine with salicylaldehyde [29], are also receiving the attention in preparing high-54 nuclearity complexes [30-31]. Incorporation of additional groups in the salicylaldehyde moiety 55 may increase the denticity of the ligand [32]. Keeping this in mind, we have planned to use the 56 N₂O donor Schiff base, derived from the condensation of N-alkyl ethylenediamine with 5-57 nitrosalicyaladehyde, to prepare several copper(II) complexes. 58

We will also like to investigate the variation of the supra-molecular architecture of the complexes with the variation in H-bonding. The supra-molecular chemistry has a great impact on how efficiently chemists prepare structures of different sizes and shapes [33]. The components of these structures are held together by a variety of non-covalent forces. Some of these (lone pair $\dots\pi$, $\pi \dots \pi$ etc.) are very common and well accepted [34-39]. These are widely used in supramolecular chemistry and are very important binding forces that determine the packing of molecules in crystals. Herein, we report the synthesis, structural features, spectroscopic

66 characterization, X-ray crystal structure analysis and supra-molecular architecture involving π 67 aromatic clouds in solid-state.

68

69 **2. Experimental**

70 2.1 Materials

All reagents were of commercially available grade and were used without furtherpurification.

73 2.2 Preparation

74 2.2.1. Preparation of $[Cu(L^{1})(dca)]_{n}(1)$

A solution of Cu(OCOCH₃)₂.H₂O (199.6 mg, 1 mmol) in methanol (20 ml) was added to the methanol solution (25 ml) of 5-Nitrosalicylaldehyde (167 mg, 1 mmol) and NaN(CN)₂ (130 mg, 2 mmol) and refluxed for 1 hr to give a green solution and then 1,2-diaminoethane (0.1 ml, 1 mmol) was added to it and refluxed for additional 2 hrs to give green precipitate. The precipitate was separated from the solution by filtration and dissolved in DMSO. Single crystals, suitable for X-ray diffraction, were obtained on slow evaporation of the DMSO solution in open atmosphere after several weeks.

82 Yield: 260 mg (77%). Anal. Calcd. (%) for $C_{44}H_{40}Cu_4N_{24}O_{12}$: C, 39.11; H, 2.98; N, 83 24.88. Found: C, 39.1; H, 2.8; N, 24.7. IR (KBr, cm⁻¹): 1648 ($v_{C=N}$), 2303, 2228, 2172 (v_{dca}), 84 1325 (v_{NO2}), UV/Vis (acetonitrile): λ_{max} (ε_{max} , dm³mol⁻¹cm⁻¹) = 581 (8.6 × 10), 361 (1.6 × 10³), 85 233 (2.0 × 10³) nm. Magnetic moment is 1.73 BM.

87 2.2.2. Preparation of $[Cu(L^2)(dca)(H_2O)]_2$ (2)

Methanol solution of 5-nitrosalicylaldehyde (170 mg, 1 mmol) and N-methyl-1,2-88 diaminoethane (0.1 ml, 1 mmol) in 1:1 ratio was refluxed for 1 hr in order to synthesize a vellow 89 solution of the ligand, HL². Then methanol solution of Cu(OCOCH₃)₂,H₂O (199.6 mg, 1 mmol) 90 91 was added to the ligand solution and refluxed for 1 hr to give a deep green solution. Thereafter aqueous solution of NaN(CN)₂ (130 mg, 2 mmol) was added to it and refluxed again for an 92 additional hour to obtain deep green solution. It was then kept at room temperature. Compound 93 obtained from the mother liquor after few days was dissolved in DMF and kept undisturbed. 94 Single crystals of the complex, suitable for X-ray diffraction, were obtained from the DMF 95 solution on slow evaporation in open atmosphere after few weeks. 96

97 Yield: 450 mg (61%). Anal. Calcd. (%) for $C_{12}H_{14}CuN_6O_4$: C, 38.97; H, 3.82; N, 98 22.72. Found: C, 38.8; H, 3.7; N, 22.5. IR (KBr, cm⁻¹): 1653 ($v_{C=N}$), 2295, 2239, 2191 (v_{dca}), 99 3430 (v_{OH}), 1327 (v_{NO2}), UV/Vis (acetonitrile): λ_{max} (ε_{max} , dm³mol⁻¹cm⁻¹) = 586 (3.4 × 10²), 360 100 (6.9 × 10³), 250 (8.1 × 10³) nm. Magnetic moment is 1.72 BM.

101 2.2.3. Preparation of $[Cu(L^3)(dca)]_n(3)$

A methanol solution of of 5-nitrosalicylaldehyde (170 mg, 1 mmol) and N,N-dimethyl-1,2-diaminoethane (0.1 ml, 1 mmol) in 1:1 ratio was refluxed for 1 hr in order to prepare a clear yellow solution of ligand, HL³. Then methanol solution of Cu(OCOCH₃)₂.H₂O (199.6 mg, 1 mmol) was added to the ligand solution and refluxed for 1 hr to give a deep green solution. Thereafter aqueous solution of NaN(CN)₂ (130 mg, 2 mmol) was added to it and refluxed again for an additional hour to obtain shiny green precipitate. The precipitate was separated from the solution by filtration and dissolved in DMSO and kept undisturbed. Single crystals of the

complex, suitable for X-ray diffraction, were obtained from DMSO solution on slow evaporation 109 in open atmosphere after few weeks. 110

