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## Polymeric polymorphs and a monomer of pseudohalide incorporated Cu(II) complexes of 2,4-dichlorido-6-((2-(dimethylamino)ethylimino) methyl)phenol]: Crystal structures and spectroscopic behavior



N. Aiswarya<sup>a</sup>, M. Sithambaresan<sup>b</sup>, S.S. Sreejith<sup>a</sup>, Seik Weng Ng<sup>c</sup>, M.R. Prathapachandra Kurup<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India <sup>b</sup> Department of Chemistry, Faculty of Science, Eastern University, Sri Lanka, Chenkalady, Sri Lanka <sup>c</sup> Chemistry Department, King Abdulaziz University, PO Box 80203, Jeddah, Saudi Arabia

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#### ABSTRACT

In the present investigation, copper(II) complexes of tridentate 2,4-dichlorido-6-((2-(dimethylamino) ethylimino)methyl)phenol] (HL) Schiff base system incorporating azido  $[Cu(L)(N_3)]_n$  (1a and 1b) and cyanato groups [Cu(L)(NCO)] (2) are prepared and characterized by elemental analysis, IR, UV–Vis and single crystal X-ray diffraction studies. While the polymeric polymorphs, **1a** and **1b** have a square-pyramidal geometry for the basic unit, complex 2 exhibits square planar topology. The polymorphs are onedimensional helical coordination polymers with azido group in single asymmetric equatorial-axial end-on bridging mode. The interestingly different combinations of intermolecular interactions have resulted in polymorphs 1a and 1b. Based on the angular preference, intermolecular distance and the size of Cl atom, type I halogen interactions which is rather rarely observed is also discussed. Solvent effect on the charge-transfer bands and d-d bands were analyzed and the former exhibits negative solvatochromic effect while latter a positive effect with increasing polarity of solvents.

Solid and solution state optical emission properties are analyzed. All the copper complexes emit in the blue region. Thermal analyses have been performed in order to understand the thermal decomposition pattern of the complexes. Spin Hamiltonian and bonding parameters have been calculated from EPR analysis. The g values, calculated for the complexes 1a, 1b in frozen DMF, indicate the presence of the unpaired electron in the  $d_{\chi^2-\gamma^2}$  orbital consistent with a square pyramidal topology whereas that of complex **2** corresponds to a rhombic symmetry.

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## 1. Introduction

The current scenario of coordination chemistry is witnessing the exploitation of coordination bonds and noncovalent interactions to generate self-assemblies of various dimensions having not only esthetic values but also countless applications and that paved way for supramolecular chemistry/crystal engineering. The structural variety, interesting properties and potential applications in the fields of catalysis [1], luminescence [2], gas adsorption [3], and magnetic materials [4,5] attracts researchers to this area. Most of such fascinating work employs Schiff bases obtained by the condensation of an amine and a carbonyl compound. The use of diamines in the synthesis of high-nuclearity complexes utilizes the bridging capacity of phenoxo atoms [6,7]. Whereas in the case of N<sub>2</sub>O donor tridentate Schiff bases (N-substituted diamines with salicylaldehyde or its derivatives), coligands are employed to generate structures of variable composition apart from satisfying the coordination number [8,9]. Among the various coligands known, pseudohalides (azido, cyanato, thiocyanato, dicyanamido) deserve special attention on account of their versatile modes of binding. Of them, azido group is the most widely studied because of its flexible coordinating ability. The family of reported metal-azido systems consist of discrete mono-/di-/oligonuclear complexes as well as 1-D, 2-D and 3-D coordination polymers [10–16]. Of the various transition metals, the chemistry of polynuclear copper(II) complexes is getting more importance now-a-days because of its relevance to various metallo-proteins and metallo-enzymes [17-21].

Structure-property correlation studies are found to be interesting in case of metallo-pseudohalide systems. For example, some of the factors governing the magnetic properties of such exchangecoupled systems are (a) type of bridge, metrical parameters like



<sup>\*</sup> Corresponding author. Tel.: +91 484 2862423; fax: +91 484 2575804. E-mail addresses: mrpcusat@gmail.com, mrp\_k@yahoo.com (M.R.P. Kurup).

the (b) metal–N–metal bridge angle (c) metal–N–N–metal torsion angle, metal–N–N angle and metal–N distance [13–17,22–24]. On the other hand, even the prediction of the nature and magnitude of the exchange interaction for some types of systems, e.g., complexes having an equatorial–axial  $\mu_{1,1}$ -azido bridge [25–29] is difficult and that makes the field evergreen.

Though several factors like the nature of metal ion, solvent, blocking organic ligand, metal:pseudohalide ratios etc. can be stated as those that control the nature of the final product, no generalization can be arrived at and therefore in many cases called 'Serendipitous self assembly' [30]. Although voluminous research work has been done in this arena, still researchers find it difficult to control the composition and nuclearity of the final product and this ambiguity intrigues us to pursue more.

Since not much of experimental work highlighting the halogen interaction is known, our group employed halogen substituted salicylaldehydes to explore more on halogen interactions [31], a new tool for crystal engineers and to discuss the role of various other weak interactions in stabilizing a specific crystal system. Herein, we have used the N<sub>2</sub>O tridentate Schiff base derived from refluxing N,N-substituted ethylene diamine and 3,5-dichlorosalicylaldehyde along with azido and cyanato ligands. We have obtained two azido linked polymeric polymorphs and a monomeric cyanato complex of 2,4-dichlorido-6-((2-(dimethylamino)ethylimino)methyl)phenol. Only azido ligand produced polymeric complexes revealing its greater ability to bridge over the other. The synthesis, spectral characterization, crystal structures, packing interactions (supramolecular assemblies including halogen interactions), photophysical studies and EPR studies are discussed here.

#### 2. Experimental

#### 2.1. Materials

All chemicals were of reagent grade and purchased from commercial sources. The solvents were purified according to standard procedures. 3,5-Dichlorosalicylaldehyde (Aldrich), *N,N*-dimethyl-1,2-diaminoethane (Aldrich), CuCl<sub>2</sub>·2H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, NaN<sub>3</sub>, NaCNO (all are BDH, AR quality) were used as received.

The Schiff bases were formed in situ.

*Caution!* Azido compounds are potentially explosive. Although no problems were encountered in the present study, it should be prepared only in small quantities and handled with care.

#### 2.2. Synthesis of copper(II) complexes

# 2.2.1. Synthesis of [Cu(L)(N<sub>3</sub>)]<sub>n</sub> (**1a**) [HL = 2,4-dichloro-6-((2-(dimethylamino)ethylimino)methyl)phenol]

3,5-Dichlorosalicylaldehyde (0.191 g, 1 mmol) and *N*,*N*-dimethyl-1,2-diaminoethane (0.088 g, 1 mmol) were dissolved in 10 mL methanol and refluxed for about an hour. A methanolic solution (10 mL) of copper(II) chloride dihydrate (0.170 g, 1 mmol) was added to the hot reaction mixture. To the resulting deep green solution, sodium azide (0.130 g, 2 mmol) in a MeOH/H<sub>2</sub>O (1:9) mixture was added dropwise with continuous stirring and filtered. Suitable single crystals for structure determination by X-ray diffraction were obtained by slow evaporation of the mother liquor in air. M.P. 231 °C.

Yield: 0.297 g (81%). *Anal.* Calc. for C<sub>11</sub>H<sub>13</sub>Cl<sub>2</sub>CuN<sub>5</sub>O (365.70): C, 36.13; H, 3.58; N, 19.15. Found: C, 36.09; H, 3.55; N, 19.10%.

UV–Vis,  $\lambda_{max}/nm$  ( $\epsilon_{max}/10^3$  M<sup>-1</sup> cm<sup>-1</sup>) (acetonitrile): 376 (7.60), 238 (28.54).

Magnetic moment:  $\mu$  = 1.89 B.M.

