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Structural, Spectral and Biological Investigations on Cu(II) and Zn(II) Complexes Derived from NNO Donor Tridentate Schiff base: Crystal Structure of a 1D Cu(II) Coordination Polymer

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Abstract

Copper(II) and zinc(II) complexes of an NNO donor tridentate Schiff base, 4-bromo-2-(((3-(methylamino)propyl)imino)methyl)phenol (HL), were synthesised and characterised by different physicochemical methods including single crystal XRD, elemental analysis, IR, electronic and EPR spectral analysis. Copper(II) complex is a 1D coordination polymer in which chlorine acts as a bridging ligand and zinc(II) complex is a bis-ligated one. Hirshfeld surface analysis of the complexes has been carried out which provided better understanding of intermolecular interactions. Effects of solvents on charge transfer bands and *d-d* bands were investigated and the former shows a negative solvatochromic behaviour and latter a positive behaviour upon increasing solvent polarity. Luminescent properties were analysed and found that copper(II) and zinc(II) complexes exhibit quenching and enhancement of fluorescence respectively which is backed by quantum yield values. Cytotoxic activity of both complexes has been screened *in vitro* against lymphoma ascites cell lines. In addition, antibacterial activity of complexes has been screened against bacterial species *Bacillus cereus, Staphylococcus aureus, Klebsiella pneumonia* and *Escherichia coli*.

Keywords

Schiff base complex; 1D coordination polymer; Solvatochromism; *In vitro* cytotoxicity; Antibacterial activity

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1. Introduction

Application of metal complexes of Schiff bases in diverse fields is of current research interest to coordination chemists all over the world. By recognizing the significance of metal complexes incorporating Schiff bases from their application perspective, a lot of efforts are being invested to develop inexpensive synthetic routes for these compounds. Several studies have been reported illustrating the biological activity of Schiff base complexes including their anticancer [1], antimicrobial [2], antioxidant [3] *etc.* activities.

Cytotoxic activity of metal complexes derived from Schiff bases against various malignant tumors have also been extensively studied and the metal which is incorporated in the complex has a great impact on the effectiveness of the compound [4]. Several attempts are being made to find suitable alternatives to platinum based metal complexes in order to broaden the spectrum of activity, to enhance clinical effectiveness and to reduce general toxicity leading to undesirable side-effects [5]. Compared to organic agents, metal complexes offer better ways of drug action due to their wide range of coordination numbers and flexible geometries as well as kinetic properties [6]. The determination of cytotoxicity and cell viability of coordination compounds can be considered as an initial step in the development of anti-cancer drugs. Transition metal complexes have been found to possess extensive antimicrobial activity which depend on the nature of metal ion as well as ligands, presence of certain functional groups, geometry of the complex etc. Schiff base ligands serve as better candidates for the synthesis of such complexes since they are characterized by the presence of biologically important azomethine functionality [7]. Copper and zinc are bioessential metal ions, involved in several biological processes and their complexes have been largely explored for their significant cytotoxic and antimicrobial activities [8].

Herein we report the synthesis and characterization of an NNO donor tridentate Schiff base ligand, formed by the facile condensation of *N*-methyl-1,3-diaminopropane and 5-bromosalicylaldehyde and its copper(II) and zinc(II) complexes. Molecular structures of the compounds were confirmed by single crystal X-ray crystallography. Presence of different intermolecular interactions responsible for various supramolecular architectures has been visualised by Hirshfeld surface analysis. Photoluminescent properties of Schiff base and complexes were investigated. *In vitro* cytotoxicity and antibacterial activity of complexes were also studied.

2. Experimental

2.1. Materials

All starting materials and solvents were of reagent grade and purchased from commercial sources. 5-Bromosalicylaldehyde (Aldrich), *N*-methyl-1,3-diaminopropane (Aldrich), $CuCl_2 \cdot 2H_2O$ (Aldrich) and $Zn(NO_3)_2 \cdot 6H_2O$ were used as received. Solvents, methanol and DMF were purchased from Spectrochem and used without further purification.

2.2. Synthesis of the ligand (HL) and its metal complexes

2.2.1. Synthesis of 4-bromo-2-(((3-(methylamino)propyl)imino)methyl)phenol (HL)

5-Bromosalicylaldehyde (0.201 g, 1 mmol) and *N*-methyl-1,3-diaminopropane (0.088 g, 1 mmol) were refluxed in H₂O/MeOH (3:1) mixture for about two hours. To the resulting hot reaction mixture, three drops of triethyl amine was added and allowed to reflux for another one hour. This yellow colored clear solution was kept for slow evaporation. Brown residue obtained within a week was separated, washed, and dried.

Yield: 0.048 g (18%). Color: Brown. *Anal.* Calc. for $C_{11}H_{15}BrN_2O$ (270.04): C, 48.72; H, 5.58; N, 10.33%. Found: C, 49.12; H, 5.28; N, 10.53%. FTIR (KBr, cm⁻¹): 3448 (–OH), 3272 (N–H), 1634 (C=N), 1382 (C–O). ¹H NMR (CDCl₃, ppm): δ H 3.10 (3H, s), 2.63 (2H, t, *J* = 5.60 Hz), 3.50 (2H, t, *J* = 7.20 Hz), 3.75 (2H, t, *J* = 6.40 Hz), 6.91 (1H, t, *J* = 8.40 Hz), 7.24 (2H, d, *J* = 9.2 Hz), 8.30 (1H, s).

