

Supramolecular structure, spectroscopic, thermal studies and antimicrobial activities of Schiff base complexes

A. Z. El-Sonbati¹ \cdot A. A. El-Bindary¹ \cdot M. A. Diab¹ \cdot M. I. Abou-Dobara² \cdot E. E. Abdo¹

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Abstract Metal(II) complexes of 4-(((2-hydroxynaphthalen-1-yl)methylene) amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (HL) were prepared, and their compositions and physicochemical properties were characterized on the basis of elemental analysis, with¹HNMR, UV-Vis, IR, mass spectroscopy and thermogravimetric analysis. All results confirm that the novel complexes have a 1:1 (M:HL) stoichiometric formulae $[M(HL)Cl_2] \quad (M = Cu(II)(1),$ Cd(II)(5)),[Cu(L)(O₂NO)(OH₂)₂](2), [Cu(HL)(OSO₃)(OH₂)₃]2H₂O(3), [Co(HL)Cl₂(OH₂)₂]3-H₂O(4), and the ligand behaves as a neutral/monobasic bidentate/tridentate forming a five/six-membered chelating ring towards the metal ions, bonding through azomethine nitrogen, exocyclic carbonyl oxygen, and/or deprotonated phenolic oxygen atoms. The XRD studies show that both the ligand and Cu(II) complex (1) show polycrystalline with monoclinic crystal structure. The molar conductivities show that all the complexes are non-electrolytes. On the basis of electronic spectral data and magnetic susceptibility measurements, a suitable geometry has been proposed. The trend in g values ($g_{11} > g_{\perp} > 2.0023$) suggest that the unpaired electron on copper has a $d_{x^2-y^2}$ character, and the complex (1) has a square planar, while complexes (2) and (3) have a tetragonal distorted octahedral geometry. The molecular and electronic structures of the ligand (HL) and its complexes (1-5) have been discussed. Molecular docking was used to predict the binding between HL ligand and the receptors of the crystal structure of Escherichia coli (E. coli) (3t88) and the crystal structure of *Staphylococcus aureus* (S. aureus) (3q8u). The activation thermodynamic parameters, such as activation energy (E_a) , enthalpy (ΔH) , entropy (ΔS), and Gibbs free energy change of the decomposition (ΔG) are

A. Z. El-Sonbati elsonbatisch@yahoo.com

¹ Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

² Botany Department, Faculty of Science, Damietta University, Damietta, Egypt

calculated using Coats-Redfern and Horowitz-Metzger methods. The ligand and its metal complexes (1-5) showed antimicrobial activity against bacterial species such as Gram positive bacteria (*Bacillus cereus* and *S. aureus*), Gram negative bacteria (*E. coli* and *Klebsiella pneumoniae*) and fungi (*Aspergillus niger* and *Alternaria alternata*); the complexes exhibited higher activity than the ligand.

Keywords Schiff base · Molecular docking · DNA binding · Molecular structure · Thermodynamic parameters

Introduction

Schiff base complexes of transition metals are of particular interest to inorganic chemists since their wide range of diverse biological activities and their chemical, structural, and spectral properties are often strongly dependent on the nature of the ligand structure [1, 2]. Also a Schiff base chromophore possesses substantial harmonic phonons, which give substantial contributions to their coordination ability with different ligands [3]. Metal chelation is involved in many biological processes, where the coordination can occur between a different metal ion and a wide range of ligands [4]. In recent years, metal-based drugs have gained much importance in the medicinal field. They are in use as medicines for the treatment of diabetes, cancer, and anti-inflammatory and cardiovascular disease [5–7].

Schiff bases derived from 2-hydroxy-1-napthaldehyde have been extensively studied due to their wide range of applications in medicinal fields [10], and they form stable complexes with metal ions due to the presence of a phenolic hydroxyl group at their *o*-position, which coordinates to the metal ion via deprotonation. Many Schiff bases derived from 2-hydroxynaphthaldehyde have been studied by NMR spectroscopy and X-ray analysis in the solid state [8–11]. The UV–Vis spectra of some 2-hydroxyl Schiff bases have been investigated in polar and non-polar solvents [12-14]. The absorption band at >400 nm belongs to a keto-amine form of the Schiff base. The results showed that the enol-imine form is dominant in a nonpolar solvent while the keto-amine form is dominant in a polar solvent for such Schiff bases. Recently, the UV-Vis spectroscopic study for quantitative analysis of undefined mixtures of the substituted Schiff bases of 2-hydroxynaphthaldehydes has been based on the chemometric approach [13]. Schiff bases can be incorporated into crown ether structures to form interesting cation binding ligands. In such structures the cation can occupy the crown cavity depending on the donor atom and cation character or form the Schiff base complex through the imine group. Some crown ether-containing ortho hydroxylated Schiff bases have been synthesized and their complexation properties with transition metal cations have been investigated [15]. However, the crown ether moieties carrying only oxygen and nitrogen donor atoms exist in these compounds. Schiff bases have been reported to possess remarkable antibacterial and antifungal activities. The C=N linkage in azomethine derivatives is an essential structural requirement for biological activity [16, 17].

Recently we have reported the synthesis, characterization and biological activities of some metal(II) complexes of Schiff bases [16]. We have synthesized

the novel Schiff base ligand 4-(((2-hydroxynaphthalen-1-yl)methylene)amino)-1,5dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (**HL**) containing carbonyl and azomethines as potential chelating sites. In order to explore the ligational behavior of this ligand, we have prepared a series of its Cu(II), Co(II) and Cd(II) complexes and characterized them by various physicochemical techniques and studied their antimicrobial activities. Study of the docking of the Schiff base ligand, as well as molecular and electronic structures of the ligand (**HL**) and its complexes are discussed

Experimental

Materials

All reagents and chemicals required were Analytical Grade (AR), purchased commercially. All the solvents were purified by distillation and used. All reactants (2-hydroxy-1-naphthaldehyde and 4-aminoantipyrine) were procured from Sigma Aldrich. Calf thymus DNA (CT-DNA) was purchased from SRL (India). Organic solvents were spectroscopically pure from BDH and included ethanol, methanol, and dimethylformamide.

Preparation of Schiff base ligand (HL)

The Schiff base ligand of 4-(((2-hydroxynaphthalen-1-yl)methylene)amino)-1,5dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (**HL**) was prepared according to the previous procedure [16]. An ethanolic solution of 4-aminoantipyrine (0.1 m mol) was added slowly to the solution of 2-hydroxy-1-naphthaldehyde (0.1 m mol) in ethanol with constant stirring and addition of two drops of piperidine. The mixture was refluxed for 4 h in in a water bath. After concentration of the solution, the precipitate was separated, filtered, washed with ethanol, and dried in vacuum over anhydrous CaCl₂ [18]. Recrystallization from ethanol afforded pure crystals, Yield: 70 %. The purity of ligand was checked by TLC. Our synthetic route of Schiff base ligand is shown in Fig. 1.

Preparation of the complexes

The metal complexes (1–5) of the different metal ions under study were prepared and purified by recrystallization when possible (Fig. 2). The following synthetic has been employed. Ethanolic solution of $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $CdCl_2 \cdot H_2O$ (0.001 mol) was added slowly to the ligand (**HL**) (0.001 mol) in ethanol, and the reaction mixture was further refluxed. The colored precipitates were filtered through a sintered glass crucible and washed several times with hot ethanol, ether, and finally dried in vacuum over anhydrous calcium chloride in desiccators. The results of elemental analysis as well as some physical properties and the suggested chemical formula are listed in Table 1.



Fig. 1 The structure route of Schiff base ligand (HL)



Fig. 2 Structure of the metal complexes (1–5)

Microbiological investigation

The newly synthesized Schiff base ligand (HL) and its metal complexes were screened for their antibacterial and antifungal activities using nutrient agar and DOX agar media, respectively, by the agar well dilution method [19, 20]. In vitro,

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Table 1

Compound	Color	M.p. (°C)	Exp. (Calcd.)%			
			C	Н	Ν	М
HL	Yellow	195	72.56 (73.95)	5.00 (5.32)	11.54 (11.76)	I
$[Cu(HL)Cl_2]$ (1)	Brown	270	53.37 (53.81)	3.57 (3.87)	8.79 (8.54)	13.55 (12.93)
$[Cu(L)NO_3H_2O] (2)$	Green	290	52.13 (52.85)	3.49(4.00)	11.13 (11.21)	12.69 (12.70)
$[Cu(HL)SO_4(H_2O)_3]2H_2O(3)$	Dark green	>300	43.50 (43.53)	3.39 (4.12)	6.73 (6.92)	10.72 (10.48)
$[Co(HL)Cl_2(H_2O)_2]3H_2O$ (4)	Green	220	45.80 (45.76)	3.82 (3.99)	7.00 (7.28)	9.63 (10.21)
[Cd(HL)Cl ₂] (5)	Pale orange	>300	48.37 (48.85)	3.49 (3.52)	7.74 (7.77)	20.53 (20.80)

antibacterial activity of the test compounds was tested against two local Gram positive bacterial strains, *Bacillus cereus* and *Staphylococcus aureus* and two local Gram negative bacterial strains, *Escherichia coli* and *Klebsiella pneumoniae* and antifungal activities were carried out against two local fungal strains, *Aspergillus niger* and *Alternaria alternata*. The stock solutions of each test compound were prepared using concentrations of 50, 100, and 150 µg mL⁻¹. By using a sterile cork borer (10 mm diameter), wells were made in agar media plates previously seeded with the test microorganism. Then 200 µl of each compound was applied in each well. The agar plates were kept at 4 °C for at least 30 min to allow the diffusion of the compound to agar medium. The plates were then incubated at 37 or 30 °C for growth of bacteria and fungi, respectively. The diameters of inhibition zone were determined after 24 h and 7 days for bacteria and fungi, respectively, taking into consideration the control values (DMF).

DNA binding experiments

The binding properties of the ligand to CT-DNA have been studied using electronic absorption spectroscopy. The stock solution of CT-DNA was prepared in 5 mM Tris–HCl/50 mM NaCl buffer (pH 7.2), which has a ratio of UV absorbances at 260 and 280 nm (A_{260}/A_{280}) of ca. 1.8–1.9, indicating that the DNA was sufficiently free of protein [21], and the concentration was determined by UV absorbance at 260 nm ($\varepsilon = 6600 \text{ M}^{-1} \text{ cm}^{-1}$) [22]. Electronic absorption spectra (300–700 nm) were carried out using 1 cm quartz cuvettes at 25 °C by fixing the concentration of ligand or complex (1.00 × 10⁻³ mol L⁻¹), while gradually increasing the concentration of CT-DNA (0.00–1.30 × 10⁻⁴ mol L⁻¹). An equal amount of CT-DNA was added to both the compound solutions and the references buffer solution to eliminate the absorbance of CT-DNA itself. The intrinsic binding constant K_b of the compound with CT-DNA was determined using the following equation [23]:

$$\frac{[\text{DNA}]}{(\varepsilon_{a} - \varepsilon_{f})} = \frac{[\text{DNA}]}{(\varepsilon_{b} - \varepsilon_{f})} + \frac{1}{K_{b}(\varepsilon_{a} - \varepsilon_{f})},$$
(1)

where [DNA] is the concentration of CT-DNA in base pairs, ε_a is the molar extinction coefficient observed for the A_{obs} /[compound] at the given DNA concentration, ε_f is the molar extinction coefficient of the free compound in solution, and ε_b is the molar extinction coefficient of the compound when fully bonded to DNA. In plots of [DNA]/(ε_a - ε_f) versus [DNA], K_b is given by the ratio of the slope to the intercept.

Measurements

Elemental microanalyses of the separated ligand and solid chelates for C, H, and N were performed on a Perkin-Elmer (2400) CHNS analyzer. The analyses were repeated twice to check the accuracy of the analyzed data. Infrared spectra were recorded as KBr discs using a Pye Unicam SP 2000 spectrophotometer. The ¹H-NMR spectrum was obtained with a Bruker WP 300 MHz using DMSO-d₆ as a

solvent containing TMS as the internal standard. Mass spectra were recorded by the EI technique at 70 eV using a MS-5988 GS-MS Hewlett-Packard.Ultravioletvisible (UV-Vis) spectra of the compounds were recorded using a Perkin-Elmer AA 800 spectrophotometer model AAS. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), [Hg{Co(SCN)₄}], was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [24] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\rm eff.} = 2.84 \left[T\chi_{\rm M}^{\rm coor.}\right]^{1/2}$. X-ray diffraction analysis of the ligand and its copper complex powder forms was recorded on X-ray diffractometer in the range of diffraction angle $2\theta^{\circ} = 5^{\circ} - 80^{\circ}$. This analysis was carried out using Cu K α radiation ($\lambda = 1.540598$ Å). The applied voltage and the tube current were 40 kV and 30 mA, respectively. The diffraction peaks in powder spectra were indexed, and the lattice parameters were determined with the aid of the computer program [25]. The value of interplanar spacing, d, and Miller indices, hkl, for each diffraction peak were determined by using the CHEKCELL program [26]. Thermal studies were computed on a Simultaneous Thermal Analyzer (STA) 6000 system using the thermogravimetric analysis (TGA) method. Thermal properties of the samples were analyzed in the temperature range up to 1000 °C at a heating rate of 10 °C min⁻¹ under dynamic nitrogen atmosphere. ESR measurements of powdered samples were recorded at room temperature (Tanta University, Egypt) using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenylpicrylhydrazyle (DPPH) as a reference material. The molecular structures of the ligands were optimized by HF method with a 3-21G basis set. The molecules were built with the Perkin Elmer ChemBioDraw and optimized using the Perkin Elmer ChemBio3D software [27, 28].

In the study simulation of the actual docking process, in which the ligand-protein pair-wise interaction energies was calculated, was done using Docking Server [29]. The MMFF94 Force field was for used energy minimization of ligand molecules using Docking Server. Gasteiger partial charges were added to the ligand atoms. Non-polar hydrogen atoms were merged, and rotatable bonds were defined. Docking calculations were carried out on a crystal structure of **HL** ligand protein model. Essential hydrogen atoms, Kollman united atom type charges, and solvation parameters were added with the aid of AutoDock tools [30]. Auto Dock parameter set- and distance-dependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively.