# 2.2.2. Synthesis of $[Cu(L)(N_3)]_n$ (**1b**) [HL = 2,4-dichloro-6-((2-(dimethylamino)ethylimino)methyl)phenol]

Complex **1b** was prepared by a method similar to that of complex **1a** except that copper(II) sulfate pentahydrate (0.249 g, 1 mmol) was added to the hot reaction mixture instead of copper (II) chloride dihydrate. To the resulting deep green solution, sodium azide (0.130 g, 2 mmol) in a MeOH/H<sub>2</sub>O (1:9) mixture was added dropwise with continuous stirring and filtered. Suitable single crystals for structure determination by X-ray diffraction were obtained by slow evaporation of the mother liquor in air. Complex **1b** was found to be a polymorph of **1a**. M.P. 234.5 °C.

Yield: 0.2123 g (66%). *Anal.* Calc. for C<sub>11</sub>H<sub>13</sub>Cl<sub>2</sub>CuN<sub>5</sub>O (365.70): C, 36.13; H, 3.58; N, 19.15. Found: C, 36.09; H, 3.55; N, 19.10%.

UV–Vis,  $\lambda_{max}/nm (\epsilon_{max}/10^3 \text{ M}^{-1} \text{ cm}^{-1})$  (acetonitrile): 376 (8.12), 237 (31.27).

Magnetic moment:  $\mu$  = 1.85 B.M.

# 2.2.3. Synthesis of [Cu(L)(NCO)] (2) [HL = 2,4-dichloro-6-((2-(dimethylamino)ethylimino)methyl)phenol]

Complex **2** was prepared by a similar method except for the pseudohalide used. Here, sodium cyanate (0.130 g, 2 mmol) in a MeOH/H<sub>2</sub>O mixture was added dropwise and the resulting solution further stirred for *ca*. 2 h and filtered. Diffraction quality single crystals for structure determination were obtained by slow evaporation of this mother liquor in air. M.P. 240 °C.

Yield: 0.2081 g (54%). *Anal.* Calc. for C<sub>11</sub>H<sub>13</sub>Cl<sub>2</sub>CuN<sub>5</sub>O (365.70): C, 39.41; H, 3.58; N, 11.49. Found: C, 39.20; H, 3.50; N, 11.52%.

UV–Vis,  $\lambda_{max}/nm$  ( $\epsilon_{max}/10^3$  M<sup>-1</sup> cm<sup>-1</sup>) (acetonitrile): 389 (5.16), 238 (25.16).

Magnetic moment:  $\mu$  = 1.75 B.M.

#### 2.3. Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out using a Vario EL III CHNS analyzer. Infrared spectra were recorded on a JASCO FT-IR-5300 Spectrometer in the range 4000–400 cm<sup>-1</sup> using KBr pellets. Electronic spectra were recorded on Ocean Optics USB 4000 UV-Vis Fiber Optic Spectrometer in the 200–1000 nm range using solutions in various solvents. Molar conductivities of the complexes in DMF solutions (10<sup>-3</sup> M) at room temperature were measured using a Systronic model 303 direct reading conductivity meter. Magnetic susceptibility measurements were made in the polycrystalline state on a Vibrating Sample Magnetometer using Hg[Co(SCN)<sub>4</sub>] as calibrant at room temperature. TG-DTG analyses of the complexes were carried out in a Perkin Elmer Pyris Diamond analyser under nitrogen at a heating rate of 10 °C min<sup>-1</sup> in the 50– 700 °C range. The solid state photoluminescence measurements were carried out using a Schimadzu Scientific spectrofluorometer (Model No: RF-5301PC) at room-temperature and the solution state studies were done in Thermo Fischer Variaskan Flash spectrofluorometer. The EPR spectra were recorded in a Varian E-112 X-band spectrometer using TCNE (g = 2.00277) as standard.

## 2.4. X-ray crystallography

Single crystals of compounds  $[Cu(L)(N_3)]_n$  (1a),  $[Cu(L)(N_3)]_n$ (1b), [Cu(L)(NCO)] (2) suitable for X-ray diffraction studies were grown from their methanol solutions by slow evaporation at room temperature. Single crystals were selected and mounted on a Bruker SMART APEX diffractometer, equipped with a graphite crystal, incident-beam monochromator, and a fine focus sealed tube with Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) as the X-ray source. The crystallographic data along with details of structure solution refinements are given in Tables 1 and 2. The unit cell dimensions were measured and the data collection was performed at 293(2) K. Bruker SMART software was used for data acquisition and Bruker SAINT software for data

#### Table 1

| Parameters   | 1a  | 1b                                       |
|--|---|--|
| Empirical formula                                  | C11H13Cl2CuN5O  | C22H26Cl4Cu2N10O2                        |
| Formula weight                                     | 365.71  | 731.43                                   |
| T (K)  | 293(2)  | 296(2)                                   |
| λ (Å)  | 0.71073   | 0.71073                                  |
| Crystal system                                     | monoclinic  | monoclinic                               |
| Space group  | $P2_1/c$  | $P2_1/n$                                 |
| Unit cell dimensions                               | a = 11.0792(5) Å  | a = 6.9187(2) Å                          |
|  | $\alpha = 90^{\circ}$                                     | $\alpha = 90^{\circ}$                    |
|  | b = 6.8477(3) Å   | b = 19.2758(7) Å                         |
|  | $\beta = 101.826(2)^{\circ}$                              | $\beta = 97.682(2)^{\circ}$              |
|  | c = 19.5346(8) Å  | <i>c</i> = 21.3470(7) Å                  |
|  | $\gamma = 90^{\circ}$                                     | $\gamma = 90^{\circ}$                    |
| V (Å <sup>3</sup> )                                | 1450.58(11)   | 2821.36(16)                              |
| Ζ  | 4   | 4  |
| $D_{\rm calc}$ (Mg m <sup>-3</sup> )               | 1.675   | 1.722                                    |
| Absorption coefficient (mm <sup>-1</sup> )         | 1.875   | 1.928                                    |
| F(000)   | 740   | 1480                                     |
| Crystal size (mm)                                  | $\textbf{0.41} \times \textbf{0.13} \times \textbf{0.10}$ | $0.40\times0.35\times0.35$               |
| $\theta$ range for data collection (°)             | 3.12-27.77  | 1.43-26.50                               |
| Limiting indices                                   | $-14\leqslant h\leqslant 14$ ,                            | $-8\leqslant h\leqslant 8$ ,             |
|  | $0\leqslant k\leqslant 8$ ,                               | $-24\leqslant k\leqslant 20$ ,           |
|  | $0 \leqslant l \leqslant 25$                              | $-26 \leqslant l \leqslant 26$           |
| Reflections collected                              | 10989   | 18807                                    |
| Unique reflections                                 | 6794 [ <i>R</i> <sub>int</sub> = 0.0000]                  | 5861 [ <i>R</i> <sub>int</sub> = 0.0307] |
| Refinement method                                  | full-matrix least-  | full-matrix least-                       |
|  | squares on $F^2$  | squares on F <sup>2</sup>                |
| Data/restraints/parameters                         | 3356/0/182  | 5853/0/366                               |
| Goodness-of-fit (GOF) on $F^2$                     | 1.084   | 1.014                                    |
| Final <i>R</i> indices $[I > 2\sigma(I)]$          | $R_1 = 0.0538,$   | $R_1 = 0.0299,$                          |
|  | $wR_2 = 0.1172$   | $wR_2 = 0.0790$                          |
| R indices (all data)                               | $R_1 = 0.0937,$   | $R_1 = 0.0444,$                          |
|  | $wR_2 = 0.1354$   | $wR_2 = 0.0901$                          |
| Largest difference in peak and hole ( $e A^{-3}$ ) | 0.764 and -0.591 <sup>3</sup>                             | 0.341 and -0.480                         |

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$ 

 $wR_2 = [\Sigma w (F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma w (F_{\rm o}^2)^2]^{1/2}.$ 