Yield: 290 mg (79%). Anal. Calcd. (%) for C₃₉H₄₂Cu₃N₁₈O₉: C, 42.68; H, 3.86; N, 22.97. 111 Found: C, 42.5; H, 3.7; N, 22.8. IR (KBr, cm⁻¹): 1638 (v_{C=N}), 2297, 2239, 2165 (v_{dca}), 1317 112 (v_{NO2}) , UV/Vis (acetonitrile): λ_{max} (ε_{max} , dm³mol⁻¹cm⁻¹) = 577 (9.5 × 10), 360 (1.9 × 10³), 253 113 Ò (2.4×10^3) nm. Magnetic moment is 1.73 BM. 114

2.2.4. Preparation of $[Cu(L^4)(dca)]_n$ (4) 115

Methanol solution of 5-Nitrosalicylaldehyde (170 mg, 1 mmol) with N,N-diethyl-1,2-116 diaminoethane (0.1 ml, 1 mmol) in 1:1 ratio was refluxed a for 1 hr in order to prepare a clear 117 yellow solution of the ligand, HL⁴. Then methanol solution of Cu(OCOCH₃)₂.H₂O (199.6 mg, 1 118 mmol)) was added to the ligand and refluxed for an additional hr to give a deep green solution. 119 Thereafter aqueous solution of NaN(CN)₂ (130 mg, 2 mmol) was added to it and refluxed again 120 for an hour to obtain shiny green precipitate. The precipitate was filtered and dissolved in DMF. 121 Single crystals, suitable for X-ray diffraction, were obtained from the DMF solution on slow 122 evaporation in open atmosphere after several weeks. 123

124 Yield: 260 mg (66%). Anal. Calcd. (%) for C₁₅H₁₈CuN₆O₃: C, 45.74; H, 4.61; N, 21.34. Found: C, 45.6; H, 4.4; N, 21.2. IR (KBr, cm⁻¹): 1640 (v_{C=N}), 2317, 2245, 2200 (dca), 1325 125 (v_{NO2}) , UV/Vis (acetonitrile): λ_{max} (ε_{max} , dm³mol⁻¹cm⁻¹) = 592 (1.1 × 10²), 358 (1.6 × 10³), 251 126 127 (2.0×10^3) nm. Magnetic moment is 1.71 BM.

2.3. Physical measurements 128

Elemental analysis (carbon, hydrogen and nitrogen) of the complexes were performed on 129 a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500-500 cm⁻¹) were 130

recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1000–200 nm) were recorded on a Jasco V-630 UV-VIS spectrophotometer. Fluorescence spectra were obtained on HORIBA Jobin Yvon FluoroMax-P spectrophotometer at room temperature. The electrochemical measurements were performed under a dry nitrogen atmosphere on a CH instrument (model CHI720D). The magnetic susceptibility measurements were done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.

138 2.4. X-ray Crystallography

Single crystals of suitable dimensions were mounted in inert oil and transferred to the 139 cold gas stream of the cooling device. Data were collected at 100 K on a STOE IPDS 2T 140 diffractometer using graphite monochromated Mo Ka radiation, and were corrected for 141 absorption effects using multiscanned reflections. Non hydrogen atoms were refined 142 anisotropically. H atoms of water molecules were located by difference Fourier maps and were 143 kept fixed. All other hydrogen atoms were placed in their geometrically idealized positions and 144 constrained to ride on their parent atoms. Programs used: SIR 2011 [40], SHELXL-97 [41], 145 DIAMOND [42], ORTEP [43] and STOE IPDS2 [44] software. The crystallographic and 146 refinement data are summarized in Table 1. 147

- 148 **3. Results and discussion**
- 149 *3.1. Synthesis* of *the complexes*

The mono-condensed ligand (HL¹) has been prepared conveniently as the copper(II) complex, [Cu(L¹)(dca)]_n (1) by the reaction of copper(II), 5-nitro salicyaldehyde and NaN(CN)₂ in 1:1:1 ratio in methanol, followed by the addition of equimolar amount of 1,2-diaminoethane

153 under reflux. It is to be noted that there is a possibility that the diamines may undergo condensation at both ends to produce a tetradentate di-Schiff base. We, therefore, repeated the 154 syntheses several times and found that, in presence of the strongly coordinating dicyanamide, the 155 tridentate ligand and dicyanamide occupy the four equatorial sites of copper(II). The formation 156 of the complex **1** can be rationalized in light of the templating effect of copper(II) modulated by 157 the counter anion. A templating agent can be said to contain the required information to organize 158 a collection of building blocks so that they can be linked together in a specific manner [45]. The 159 dicyanamide ion, having a more or less similar crystal field stabilization energy as the Schiff 160 base, occupies a coordination site of copper(II), leaving the other three sites to be coordinated by 161 a Schiff base and that can be achieved most efficiently by a tridentate Schiff base ligand. Similar 162 examples are already reported in the literature [46]. 163

