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Cyano and end-to-end azido bridged 3D copper(II)-copper(I) mixed-valence coordination polymer and its transformation to copper nitride nanoparticles

Manoj Trivedi,[a]* Gurmeet Singh,[a] Abhinav Kumar,[b] and Nigam P. Rath[c]*

A new cyano and end-to-end azido bridged 3D copper(II)-copper(I) mixed valence polymer, $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**), copper-azide systems without cyanide $\{[Cu(NH_3)_2(N_3)_2]_4\}_n$ (**2**), and cyano-bridged copper analogue without azide $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (**3**) have been prepared and their
10 structures have been revealed by X-ray crystallography. The cyano groups acting as μ_2,η^2 and azido anions with rare asymmetric μ-1,1,3 bridging mode connecting the copper centers in **1** to form an infinite 3-D layered motif, whereas **2** is a one dimensional polymer chains bridged by two azide moieties which are μ-1 and μ-1,1,3 mode and **3** is a two dimensional $Cu^{II}Cu^{I}$ infinite polymeric network formed by cyanide bridges. The solid-state transformation of all the three compounds has also been investigated. The
15 present investigation suggests application of $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**) as a precursor for copper nitride nanoparticles.

Introduction

Metal-azido complexes have attracted considerable research interest for many years due to their fascinating structural
20 diversities, their importance in understanding magneto-structural correlations, and their promising potential applications in functional materials.[1] The azido ligand is well-known for its versatile bridging modes (Scheme 1) besides its monodentate terminal coordination.[2] Commonly, it binds the metal ions either
25 through μ-1,1-N_3 (end-on, EO) or μ-1,3-N_3 (end-to-end, EE) bridging modes.[3] Other possible bridging modes of azido ligand are μ-1,1,1-N_3 and μ-1,1,3-N_3.[4] The rare variety of coordination modes, e.g., μ-1,1,1,1-N_3, μ-1,1,3,3-N_3 and μ-1,1,1,3,3,3-N_3 have also been reported in some compounds.[5] It is to be noted that in
30 all these cases, only the two terminal nitrogen atoms of the azido ligand are involved in bonding. More significantly, azides are able to predictably transmit certain types of magnetic exchange, depending on their bridging modes. The general rule is that end-on azides transmit ferromagnetic interactions and end-to-end
35 azides transmit antiferromagnetic interactions.[6] Other interesting magnetic phenomena have also been observed in systems with mixed azide bridging modes.[7] In the past two decades, several mono- or multi-dimensional metal-azido derivatives have been reported[8], and high dimensional metal- azido complexes are still
40 the focus for researchers for their interesting topology and magnetic properties.[9] The common strategies for this purpose reported in the literature include the further extension of metal-azido assemblies by introducing a second bridging ligand[10] or the use of more azido ligands by adding a counter-cation, such as Cs^+
45 or $N(CH_3)_4^+$,[11] or by employing chelating diamine ligands, such
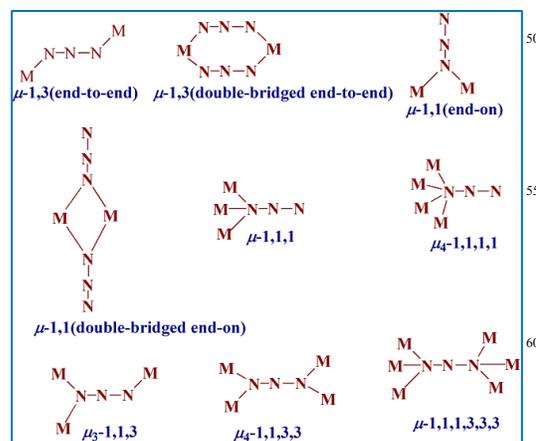
Scheme 1. Various Azido bridging modes.

as ethylenediamine and its derivatives,[12] to alter the network
65 topology. When secondary bridging ligands are used for constructing high-dimensional metal-azido systems, neutral organic ligands have been most popular, while the use of bridging anionic ligands is relatively rare. Incorporation of bridging
70 anionic ligands into metal-azido systems is still a challenge due to the competition of the negatively charged ligand with azide in the self-assembly process.[13,14] Metal nitrides have attracted considerable attention because of unique catalytic, optic, and magnetic properties. Recently, Copper nitride (Cu_3N), which has
75 a cubic anti-ReO_3 crystal structure, has engendered wide attention because of their versatile properties and potential applications in electronic devices.[15] Various investigators have reported the

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preparation of Cu_3N nanoparticles at high pressure or high temperature.[15,16] If Cu_3N could be prepared without the need for high pressure or temperature, Cu_3N nanoparticles could be easily mass produced. Keeping these aspects in mind, herein, we report the synthesis, spectroscopic characterization of a new cyano and end-to-end azido bridged copper(II)-copper(I) mixed valence polymer, $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**), and its solid-state transformation to pure copper nitride nanoparticles. In addition, we also describe the synthesis, and spectroscopic characterization of cyano-bridged Cu(II) analogue (without azide) and Cu-azide systems (without cyanide) and their decomposition studies.