Results and discussion

Metal complexes

The Schiff base 4-(((2-hydroxynaphthalen-1-yl)methylene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (**HL**) analogues were carried out according to a convenient one-step procedure, that is, by the condensation of 4-amino-1-phenyl-2,3-dimethylpyrazolin-5-one and 2-hydroxy-1-naphthaldehyde in ethanol, which

provided excellent yield (\sim 70 %). The elemental analyses data confirmed the assigned composition of the Schiff base and its complexes. The Schiff base is soluble in all common organic solvents and strong polar solvents such as DMF and DMSO. All the complexes (1–5) are stable at room temperature, insoluble in water, but soluble in ethanol, DMF, and DMSO.

All the complexes were prepared by direct reaction between ligand (HL) and the hydrated copper(II) chloride, nitrate, sulfate, cadmium, and cobalt(II) chlorides in ethanol to yield the complexes (1-5) (Fig. 2).

The products were purified by washing with dry ethanol, and gave elemental analyses compatible with the suggested formulae given in Table 1 according to the following general equations:

$$CuCl_2 \cdot 2H_2O + HL \rightarrow [Cu(HL)Cl_2], \tag{2}$$

$$Cu(NO_3)_2 \cdot 6H_2O + HL \rightarrow [CuL(O_2NO)H_2O] + HNO_3, \tag{3}$$

$$CuSO_4 \cdot 5H_2O + HL \rightarrow [Cu(HL)(OSO_3)(3H_2O)] 2H_2O, \tag{4}$$

$$CoCl_2 \cdot 6H_2O + HL \rightarrow \left[Co(HL)Cl_2(H_2O)_2\right] 3H_2O,$$
(5)

$$CdCl_2 \cdot H_2O + HL \rightarrow [Cd(HL)Cl_2].$$
 (6)

L is the deprotonated ligand.

The observed molar conductance ($\Lambda m = 6.4-11.6 \text{ O}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of all the complexes in 10^{-3} molar solution in DMF suggest the non-electrolytic nature of these complexes [31]. Such a non-zero molar conductance value for each of the complexes in the present study is most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligands and change of electrolyte type [31].

Formulation of the complexes was based on their elemental analytical data, molar conductance values, and magnetic susceptibility data. Cu(II), Co(II) and Cd(II) complexes showed 1:1 metal–ligand stoichiometry (Table 1).

Structure of the ligand and its metal complexes

The ESI mass spectrum of the Schiff base ligand (**HL**) showed a molecular ion peak recorded at m/z = 357, which is equivalent to its molecular weight. Generally, the fragmentation of mass spectra of the ligand showed four main pathways as shown in Scheme 1.

Introduction of a hydroxyl group at the *ortho* position to the azomethine linkage raises the possibility of phenolimine–quinoneamine tautomerism. It has been reported that the tautomeric equilibrium depends on the extent of conjugation, nature, and position of the substituent and polarity of the solvent, and this phenomenon has drawn considerable attention both from the theoretical and experimental point views [32]. Anonove et al. [32] explained this type of tautomerism exhibited by 2-hydroxy-1-naphthaldehyde Schiff base and arrived at the conclusion that the compound exists in the quinonoid form. The ligand under



Scheme 1 The fragmentation of mass spectra of the ligand

investigation is also capable of exhibiting phenolimine–quinoneamine tautomerism (Fig. 1b, d). On the basis of the spectral data, a phenolimine structural form [3921 cm⁻¹ ($\pi \rightarrow \pi^*$) and 31,940 cm⁻¹ ($n \rightarrow \pi^*$)] of the ligand has been established (Fig. 1b).

The infrared spectrum of **HL** ligand gives interesting results and conclusions. In the spectrum of 4-aminoantipyrine, a pair of medium intensity bands present at ~ 3150 to 3400 cm⁻¹ corresponds to $v(NH_2)$, but these were absent in the infrared spectra of all the complexes. Furthermore, no strong absorption band was observed

at ~1760 cm⁻¹ indicating the absence of a v(C=O) group of 4-aminoantipyrine [33]. This indicated that the coordination of the carbonyl group of 4-aminoantipyrine and the amino group of 4-aminoantipyrine might have taken place [34]. These results provide strong evidence for the formation of a ligand frame [35]. A strong absorption band in the ~1643 cm⁻¹ may be attributed to the v(C=N) group. The lower value of v(C=N) may be explained on the basis of a drift of the lone pair density of azomethine nitrogen towards the metal atom [16].

Infrared spectrum of the ligand was in a broad absorption band located at ~3210 cm⁻¹, which could be attributed to hydrogen bonded phenolic v(O-H). The low frequency bands indicated that the hydroxy hydrogen atom was involved in (B \Leftrightarrow D) tautomerism through hydrogen bonding (Fig. 1). The region between 1219 and 1323 cm⁻¹ was due to C–OH stretching, to C–OH in plane or out of plane bending and out-of-plane C–OH bending vibrations. The strong band at 1620 cm⁻¹ was due to a carbonyl stretching vibration mode. An intramolecular hydrogen bridge linking of the C=N and carbonyl groups to the OH moiety was found to be a characteristic feature of this compound class (Fig. 1b). The five/six membered intramolecular hydrogen bonding ring is shown in Fig. 1b. The IR spectrum of the ligand shows an intense carbonyl band ($vC=O\cdots$ H), ($vC=O/vC=N\cdots$ H)(vC=N) formed with extensive five/six membered intramolecular hydrogen bonding, and this has been confirmed by El-Sonbati et al. [20].

IR spectrum of the ligand shows a broad band located at $\sim 3210 \text{ cm}^{-1}$ due to the stretching vibration of some hydrogen bonding. El-Sonbati et al. [16, 20] made detailed studies for the different types of hydrogen bonding, which are favorable in the molecule under investigation:

- 1. Intramolecular hydrogen bond between the nitrogen atom of the -C=N-/C=O system and hydrogen atom of the hydroxy hydrogen atom (Fig. 1b).
- 2. Intramolecular hydrogen bond between the oxygen atoms of the -C=O/C=O(exocyclic) system and the hydrogen atom of the NH atom (Fig. 1d).
- 3. Intermolecular hydrogen bonding is possible forming cyclic dimmer through OH…N=C (F) (Fig. 1).
- 4. Intermolecular hydrogen bonding is possible forming cyclic dimmer through NH…O=C(exocyclic) (H) or OH…O=C (G) (Fig. 1).

By comparing the infrared spectrum of the ligands of its complexes, the following features for some of the prepared complexes were observed.

The exocyclic carbonyl absorption band v(CO) was shifted to frequencies higher by 25–10 cm⁻¹ for all complexes (1–5) indicating that the carbonyl group was coordinated to the metals ions (Fig. 2). New bands were found in the spectra of complexes in the regions 560–585 and 417–452 cm⁻¹, which were assigned to v(M-O) and v(M-N) stretching vibrations, respectively.

A strong band observed at ~1760 cm⁻¹ in the free ligand was attributed to v(C=O) of the exocyclic carbonyl oxygen. The infrared spectrum of the coordination ligand showed a considerable negative shift of 15–20 cm⁻¹ in the v(C=O) absorption of the exocyclic carbonyl oxygen group, indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the

exocyclic carbonyl oxygen atom of the ligand. This band shifted in all the complexes (1–5) indicating the participation of the exocyclic carbonyl oxygen in bonding with metal ions. A medium-to-strong intensity band at cm⁻¹ in the free ligand was attributed to the v(C=N) stretch of the azomethine group. Coordination of the Schiff base to the metal ions through the nitrogen atom is expected to reduce electron density in the azomethine link and lower the v(C=N) absorption frequency. This band shifted to a lower wavenumber side in all the complexes (1–5) indicating the participation of the azomethine nitrogen in coordination with metal ions.

The broad band due to the internally hydrogen-bonded phenolic –OH group disappeared from the region $3300-3000 \text{ cm}^{-1}$ indicating deprotonation and formation of a metal–oxygen bond. Consequently, the band due to v(C-O) was increased by ~25 cm⁻¹ in the metal complex (2) and this adequately supported the bond formation by phenolate oxygen.

Moreover, the IR spectrum of the $[CuL(O_2NO)OH_2)]$ (2) complex reflects that the HL acts as a monobasic tridentate ligand coordinating via the oxygen atom of phenolic (OH), azomethine nitrogen, and exocyclic carbonyl oxygen, while $[Cu(HL)Cl_2]$ (1), $[Cu(HL)(OSO_2)(OH_2)_3]2H_2O$ (3), $[Co(HL)(Cl_2)(OH_2)_2]3H_2O$ (4) and $[Cd(HL)Cl_2]$ (5) complexes reflect that the HL acts as a neutral bidentate ligand coordinating via the azomethine nitrogen and exocyclic carbonyl oxygen. Apart from these bands, the non-ligand bands of low intensity appearing in the region 560–585 and 417–452 cm⁻¹ could be assigned to v(M-O) and v(M-N)vibrations, respectively [16]. The above mode of bonding suggested by infrared spectral studies was reinforced by the proton NMR spectral study of the Cd(II) complex.

Additionally, the IR spectra of the complexes show the bands due to coordinated anions. In the spectrum of complex (2), three additional bands, which were not present in the spectrum of free ligand, were observed. Of these, the band ~1030 cm⁻¹ was assigned to the v_2 mode of the nitrate group. The bands at 1470 and 1260 cm⁻¹ are the two split bands of v_4 and v_1 , respectively, of the coordinated nitrate group. The magnitude of v_4 - v_1 is about 200 cm⁻¹ in the complex (2), which indicated that the nitrate group was coordinated to the copper(II) ion in bidentate fashion [36]. The sulphato complex (3) showed IR bands in 1130 and 1110 cm⁻¹ (v_3), 965 cm⁻¹ (v_1) and 665 cm⁻¹ (v_4) indicating the unidentate [37] nature of sulpate group. The spectra of complexes, which contain water molecules, showed a broad band ~3475 to 3380 cm⁻¹, assigned to v(OH) of crystallization water involved in the complexes [20]. Moreover, the spectra of complexes containing coordinated water molecules showed an additional two bands ~965 and 650 cm⁻¹, owing to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively [20, 38]. The appearance of the latter two modes indicated coordinated water rather than hydrated water.

The ¹H NMR spectrum of the ligand was recorded in DMSO-d₆ (Fig. 3). The signal at $\delta(14.965 \text{ ppm})(\text{s. 1H})$ is assigned to phenolic proton of (–OH–) group The downward shift of the proton is presumably due to strong hydrogen bonding [16]. The signal at $\delta(10.657 \text{ ppm}; \text{ s. 1H})$ is assigned to the azomethine proton, in the Schiff base ligand (Table 2). The aromatic proton at $\delta(7.169-8.097 \text{ ppm}; \text{ m. H})$ shifted downfield in the complexes. A sharp singlet at $\delta(2.437)$ was assigned to methyl proton. On the basis of the spectral values, a hydrogen bonded phenolimine



Fig. 3 1 H NMR spectra of (a) ligand (HL) and (b) Cd(II) complex (5)

Table 2 ¹ H NMR spectral data of Schiff base ligand (HL) and its Cd(II) complex (5)	Compound	¹ H NMR data (ppm)
	HL	14.965 (s, 1H, Phenolic OH) 10.657 (s, 1H, HC=N) 7.169–8.097 (m, 12H, ArH)
	5	2.437 (m,C-CH ₃) 14.966 (s, 1H, Phenolic OH) 10.664 (s, 1H, HC=N) 7.760–8.100 (m, 12H, ArH) 2.456 (m,C-CH ₃)

structure has been proposed for the ligand. The above in the spectrum of the Cd(II) complex (Fig. 3), with the presence of an –OH (14.966 ppm) proton signal is a clear indication that phenolic oxygen is not bonded to the metal ion. A careful comparison of the position of other signals in this complex with those of the ligand indicated a downward shift of the other protons by $\sim \delta(0.10-0.25 \text{ ppm})$ in the metal complexes. Thus, the azomethine proton signal observed at $\delta(10.664 \text{ ppm})$ in the complex was shifted down field by 0.007 ppm.

The IR spectrum showed that the ligand (HL) acted as monobasic bidentate/ tridentate through the (-C=N) and (C=O)/proton displacement from the phenolic OH moiety groups forming a five/six membered structure (Fig. 1).

