

REGULAR ARTICLE

# Copper(II) complex as a precursor for formation of cyano-bridged pentanuclear Fe<sup>III</sup>-Cu<sup>II</sup> bimetallic assembly: Synthesis, characterization, crystal structure and antibacterial activity

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**Abstract.** [CuL(ClO<sub>4</sub>)<sub>2</sub>] (**1**) (L = 3,10-diisobutyl-1,3,5,8,10,12-hexaazacyclotetradecane) was synthesized by condensation reaction of ethylenediamine, formaldehyde and *iso*-butylamine in absolute ethanol. Characterization of **1** utilized various spectroscopic techniques, *viz.* elemental analysis, electrospray ionization-mass spectrometry (ESI-MS), Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis), diffuse reflectance spectroscopy (DRS) and thermogravimetric analysis (TGA). Based on these techniques, the structure of **1** was proposed as Cu(II) ion occupying octahedral geometry with four secondary amine nitrogens of the hexaazamacrocyclic ligand and two perchlorato anions. **1** was used as a precursor in the preparation of cyano-bridged bimetallic compound, [CuL]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·5H<sub>2</sub>O (**2**), by reaction with K<sub>3</sub>[Fe(CN)<sub>6</sub>] in aqueous solution. Single-crystal X-ray analysis indicated that **2** crystallized in the monoclinic system with space group *P*2<sub>1</sub>/*n*. The structure of **2** consisted of cyano-bridged Fe<sup>III</sup>-Cu<sup>II</sup> pentanuclear molecules having two [Fe(CN)<sub>6</sub>]<sup>3-</sup> anions connected to three *cis*-[CuL]<sup>2+</sup> cations *via* two *cis*-cyanide ligands from each ferrate unit. In each of pentanuclear unit, the central [CuL]<sup>2+</sup> cation exhibited a distorted octahedral geometry while the other two units exhibited a distorted square pyramidal geometry. The room temperature magnetic moments of both complexes were measured to be 1.92 B.M. for **1** and 5.61 B.M. for **2**. The *in vitro* antibacterial activity of **1** against *Staphylococcus aureus* ATCC 25923, *Escherichia coli* ATCC 25922, and *Pseudomonas aeruginosa* ATCC 27853 strains were studied and compared with standard drugs, which showed moderate antibacterial activity compared with Penicillin and Gentamicin.

**Keywords.** Hexacyanoferrate(III); copper(II) complex; cyano-bridged complex; crystal structure; antibacterial activity.

## 1. Introduction

The coordination chemistry of hexaazamacrocyclic complexes has become an attractive topic of research because of their various applications in biological field. The importance of these hexaazamacrocyclic ligands and their complexes lie in the fact that they display the structural similarities to the natural hexaazamacrocyclic complexes such as heme in human red blood cell, chlorophyll A and B, and vitamin B12.<sup>1</sup> Especially, the copper(II), nickel(II) and zinc(II) complexes<sup>2,3</sup> of the hexaazamacrocyclic with nitrogen-donor ligands have received much attention recently because of the enhanced thermodynamic and kinetic stability of the

resulting complexes<sup>4</sup> and their applications as anti-fungal,<sup>5</sup> antibacterial,<sup>6</sup> antitumor,<sup>7</sup> and antiviral agents.<sup>8</sup>

Furthermore, the bridged-cyanide bimetallic assemblies based upon hexacyanometalate building blocks [M(CN)<sub>6</sub>]<sup>n-</sup>, such as, [Fe(CN)<sub>6</sub>]<sup>3-</sup> or [Cr(CN)<sub>6</sub>]<sup>3-</sup>, have several types of molecular-based materials with interesting magnetic properties.<sup>9</sup> The terminal nitrogen atoms of the cyanide ligands of hexacyanoferrate(III) are strong donor atoms that could link two metal ions. Bridged-cyanide transition metal complexes of 3d-3d or 4f-3d electron configurations have received much interest due to the possible uses as magnetic, catalytic, and magneto-optical materials.<sup>10</sup> Recently, six-coordinate hexaazamacrocyclic copper(II) complexes were used as the complex ligand to construct a dinuclear (CuFe),<sup>11,12</sup> trinuclear (CuFe<sub>2</sub>),<sup>13</sup> and pentanuclear (Cu<sub>3</sub>Fe<sub>2</sub>)<sup>14</sup>

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complexes. It is expected that the coordinated  $[\text{CuL}]^{2+}$  cation ( $\text{L} =$  macrocyclic ligands) could accept donor atoms at the axial planes giving rise to a five- or six-coordinate environment around the copper(II) ion.

In this paper, we report part of our work in the realm of copper(II) complexes and bridged-cyanide complexes covering the synthesis, spectroscopic characterization, antibacterial study of  $[\text{CuL}(\text{ClO}_4)_2]$  (**1**), and X-ray crystal structure of  $[\text{CuL}]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$  (**2**) ( $\text{L} = 3,10$ -diisobutyl-1,3,5,8,10,12-hexaazacyclotetradecane).

