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[Dichlorido (2-(2-(1H-benzo[*d*]thiazol-2-yl)hydrazono)propan-1-ol) Cu(II)]: Crystal structure, Hirshfeld surface analysis and correlation of its ESI-MS behavior with [Dichlorido 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone Cu(II)]

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[Dichlorido (2-(2-(1H-benzo[d]thiazol-2-yl)hydrazono)propan-1-ol) Cu(II)]: Crystal structure, Hirshfeld surface analysis and correlation of its ESI-MS behavior with [Dichlorido 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone Cu(II)]

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#### Abstract

In the present work, Cu(II) complexes of 2-(2-benzo[d]thiazol-2-yl)hydrazono)propan-1-ol ( $L^1$ ) 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone (L<sup>2</sup>) are synthesized and and characterized by various spectro-analytical techniques. The structure of Cu(II) complex of L<sup>1</sup> i.e., [CuL<sup>1</sup>Cl<sub>2</sub>], is unambiguously determined by single crystal X-ray diffraction method. While similar efforts were unsuccessful in the case of Cu(II) complex of  $L^2$  i.e.,  $[CuL^2Cl_2]$ . Hence, to avail the structural facts, various cationic/anionic fragments or adducts formed during positive/negative mode electrospray ionization (ESI) of CuL<sup>1</sup>Cl<sub>2</sub> and CuL<sup>2</sup>Cl<sub>2</sub> have been identified with the help of their charge, monoisotopic masses and isotopic distributions. The similarity in the ESI behavior of two complexes has inferred their structural resemblance, which is further supported by DFT optimized structures, EPR spectral studies and analytical measurements. The EPR spectral behavior ( $g_{11} > g_{\perp} > 2.02$ ) of the complexes are attributed to an axial symmetry with the  $dx^2-y^2$  ground state having square pyramidal Cu(II) ion. CuL<sup>1</sup>Cl<sub>2</sub> has crystallized in monoclinic crystal system in P2<sub>1</sub>/c space group. The molecular complex has ring-metal (Cg-Me) interactions of the type Cg···>Cu, which contributes to the crystal packing. The Cl···H (30.6%) interactions have the major contribution among all intermolecular contacts and have played a vital role in the stabilization of the molecular structure, which is extended to 3D network through  $C-H\cdots Cg$  and Cg-Cg interactions.

#### Keywords

Copper complexes of benzothiazol hydrazone, Crystal structure of the copper complex, Hirshfeld analysis of metal complex, ESI-MS of a coordination complex.

# Highlights

- Two complexes, [Dichlorido (2-(2-(1H-benzo[d]thiazol-2-yl)hydrazono)propan-1-ol) Cu(II)] and [Dichlorido 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone Cu(II)] are synthesized.
- X-ray structure, intermolecular interactions and Hirshfeld surface analysis of [Dichlorido (2-(2-(1H-benzo[d]thiazol-2-yl)hydrazono)propan-1-ol) Cu(II)] are explored.
- Various cationic/anionic fragments or adducts formed during positive/negative mode electrospray ionization of the complexes have been identified with the help of their charge, monoisotopic masses and isotopic distributions.

# **Graphical abstract**





#### 1. Introduction

Polydentate heterocyclic ligands containing both sulfur and nitrogen atoms possess versatile coordination ability toward various transition metal ions. Hence, polyfunctional benzothiazole-based derivatives assume an exceptional importance in the construction of metal complexes of different types [1]. Due to this fact, a wide variety of copper (II) complexes derived from benzothiazole core have been reported in the literature [2-4].

X-ray crystallography remains the method of choice for definitive determination of the structure of a new coordination complex, despite the tremendous advances in spectroscopic methods for structure elucidation [5]. Hence, X-ray crystallography is often touted as the ultimate technique for substance characterization. While this is often true, limitations in growing the single crystals suitable for diffraction need to be recognized.

Recent developments of new soft ionization methods have made possible the application of mass spectrometry in various fields of analytical chemistry. Electrospray Ionization (ESI) is one such soft ionization method, that keeps any weakly bound ligands intact to the metal ion in a coordination complex. Because of this advantage of ESI, it has become increasingly popular as an analytical tool in inorganic and organometallic chemistry [6, 7]. Hence electrospray ionization mass spectrometry (ESI-MS) can be used as a complementary tool in the characterization of coordination species. However, due to susceptibility to thermal decomposition, ESI-MS may not always detect molecular ions in most of the cases [8, 9]. This makes it extremely important to identify the various species formed during ESI of coordination complexes.