The preparation of other tridentate Schiff-base ligands, HL^2 , HL^3 and HL^4 were routinely 164 achieved by the condensation of the N-substituted diamines, N-methyl-1,2-diaminoethane, N,N-165 dimethyl-1,2-diaminoethane and N,N-diethyl-1,2-diaminoethane with 5-Nitrosalicylaldehyde 166 separately in 1:1 molar ratio, following the literature method [32]. They are then reacted with 167 copper(II) and dca to form the complexes 2, 3 and 4 respectively. The formation of all the 168 complexes is shown in Scheme 1. The four tridentate Schiff base blocking ligands are very 169 similar; all the complexes have the same general empirical formula [CuL(dca)]_n, yet the bridging 170 topologies are drastically different. The complexes of the ligands HL^1 and HL^4 are single μ -1,5-171 dca bridged polymers, that of HL^2 is double μ -1,5-dca bridged dimer and the complex of HL^3 is 172 a 1-D chain with alternate two μ -1,3 and one μ -1,5-dca bridges. The structure of the complex of 173 HL^4 is very interesting for the presence of alternate two μ -1,3 and one μ -1,5-dca bridges. 174



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176



- 1773.2. Description of the structures
- 178 3.2.1. $[Cu(L^{1})(dca)]_{n}(1)$

An ORTEP drawing of the helical complex, [Cu(L¹)(dca)]_n, is shown in Fig. 1. Selected
bond lengths are summarized in Table 2. Selected bond angles are given in supplementary

181 material, Table S1. The structure determination reveals that the copper(II) are bridged singly by 182 end-to-end dca ligands. The asymmetric unit contains four independent copper(II), Cu(1), Cu(2), Cu(3) and Cu(4), having different environments. All the copper ions possess distorted square-183 pyramidal geometries. Each copper center is linked to two neighboring copper(II) centers by two 184 dca in end-to-end fashions to form the helix. Cu(1) is coordinated equatorially by one amine 185 nitrogen atom, N(1), one imine nitrogen atom, N(4) and one oxygen atom O(1), of the tridentate 186 Schiff base ligand, HL^1 and a nitrogen atom, N(12), of the $\mu_{1,5}$ bridged dca; this defines the basal 187 plane. The apical position is occupied by one nitrogen atom N(316)^a {Symmetry code, a=x,-188 3+y,z} of the another end-to-end bridged dca ligand from a crystallographically related unit to 189 complete the square pyramidal geometry of Cu(1). Other three copper ions in the asymmetric 190 unit also assume square pyramidal geometries (See the supplementary information for details). 191 Addison parameters [47] for all the four copper(II) are in the range of 0.1 - 0.3. In the equatorial 192 plane, the Cu-N_{imine} distances (1.959-1.970 Å) are shorter than the Cu-N_{amine} (1.915-2.028 Å) 193 distances as were also observed in similar systems [48-49]. The closest conformation of the five-194 membered chelate rings [Cu(2)-N(101)-C(102)-C(103)-N(104)] and [Cu(4)-N(301)-C(302)-195 C(303)-N(304)], is envelope with puckering parameters [50] q(2)=0.442(8) and 258.3(8) Å; 196 $\phi(2)=258.3(8)^{\circ}$ and $254.8(9)^{\circ}$ respectively, whereas similar type chelate rings formed by the same 197 diamine with Cu(1) and Cu(3), [Cu(1)-N(1)-C(2)-C(3)-N(4)] and [Cu(3)-N(2)-C(202)-198 C(203)-N(204)] are twisted on C(2)-C(3) and C(202)-C(203) with puckering parameters q(2)199 =0.398(8) Å and 0.415(8) Å, $\phi(2)=277.3(8)^{\circ}$ and $273.7(8)^{\circ}$ respectively. 200

It has also been observed that the formation of a 2D supramolecular network is ensured by two strong face-to-face $\pi \cdots \pi$ stacks (Table 3). Such multilayered $\pi \cdots \pi$ interactions contribute

to the formation of the 2D assembly in **1** {Fig. 2}. The details description of $\pi \cdots \pi$ stacking is given in supplementary information.

205

206 3.2.2. $[Cu(L^2)(dca)(H_2O)]_2(2)$

The ORTEP diagram of the complex is given in Fig. 3. Selected bond lengths are 207 summarized in Table 4. Selected bond angles are given in supplementary material, Table S2. 208 The compound features a double µ-1,5-dca bridged copper(II) dimer, in which two distorted 209 octahedral copper(II) centers are bridged by the two centrosymmetrically related dca ions in end-210 to-end fashion. The end to end bridges assume asymmetric apical-basal disposition between 211 neighboring copper(II) ions; i.e., the same dca bridge resides on the apical position of one copper 212 but in the basal plane of the neighboring copper, with the apical Cu–N distance (2.626 Å) being 213 significantly longer than the basal one (1.960-2.041 Å). Within the dimeric units, each of the two 214 copper atoms is six-coordinated, being bonded to one amine nitrogen atom, N(2), one imine 215 nitrogen atom, N(1) and one oxygen atom O(1), of the tridentate Schiff base ligand and a 216 nitrogen atom, N(4), of the end-to-end bridged dca in the basal plane. A nitrogen atom, N(6)^b, 217 from a symmetry related (-x,2-y,1-z) end-to-end bridged dca and one oxygen atom O(4) from a 218 water molecule coordinate axially at rather long distances (Cu–O=2.485(4) Å, Cu(1)–N(6)^b = 219 2.626(4) Å). to form a tetragonally distorted octahedron. In the equatorial plane, the Cu-N_{imine} 220 distance (1.960 Å) is shorter than the Cu-N_{amine} (2.041 Å) distance. The closest conformation of 221 the five-membered chelate ring [Cu(1)-N(1)-C(8)-C(9)-N(2)] is twisted on C(8)-C(9) with 222 puckering parameters q(2) = 0.425(4) Å; $\phi(2) = 92.4(4)^{\circ}$. The copper separation within the 223 dinuclear unit is 7.444 Å, and the shortest inter-dimer copper distance is 6.542 Å. 224