#### Table 2

| Crystal data and refinement | details of complex <b>2</b> . |
|-----------------------------|-------------------------------|
|-----------------------------|-------------------------------|

| Parameters   | 2   |
|--|---|
| Empirical formula                                  | $C_{12}H_{18}Cl_2CuN_3O_2$                      |
| Formula weight                                     | 366.71  |
| T (K)  | 296(2)  |
| λ (Å)  | 0.71073   |
| Crystal system                                     | orthorhombic                                    |
| Space group  | Pnma  |
| Unit cell dimensions                               | $a = 18.5526(12)$ Å $\alpha = 90^{\circ}$       |
|  | $b = 6.8128(3) \text{ Å } \beta = 90^{\circ}$   |
|  | $c = 11.1901(6) \text{ Å } \gamma = 90^{\circ}$ |
| $V(Å^3)$   | 1414.37(13)                                     |
| Ζ  | 4   |
| $D_{\text{calc}}$ (Mg m <sup>-3</sup> )            | 1.722   |
| Absorption coefficient (mm <sup>-1</sup> )         | 1.925   |
| F(000)   | 744.0   |
| Crystal size (mm <sup>3</sup> )                    | $0.35 \times 0.25 \times 0.20$                  |
| $\theta$ range for data collection (°)             | 2.85-28.25                                      |
| Limiting indices                                   | $-24 \leqslant h \leqslant 24$ ,                |
|  | $-8 \leqslant k \leqslant 9$ ,                  |
|  | $-14 \leqslant l \leqslant 14$                  |
| Reflections collected                              | 10832   |
| Unique reflections                                 | $1892 [R_{int} = 0.0342]$                       |
| Refinement method                                  | full-matrix least-squares on $F^2$              |
| Data/restraints/parameters                         | 1882/2/145                                      |
| Goodness-of-fit (GOF) on $F^2$                     | 1.044   |
| Final R indices $[I > 2\sigma(I)]$                 | $R_1 = 0.0300, wR_2 = 0.0715$                   |
| R indices (all data)                               | $R_1 = 0.0407, wR_2 = 0.0774$                   |
| Largest difference in peak and hole ( $e A^{-3}$ ) | 0.544 and -0.450                                |
| , , , , , , , , , , , , , , , , , , ,              |   |

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$ 

 $wR_2 = [\Sigma w (F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma w (F_{\rm o}^2)^2]^{1/2}.$ 

integration [32]. Absorption corrections were carried out using sAD-ABS based on Laue symmetry using equivalent reflections [33]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the WINGX software package [34a] and the sHELXL-97 software package [34b]. The molecular and crystal structures were plotted using DIAMOND version 3.2 g [35a] and ORTEP-3 for *Windows* [34a]. All non-hydrogen atoms were refined anisotropically, and all H atoms on C and N were placed in calculated positions, guided by difference maps and refined isotropically, with C–H and N–H bond distances of 0.93 Å and 0.86 Å respectively.

The crystal of **1a** is a non-merohedral twin, and the diffraction intensities were separated into two sets by using PLATON [35b]. The minor component refined to 17.8(2)%. Complex **2** possess a crystallographic mirror symmetry with all the atoms lying on a mirror plane and hence enjoys an occupancy factor of 0.50 (special position constraint). The occupation site of atoms in disorder refinement is 50:50.

#### 3. Results and discussion

#### 3.1. Synthetic protocol of ligand and its copper(II) complexes

Facile condensation of 3,5-dichlorosalicylaldehyde with *N*,*N*-dimethyl-1,2-diaminoethane in equimolar ratio (1:1) resulted in the formation of the tridentate Schiff base ligand (Scheme 1). Since the isolation of the Schiff base was difficult, one-pot synthetic strategy was adopted for the preparation of all complexes.

The Schiff-base on reaction with copper(II) chloride dihydrate and copper(II) sulfate pentahydrate, followed by the addition of sodium azide in the ratio 1:1:2 yielded the polymeric polymorphs **1a** and **1b** respectively whereas the monomeric complex **2** was obtained by adding sodium cyanate in the same ratio (Scheme 2). The polymorphic complexes show only marginal variation in the cell parameters.

All the complexes are analytically pure as confirmed from their elemental analysis. They are soluble in polar solvents like methanol, DMF and DMSO. The conductivity measurements were made in DMF solution and all complexes are found to be non-electrolytic in nature [36]. According to Boudreaux, theoretically calculated value for the magnetic moment of square-pyramidal copper(II) complexes lies in the range 2.11–2.21 B.M. at room temperature [37,38], though experimental measurements usually give a slightly lesser value (1.88 B.M.). Room temperature magnetic moment values of the polymorphs **1a** and **1b** are 1.89 and 1.85 B.M. respectively [39], thus confirming the square pyramidal environment of Cu(II). While the magnetic moment of complex **2** has a value very close to the expected spin only value of 1.73 B.M. for a  $d^9$  copper system.

#### 3.2. Description of crystal structures

## 3.2.1. $[Cu(L)(N_3)]_n$ (**1a**)

Compound crystallizes in monoclinic  $P2_1/c$  space group. A perspective view of the complex with atom labeling scheme is shown in Fig. 1. Selected bond lengths and angles are given in Table S1. The single crystal X-ray analysis reveals the asymmetric unit as a crystallographically distinct square planar Cu(II) center with its plane accommodated by amino nitrogen (N2), imine nitrogen (N1), phenoxo oxygen (O1) and the N3 of the azido group (Fig. 2) although in the entire polymeric structure, each unit has pentacoordinated (4+1) geometry, with the fifth coordination site being satisfied by the nitrogen of the azido group of the adjacent unit *via*  $\mu_{1,1}$ -bridging. In brief, the coordination modes are satisfied by



Scheme 1. Formation of tridentate Schiff base ligand.



Scheme 2. Synthetic route to the complexes.



**Fig. 1.** Perspective view of complex **1a**. Only relevant atoms are labeled. Symmetry element: \* = x, 5.5 - y, -0.5 + z.



Fig. 2. ORTEP plot showing the atom labeling of the asymmetric unit of the complex 1a (drawn with 50% thermal ellipsoid).

tridentate monoanionic Schiff base system and two azido ions, both of which are involved in end-on bridging (Fig. 1).

The pattern of propagation of the chain is in such a manner that each azido group exhibits dual nature – while it is axially disposed with respect to one metal ion, the same  $N_3^-$  is equatorially aligned with respect to the adjacent metal ion. Bridging Cu–N bond lengths are significantly different with values 1.975(4)/2.694(5) for basal/axial bonds. Therefore the mode of end-on azido bridging is asymmetric in terms of the type of the coordination position it occupies [40].

The extent of distortion of the pentacoordinated geometry can be conveniently measured by Addison parameter, given by the equation  $\tau = (\beta - \alpha)/60$  [41] (for perfect square pyramidal and trigonal bipyramidal geometries the values of  $\tau$  are zero and unity respectively). The value of  $\tau$  – the angular structural parameter, an index of degree of trigonality is 0.051, suggestive of an almost square pyramidal geometry. Also the metal center deviates from the least squares plane by a distance of 0.0442 Å towards apical donor atom and among the other donor atoms, the imino nitrogen deviates the most (0.0533 Å) from the plane.

The *trans*- $\mu_{1,1}$  bridging mode of azido group constructs the whole molecule into a one-dimensional polymeric structure along '*b*' axis. Also, each monomeric unit is related to its adjacent one by a 2<sub>1</sub> screw axis. This translational element of symmetry coupled with the *trans* bridging mode of N<sub>3</sub><sup>-</sup> generates a helical chain (Fig. 3).

It is interesting to note that although several  $\mu_{1,3}$ -N<sub>3</sub> bridged helical chains have been reported, there are very few examples reported for helical *trans*- $\mu_{1,1}$  chains with Cu(II) [42a,b,c]. The *trans*  $\mu_{1,1}$ -azido ligand packs the succeeding units in such a fashion that the alternate units can be stacked one over the other with a dihedral angle of 0° between them, further evidencing the piling of the units. Two adjacent 1-D strands fit into a zipper-like structure where the alternate teeth are spaced at a distance of 6.8477(3) Å (Fig. 4).

The Cu···Cu non-bonded distance along a chain is 4.2548(10) Å and the interchain Cu···Cu distance is 10.1471(10) Å. The bridging pseudo-halide is quasi-linear as revealed by the N–N–N bond angle of  $177.0(6)^{\circ}$ .

The metrical parameters like metal–N–metal bridge angle (Cu1-N3-Cu1) in this metal-azido complex is  $130.8(2)^{\circ}$  and the



Fig. 4. The two adjacent chains of complex 1a fit to form a zipper-like structure with teeth tilted.