The X-ray diffraction (XRD) patterns powder forms of **HL** and Cu(II) complexes (1) are presented in Fig. 4. The XRD of **HL** and Cu(II) complex (1) show many diffraction peaks, which indicated the polycrystalline phase. The average crystallite size (ξ) can be calculated from the XRD pattern according to Debye–Scherrer Eq. [28, 39]:

$$\xi = \frac{K\lambda}{\beta_{1/2}\cos\theta}.\tag{7}$$

The equation uses the reference peak width at angle (θ), where λ is the wavelength of X-ray radiation (1.541874 Å), *K* is constant taken as 0.95 for organic compounds [40] and $\beta_{1/2}$ is the width at half maximum of the reference diffraction peak measured in radians. The dislocation density, δ , is the number of dislocation lines per unit area of the crystal. The value of δ is related to the average particle diameter (ξ) by relation [39, 40]:

$$\delta = \frac{1}{\xi^2}.$$
(8)

The value of ξ was calculated and found to be 315 nm and 630 nm and the value of δ was 33.78 × 10⁻⁴ and 15.86 × 10⁻⁴ nm⁻² for ligand (**HL**) and Cu(II) complex (1), respectively. The diffraction peaks in powder spectra were indexed, and the lattice parameters were determined with the aid of the CRYSFIRE computer program [40–43]. The values of interplanar spacing (*d*) and Miller indices (hkl) for each diffraction peak before and after refinement are determined by using the CHEKCELL program [40–43]. The values of *d* and corresponding hkl for **HL** and



Fig. 4 X-Ray diffraction pattern for a ligand (HL) and b complex (2) in powder forms

Cu(II) complex (1) are listed in Tables 3 and 4, respectively. The results show that the **HL** ligand and Cu(II) complex (1) have monoclinic crystal structure with space group P2 and P21/C, respectively. The lattice parameters are estimated as:

$$\begin{array}{l} a = 8.6156 \text{ Å}; \quad b = 13.5885 \text{ Å}; \quad c = 7.4372 \text{ Å} \\ \alpha = 90^{\circ}, \quad \gamma = 114^{\circ}, \quad \beta = 90^{\circ} \end{array} \right\} \quad \text{for ligand.}$$

and

$$\begin{array}{l} a = 15.5084 \,\text{\AA}; \quad b = 18.5706 \,\text{\AA}; \ c = 7.0558 \,\text{\AA} \\ \alpha = 90^{\circ}, \quad \gamma = 114^{\circ}, \quad \beta = 90^{\circ} \end{array} \right\} \quad \text{for Cu(II) complex.}$$

Table 3Crystallographic datafor HL Schiff base ligand	Peak no.	$2\theta_{\rm obs.}$ (°)	$d_{\rm obs.}$ (Å)	$d_{\text{cal.}}$ (Å)	(h	k	1)
	1	6.5255	13.53541	13.59033	0	1	0
	2	13.0339	6.786964	6.773119	ī	1	0
	3	17.3054	5.120178	5.12683	ī	2	0
	4	18.6222	4.760963	4.765656	ī	2	1
	5	19.5618	4.534377	4.529578	0	3	0
	6	20.8833	4.2504	4.244241	$\bar{2}$	0	1
	7	21.7006	4.09204	4.089748	1	1	1
	8	22.7498	3.905636	3.906405	2	0	0
	9	26.3207	3.383302	3.38655	$\bar{2}$	2	0
	10	26.651	3.342115	3.343187	$\bar{2}$	0	2
	11	29.4075	3.034828	3.033946	0	4	1

Table 4	Crystallographic data
for Cu(II) complex (1)

Peak no.	$2\theta_{\rm obs.}$ (°)	$d_{\rm obs.}$ (Å)	$d_{\text{cal.}}$ (Å)	(h	k	1)
1	7.7015	11.47002	11.48707	ī	1	0
2	11.2895	7.831436	7.838002	ī	2	0
3	13.0047	6.802132	6.801712	$\bar{2}$	1	0
4	13.5337	6.537418	6.548589	ī	1	2
5	15.4656	5.724865	5.726797	$\bar{2}$	1	1
6	15.8558	5.584846	5.588647	ī	2	1
7	16.3792	5.407538	5.407147	0	1	2
8	17.558	5.047057	5.051366	$\bar{2}$	2	1
9	18.7549	4.727594	4.723883	$\bar{2}$	3	0
10	19.1035	4.642085	4.642655	0	4	0
11	20.0602	4.422805	4.42488	ī	4	0
12	20.5511	4.318254	4.31576	$\bar{2}$	3	1
13	20.9496	4.237004	4.236494	3	2	1
14	21.7995	4.073697	4.074177	1	3	1
15	22.657	3.921423	3.938893	$\bar{2}$	4	0
16	22.9687	3.868906	3.868706	ī	4	1
17	24.0145	3.703365	3.703437	$\bar{4}$	1	1
18	25.371	3.507757	3.505687	ī	0	2
19	25.8711	3.441082	3.43856	$\bar{2}$	1	2
20	27.2131	3.274389	3.274285	$\overline{2}$	2	2
21	28.4953	3.129856	3.129459	0	2	2

Molecular structures of the ligand and its complexes

The forms A–D of ligand (HL) are shown in Fig. 1. Primary calculations reveal that the form (A) is more stable and reactive than other forms (Fig. 1). The selected geometrical structures of the Schiff base ligand (HL) [form (A)] and its complexes



Fig. 5 Optimized structure for Schiff base (HL)

(1–5) are shown in Figs. 5 and 6. The bond lengths and bond angles for ligand (HL)[form (A)] and its metal complexes (1–5) are listed in Tables 5, 6, 7, 8, 9 and 10. The form (A) is more reactive than the other forms as reflected from energy gap values (Table 11). The HOMO–LUMO energy gap, ΔE , which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems [16, 39]. The value of ΔE for form (A), form (B), form (C), and form (D) was found to be 3.229, 3.678, 5.143, and 3.440 eV, respectively, so the form (A) is more stable than the other forms. The HOMO and LUMO of the Schiff base ligand (HL) and its complexes (1–5) are shown in Fig. 7. The calculated quantum chemical parameters are given in Table 11. Additional parameters such as ΔE , absolute electronegativities, χ , chemical potentials, Pi, absolute hardness, η , absolute softness, σ , global electrophilicity, ω , global softness, *S*, and additional electronic charge, ΔN_{max} , have been calculated according to the following equations [20, 39]:

$$\Delta E = E_{\rm LUMO} - E_{\rm HOMO},\tag{9}$$

$$\chi = \frac{-(E_{\rm HOMO} + E_{\rm LUMO})}{2},\tag{10}$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2},\tag{11}$$

$$\sigma = \frac{1}{\eta},\tag{12}$$

$$Pi = -\chi, \tag{13}$$

$$S = \frac{1}{2\eta},\tag{14}$$

$$\omega = \frac{\mathrm{Pi}^2}{2\eta},\tag{15}$$

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Fig. 6 Optimized structures for complexes (1–5)

Bond lengths (Å)		Bond angles (°)	
C(27)–H(46)	1.104	H(37)-C(13)-C(14)	120.169
C(26)-H(45)	1.103	H(37)-C(13)-C(12)	119.783
C(25)-H(44)	1.104	C(14)-C(13)-C(12)	120.044
C(24)-H(43)	1.099	H(36)-C(12)-C(13)	120.491
C(22)-H(42)	1.09	H(36)-C(12)-C(11)	120.518
O(21)-H(41)	0.967	C(13)-C(12)-C(11)	118.99
C(18)-H(40)	1.104	H(35)-C(11)-C(12)	119.573
C(17)-H(39)	1.104	H(35)-C(11)-C(10)	120.111
C(14)-H(38)	1.103	C(12)-C(11)-C(10)	120.314
C(13)-H(37)	1.103	H(38)-C(14)-C(7)	120.887
C(12)-H(36)	1.103	H(38)-C(14)-C(13)	116.816
C(11)-H(35)	1.103	C(7)-C(14)-C(13)	122.266
C(10)-H(34)	1.101	H(34)-C(10)-C(11)	116.055
C(9)-H(33)	1.112	H(34)-C(10)-C(7)	121.952
C(9)-H(32)	1.113	C(11)-C(10)-C(7)	121.961
C(9)–H(31)	1.112	H(30)-C(8)-H(29)	109.053
C(8)-H(30)	1.113	H(30)-C(8)-H(28)	103.771
C(8)–H(29)	1.114	H(30)-C(8)-N(3)	112.568
C(8)-H(28)	1.112	H(29)-C(8)-H(28)	109.375
C(18)–C(17)	1.335	H(29)-C(8)-N(3)	110.706
C(15)–C(17)	1.341	H(28)-C(8)-N(3)	111.122
C(16)–C(15)	1.354	C(14)-C(7)-C(10)	116.414
C(27)–C(15)	1.347	C(14)-C(7)-N(4)	119.602
C(26)–C(27)	1.338	C(10)-C(7)-N(4)	123.965
C(25)–C(26)	1.337	C(5)–N(4)–N(3)	102.355
C(24)–C(25)	1.342	C(5)–N(4)–C(7)	130.25
C(16)-C(24)	1.353	N(3)–N(4)–C(7)	123.336
C(20)–C(16)	1.363	H(45)-C(26)-C(27)	120.903
C(19)-C(20)	1.36	H(45)-C(26)-C(25)	120.707
C(18)–C(19)	1.343	C(27)-C(26)-C(25)	118.389
C(7)–C(14)	1.349	H(44)-C(25)-C(26)	119.413
C(13)-C(14)	1.342	H(44)-C(25)-C(24)	120.476
C(12)–C(13)	1.34	C(26)-C(25)-C(24)	120.111
C(11)–C(12)	1.34	H(41)-O(21)-C(19)	116.69
C(10)–C(11)	1.343	H(40)-C(18)-C(17)	118.513
C(7)–C(10)	1.349	H(40)-C(18)-C(19)	119.305
N(3)-C(2)	1.277	C(17)-C(18)-C(19)	122.182
C(1)–C(2)	1.345	H(46)-C(27)-C(15)	121.386
C(5)–C(1)	1.364	H(46)-C(27)-C(26)	117.701
N(4)–C(5)	1.273	C(15)-C(27)-C(26)	120.913
N(3)-N(4)	1.363	H(39)-C(17)-C(18)	118.565

Table 5 The selected geometric parameters for HL [form (A)]

Bond lengths (Å)		Bond angles (°)	
C(1)–N(23)	1.263	H(39)–C(17)–C(15)	121.917
C(22)-N(23)	1.26	C(18)-C(17)-C(15)	119.518
C(20)-C(22)	1.355	H(43)-C(24)-C(25)	113.024
C(19)-O(21)	1.369	H(43)-C(24)-C(16)	123.716
C(2)–C(9)	1.508	C(25)-C(24)-C(16)	123.26
N(3)-C(8)	1.485	C(17)-C(15)-C(16)	119.967
N(4)-C(7)	1.279	C(17)-C(15)-C(27)	117.84
C(5)-O(6)	1.216	C(16)-C(15)-C(27)	122.194
		C(20)-C(19)-C(18)	118.769
		C(20)-C(19)-O(21)	126.037
		C(18)-C(19)-O(21)	115.187
		C(15)-C(16)-C(24)	115.132
		C(15)-C(16)-C(20)	120.217
		C(24)-C(16)-C(20)	124.651
		C(16)-C(20)-C(19)	119.346
		C(16)-C(20)-C(22)	121.281
		C(19)-C(20)-C(22)	119.373
		H(42)-C(22)-N(23)	113.455
		H(42)-C(22)-C(20)	121.079
		N(23)-C(22)-C(20)	125.454
		C(1)-N(23)-C(22)	131.352
		C(1)-C(5)-N(4)	111.093
		C(1)-C(5)-O(6)	123.024
		N(4)-C(5)-O(6)	125.744
		H(33)-C(9)-H(32)	107.971
		H(33)-C(9)-H(31)	103.753
		H(33)–C(9)–C(2)	112.395
		H(32)-C(9)-H(31)	110.294
		H(32)-C(9)-C(2)	110.827
		H(31)-C(9)-C(2)	111.344
		C(2)–N(3)–N(4)	114.409
		C(2)–N(3)–C(8)	115.901
		N(4)-N(3)-C(8)	129.133
		N(3)-C(2)-C(1)	104.075
		N(3)-C(2)-C(9)	128.703
		C(1)-C(2)-C(9)	127.049
		C(2)-C(1)-C(5)	106.932
		C(2)-C(1)-N(23)	135.358
		C(5)-C(1)-N(23)	117.706

Table 5 continued

Bond lengths (Å)		Bond angles (°)	
C(26)–H(49)	1.104	H(41)-C(20)-C(21)	120.102
C(25)-H(48)	1.102	H(41)-C(20)-C(19)	119.658
C(24)-H(47)	1.104	C(21)-C(20)-C(19)	120.239
C(23)-H(46)	1.095	H(40)-C(19)-C(20)	120.442
C(22)-H(45)	1.113	H(40)-C(19)-C(18)	120.451
C(22)-H(44)	1.112	C(20)-C(19)-C(18)	119.1
C(22)-H(43)	1.112	H(39)-C(18)-C(19)	119.759
C(21)-H(42)	1.103	H(39)-C(18)-C(17)	120.125
C(20)-H(41)	1.103	C(19)–C(18)–C(17)	120.111
C(19)-H(40)	1.103	H(42)-C(21)-C(16)	121.625
C(18)-H(39)	1.103	H(42)-C(21)-C(20)	116.571
C(17)-H(38)	1.102	C(16)-C(21)-C(20)	121.801
C(15)-H(37)	1.114	H(38)-C(17)-C(18)	116.885
C(15)-H(36)	1.112	H(38)–C(17)–C(16)	121.11
C(15)-H(35)	1.113	C(18)-C(17)-C(16)	121.986
C(8)-H(34)	1.106	C(21)–C(16)–C(17)	116.73
O(7)-H(33)	0.969	C(21)–C(16)–N(12)	122.132
C(4)-H(32)	1.104	C(17)–C(16)–N(12)	121.093
C(3)–H(31)	1.104	H(37)-C(15)-H(36)	108.537
C(16)–C(21)	1.35	H(37)–C(15)–H(35)	107.194
C(20)–C(21)	1.343	H(37)–C(15)–N(13)	110.153
C(19)-C(20)	1.34	H(36)-C(15)-H(35)	108.596
C(18)–C(19)	1.34	H(36)-C(15)-N(13)	112.416
C(17)–C(18)	1.342	H(35)-C(15)-N(13)	109.79
C(16)–C(17)	1.349	C(16)–N(12)–N(13)	119.902
C(4)–C(3)	1.334	C(16)–N(12)–C(11)	121.169
C(1)–C(3)	1.341	N(13)–N(12)–C(11)	113.226
C(2)–C(1)	1.356	Cu(28)–O(27)–C(11)	111.086
C(26)–C(1)	1.347	H(45)-C(22)-H(44)	111.688
C(25)–C(26)	1.338	H(45)-C(22)-H(43)	105.669
C(24)-C(25)	1.336	H(45)-C(22)-C(14)	111.73
C(23)-C(24)	1.342	H(44)-C(22)-H(43)	103.97
C(2)–C(23)	1.353	H(44)-C(22)-C(14)	112.214
C(6)–C(2)	1.365	H(43)-C(22)-C(14)	111.109
C(5)–C(6)	1.361	C(15)–N(13)–C(14)	123.706
C(4)–C(5)	1.341	C(15)–N(13)–N(12)	135.261
Cu(28)–Cl(30)	2.16	C(14)–N(13)–N(12)	99.062
Cu(28)–Cl(29)	2.158	C(22)-C(14)-C(10)	134.701
O(27)-Cu(28)	1.819	C(22)-C(14)-N(13)	126.7
N(9)-Cu(28)	1.312	C(10)-C(14)-N(13)	98.297
C(11)-O(27)	1.247	O(27)–C(11)–N(12)	168.433