Adjacent dimeric units are connected to one another along a axis by strong self-225 complementary O(4)-H(4B)...N(6) {2.998(5) Å} hydrogen bonds (Table 5), giving rise to the 226 formation of a $R_2^2(16)$ hydrogen bonding motif (Fig 4a). This self-assembly propagates along an 227 228 axis, generating an infinite 1D chain. Another infinite 1D chain of complex 2 propagates along the b axis where neighboring $[Cu(L^2)(dca)(H_2O)]_2$ units are connected to one another by 229 comparatively weaker self-complementary N(2)-H(2)...N(5) {3.269(5) Å} hydrogen bonds, 230 giving rise to the formation of a $R_2^2(12)$ hydrogen bonding motif (Fig 4b). The nitro group 231 interacts with water molecule $[O(4)-H(4A)\cdots O(3) (2.994(4) Å)]$, giving rise to the formation of a 232 $R_2^{(22)}$ hydrogen bonding motif (Fig 4c). Thus another 1D chain along c axis is formed. The 233 association of several weak lone pair π interactions (Table 6) contributes to the formation of the 234 2D assembly in 2 (Fig 5). The further details of H-bonding and lone pair... π interactions 235 interactions are given in the supplementary material. 236

237

238 3.2.3 $[Cu(L^3)(dca)]_n(3)$

A 1-D linear chain structure is present in complex 3. Two consecutive dca units are 239 serving as 1,3-bridging ligand, while the third one exhibits end-to-end 1,5-bridging mode. The 240 structural building block of it is a trinuclear copper(II) moiety. The ORTEP diagram of the 241 complex is given in Fig. 6a. Three independent copper atoms Cu(1), Cu(2) and Cu(3) having 242 different environments, possess distorted square-pyramidal geometries (trigonality parameter τ 243 are in the range of 0.04–0.07). The trinuclear units connect each other to form a 1D polymer 244 where two consecutive dca anions units serving as 1,3-bridging ligand while the third one 245 246 exhibits end-to-end 1,5-bridging mode (Fig. 6b). Selected bond lengths are summarized in Table

247 7. Selected bond angles are given in supplementary material, Table S3. The dca bridges assume an asymmetric apical-basal disposition between neighboring copper(II) ions; i.e., the same $\mu_{-1,3}$ 248 or $\mu_{-1,5}$ dca bridge resides on the apical position of one copper but in the basal plane of the 249 250 neighboring copper, with the apical Cu–N distance (2.363-2.449 Å) being significantly longer than the basal one (1.947-2.054 Å), as an obvious result of Jahn Teller effect in d^9 copper(II) 251 system. In the equatorial plane, the Cu-N_{imine} distances (1.947-1.958 Å) are shorter than the Cu-252 N_{amine} (2.023-2.054 Å) distances. Deviation of the Cu(1), Cu(2) and Cu(3) atoms from the mean 253 plane towards the apical donor atom is about 0.152, 0.142, and 0.132 Å respectively. The intra-254 chain Cu. Cu distances are 5.778, 5.680 and 6.467 Å. The five-membered chelate rings [Cu(1)– 255 N(1)-C(2)-C(3)-N(4)], [Cu(2)-N(101)-C(102)-C(103)-N(104)] and [Cu(3)-N(201)-C(20256 C(203)–N(204)] connected with Cu(1), Cu(2) and Cu(3) assume envelope conformations with 257 puckering parameters q(2) = 0.424(5), 0.404(5) and 0.413(6) Å; $\phi(2) = 243.7(6)^{\circ}$, $66.2(6)^{\circ}$ and 258 $248.2(6)^{\circ}$ respectively. 259

260 The π ··· π /lone pair··· π interactions (Table 3 and Table 6) are responsible for the formation 261 of the 2D assembly in **3** (Fig. 7).