N3–Cu1–N3 bond angle emerges to 99.09(18)°. The bond distances in the azido complex follow the order: metal-axial azido nitrogen (2.694(5) Å) > metal-amino nitrogen (2.071(4) Å) > metal-equatorial azido nitrogen (1.975(4) Å) > metal-imino nitrogen (1.951 (4) Å) > metal-phenoxo oxygen (1.924(3) Å). The Cu–N distance in apical position is longer than the basal distance, which is an obvious consequence of Jahn–Teller distortion in a  $d^9$  copper(II) system (Table S1). Also the metal-imine bond distance is shorter than metal-amino nitrogen, as seen in many other similar systems [43a,b]. The five membered chelate ring incorporating the amino fragment *i.e.*: Cg(1) adopts an envelope conformation with C(9) as the flap atom of the envelope, with a puckering amplitude of



Fig. 3. Helical propagation of polymeric complex 1a.

Q = 0.422(6) Å and  $\varphi = 108.8(6)^{\circ}$  [44]. The puckering of the metallocycle is also calculated in terms of pseudorotation parameters *P* and  $\tau_m$  [45] and the envelope conformation was confirmed with  $P = 264.6(3)^{\circ}$  and  $\tau = 47.3(3)^{\circ}$  for reference bond Cu(1)–N(1). The six membered chelate ring formed by the aldehydic moiety, Cg (2) also assumes an envelope conformation with puckering amplitude, Q = 0.163(4) Å and  $\varphi = 182(2)^{\circ}$ .

#### 3.2.2. $[Cu(L)(N_3)]_n$ (**1b**)

The polymorphic counterpart crystallizes in monoclinic  $P_{2_1/n}$  space group. The asymmetric unit of this polymeric polymorph houses two crystallographically distinct molecules, with both the Cu(II) centers, (Cu1 and Cu2) disposing in square planar topology (Fig. 5) and the polymeric one dimensional chain constituting both Cu1 and Cu2 (Fig. 6) units are built by the end-on bridging of azido group in axial-equatorial fashion along 'a' axis (Fig. S1).

The asymmetric alignment of the pseudohalide is further evidenced by the metrical parameters like metal-nitrogen distance, metal-N-N bond angle, metal-N-metal bridge angle etc. unveils the fact that the higher value of Addison parameter is due to variation in the non-linear trans angle value involving azido nitrogen atoms (N1–Cu1–N3, 169.73(9)°/N6–Cu2–N8, 167.39(9)° over N1–Cu1–N3, 173.8(2)° of former crystal). A measure of the relative strength of bonding follows the same order as that of **1a** *i.e.*: metal-phenoxo oxygen > metal-imino nitrogen > metal-equatorial azido nitrogen > metal-amino nitrogen > metal-axial azido nitrogen although slight variations do exist in the bonding distances (Table S2).

In complex **1b**, the five membered ring involving amine is twisted on C9–N2 bond with puckering parameters, Q = 0.443 (3) Å and  $\varphi = 120.9(3)^\circ$ . The metallocycle (Cu2–N6–C19–C20–N7) assumes an envelope conformation with C20 as the flap atom of the envelope with parameters Q = 0.419(3) Å and  $\varphi = 113.2(3)^\circ$ . Puckering of both metallocycles is further confirmed by the pseudorotation parameters – *i.e.*;  $P = 274.5(2)^\circ$  and  $\tau_m = 47.2(2)^\circ$  for reference bond Cu(1)–N(1) in Cg(1) and  $P = 267.9(2)^\circ$  and  $\tau_m = 46.3$  (2)° for reference bond Cu(2)–N(6) in Cg(2). No puckering was

| Metrical parameters            | With respect to Cu1       |            | With respect to Cu2       |            |
|--------------------------------|---------------------------|------------|---------------------------|------------|
| Metal-nitrogen distance (Å)    | Cu1–N3 <sup>a</sup> basal | 1.980(2)   | Cu2–N3 <sup>c</sup> axial | 2.713(2)   |
|                                | Cu1–N8 <sup>b</sup> axial | 2.629(2)   | Cu2–N8 <sup>b</sup> basal | 1.967(2)   |
| Metal–N–N bond angle (°)       | Cu1-N3-N4                 | 120.1(1)   | Cu2-N3-N4                 | 106.97(16) |
|                                | Cu1-N8-N9                 | 110.29(16) | Cu2-N8-N9                 | 117.7(1)   |
| Metal–N–metal bridge angle (°) | Cu1-N3-Cu2                | 132.01(10) | Cu1-N8-Cu2                | 131.93(10) |
| _                              |                           |            |                           |            |

a = 1.5 - x, -0.5 + y, 0.5 - z; b = -1 + x, -1 + y, -1 + z; c = 0.5 - x, -0.5 + y, 0.5 - z.

The azido groups in the crystallographically distinct units are quasi-linear with N–N–N bond angle of  $177.3(3)^\circ$ . The non-bonded distances of Cu1 with the symmetrically related copper centers [Cu2 (x, -1 + y, -1 + z)] along this chain are 4.2061(5) and 4.2965(5) Å respectively. This complex is much more closely packed as revealed by the comparatively lower interchain Cu-··Cu distances of 9.7985(6) and 9.8565(6) Å, with respect to **1a**. The polymorphic form also exhibits a zipper like structure with a spacing of 6.9187(2) Å between alternate teeth (Fig. 7).

The central metal atoms, Cu1 and Cu2 deviate by 0.0720 and 0.0724 Å from the respective least square planes. Though both forms have axially elongated pentacoordinated environment, this crystallographic form with two different copper centers exhibits a greater distortion as revealed by a trigonality index value of 0.11 and 0.1565 respectively, which is almost and more than twice of its counterpart. A closer examination of the transoid angles

found for the six membered ring unlike seen in its polymorphic counterpart.

3.2.2.1. Comparison of the polymorphic structures. An overall comparison brings out that the strongest axial bond and the strongest equatorial bonds are seen in complex **1b** (Table 3). The value of Addison parameter,  $\tau$  and the deviation of metal center from the least squares plane are taken as indicators of the relative extent of distortion of a square-pyramidal environment [45]. In the case of polymorphic compounds we obtained, the  $\tau/d$  (Å) values are 0.051/0.0442 (**1a**), 0.11/0.0720 (Cu1 of **1b**), 0.1565/0.0724 (Cu2 of **1b**) from which the extent of distortion follows the order: Cu2



**Fig. 5.** ORTEP plot showing the atom labeling of asymmetric unit of complex **1b** (drawn with 50% thermal ellipsoid).



**Fig. 6.** Perspective view of complex **1b**. Only relevant atoms are labeled. Symmetry element: \* = 4 - x, 2 - y, 2 - z.



Fig. 7. The two adjacent chains of complex 1b fit to form a zipper-like structure.

| Table 3   |
|---|
| Comparative analysis of metal-donor atom bond distances in the polymorphic forms. |

|                                 | Crystallographic<br>distinct form ( <b>1</b> | c<br>a)  | Two distinct cry<br>entities ( <b>1b</b> ) | /stallographic |                      |            |
|---------------------------------|--|----------|--|----------------|----------------------|------------|
| Metal-axial azido nitrogen      | Cu1-N3 <sup>1a</sup>                         | 2.694(5) | Cu1-N8 <sup>2b</sup>                       | 2.629(2)       | Cu2-N3 <sup>2c</sup> | 2.713(2)   |
| Metal-amino nitrogen            | Cu1-N2                                       | 2.071(4) | Cu1-N2                                     | 2.053(2)       | Cu2-N7               | 2.051(1)   |
| Metal-equatorial azido nitrogen | Cu1-N3 <sup>1b</sup>                         | 1.975(4) | Cu1-N3 <sup>2a</sup>                       | 1.980(2)       | Cu2-N8 <sup>2b</sup> | 1.967(2)   |
| Metal-imino nitrogen            | Cu1-N1                                       | 1.951(4) | Cu1-N1                                     | 1.943(2)       | Cu2-N6               | 1.931(2)   |
| Metal-phenoxo oxygen            | Cu1-01                                       | 1.924(3) | Cu1-01                                     | 1.9069(17)     | Cu2-02               | 1.9067(17) |

1a = 1 - x, 1 - y, 1 - z; 1b = x, 0.5 - y, -0.5 + z.