 Table 6 The selected geometric parameters for complex (1)

Bond lengths (Å)		Bond angles (°)	
C(14)–C(22)	1.507	O(27)-C(11)-C(10)	86.55
N(12)-C(16)	1.281	N(12)-C(11)-C(10)	81.959
N(13)-C(15)	1.47	Cl(30)-Cu(28)-Cl(29)	110.925
C(14)–C(10)	1.372	Cl(30)-Cu(28)-O(27)	109.108
N(13)-C(14)	1.252	Cl(30)-Cu(28)-N(9)	112.711
N(12)-N(13)	1.347	Cl(29)-Cu(28)-O(27)	113.474
C(11)–N(12)	1.272	Cl(29)-Cu(28)-N(9)	120.667
C(10)–C(11)	1.458	O(27)-Cu(28)-N(9)	87.562
N(9)-C(10)	1.286	C(14)-C(10)-C(11)	115.718
C(8)-N(9)	1.279	C(14)-C(10)-N(9)	121.936
C(6)–C(8)	1.364	C(11)-C(10)-N(9)	122.037
C(5)–O(7)	1.367	Cu(28)–N(9)–C(10)	90.222
		Cu(28)-N(9)-C(8)	111.046
		C(10)–N(9)–C(8)	127.671
		H(48)-C(25)-C(26)	121.092
		H(48)-C(25)-C(24)	120.871
		C(26)-C(25)-C(24)	118.025
		H(47)-C(24)-C(25)	119.328
		H(47)-C(24)-C(23)	120.585
		C(25)-C(24)-C(23)	120.083
		H(46)-C(23)-C(24)	111.803
		H(46)-C(23)-C(2)	124.189
		C(24)-C(23)-C(2)	123.996
		H(34)-C(8)-N(9)	116.827
		H(34)–C(8)–C(6)	113.7
		N(9)-C(8)-C(6)	129.458
		H(33)–O(7)–C(5)	110.921
		C(2)–C(6)–C(5)	118.415
		C(2)–C(6)–C(8)	126.065
		C(5)–C(6)–C(8)	115.519
		C(6)–C(5)–C(4)	120.075
		C(6)–C(5)–O(7)	123.96
		C(4)–C(5)–O(7)	115.843
		H(32)-C(4)-C(3)	118.919
		H(32)–C(4)–C(5)	119.596
		C(3)–C(4)–C(5)	121.481
		H(49)-C(26)-C(1)	121.522
		H(49)-C(26)-C(25)	117.407
		C(1)-C(26)-C(25)	121.069
		H(31)-C(3)-C(4)	118.393
		H(31)–C(3)–C(1)	122.193

Table 6 continued

Table 6 continued		
Bond lengths (Å)	Bond angles (°)	
	C(4)-C(3)-C(1)	119.414
	C(1)–C(2)–C(23)	114.146
	C(1)–C(2)–C(6)	120.09
	C(23)–C(2)–C(6)	125.742
	C(3)–C(1)–C(2)	120.464
	C(3)–C(1)–C(26)	116.906
	C(2)–C(1)–C(26)	122.629

and

$$\Delta N_{\rm max} = -\frac{{\rm Pi}}{\eta}.$$
 (16)

The value of ΔE for complexes (1–5) was found to be 1.742, 1.428, 0.492, 0.218, and 2.532 eV, respectively, so the complex (4) is more stable than the other complexes.

Electronic spectra

The electronic spectrum Co(II) complex (4) display of bands ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F) \quad (\sim 94,500 \text{ cm}^{-1}), \ {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F) \quad (\sim 14,450 \text{ cm}^{-1}) \text{ and}$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P) \ (\sim 21,250 \text{ cm}^{-1}) \text{ transitions. This indicates that this complex}$ has octahedral geometry. The value of Dq (945 cm^{-1}) was calculated from the transition energy ratio diagram using the v_3/v_2 ratio (1.471 cm⁻¹) [44]. The naphelaxetic parameter β (0.84) was readily obtained by using the relation $\beta = B(\text{complex})/B$ (free ion), where B free for the Co(II) complex is 1120 cm⁻¹ [45]. From the position of the bands, the chelates are octahedral with largely covalent bonds between the organic ligand and the metal ion [20]. The magnetic susceptibility measurements lie in the 4.91 B.M. range, corresponding to three unpaired electrons (normal range for octahedral Co(II) complexes is 4.3-5.2 B.M.), and is an indication of octahedral geometry [46].

Magnetic moment values for Cu(II) complexes (1–3) recorded at room temperature lie in the range 1.89–2.04 B.M. corresponding to one unpaired electron on a Cu(II) ion in an ideal square planar and/or octahedral environment (Table 1). The electronic spectrum of complex (1) showed two bands at ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ (17,825 cm⁻¹) and ${}^{2}B_{1g} \rightarrow {}^{2}E$ (22,270 cm⁻¹), transitions, for square planar geometry [47, 48]. The observed magnetic moment of 1.72 B.M. further supported the electronic results. Also, the electronic spectra of six-coordinated Cu(II) complexes have either D_{4h} or C_{4v} symmetry, and the E_g and T_{2g} levels of the ${}^{2}D$ free ion term will split into B_{1g}, A_{1g}, B_{2g}, E_g levels, respectively. Copper complexes (2 and 3) under study display bands in the range 13,210–15,720 and 15,590–16,660 cm⁻¹. These bands were assigned to the following transitions in order of increasing energy [49, 50].

		· · ·	
Bond lengths (Å)		Bond angles (°)	
O(30)–H(53)	1.001	O(33)-N(31)-O(32)	119.767
O(30)-H(52)	1.049	O(33)–N(31)–O(29)	85.234
C(26)–H(51)	1.104	O(32)–N(31)–O(29)	119.608
C(25)-H(50)	1.103	H(43)-C(20)-C(21)	120.157
C(24)-H(49)	1.103	H(43)-C(20)-C(19)	119.609
C(23)-H(48)	1.1	C(21)-C(20)-C(19)	120.224
C(22)-H(47)	1.113	H(42)-C(19)-C(20)	120.552
C(22)-H(46)	1.112	H(42)-C(19)-C(18)	120.544
C(22)-H(45)	1.112	C(20)-C(19)-C(18)	118.899
C(21)-H(44)	1.1	H(41)-C(18)-C(19)	119.614
C(20)-H(43)	1.103	H(41)-C(18)-C(17)	120.195
C(19)-H(42)	1.103	C(19)-C(18)-C(17)	120.191
C(18)–H(41)	1.103	H(44)-C(21)-C(16)	121.687
C(17)-H(40)	1.103	H(44)-C(21)-C(20)	115.988
C(15)-H(39)	1.114	C(16)-C(21)-C(20)	122.302
C(15)-H(38)	1.113	H(40)-C(17)-C(18)	115.471
C(15)-H(37)	1.112	H(40)-C(17)-C(16)	122.255
C(8)-H(36)	1.098	C(18)-C(17)-C(16)	122.273
C(4)-H(35)	1.101	C(21)-C(16)-C(17)	116.091
C(3)-H(34)	1.105	C(21)-C(16)-N(12)	122.421
C(16)–C(21)	1.348	C(17)-C(16)-N(12)	121.414
C(20)–C(21)	1.342	H(39)-C(15)-H(38)	107.296
C(19)-C(20)	1.34	H(39)-C(15)-H(37)	108.199
C(18)–C(19)	1.339	H(39)–C(15)–N(13)	109.943
C(17)–C(18)	1.342	H(38)-C(15)-H(37)	108.901
C(16)–C(17)	1.352	H(38)–C(15)–N(13)	109.994
O(33)-Cu(28)	1.814	H(37)–C(15)–N(13)	112.359
N(31)-O(33)	1.359	H(47)-C(22)-H(46)	107.12
N(31)-O(32)	1.565	H(47)-C(22)-H(45)	110.925
O(29)-N(31)	1.35	H(47)-C(22)-C(14)	110.774
O(7)-Cu(28)	2.003	H(46)-C(22)-H(45)	104.669
O(30)-Cu(28)	1.849	H(46)-C(22)-C(14)	110.732
Cu(28)–O(29)	1.828	H(45)-C(22)-C(14)	112.336
O(27)-Cu(28)	1.828	C(15)-N(13)-C(14)	123.317
N(9)-Cu(28)	1.575	C(15)–N(13)–N(12)	135.702
C(11)-O(27)	1.231	C(14)–N(13)–N(12)	99.822
C(26)–C(1)	1.349	C(22)-C(14)-C(10)	131.812
C(25)-C(26)	1.34	C(22)-C(14)-N(13)	127.91
C(24)-C(25)	1.338	C(10)-C(14)-N(13)	99.849
C(23)-C(24)	1.341	C(16)–N(12)–N(13)	124.265
C(2)–C(23)	1.348	C(16)–N(12)–C(11)	119.276

 Table 7 The selected geometric parameters for complex (2)

Supramolecular	structure,	spectroscopic,	thermal	studies
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Bond lengths (Å)		Bond angles (°)	
C(14)–C(22)	1.504	N(13)-N(12)-C(11)	115.935
N(12)-C(16)	1.283	O(27)–C(11)–N(12)	165.505
N(13)-C(15)	1.469	O(27)-C(11)-C(10)	83.352
C(14)-C(10)	1.361	N(12)-C(11)-C(10)	83.209
N(13)-C(14)	1.253	Cu(28)–O(33)–N(31)	68.443
N(12)-N(13)	1.346	H(53)-O(30)-H(52)	71.707
C(11)–N(12)	1.275	H(53)-O(30)-Cu(28)	92.777
C(10)-C(11)	1.457	H(52)-O(30)-Cu(28)	163.598
N(9)-C(10)	1.286	N(31)-O(29)-Cu(28)	68.151
C(8)-N(9)	1.498	Cu(28)–O(27)–C(11)	110.038
C(6)–C(8)	1.626	O(33)–Cu(28)–O(7)	58.207
C(5)–O(7)	1.789	O(33)-Cu(28)-O(30)	101.626
C(6)–C(2)	1.35	O(33)–Cu(28)–O(29)	60.481
C(5)-C(6)	1.628	O(33)-Cu(28)-O(27)	147.768
C(4)–C(5)	1.336	O(33)-Cu(28)-N(9)	118.049
C(3)–C(4)	1.34	O(7)-Cu(28)-O(30)	134.033
C(1)–C(3)	1.349	O(7)–Cu(28)–O(29)	102.169
C(1)-C(2)	1.355	O(7)–Cu(28)–O(27)	91.013
		O(7)-Cu(28)-N(9)	107.588
		O(30)-Cu(28)-O(29)	100.414
		O(30)-Cu(28)-O(27)	93.252
		O(30)-Cu(28)-N(9)	118.053
		O(29)–Cu(28)–O(27)	144.439
		O(29)–Cu(28)–N(9)	66.744
		O(27)-Cu(28)-N(9)	77.83
		C(14)-C(10)-C(11)	116.292
		C(14)-C(10)-N(9)	117.217
		C(11)-C(10)-N(9)	126.192
		Cu(28)-N(9)-C(10)	101.862
		Cu(28)-N(9)-C(8)	122.904
		C(10)–N(9)–C(8)	131.553
		H(50)-C(25)-C(26)	120.548
		H(50)-C(25)-C(24)	120.231
		C(26)-C(25)-C(24)	119.221
		H(49)-C(24)-C(25)	119.915
		H(49)-C(24)-C(23)	120.46
		C(25)-C(24)-C(23)	119.625
		H(48)-C(23)-C(24)	115.786
		H(48)-C(23)-C(2)	122.346
		C(24)-C(23)-C(2)	121.867
		H(36)-C(8)-N(9)	116.09

Bond lengths (Å)	Bond angles (°)	
	H(36)–C(8)–C(6)	115.606
	N(9)-C(8)-C(6)	128.152
	Cu(28)–O(7)–C(5)	112.218
	C(8)-C(6)-C(2)	126.282
	C(8)-C(6)-C(5)	118.103
	C(2)-C(6)-C(5)	115.505
	O(7)–C(5)–C(6)	117.624
	O(7)-C(5)-C(4)	124.144
	C(6)-C(5)-C(4)	118.221
	H(35)-C(4)-C(5)	119.334
	H(35)–C(4)–C(3)	121.615
	C(5)-C(4)-C(3)	119.049
	H(51)-C(26)-C(1)	121.239
	H(51)-C(26)-C(25)	117.165
	C(1)-C(26)-C(25)	121.596
	H(34)-C(3)-C(4)	115.841
	H(34)–C(3)–C(1)	120.125
	C(4)–C(3)–C(1)	124.029
	C(23)-C(2)-C(6)	121.658
	C(23)–C(2)–C(1)	118.382
	C(6)-C(2)-C(1)	119.955
	C(26)–C(1)–C(3)	117.469
	C(26)–C(1)–C(2)	119.309
	C(3)-C(1)-C(2)	123.222

 Table 7
 continued

 $^2B_{1g} \rightarrow ^2A_{1g}(\upsilon_1), \quad ^2B_{1g} \rightarrow ^2B_{2g}(\upsilon_2)$

The complex of Cd(II) is diamagnetic. In analogy with those described for the Cd(II) complex containing N–O donor Schiff bases and according to the empirical formulae of this complex, a square planar geometry was proposed for the Cd(II) complex [51].