## 2. Experimental

### 2.1 Materials and physical measurements

All chemicals and solvents were of reagent grade and used without further purification. Complex **1** was prepared according to the method previously reported.<sup>15</sup> Mass spectrum of **1** was recorded by electrospray ionization (ESI) technique operating in the positive ion mode by directly injecting the solution into the mass spectrometer (Waters Micro-mass). The simulated isotopic pattern of **1** was generated by mMass version 5.5 - Open Source Mass Spectrometry Tool (<http://www.mmass.org/>). Electronic absorption spectrum of **1** was obtained on a Shimadzu Lambda-1600 UV-Vis spectrophotometer in the range 400–800 nm. Solid state UV-Vis diffuse reflectance spectra (sample diluted with  $\text{BaSO}_4$ ) were recorded with a Shimadzu 2450 PC UV-Vis recording spectrophotometer in the range 400–800 nm. Infrared spectra of solid samples (in KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the range 4000–400  $\text{cm}^{-1}$ . Elemental analysis of CHN was performed using a CE instruments Flash EA 1112 series, Thermo Quest analyzer. The thermal curves (TGA) were recorded using a TGA7 Perkin Elmer, USA, with sample mass of 1.96 mg for complex **1** and 0.50 mg for complex **2** over the temperature range 50–1000°C and a heating rate 10°C  $\text{min}^{-1}$ . Powder X-ray diffraction (PXRD) patterns were recorded on a X'Pert, Philips diffractometer with  $\text{CuK}\alpha$  radiation. The simulation of PXRD patterns was carried out with the Mercury 3.8 software. Magnetic measurements were performed at room temperature on Lake Shore's fully integrated Vibrating Sample Magnetometer (VSM) system 7400.

*Synthesis safety note!* Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution.

### 2.2 Synthesis of $[\text{CuL}(\text{ClO}_4)_2]$ (**1**)

To a stirred solution of copper(II) chloride dihydrate (0.171 g, 1 mmol) and ethylenediamine (2 mmol) in absolute ethanol (10 mL) was added dropwise a solution of formaldehyde (4 mmol) and *iso*-butylamine (2 mmol) in absolute ethanol (10 mL). The reaction mixture was refluxed for 24 h. The hot solution was filtered, cooled, and perchloric acid

was added slowly. The pink color precipitate formed was filtered off, washed with absolute ethanol, and dried in air. The yield was 0.489 g (~75%). M.p.: 262–264°C. Anal. calc. for  $\text{C}_{16}\text{H}_{38}\text{CuN}_6\text{O}_8\text{Cl}_2$ : C, 33.32; H, 6.59; N, 14.58%. Found: C, 33.23; H, 6.51; N, 14.77%.

### 2.3 Synthesis of $[\text{CuL}]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$ (**2**)

To an aqueous solution (15 mL) of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (0.033 g, 0.10 mmol) was added a DMF solution (15 mL) containing complex **1** (0.056 g, 0.10 mmol) with stirring at room temperature. The resulting brown color precipitate was filtered off and washed several times with water, and dried in air. Well shaped brown single crystals suitable for X-ray structure analysis were grown at room temperature by the slow diffusion of two solutions of the reactants into a H-tube. The yield was 0.039 g (~44%). M.p.: 289–291°C. Anal. calc. for  $\text{C}_{60}\text{H}_{122}\text{Cu}_3\text{Fe}_2\text{N}_{30}\text{O}_5$ : C, 43.74; H, 6.80; N, 25.51%. Found: C, 43.71; H, 6.78; N, 25.49%.

### 2.4 Antibacterial activity of $[\text{CuL}(\text{ClO}_4)_2]$ (**1**)

The *in vitro* antibacterial activity of **1** was tested using agar disc diffusion method and each testing was performed in triplicate. The tests were carried out with three species of Gram-positive and Gram-negative bacteria, namely: *Staphylococcus aureus* (*S. aureus* ATCC 25923), *Escherichia coli* (*E. coli* ATCC 25922), and *Pseudomonas aeruginosa* (*P. aeruginosa* ATCC 27853). Solution of **1** (1 mg  $\text{mL}^{-1}$ ) in dimethylsulfoxide (DMSO) was compared with standard drugs, Penicillin (10  $\mu\text{g}$  disc $^{-1}$ ) and Gentamicin (10  $\mu\text{g}$  disc $^{-1}$ ), as the positive control. The inoculums were prepared using a 4–6 h broth culture of each bacterium and adjusted to a turbidity equivalent to a 0.5 McFarland of standard containing approximately  $10^4$ – $10^6$  CFU  $\text{mL}^{-1}$ . A sterile cotton swab was dipped into the inoculums and the surface of the nutrient agar (NA) was inoculated by streaking the swab. The paper disks impregnated with the test complex **1** was placed on the solidified medium. The plates were incubated immediately at 37°C for 24 h. The antibacterial activity was evaluated by measuring the diameter of zones showing complete inhibition (mm). Percentage of inhibition was determined by comparing between the distance of the complex **1** and positive control (Penicillin and Gentamicin) as follows:<sup>16</sup>

$$\% \text{inhibition} = \left( \frac{\text{Diameter of the sample}}{\text{Diameter of the positive control}} \right) \times 100$$

### 2.5 Crystal structure determination and refinement

Selected crystallographic data for **2** are given in Table 1. X-ray data were collected on a Bruker APEXII D8 QUEST CMOS diffractometer, using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) in the  $\omega$  scanning mode at 298(2) K. Data reduction was carried out by using SAINT Program<sup>17</sup> and a semi-empirical absorption-correction (multi-scan,