2a = 1.5 - x, -0.5 + y, 0.5 - z; 2b = -1 + x, -1 + y, -1 + z; 2c = 0.5 - x, -0.5 + y, 0.5 - z.

(**1b**) > Cu1 (**1b**) > Cu1 (**1a**). Coupled to the above values, the wide variation in transoid bond angle values [(176.72(8)°/167.39(9)°] also contribute to the greater distortion of Cu2 environment of complex **1b**.

#### 3.2.3. [Cu(L)(NCO)] (2)

Complex 2 crystallizes in the orthorhombic space group *Pnma*. The complex assumes a square planar geometry, with the tetracoordination of Cu(II) being satisfied by the imino nitrogen (N1), amino nitrogen (N2), phenoxo oxygen (O1) of the tridentate Schiff base ligand (L1) and N3 atom of the cyanato group (Fig. 8). The extent of deformation in a tetracoordinated complex is given by the  $\tau_4$  index, a measure of the extent of distortion between a perfect tetrahedron ( $\tau_4 = 1$ ) and perfect square planar geometry  $(\tau_4 = 0)$ , given by the formula:  $\tau_4 = [360^\circ - (\alpha + \beta)]/(141^\circ)$ ,  $\alpha$  and  $\beta$ being the two largest angles around the central metal atom in the complex [46]. The  $\tau_4$  value of 0.1084, for this complex confirms a slightly distorted square planar geometry. Moreover, the different angles around the copper metal summate to 359.36° indicating negligible deviation from the coordination polyhedron. Of the various coordinating atoms O1, N1, N2 and N3, imino nitrogen (N1) and amino nitrogen (N2) shows 0.2081 and 0.2299 Å deviation from the least square mean plane whereas O1 and N3 lies exactly in the plane. No deviation was found for Cu(II) from the reference plane. The metal-donor bond strength follows the order Cu1-N3 (cyanato nitrogen) > Cu1-O1 (phenoxo oxygen) > Cu1-N1 (amino nitrogen) > Cu1-N2 (imino nitrogen) which in turn reflects the reverse order of the metal-donor bond distances (Table S3). The pseudolinearity of the cyanato ligand is evidenced by the bond



Fig. 8. ORTEP plot showing the atom labeling of asymmetric unit of complex 2 (drawn with 50% thermal ellipsoid).

angle value of  $179.6(4)^{\circ}$  for N(3)–C(12)–O(2). The tridentate ligand forms six and five membered metallocycles with chelate bite angles of  $91.59(6)^{\circ}$  and  $83.13(11)^{\circ}$  for the rings respectively.

Ring puckering analyses and least square plane calculations shows that the five membered metallocycle, Cg(1) is twisted on C(8)-C(9) bond with puckering amplitude, Q = 0.400(6) Å and

 $\varphi$  = 97.8(7)°. A boat conformation is found for the six membered metallocycle, Cu1–N1–C7–C6–C7a–N1a [C7a, N1a stands for the disordered atoms] with puckering parameters Q = 1.524(8) Å, and  $\varphi$  = 180.0(5)°. Another six membered metallocycle, Cg(3) is also puckered with an amplitude of Q = 0.106(6) Å and  $\varphi$  = 165(5)°.

#### 3.2.4. Supramolecular features as structural adhesives

While one of the hydrogen atoms, H(11B) borne by the C(11) atom of the methyl group forms an (intermolecular) intrachain hydrogen bonding interaction with the deprotonated phenoxy oxygen atom (O1), the other hydrogen atom H(11C) of the same carbon is involved in two intramolecular interactions with N(3) and N(4) of the azido group, thus forming a bifurcated, three center H bonding interaction (Fig. 9), leading to S(3) ring motif. Due to the involvement of azido nitrogens in H bonding, S(5) and S(6) motifs are also formed.

The H bonding between H(5) atom on C(5) with that of the N(5) of the azido group of a similar molecule in the adjacent chain stitches the neighboring one-dimensional polymeric chains in such a manner that the molecules pack in '*bc*' plane (Table S4, Fig. S2). No significant ring interactions are found in the complex.

In the polymorphic form, the three intermolecular interactions, namely C(7)–H(7)···N(5), C(16)–H(16)···N(10) and C(18)–H(18)··· N(10) sews together adjacent one-dimensional chains and pack the molecules in '*ab*' plane (Fig. S3).

A trifurcated H bonding interaction is established by H(10C), H (18) and H(16) with a common acceptor, N(10) (Fig. 10). A  $R_2^1(6)$  pattern is generated considering only the H bond interaction of H (18) and H(16) with the common acceptor, N(10) (bifurcated interaction, Fig. 10).

One of the phenoxy oxygens, O(1) is engaged in an intermolecular H bonding with the hydrogen [H(21A)] of the methyl carbon C



Fig. 9. Intrachain intermolecular and intramolecular H bonding interactions in complex 1a.



Fig. 10. Plot highlighting the trifurcated and bifurcated hydrogen bonding interaction in complex 1b.

(21). The other phenoxy oxygen O(2), is involved in an intrachain intermolecular H bonding with the hydrogens (H10B & H11A) of methyl carbons, C(10) and C(11) of two different adjacent units, creating a bifurcated interaction and bringing them closer together. Apart from this, an intramolecular H bond is formed by the nitrogen of azido functional group, N(4) with the hydrogen [H(11B)] borne by the methyl carbon, C(11) thus forming a S(6) ring motif (Fig. S4). The two interactions arising from H(10B) & H (10C) of C(10) to O(2) & N(10) forms a  $R_2^2(8)$  pattern (Table S5). No classic hydrogen bonds are present in the complexes.

In form **1b**, the halogen bearing aromatic ring of one copper unit is involved in a face to face  $\pi$ – $\pi$  [Cg(5)–Cg(6)] interaction [3.7106 (15) Å] with a similar ring of the adjacent unit in the nearby polymeric chain (Table S6, Fig. S5).

The azido nitrogens, N(5) and N(10) establishes a non-covalent interaction with the six membered metallocycles, Cg(4) and Cg(3) respectively. Also the halogen atom, Cl(4) establishes a contact with the halogen bearing aromatic ring, [Cg(5)] of the nearby one dimensional chain (Table S7, Fig. S6).

Complex **1a** doesn't have any halogen halogen interaction whereas two intermolecular halogen interactions are seen in its polymorphic counterpart. Halogen-halogen interaction is seen between Cl1···Cl1 and Cl2···Cl3 atoms with distances, 3.266 and 3.6222(11) Å respectively between them which is definitely less than the sum of their van der Waals radii (Fig. 11). According to Desiraju and co-workers [47,48], halogen interactions are classified as type I and II based on bond angles ' $\theta$ 1' and ' $\theta$ 2' made at the halogen atoms and the intermolecular distances. So considering the angular preference, intermolecular distance and the size of Cl atom [48], we conclude these to be Type 1 halogen interaction where  $0^{\circ} \leq |\theta 1 - \theta 2| \leq 15^{\circ}$  (Table 4). Type 1 interaction is geometry based contact that arises from close packing and this is most effective in Cl due to its small polarisability over other halogens.

An intramolecular interaction  $C(2)-Cl1\cdots O1$  is seen in the complex **1a** with a donor-acceptor distance of 2.912(4) Å (Fig. S7). Similar interactions,  $C(2)-Cl(1)\cdots O(1)$  and  $C(13)-Cl(3)\cdots O(2)$  with X $\cdots$ B distances of 2.889(1) and 2.906(1) Å respectively are seen in the complex **1b** (Fig. S8). Still they cannot be categorized as halogen bonding since the halogen in both cases are bonded to a less electronegative carbon and hence chances for chlorine to become electrophilic is meagre [49].