Experimental

Materials and Physical Measurements

All the synthetic manipulations were performed under oxygen atmosphere. The solvents were dried and distilled before use following the standard procedures.[17] Copper cyanide, Ammonia solution, Sodium azide, and Copper(II) chloride anhydrous (all Aldrich) were used as received. Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within ±0.4% of calculated values. IR(KBr) was recorded using Perkin-Elmer FT-IR spectrophotometer. The structural characterization of the fired products at 250°C and 450°C were done using X-ray diffraction (XRD) measurements using a Bruker D8 Discover X-ray diffractometer, with Cu Kα1 radiation (λ = 1.5405 Å). Small quantities of the pyrolyzed products were dispersed in isopropyl alcohol by sonicating for about 30 min. 5 ml of the suspension was put on copper grids using a microliter pipette for TEM measurements that was carried out using a FEI TECNAI G2 200 kV transmission electron microscope. X-ray photoelectron spectrometer (XPS), Perkin-Elmer model 1257, was employed to study the chemical states, structure and composition of different elements present in the specimen. Crystals suitable for single crystal X-ray analyses for $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**), $\{[Cu(NH_3)_2(N_3)_2]\}_n$ (**2**), and $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (**3**) were grown from slow evaporation at room temperature. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on X-calibur S oxford diffractometer using graphite monochromaed M_o-K_α radiation. CrysAlisPro, Agilent Technologies software packages[18] were used for data collection and data integration for **1**, to **3**. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[19] The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the interaction and stacking distances.[19]

Syntheses and Characterization

Synthesis of $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (1)

Copper cyanide (0.178 g, 2 mmol) was added slowly to a solution of CH_3OH (10 mL), and CH_2Cl_2 (10 mL) containing ammonia solution (10 mL, 25%). The resulting solution was stirred at room temperature for 1 hour. Slowly, color of the solution changes from creamy to light blue color. After 1 hours of stirring, 4 equivalents of NaN_3 salt (8 mmol, 520 mg) was added to this solution and again stirred overnight. The resulting dark blue color solution was filtered and left for slow evaporation. Dark blue color block shaped crystals suitable for single crystal X-ray studies were found after three weeks. Yield: (0.792 g, 60%). Anal. Calc. for $C_{25}H_{20}N_9Cu_4$: C, 10.91; H, 2.73; N, 19.09. Found: C, 10.93; H, 2.85; N, 19.20. IR (cm^{-1}, KBr): ν = 3408, 2137(CN), 2092 (N$_3^-$), 2068 (N$_3^-$), 2036(N$_3^-$), 1640, 1558, 1417, 1322, 1275, 1052, 1020, 939, 802, 683, 625, 527.

Synthesis of $\{[Cu(NH_3)_2(N_3)_2]\}_n$ (2)

Copper chloride (0.268 g, 2 mmol) was added slowly to a solution of CH_3OH (10 mL), and CH_2Cl_2 (10 mL) containing ammonia solution (10 mL, 25%). The resulting solution was stirred at room temperature for 1 hour. After 1 hour of stirring, 4 equivalents of NaN_3 salt (8 mmol, 520 mg) was added to this solution and again stirred overnight. Slowly, color of the solution changes from blue to green. The resulting dark green color solution was filtered and left for slow evaporation. Dark green colour needle shaped crystals suitable for single crystal X-ray studies were found after six days. Yield: (0.218 g, 60%).

Synthesis of $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (3)

Copper cyanide (0.178 g, 2 mmol) was added slowly to a solution of CH_3OH (10 mL), and CH_2Cl_2 (10 mL) containing ammonia solution (10 mL, 25%). The resulting solution was stirred at room temperature for 24 hour. Slowly, color of the solution changes from creamy to blue color. The resulting solution was filtered and layered with methanol. Blue needle shaped crystals suitable for single crystal X-ray studies were found after two weeks. Yield: (0.553 g, 80%). Anal. Calc. for $C_4H_9N_7Cu_3$: C, 13.91; H, 2.61; N, 28.41. Found: C, 13.96; H, 2.70; N, 28.60. IR(cm^{-1}, nujol): ν = 3355, 3271, 2927, 2143, 2104, 1603, 1411, 1265, 1244, 1217, 1074, 1008, 812, 669, 634, 569, 497.