262

263 3.2.4. $[Cu(L^4)(dca)]_n(4)$

X-ray single crystal structure analyses reveal that complex **4** is a 1D helical system. It crystallized in the space group $P2_1/c$. Fig. 8 shows a perspective ORTEP view of the complex. Selected bond lengths are summarized in Table 8. Selected bond angles are given in supplementary material, Table S4. The overall geometry at the metal centre is best described as a distorted square pyramid, τ (Addison parameter) = 0.34 with a CuN4O chromophore. Cu(1) is

coordinated equatorially by one amine nitrogen atom, N(1), one imine nitrogen atom, N(4) and 269 one oxygen atom O(1), of the tridentate Schiff base ligand, HL^4 and a nitrogen atom, N(20), of 270 the end-to-end bridged dca; this defines the basal plane. The apical position is occupied by one 271 nitrogen atom N(20)^d {Symmetry code, d=-x, 1/2+y, 1/2-z} of the another end-to-end bridged dca 272 ligand from a crystallographically related unit. The dca bridges assume an asymmetric apical-273 basal disposition between neighboring copper(II) ions; i.e., the same end-to-end dca bridge 274 resides on the apical position of one copper but in the basal plane of the neighboring copper, with 275 the apical Cu–N distance (2.282 Å) being significantly longer than the basal one (1.938-2.096 276 Å), as an obvious result of Jahn Teller effect in d⁹ copper(II) system. In the equatorial plane, the 277 Cu-N_{imine} distance (1.938 Å) is shorter than the Cu-N_{amine} (2.096 Å) distance. The five-membered 278 chelate rings [Cu(1)-N(1)-C(2)-C(3)-N(4)] connected with Cu(1) assume envelope 279 conformation with puckering parameters q(2) = 0.442(4) Å; $\phi(2) = 283.7(4)^{\circ}$. 280

In complex **4**, the nitro oxygen atom, O(2) of the host molecule participates in weak lone pair π interactions (Table 7) with a chelate ring, Cu(1)–O(1)–C(7)–C(6)–C(5)–N(4) and a phenyl ring, C(6)–C(7)–C(8)–C(9)–C(10)–C(11) of the neighbouring molecule of symmetry, 1x,1-y,1-z. The lone pair π interactions contribute to the formation of the 2D assembly in **4** (Fig 9).

286

287 *3.3. IR and electronic spectra, luminescence studies and magnetic moments*

The dicyanamide anion has three characteristic IR absorptions located in the 2300–2170 cm⁻¹ region: v_{as} + v_s (C=N) at 2286 cm⁻¹, v_{as} (C=N) at 2232 cm⁻¹ and v_s (C=N) at 2179 cm⁻¹ for NaN(CN)₂ [51]. The IR spectrum of complex **1**, **2**, **3** and **4** also exhibits three strong bands:

 $v_{as}(C \equiv N) + v_s(C \equiv N)$ at 2303, 2295, 2297 and 2317 cm⁻¹, $v_{as}(C \equiv N)$ at 2228, 2239, 2239 and 2245 291 cm⁻¹ and v_s (C=N) at 2172, 2191, 2165 and 2200 cm⁻¹ respectively. These bands can be assigned 292 to the stretching frequencies $v(C \equiv N)$ of the dicyanamide ligand, linked in a bidentate μ -1,5- n^{1} : 293 η^1 coordination mode [51], as X-ray diffraction studies demonstrated. In the IR spectra of all the 294 complexes, stretching vibrations corresponding to the azomethine group appear in the range 295 1638–1653 cm⁻¹. Two satellite peaks at 2276 cm⁻¹ and 2184 cm⁻¹ may be attributed to μ -1,3 296 bridging mode of dca ligand. The infrared spectrum of complex 3 is depicted in Fig. 10. An 297 intense band within 1317–1327 cm⁻¹ may be attributed to v_{NO3} vibration [52]. In the IR spectra of 298 complex 2, a broad band at 3430 cm⁻¹ was observed may be assigned to OH stretching vibration 299 of the lattice water molecule. The presence of lattice water was also supported by the X-ray 300 crystal structure analysis. 301

The electronic spectra of all the complexes in acetonitrile were recorded 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 600 nm may be assigned to d–d transitions. The Uv–Vis spectra in acetonitrile solutions of the complexes are given in Fig 11. The concentrations of the solutions of **1**, **2**, **3** and **4** are 2.1×10^{-4} (M), 5.4×10^{-5} (M), 1.9×10^{-4} (M) and 1.0×10^{-4} (M) respectively.

The complexes 1-4 exhibit luminescence in acetonitrile medium. On excitation at 350 nm, emissions observed at 423.5, 424, 422.5 and 423 nm respectively for complexes 1, 2, 3 and 4. These are assigned as intra-ligand ${}^{1}(\pi-\pi^{*})$ fluorescence [53]. The fluorescence spectra of the complexes in acetonitrile solutions are given in Fig 12. The concentrations of the solutions of 1, 2, 3 and 4 are 8.9×10^{-6} (M), 4.0×10^{-6} (M), 8.2×10^{-6} (M) and 7.6×10^{-6} (M) respectively.

Room temperature magnetic susceptibility measurements showed that all have magnetic moments close to 1.73 BM as expected for discrete magnetically non-coupled spin-only value for copper(II) ion, as was observed in similar systems [30].

317

318 *3.4 Cyclic Voltammetry*

The cyclic voltammograms were recorded in acetonitrile solution containing TBAP as supporting electrolyte at a glassy carbon, Ag/Ag^+ (nonaquous) and a platinum wire as working, reference and auxiliary electrodes respectively at ambient temperature (300 K) with no trace of decomposition as reflected in the smooth curve, in the potential range from -2 to 2 V and were uncorrected for junction contribution. The value for the Fc–Fc+ couple under our conditions is 0.39 V.