Considering these facts, herein we have tried to correctly establish the structure of two copper complexes derived from benzothiazole moiety, through detailed comparative analysis of their ESI-MS behavior. Further, the structures have been correlated with the structure obtained from X-ray crystallography of one of the complex. In addition, to explore the packing modes and intermolecular interactions in molecular crystal, Hirshfeld surface(HS) analysis of the complex is also carried out.

#### 2. Experimental

#### 2.1. Materials and physical measurements

In the present studies, hydroxyacetone obtained from Sigma-Aldrich and diacetyl monoxime obtained from Thomas-Baker were used as supplied. The other reagents were obtained from SD-Fine Chemicals. Solvents were purified and dried according to the standard procedures. The metal salt used

was in its hydrated form, CuCl<sub>2</sub>.2H<sub>2</sub>O. The reaction progresses were maintained through silica gel thin layer chromatographic technique.

The CHN analysis was performed on a Thermo quest elemental analyzer. The <sup>1</sup>H NMR spectra of the ligands were recorded on AGILENT VNMRS-400 spectrometer, in a DMSO- $d_6$  solvent. The EI mass spectrum of the ligands was obtained with a Shimadzu GCMS-QP2010S spectrometer. Infrared spectra were recorded in KBr discs in the region 4000–400 cm<sup>-1</sup> on a Nicolet-6700 FT-IR spectrometer. The solution state UV–Vis spectra of all the compounds in DMF were recorded on a JASCO V-670 UV-Vis spectrophotometer. The room temperature electron paramagnetic resonance (EPR) spectrum of the complexes was recorded on the polycrystalline samples with an X-band JEOL-JES-200 spectrometer.

#### 2.2. Synthesis

# [Dichlorido (2-(2-(1H-benzo[d]thiazol-2-yl)hydrazono)propan-1-ol) Cu(II)] ([CuL<sup>1</sup>Cl<sub>2</sub>]) and [Dichlorido 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone Cu(II)] ([CuL<sup>2</sup>Cl<sub>2</sub>])

As depicted in scheme 1, the complexes were synthesized in two steps. First, the free ligands ( $L^1$  and  $L^2$ ) were synthesized according to the previous reports [10, 11]. In the next step, 10 mmol of ligands (2.21g of  $L^1$  or 2.48g of  $L^2$ ) were refluxed with 10 mmol of CuCl<sub>2</sub>.2H<sub>2</sub>O (1.70g) in ethanol/methanol for 4 hours. The obtained brown colored precipitates were filtered off and air dried. Single crystals of [CuL<sup>1</sup>Cl<sub>2</sub>] suitable for X-ray diffraction were obtained from the slow evaporation of its ethanolic filtrate.

L<sup>1</sup>: Isolated yield: 75%. m.p. 150 <sup>o</sup>C. Anal. Calc. for C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>OS (%): C, 54.28; H, 5.01; N, 18.99. Found for L<sup>1</sup>: C, 54.03; H, 5.10; N, 18.63. <sup>1</sup>H NMR (400 MHz, DMSO- d<sub>6</sub>):  $\delta$  ppm: 11.10 (s, 1H, NH), 7.60 (d, 1H, J =7.7 Hz, aromatic H), 7.36 (d, 1H, J =7.7 Hz, aromatic H), 7.23 (dd, 1H, J = 7.6 Hz, J = 7.6 Hz, aromatic H), 7.04 (dd, 1H, J = 7.6 Hz, J = 7.6 Hz, aromatic H), 5.08 (t, 1H, OH, J = 5.9Hz), 3.97 (d, 2H, methylene H, J = 5.9 Hz), 2.01 (s, 3H, methyl H). EI-MS (m/z): 221 (M<sup>+</sup>). IR (KBr,  $\upsilon$ , cm<sup>-1</sup>): 3346, 1602, 1549, 1020, 755.  $\lambda_{max}$  (nm): 250 ( $\pi \rightarrow \pi^*$ ), 295 ( $n \rightarrow \pi^*$ ).