Results and Discussions

Syntheses

1 and **2** were prepared as dark blue and green colored crystals by the reaction of CuCN/anhydrous $CuCl_2$ with a concentrated solution of NH_3 (25%) containing four equivalent of NaN_3 under stirring at room temperature, while **3** (without azide) was synthesized by the reaction of CuCN with a concentrated solution of NH_3 (25%) at room temperature. These coordination polymers $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**), $\{[Cu(NH_3)_2(N_3)_2]_4\}_n$ (**2**), and $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (**3**) were obtained in good yield by slow evaporation (Scheme 2). Complex **1-3** are air stable solids, insoluble in water and other common organic solvents but soluble in dimethyl sulfoxide and do not show any signs of decomposition in solution upon exposure to air for days.
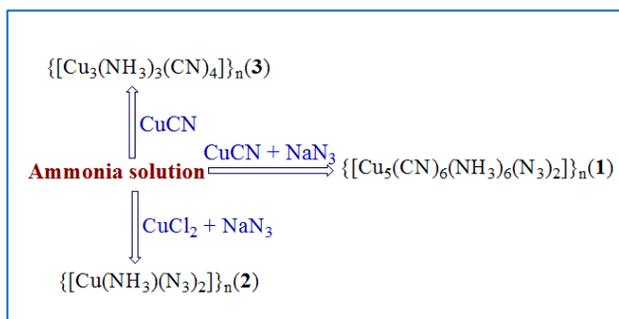
Scheme 2. Synthetic routes for the coordination polymers **1-3**.

Spectroscopy

The elemental analyses for **1** and **3** were consistent with their chemical formula, while we drop to record the elemental analysis
[5] of **2** because of explosive nature. IR spectrum of complex **1** shows the characteristic band at 2036 cm^{-1}, 2068 cm^{-1}, and 2092 cm^{-1} corresponding to bridging azide group in asymmetric μ-1,1,3 manner which are in good agreement with the literature values for bridging azido group.[20] The cyano stretching band observed in **1**
[10] at 2137 cm^{-1} indicate the existence of cyanide group in μ_2-bridging modes, while in **3**, cyano stretching band appeared at 2143 cm^{-1}, and 2104 cm^{-1} indicate the existence of two types of cyanide groups with μ_2 and μ_3-bridging modes.

Description of Crystal Structures

[15] The single crystal X-ray structural analysis of $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$(**1**) reveals an infinite three-dimensional architecture with three crystallographically independent Cu atoms bridged by μ_2,η^2 cyanide an asymmetric μ-1,1,3 azido groups (Fig. 1). There are three kinds of
[20] coordination modes for the Cu atoms. The first divalent Cu atom (Cu1) is coordinated by nitrogen atom of three ammonia molecules (N4, N5 and N6) [Cu(1)-N(4) 2.018(7) Å; Cu(1)-N(5) 2.016(8) Å; Cu(1)-N(6) 2.029(7) Å], one (μ_2,η^2)-cyanide [C(7)-N(7) = 1.152(12) Å], and one μ-1,1,3 azido group [Cu(1)-N(1) =
[25] 2.398(8) Å] and exhibits a distorted square pyramidal coordination environment. The second divalent Cu atom (Cu2) is coordinated by four (μ_2,η^2)-cyanide [N(8)-C(8)= 1.143(12) Å ; N(9)-C(9) = 1.155(12) Å] groups, and two μ-1,1,3 azido groups [Cu(2)-N(3) = 2.547 Å] and exhibits distorted octahedral
[30] coordination environment. The third monovalent Cu atom (Cu3) displays primary CuC$_3$ trigonal geometry consisting of three cyanides in (μ_2,η^2)-manner [N(8)-C(8)= 1.143(12)Å ; N(9)-C(9) = 1.155(12) Å; C(7)-N(7) = 1.152(12) Å], which is very common for Cu(I) and one μ-1,1,3 azido group is very weakly bonded to
[35] Cu$_3$. All Cu-N and Cu-C bond distances are in the range of 1.980(8) to 2.398(8) Å and 1.926(9) to 1.966(10) Å, respectively and comparable to the values reported in the literature.[20,21,22] The alternating linkages of the five Cu atoms and four cyanide and one azido groups form an 16-membered pentagonal repeating unit
[40] [Cu$_5$(CN)$_4$(N$_3$)] in the lattice (Fig. 2). The approximate size of 16-membered pentagonal rings is 8.960 × 6.759 Å^2 based on the metal–metal distances.
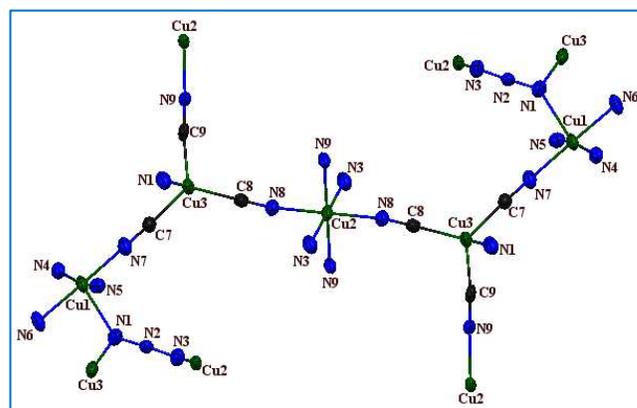
[45]