2.2.2. Synthesis of Cu(II) complex (1)

5-Bromosalicylaldehyde (0.201 g, 1 mmol) and *N*-methyl-1,3-diaminopropane (0.088 g, 1 mmol) were refluxed in 10 mL methanol for about two hours. A methanolic solution of copper(II) chloride (0.170 g, 1 mmol) was added with continuous stirring and refluxed for about 3 hours. Suitable single crystals for structure determination by X-ray diffraction were obtained by slow evaporation of the mother liquor in air.

Yield: 0.295 g (80%). Color: Green. *Anal*. Calc. for $C_{11}H_{14}BrClCuN_2O$ (369.14): C, 35.79; H, 3.82; N, 7.59%. Found: C, 35.99; H, 4.12; N, 7.39%. FTIR (KBr, cm⁻¹): 3394 (N–H), 1631 (C=N), 1352 (C–O). λ_M (DMF): 6.8 mho cm² mol⁻¹.

2.2.3. Synthesis of Zn(II) complex (2)

Complex **2** was prepared by a method similar to that of complex **1** except that zinc(II) nitrate (0.297 g, 1 mmol) was added to the hot reaction mixture instead of copper(II) chloride. Diffraction quality single crystals for structure elucidation were obtained by slow evaporation of the mother liquor in air.

Yield: 0.600 g (82%). Color: Yellow. *Anal.* Calc. for $C_{22}H_{30}Br_2N_6O_8Zn$ (731.71): C, 36.11; H, 4.13; N, 11.49%. Found: C, 36.41; H, 4.53; N, 11.19%. FTIR (KBr, cm⁻¹): 3326 (N–H), 1624 (C=N), 1344 (C–O), 1382 (N–O). λ_M (DMF): 87 mho cm² mol⁻¹.

2.3. Methods and measurements

Microanalysis studies of compounds were carried out using a Vario E III CHNS analyser. FT-IR spectra were recorded on a JASCO FT-IR-5300 spectrometer in the range 400-4000 cm⁻¹ using KBr discs. Electronic spectra in DMF solution were recorded in Thermo Scientific Evolution 220 spectrophotometer in the 200-900 nm range. Molar conductivities of the synthesised complexes were measured in DMF (10⁻³ M) at room temperature using Systronic model 303 direct reading conductivity meter. Photoluminescent properties were investigated using Fluorolog, Horiba Scientific (solution). ¹H NMR spectrum of the Schiff base was recorded in CDCl₃ using Bruker AMX 400 FT-NMR spectrometer with TMS as internal standard at ambient temperature. The EPR spectra of the copper complex in the solid state at 298 K and in DMF at 77 K were recorded on a JES- FA200 ESR Spectrometer at SAIF, IIT Bombay, India.

2.4. Description of crystal structures

Diffraction data for complexes **1** and **2** were collected at room temperature on a Bruker SMART APEXII CCD diffractometer using graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The unit cell dimensions were measured, and the data collection was carried out. Data acquisition and integration were accomplished through Bruker SMART software and Bruker SAINT Software respectively [9]. Absorption corrections were done using SADABS based on Laue symmetry using equivalent reflections [10]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXL-2018/1 software [11] in the WINGX software package [12]. Molecular and crystal structures were drawn using ORTEP-3 [12], DIAMOND version 3.10. [13] and MERCURY 3.8 programs [14]. Anisotropic refinement for all non-hydrogen atoms was performed and all H atoms on C atoms were placed in calculated positions, with the aid of difference maps, with C–H bond distances of 0.93 - 0.97 Å. and refined in the riding model approximation with $U_{iso}(H)$ set to 1.2 $U_{eq}(C)$ (1.5 for Me). Crystallographic data along with relevant bond lengths and bond angles are listed in Tables 1-2.

2.5. Hirshfeld surface analysis

. Hirshfeld surfaces (HSs) which are unique for a given crystal structure have been generated and mapped with d_{norm} (range of -0.21 to 1.24 Å) and shape index functions (-1 to 1 Å) using CrystalExplorer 17.5 software [15,16]. The d_{norm} plot is based on the distances to the surface from nuclei outside and inside the Hirshfeld surface (d_e and d_i respectively) and vdW radii of the atom. Negative d_{norm} value corresponds to contacts shorter than vdW separation and positive d_{norm} value corresponds to contacts greater than vdW separation and are plotted using a red-white-blue colour scheme where red represents shorter contacts, white implies contacts around the vdW separation and blue indicates longer contacts. Shape index function specifies the subtle changes in surface shape. 2D fingerprint plots, plot of d_i vs d_e , were displayed in the range of 0.8 to 2.8 Å, which includes reciprocal contacts too [17].