The difference in the intermolecular interactions present in complexes enabled a variation in the packing motifs, thus resulting in packing polymorphism [50]; polymorph **1a** and **1b**. The various packing interactions and the calculated density values (1.675 and

#### Table 4

Type I halogen contacts in complex **1b**.

| Interaction | θ1 (°)                     | θ2 (°)                      | $(\theta 1 - \theta 2)$ | $\begin{array}{c} X \cdots X \\ ({\mathring{A}}) \end{array}$ |
|-------------|----------------------------|-----------------------------|-------------------------|---|
| Cl1···Cl1   | C2–Cl1···Cl1<br>162.66(9)  | Cl1…Cl1–C2<br>162.66(9)     | 0                       | 3.266   |
| Cl2···Cl3   | C4–Cl2···Cl3<br>165.57(11) | C13-Cl3···Cl2<br>170.07(11) | 4.5                     | 3.622   |

1.722 Mg m<sup>-3</sup> for **1** and **2** respectively), is supportive of the greater close packing of molecules in form **1b** as compared to that of **1a**. Apart from the Cg...Cg stacking interaction between rings and the hydrogen bonding interactions, these polymorphs are characterized by a difference in the halogen bonding interactions.

In the cyanato complex (**2**), an intramolecular H bonding between the nitrogen (N3) of the cyanato group and the methyl carbon, C(10) generates a S(5) ring motif. A bifurcated, 3c-2 electron bond is seen between the phenoxy oxygen, O(2) [acceptor] and H(7) & H(8B) of the donor atoms C(7) [azomethine carbon] and C(8) respectively which creates a  $R_2^1(6)$  pattern (Table S8, Fig. 12) and interconnects the molecules along '*c*' axis.

Ring interactions exist between the halogen bearing ring, Cg(6) and metallocycles Cg(3) & Cg(4). Also aromatic rings, Cg(6) interact face to face with each other (Table S9, Fig. 13).

There is the presence of  $Y-X \cdots Cg$  interaction between the halogen, Cl(2) and aromatic rings Cg(3) and Cg(4) (Table S10, Fig. S9).

## 3.3. Spectral characterization

#### 3.3.1. IR and electronic spectra

The C=N stretching vibrations for all the four complexes lie in the region 1625–1634 cm<sup>-1</sup> [43a]. The polymorphic pair shows a single band consistent with the presence of only one type of azido bridge in the structures and this characteristic strong band at 2045 cm<sup>-1</sup> can be ascribed to the presence of asymmetric bridging [51a,b]. Moreover, the IR spectra also exhibits peaks at 1319 and 758 cm<sup>-1</sup> corresponding to symmetric stretching,  $v_s(N_3)$  and bending mode  $\delta(N_3)$  of the pseudohalide present [52]. One sharp and strong band at 2234 cm<sup>-1</sup> in the IR spectrum of complex **2** indicates the presence of N bonded cyanato group [43a]. The IR band in the region 2918–2930 cm<sup>-1</sup> seen in complexes is assignable to alkyl C–H stretching vibrations [53].

The electronic spectra of all the three complexes were recorded in acetonitrile in the 200–1000 nm region at room temperature.



Fig. 11. Intermolecular Cl1…Cl1 (pink) and Cl2…Cl3 (green) interaction in 1b. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. Hydrogen bonding interactions in 2 (The C10 and H10C atoms are disordered and treated).



Fig. 13. Ring interactions in complex 2 (disordered atoms are omitted for clarity).

#### Table 5 The $\lambda_{max}$ (nm) values along with their $\epsilon$ (M<sup>-1</sup> cm<sup>-1</sup>) in various solvents.

| Polarity index <sup>*</sup> | Solvents (decreasing order of polarity) | Complex <b>1a</b> $\lambda_m$<br>$\epsilon * 10^3$ (M <sup>-1</sup> cm | Complex <b>1a</b> $\lambda_{max}$ (nm) $\epsilon * 10^3$ (M <sup>-1</sup> cm <sup>-1</sup> ) |            | <sub>ax</sub> (nm)<br>1 <sup>-1</sup> ) | Complex <b>2</b> $\lambda_{max}$ (nm) $\epsilon^* 10^3 (M^{-1} cm^{-1})$ |                        |
|-----------------------------|---|--|--|------------|---|--|------------------------|
| 5.1                         | Methanol                                | 384<br>235   | 5.32<br>27.56  | 385<br>235 | 7.29<br>30.32                           | 389<br>238<br>209  | 5.12<br>23.61<br>24.32 |
| 5.8                         | Acetonitrile                            | 376<br>238   | 7.60<br>28.54  | 376<br>237 | 8.12<br>31.27                           | 389<br>238   | 5.16<br>25.16          |
| 5.1                         | Acetone                                 | 378  | 8.73   | 378        | 8.80                                    | 388  | 5.73                   |
| 4.4                         | Ethylacetate                            | 384  | 8.27   | 385        | 8.35                                    | 395  | 4.58                   |
| 4.0                         | Tetrahydrofuran                         | 385  | 8.39   | 385        | 9.09                                    | 398  | 4.43                   |
| 4.1                         | Chloroform                              | 387<br>245   | 7.39<br>22.52  | 387<br>245 | 8.89<br>26.44                           | 404<br>273   | 4.33<br>14.75          |
| 2.4                         | Toluene                                 | 390  | 8.66   | 390        | 9.62                                    | 402  | 5.45                   |

\* Relative measure of degree of interaction of the solvents with various polar test solutes.

The electronic spectra of all complexes show broad bands in the high energy 370–390 nm region consistent with the LMCT bands comprising of transitions from the coordinating atoms of respective pseudohalides to the metal center [51b,54] apart from  $O \rightarrow Cu$ ,  $N \rightarrow Cu$  transitions. The bands *ca.* 235 nm correspond to intraligand transitions [55a,b]. The high  $\varepsilon$  values for these bands is supportive of the charge transfer and intraligand transitions

(Table 5). The absorption at low energy region, 590–650 nm corresponds to *d*–*d* transition. For complexes **1a** and **1b**, peak at 593 nm typical of a square pyramidal environment of the Cu(II) center is seen, enclosing  ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$ ,  ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$ , and  ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$  transitions [28,56a,b] and peak *ca*. 630 nm can be assigned to a square-planar environment with transitions  ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$ ,  ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$ , and  ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$ . It is difficult to interpret the

electronic spectra of Cu(II) complexes as they possess flexible stereochemistry due to Jahn–Tellar distortion [57].

#### 3.3.2. Solvatochromism and photo-physical studies

The electronic spectra of all the three complexes were recorded in different solvents of varying polarity to investigate the effect of solvents on the absorption bands (CT and *dd*) of the copper complexes. Solvents chosen for the study included polar protic (methanol), polar aprotic (tetrahydrofuran, ethyl acetate, acetone and acetonitrile) and non-polar solvents (toluene, chloroform). All the three complexes exhibited interesting solvatochromic behavior.

All the complexes are soluble in a wide range of organic solvents that make their solvatochromic study easy. Both charge transfer bands and d-d bands exhibited solvatochromism although significant shift in energy was seen for the d-d bands.

The charge-transfer and intraligand transitions exhibited negative solvatochromism (Figs. 14 and S10), though the variation occurs within a narrow range. With increasing solvent polarity, within each classification of solvents (polar protic, polar aprotic and non-polar), hypsochromic (or blue) shift of these bands are observed. This is called "negative solvatochromism" and this occurs due to differential solvation of the ground and first excited state of the light-absorbing molecule (or its chromophore): if, with increasing solvent polarity, the ground-state molecule is better stabilized by solvation than the molecule in the excited state, negative solvatochromism will result [58]. This is due to a solvent-induced change of the electronic ground-state structure from a less dipolar (in non-polar solvents) to a more dipolar chromophore (in polar solvents) with increasing solvent polarity. The  $\lambda_{max}$  (nm) along with their  $\varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>) values in various solvents are tabulated (Table 5).

The solvents apart from influencing the chromophoric groups also affects the coordination environment of the metal center which is reflected as a shift in the d-d absorption band. The color change of the complexes can be attributed to this shift. Pseudo-halogeno complexes appear in various shades of green [59] (Fig. S11).

The influence of the donor power of the solvent on the  $v_{max}$  values of the d-d bands of the complexes have been investigated by means of visible spectroscopy. Four solvents of varying donor powers – DMSO, MeOH, CH<sub>3</sub>CN and DCM were chosen for the study and it was found that the d-d band shifts to red with increasing donor number of the solvent. Observed shift in this region as a function of donor power of chosen solvents was significant and a positive solvatochromism was noted (Figs. 14 and S12, Table 6).