L<sup>2</sup>: Isolated yield: 83%. m.p.: 280°C. Anal. Calc. for  $C_{11}H_{12}N_4OS$  (%): C, 53.21; H, 4.87; N, 22.56. Found for L<sup>2</sup> (%): C, 53.53; H, 5.01; N, 22.32. <sup>1</sup>H NMR (400 MHz, DMSO- d<sub>6</sub>):  $\delta$  (ppm) 11.66 (s, 1H, OH), 11.46 (s, 1H, NH), 7.70 (s, 1H, aromatic H), 7.37 (s, 1H, aromatic H), 7.76 (m, 1H, aromatic H) 7.07 (m, 1H, aromatic H), 2.11 (s, 3H, C<sub>1</sub>H), 2.01 (s, 3H, C<sub>4</sub>H). EI-MS (m/z): 248 (M<sup>+</sup>). IR (KBr, v, cm<sup>-1</sup>): 3442, 1612, 1571, 1545, 750.  $\lambda_{max}$  (nm): 231 ( $\pi \rightarrow \pi^*$ ), 313 ( $n \rightarrow \pi^*$ ).

[CuL<sup>1</sup>Cl<sub>2</sub>]: Isolated yield: 2.10g, (59%). m.p. >300<sup>0</sup>C. Anal. Calc. for C<sub>10</sub>H<sub>11</sub>Cl<sub>2</sub>CuN<sub>3</sub>OS (%): C, 35.43; H, 3.47; N, 13.15. Found for [CuL<sup>1</sup>Cl<sub>2</sub>] (%): C, 35.28; H, 3.58; N, 12.92. IR (KBr, υ, cm<sup>-1</sup>): 3446, 1540, 1449, 1051, 753.  $\lambda_{max}$  (nm): 250 ( $\pi \rightarrow \pi^*$ ), 338 (n $\rightarrow \pi^*$ ), 500 (d-d transition).

[CuL<sup>2</sup>Cl<sub>2</sub>]: Isolated yield: 1.95g, (51%). m.p. >300<sup>0</sup>C. Anal. Calc. for C<sub>11</sub>H<sub>12</sub>Cl<sub>2</sub>CuN<sub>4</sub>OS (%): C, 34.52; H, 3.16; N, 14.64. Found for [CuL<sup>2</sup>Cl<sub>2</sub>] (%): C, 34.28; H, 3.38; N, 14.82. IR (KBr, υ, cm<sup>-1</sup>): 3439, 1560, 1521, 1494, 760.  $\lambda_{max}$  (nm): 271 ( $\pi \rightarrow \pi^*$ ), 317 ( $n \rightarrow \pi^*$ ), 454 (d-d transition).



Scheme 1. Synthesis of complexes.

# 2.3. SC-XRD Data collection and refinement of [CuL<sup>1</sup>Cl<sub>2</sub>]

A single crystal of dimensions  $0.29 \times 0.27 \times 0.26$  was mounted on a glass fiber. The X-ray intensity data were collected at a temperature of 130 K on a Bruker Proteum2 CCD diffractometer with X-ray generator operating at 45 kV and 10 mA, using Cu-K $\alpha$  radiation of wavelength 1.54178 Å. Data were collected for 24 frames per set with different settings of  $\phi(0^\circ$  and 90°), keeping the scan width of 0.5°, exposure time of 5 s, the sample to detector distance of 45.10 mm and 20 value at 46.6°. A complete data set was processed using *SAINT PLUS* [12]. All the frames were indexed using a primitive monoclinic lattice. The structure was solved on Olex2 [13] with ShelXT [14] structure solution program using intrinsic phasing and refined with the XL [15] refinement package using least squares minimization. All non-hydrogen atoms were identified in the first difference Fourier map and were refined anisotropically. Further, all the hydrogen atoms were geometrically positioned. After several cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residual was saturated to

0.048. The mercury-3.8 package was used to generate molecular graphics [16]. The crystal data and the structure refinement details are given in Table 1.

Crystal data	CCDC 1532568		
Chemical formula	C <sub>10</sub> H <sub>11</sub> Cl <sub>2</sub> CuN <sub>3</sub> OS		
M <sub>r</sub>	355.72		
Crystal system, space group	Monoclinic, $P2_1/c$		
Temperature (K)	296		
a, b, c (Å)	8.0596 (3), 19.9590 (7), 9.0924 (3)		
β (°)	115.285 (1)		
$V(Å^3)$	1322.49 (8)		
Z	4		
Radiation type	Cu <i>K</i> α		
$\mu (mm^{-1})$	7.46		
Crystal size (mm)	$0.29 \times 0.26 \times 0.22$		
Data collection			
Diffractometer	Bruker X8 Proteum		
Absorption correction	Multi-scan SADABS		
T <sub>min</sub> , T <sub>max</sub>	0.221, 0.291		
No. of measured, independent and	10513, 2062, 1848		
observed $[I > 2\sigma(I)]$ reflections			
R <sub>int</sub>	0.042		
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.584		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.048, 0.168, 1.19		
No. of reflections	2062		
No. of parameters	164		
H-atom treatment	H-atom parameters constrained		

Table 1. Crystal data and the structure refinement details.