2.6. In vitro cytotoxicity studies

Complexes 1 and 2 were investigated for short-term *in vitro* cytotoxicity using Dalton's lymphoma ascites cell lines (DLA). Tumour cells were aspirated from the peritoneal cavity of mice and washed with phosphate buffer saline (PBS). Concentration of the cell suspension was made up to 1×10^6 cells in 0.1 mL. The stock solution of test compounds were prepared in DMSO. Then the viable cell suspension was added to tubes containing different concentration of compounds under investigation and volume was made up to 1 mL using PBS. In control tube, only cell suspension was maintained. These assay mixtures were incubated at 37 °C for 3 hours. After that, 0.1 mL of Trypan blue was added to each test tube and kept for 2-3 minutes. Later these were loaded on a haemocytometer. Trypan blue stains the dead cells and they will have blue cytoplasm whereas live cells do not take up the dye and they will have a clear cytoplasm. The number of stained and unstained cells were counted separately and percentage cytotoxicity was determined using Eq. 1 [18],

% Cytotoxicity =
$$\frac{\text{No.of dead cells}}{\text{No.of live cells + No.of dead cells}} \times 100$$
 (1)

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2.7. Antibacterial activity studies

In vitro antibacterial activity of complexes 1 and 2 were studied using both Gram(+) and Gram(-) pathogenic bacterial strains. Bacillus cereus and Staphylococcus aureus were used as Gram(+) bacterial strains whereas Klebsiella pneumonia and Escherichia coli were used as Gram(-) bacterial strains. Activity of complexes was tested by the well diffusion method using nutrient agar medium. Nutrient agar medium was prepared using 0.5 g peptone, 0.3 g yeast extract, 0.5 g NaCl, 3 g agar and 100 mL distilled water whose pH was maintained to be 7.2. It was then sterilised by autoclaving. Later they were poured into sterile petri dishes aseptically to uniform depth of 4 mm and then allowed to solidify at room temperature (37 °C). After solidification, the test organism was inoculated by sterile swab, which provides uniform surface growth of microorganism. After that, a well with a diameter of 7 mm was made aseptically with a sterile cup borer. The compounds under investigation were dissolved in DMSO solvent to get a final concentration of 100 mg/L and introduced into the well along with standard antibiotic, ampicillin into another well (positive control). DMSO solvent was used as the negative control. The petri dishes were incubated at 37 °C for 24 hrs and the experiments were repeated under aseptic condition. After 24 hrs of incubation, the zone of inhibition produced by the different organism in different plates were measured with reference to positive control.

3. Results and discussion

Copper(II) and zinc(II) complexes of a tridentate Schiff base (HL), derived by the facile condensation of 5-bromosalicylaldehyde and *N*-methyl-1,3-diaminopropane, were synthesized (Schemes 1 & 2) and characterized by various physicochemical methods.

Scheme 1. Formation of tridentate Schiff base ligand.

Scheme 2. Synthetic pathway to complexes 1 and 2.

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Complex 1 (Cu(II) complex) is a 1D coordination polymer in which, HL acts as a tridentate NNO donor ligand which coordinates to the central metal ion through phenoxo oxygen, imine nitrogen and amino nitrogen. Complex 2 (Zn(II) complex) is a bis-ligated one, whose crystal structure was reported previously [19], in which HL acts as a bidentate ligand coordinating to the metal centre through phenoxo oxygen and imine nitrogen only.

Analytical purity of the complexes was confirmed by elemental analysis. They are moisture insensitive and stable in air and are soluble in dipolar aprotic solvents like DMF and DMSO. From the molar conductivity values it has been found that complexes **1** and **2** are non- electrolytic and electrolytic respectively in nature. Investigation of the photophysical properties of the Schiff base and complexes was also carried out.

| Parameters | Complex 1 | Complex 2 |
|---|--------------------------|--------------------------------|
| T urumeters | | |
| | | ~ ~ ~ ~ ~ ~ ~ |
| Empirical formula | $C_{11}H_{14}BrClCuN_2O$ | $C_{22}H_{30}Br_2N_6O_8Zn$ |
| Formula weight | 369.14 | 731.71 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | Cc | Fdd2 |
| Cell parameters | | |
| a (A) | 13.369(3) | 22.057(3) |
| b (A) | 15.430(3) | 47.507(5) |
| c (A) | 6.7670(9) | 5.4550(6) |
| α (°) | 90 | 90 |
| β (°) | 117.221(8) | 90 |
| γ (°) | 90 | 90 |
| Volume V ($Å^3$) | 1241.4(4) | 5716.1(11) |
| Z | 4 | 8 |
| Calculated density (ρ) (Mg m ⁻³) | 1.975 | 1.700 |
| Absorption coefficient, μ (mm ⁻¹) | 5.177 | 3.710 |
| F(000) | 732 | 2944 |
| Crystal size mm ³ | 0.350 x 0.300 x 0.300 | 0.320 x 0.170 x 0.120 |
| θ (°) range for data collection | 3.291 to 31.601 | 2.520 to 28.244 |
| Limiting indices | -18≤h≤19 | -28≤h≤29 |
| - | -22≤k≤22 | -62≤k≤61 |
| | -9 <u>≤</u> 1≤5 | -5 <u><</u> 1 <u><</u> 7 |
| Reflections collected | 5959 | 11983 |
| Unique Reflections (R _{int}) | 4151 (0.0370) | 3546 (0.0524) |
| Completeness to θ | 25.242 (99.7 %) | 25.242 (99.9 %) |
| Maximum and minimum | 0.215 and 0.176 | 0.620 and 0.450 |
| transmission | | |
| Data / restraints / parameters | 4151 / 2 / 155 | 2979 / 1 / 178 |
| Goodness-of-fit on F ² | 0.892 | 1.017 |