ESR spectroscopy

ESR spectra of the polycrystalline were recorded at room temperature and presented in Table 12. The values of *g* factors were assessed following the method described by Searl et al. [52]. The *g* tensor values of Cu(II) complex can be used to derive the ground state. In tetragonal and square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ²B_{1g} as the ground state with the $g_{11} > g_{\perp} > 2.0023$ [20]. From the observed values for complexes (1–3), it is clear that $g_{11} > g_{\perp}$. These data are in agreement with those obtained from the electronic spectra and confirm the

O(31)-H(61)1.081 $O(32)$ -S(33)-O(36)115.267 $O(31)$ -H(60)1.088 $O(32)$ -S(33)-O(35)113.457 $O(30)$ -H(59)1.068 $O(32)$ -S(33)-O(34)115.449 $O(30)$ -H(58)1.25 $O(36)$ -S(33)-O(34)97.365 $O(29)$ -H(57)1.132 $O(36)$ -S(33)-O(34)97.365 $O(29)$ -H(56)1.079 $O(35)$ -S(33)-O(34)122.263 $C(26)$ -H(55)1.09H(47)-C(20)-C(21)129.984 $C(25)$ -H(54)1.091H(47)-C(20)-C(19)109.495 $C(24)$ -H(53)1.114 $C(21)$ -C(20)-C(19)126.203 $C(22)$ -H(51)1.1H(46)-C(19)-C(20)126.203 $C(22)$ -H(50)1.108 $C(20)$ -C(19)111.157 $C(22)$ -H(49)1.13H(45)-C(18)-C(17)118.949 $C(21)$ -H(48)1.108H(45)-C(19)-C(18)111.150 $C(21)$ -H(48)1.108H(44)-C(17)125.897 $C(19)$ -H(46)1.116H(48)-C(21)-C(20)100.426 $C(17)$ -H(44)1.09 $C(16)$ -C(21)-C(20)131.179 $C(15)$ -H(43)1.168H(44)-C(17)-C(16)112.387 $C(15)$ -H(41)1.099 $C(18)$ -C(12)-C(16)128.895 $C(3)$ -H(40)1.13 $Cu(28)$ -O(32)-S(33)121.204 $O(7)$ -H(39)0.967H(61)-O(31)-H(60)83.093 $C(4)$ -H(38)1.103H(61)-O(31)-Cu(28)78.195 $C(3)$ -H(37)1.096H(60)-O(31)-Cu(28)148.923 $C(16)$ - $C(21)$ 1.331H(55)-O(29)-Cu(28)111.033 $C(16)$ - $C(12)$ 1.3	Bond lengths (Å)		Bond angles (°)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(31)–H(61)	1.081	O(32)-S(33)-O(36)	115.267
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(31)-H(60)	1.088	O(32)–S(33)–O(35)	113.457
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(30)-H(59)	1.068	O(32)–S(33)–O(34)	115.449
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(30)-H(58)	1.25	O(36)-S(33)-O(35)	87.909
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(29)-H(57)	1.132	O(36)-S(33)-O(34)	97.365
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(29)-H(56)	1.079	O(35)-S(33)-O(34)	122.263
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(26)-H(55)	1.09	H(47)-C(20)-C(21)	129.984
$\begin{array}{ccccccc} C(24)-H(53) & 1.114 & C(21)-C(20)-C(19) & 120.444 \\ C(23)-H(52) & 1.078 & H(46)-C(19)-C(20) & 126.203 \\ C(22)-H(51) & 1.1 & H(46)-C(19)-C(18) & 122.635 \\ C(22)-H(50) & 1.108 & C(20)-C(19)-C(18) & 111.157 \\ C(22)-H(49) & 1.13 & H(45)-C(18)-C(19) & 115.069 \\ C(21)-H(48) & 1.108 & H(45)-C(18)-C(17) & 118.949 \\ C(20)-H(47) & 1.109 & C(19)-C(18)-C(17) & 125.897 \\ C(19)-H(46) & 1.116 & H(48)-C(21)-C(16) & 128.395 \\ C(18)-H(45) & 1.104 & H(48)-C(21)-C(20) & 100.426 \\ C(17)-H(44) & 1.09 & C(16)-C(21)-C(20) & 131.179 \\ C(15)-H(43) & 1.168 & H(44)-C(17)-C(18) & 117.719 \\ C(15)-H(42) & 1.151 & H(44)-C(17)-C(16) & 112.387 \\ C(15)-H(41) & 1.099 & C(18)-C(17)-C(16) & 129.857 \\ C(8)-H(40) & 1.13 & Cu(28)-O(32)-S(33) & 121.204 \\ O(7)-H(38) & 1.103 & H(61)-O(31)-H(60) & 83.093 \\ C(4)-H(38) & 1.103 & H(61)-O(31)-H(60) & 83.093 \\ C(16)-C(21) & 1.426 & H(59)-O(30)-H(58) & 134.231 \\ C(20)-C(21) & 1.376 & H(59)-O(30)-H(58) & 134.231 \\ C(20)-C(21) & 1.331 & H(57)-O(29)-H(56) & 58.116 \\ C(17)-C(18) & 1.349 & H(57)-O(29)-H(28) & 116.346 \\ C(16)-C(21)-C(16) & 1.334 & H(57)-O(29)-C(28) & 116.4646 \\ \end{array}$	C(25)-H(54)	1.091	H(47)-C(20)-C(19)	109.495
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(24)-H(53)	1.114	C(21)-C(20)-C(19)	120.444
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(23)-H(52)	1.078	H(46)-C(19)-C(20)	126.203
C(22)-H(50)1.108 $C(20)$ -C(19)-C(18)111.157 $C(22)$ -H(49)1.13H(45)-C(18)-C(19)115.069 $C(21)$ -H(48)1.108H(45)-C(18)-C(17)118.949 $C(20)$ -H(47)1.109 $C(19)$ -C(18)-C(17)125.897 $C(19)$ -H(46)1.116H(48)-C(21)-C(16)128.395 $C(18)$ -H(45)1.104H(48)-C(21)-C(20)100.426 $C(17)$ -H(44)1.09 $C(16)$ -C(21)-C(20)131.179 $C(15)$ -H(43)1.168H(44)-C(17)-C(18)117.719 $C(15)$ -H(42)1.151H(44)-C(17)-C(16)122.877 $C(15)$ -H(41)1.099 $C(18)$ -C(17)-C(16)129.857 $C(8)$ -H(40)1.13 $Cu(28)$ -O(32)-S(33)121.204 $O(7)$ -H(39)0.967H(61)-O(31)-H(60)83.093 $C(4)$ -H(38)1.103H(61)-O(31)-Cu(28)78.195 $C(3)$ -H(37)1.096H(60)-O(31)-Cu(28)148.923 $C(16)$ - $C(21)$ 1.336H(59)-O(30)-Lu(28)111.033 $C(19)$ - $C(20)$ 1.333H(58)-O(30)-Cu(28)111.033 $C(19)$ - $C(20)$ 1.331H(57)-O(29)-H(56)58.116 $C(17)$ - $C(18)$ 1.349H(57)-O(29)-Cu(28)153.166 $C(17)$ - $C(18)$ 1.343H(55)- $O(29)$ - $Cu(28)$ 116.466	C(22)-H(51)	1.1	H(46)-C(19)-C(18)	122.635
C(22)-H(49)1.13 $H(45)$ - $C(18)$ - $C(19)$ 115.069 $C(21)$ -H(48)1.108 $H(45)$ - $C(18)$ - $C(17)$ 118.949 $C(20)$ -H(47)1.109 $C(19)$ - $C(18)$ - $C(17)$ 125.897 $C(19)$ -H(46)1.116 $H(48)$ - $C(21)$ - $C(16)$ 128.395 $C(18)$ -H(45)1.104 $H(48)$ - $C(21)$ - $C(20)$ 100.426 $C(17)$ -H(44)1.09 $C(16)$ - $C(21)$ - $C(20)$ 131.179 $C(15)$ -H(43)1.168 $H(44)$ - $C(17)$ - $C(16)$ 112.387 $C(15)$ -H(42)1.151 $H(44)$ - $C(17)$ - $C(16)$ 129.857 $C(15)$ -H(41)1.099 $C(18)$ - $C(17)$ - $C(16)$ 129.857 $C(8)$ -H(40)1.13 $Cu(28)$ - $O(32)$ - $S(33)$ 121.204 $O(7)$ -H(39)0.967 $H(61)$ - $O(31)$ - $H(60)$ 83.093 $C(4)$ -H(38)1.103 $H(61)$ - $O(31)$ - $Cu(28)$ 148.923 $C(16)$ - $C(21)$ 1.426 $H(59)$ - $O(30)$ - $H(58)$ 134.231 $C(20)$ - $C(21)$ 1.331 $H(58)$ - $O(30)$ - $Cu(28)$ 111.033 $C(19)$ - $C(18)$ 1.343 $H(56)$ - $O(29)$ - $Cu(28)$ 153.166 $C(17)$ - $C(18)$ 1.343 $H(56)$ - $O(29)$ - $Cu(28)$ 146.466	C(22)-H(50)	1.108	C(20)–C(19)–C(18)	111.157
C(21)-H(48)1.108H(45)-C(18)-C(17)118.949 $C(20)$ -H(47)1.109 $C(19)$ -C(18)-C(17)125.897 $C(19)$ -H(46)1.116H(48)-C(21)-C(16)128.395 $C(18)$ -H(45)1.104H(48)-C(21)-C(20)100.426 $C(17)$ -H(44)1.09 $C(16)$ -C(21)-C(20)131.179 $C(15)$ -H(43)1.168H(44)-C(17)-C(18)117.719 $C(15)$ -H(42)1.151H(44)-C(17)-C(16)122.387 $C(15)$ -H(41)1.099 $C(18)$ -C(17)-C(16)129.857 $C(8)$ -H(40)1.13 $Cu(28)$ -O(32)-S(33)121.204 $O(7)$ -H(39)0.967H(61)-O(31)-H(60)83.093 $C(4)$ -H(38)1.103H(61)-O(31)-Cu(28)78.195 $C(3)$ -H(37)1.096H(60)-O(31)-Cu(28)148.923 $C(16)$ - $C(21)$ 1.376H(59)-O(30)-H(58)134.231 $C(20)$ - $C(20)$ 1.333H(58)-O(30)-Cu(28)110.33 $C(19)$ - $C(20)$ 1.331H(57)-O(29)-H(56)58.116 $C(17)$ - $C(18)$ 1.349H(57)-O(29)-Cu(28)153.166 $C(16)$ - $C(17)$ 1.343H(56)-O(29)-Cu(28)153.166	C(22)-H(49)	1.13	H(45)-C(18)-C(19)	115.069
C(20)-H(47)1.109 $C(19)-C(18)-C(17)$ 125.897 $C(19)-H(46)$ 1.116 $H(48)-C(21)-C(16)$ 128.395 $C(18)-H(45)$ 1.104 $H(48)-C(21)-C(20)$ 100.426 $C(17)-H(44)$ 1.09 $C(16)-C(21)-C(20)$ 131.179 $C(15)-H(43)$ 1.168 $H(44)-C(17)-C(18)$ 117.719 $C(15)-H(42)$ 1.151 $H(44)-C(17)-C(16)$ 112.387 $C(15)-H(41)$ 1.099 $C(18)-C(17)-C(16)$ 129.857 $C(8)-H(40)$ 1.13 $Cu(28)-O(32)-S(33)$ 121.204 $O(7)-H(39)$ 0.967 $H(61)-O(31)-H(60)$ 83.093 $C(4)-H(38)$ 1.103 $H(61)-O(31)-Cu(28)$ 78.195 $C(3)-H(37)$ 1.096 $H(60)-O(31)-Cu(28)$ 148.923 $C(16)-C(21)$ 1.426 $H(59)-O(30)-H(58)$ 134.231 $C(20)-C(21)$ 1.376 $H(59)-O(30)-Cu(28)$ 111.033 $C(19)-C(20)$ 1.331 $H(57)-O(29)-H(56)$ 58.116 $C(17)-C(18)$ 1.349 $H(57)-O(29)-Cu(28)$ 1153.166 $C(16)-C(17)$ 1.343 $H(56)-O(29)-Cu(28)$ 116.446	C(21)-H(48)	1.108	H(45)-C(18)-C(17)	118.949
C(19)-H(46)1.116H(48)-C(21)-C(16)128.395 $C(18)$ -H(45)1.104H(48)-C(21)-C(20)100.426 $C(17)$ -H(44)1.09 $C(16)$ -C(21)-C(20)131.179 $C(15)$ -H(43)1.168H(44)-C(17)-C(18)117.719 $C(15)$ -H(42)1.151H(44)-C(17)-C(16)112.387 $C(15)$ -H(41)1.099 $C(18)$ -C(17)-C(16)129.857 $C(8)$ -H(40)1.13 $Cu(28)$ -O(32)-S(33)121.204 $O(7)$ -H(39)0.967H(61)-O(31)-H(60)83.093 $C(4)$ -H(38)1.103H(61)-O(31)-Cu(28)78.195 $C(3)$ -H(37)1.096H(60)-O(31)-Cu(28)148.923 $C(16)$ - $C(21)$ 1.426H(59)-O(30)-H(58)134.231 $C(20)$ - $C(21)$ 1.376H(59)-O(30)-Cu(28)111.033 $C(19)$ - $C(20)$ 1.331H(57)-O(29)-H(56)58.116 $C(17)$ - $C(18)$ 1.349H(57)-O(29)-Cu(28)153.166 $C(16)$ - $C(17)$ 1.343H(56)-O(29)-Cu(28)116.446	C(20)-H(47)	1.109	C(19)–C(18)–C(17)	125.897
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(19)-H(46)	1.116	H(48)-C(21)-C(16)	128.395
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(18)-H(45)	1.104	H(48)-C(21)-C(20)	100.426
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(17)-H(44)	1.09	C(16)-C(21)-C(20)	131.179
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(15)-H(43)	1.168	H(44)–C(17)–C(18)	117.719
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(15)-H(42)	1.151	H(44)–C(17)–C(16)	112.387
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(15)-H(41)	1.099	C(18)–C(17)–C(16)	129.857
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(8)-H(40)	1.13	Cu(28)–O(32)–S(33)	121.204
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(7)-H(39)	0.967	H(61)–O(31)–H(60)	83.093
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4)-H(38)	1.103	H(61)–O(31)–Cu(28)	78.195
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3)–H(37)	1.096	H(60)–O(31)–Cu(28)	148.923
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(16)–C(21)	1.426	H(59)–O(30)–H(58)	134.231
C(19)-C(20) 1.333 H(58)-O(30)-Cu(28) 102.063 C(18)-C(19) 1.331 H(57)-O(29)-H(56) 58.116 C(17)-C(18) 1.349 H(57)-O(29)-Cu(28) 153.166 C(16)-C(17) 1.343 H(56)-O(29)-Cu(28) 116.446	C(20)–C(21)	1.376	H(59)–O(30)–Cu(28)	111.033
C(18)-C(19) 1.331 H(57)-O(29)-H(56) 58.116 C(17)-C(18) 1.349 H(57)-O(29)-Cu(28) 153.166 C(16)-C(17) 1.343 H(56)-O(29)-Cu(28) 116.446	C(19)–C(20)	1.333	H(58)–O(30)–Cu(28)	102.063
C(17)–C(18) 1.349 H(57)–O(29)–Cu(28) 153.166 C(16)–C(17) 1.343 H(56)–O(29)–Cu(28) 116.446	C(18)–C(19)	1.331	H(57)–O(29)–H(56)	58.116
C(16) - C(17) 1.343 $H(56) - O(29) - Cu(28)$ 116.446	C(17)–C(18)	1.349	H(57)–O(29)–Cu(28)	153.166
C(10)-C(17) 1.545 $II(50)-C(27)-Cu(20)$ 110.440	C(16)–C(17)	1.343	H(56)–O(29)–Cu(28)	116.446
C(4)–C(3) 1.338 C(21)–C(16)–C(17) 101.157	C(4)–C(3)	1.338	C(21)–C(16)–C(17)	101.157
C(1)–C(3) 1.337 C(21)–C(16)–N(12) 135.222	C(1)–C(3)	1.337	C(21)–C(16)–N(12)	135.222
C(2)–C(1) 1.34 C(17)–C(16)–N(12) 123.565	C(2)–C(1)	1.34	C(17)–C(16)–N(12)	123.565
C(26)–C(1) 1.351 H(43)–C(15)–H(42) 78.856	C(26)–C(1)	1.351	H(43)-C(15)-H(42)	78.856
C(25)–C(26) 1.335 H(43)–C(15)–H(41) 97.921	C(25)–C(26)	1.335	H(43)–C(15)–H(41)	97.921
C(24)–C(25) 1.317 H(43)–C(15)–N(13) 119.332	C(24)-C(25)	1.317	H(43)–C(15)–N(13)	119.332
C(23)–C(24) 1.337 H(42)–C(15)–H(41) 100.985	C(23)–C(24)	1.337	H(42)–C(15)–H(41)	100.985
C(2)–C(23) 1.35 H(42)–C(15)–N(13) 120.149	C(2)–C(23)	1.35	H(42)–C(15)–N(13)	120.149
C(6)–C(2) 1.373 H(41)–C(15)–N(13) 127.687	C(6)–C(2)	1.373	H(41)–C(15)–N(13)	127.687
C(5)–C(6) 1.345 C(16)–N(12)–N(13) 142.175	C(5)–C(6)	1.345	C(16)–N(12)–N(13)	142.175