$\Delta \rangle_{\text{max}}, \Delta \rangle_{\text{min}} (e \text{ Å}^{-3})$	0.83, -0.89

#### 2.4. Computational methods

The geometry of the molecules,  $[CuL^1Cl_2]$  and  $[CuL^2Cl_2]$ were optimized using density functional theory. ORCA program package (version 3.0.3) was used for DFT calculations. Tight convergence criteria were chosen for all calculations. All calculations were performed using the hybrid functional BP in combination with Ahlrichs split-valence double- $\xi$  basis set def2-SVP [17] for all atoms. ORCA calculation times were minimized using the RI approximation [18] [19] using SVP/J auxiliary basis sets [18] from the TurboMole basis set library II. The outputs were visualized using molecular visualizer tool Avogadro 1.1.1 [20] and Mercury-3.8 package [16].

## **2.5.** Hirshfeld surface analysis of [CuL<sup>1</sup>Cl<sub>2</sub>]

The molecular HS in the crystal structure was created based on the electron distribution calculated as the sum of spherical atom electron densities. The normalized contact distance ( $d_{norm}$ ) based on both  $d_e$ ,  $d_i$  and the van Der Waals radii enables identification of the regions of particular interest to intermolecular interactions. The HSs and 2D fingerprint plots(FP) presented here were plotted using the software Crystal Explorer 3.0 [21]. The  $d_{norm}$  plots were mapped with color scale in between -0.491 au (blue) and 1.541 au (red). The FPs [22, 23] were displayed by using the expanded 0.6–2.8 Å view with the  $d_e$  and  $d_i$  distance scales displayed on the graph axes. Shape-index and Curvedness surfaces are specified on the basis of local curvature of the Hirshfeld surface [24].

#### 2.6. ESI-MS analysis

The positive and negative mode ESI measurements were performed in DMF solvent, on Waters Q-TOF Premier-HAB213 mass spectrometer in the mass range 0-1300 Da. The Sample was dissolved in DMF to form a 10<sup>-5</sup>M solution. The resulting solution was directly infused into the instrument's ESI source at a flow rate of 0.2 mL min<sup>-1</sup>. The data was acquired at a capillary voltage of 3.5 kV, sampling cone voltage of 10 V, and a source temperature of 100 °C.

#### 3. Results and discussion

#### 3.1. Spectral characterization

The IR spectrum of ligand  $L^1$  has shown u(O-H) band at 3346 cm<sup>-1</sup>. The sharp intense bands at 1597 cm<sup>-1</sup> and 1549 cm<sup>-1</sup> in  $L^1$  are assigned to azomethine and benzothiazole ring u(C=N) vibrations. In

the complex, these bands have broadened and intensified due to the coupling of the exo-azomethine band with azomethine of benzothiazole ring with a low energy shift. This suggests the coordination of the benzothiazole ring nitrogen and azomethine nitrogen to the Cu(II) ion [25]. A sharp intense band at  $1020 \text{ cm}^{-1}$  in the ligand L<sup>1</sup>, is assigned to u(C-O), which has shifted to  $1051 \text{ cm}^{-1}$  in the complex indicating the coordination of –OH to the metal ion upon complexation.

In the free ligand  $L^2$  the u(O-H) of oxime functionality, has given stretching vibrations at 3442 cm<sup>-1</sup>. This has shifted to 3439cm<sup>-1</sup> in the complex. The low energy shift of this band in the complex is due to the coordination of oxime nitrogen[26]. The sharp intense bands observed at 1612, 1571 and 1545 cm<sup>-1</sup> in  $L^2$  are assigned to azomethine, oxime and ring u(C=N) vibrations respectively [27, 28]. In the complex, these bands have suffered from low energy as well as significant low-intensity shifts, indicating the coordination azomethine, oxime and ring nitrogens [29].

In the Uv-Vis spectrum of L<sup>2</sup>, it has exhibited broad bands in the UV region at a  $\lambda_{max}$  of 231 and 313 nm respectively. These bands are assigned to the intra ligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions respectively. L<sup>1</sup> has shown these transitions at 250 and 295 nm. These bands have appeared in complexes with a slight shift in their  $\lambda_{max}$ . This shift is attributed to the change in  $\pi$  conjugation and coordination of azomethine nitrogens upon complexation [30]. The absorption spectrum of [CuL<sup>1</sup>Cl<sub>2</sub>] and [CuL<sup>2</sup>Cl<sub>2</sub>] have given a *d*-*d* electronic bands at 500 and 454 nm respectively.