Table 1. Crystal data and refinement details of complexes 1 and 2

| | ð | |
|-------------------------------------|------------------|------------------|
| | ournal Pre-proof | |
| Final R indices $[I > 2\sigma (I)]$ | $R_1 = 0.0359,$ | $R_1 = 0.0404,$ |
| | $wR_2 = 0.0685$ | $wR_2 = 0.0781$ |
| R indices (all data) | $R_1 = 0.0553,$ | $R_1 = 0.0793,$ |
| | $wR_2 = 0.0746$ | $wR_2 = 0.0904$ |
| Largest difference peak and hole (e | 0.377 and -0.564 | 0.481 and -0.481 |
| A^{-3}) | | |

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0| \qquad w R_2 = [\Sigma w ({F_0}^2 - {F_c}^2)^2 / \Sigma w ({F_0}^2)^2]^{1/2}.$

Table 2

Selected bond lengths (Å) and bond angles (°) of complexes 1 and 2

| Comple | ex 1 | Comple | ex 2 |
|------------------|------------|------------------------------|------------|
| | Bond | lengths (Å) | |
| Cu(1)–N(1) | 1.983(4) | Zn(1)–N(1) | 1.986(4) |
| Cu(1)–N(2) | 2.045(4) | Zn(1)–O(1) | 1.930(4) |
| Cu(1)–O(1) | 1.929 (4) | C(7)–N(1) | 1.272(6) |
| Cu(1)–Cl(1) | 2.293(17) | 2.293(17) C(8)–N(1) 1.468(7) | |
| | Bond | angles (°) | |
| O(1)-Cu(1)-N(1) | 87.9(2) | O(1)-Zn(1)-O(1a) | 113.9(2) |
| O(1)-Cu(1)-N(2) | 176.1(2) | O(1)-Zn(1)-N(1) | 95.71(16) |
| N(1)-Cu(1)-N(2) | 95.69(19) | O(1)-Zn(1)-N(1a) | 117.13(17) |
| O(1)-Cu(1)-Cl(1) | 84.74(13) | N(1)-Zn(1)-N(1a) | 118.7(2) |
| N(1)-Cu(1)-Cl(1) | 165.22(14) | | |
| N(2)-Cu(1)-Cl(1) | 91.42(15) | | |

3.1. Crystal structures of complexes

3.1.1. Crystal structure complex 1

Molecular structure of complex **1** was confirmed by X-ray crystallography and is shown in Fig.1 with atom numbering scheme.

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

When the tridentate Schiff base ligand (HL) reacts with $CuCl_2$ it forms a 1D polymeric complex. Complex crystallized in a monoclinic *C*c space group and asymmetric

unit consists of a distinct square planar Cu(II) centre with its plane accommodated by phenoxo oxygen (O1), imine nitrogen (N1), amino nitrogen (N2) and a chlorido ligand. However in the entire polymeric structure, each unit has a pentacoordinated geometry with its apical position occupied by chlorido ligand of the adjacent unit *via* μ_2 bridging. In the polymeric chain, chlorido ligand exhibits a dual nature in such a manner that it is axially aligned with respect to one metal ion and is equatorially positioned with respect to the adjacent metal ion (Fig 2). The central metal atom, Cu1, deviate by 0.1017 Å from the least square plane. The Addison parameter, an index of degree of trigonality, gives the extent of distortion of the pentacoordinated geometry of the complex which can be obtained by the equation $\tau = (\beta - \alpha)/60$ [20]. The value of τ is 0.1813 for this complex which confirms a slightly distorted square pyramidal geometry.

Fig. 2. (a) The coordination geometry of Cu(II) metal centre and the nature of chlorido ligand (b) 1D polymeric chain of Cu(II) complex.

Bridging Cu···Cl distance is ~0.6 Å longer than normal Cu–Cl distance (normal Cu–Cl, 2.2933(15)Å, bridging Cu···Cl, 2.8922(21) Å). This is comparable with Cu–Cl distance found in similar chloride bridged Cu(II) polymers [21]. The Cu···Cu non bonded distance along the polymeric chain in 3.5171(11) Å and the interchain Cu···Cu distance is 6.7670(13) Å. The Cu(1)–Cl(1)–Cu(1) bond angle is $84.57(4)^{\circ}$ and the Cl(1)–Cu(1)–Cl(1) bond angle is $105.49(5)^{\circ}$. A relative measure of the bond strength follows the order metal-phenoxo oxygen> metal-imino nitrogen> metal-amino nitrogen> metal-equatorial chlorine> metal-amino nitrogen> metal-equatorial chlorine>

Cremer and Pople ring puckering analysis [22] showed that in this copper complex, two pairs of fused six membered chelate rings Cu(1)/O(1)/C(1)/C(6)/C(7)/N(1) and Cu(1)/N(1)/C(8)/C(9)/C(10)/N(2) are puckered around the metal centers with puckering parameters Q = 0.477(4) Å and φ =196.1(8)° and Q = 0.532(7) Å and φ =180(18)° respectively.