The *d*-*d* band spectra of all the three complexes show almost a broad band in the visible region assignable to the promotion of electron in the low energy orbitals to the hole in  $d_{x-y}^{2}$  orbital of the copper(II) ion ( $d^9$ ). The position of this band is shifted to longer wavelengths as the DN (donor number) of the solvent increases. As



**Fig. 14.** The spectra showing solvatochromic behavior of LMCT, intraligand transitions (top row, con: 1 \* 10<sup>-3</sup> M) and *d*-*d* transitions (bottom, con: 2 \* 10<sup>-3</sup> M) of complex **1a** in various solvents.

| Tabl | e 6 |
|------|-----|
|------|-----|

| The λmm (     | nm) va    | lues along     | with their | ε (M <sup>−1</sup> | $cm^{-1}$ ) of d | -d hands in  | various solvents  |
|---------------|-----------|----------------|------------|--------------------|------------------|--------------|-------------------|
| I III. Amay I | 11111/ Va | וווועבא מוטווצ |            | GUN                | u = 101 u        | =u Danus III | various solvenus. |

| Solvents     | Donor number of solvents (DN) | Complex <b>1</b> a<br>ε (M <sup>-1</sup> cm <sup>-</sup> | Complex 1a $\lambda_{max}$ (nm) $\varepsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) |     | $\lambda_{max} (nm)$ | Complex <b>2</b><br>ε (M <sup>-1</sup> cm <sup>-1</sup> | $\lambda_{\max} (nm)$ |
|--------------|-------------------------------|--|---|-----|----------------------|---|-----------------------|
| DMSO         | 29.8                          | 639  | 164   | 639 | 128                  | 656   | 152                   |
| Methanol     | 19.0                          | 613  | 142   | 619 | 151                  | 640   | 204                   |
| Acetonitrile | 14.1                          | 593  | 213   | 591 | 195                  | 633   | 162                   |
| DCM          | 0.0                           | 583  | 250   | 583 | 214                  | 632   | 151                   |
|              |                               | 535  | 259   | 535 | 223                  |   |                       |
|              |                               | 509  | 262   | 509 | 225                  |   |                       |

the solvent molecules approach along the *z* axis of the complex the ligands in the *x*, *y* plane move out and the interactions become more with orbitals that have *z* characters  $(d_z^2, d_{xz}, \text{ and } d_{yz})$ . These orbitals are thus destabilized, while the other orbitals energetically decreases and eventually a typical octahedral *d* orbital splitting is formed and in this process the *d*-*d* bands shift to red region. The change in the color of the complex with solvent molecules is because of weak coordination of the solvent molecules which is attributable to a strong Jahn–Teller effect of the Cu(II) center with a  $d^9$  configuration [60a,b].

Among the three complexes, greatest solvatochromic effect was seen for the azido pair and there is a difference of  $1500 \text{ cm}^{-1}$  as we move from DCM to DMSO whereas for **2** that difference is only around 580 cm<sup>-1</sup>. It was observed that in solvent with the highest donor number (DMSO), the absorption maxima for the complexes is hardly noticeable (406 cm<sup>-1</sup>) and in weakly coordinating solvent like DCM, there is considerable difference (1330 cm<sup>-1</sup>).

Spectral analysis of the optical emission of all the three complexes were investigated in acetonitrile solution and in solid state at room temperature. The fluorescent emission spectra are shown in Fig. 15. The luminescent data of the complexes are summarized in Table 7. All copper(II) complexes showed fluorescence behavior. Complexes 1a, 1b and 2 on photoexcitation in the range 386-400 nm in their solid state, showed almost same behavior with an emission in the blue region (ca. 465 nm). The solution state emission of the same complexes showed only violet luminescence (ca. 420 nm) when excited at 345 nm. There is a red shift in the major emissive peak in solid state when compared with that of solution state. The possibility of greater stacking due to the presence of stronger non-covalent interactions between molecules may be responsible for the larger red shifts of the solid state emission bands compared to their respective counterparts in solution [61]. The coordination of a metal ion with the ligand produces

metallocycles which increases the conjugation length and conformational coplanarity thereby reducing transition energy of intraligand charge transfer [62].

## 3.3.3. Thermal analysis

The thermogravimetric analysis of complex **1a** shows a single weight loss of 25.50% (calcd. 23.70%) in the temperature range of 230-260 °C corresponding to the loss of amine part. The process is exothermic as seen in DSC curves (Fig. 16-1a). Beyond 400 °C a gradual weight loss occurs due to the thermal degradation of the remaining part of the complex and the decomposition is not completed even at 700 °C. While its polymorphic counterpart exhibits three stage decomposition – an initial weight loss of 7.45% (calcd. 7.65%) corresponding to the loss of nitrogen from the amine portion in the range 220-240 °C, then the decomposition of azide group as N<sub>3</sub>H coinciding with a mass loss of 13.99% (calcd. 12.43%) in the 240-271 °C range and finally there is a loss of chloride ion as HCl in 320-360 °C fitting to a 12.66% (calcd. 12.72%) mass loss. Unlike seen in complex 1a, here a plateau like formation is observed at higher temperatures indicating the formation of a stable metal oxide. The DSC curves show exothermic peaks for all the three stages (Fig. 16-1b).

The thermogram of complex **2** shows a 29.54% (calcd. 30.89%) weight loss (230–263 °C), exothermically corresponding to the loss

#### Table 7

Р

| hotophysical | data | of | comp | lexes. |
|--------------|------|----|------|--------|
|              |      |    |      |        |

| Complex | Excitation (nm) | Solid state<br>emission (nm) | Solution state emission (nm)<br>at excitation of 345 nm |
|---------|-----------------|------------------------------|---|
| 1a      | 386             | 466                          | 424   |
| 1b      | 386             | 465                          | 424   |
| 2       | 399             | 464                          | 428   |



Fig. 15. Solid state (left) and solution state (right) [acetonitrile, 1 \* 10<sup>-3</sup> M concentration] fluorescence spectra of the complexes.



Fig. 16. Thermogram of complexes 1a and 1b.

of HCN and  $Cl_2O$  (Fig. S13) after which a stable metal oxide is formed.

#### 3.3.4. EPR studies

The EPR spectra of the copper(II) complexes in polycrystalline state at 298 K and in DMF at 77 K were recorded in the X-band, using 100-kHz modulation frequency and 9.1 GHz microwave frequency and *g* factors were quoted relative to the standard marker TCNE (g = 2.00277). All the EPR spectra are simulated using EASYSPIN 54.0.2 package [63] and the experimental (red) and simulated (blue) best fits are included (Figs. 17 and S14). EPR parameters of the copper(II) complexes are presented in Table 8.

The EPR spectra of the polycrystalline polymeric complexes **1a** and **1b** at room temperature are of axial type giving rise to two *g* values,  $g_{\parallel}$  and  $g_{\perp}$  with  $g_{\parallel} > g_{\perp} > g_e$  (2.0023), with no hyperfine lines in the parallel and perpendicular region. The variation in the  $g_{\parallel}$  and  $g_{\perp}$  values indicate that in the solid state, the geometry of the compounds is affected by the nature of coordinating ligands.

The *g*-values in axial symmetry are correlated by the expression,

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023) \quad [64]$$

which reflects the exchange interaction between Cu(II) centers in the solid polycrystalline complexes. Accordingly, if *G* is greater than 4, the exchange interaction may be negligible; however, if *G* is less than 4, a considerable exchange interaction is indicated in the solid complex [65]. The *G* values for the polymer complexes were found to be less than 4.0, indicative of considerable exchange interaction between the copper centers in the solid.

The EPR spectra of the complexes recorded in frozen state at 77 K gives more information on the geometry of the complexes. Both the complexes, **1a** and **1b** display axial features  $[(g_{\parallel} = 2.232, g_{\perp} = 2.085)$  and  $(g_{\parallel} = 2.202, g_{\perp} = 2.120)]$  with well resolved hyperfine splittings in parallel and perpendicular region due to the interaction of the odd electron with the nuclear spin (<sup>63,65</sup>Cu, *I* = 3/2). Although expected superhyperfine splittings are not seen for complex **1a**, its polymorphic counterpart shows quintet splittings in the perpendicular region due to the coupling of electron spin with the nuclear spin of the two nitrogen atoms (*I* = 1) with super exchange splitting constant,  $A - N_{\perp} = 15.83 * 10^{-4}$  cm<sup>-1</sup>. However, the superhyperfine splittings are not visible in the parallel region.