 Table 8 The selected geometric parameters for complex (3)

Bond lengths (Å)		Bond angles (°)	
C(4)–C(5)	1.339	C(16)-N(12)-C(11)	96.352
O(31)–Cu(28)	1.792	N(13)–N(12)–C(11)	116.553
O(30)-Cu(28)	1.933	Cu(28)–O(27)–C(11)	112.384
O(29)–Cu(28)	1.903	H(51)-C(22)-H(50)	109.838
Cu(28)–O(32)	1.931	H(51)-C(22)-H(49)	106.109
O(27)–Cu(28)	1.849	H(51)-C(22)-C(14)	111.976
N(9)-Cu(28)	1.409	H(50)-C(22)-H(49)	101.344
C(11)–O(27)	1.264	H(50)-C(22)-C(14)	121.063
C(14)–C(22)	1.583	H(49)-C(22)-C(14)	104.765
N(12)-C(16)	1.39	C(15)-N(13)-C(14)	90.377
N(13)-C(15)	1.809	C(15)-N(13)-N(12)	151.893
C(14)–C(10)	1.407	C(14)-N(13)-N(12)	106.749
N(13)-C(14)	1.219	C(22)-C(14)-C(10)	118.828
N(12)–N(13)	1.418	C(22)-C(14)-N(13)	95.37
C(11)–N(12)	1.295	C(10)-C(14)-N(13)	85.009
C(10)–C(11)	1.365	O(27)-C(11)-N(12)	166.882
N(9)–C(10)	1.295	O(27)-C(11)-C(10)	83.465
C(8)–N(9)	1.292	N(12)-C(11)-C(10)	83.425
C(6)–C(8)	1.359	O(31)-Cu(28)-O(30)	64.311
C(5)–O(7)	1.364	O(31)-Cu(28)-O(29)	84.853
O(32)–S(33)	1.759	O(31)-Cu(28)-O(32)	69.112
S(33)–O(36)	1.717	O(31)-Cu(28)-O(27)	73.986
S(33)–O(35)	1.566	O(31)-Cu(28)-N(9)	151.272
S(33)–O(34)	1.444	O(30)-Cu(28)-O(29)	53.14
		O(30)-Cu(28)-O(32)	79.986
		O(30)-Cu(28)-O(27)	122.012
		O(30)-Cu(28)-N(9)	135.405
		O(29)-Cu(28)-O(32)	132.91
		O(29)-Cu(28)-O(27)	85.974
		O(29)-Cu(28)-N(9)	93.894
		O(32)-Cu(28)-O(27)	120.722
		O(32)-Cu(28)-N(9)	127.514
		O(27)-Cu(28)-N(9)	77.294
		C(14)-C(10)-C(11)	125.631
		C(14)-C(10)-N(9)	116.605
		C(11)-C(10)-N(9)	109.324
		Cu(28)–N(9)–C(10)	118.063
		Cu(28)–N(9)–C(8)	110.829
		C(10)–N(9)–C(8)	125.215
		H(54)-C(25)-C(26)	128.232
		H(54)–C(25)–C(24)	116.282

Table 8 continued

Bond lengths (Å)	Bond angles (°)	
	C(26)-C(25)-C(24)	115.446
	H(53)-C(24)-C(25)	122.142
	H(53)-C(24)-C(23)	122.95
	C(25)-C(24)-C(23)	114.906
	H(52)-C(23)-C(24)	101.744
	H(52)-C(23)-C(2)	125.902
	C(24)-C(23)-C(2)	132.184
	H(40)-C(8)-N(9)	122.76
	H(40)-C(8)-C(6)	122.377
	N(9)-C(8)-C(6)	114.01
	H(39)–O(7)–C(5)	110.78
	C(2)–C(6)–C(5)	117.705
	C(2)–C(6)–C(8)	124.161
	C(5)–C(6)–C(8)	117.897
	C(6)–C(5)–C(4)	117.819
	C(6)–C(5)–O(7)	122.551
	C(4)–C(5)–O(7)	119.341
	H(38)–C(4)–C(3)	118.579
	H(38)–C(4)–C(5)	118.4
	C(3)–C(4)–C(5)	123.019
	H(55)-C(26)-C(1)	121.286
	H(55)-C(26)-C(25)	113.149
	C(1)-C(26)-C(25)	125.42
	H(37)-C(3)-C(4)	119.735
	H(37)-C(3)-C(1)	119.209
	C(4)–C(3)–C(1)	121.034
	C(1)-C(2)-C(23)	106.795
	C(1)–C(2)–C(6)	124.24
	C(23)–C(2)–C(6)	128.506
	C(3)–C(1)–C(2)	115.716
	C(3)–C(1)–C(26)	122.692
	C(2)–C(1)–C(26)	121.56

Table 8 continued

square planar geometry for complex (1) and the tetragonal geometry for complexes (2) and (3). The term of the fundamental state is thus defined by the orbital $d_{x^2-y^2}$.

The ESR spectrum of the copper(II) complex (1) has been reported such that $g_{\rm II}$ can be used as a measure of the covalent character of the metal–ligand bond. If the value is more than 2.3, the metal–ligand bond is essentially ionic, and the value less than 2.3 is indicative of covalent character [53]. Apart from this, the covalency parameter (α^2) has been calculated using the Kivelson and Neinant equation [45]. The covalency parameter ($\alpha^2 = 0.58$) indicates considerable covalent character for the metal–ligand bond [54]. Also, the trend $g_{\rm II} > g_{\perp} > 2.0023$ observed for this

	*	* '''	
Bond lengths (Å)		Bond angles (°)	
O(32)–H(55)	1.15	H(43)-C(20)-C(21)	120.119
O(32)-H(54)	1.15	H(43)-C(20)-C(19)	119.578
O(31)-H(53)	1.149	C(21)-C(20)-C(19)	120.302
O(31)-H(52)	1.15	H(42)-C(19)-C(20)	120.533
C(26)-H(51)	1.104	H(42)-C(19)-C(18)	120.526
C(25)-H(50)	1.102	C(20)-C(19)-C(18)	118.939
C(24)-H(49)	1.104	H(41)-C(18)-C(19)	119.752
C(23)-H(48)	1.094	H(41)-C(18)-C(17)	120.179
C(22)-H(47)	1.11	C(19)-C(18)-C(17)	120.063
C(22)-H(46)	1.113	H(44)-C(21)-C(16)	122.21
C(22)-H(45)	1.113	H(44)-C(21)-C(20)	115.689
C(21)-H(44)	1.1	C(16)-C(21)-C(20)	122.067
C(20)-H(43)	1.103	H(40)-C(17)-C(18)	116.647
C(19)-H(42)	1.103	H(40)-C(17)-C(16)	120.971
C(18)-H(41)	1.103	C(18)-C(17)-C(16)	122.345
C(17)-H(40)	1.102	H(55)-O(32)-H(54)	120.177
C(15)-H(39)	1.111	H(55)-O(32)-Co(28)	114.473
C(15)-H(38)	1.113	H(54)-O(32)-Co(28)	124.711
C(15)-H(37)	1.113	H(53)-O(31)-H(52)	122.792
C(8)-H(36)	1.105	H(53)-O(31)-Co(28)	122.353
O(7)-H(35)	0.969	H(52)-O(31)-Co(28)	114.316
C(4)-H(34)	1.104	C(21)-C(16)-C(17)	116.273
C(3)-H(33)	1.104	C(21)-C(16)-N(12)	123.83
C(16)-C(21)	1.349	C(17)–C(16)–N(12)	119.876
C(20)-C(21)	1.343	H(39)-C(15)-H(38)	104.323
C(19)-C(20)	1.34	H(39)-C(15)-H(37)	107.721
C(18)-C(19)	1.34	H(39)–C(15)–N(13)	113.487
C(17)-C(18)	1.342	H(38)-C(15)-H(37)	109.895
C(16)-C(17)	1.349	H(38)–C(15)–N(13)	110.846
C(4)–C(3)	1.334	H(37)–C(15)–N(13)	110.356
C(1)–C(3)	1.342	C(16)-N(12)-N(13)	123.74
C(2)–C(1)	1.356	C(16)–N(12)–C(11)	129.021
C(26)–C(1)	1.347	N(13)–N(12)–C(11)	103
C(25)-C(26)	1.338	Co(28)–O(27)–C(11)	109.707
C(24)-C(25)	1.336	H(47)-C(22)-H(46)	106.664
C(23)-C(24)	1.342	H(47)-C(22)-H(45)	107.101
C(2)–C(23)	1.353	H(47)–C(22)–C(14)	112.573
C(6)–C(2)	1.364	H(46)-C(22)-H(45)	109.306
C(5)–C(6)	1.359	H(46)-C(22)-C(14)	110.557
C(4)–C(5)	1.341	H(45)-C(22)-C(14)	110.485
O(32)-Co(28)	1.193	C(15)–N(13)–C(14)	115.539

Table 9 The selected geometric parameters for complex (4)

Table 9 continued

Bond lengths (Å)		Bond angles (°)	
O(31)–Co(28)	1.196	C(15)-N(13)-N(12)	129.467
Cl(30)-Co(28)	2.213	C(14)-N(13)-N(12)	114.781
Co(28)–Cl(29)	2.197	C(22)-C(14)-C(10)	126.066
O(27)–Co(28)	1.069	C(22)-C(14)-N(13)	131.689
N(9)-Co(28)	1.885	C(10)-C(14)-N(13)	102.238
C(11)–O(27)	1.252	O(27)-C(11)-N(12)	128.739
C(14)-C(22)	1.503	O(27)-C(11)-C(10)	121.863
N(12)-C(16)	1.279	N(12)-C(11)-C(10)	109.156
N(13)-C(15)	1.484	O(32)-Co(28)-O(31)	157.516
C(14)-C(10)	1.336	O(32)-Co(28)-Cl(30)	79.203
N(13)-C(14)	1.279	O(32)-Co(28)-Cl(29)	89.071
N(12)-N(13)	1.367	O(32)-Co(28)-O(27)	101.629
C(11)–N(12)	1.279	O(32)-Co(28)-N(9)	90.273
C(10)-C(11)	1.343	O(31)-Co(28)-Cl(30)	78.337
N(9)-C(10)	1.259	O(31)-Co(28)-Cl(29)	89.342
C(8)-N(9)	1.276	O(31)-Co(28)-O(27)	100.785
C(6)–C(8)	1.359	O(31)-Co(28)-N(9)	85.229
C(5)-O(7)	1.366	Cl(30)-Co(28)-Cl(29)	83.284
		Cl(30)–Co(28)–O(27)	172.809
		Cl(30)-Co(28)-N(9)	81.024
		Cl(29)-Co(28)-O(27)	89.579
		Cl(29)-Co(28)-N(9)	164.134
		O(27)-Co(28)-N(9)	106.069
		C(14)-C(10)-C(11)	110.206
		C(14)-C(10)-N(9)	141.075
		C(11)-C(10)-N(9)	108.686
		Co(28)-N(9)-C(10)	93.352
		Co(28)-N(9)-C(8)	125.192
		C(10)-N(9)-C(8)	108.418
		H(50)-C(25)-C(26)	121.074
		H(50)-C(25)-C(24)	120.854
		C(26)-C(25)-C(24)	118.071
		H(49)-C(24)-C(25)	119.29
		H(49)-C(24)-C(23)	120.597
		C(25)-C(24)-C(23)	120.113
		H(48)-C(23)-C(24)	111.498
		H(48)-C(23)-C(2)	124.615
		C(24)-C(23)-C(2)	123.885
		H(36)-C(8)-N(9)	113.537
		H(36)–C(8)–C(6)	116.584
		N(9)-C(8)-C(6)	129.862