In this complex, there are four different types of non-classical intermolecular hydrogen bonding interactions exist (Fig. 3). The interaction parameters are listed in Table S1. Two hydrogen atoms, H8A borne by the C8 atom and H10B borne by the C10 atom form an intermolecular hydrogen bonding interaction with chlorine atom Cl1. As a result a ring motif R_2^{1} (6) is generated. The same chlorine atom forms another intermolecular hydrogen

bond with hydrogen atom H1A borne by the amino nitrogen N2 and an intramolecular hydrogen bond with hydrogen atom H11B borne by C11 atom of the methyl group. All these four interactions thus result in a quadfurcated hydrogen bonding interaction with Cl1 as the common acceptor. Phenoxo oxygen, O1, is also engaged in an intermolecular hydrogen bonding with hydrogen atom H1A borne by the amino nitrogen N2. The polymeric chain formed by chloride bridging is further enhanced by all these intermolecular hydrogen bonding interactions.

Fig. 3. Inter- and intramolecular hydrogen bonding interactions (dashed lines) in complex 1.

3.1.2. Crystal structure of complex 2

Crystal structure of complex 2 has been reported by Wang *et al* before [19]. But we could isolate X-ray quality single crystals with better R factor. This centrosymmetric mononuclear zinc(II) complex got crystallized in orthorhombic Fdd2 space group and asymmetric unit consists of half of the molecule along with a nitrate ion in the lattice (Fig. 4). Although the crystal structure is reported, herein we are attempting to explore more of its structural and supramolecular aspects.

Fig. 4. ORTEP plot showing the atom labeling of the asymmetric unit of the complex **2** (drawn with 50% thermal ellipsoid).

Complex is bis-ligated and only azomethine nitrogens (N1 and N1a) and phenoxo oxygens (O1 and O1a) coordinate to the metal centre hence making it a four coordinated complex. Both amino nitrogens are protonated and two nitrate ions are present in the lattice making the whole charge of the complex neutral. Whether the coordination geometry of Zn(II) ion is perfect tetrahedron or perfect square planar can be found out from τ_4 index ($\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$ where α and β (in °) are the largest angles around central metal ion). For a perfect tetrahedron, $\tau_4 = 1$ and for perfect square planar geometry, $\tau_4 = 0$ [23]. The τ_4 value of 0.8865, for this complex confirms a slightly distorted tetrahedral geometry.

Fig. 5. Molecular structure of complex 2 along with the atom-numbering scheme of the non-hydrogen atoms.

Cremer and Pople ring puckering analysis showed that the six membered chelate ring (Zn1/O1/C1/C6/C7/N) and its counterpart are puckered and adopts S form (Screw-Boat) conformation with puckering parameters Q= 0.208(4) Å and $\phi = 207.4(14)^{\circ}$.

In the crystal structure, N–H···O, N–H···N and C–H···O hydrogen bonding interactions exist (Fig. S1). Molecules are linked through N–H···O hydrogen bonds along crystallographic 'c' axis forming a polymeric chain (Fig. S2) and the rest of all the interactions result in the formation of a 3D supramolecular architecture (Fig. S3). In addition to this, non-covalent C–H··· π interaction involving C3–H3···Cg(3) enhance the stability of crystal packing (Fig S4, Table S2).

Quality of the crystals that we have obtained is very much greater than that reported by Wang *et al.* as it is indicated from the R factor (R factor of crystals that we have reported is 0.04 and that reported by Wang *et al* is 0.08). Also, slight differences in the bond length and bond angles are observed. In addition to N–H···O hydrogen bonds, reported by Wang *et al*, all other interactions could be studied in detail from the crystal structure reported by us which helped in the analysis of the formation of supramolecular architectures. A similar bisligated nickel(II) complex with the same ligand is reported by Bhattacharyya *et al* [24] which got crystallised in monoclinic $P2_1/c$ space group. Here, in addition to the two imino nitrogens and the two phenoxo oxygens, two amino nitrogens from the two deprotonated Schiff base ligands are coordinating to the nickel(II) centre, thus making a six-coordinate octahedral environment for the metal ion. Also, here there are no nitrate ions present in the crystal lattice.

3.2. Hirshfeld surface and 2D fingerprint analyses

Presence of different types of intermolecular interactions in the crystal systems was further supported by Hirshfeld surface analysis and associated fingerprint plots. Hirshfeld surfaces (HSs) for complexes **1** and **2** have been generated and mapped with d_{norm} and shape index functions (Fig. 6). Intermolecular hydrogen bonding interactions in complexes **1** and **2**, visualised using Hirshfeld surfaces mapped with d_{norm} are shown in Figs. 7 & 8 respectively. The red hot spots on the HS of complexes **1** and **2** indicate prominent intermolecular hydrogen bonding interactions present in the crystal structures.

Fig. 6. Hirshfeld surfaces of complexes **1** and **2** mapped over (a) d_{norm} and (b) shape index functions.

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Fig. 7. (a) Intermolecular hydrogen bonding interactions in 1, (b) viewing the same short contacts in Hirshfeld surface mapped with d_{norm} .

Fig. 8. (a) Intermolecular hydrogen bonding interactions in 2, (b) viewing the same short contacts in Hirshfeld surface mapped with d_{norm} .

While the non-covalent C–H··· π interaction present in crystal structure of complex 2 can be envisioned from the orange concave depressions (π acceptor regions) and blue convex regions (C–H donors) on the shape index plot drawn (Fig. S5) [25].