**Table 1.** Crystal data and structure refinement parameters of **2**.

Complex	<b>2</b>
Empirical formula	C <sub>60</sub> H <sub>112</sub> Cu <sub>3</sub> Fe <sub>2</sub> N <sub>30</sub>
Formula weight	1556.12
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimension	<i>a</i> = 11.8658(5) Å, <i>α</i> = 90° <i>b</i> = 9.7447(3) Å, <i>β</i> = 96.8990(12)° <i>c</i> = 37.7968(14) Å, <i>γ</i> = 90°
<i>V</i> (Å <sup>3</sup> )	4338.7(3)
<i>Z</i>	2
<i>D</i> <sub>cal</sub> (g·cm <sup>-3</sup> )	1.191
<i>μ</i> (mm <sup>-1</sup> )	1.100
<i>F</i> (000)	1642
Crystal size (mm)	0.30 × 0.28 × 0.20
<i>θ</i> range for data collection	3.01–25.75°
Index ranges	–14 ≤ <i>h</i> ≤ 14, –11 ≤ <i>k</i> ≤ 11 –46 ≤ <i>l</i> ≤ 46
Reflections collected	57347
Independent reflections	8205 [ <i>R</i> <sub>int</sub> = 0.0737]
Data / restraints / parameters	8205 / 135 / 430
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.021
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0491, <i>wR</i> <sub>2</sub> = 0.1241
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0775, <i>wR</i> <sub>2</sub> = 0.1340
Largest diff. peak and hole (eÅ <sup>-3</sup> )	0.57 and –0.40
Completeness to <i>θ</i>	98.8% ( <i>θ</i> = 25.75°)

SADABS<sup>18</sup>) based on the intensities of equivalent reflections. The structures were solved by direct methods using *OLEX2* program<sup>19</sup> and refined by a full-matrix least-squares procedure based on *F*<sup>2</sup>. All non-hydrogen atoms were found from the different map and refined with anisotropic displacement parameters. All hydrogen atoms on carbon atoms were constrained at calculated positions and refined as riding atoms. The molecular structure with atomic labeling scheme and the crystal packing were plotted by Mercury 3.8 program.<sup>20</sup> The crystal structure of **2** displayed disordered solvent water molecules occupancy. An acceptable model for the disordered solvent water molecules was not found, so the disordered density was masked out by using solvent mask route in *OLEX2*. The *OLEX2* program revealed two voids per unit cell at (0.0, 0.5, 0.5) and (0.5, 0.0, 0.0) of 401.3 Å<sup>3</sup> with total electron count per unit cell of 13.2 electrons each. Furthermore, this structure was implicated by the orientation disorder of carbon atoms. The molecule was refined at two positions, the major position of the atoms C16A (51%), C17A (51%), C18A (51%), C20A (56.7%), C21A (56.7%), C22A (56.7%) and the minor position of the atoms C16B

(49%), C17B (49%), C18B (49%), C20B (43.3%), C21B (43.3%), C22B (43.3%).

### 3. Results and Discussion

#### 3.1 Synthesis of the complexes

The condensation reaction of **1** began with the reaction of copper(II)-ethylenediamine complex with formaldehyde to form an imine (C=N) with the loss of two water molecules. Further reaction with *iso*-butylamine which acted as pendant arms yielded a *gem*-diamine to give the first six-membered ring. The same reaction path could also take place on the other side to form the second six-membered ring. Finally, the target hexaazamacrocyclic complex **1** was obtained. For complex **2**, the complex **1** was used as a precursor to react with hexacyanoferrate(II) ion. The cyanide ions replaced the perchlorate anions due to its stronger ligand field power in spectrochemical series resulting in a new structure that is different from those ever reported in the literatures.

#### 3.2 FT-IR spectroscopy

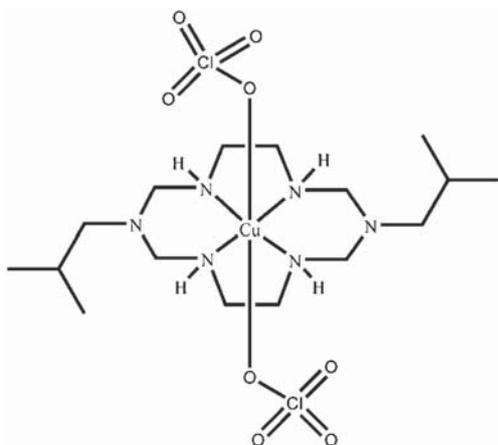
The FT-IR spectrum (Figure S1, in Supplementary Information) of **1** showed the absence of a strong band in the range 1720–1740 cm<sup>-1</sup> corresponding to carbonyl group of aldehydic moiety confirming the completion of condensation reaction.<sup>3</sup> A sharp band around 3244 cm<sup>-1</sup> was assigned to ν(N-H) stretching vibration of the secondary amine groups of the hexaazamacrocyclic ligands. A medium band appearing in the range 2872–2961 cm<sup>-1</sup> was assigned to ν(*sp*<sup>3</sup> C-H). In the region 1100 cm<sup>-1</sup>, splitting to two bands at 1080 and 1119 cm<sup>-1</sup> corresponded to ν(Cl-O) stretching and a sharp band at 627 cm<sup>-1</sup>, was assigned to δ(Cl-O) bending vibration of the perchlorate ions. The splitting of ν(Cl-O) band clearly indicated the presence of coordinated perchlorate.<sup>21</sup> In complex **2**, the FT-IR spectrum (Figure S2, in Supplementary Information) showed strong band at 3247 cm<sup>-1</sup> which was assigned to secondary amine group. The vibrations from cyanide ligand may vary depending on the bonding mode,<sup>22–24</sup> the two absorption bands observed at 2117 and 2097 cm<sup>-1</sup> were assigned to the terminal cyanide and the bridging cyanide ions, respectively. The assignment of the former was based on the comparison with that of K<sub>3</sub>[Fe(CN)<sub>6</sub>] which shows a sharp band at 2117 cm<sup>-1</sup> while the bridging mode of the type M-C≡N-M' appears at the lower energy<sup>25</sup>. The bands of the ν(Cl-O) of perchlorate ions disappeared due to the perchlorate being replaced by hexacyanoferrate(III) ions.