The singlet at 11.10 ppm in L<sup>1</sup> is ascribed to the hydrazine NH, while it is observed at 11.46 in L<sup>2</sup>. A triplet is observed at 5.08 ppm in L<sup>1</sup>, due to the OH proton. The oxime proton in L<sup>2</sup> has given a broad singlet at 11.66 ppm. Methylene protons of L<sup>1</sup>, have resonated as a doublet at 3.97 ppm. The methyl protons in L<sup>1</sup> have resonated as a singlet at 2.01 ppm, while in L<sup>2</sup>, they are observed at 2.01 and 2.11 ppm. The proton signals in the aromatic region are discussed in the syntheses section.

# 3.2. Crystal structure data and description of [CuL<sup>1</sup>Cl<sub>2</sub>]

The title compound  $C_{10}H_{11}Cl_2CuN_3OS$  has crystallized in the monoclinic crystal system with the space group P2<sub>1</sub>/c. The unit cell dimensions *a*, *b* and *c* are 8.0596 (3) Å, 19.9590 (7) Å and 9.0924 (3) Å respectively.  $\beta = 115.285^{\circ}$  (1), Z = 4 and V = 1322.49 (8) Å<sup>3</sup> for the unit cell. Mercury rendered ORTEP of the molecule with displacement ellipsoids drawn at 50 % probability level is shown in Fig.1. The bond lengths and bond angles given in Table 1 and Table 2 of supplementary information (SI) are in good agreement with the standard values.



Figure 1. ORTEP diagram of the title molecule with 50 % probability displacement thermal ellipsoids.

The asymmetric unit contains a neutral complex molecule with no crystal held solvent or water molecules. The ligand is coordinated to the central metal ion in an NNO tridentate fashion with the benzothiazole-N (N1), imine-N (N3) and hydroxyl-O (O1) as donor atoms. In addition, two coordinated chlorides have given a penta coordinated tetragonally distorted square pyramidal complex. The ligand has formed two five-membered chelate rings with the metal center. The deviation of metal centered bond angles from 90° indicates the deviation from ideal square pyramidal geometry. In the structure, the axial chloride-metal distance (Cu1-Cl1) 2.56 Å is considerably longer than the basal distance (Cu1-Cl2) 2.21 Å as ascertained by geometry index ( $\tau_5$ ) of 0.198. ( $\tau = 0$  for a square pyramid, and  $\tau = 1$  for a trigonal bipyramid)[25].

The ligand has adopted + *syn-periplanar* conformation at both the chelate rings Cu(1)-->O(1)-->C(1)-->C(2)-->N(3) (ring A, torsion angle + 8.41°) and Cu(1)-->N(1)-->C(4)-->N(2)-->N(3) (ring B, torsion angle +7.12°). The nine membered benzothiazole ring (S(1)-->C(4)-->N(1)-->C(10)-->C(9)-->C(8)-->C(7)-->C(6)-->C(5)) has accepted +*anti-clinal* conformation with the ring average torsion angle of +105.52°.

The ring puckering analysis of two chelate rings can be carried out with the help of pseudo rotation parameters, P and  $\tau$  [31]. The values of P (phase angle of pseudorotation) and  $\tau$  (amplitude of puckering) signify the variations in endocyclic bond angles [32]. The chelate ring A is characterized by P = 193.9(14)° and  $\tau$  = 11.9(2)°. This substantiates the twisted conformation on Cu(1)--O(1) on ring A. While ring B has adopted envelope conformation on Cu(1), as ascertained by P = 334.2(19)° and  $\tau$  = 9.4(3)°.

The molecular complex exhibits C—H···Cg interaction; C(1)—H(1B)···Cg4 (Cg4 is the centroid of the ring C5/C6/C7/C8/C9/C10) with a C—Cg distance of 3.406(5) Å, H···Cg distance of 2.61Å, C—H···Cg angle of 139° with the symmetry code 1-x,1-y,1-z. The C—H···Cg interaction; C(3)—H(3A)···Cg3 (Cg3 is the centroid of the ring S1/C4/N1/C10/C5) is with a C—Cg distance of 3.648(6) Å, H···Cg distance of 2.77 Å, C—H···Cg angle of 153° with the symmetry code -x,1-y,1-z. The complex shows ring-metal (Cg-Me) interactions of the type Cg(2)···>Cu(1) and Cg(3)···>Cu(1) with the ring to metal distance of 3.637 Å and 3.849 Å respectively. These interactions contribute to the crystal packing.