The 2D fingerprint plots of Hirshfeld surfaces for both complexes are shown in Fig. 9. Dihydrogen interactions have highest contribution to the total Hirshfeld surfaces of both the complexes. In complex **1**, the next highest contribution to the total Hirshfeld surface is from Br····H contacts (16.8%) with $d_i + d_e$ distance of ~ 3.3 Å followed by Cl···H (identified as two sharp spikes which are seen on the top left and at the bottom right), C···H and O···H contacts (11.7%, 9.4% and 4.1% respectively). Whereas in complex **2**, O···H contacts have almost equal contribution (28.2%) as that of H···H (28.6%) to the total Hirshfeld surface which is obvious due to the presence of N–H···O and C–H···O hydrogen bonding interactions in the crystal system. The next highest contribution is from C···H contacts (18.3%) which appeared as two sharp spikes followed by Br···H (17.3%) and N···H (2.3%) contacts. Relative contributions of all interactions in all the two complexes are shown in Fig. 10.

Fig. 9. Fingerprint plots for complexes 1-2. Close contacts are labelled as (1) $H \cdots H$, (2) $C \cdots H$, (3) $Br \cdots H$, (4) $O \cdots H$ and (5) $Cl \cdots H$.

Fig. 10. Relative contribution of intermolecular interactions to the Hirshfeld surface in 1-2.

3.3. Spectroscopic analysis

3.3.1. IR Spectra

FT-IR spectra of Schiff base and complexes were recorded in the range 400-4000 cm⁻¹ using KBr pellets. Tentative assignment of spectral values are presented in Table S4 and spectra are given in Figs. S7-S9. In the IR spectrum of Schiff base, a sharp band is observed at 3448 cm⁻¹ which can be assigned due to the stretching mode of the O–H group in the

ligand. The absence of such a band in the IR spectra of complexes **1** and **2** confirms the deprotonation of the ligand and coordination to the metal centre through oxygen atom [26]. The azomethine stretching frequency observed in the Schiff base (1634 cm⁻¹) was shifted to lower frequencies 1624-1631 cm⁻¹ upon complexation. This implies the coordination of the imine nitrogen atoms to the metal center [27]. The new peak at 1382 cm⁻¹ in complex **2** can be assignable to asymmetrical stretching frequency of nitrate moiety present in the lattice [28].

3.3.2. Electronic spectra and solvatochromic studies

The linear optical properties of complexes **1** and **2** were scanned in the UV-Vis region in DMF medium and spectral values are summarized in Table S5. The electronic spectrum of Schiff base shows two absorption maxima at 285 and 324 nm corresponding to π - π * and n- π * transitions respectively [29]. Complexes **1** and **2** showed LMCT bands at 379 and 369 nm respectively indicating transitions from the coordinating atoms of the Schiff base to the metal centres [30]. The high ϵ values for these bands are supportive of the charge transfer transitions. It is very difficult to resolve the three spin allowed transitions (${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$, ${}^{2}B_{2g}$ $\leftarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$) into individual bands in the electronic spectra of copper complexes since the energy difference between these bands are very low. Complex **1**, shows absorption in the low energy region, 650-653 nm which corresponds to *d*-*d* transitions [31].

In order to have an understanding of the dependency of electronic response on solvents, solvatochromic studies were carried out by choosing eight different sovents of varying polarity. A negative solvatochromic effect (hypsochromic (or blue) shift of charge transfer bands as solvent polarity increases) was observed for the charge transfer bands of both the complexes which is a result of greater stabilization of ground electronic state than the excited one (Fig. S10 & S11) [32]. The absorption maxima (λ_{max} , nm) along with their ϵ (M⁻¹cm⁻¹) of complexes in different solvents are compiled in Table S5.

Low energy metal based *d*-*d* transitions are also affected by solvent environment as a result of their influence on coordination environment of the metal centre. Four solvents having different donor power (DCM, acetonitrile, methanol and DMSO) were chosen for the investigation and found that there is a bathochromic (or red) shift for the *d*-*d* bands as the donor power of the solvent increases, which is known as positive solvatochromism (Table S7, Fig. S13). When the solvents approach the complex along the 'z' axis, ligands in *x*, *y* plane move out, orbitals which are having *z* character will experience greater repulsion as result of

greater interaction and thus they get energetically destabilized and other orbitals get stabilized leading to a typical octahedral d orbital splitting. As a result d-d bands are shifted to higher wavelength region [33].

3.3.3. Photoluminescent properties

Optical emissive responses of Schiff base and both the complexes were studied in DMF solution (10^{-5} M) at room temperature. The emission spectra of the Schiff base and complexes are shown in Fig. S12 and the luminescent data are summarised in Table S6. On excitation at 320 nm, emission maxima are observed at 417, 411 and 437 nm for Schiff base, complexes 1 and 2 respectively.

The fluorescence emission intensity of Schiff base has been decreased on complexation with Cu(II) ion. The decrease in intensity may be attributed to the decrease in electron density on Schiff bases as a result of complex formation [34]. But in zinc complex, there is an enhancement in the fluorescent intensity which is of great significance since this complex can serve as potential photoactive material. This enhancement may be due to the prevention of photoinduced electron transfer process by the complexation of ligand with metal ions [35]. Also, because of its stable d^{10} electronic configuration, zinc ion is difficult to oxidise or reduce which clearly indicates that the emission observed in the complex is purely intraligand fluorescence [36].