### 3.3 ESI-MS spectroscopy

The ESI mass spectrum (Figure S3, in Supplementary Information) of **1** showed the parent ion peaks of  $[\text{CuL}(\text{ClO}_4)-2\text{H}]^+$  at  $m/z$  476.1 (100%). This molecular ion underwent fragmentation in two ways. First, with the release of  $\text{C}_3\text{N}_2$  radical, the new fragment ion coresponding to  $[\text{Cu}(\text{C}_{13}\text{H}_{38}\text{N}_4)-\text{ClO}_4]^+$  species was observed with  $m/z$  412.2 (28%). The other path was the release of perchlorate anion which gave fragment ion peak at  $m/z$  376.2 (5%) coresponding to  $[\text{Cu}(\text{C}_{16}\text{H}_{38}\text{N}_6)]^{2+}$  species, which on further release of  $\text{C}_5\text{H}_{11}\text{N}$  radical gave a fragment ion peak at  $m/z$  291.2 (5%) coresponding to  $[\text{Cu}(\text{C}_{11}\text{H}_{27}\text{N}_5)]^{2+}$  species. Fragmentation of the last species continued to  $[\text{Cu}(\text{C}_9\text{H}_{20}\text{N}_4)]^{2+}$  with  $m/z = 247.1$  (10%),  $[\text{Cu}(\text{C}_8\text{H}_{18}\text{N}_4)]^{2+}$  with  $m/z = 233.1$  (8%), and  $[\text{Cu}(\text{C}_6\text{H}_{13}\text{N}_3)]^{2+}$  with  $m/z = 190.0$  (35%), respectively. Further confirmation for the proposed structure of **1** came from the appearance of other peaks containing  $^{65}\text{Cu}$  besides the peaks due to successive degradation of the target complex to various fragments.<sup>26</sup> The simulated isotopic pattern is in good agreement with the measured spectrum (Figure S4, in Supplementary Information). Similar type of ESI mass spectral pattern was also observed in the hexaazamacrocyclic copper(II) complex reported previously.<sup>21</sup> Based on the physico-chemical and the spectral studies, the structure proposed for **1** is shown in Figure 1.

### 3.4 Electronic absorption spectra

Complex **1** showed a distinct single  $d-d$  transition band (Figure S5, in Supplementary Information) which could be assigned to  ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$  transition. In solution,  $\lambda_{\text{max}}$  appeared at 514 nm ( $\epsilon = 38 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) while in the solid state it was at 512 nm. The peak was slightly



**Figure 1.** The proposed structure of  $[\text{CuL}(\text{ClO}_4)_2]$  (**1**).

unsymmetrical as a result of the Jahn-Teller distortion inherited with the  $d^9$  configuration of  $\text{Cu}^{2+}$  ion. Distorted octahedral geometry due to Jahn-Teller distortion normally shows weak absorption bands at around 625 nm and often a broad band in the near infrared region.<sup>27</sup> Solid state DRS of complex **2** exhibited a shoulder absorption band at 530 nm in the visible region which could be attributed to  $d-d$  transition occurred from overlay between  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions. The shift to longer wavelengths was assigned to stabilization of the  $\text{Fe}^{3+}$   $d$ -orbital because the weakening of the  $\sigma$ -donor types of the cyanide ligands.<sup>28,29</sup> Other absorption bands below 380 nm were assigned to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ , and  $n \rightarrow \sigma^*$  transitions, and the maximum absorption band at 431 nm was assigned to the ligand-to-metal charge transfer (LMCT) due to the presence of  $[\text{Fe}(\text{CN})_6]^{3-}$  ions.<sup>30</sup>

### 3.5 Thermal analysis

Thermogravimetric analyses (TGA) of **1** and **2** were recorded in  $\text{N}_2$  atmosphere in the temperature range 50–1000°C (Figure S6, in Supplementary Information). TGA curve of **1** revealed three steps of weight losses. The first weight loss (47.5%) appeared in the range 200–260°C corresponding to the loss of one *iso*-butyl molecule and two perchlorate anion (calculated 47.60%). The second stage at 260–650°C with a weight loss of 27.83% corresponded to the weight loss of one *iso*-butyl molecule and hexaazamacrocyclic ligand (calculated 22.88%). The final residue, presumably  $\text{CuO}$ , was obtained with weight loss of 24.64% (calculated 24.71%). Complex **2** also exhibited four steps of dissociation in TGA curve. The first decomposition started in the temperature range 120–200°C with the weight loss of 5.06% (calculated 5.46%) corresponding to release of five lattice water molecules. The second weight loss of 40.37% took place at 200–285°C was attributed to the loss of hexaazamacrocyclic ligand and cyanide group (calculated 40.20%). The third step of 20.54% at 285–600°C corresponded to loss of one hexaazamacrocyclic ligand (calculated 20.15%). The remaining mass of 2.47% (calculated 2.51%), mixture product of  $\text{CuO} + \text{FeO}$ , was obtained above 600°C.