The molecule also exhibits  $Cg \cdots Cg$  interaction;  $Cg1 \cdots Cg3$  (Cg1 is the centroid of the ring Cu1/O1/C1/C2/N3) and Cg3 is the centroid of the ring S1/C4/N1/C10/C5) with a Cg-Cg distance of 3.555(2) Å,  $\alpha = 4.08(19)^\circ$ ,  $\beta = 18.7^\circ$ ,  $\gamma = 19.3^\circ$ , a perpendicular distance of Cg1 on ring S1/C4/N1/C10/C5 = 3.3553(16) Å, a perpendicular distance of Cg3 on ring Cu1/O1/C1/C2/N3 = 3.3680(17) Å with the symmetry code 1-x, 1-y, 1-z.

The molecules are further connected through inter and intra molecular O-H-Cl, N-H-Cl and C-H-Cl hydrogen bond interactions [33], which helps to stabilize the molecular structure by forming a three-dimensional network. The hydrogen bonding geometry is listed in Table 2. The hydrogen bonding interactions arising from axial chloride(Cl1), are depicted in Fig.2. The packing of molecules along 'c' axis (Fig.3) shows that the molecules form layered stacking along (0 0 1) plane.

D—HA	D—H	НА	DA	D—H…A
C(9)H(9)Cl(2)*	0.93	2.76	3.536(5)	142
O(1)H(1)Cl(1) <sup>i</sup>	0.93	2.26	2.991(3)	134
N(2)H(2)Cl(1) <sup>ii</sup>	0.86	2.25	3.040(4)	153

Table 2. Geometric parameters for hydrogen bond interactions (Å, °).

\*Intra; i:1-x,1-y,2-z; ii:-x,1-y,1-z.



Figure 3. The packing of molecules along 'c' axis.

#### 3.3. DFT optimized structures

Repeated attempts to grow the single crystals of  $[CuL^2Cl_2]$  suitable for X-ray diffraction were not fruitful. Hence the structure of  $[CuL^2Cl_2]$  is obtained from DFT calculations. The DFT optimized structures of  $[CuL^1Cl_2]$  and  $[CuL^2Cl_2]$  are given in Fig.4. These structures are quite close to the structure of  $[CuL^1Cl_2]$  obtained from the single crystal. The calculated single point energies (SPE) for  $[CuL^1Cl_2]$  and  $[CuL^2Cl_2]$  are found to be -3679.27 and -3585.91 kJ/mol respectively. SPE calculates the wave function and charge density, and hence the energy, of a particular arrangement of nuclei [34].



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# Figure 4. DFT optimized structures of [CuL<sup>1</sup>Cl<sub>2</sub>] and [CuL<sup>2</sup>Cl<sub>2</sub>]

The optimized structures were used to calculate the energies of the molecular orbitals (MOs). Besides the HOMO and LUMO, HOMO-1 and LUMO+1 are also considered for both the structures. The contributions of each atom in the molecular orbital are reflected in the molecular density distribution through the MO. The localization of the density for the orbitals and energies of [CuL<sup>1</sup>Cl<sub>2</sub>]and [CuL<sup>2</sup>Cl<sub>2</sub>]are depicted in Fig.5. The highest contribution for the HOMO for all the structures is attributed to the chloride ligands. In the LUMO orbital, in addition to the localized density from the benzene ring, there is some contribution from other atoms as shown in Fig.5.



Figure 5. The localization of the density for the orbitals and energies of  $[CuL^{1}Cl_{2}]$  and  $[CuL^{2}Cl_{2}]$ .

#### **3.3.** Hirshfeld Surface studies of [CuL<sup>1</sup>Cl<sub>2</sub>]

HS analysis provides surface features characteristic of different types of intermolecular interactions. These features can be revealed by color coding distances from the surface to the nearest atom exterior ( $d_e$  plots) or interior ( $d_i$  plots) to the surface. This gives a visual picture of different types of interactions present and also reflects their relative contributions from molecule to molecule. FPs, in particular, the breakdown of these plots into specific atom...atom contacts in a crystal can provide a quantitative idea of the types of intermolecular contacts experienced by molecules in the bulk [22, 35, 36].