In the positive range, from 0 to +2 V, the oxidation and reduction processes due to ligand 325 326 are observed. Cyclic scanning between 0 and -2 V permitted the study of the copper centered 327 reduction processes. A representative example of this behavior is shown in Fig. 13 for complex 4. The cyclic voltammogram shows a reduction peak (Ic) at about the potential -343 mV. This 328 can be assigned as Cu^{II}/Cu^{I} reduction process. Other peaks at more negative potentials may be 329 due to the reduction to further lower oxidation states of copper. A wave (Ia) at -606 mV is 330 observed during the reverse scan. All the redox signals are similar under different scan rates at 331 332 ambient temperature (300 K). Electrochemical responses in the total range studied for complexes 1-4 show a similar pattern. However, the differences between cathodic and anodic peaks are 333 334 more than 200 mV for the complexes 1 and 4 and this fact suggests the quasi-reversible character of the electron transfer processes in 1 and 4. On the other hand, the differences between cathodic 335

and anodic peaks are 101 and 191 mV for the complexes 2 and 3 respectively, and this suggests the reversible nature of the electron transfer processes in 2 and 3. Electrochemical data for the reduction of the copper(II) centers of the complexes 1, 2, 3 and 4 are given in Table 9.

339

340 **4.** Conclusion

In the present work, four dca bridged copper(II) complexes with N₂O donor Schiff bases 341 were synthesised and characterized. In all the complexes, we have used N₂O donor tridentate 342 Schiff bases, all of which contain additional nitro groups in them. Although the nitro groups 343 remain pendant in the complexes, the presence of pendant nitro groups in each of the complexes 344 is the key advantages of synthesizing the complexes. A set of pendant donors can perturb the 345 metal ion at additional coordination sites, in competition with external substrates, or can be used 346 as attachment points for other molecules. That is why these types of structural motif as an 347 important one with the potential to influence the future development in chemistry in a major 348 349 way.

350

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357 Supplementary data

- Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC Nos. 921569 (Complex 1), 921570 (Complex 2), 921568 (Complex 3) and 915573 (Complex 4). Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail:
- 362 <u>deposit@ccdc.cam.ac.uk</u> or www: <u>http://www.ccdc.cam.ac.uk</u>).

363

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- 446
- 447 **Table 1:** Crystal data and refinement details of complexes 1-4

	1	2	3	4
Formula	$C_{11}H_{10}CuN_6O_3$	$C_{24}H_{28}Cu_2N_{12}O_8$	$C_{13}H_{14}CuN_6O_3$	$C_{15}H_{18}CuN_6O_3$
Formula Weight	337.79	739.66	365.84	393.89
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	Pna21	P-1	P21/c	P21/c

a(Å)	19.9332(7)	6.5415(7)	14.0892(5)	18.2284(15)
b(Å)	8.3531(2)	6.9196(8)	11.7467(5)	6.6962(4)
c(Å)	30.4128(14)	17.7611(18)	27.6456(12)	14.9753(10)
α	90	85.719(9)	90	90
β	90	80.630(9)	102.090(3)	114.218(5)
γ	90	63.759(9)	90	90
Z	16	1	16	4
$d_{\rm calc} ({\rm g \ cm}^{-3})$	1.772	1.726	1.630	1.569
μ (mm ⁻¹)	1.747	1.567	1.490	1.339
F(000)	2736	378	2244	812
Total Reflections	36416	5425	28680	11034
Unique Reflections	9130	2576	8071	3009
Observed data [I >2 σ (I)]	5630	1705	4224	2414
No. of parameters	757	212	628	229
R(int)	0.105	0.078	0.095	0.060
R1, wR2 (all data)	0.0893, 0.0596	0.0694, 0.0842	0.1284, 0.0746	0.0402, 0.0686
R1, wR2 $[I > 2 \sigma(I)]$	0.0431, 0.0498	0.0385, 0.0789	0.0471, 0.0577	0.0311, 0.0670
48	1	1		

Fuble 2: Beleeted bond lengths of complex	d bond lengths of complex	Table 2: Selecte	450
--	---------------------------	------------------	-----

Cu(1)–O(1)	1.948(4)	Cu(3)–O(201)	1.922(4)
Cu(1)–N(1)	2.028(6)	Cu(3)–N(2)	2.012(6)

$Cu(1)-N(4)$ $1.959(6)$ $Cu(3)-N(116)$ $2.268(6)$ $Cu(1)-N(12)$ $1.976(7)$ $Cu(3)-N(204)$ $1.962(6)$ $Cu(1)-N(316)^a$ $2.270(6)$ $Cu(3)-N(212)$ $2.003(7)$	
Cu(1)-N(12)1.976(7)Cu(3)-N(204)1.962(6)Cu(1)-N(316)^a2.270(6)Cu(3)-N(212)2.003(7)	
$Cu(1) = N(316)^a$ 2 270(6) $Cu(3) = N(212)$ 2 003(7)	
Cu(2)-O(101) 1.921(5) Cu(4)-O(301) 1.915(5)	
Cu(2)–N(16) 1.990(6) Cu(4)–N(216) 1.975(6)	
Cu(2)-N(101) 2.025(9) Cu(4)-N(301) 1.982(9)	
Cu(2)–N(104) 1.959(6) Cu(4)–N(304) 1.970(6)	
Cu(2)-N(112) 2.277(7) Cu(4)-N(312) 2.268(7)	