### 3.6 Crystal structure of $[\text{CuL}]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$ (**2**)

Selected bond lengths and bond angles are listed in Table 2. The molecular structure of **2** is presented in Figure 2, together with the atomic labeling scheme and the unit cell packing diagram are illustrated in Figure 3. X-ray crystallographic study revealed that complex **2** belonged to the monoclinic system with space group

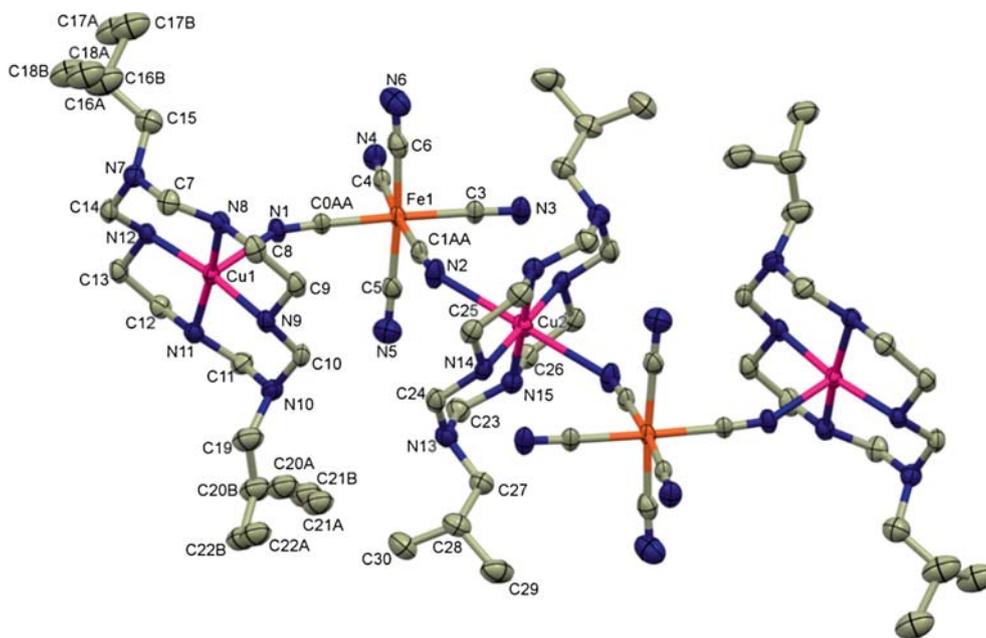
$P2_1/n$ . The asymmetric unit of **2** consisted of core structure of three  $[\text{CuL}]^{2+}$  cations, two  $[\text{Fe}(\text{CN})_6]^{3-}$  anions and five water molecules as lattice solvent. Addison *et al.*,<sup>31</sup> have suggested the angular structural parameter ( $\tau$ ) to differentiate between trigonal bipyramidal (TBP,  $\tau = 1$ ) and square pyramidal (SP,  $\tau = 0$ ) in five-coordinated metal complexes. The parameter  $\tau$  is defined as  $\tau = (\beta - \alpha)/60$  where  $\alpha$  and  $\beta$  are the two largest coordination angles. In our case, the five-coordinated Cu1 center exhibited  $\tau = 0.115$  which favored the square pyramidal geometry defined by the bondings to four nitrogen atoms of the macrocyclic