HSs comprising  $d_{norm}$  surface and FPs were generated and analyzed for  $[CuL^1Cl_2]$  in order to explore the packing modes and intermolecular interactions. Fig.6 illustrates the two-dimensional FPs from HS analysis. This shows the difference between the intermolecular interaction patterns and the relative contributions to the HS for the major intermolecular contacts associated [35]. Importantly, H...Cl (30.6%) bonding appears to be a major contributor in the crystal packing, whereas the H...H (30.0%), C...H/H...C (17.1%), S...H/H...S (7.1%), S...Cl/Cl...S(3.0%) being the other contributors. Fig.7 shows the intermolecular contacts which are highlighted by the conventional mapping of  $d_{norm}$  on molecular HSs. The red spots over the HS indicate the intercontacts involved in a hydrogen bond. The dark-red spots on the  $d_{norm}$  surface arise as a result of the short interatomic contacts [35, 37, 38], i.e., strong hydrogen bonds, while the other intermolecular interactions appear as light-red spots.

Fig.8 shows the shape index and curvedness mapped on HS. The shape index shows a red concave region on the surface around the acceptor atom and a blue region around the donor H-atom. The adjacent red and blue triangles on the shape index surface shows that the  $\pi$ - $\pi$  stacking interaction is almost identical in the total crystal structures [39]. Curvedness on the Hirshfeld surface has divided the surface into contact patches with each neighboring molecules. On the curvedness surface, the flat region towards the bottom of the molecule indicates  $\pi$ - $\pi$  stacking interactions.







Figure 6. Two-dimensional Fingerprint plots of the showing Cl...H, H...H, C...H, S...H and S...Cl interactions. ( $d_i$  is the closest internal distance from a given point on the Hirshfeld surface and  $d_e$  is the closest external contacts).



Figure 7.  $d_{norm}$  mapped on Hirshfeld surface for visualizing the molecular interactions.

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Figure 8. Hirshfeld surface mapped with (a) shape index and (b) curvedness.

#### 3.4. ESI-MS analysis

Electrospray technique is a powerful tool in the study of coordination complexes, due to its ability to sample various molecular species in solution systems. The ESI-MS of the complexes has shown several peaks due to the molecular species (cation/anion) of the various fragments formed during ESI. Only singly charged complex ions were identified, presenting various metal to ligand stoichiometries. Table 3 and 4 of SI presents the assignments for all the peaks observed in positive and negative mode ESI-MS of both the complexes. The corresponding spectra are depicted in Fig.1-4 of SI. The assignment of every peak in ESI-MS has been further supported by calculated isotopic distribution for the moiety formula. For [CuL<sup>1</sup>Cl<sub>2</sub>], the expanded portions of positive mode ESI-M spectrum and calculated isotopic mass distributions of various species are provided in SI.

In the positive mode ESI, the title compounds have shown very close fragmentation pattern. Complexes have lost 2 chloride ligands, generating two mono-positive cations (Scheme 2). This is evident in the intense peaks observed at an m/z of 318.96, 282.98 for [CuL<sup>1</sup>Cl<sub>2</sub>] and 345.97, 309.99 for [CuL<sup>2</sup>Cl<sub>2</sub>]. These peaks support the structure obtained from X-ray crystallography for [CuL<sup>1</sup>Cl<sub>2</sub>]. The base peaks at an m/z of 222.06 and 249.08 are due to the protonated ligands. Complexes have shown peaks at an m/z of 356.04 and 383.06, which closely resembles the mass of whole molecules. But from calculated isotopic distributions, these peaks are more precisely assigned to [Cu+L+4(H<sub>2</sub>O)]<sup>+</sup> type aqua adducts of the complexes. Peaks at 504.04 and 558.07 exactly correspond to in situ generated ML<sub>2</sub> type species [Cu+2L-H]<sup>+</sup>. The complex [CuL<sup>1</sup>Cl<sub>2</sub>] has shown an additional peak at 473.03, which accounts for the mass of [Cu+2L-CH<sub>2</sub>OH-H]<sup>+</sup> species formed by the loss of methanol fragment from the ML<sub>2</sub> species [25]. In the case of [CuL<sup>2</sup>Cl<sub>2</sub>], this peak is not expected due to its structure. Additional less intense peaks at a higher m/z are assigned to various mono-positive cations, as identified in Table 3 of SI.