The relative fluorescent quantum yields for Schiff base and both the complexes were measured in DMF using quinine sulfate (in 0.5 M H₂SO₄, $\phi = 0.54$) as the quantum yield standard. The fluorescent quantum yields of Schiff base and complexes **1** and **2** are 0.0147 and 0.0078 respectively. The quenching and enhancement of fluorescence in complexes **1** and **2** respectively are backed by the quantum yield values.

3.3.4. EPR spectral analysis

The X band EPR spectrum of complex **1** in polycrystalline state at 298 K and in DMF at 77 K was recorded using JES- FA200 ESR Spectrometer. Simulation of ESR spectrum was carried out using the EasySpin 5.0.25 package [37] and the experimental (red) and simulated (blue) best fits are included. EPR spectral parameters are given in Table 3.

EPR spectrum of complex **1** at 298 K is of axial type providing two g values, g_{\parallel} and g_{\perp} , with g_{\parallel} (2.209) > g_{\perp} (2.035) > g_e (2.0023) (Fig. 11) which indicates that the unpaired

electron is in $d_x^2 - y^2$ orbital. There are no hyperfine lines in the parallel and perpendicular region. The fact $g_{//} > g_{\perp}$ proposes a distorted square pyramidal geometry which is consistent with the X-ray crystallographic studies.

The geometric parameter, G, for an axial spectrum is obtained by the expression, $G = (g_{||} - 2.0023)/(g_{\perp} - 2.0023)$ [38] which indicates the exchange interaction between copper centres in polycrystalline state. G value less than 4 implies there is considerable exchange interaction and G value greater than

value less than 4 implies there is considerable exchange interaction and G value greater than 4 indicates negligible interaction. For complex **1**, G value was found to be greater than 4, indicative of no exchange interaction.

In solution state, at 77 K, EPR spectrum has axial features and consists of four wellresolved hyperfine lines in the parallel region with $g_{||} = 2.233$ and $g_{\perp} = 2.047$. There are no hyperfine lines in perpendicular region (Fig. 12).

 α^2 , β^2 and γ^2 are the bonding parameters which correspond to covalency of the inplane σ bonds, in-plane π bonds and out-of plane π bonds respectively. α^2 can also be regarded as a measure of the fraction of the unpaired electron density located on the copper ion and is obtained from the equation [39],

 $\alpha^2 = -A_{||} / 0.036 + (g_{||} - 2.003) + 3/7 (g_{\perp} - 2.0023) + 0.04$

Value of α^2 implies the nature of metal-ligand bond. If its value is unity, M–L bond has ionic nature and if $\alpha^2 = 0.5$, it is completely covalent [40]. For complex **1** it was found to be 0.8307, lie in between 0.5 and 1 and which implies that the nature of metal-ligand bond is partially ionic and partially covalent.

The value of other bonding parameters can be obtained through the following expressions.

$$K_{||}^{2} = (g_{||} - 2.0023) E_{d-d} / 8\lambda o$$

$$K_{\perp}^{2} = (g_{\perp} - 2.0023) E_{d-d} / 2\lambda o$$

$$K_{||}^{2} = \alpha^{2} \beta^{2}$$

$$K_{\perp}^{2} = \alpha^{2} \gamma^{2}$$

Where $K_{//}^2$ and K_{\perp}^2 are the orbital reduction factors and λo denotes the spin orbit coupling constant with a value of -828 cm⁻¹.

According to Hathaway [40], for pure σ bonding, $K_{//} \approx K_{\perp} \approx 0.77$, for in-plane π bonding, $K_{//} < K_{\perp}$ and for out of-plane π bonding, $K_{\perp} < K_{//}$. In our case K_{\perp} (0.644) $< K_{//}$ (0.732) which implies significant out of-plane π bonding. Another parameter, *f*, index of tetragonal distortion can be calculated as $f = g_{//} / A_{//}$, whose value may differ from 105 to 135 for small

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to medium distortion and depends on the nature of coordinated atom [41]. In our complex its value is found to be 112.77 indicating medium distortion.

Fig. 11. EPR spectrum of complex 1 in polycrystalline state at 298 K.

Fig. 12. EPR spectrum of complex 1 in DMF at 77 K

Table 3

EPR spectral parameters of the complex 1.

| | 8// | g_\perp | g_{av} | G | $A_{//}$ | A_{\perp} | α^2 | β^2 | γ^2 | f |
|----------------------------------|-------|-----------|----------|-------|----------|-------------|------------|-----------|------------|--------|
| Polycrystalline state (298 K) | 2.209 | 2.035 | 2.093 | 6.321 | | 6, | | | | |
| DMF solution (77 K) | 2.233 | 2.047 | 2.109 | 0 | 198 | | 0.830 | 0.881 | 0.775 | 112.77 |

A values in 10⁻⁴ cm⁻¹

3.4. Cytotoxic activity

In vitro cytotoxic activity of complexes 1 and 2 were evaluated against Dalton's lymphoma ascites cells. Percentage cytotoxicity exhibited by each compound against DLA cell lines are summarized in Table 4 and the drug concentration is varied from 10 to 200 μ g/mL.