Bond lengths (Å)	Bond angles (°)	
	H(35)–O(7)–C(5)	110.623
	C(2)–C(6)–C(5)	118.851
	C(2)–C(6)–C(8)	126.104
	C(5)–C(6)–C(8)	115.044
	C(6)-C(5)-C(4)	119.971
	C(6)–C(5)–O(7)	123.711
	C(4)–C(5)–O(7)	116.253
	H(34)–C(4)–C(3)	119.033
	H(34)–C(4)–C(5)	119.619
	C(3)–C(4)–C(5)	121.347
	H(51)–C(26)–C(1)	121.519
	H(51)-C(26)-C(25)	117.408
	C(1)-C(26)-C(25)	121.073
	H(33)–C(3)–C(4)	118.321
	H(33)–C(3)–C(1)	122.128
	C(4)–C(3)–C(1)	119.549
	C(1)–C(2)–C(23)	114.297
	C(1)–C(2)–C(6)	119.751
	C(23)–C(2)–C(6)	125.949
	C(3)–C(1)–C(2)	120.527
	C(3)-C(1)-C(26)	116.917
	C(2)–C(1)–C(26)	122.556

 Table 9
 continued

complex indicated that the unpaired electron was most likely in the $d_{x^2-y^2}$ orbital, which supported a square planar structure [55]. The calculated g_{av} , suggests the high covalency property of complex. The *g*-values can be used to calculate the G value; with this factor indicating that the ligand is a weak field or a strong field ligand. The equation used is as follows:

$$G = (g_{\rm ll} - 2.0023)/(g_{\perp} - 2.0023), \tag{17}$$

where *G* is <4.0, the ligand forming Cu^{2+} complex is regarded as a strong field ligand [45]. In this case the G value is 4.44, which is indicating the formation of a weak field ligand [56]. Based on this observation, a distorted square planar geometry is proposed for the complex. The ESR study of the copper(II) complex has provided supportive evidence to a conclusion obtained on the basis of the electronic spectrum and magnetic moment value. The spin Hamiltonian, orbital reduction, and bonding parameters of these complexes are given in Table 12.

The ESR parameters and d-d transition energies were used to evaluate the bonding parameters α^2 , β^2 and γ^2 , which may be regarded as measures of the covalency of the in-plane σ -bonds and the in-plane and out-of-plane π -bonds,

Bond lengths (Å)		Bond angles (°)	
C(26)–H(49)	1.104	H(41)-C(20)-C(21)	120.137
C(25)-H(48)	1.102	H(41)-C(20)-C(19)	119.496
C(24)-H(47)	1.104	C(21)-C(20)-C(19)	120.367
C(23)-H(46)	1.095	H(40)-C(19)-C(20)	120.593
C(22)-H(45)	1.112	H(40)-C(19)-C(18)	120.573
C(22)-H(44)	1.113	C(20)-C(19)-C(18)	118.828
C(22)-H(43)	1.113	H(39)-C(18)-C(19)	119.739
C(21)-H(42)	1.099	H(39)-C(18)-C(17)	120.217
C(20)-H(41)	1.103	C(19)–C(18)–C(17)	120.037
C(19)-H(40)	1.102	H(42)-C(21)-C(16)	122.383
C(18)-H(39)	1.103	H(42)-C(21)-C(20)	115.396
C(17)-H(38)	1.102	C(16)-C(21)-C(20)	122.205
C(15)-H(37)	1.113	H(38)–C(17)–C(18)	116.348
C(15)-H(36)	1.113	H(38)-C(17)-C(16)	121.053
C(15)-H(35)	1.113	C(18)-C(17)-C(16)	122.568
C(8)–H(34)	1.107	C(21)-C(16)-C(17)	115.961
O(7)-H(33)	0.969	C(21)-C(16)-N(12)	124.481
C(4)–H(32)	1.104	C(17)-C(16)-N(12)	119.508
C(3)–H(31)	1.104	H(37)-C(15)-H(36)	104.567
C(16)-C(21)	1.349	H(37)-C(15)-H(35)	108.227
C(20)–C(21)	1.343	H(37)-C(15)-N(13)	112.584
C(19)-C(20)	1.34	H(36)-C(15)-H(35)	109.639
C(18)–C(19)	1.339	H(36)-C(15)-N(13)	110.914
C(17)–C(18)	1.342	H(35)-C(15)-N(13)	110.696
C(16)–C(17)	1.35	C(16)–N(12)–N(13)	124.258
C(4)–C(3)	1.334	C(16)–N(12)–C(11)	131.602
C(1)–C(3)	1.342	N(13)–N(12)–C(11)	100.608
C(2)–C(1)	1.355	Cd(28)–O(27)–C(11)	108.807
C(26)–C(1)	1.347	H(45)-C(22)-H(44)	107.777
C(25)-C(26)	1.338	H(45)-C(22)-H(43)	106.462
C(24)–C(25)	1.337	H(45)-C(22)-C(14)	112.293
C(23)–C(24)	1.342	H(44)-C(22)-H(43)	109.044
C(2)–C(23)	1.352	H(44)-C(22)-C(14)	110.318
C(6)–C(2)	1.364	H(43)-C(22)-C(14)	110.798
C(5)–C(6)	1.36	C(15)-N(13)-C(14)	115.24
C(4)–C(5)	1.341	C(15)–N(13)–N(12)	129.845
Cd(28)-Cl(30)	2.475	C(14)–N(13)–N(12)	114.51
Cd(28)–Cl(29)	2.475	C(22)-C(14)-C(10)	124.469
O(27)–Cd(28)	2.133	C(22)-C(14)-N(13)	130.19
N(9)–Cd(28)	2.176	C(10)–C(14)–N(13)	105.147
C(11)-O(27)	1.227	O(27)-C(11)-N(12)	131.302

Table 10 The selected geometric parameters for complex (5)

Bond lengths (Å)		Bond angles (°)	
C(14)-C(22)	1.506	O(27)-C(11)-C(10)	116.31
N(12)-C(16)	1.279	N(12)-C(11)-C(10)	112.289
N(13)-C(15)	1.484	Cl(30)-Cd(28)-Cl(29)	113.882
C(14)-C(10)	1.344	Cl(30)-Cd(28)-O(27)	115.028
N(13)-C(14)	1.277	Cl(30)-Cd(28)-N(9)	114.35
N(12)-N(13)	1.364	Cl(29)-Cd(28)-O(27)	115.025
C(11)–N(12)	1.272	Cl(29)-Cd(28)-N(9)	114.485
C(10)–C(11)	1.377	O(27)-Cd(28)-N(9)	79.879
N(9)-C(10)	1.289	C(14)-C(10)-C(11)	104.617
C(8)-N(9)	1.276	C(14)-C(10)-N(9)	125.146
C(6)–C(8)	1.359	C(11)-C(10)-N(9)	130.168
C(5)-O(7)	1.366	Cd(28)-N(9)-C(10)	97.075
		Cd(28)-N(9)-C(8)	102.196
		C(10)–N(9)–C(8)	113.766
		H(48)-C(25)-C(26)	121.044
		H(48)-C(25)-C(24)	120.828
		C(26)-C(25)-C(24)	118.123
		H(47)-C(24)-C(25)	119.354
		H(47)-C(24)-C(23)	120.557
		C(25)-C(24)-C(23)	120.088
		H(46)-C(23)-C(24)	112.071
		H(46)-C(23)-C(2)	124.113
		C(24)-C(23)-C(2)	123.811
		H(34)-C(8)-N(9)	112.703
		H(34)-C(8)-C(6)	116.872
		N(9)-C(8)-C(6)	130.345
		H(33)–O(7)–C(5)	111.209
		C(2)-C(6)-C(5)	118.743
		C(2)–C(6)–C(8)	125.927
		C(5)-C(6)-C(8)	115.324
		C(6)-C(5)-C(4)	119.931
		C(6)–C(5)–O(7)	123.872
		C(4)–C(5)–O(7)	116.178
		H(32)–C(4)–C(3)	118.997
		H(32)–C(4)–C(5)	119.577
		C(3)–C(4)–C(5)	121.425
		H(49)-C(26)-C(1)	121.488
		H(49)-C(26)-C(25)	117.467
		C(1)-C(26)-C(25)	121.044
		H(31)-C(3)-C(4)	118.387
		H(31)–C(3)–C(1)	122.107

Table 10 continued

Table	10	continued

Bond lengths (Å)	Bond angles (°)	
	C(4)–C(3)–C(1)	119.498
	C(1)–C(2)–C(23)	114.436
	C(1)–C(2)–C(6)	119.936
	C(23)–C(2)–C(6)	125.623
	C(3)–C(1)–C(2)	120.434
	C(3)–C(1)–C(26)	117.085
	C(2)-C(1)-C(26)	122.48

respectively. The in-plane σ -bonding parameters α^2 was calculated using the expression of Kivelson and Neiman [45].

$$\alpha^2 = (A_{\rm ll}/0.036) + (g_{\rm ll}-2.0023) + 3/7(g_{\perp}-2.0023) + 0.04 \tag{18}$$

The calculated values, $\alpha^2 = 0.57$ -0.60, suggests the covalent character [20]. The orbital reduction factors K_{11} and K_{\perp} were estimated from the expressions [57].

$$K_{\rm ll}^2 = (g_{\rm ll} - 2.0023) E_{\rm d-d} / 8\lambda_{\rm o}, \tag{19}$$

$$K_{\perp}^{2} = (g_{\perp} - 2.0023) E_{\rm d-d} / 2\lambda_{\rm o}, \qquad (20)$$

where $K_{\rm II} = \alpha^2 \beta^2$, $K_{\perp} = \alpha^2 \gamma^2$, and $\lambda_{\rm o}$ represents the one electron spin–spin coupling constant for the free ion, ($\lambda_{\rm o} = -828 \text{ cm}^{-1}$) for the copper(II) d⁹ system.

According to Hathaway [58] for pure σ -bonding, $K_{\rm ll} \approx K_{\perp} \approx 0.77$, whereas $K_{\rm ll} < K_{\perp}$ implies considerable in-plane π -bonding, while for out of plane π -bonding $K_{\rm ll} > K_{\perp}$.

In the present investigations of Cu(II) complexes, it is observed that $K_{\rm II} < K_{\perp}$, in complex (3), which indicates the presence of significant in-plane π -bonding. While, $K_{\rm II} > K_{\perp}$ (in complexes 1 and 2) is for out-of-plane π -bonding. The values of K (0.62–0.69) for copper(II) complexes are indicative of their covalent nature with the ligand. The $\beta^2 = 1.06-1.14$, assigns an ionic character to the out-of-plane π -bonding [59]. The use of β^2 as a measure of out-of-plane metal–ligand π -bonding is not always reliable.

Thermal studies

In order to study the thermal stability of the Schiff base ligand (**HL**) and its metal complexes, thermogravimetrics (TG) were carried out for ligand and complexes (1–4) as shown in Fig. 8. The suggested stepwise thermal degradation pattern of ligand and its complexes, with respect to temperature and formation of respective metal oxides, are depicted in Table 13. The TGA analysis curve of the ligand (HL), showed that the complex was stable up to 185 °C and no weight loss occurs before this temperature. The ligand underwent degradation in two successive stages. The first stage of degradation occurred at 185 °C, due to the loss of $C_{11}H_{12}N_3O$ with a

Table 11 Th	e calculated quantur	m chemical paramet	ters for HL [for	ms (A-D)] an	d its complex	es (1–5) ^a				
Compound	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	$\sigma (eV)^{-1}$	Pi (eV)	$S (eV)^{-1}$	ω (eV)	$\Delta N_{\rm max}$
¥	-6.569	-3.340	3.229	4.955	1.615	0.619	-4.955	0.309	7.602	3.068
В	-3.305	0.373	3.678	1.466	1.839	0.544	-1.466	0.272	0.584	0.797
С	-8.324	-3.181	5.143	5.753	2.572	0.389	-5.753	0.194	6.434	2.237
D	-3.070	0.370	3.440	1.350	1.720	0.581	-1.350	0.291	0.675	0.785
(1)	-3.907	-2.165	1.742	3.036	0.871	1.148	-3.036	0.574	5.291	3.486
(2)	-2.154	-0.726	1.428	1.440	0.714	1.401	-1.440	0.700	1.452	2.017
(3)	-3.224	-2.732	0.492	2.978	0.246	4.065	-2.978	2.033	18.025	12.106
(4)	-4.355	-4.137	0.218	4.246	0.109	9.174	-4.246	4.587	82.699	38.954
(5)	-6.604	-4.072	2.532	5.338	1.266	0.789	-5.338	0.395	11.254	4.216
^a Numbers as	given in Table 1									



Fig. 7 The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Schiff base (HL) and its complexes (1-5)

	1	1		11	· /	1					
Complex ^a	g_{11}	g_{\perp}	g _{av.}	G	α^2	K_{11}^2	K_{\perp}^2	K^2	β^2	B_1^2	$A_{\rm ll} \times 10^{-4} {\rm ~cm}^{-1}$
(1)	2.232	2.049	2.110	4.5	0.58	0.62	0.63	0.63	1.08	1.07	105
(2)	2.279	2.078	2.145	3.70	0.57	0.65	0.61	0.62	1.14	1.06	80
(3)	2.268	2.089	2.149	3.10	0.60	0.64	0.71	0.69	1.06	1.18	93

Table 12 ESR spectral parameter of copper(II) complexes

^a Numbers as given in Table 1



Fig. 8 TGA curves of ligand (HL) and its complexes (1-4)

practical weight loss of 55.91 % (Calcd. 56.58 %). The second stage of degradation occurred at 460 °C, due to the loss of $C_{10}H_7O$ with a practical weight loss of 41.19 % (Calcd. 40.06 %). The weight of the residue corresponds to the carbon atom.