In the negative mode ESI of complexes, molecular ion peaks are expected at an m/z of 354.92 and 316.94 for the species [Cu+L+2Cl-H]<sup>-</sup> However, due to the presence of labile chloride ligands, these peaks are observed with very less intensity. But the peaks due to [Cu+L+Cl-2H]<sup>-</sup> at an m/z of 381.93 and 343.96 are sufficiently intense to index the presence of MLCl<sub>2</sub> complex. Spectra have even detected the formation of M<sub>2</sub>L<sub>2</sub> type species [2Cu+2L+Cl-4H]<sup>-</sup>, in the form of intense peaks at an m/z of 600.92 and 654.94. The base peaks at an m/z of 134.86 in these spectra, exactly correspond to in situ generated [CuCl<sub>2</sub>]<sup>-</sup> species. Additional less intense peaks at a higher m/z are assigned to various mono-negative anions varying from M<sub>4</sub>L<sub>4</sub> to M<sub>2</sub>L<sub>2</sub> type species, as identified in Table 4 of SI. Most of the coordination entities formed here have maintained 1:1 metal to ligand ratio. Overall, in all the peaks of negative mode ESI, spectrum has shown a maximum of 2 ionizable hydrogens per ligand and 2 ionizable chlorides per metal ion for both the complexes. In conclusion, comparative account of ESI behavior of the complexes strongly suggest the structural similarities.





Scheme 2. Positive mode ESI-fragmentation of the complexes.

## 3.5. EPR spectral analysis

The room temperature EPR spectrum of  $[CuL^1Cl_2]$  and  $[CuL^2Cl_2]$  was recorded on polycrystalline samples, to get the insights into the geometry of complexes. Corresponding spectra are given in Fig.5 and Fig.6 of SI. The  $g_{||}$  and  $g_{\perp}$  values observed for the complexes are 2.28, 2.09 (for  $[CuL^1Cl_2]$ ) and 2.24, 2.09 (for  $[CuL^2Cl_2]$ ) respectively. This spectral behavior ( $g_{||} > g_{\perp} > 2.02$ ) of the complexes are attributed to an axial symmetry with the dx<sup>2</sup>-y<sup>2</sup> ground state having elongated octahedral, square pyramidal or square planar coordination geometry around the Cu(II) ion [40]. This observation is clearly in support of observed square pyramidal X-ray structure of  $[CuL^1Cl_2]$ . When the geometry is compressed octahedral or trigonal bipyramidal, an EPR spectrum will be characterized by  $g_{\perp} > g_{||} = 2.0023$  [41]. Hence the present trend ( $g_{||} > g_{\perp} > 2.02$ ) rules out the possibility of trigonal bipyramidal geometry around the pentacoordinated Cu(II). In both the complexes,  $g_{||}$  values (2.28, 2.24) are less than 2.3, indicating a larger percentage of covalency of metal–ligand bonding [42].

#### 4. Conclusions

In the present studies, two new transition metal complexes, [Dichlorido (2-(2-(1H-benzo[d]thiazol-2-yl)hydrazono)propan-1-ol) Cu(II)] and 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone are synthesized and characterized by various spectro-analytical techniques.

The structure of  $[CuL^1Cl_2]$  is determined by single crystal X-Ray diffraction method. In  $[CuL^1Cl_2]$ , the ligand is coordinating to the central metal ion Cu(II), in an N, N, O-tridentate fashion. Along with the two chloride ligands, the organic moiety has produced a penta-coordinated tetragonally distorted square pyramidal complex. The molecular complex involves ring-metal (Cq-Me) interactions of the type Cg···>Cu. The molecular and crystal structure of the molecule is stabilized by hydrogen bond interactions arising from axial chloride ligand, which is visualized with the help of dark red spots on the Hirshfeld surface of the molecule. 2D fingerprint plots reveal that H...Cl (30.6%) interaction to be a major contributor in the crystal packing, which extends to the 3D network through C-H-Cq and Cq-Cqinteractions. EPR spectral behavior ( $g_{\parallel} > g_{\perp} > 2.02$ ) of the complexes are attributed to an axial symmetry with the  $dx^2-y^2$  ground state having square pyramidal geometry around the Cu(II) ion. In the positive mode, ESI of both the complexes, along with the mono-cationic molecular fragments, various adducts of  $M_2L_2$  and  $ML_2$  type species have been identified. Most of the coordination entities formed in the negative mode ESI have maintained 1:1 metal to ligand ratio. This observation strongly supports the crystal structure.  $M_2L_2$   $M_3L_3$  and  $M_4L_4$  type anionic molecular adducts of higher m/z have been generated during ESI. Comparative account of ESI behavior of the complexes, EPR analysis and DFT optimized structures strongly suggest the structural similarities in the synthesized complexes.

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