**Table 2.** The selected bond lengths (Å) and bond angles (°) of **2**.

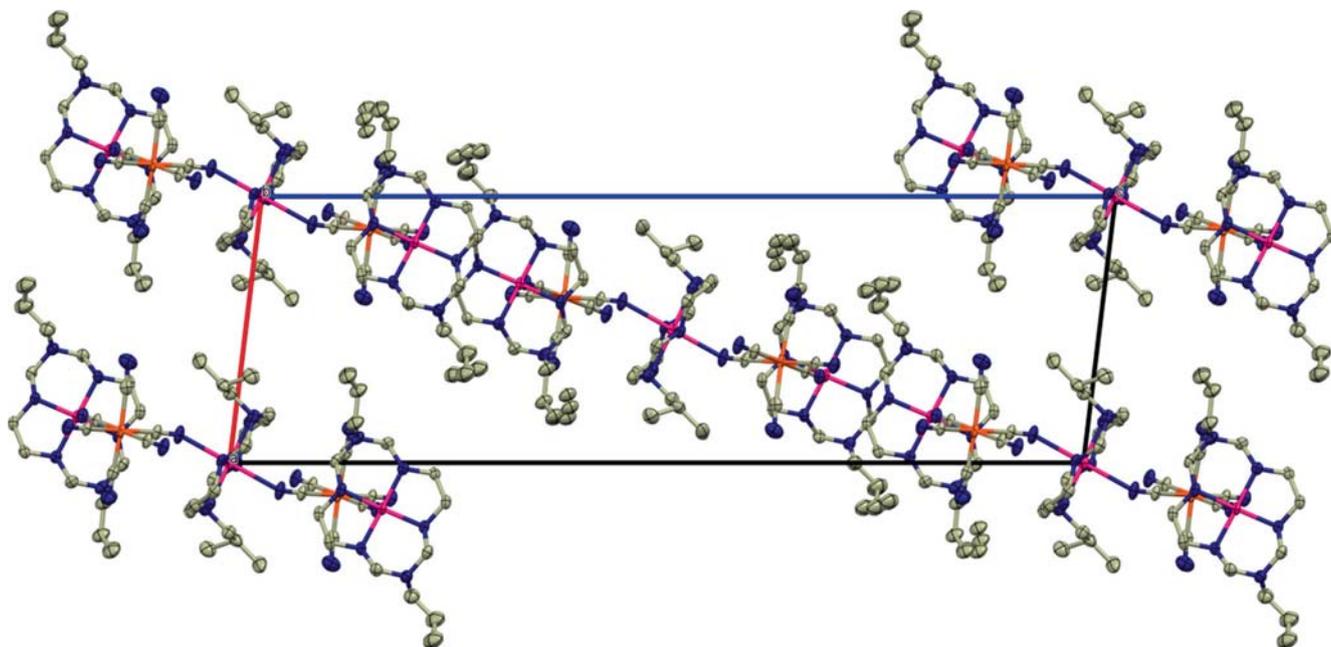
Bond lengths			
Cu1-N1	2.303(3)	Cu2-N2	2.579(3)
Cu1-N8	2.009(3)	Cu2-N14 <sup>1</sup>	2.011(3)
Cu1-N9	2.013(3)	Cu2-N15 <sup>1</sup>	2.007(3)
Cu1-N11	2.008(3)	Fe1-C3	1.942(3)
Cu1-N12	2.022(3)	Fe1-C4	1.944(3)
Fe1-C0AA	1.941(3)	Fe1-C5	1.941(5)
Fe1-C1AA	1.944(3)	Fe1-C6	1.940(5)
Bond angles			
N8-Cu1-N1	92.85(11)	N14 <sup>1</sup> -Cu2-N14	179.99(1)
N9-Cu1-N1	93.13(10)	N15 <sup>1</sup> -Cu2-N15	180.00(1)
N9-Cu1-N12	170.77(10)	N15-Cu2-N2	86.61(12)
N11-Cu1-N8	170.07(11)	C0AA-Fe1-C4	93.55(12)
N14-Cu2-N2	92.17(10)	C1AA-Fe1-C4	175.67(13)

Symmetry transformations used to generate equivalent atoms: 1 = 1-x, 1-y, 1-z.

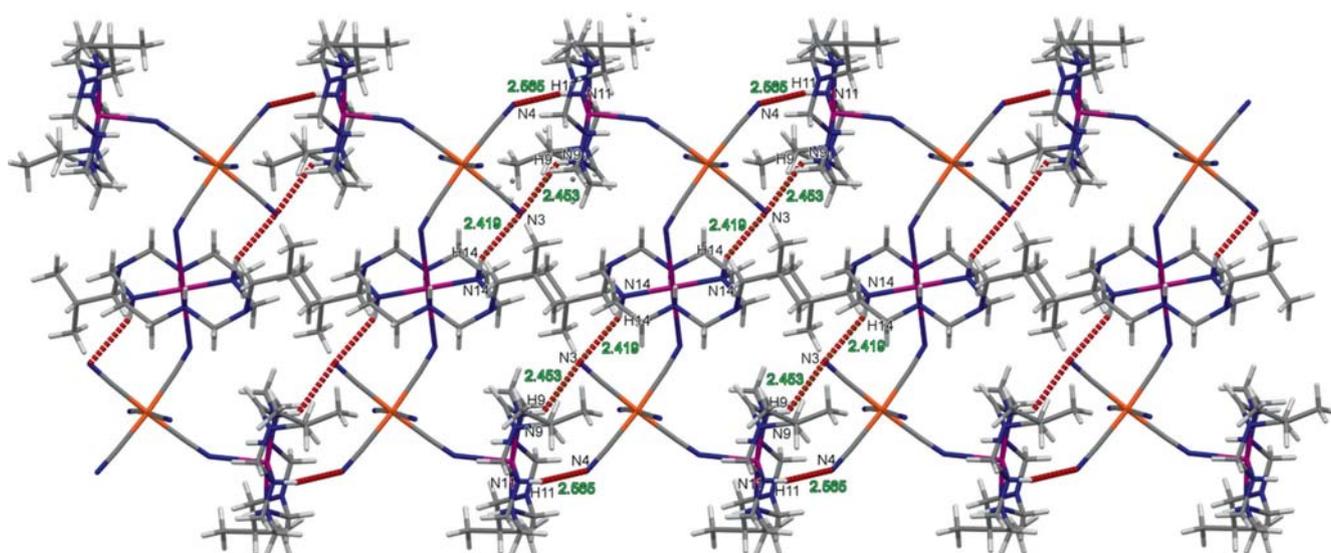
ligand with the average Cu1-N<sub>macrocyclic</sub> bond length of 2.013(3) Å and one nitrogen atom of cyanide ligand from  $[\text{Fe}(\text{CN})_6]^{3-}$  anion with the Cu1-N1 distance of 2.303(3) Å. The Cu2 center showed distorted octahedral geometry with the equatorial planes composed of four nitrogen atoms of the macrocyclic ligand with the average Cu2-N<sub>eq</sub> bond distance of 2.009(3) Å and the axial sites coordinated to two nitrogen atoms from cyanide ions with the Cu2-N<sub>ax</sub> distance of 2.579(3) Å. The fact that the Cu2-N<sub>ax</sub> distances were much longer than the Cu2-N<sub>eq</sub> distances could be attributed to the Jahn-Teller distortion of the  $d^9$  configuration of the  $\text{Cu}^{2+}$  ion.<sup>32-35</sup> In the crystal structure, each  $\text{Fe}^{3+}$  ion coordinated to six carbon atoms from the cyanide ligands in an octahedral geometry. The bond angles of the *cis*-N-C-Fe for the terminal cyanide ligands were  $\sim 177.0^\circ$  and those for the bridging cyanide ligands were slightly bent to  $\sim 176.2^\circ$ . The average bond distance of cyanide-bridge was 1.147(4) Å while those of the terminal cyanide ligands were in the range 1.146–1.154 Å which were in the normal range for low spin cyanide complexes of  $\text{Fe}^{3+}$  ion.<sup>36,37</sup> Hydrogen bonding interactions were observed between the hydrogen atoms (H9, H11 and H14) from the secondary amine (N9, N11 and N14) of the macrocyclic ligand with the nitrogen atoms (N3 and N4) of the terminal cyanide ligands with the contacts of N9-H9...N3 = 2.453 Å, N11-H11...N4 = 2.565 Å, and N14-H14...N3 = 2.419 Å generating a 2D supramolecular interactions as depicted in Figure 4 (plotted along *a*-axis).