451	Symmetry element, $a = x, -3+y, z$.		
452	Table 3: Geometrical Parameters (Å,	deg) for the π -Stacking Moieties involved in the	π…π
453	interactions for the complexes 1 and 3.		

				r				
Complex	rings I–J	Rc ^d	$R1v^{e}$	R2v ^r	α	β	γ	symmetry
	Cg(9)-Cg(10)	3.650(5)	3.433(3)	3.404(3)	3.8(4)	21.14	19.87	1/2+x,-1/2-y,z
1	Cg(12)-Cg(11)	3.708(5)	3.436(3)	3.588(3)	9.9(4)	14.65	22.09	1/2+x,5/2-y,z
	Cg(7)-Cg(8)	3.941(3)	3.223(2)	3.444(2)	6.0(2)	29.12	35.14	2-x,1/2+y,3/2-z
3	Cg(9)-Cg(9)	3.963(3)	3.246(2)	3.247(2)	0	34.99	34.99	1-x,1-y,1-z

^d Distance between the centroids of ring I and ring J. ^e Perpendicular distance from the centroid 454

455	of ring I to ring J. ^f Perpendicular distance from the centroid of ring J to ring I. α = Dihedral
456	Angle between ring I and ring J(°); β =Angle Cg(I)–Cg(J) vector and normal to plane I (°);
457	γ =Angle Cg(I)–Cg(J) vector and normal to plane J (°).For complex 1 , Cg(9) = Centroid of ring
458	[C(6)-C(7)-C(8)-C(9)-C(10)-C(11)]; Cg(10) = Centroid of ring [C(106)-C(107)-C(108)-C(107)-C(108)-C(107)-C(108)-C(107)-C(108)-C(107)-C(108)-C(107)-C(108)-C
459	C(109)-C(110)-C(111); $Cg(11) = Centroid of ring [C(206)-C(207)-C(208)-C(209)-C(210)-C(210)-C(208)-C(209)-C(210)-C(210)-C(208$

- C(211)] and Cg(12) = Centroid of ring [C(306)-C(307)-C(308)-C(309)-C(310)-C(311)]; for 460
- complex 3, Cg(7) = Centroid of ring [C(6)-C(7)-C(8)-C(9)-C(10)-C(11)]; Cg(8) = Centroid of461
- ring [C(106)-C(107)-C(108)-C(109)-C(110)-C(111)] and Cg(9) = Centroid of ring [C(206)-C(107)-C(108)-C(109)-C(109)-C(110)]462
- 463 C(207)-C(208)-C(209)-C(210)-C(211].

464

Table 4: Selected bond lengths of complex 2 465

			2
Selected bond lengths o	f complex 2		0
Cu(1)–O(1)	1.940(3)	Cu(1)–N(2)	2.041(3)
Cu(1)–O(4)	2.485(4)	Cu(1)–N(4)	1.971(3)
Cu(1)–N(1)	1.960(3)	$Cu(1)-N(6)^b$	2.626(4)

Symmetry element, b = -x, 2-y, 1-z466

467

Table 5: Hydrogen bond distances (Å) and angles (°) of complex 2. 468

	×			
D-H···A	D–H	D····A	H···A	∠D–H…A
N(2)–H(2)···N(5)	0.9300	3.269(5)	2.4500	147.00
O(4)–H(4A)···O(3)	0.8500	2.994(4)	2.2000	155.00
O(4)–H(4B)····N(6)	0.8500	2.998(5)	2.2100	155.00

D: Donor, A: Acceptor, H: Hydrogen 469

470

Table 6: Geometrical Parameters (Å, deg) for the Lone Pair $\cdot\cdot\cdot\pi$ interactions for the complexes 2-471

472 **4**.

Complex	Y-X(I)···· $Cg(J)$	X•••Cg(J)	Y•••Cg(J)	Y–X•••Cg(J)	X-Perp	symmetry
	N(3)–O(2)•••Cg(3)	3.414(4)	3.342(5)	76.2(3)	3.300	-x,2-y,-z
2	N(3)–O(3)•••Cg(3)	3.586(4)	3.342(5)	68.7(3)	3.314	-x,2-y,-z
	N(3)–O(2)•••Cg(3)	3.187(4)	3.457(5)	91.9(3)	3.159	1-x,2-y,-z
	N(108)–O(102)····Cg(4)	3.273(5)	3.370(5)	83.7(3)	3.227	
3	N(108)–O(103)•••Cg(4)	3.778(4)	3.370(5)	61.6(3)	3.337	2-x,-1/2+y,3/2-z
	N(208)–O(202)····Cg(9)	3.792(4)	3.699(5)	76.3(3)	3.404	1-x,1-y,1-z
	N(10)–O(2)•••Cg(2)	3.412(3)	3.643(4)	90.8(2)	3.339	
4	N(10)–O(2)•••Cg(3)	3.778(3)	4.016(4)	92.1(2)	3.359	1-x,1-y,1-z

474 For complex 2, Cg(3) = Centroid of ring [C(2)-C(3)-C(4)-C(5)-C(6)-C(7)]; for complex 3,

Cg(4) = Centroid of ring [Cu(1)-O(1)-C(7)-C(6)-C(5)-N(4)] and Cg(9) = Centroid of ring

[C(206)-C(207)-C(208)-C(209)-C(210)-C(211)] and for complex 4, Cg(2) = Centroid of ring

C(10)-C(11)]. X-Perp=Perpendicular distance between X and the ring J (Å).