Fig. 1. Molecular representation of complex **1** with thermal ellipsoids
[50] shown at the 50% probability level. Selected bond lengths and angles: Cu(1)-N(7) 2.006(8), Cu(1)-N(5) 2.016(8), Cu(1)-N(4) 2.018(7), Cu(1)-N(6) 2.029(7), Cu(2)-C(8) 1.980(8), Cu(2)-N(9) 2.017(8), Cu(3)-C(7) 1.926(9), Cu(3)-C(9) 1.962(11), Cu(3)-N(8) 1.966(10), N(9)-C(9) 1.155(12), N(7)-C(7) 1.152(12), N(8)-C(8)
[55] 1.143(12), N(2)-N(3) 1.175(11), N(2)-N(1) 1.174(11), N(7)-Cu(1)-N(5) 88.1(3), N(7)-Cu(1)-N(4) 90.9(3), N(5)-Cu(1)-N(4) 164.8(3), N(7)-Cu(1)-N(6) 178.0(3), N(3)-N(2)-N(1) 176.4(10), N(5)-Cu(1)-N(6) 90.5(3), N(4)-Cu(1)-N(6) 90.0(3), N(7)-Cu(1)-N(1) 94.5(3), N(5)-Cu(1)-N(1) 105.1(3), N(4)-Cu(1)-N(1) 90.1(3), N(6)-Cu(1)-N(1) 87.2(3), N(9)-Cu(2)-N(9)
[60] 180.0, C(7)-Cu(3)-C(9) 124.3(4), C(7)-Cu(3)-C(8) 122.3(4), C(9)-Cu(3)-C(8) 111.9(4), C(9)-N(9)-Cu(2) 175.3(8), N(8)-C(8)-Cu(3) 178.5(8), C(7)-N(7)-Cu(1) 176.3(8), C(8)-N(8)-Cu(2) 172.6(7), N(9)-C(9)-Cu(3) 170.3(9), N(7)-C(7)-Cu(3) 173.7(9), N(2)-N(1)-Cu(1) 122.7(7).

[65] The copper atoms are bridged by the μ_2,η^2-cyanide and μ-1,1,3 azido ligands to afford a three dimensional (3-D) layered motif (Fig. 3a). Pentagonal channels are present within the framework of **1**(Fig. 3b). Crystal packing in complex **1** is stabilised by N-H···N hydrogen bond interactions (See Fig. S1, supporting
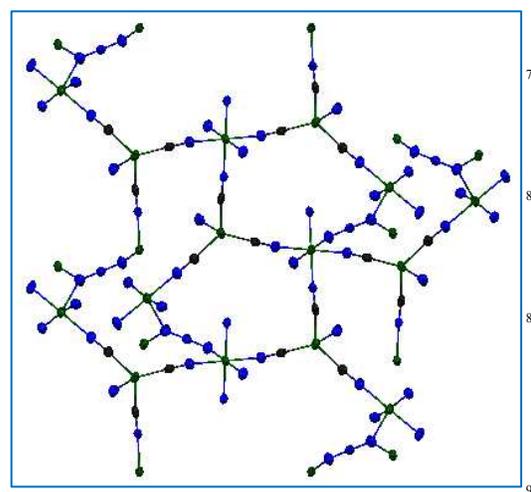[70] material). The N-H···N interactions are in the range of 2.27-2.61Å.

Fig. 2. Layered structure of the **1** showing the 16-membered pentagonal rings viewed along the *c*-axis.