Table 4

| Drug concentration(µg/mL) | Percentage cell death (DLA) % | | |
|---------------------------|-------------------------------|-----------|--|
| | Complex 1 | Complex 2 | |
| 200 | 83 | 78 | |
| 100 | 63 | 62 | |
| 50 | 51 | 56 | |
| 20 | 47 | 35 | |
| 10 | 32 | 17 | |
| | | | |

In vitro cytotoxicity of complexes

While analyzing the results we can see that although both the complexes showed significant cytotoxic activity against DLA cells, copper complex is having higher activity. Both of them exhibit concentration dependent inhibition of the growth of DLA cells. As the drug concentration increases, cytotoxic activity of test compounds also increases. We have also calculated the IC₅₀ values (concentration of drug when the response is reduced by half) for both complexes and complex 1 is having 36 μ g/mL as IC₅₀ value and for complex 2 it is 42 µg/mL. The increased cytotoxic activity of copper complexes may be attributed to the extended planar structure induced by $\pi - \pi^*$ conjugation resulting from the chelation of copper ion with the ligand [42]. In addition, the flexible redox properties of copper complexes leading to a distorted geometry form another reason for the increased bioactivity compared to zinc complexes [43].

3.5. Antibacterial activity

In vitro antibacterial activity of complexes 1 and 2 were investigated using both Gram(+) and Gram(-) pathogenic bacterial strains and both of them were found to be active against both Gram(+) and Gram(-) bacterial strains. Zone of inhibition of both the compounds in mm against four bacterial strains chosen for the study are compiled in Table 5. Between the bacterial strains, complexes showed very good activity against Klebsiella pneumonia (Fig. 13). DMSO control did not show any zone of inhibition.

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Table 5

Antibacterial activity of complexes

| Bacteria | Zone of inhibition (mm) | | | |
|------------------------------------|-------------------------|-----------|------------|--|
| | Complex 1 | Complex 2 | Antibiotic | |
| Staphylococcus aureus ^a | 22 | 21 | 32 | |
| Bacillus cereus ^a | 16 | 20 | 30 | |
| Escherichia coli ^b | 15 | 18 | 28 | |
| Klebsiella pneumonia ^b | 20 | 21 | 26 | |

^a Gram positive bacteria

^b Gram negative bacteria

Fig. 13. Petri plates showing the zone of inhibition of antibacterial activity of complexes against *Klebsiella pneumonia*.

Although the complexes behaved somewhat in similar way to the pathogenic strains, complex 2 (zinc complex) showed more activity against *Bacillus cereus* and *Escherichia coli*. Usually biomolecules show stronger affinity for copper centered complexes which help them to pass through the cell membrane [44]. The increased antibacterial activity of zinc complex can be explained in connection with its structure. Complex 2 is bis-ligated in which amino nitrogens of both ligands are free from coordinating to the metal center. The presence of uncoordinated hetero atoms increases the activity of coordination compounds by bonding with the trace elements present in the microorganism which leads to the inhibition of microbial growth [45].

4. Conclusion

In the present endeavor, we have discussed the synthesis and physicochemical characterizations of 4-bromo-2-(((3-(methylamino)propyl)imino)methyl)phenol Schiff base system and its copper(II) and zinc(II) complexes. Copper(II) complex is a chloro bridged 1D coordination polymer which crystallized in a monoclinic Cc space group. We could successfully isolate the single crystals of zinc(II) complex with improved R factor though its structure has been reported before. Structural and supramolecular aspects of both the complexes were investigated in detail. Various intermolecular interactions present in crystal systems were visually analysed with the help of Hirshfeld surfaces and associated 2D

fingerprint plots. Charge transfer bands of both the complexes showed negative solvatochromic behaviour and *d-d* bands exhibited a positive nature. From the photoluminescence studies it has been found that copper(II) complex exhibits quenching of fluorescence whereas in the case of zinc(II) complex there is an enhancement of fluorescence with respect to Schiff base ligand and these observations are supported by the obtained quantum yield values. Cytotoxic activity of both complexes has been screened *in vitro* against lymphoma ascites cell lines and copper complex showed better activity with IC₅₀ value 36 μ g/mL. Also, *in vitro* antibacterial activity of complexes has been screened against bacterial species *Bacillus cereus, Staphylococcus aureus, Klebsiella pneumonia* and *Escherichia coli* and found that complex **2** (zinc complex) showed more activity against *Bacillus cereus* and *Escherichia coli* than complex **1**.

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Appendix A. Supplementary data

CCDC 1948191 and 1948192 contain the supplementary crystallographic data for complexes **1** and **2** respectively. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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N-methyl-1,3-diaminopropane 5-bromosalicylaldehyde

4-bromo-2-(((3-(methylamino)propyl)imino)methyl)phenol

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4-bromo-2-(((3-(methylamino)propyl)imino)methyl)phenol



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Highlights

- Copper(II) and zinc(II) complexes derived from a Schiff base system are discussed.
- Copper(II) complex is a chloro bridged 1D coordination polymer.
- Complexes exhibit in vitro cytotoxicity against Dalton's lymphoma ascites cell lines.
- They show antibacterial activity against both Gram(+) and Gram(-) bacterial strains.

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All the three authors contributed equally to the work.

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There are no conflicts of interest

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