**Figure 2.** Crystal structure of **2** with the atomic labeling scheme. Solvent molecules and all hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.



**Figure 3.** The molecular packing arrangement of **2** plotted along the *b* axis.



**Figure 4.** The 2D supramolecular structure of **2**, showing hydrogen bonding (N-H...N) indicated by dotted lines.

In addition, the structural parameters of the hexaazamacrocyclic ligand were similar to those found in linked metal complexes reported in literatures. It should be indicated that in the  $[ML]^{2+}$  cation and  $[Fe(CN)_6]^{3-}$  anions (where  $M = Cu(II)$  or  $Ni(II)$  and  $L = 3,10$ -dialkyl-1,3,5,8,10,12-hexaazacyclotetradecane), the  $[Fe(CN)_6]^{3-}$  revealed different coordination styles depending on pendant arms of the hexaazamacrocyclic ligand. In the work by Shen *et al.*,<sup>33</sup> on the complex  $[CuL^4]_3[Fe(CN)_6]_2 \cdot 2H_2O$  ( $L^4 = 3,10$ -dibutyl-1,3,5,8,10,12-hexaazacyclotetradecane), each  $[Fe(CN)_6]^{3-}$  anion linked to three

$[CuL^4]^{2+}$  cations via three *mer*- $C \equiv N$  and each  $[CuL^4]^{2+}$  cation was connected to two  $[Fe(CN)_6]^{3-}$  anions in *trans* positions resulting in a 2D ring-like structure. Yuan *et al.*,<sup>38</sup> reported the complex  $[CuL]_2[Fe(CN)_6]ClO_4 \cdot H_2O$  ( $L = 3,10$ -dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) where each  $[Fe(CN)_6]^{3-}$  anion connected to four  $[CuL]^{2+}$  cations using four co-planar cyanide groups to axially bind to the  $[CuL]^{2+}$  cations in the *trans* position forming *trans*- $CuL(N \equiv C)_2$  moieties resulting in a novel 3D honeycomb-like structure. Thus, by reasonably designing the organic ligands, it

is possible to synthesize complexes with a variety of crystal structures giving advantage in searching for the expected physicochemical properties.

### 3.7 Powder X-ray diffraction of $[\text{CuL}]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$ (**2**)

Complex **2** was characterized by powder X-ray diffraction and compared with the simulated one based on the single crystal data (Figure S7, in Supplementary Information). Both spectra are identical indicating that the bulk synthesized material and the as-grown crystals were homogeneous.

### 3.8 Magnetic measurements

The effective magnetic moment ( $\mu_{\text{eff}}$ ) of **1** was 1.92 B.M. corresponding to the  $d^9$  electronic configuration. The observed value is slightly higher than the spin-only value of one unpaired electron 1.73 B.M. suggesting the octahedral coordination geometry.<sup>39</sup> The  $\mu_{\text{eff}}$  values of copper(II) octahedral complexes normally lie between 1.8–2.2 B.M. depending on the magnitudes of orbital contribution and spin-orbit coupling.<sup>40–42</sup> The  $\mu_{\text{eff}}$  of **2** was 5.61 B.M. which was higher than the combined magnetic moment one would expect in the multinuclear complexes calculated from the simple relation:<sup>43</sup>  $\mu_{\text{eff-T}} = \{3(\mu_{\text{eff}} \text{ of } \mathbf{1})^2 + 2(\mu_{\text{eff}} \text{ of } \text{K}_3[\text{Fe}(\text{CN})_6])^2\}^{1/2}$ , where the magnetic moment of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is 2.31 B.M. The observed value of **2** indicated that the ferromagnetic interaction in  $\mu_{\text{eff-T}}$  was much greater than  $\mu_{\text{spin-only}}$  due to the combination effect of the spins coupling in parallel which occurred between the  $\text{Cu}^{2+}$  and the low-spin configuration  $\text{Fe}^{3+}$  as a result of the strict orthogonality.<sup>44</sup> From the crystal structure of **2**,  $\text{Cu}^{2+}$  ions in square-pyramidal and octahedral surrounding had one unpaired electron (per each ion) in  $d_{x^2-y^2}$  orbital which interacted with the molecular orbitals of bridged-cyanide having appropriate symmetry giving a magnetic orbital with  $\sigma$  type.<sup>43</sup> Meanwhile, each low-spin  $\text{Fe}^{3+}$  ion in octahedral geometry environment had one unpaired electron in  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  which interacted with other molecular orbitals of bridged-cyanide of the same symmetry to give a magnetic orbital with  $\pi$  type.<sup>45</sup> From this scenario, we may expect the ferromagnetic behaviour in this pentanuclear complex **2**.