The asymmetric unit of complex **2** can be described as a Cu(II) ion coordinated by two azide ligands, one acting as a bridge
[95] between the metal centres and, the other one in μ-1 coordination mode. A similar system was previously reported by Tommasino

et al.[23] in 2012. They have described as an azide-bridged Cu(II) one dimensional polymer $\{Cu(\mu_{1,1,3}\text{-}N_3)(\mu_1\text{-}N_3)(NH_3)_{0.8}(H_2O)_{1.2}\}_n$, where statistical distribution of water and ammonia were present along the chain. In our case, we isolated
5 an azide-bridged Cu(II) one dimensional polymer $\{Cu(\mu\text{-}1,1,3\text{-}N_3)(\mu\text{-}1\text{-}N_3)(NH_3)_2\}_n$, where only ammonia molecules are present. In complex **2**, the Cu(II) ion is located in a distorted octahedral environment comprising of four azide ligands at the equatorial plane and two coordinated ammonia molecules located
10 at the apical positions (Fig. 4). The bridging N_3^- ion exhibits a μ-1,1,3 coordination mode linking three Cu(II) ions to grow a 1D polymer chain running along the *b*-axis of the unit-cell (Fig. 5). The coordination polyhedron of the metal centre is completed by two ammonia molecules perpendicular to the chain.
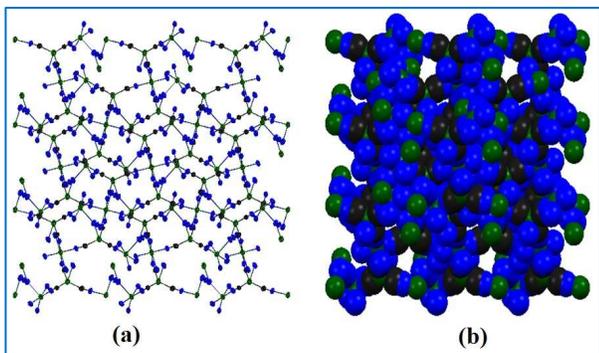

15 Fig. 3.(a) 3-D layered network of **1**, and (b) Spacefill model of **1** showing the channels in the 3D framework.

The first azide moiety is mono-coordinated (N1, N2 and N3) while the second one (N4, N5 and N6) links one copper cation to two other ones through a μ-1,1,3 coordination mode (Fig. 4). Two
20 adjacent Cu ions in the chain are linked through a rather uncommon double azide-bridge: one EO and one EE.
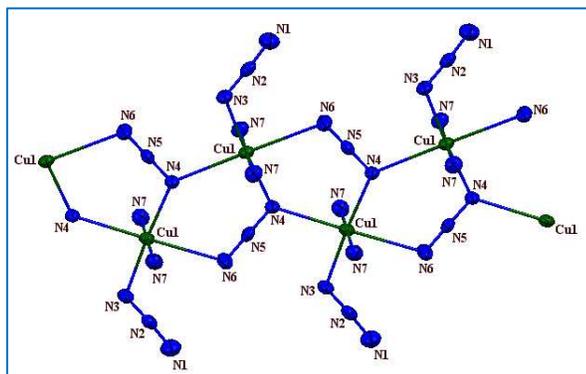

Fig. 4. Molecular representation of complex **2** with thermal ellipsoids
25 shown at the 50% probability level. Selected bond lengths and angles: Cu(1)-N(7) 1.973(3)), Cu(1)-N(3) 2.045(3), Cu(1)-N(4) 2.064(3), N(1)-N(2) 1.146(6), N(2)-N(3) 1.183(5), N(4)-N(5) 1.188(5), N(5)-N(6) 1.148(5), N(7)-Cu(1)-N(7) 177.92(17), N(7)-Cu(1)-N(3) 89.38(8), N(7)-Cu(1)-N(4) 90.57(8), N(3)-Cu(1)-N(4) 176.12(13), N(1)-N(2)-N(3)
30 177.2(4), N(2)-N(3)-Cu(1) 121.1(3), N(5)-N(4)-Cu(1) 115.6(3), N(6)-N(5)-N(4) 179.2(4).