Cu(1)–O(1)	1.930(4)
Cu(1)–N(1)	2.034(5)
Cu(1)–N(4)	1.958(4)
Cu(1)–N(14)	2.363(5)
Cu(1)–N(114)	1.982(4)

Table 7: Selected bond lengths of complex **3**

481	Cu(2)–O(101)	1.914(4)	
482	Cu(2)–N(101)	2.023(5)	
	Cu(2)–N(104)	1.956(4)	
483	Cu(2)–N(116)	2.407(4)	
484	Cu(2)–N(214)	1.976(4)	
485	Cu(3)–O(201)	1.919(4)	
	Cu(3)–N(201)	2.054(5)	0
486	Cu(3)–N(204)	1.947(4)	2
487	Cu(3)–N(216)	2.449(4)	
488	Cu(3)–N(18) ^c	1.953(6)	
489	~		

Symmetry element, c = -1+x, 1/2-y, -1/2+z

 Table 8: Selected bond lengths of complex 4

Cu(1)–O(1)	1.949(3)
Cu(1)–N(1)	2.096(3)
Cu(1)–N(4)	1.938(3)
Cu(1)–N(16)	2.282(3)
$Cu(1)-N(20)^d$	1.959(3)

Symmetry elements d = -x, 1/2+y, 1/2-z;

Table 9: Electrochemical data for the oxidation and reduction of the copper(II) center of the

497 complexes **1-4**.

Complex	$E_{pa}(V)$	$E_{pc}(V)$	$E_{1/2}(V)$	$\Delta E_p(mV)$	
-	1	1		1	
1	-0.654	-0.412	-0.533	242	5
2	-0.604	-0.503	-0.553	101	
3	-0.588	-0.397	-0.492	191	
4	-0.606	-0.343	-0.474	263	
L					

 $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials;

 $\Delta E_p = (E_{pa} - E_{pc}).$

512 **Legends to the figures**

- **Figure 1:** ORTEP3 diagram of **1** with 30% ellipsoid probability. Symmetry code, a = x, -3+y, z.
- **Figure 2:** (a) 2D array in crystal packing of 1, generated through $\pi \cdots \pi$ interactions. (b) $\pi \cdots \pi$
- 515 interactions are highlighted in complex **1**.
- **Figure 3:** ORTEP3 diagram of **2** with 30% ellipsoid probability. Symmetry code, b = -x,2-y,1-z.
- **Figure 4:** Formation of a 1D hydrogen bonding chain of **2**, **a**) along a axis, **b**) along b axis and **c**)
- 518 along c axis.
- 519 Figure 5: Two-dimensional assembly of 2 via lone pair... π interactions.
- **Figure 6: a)** ORTEP3 diagram of **3** with 30% ellipsoid probability. Symmetry code, c=-1+x,1/2-
- 521 y,-1/2+z. b) μ -1,5 and μ -1,5-dca bridged polynuclear chain in **3**. Only the relevant atoms are 522 shown.
- **Figure 7:** Two-dimensional assembly in **3**, generated through lone pair $\cdot\cdot\cdot\pi/\pi\cdot\cdot\pi$ interactions.
- **Figure 8:** The ORTEP3 diagram of **4** with 30% ellipsoid probability. Symmetry code, d =x,1/2+y,1/2-z.
- 526 Figure 9: Supramolecular network in 4, generated through lone pair π interactions.
- **Figure 10:** IR spectrum $(500-3500 \text{ cm}^{-1})$ of **3**.
- 528 **Figure 11:** The Uv–Vis spectra of the complexes in acetonitrile.
- 529 Figure 12: The fluorescence spectra of the complexes in acetonitrile.
- **Figure 13:** Cyclic voltammogram of **4** in acetonitrile.















(a)

















Graphical Abstract (Synopsis)

Synthesis and characterization of four dicyanamide bridged copper(II) complexes with N₂O donor tridentate Schiff bases as blocking ligands

Prasanta Kumar Bhaumik, Klaus Harms, Shouvik Chattopadhyay

Four copper(II) complexes have been synthesized and characterized by elemental analysis, IR and Uv–Vis spectroscopy and X-ray crystallography. Dicyanamide act as a purely μ -1,5-bridging ligand in complexes **1**, **2** and **4**, whereas in **3**, two consecutive dicyanamide units serve as 1,3-bridging ligand and the third one exhibits end-to-end 1,5-bridging mode.

Graphical Abstract (Pictogram)

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Synthesis and characterization of four dicyanamide bridged copper(II) complexes with N₂O donor tridentate Schiff bases as blocking ligands

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Research Highlights

- Synthesis and characterization of four copper(II) complexes.
- Use of N_2O donor Schiff bases with dicyanamide as co-ligand.
- Versatile coordination modes of dicyanamide.
- The molecular structures on the basis of X-ray crystallography.