### 3.9 Antibacterial activity

Complex **1** was tested for antibacterial activity *in vitro* using one Gram-positive (*S. aureus*) and two Gram-negative (*E. coli* and *P. aeruginosa*) bacteria. The sensitivity of the bacterial strains to **1** evaluated by measuring

the diameter of the inhibition zone and % inhibition are shown in Figures 5 and 6. The results showed moderate activity against all bacteria under investigation compared with inert non-complexed starting materials. The increase in activity upon coordination formation could be described on the basis of Overtone's concept<sup>46</sup> and Tweedy's chelation theory.<sup>47,48</sup> According to the Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble materials owing to liposolubility is considered to be an important factor controlling antimicrobial activity. On Tweedy's chelation, the polarity of metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with the ligand donor atoms.<sup>49</sup> Besides, it increases the delocalization of electrons over the whole chelate ring. This may increase the lipophilic feature of the metal complex, enabling it to permeate the lipid membrane of the bacteria and thus killing them more effectively. Also, factors such as

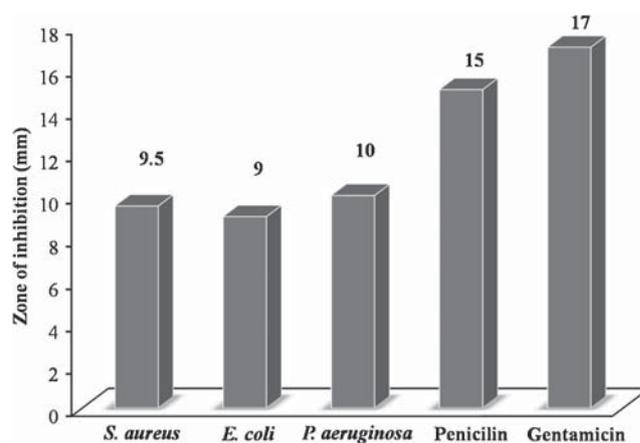


Figure 5. The antibacterial activity of  $[\text{CuL}(\text{ClO}_4)_2]$  (**1**).

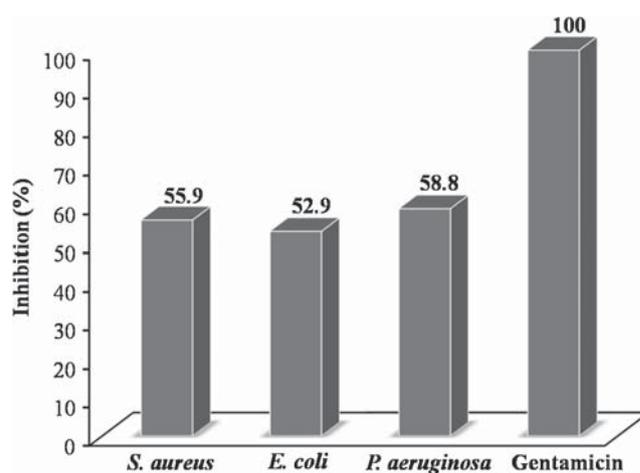


Figure 6. Percentage of inhibition of  $[\text{CuL}(\text{ClO}_4)_2]$  (**1**).

solubility, different dipole moments and cell permeability mechanisms may be affected by the presence of the different anions and this affects the mechanism of permeation through the lipid layer of the organisms killing more of them effectively.<sup>50</sup>

#### 4. Conclusions

In summary, we have reported the synthesis of a new hexaazamacrocyclic copper(II) complex, [CuL(ClO<sub>4</sub>)<sub>2</sub>] (**1**), and bimetallic pentanuclear complex, [CuL]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·5H<sub>2</sub>O (**2**). The structural characterizations of the synthesized complexes were investigated by elemental analyses, spectroscopic techniques, and X-ray diffraction. The proposed structure of **1** was octahedral geometry in which the copper(II) ion is coordinated to four nitrogen atoms from hexaazamacrocyclic ligand and two oxygen atoms from perchlorate anions. In the crystal structure of **2**, one of the [Fe(CN)<sub>6</sub>]<sup>3-</sup> ions used two *cis*-cyanide ligands to link with *cis*-[CuL]<sup>2+</sup> cations in which each of the copper(II) ion had a five- or six-coordinated geometry leading to the formation of a pentanuclear Cu<sub>3</sub>Fe<sub>2</sub> bimetallic structure. Complex **1** simply showed a paramagnetic property while **2** showed strong paramagnetism which very likely puts it in the ferromagnetic class. With regard to application, **1** displayed moderate antibacterial activity against *S. aureus*, *E. coli* and *P. aeruginosa*, thus, the exploitation of this complex could be in the treatment of bacterial infections.

#### Supplementary Information (SI)

CCDC 1510377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk>, or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2, 1EZ, UK; fax: +44(0)1223-336033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). FT-IR spectra (Figures S1, S2), ESI-MS spectrum (Figure S3), simulated isotopic pattern (Figure S4), electronic absorption spectrum (Figure S5), TGA curves (Figure S6), and PXRD pattern (Figure S7) are given in Supplementary Information, available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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