This dimeric unit is characterized by two short Cu(1)-N(3) and Cu(1)-N(4) (2.045(3)-2.064(3)Å) and two long Cu(1)-N(4) and
35 Cu(1)–N(6) (2.532(2)Å and 2.642(2)Å) bond lengths. The Cu(1)–

N(4)–Cu(1) angle θ of 134.00° induces a separation of 4.24Å between the Cu(II) centres. Cu(1) is also connected to a second Cu(II) neighbour through a single end-to-end bridging mode characterized by the two long Cu(1)–N(6) and Cu(1)-N(4) bonds
40 (2.642(2)Å and 2.532(2)Å, respectively). This in turn results in a distance of 6.38Å between the metal centres. Crystal packing in complex **2** is stabilised by N-H···N hydrogen bond interactions (Fig. 6). The N-H···N interactions are in the range of 2.34-2.48Å. Complex **3** is a two dimensional $Cu^{II}Cu^{I}$ infinite polymeric
45 network formed by cyanide bridges as was previously reported by William et al.[24a], Vrábel et al.[24b], and Song et al.[24c].
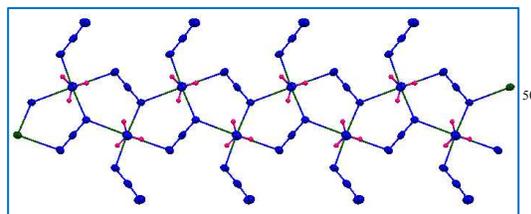

55 Fig. 5. 1D polymer chain running along *b*-axis of the unit cell for **2**.
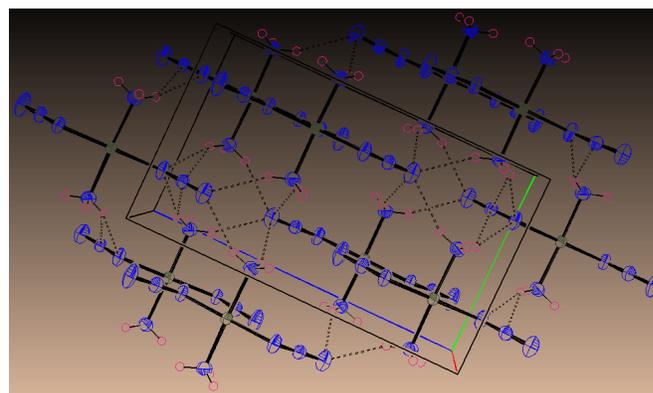

Fig. 6. Ortep diagram of **2** showing N-H···N hydrogen bond interactions in the crystal lattice.

60 To assign the oxidation state of the copper centers in **1**, we have taken recourse to the calculation based on the bond valence sum (BVS) model.[25] In this method, the valence S of a bond between two atoms i and j is related by an empirical expression (eqn (1)) where R_{ij} is the length of the bond (expressed in Å) and R_0 a
65 parameter characteristic of the bond.

$$S_{ij}= \exp[(R_0 - R_{ij})/0.37] \qquad (1)$$

This R_0, known as bond valence parameter, is however geometry and coordination number specific. The oxidation number N_i of the atom i is simply the algebraic sum (eqn (2)) of these S values of
70 all the bonds (n) around the atom i.

$$N_i = \sum_{i=1}^{n} Si \qquad (2)$$

Brown had refined R_0 values for Cu(I)–N, Cu(II)–N, Cu(I)–C and
75 Cu(II)–C bonds as 1.571, 1.731, 1.716 and 1.716 Å, respectively.[25] Taking these R_0 values, when we apply this BVS method (Table 1) to our copper compound following eqn (1), the BVS values for copper atoms in **1** are found to be 1.316 for Cu1, 1.416 for Cu2 and 1.146 for Cu3 respectively, which agreed with
80 our theoretical ones.

Table1. Bond valence values for copper centres in **1**.

Bond type	Bond distance/Å	Bond valence I(1.571, 1.716)	Bond valence II(1.731, 1.716)	Bond valance sum
Cu(3)-C(8)	1.966	0.347		1.146 for Cu3
Cu(3)-C(9)	1.962(11)	0.351		
Cu(3)-C(7)	1.926(9)	0.386		
Cu(3)-N(1)	2.602	0.062		
Cu(1)-N(4)	2.018(7)		0.301	1.316 for Cu1
Cu(1)-N(5)	2.016(18)		0.303	
Cu(1)-N(6)	2.029(7)		0.293	
Cu(1)-N(7)	2.006(8)		0.311	
Cu(1)-N(1)	2.398(8)		0.108	
Cu(2)-N(8	1.980		0.334	1.416 for Cu2
Cu(2)-N(9)	2.017		0.302	
Cu(2)-N(3)	2.547		0.072	