For these pentacoordinate complexes **1a** and **1b**, the fact that  $g_{\parallel}$  is greater than  $g_{\perp}$  suggests a distorted square-pyramidal structure

consistent with the X-ray structural analysis and rules out the possibility of a trigonal bipyramidal structure, which would be expected to have  $g_{\perp} > g_{\parallel}$ .

Complex **2** also presents a typical axial spectra in the polycrystalline state with well-defined  $g_{\parallel}$  and  $g_{\perp}$  values. The spectra is broad because of the fast spin lattice relaxation and exchange coupling. Eventhough axial features are displayed, since it is magnetically concentrated, hyperfine splitting was not clear both in parallel and perpendicular regions. Calculated *G* values for complex **2** is slightly greater than 4 ruling out the possibility of an exchange interaction. The spectrum of compound **2** in DMF gave three *g* values, *viz*.  $g_1 = 2.056$ ,  $g_2 = 2.180$  and  $g_3 = 2.293$ , indicating a rhombic distortion in the geometry.

The bonding parameters  $\alpha^2$ ,  $\beta^2$  and  $\gamma^2$ , considered to be the measure of the covalency of in-plane  $\sigma$ -bonds, in-plane  $\pi$ -bonds and out-of-plane  $\pi$ -bonds respectively are evaluated using the EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{av}$ ,  $A_{\parallel}$  (Cu) and  $A_{\perp}$  (Cu) along with the energies of d-d transition.

The value of in-plane sigma bonding parameter  $\alpha^2$  was estimated from the expression [66]

$$\chi^{2} = -A_{\parallel}/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

The following simplified expression were used to calculate the bonding parameters

$$egin{aligned} & \mathcal{K}_{\|}^2 = (g_{\|} - 2.0023) E_{d-d} / 8\lambda_o \ & \mathcal{K}_{\perp}^2 = (g_{\perp} - 2.0023) E_{d-d} / 2\lambda_o \ & \mathcal{K}_{\|}^2 = lpha^2 eta^2 \end{aligned}$$

 $K^2_{\perp} = \alpha^2 \gamma^2$ 

where  $K_{\parallel}$  and  $K_{\perp}$  are orbital reduction factors and  $\lambda_0$  represents the one electron spin orbit coupling constant which equals  $-828 \text{ cm}^{-1}$ .

Hathaway [58a] has pointed out that for pure sigma bonding  $K_{\parallel} \approx K_{\perp} \approx 0.77$ , for in plane  $\pi$ -bonding  $K_{\parallel} < K_{\perp}$  and for out-of-plane  $\pi$ -bonding,  $K_{\perp} < K_{\parallel}$ . For complexes **1a**, **1b** and **2**, it is observed that  $K_{\parallel} < K_{\perp}$  which indicates the presence of significant in-plane  $\pi$ -bonding. The nature of metal–ligand bond is evaluated by comparing the value of in-plane sigma bonding parameter  $\alpha^2$  *i.e.*, if the M–L bond is purely ionic, the value of  $\alpha^2$  is unity and it is completely covalent, if  $\alpha^2 = 0.5$  [56a]. Here  $\alpha^2$  values calculated



(1b)

Fig. 17. EPR spectra of complexes (1a and 1b) in polycrystalline (left) and frozen DMF at 77 K (right).

 Table 8

 Spin Hamiltonian and bonding parameters of copper(II) complexes.

| Compounds  | Polycrystalline state (298 K) |                       |                        | DMF solution (77 K)       |                         |                                   |                            |                   |                |                 |                            |                           |                            |                            |                            |                            |
|--|-------------------------------|-----------------------|------------------------|---------------------------|-------------------------|-----------------------------------|----------------------------|-------------------|----------------|-----------------|----------------------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
|  | g <sub>iso</sub>              | $g_{\parallel}$       | $g_{\perp}$            | G                         | $g_{\parallel}/g_3$     | $g_{\perp}/g_1, g_2$              | g <sub>av</sub>            | $A_{\parallel}$   | $A_{\perp}$    | A <sub>av</sub> | $\alpha^2$                 | $\beta^2$                 | $\gamma^2$                 | $K_{\parallel}$            | $K_{\perp}$                | f                          |
| $\begin{array}{l} [Cu(L^1)(N_3)]_n \ (\textbf{1a}) \\ [Cu(L^1)(N_3)]_n \ (\textbf{1b}) \\ [Cu(L^1)(NCO)] \ (\textbf{2}) \end{array}$ | -<br>-<br>-                   | 2.20<br>2.195<br>2.22 | 2.056<br>2.06<br>2.056 | 3.6816<br>3.3397<br>4.054 | 2.232<br>2.202<br>2.293 | 2.085<br>2.120<br>2.056,<br>2.180 | 2.1337<br>2.1471<br>2.1384 | 200<br>214<br>208 | 36<br>39<br>34 | -               | 0.8602<br>0.8863<br>0.8982 | 0.889<br>0.8058<br>0.3985 | 1.0668<br>1.2373<br>1.4496 | 0.7647<br>0.7142<br>0.3579 | 0.9177<br>1.0966<br>1.3020 | 111.60<br>102.48<br>110.10 |

A values in  $10^{-4}$  cm<sup>-1</sup>.

for all the complexes lie in between 0.5 and 1, which means that the metal-ligand bonds in the complexes under study are partially ionic and partially covalent in nature.

# The $g_{\parallel}$ values also provide information regarding the nature of metal–ligand bond [67]. The $g_{\parallel}$ value is normally 2.3 or larger for ionic and less than 2.3 for covalent metal–ligand bonds. The $g_{\parallel}$ values obtained for our complexes indicate a significant degree of covalency in the metal–ligand bonds [68]. The index of tetragonal distortion f is calculated as $f = g_{\parallel}/A_{\parallel}$ , whose value may vary from 105 to 135 for small to medium distortion and depends on the nature of the coordinated atom [69]. In all complexes distortion is medium and is found to be in the range 105–115 cm [70].

#### 4. Conclusions

In the present work, we have discussed the pseudohalide incorporated 2,4-dichloro-6-((2-(dimethylamino)ethylimino)methyl) phenol] Schiff base system. Of these, the azido ligand forms a polymeric polymorph, formed by varying the copper salt used for synthesis and the cyanato forms a simple square planar monomeric form. Both the polymers involve  $\mu_{1,1}$ -azido linkage which is rather rare. The role of various weak interactions responsible for packing polymorphism and stability of a particular crystalline structure are discussed. It was a deliberate attempt of our group to introduce halogen substituted carbonyl compounds so as to experimentally

verify another interesting area of supramolecular chemists - the various halogen involving interactions. On account of various interactions involved and the density calculated, polymorph 1b was found to be closely packed and hence more stable than 1a. Solvatochromic studies were conducted for all the complexes in various polar solvents and the charge-transfer bands were found to exhibit negative solvatochromism while the d-d bands showed positive effect. Optical emission behavior in the solid and solution state showed almost the same behavior except for the red shift of the emissive peaks in solid state. All complexes luminesces in the blue region of the visible spectrum. The thermal decomposition studies were done in the solid state. The EPR studies in polycrystalline state showed typical of an axial spectra for all the complexes and the same done at 77 K is consistent with square pyramidal/square planar geometry for all the complexes except for cvanato complex which showed rhombic distortion. In our study on the polymorphic pair, no significant variation of its spectroscopic behavior was found. But they differ widely in the various types of interactions involved in their crystal packing.

Though magneto-structural correlations are usually studied in such systems, for basal-apical end-on azido linkers such studies remain unpredictable on account of variation in subtle structural features which remains unexplored till date. Work involving similar halogen substituted systems are ongoing in our lab and we anticipate some interesting results out of it.

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#### **Appendix A. Supplementary material**

CCDC 1407849, 1407850 and 1407851 contain the supplementary crystallographic data for compounds  $[Cu(L^1)(N_3)]_n$  (1a),  $[Cu(L^1)(N_3)]_n$  $(L^{1})(N_{3})]_{n}$  (**1b**) and  $[Cu(L^{1})(NCO)]$  (**2**), respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.01.008.

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