Thermal and PXRD Analysis

To check the thermal stability of complexes **1-3**, thermo gravimetric analysis (TGA) was carried out in the temperature range of 30 - 900 °C under a flow of N_2 with a heating rate of 10. °C min^{-1} (Fig.7 & Fig. S2-S3). Complex **1** is thermally stable and gives rise to clean vaporization, free from undesired side reactions. The TGA curve displays smooth loss of cyanide and ammonia, releasing N_2, occurring in two stages and always leaves copper nitride. This process began around 100°C and is completed around 450°C. In this case, complex **1** showed plateaus prior to the ultimate formation of copper nitride. Complex **2** is explosive in nature. The sample exploded when collecting the TGA around 162°C so further characterization has not been carried out due to safety concerns. Complex **3** is thermally stable and shows smooth loss of cyanide and ammonia, releasing N_2, occurring in two stages and always results in copper oxide. Inspired by the above findings, decomposition experiments in an air flow were also performed for **1** at 250°C and 450°C for 10h. The PXRD pattern recorded for decomposition product at 250°C (Fig. S7) is consistent with the d values of **1**, while the PXRD pattern recorded for product decomposed at 450°C (Fig. S8) is consistent with mixed phases of Cu, Cu_3N, CuO and Cu_2O. We have performed decomposition experiment under argon atmosphere for **1** at 450°C for 10h. The PXRD pattern attributed to Cu_3N having anti-ReO$_3$ structure (JCPDS No. 47-1088). No peaks deriving from Cu, Cu_2O and CuO were observed (Fig. 8). Morphology and size of Cu_3N powder was observed by using a TEM image which indicates that this agglomerate is crystalline in the nanometer range. The chemical states of Cu and N were determined by the displacement of the core electron binding energies measured by XPS (Fig. 9). In Fig. 9a, the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks are centered at 932.2 and 952.9eV, respectively, which are the typical values for Cu in Cu_3N. The presence of N has been confirmed in Fig. 9b by the N 1s peak. The N1s peak can be decomposed into two distinct peaks, with the main peak centered at 397.80eV being attributed to the Cu-N bonds of Cu_3N.[26] A broad peak centered at 403 eV, of minor intensity, may be most probably attributed to weakly bound nitrogen or molecular nitrogen adsorbed at the surface. We have also performed decomposition experiments in air at 450°C for 10h for complex **3**. On decomposition, complex **3** was converted to pure copper oxide. The results of the powder XRD analysis are shown in Fig. 10. The diffraction peaks correspond to the reflection of

CuO (PDF 892530). However, decomposition of complex **3** under argon exploded so further characterization was not possible.
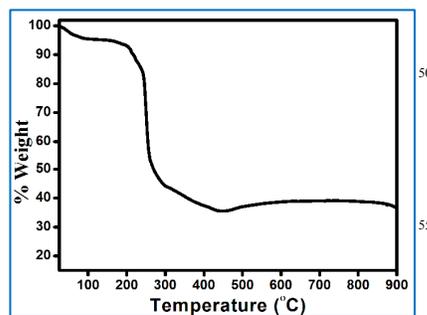
Fig. 7. TGA curve for the complex **1**.
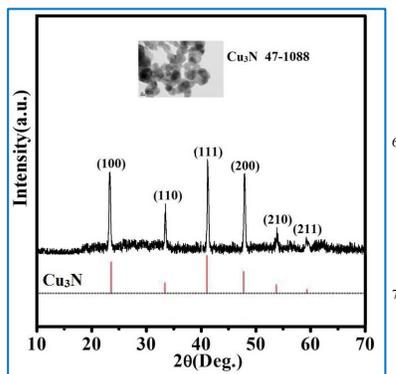
Fig. 8. XRD pattern of prepared Cu_3N nanoparticles from $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**) heated at 450°C for 10 h under argon atmosphere.
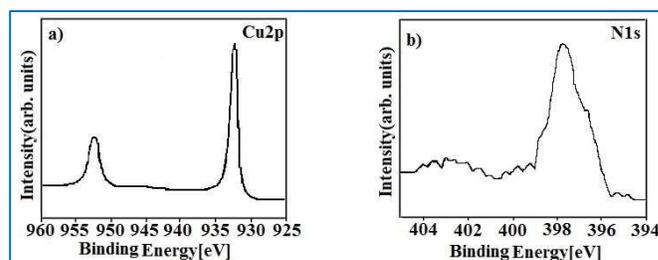
Fig. 9. XPS Spectra of Cu_3N; (a**)** Cu 2p line and (b**)** N 1s line.

Conclusions

In conclusion, we have synthesized and characterized the 3-D layered coordination motif in which Cu(II) and Cu(I) centers are linked *via* μ_2,η^2 cyano and μ-1,1,3 azido anions. In addition, we also describe the synthesis, and spectroscopic characterization of Cu-azide systems (without cyanide) $\{[Cu(NH_3)_2(N_3)_2]_4\}_n$ (**2**), and cyano-bridged Cu(II) analogue (without azide) $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (**3**), respectively. The TGA analyses and PXRD data show a clean vaporization process without premature side decompositions, and of a clear PXRD pattern dominated by the loss of the cyanide and ammonia ligands and releasing N_2 in complex **1**. Complexes **2** and **3** are explosive under argon

atmosphere; however, pyrolysis of complex **3** in air gave copper oxide. Taken together, these results make the $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$, an attractive candidate for pure copper nitride nanoparticles.

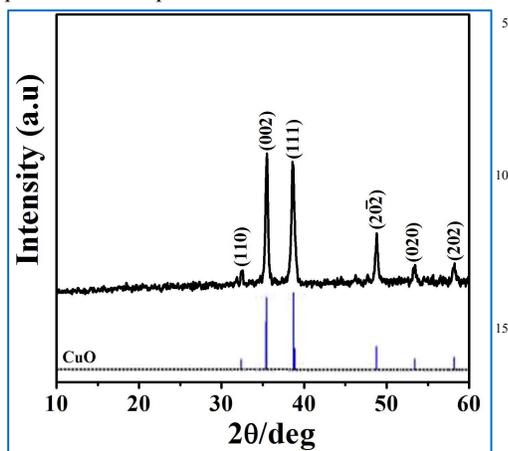Fig. 10. XRD pattern of prepared CuO from $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (**3**) heated at 450°C for 10 h in air.

Notes and references

^{a}Department of Chemistry, University of Delhi, Delhi-110007, INDIA Email: manojtri@gmail.com

^{b}Department of Chemistry, Faculty of Science, University of Lucknow, Lucknow-226 007, INDIA

^{c}Department of Chemistry & Biochemistry and Centre for Nanoscience, University of Missouri-St. Louis, One University Boulevard, St. Louis, MO 63121-4499, USA
Email: rathn@umsl.edu

§ Crystal data for **1** (CCDC 971692): $C_6H_{18}Cu_5N_{18}$, FW= 660.08, monoclinic, $P2_1/n$, a = 9.2061(11) Å, b = 11.3907(15) Å, c = 9.9910(18) Å, β=107.692(16)°, V = 998.1(3) Å^3, T = 293(2) K, Z = 2, μ, mm^{-1} = 5.276, d$_{calc}$, g cm^{-3} = 2.196, R$_1$ [I > 2σ(I)] = 0.0642, wR$_2$ = 0.1514, S = 1.061.

Crystal data for **2** (CCDC 989191): H_6N_8Cu, FW= 181.67, orthorhombic, $P n m a$, a = 6.3785(7) Å, b = 7.4502(15) Å, c = 12.6761(15) Å, β= 90°, V = 602.38(16) Å^3, T = 293(2) K, Z = 4, μ, mm^{-1} = 3.546, d$_{calc}$, g cm^{-3} = 2.003, R$_1$ [I > 2σ(I)] = 0.0267, wR$_2$ = 0.0692, S = 1.120.

Crystal data for **3** (CCDC 952627): $C_4H_9N_7Cu_3$, FW= 345.80, Monoclinic, $P2_1/n$, a = 9.3703(3) Å, b = 12.6234(3) Å, c = 9.3981(3) Å, β= 98.559(3)°, V = 1099.27(6) Å^3, T = 150(2) K, Z = 4, μ, mm^{-1} = 5.723, d$_{calc}$, g cm^{-3} = 2.089, R$_1$ [I > 2σ(I)] = 0.0890, wR$_2$ = 0.2171, S = 1.294.

† Electronic Supplementary Information (ESI) available: CCDC reference numbers 971692 (**1**), 989191(**2**), 952627(**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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Graphical Abstract: Synopsis and Pictogram

The synthesis and characterization of a cyano and end-to-end azido bridged three-dimensional copper(II)-copper(I) mixed valence polymer, $\{[Cu_5(CN)_6(NH_3)_6(N_3)_2]\}_n$ (**1**), a copper-azide systems without cyanide $\{[Cu(NH_3)_2(N_3)_2]_4\}_n$ (**2**), and a cyano-bridged copper analogue without azide $\{[Cu_3(NH_3)_3(CN)_4]\}_n$ (**3**) are reported. The solid-state transformation of the complex **1** to copper nitride nanoparticles at 450°C under argon atmosphere, suggests an attractive candidate for copper nitride nanoparticles.