In the thermogram of the compounds (1) and (2) (Fig. 8), both of them underwent degradation in two stages. In case of compound (1), the first stage of decomposition represents the weight loss of two hydrochloric acid molecules and C_6H_5 with a practical weight loss of 21.11 % (Calcd. 21.97 %) at 42–403 °C. The resultant complex underwent further degradation and gave a break at 403 °C with a practical weight loss of 56.8 % (Calcd. 56.387 %), which corresponds to the successive decomposition of $C_{15}H_{14}N_3O$. The weight of the residue corresponds to copper oxide and two carbon atoms. The thermogram of compound (2) showed a first stage of decomposition due to loss of $C_6H_{13}NO_5$ at 200 °C with a practical weight loss of 40.54 % (Calcd. 41.24 %). Furthermore, the complex underwent a second stage of decomposition due to the loss of $C_{11}H_7N$ and gave a break at 352 °C with a

Compound	TG range (°C)	Mass loss exp. (Calcd.) %	Total mass loss Exp. (Calcd.) %	Assignment	Residue
HL	185-460	55.91 (56.58)	97.188 (96.64)	C ₁₁ H ₁₂ N ₃ O	С
	461-662	41.19 (40.06)		C10H2O	
(1)	200-403	21.11 (21.97)	77.92 (76.51)	$C_6H_5 + 2HCl$	CuO + 2C
	403-1000	56.8 (56.387)		C15H14N3O	
(2)	200-352	40.54 (41.24)	72.13 (72.06)	C ₆ H ₁₃ NO ₅	CuO + 5C
	352-1000	30.47 (30.63)		C ₁₁ H ₇ N	
(3)	29-125	5.01 (5.94)	80.5 (80.95)	$2H_2O$	CuO + 3C
	125-532	23.15 (23.9)		$3H_2O + C_6H_5N$	
	532-1000	51.404 (51.1)		$C_{13}H_{14}N_2O_5S$	
(4)	42-128	9.693 (9.365)	83.84 (86.23)	3H ₂ O	CoO + 2C
	128-365	18.26(18.89)		$2H_2O + 2HCL$	
	365-520	13.38 (13.35)		C ₆ H ₅	
	521-1000	42.47 (42.57)		C ₁₅ H ₁₂ N ₃ O	

 Table 13 Weight losses percentage of ligand and its metal complexes

Numbers as given in Table 1

practical weight loss of 30.47 % (Calcd. 30.63 %). The weight of the residue corresponds to copper oxide and five carbon atoms.

The TGA curves of compound (**3**) showed that the complex underwent degradation in three successive stages. The first stage of degradation occurred at 29-125 °C due to the loss of two uncoordinated water molecules with a practical weight loss of 5.01 % (Calcd. 5.94 %). The resultant complex on further degradation gave a break at 125–532 °C by the loss of three coordinated water molecules and C₆H₅N with a practical weight loss of 23.15 % (Calcd. 23.9 %). Furthermore, the complex underwent a third stage of decomposition at 532–1000 °C due to loss of C₁₃H₁₄N₂O₅S with a practical weight loss of 51.404 % (Calcd. 51.1 %). The final weight of the residue corresponds to the respective copper oxide and three atoms of carbon.

Kinetic studies

The kinetic parameters such as activation energy (Ea), enthalpy (ΔH^*), entropy (ΔS^*), and Gibbs free energy change of the decomposition (ΔG^*) are evaluated graphically by employing the Coast-Redfern [60] and Horowitz-Metzger [61] methods.

Coast-Redfern equation

The Coast-Redfern equation, which is a typical integral method, can represent as:

$$\int_0^a \frac{\mathrm{d}x}{(1-\alpha)^n} = \frac{A}{\phi} \int_{T_1}^{T_2} \exp\left(-\frac{E_a}{RT}\right) \mathrm{d}t.$$
(21)



Fig. 9 Coats-Redfern (CR) of Schiff base (HL) and its metal complexes (1-4)

For convenience of integration, the lower limit T_1 is usually taken as zero. This equation on integration gives:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E_a}{RT} + \ln\left[\frac{AR}{\phi E_a}\right].$$
 (22)



Fig. 9 continued

A plot of left-hand side (LHS) against 1/T was drawn (Fig. 9). E_a is the energy of activation and calculated from the slope and A in (s⁻¹) from the intercept value. The entropy of activation calculated by using the equation:

$$\Delta S^* = 2.303 \left[\log \left(\frac{Ah}{k_{\rm B} T_{\rm s}} \right) \right] R,\tag{23}$$

where $k_{\rm B}$ is the Boltzmann constant, *h* is the Plank's constant, and $T_{\rm s}$ is the TG peak temperature.

Horowitz-Metzger equation

The Horowitz–Metzger equation is illustrative of the approximation methods. These authors derived the relation:

$$\log\left[\frac{1 - (1 - \alpha)^{1 - n}}{1 - n}\right] = \frac{E_{a}\theta}{2.303RT_{S}^{2}} \quad \text{for } n \neq 1,$$
(24)

when n = 1, the LHS of Eq. (24) would be $\log[-\log(1-\alpha)]$ (Fig. 10). For a first order kinetic process, the Horowitz-Metzger equation may be written in the form:



Fig. 10 Horowitz-Metzger (HM) of the Schiff base (HL) and its metal complexes (1-4)

$$\log\left[\log\left(\frac{W_{\alpha}}{W_{\gamma}}\right)\right] = \frac{E_{a}\theta}{2.303RT_{S}^{2}} - \log 2.303,$$
(25)

where $\theta = T - T_s$, $w_{\gamma} = w_{\alpha} - w$, $w_{\alpha} = mass$ loss at the completion reaction; w = mass loss up to time *t*. The plot of log [log (w_{α}/w_{γ})] versus θ was drawn and found to be linear from the slope from which E_a was calculated. The pre-exponential factor, *A*, was calculated from equation:



Fig. 10 continued

$$\frac{E_{\rm a}}{RT_{\rm S}^2} = \frac{A}{\left[\varphi \, \exp\left(-\frac{E_{\rm a}}{RT_{\rm s}}\right)\right]}.\tag{26}$$

The entropy of activation, ΔS^* , is calculated from Eq. (23). The enthalpy activation, ΔH^* , and Gibbs free energy, ΔG^* , are calculated from:

$$\Delta H^* = E_{\rm a} - RT, \tag{27}$$

$$\Delta G^* = \Delta H^* - T \Delta S^*. \tag{28}$$

The calculated values of E_a , A, ΔS^* , ΔH^* , and ΔG^* for the decomposition steps for the ligand (**HL**) and its metal complexes (1–4) are summarized in Table 14. The kinetic data obtained from the two methods are comparable and can be considered in good agreement with each other [16, 38].

Microbiological investigation

The antibacterial action of the Schiff base ligand may be significantly enhanced by the presence of azomethine groups, which have chelating properties. These properties may be used in metal transport across the bacterial membranes or to

HL $Ea (AI mol-1) A(s-1) A(s-1) A(s-1) A(s-1 (AI mol-1) A(s-$	Compound	Temp. range (°C)	Method	Parameter					Correlation
				Ea (kJ mol ⁻¹)	A (s ⁻¹)	ΔS^{*} (J mol ⁻¹ K ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)	coefficient (r)
$ \begin{array}{ ccccccccccccccccccccccccccccccccccc$	HL	185-460	CR	87.9	7.38E+04	-1.57E+02	82.9	177	0.99318
			HM	107	1.62E+07	-1.13E+02	103	170	0.9897
		460–662	CR	156	1.49E + 07	-1.16E+02	149	246	0.99833
			HM	171	2.49E+08	-9.27E+01	164	241	0.99766
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	(1)	42-403	CR	4.57	7.63E-03	-2.91E+02	-0.209	167	0.99647
			HM	54.8	3.20E + 02	-2.02E+02	50	166	0.99472
		403 - 1000	CR	43.5	3.04E - 01	-2.65E+02	35.3	293	0.99982
			HM	60.8	2.31E+00	-2.48E+02	52.7	294	0.99111
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	(2)	200-352	CR	163	2.06E+12	-1.42E+01	159	167	0.99736
			HM	175	5.66E+14	$3.24E \pm 01$	171	153	0.99599
		352 - 1000	CR	113	2.71E+05	-1.49E+02	106	218	0.98227
			ΗM	124	1.85E+06	-1.33E+02	118	218	0.99597
$ \begin{array}{lcccccccccccccccccccccccccccccccccccc$	(3)	29-125	CR	54.9	3.69E + 05	-1.40E+02	51.9	101	0.99811
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			ΗM	59.5	7.28E+06	-1.15E+02	56.6	96.8	0.99614
		125-532	CR	25.7	1.87E - 01	-2.65E+02	-0.265	180	0.99981
			ΗM	35.6	2.41E+00	-2.43E+02	30.6	177	0.99375
HM 56.6 1.61E+06 -1.28E+02 53.7 99.4 0.99969 128-365 CR 24.7 1.84E-01 -2.64E+02 20.4 157 0.99769 HM 34.4 7.40E+00 -2.33E+02 30.1 151 0.99901	(4)	42-128	CR	49.5	1.70E + 05	-1.46E+02	46.6	66	0.99993
128-365 CR 24.7 1.84E-01 -2.64E+02 20.4 157 0.99978 HM 34.4 7.40E+00 -2.33E+02 30.1 151 0.99901			HM	56.6	1.61E + 0.6	-1.28E+02	53.7	99.4	0.99969
HM 34.4 7.40E+00 -2.33E+02 30.1 151 0.99901		128–365	CR	24.7	1.84E - 01	-2.64E+02	20.4	157	0.99978
			MH	34.4	7.40E+00	-2.33E+02	30.1	151	0.99901

Table 15 A	ntibacterial and an	ititungal activity dat	a of the Schiff base (HL)	and its complexes			
Compound	Conc. (µg/ml)	Gram positive ba	cteria	Gram negative bac	teria	Fungi	
		Bacillus cereus	Staphylococcus aureus	Escherichia coli	Klebsiella pneumoniae	Aspergillus niger	Alternaria alternata
HL	50	-ve	-ve	ve	-ve	-ve	-ve
	100	-ve	-ve	-ve	-ve	-ve	-ve
	150	-ve	-ve	-ve	-ve	-ve	-ve
1	50	-ve	4	2	10	-ve	10
	100	-ve	8	-ve	14	-ve	10
	150	-ve	8	-ve	10	-ve	10
2	50	-ve	5	-ve	14	3	10
	100	-ve	5	-ve	10	-ve	10
	150	-ve	4	-ve	10	-ve	14
3	50	-ve	2	-ve	10	-ve	10
	100	-ve	2	-ve	10	-ve	10
	150	-ve	2	-ve	10	-ve	10
4	50	-ve	-ve	-ve	-ve	-ve	-ve
	100	-ve	-ve	-ve	-ve	-ve	-ve
	150	-ve	-ve	-ve	-ve	-ve	6
S	50	-ve	20	-ve	10	3	4
	100	-ve	20	-ve	14	3	14
	150	-ve	20	-ve	20	3	14
The results w	vere recorded as th	ne diameter of the in	nhibition zone (mm)				

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Numbers as given in Table 1

attach to the bacterial cells at a specific site, from which it can interfere with their growth [16]. The antimicrobial activity of the Schiff base ligand (**HL**) and its metal complexes were tested against some local bacteria and fungi [62]. More than one test organism was used to increase the chance of detection of their antimicrobial activities. The organisms used in the present investigation included two Gram positive bacteria (*B. cereus* and *S. aureus*) and two Gram negative bacteria (*E. coli*)



Fig. 11 The ligand **HL** (*green* in **a** and *blue* in **b**) in interaction with receptors of the crystal structure of *E. coli* (3t88) and the crystal structure of *S. aureus* (3q8u). (For interpretation of the references to *color* in this figure legend, the reader is referred to the web version of this article). (Color figure online)

Receptors	Est. free energy of binding (kcal mol ⁻¹)	Est. inhibition constant (<i>K_i</i>) (μM)	vdW+ bond+ desolv energy (kcal mol ⁻¹)	Electrostatic energy (kcal mol ⁻¹)	Total intercooled energy (kcal mol ⁻¹)	Interact surface
3t88	-6.91	8.59	-7.77	-0.07	-7.84	899.146
3q8u	-4.81	296.07	-5.61	-0.01	-5.62	692.879

Table 16 Energy values obtained in docking calculations of ligand (**HL**) with receptors of the crystal structure of *E. coli* (3t88) and crystal structure of *S. aureus* (3q8u)



Fig. 12 HB plot of interaction between ligand **HL** and receptor **a** crystal structure of *E. coli* (3t88) and **b** crystal structure of *S. aureus* (3q8u)

and *K. pneumoniae*) in addition to different kinds of fungi (*A. niger* and *A. alternara*).

The results of the antibacterial activities of the synthesized compounds are recorded in Table 15. Schiff base 4-(((2-hydroxynaphthalen-1-yl) methylene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (HL) and compound (4) have no antimicrobial activities. All of the synthesized complexes were found to have no antibacterial activities against B. cereus and E. coli, but compound (1) was found to have low antibacterial activity at a conc. of 50 µg/mL (inhibition zone = 2 mm) against *E. coli*. In the case of *S. aureus*, compound (1) was found to have antibacterial activities at a conc. of 50 μ g/mL (inhibition zone = 4 mm) and at 100 and 150 μ g/mL (inhibition zone = 8 mm); compound (2) has low antibacterial activities at 50 and 100 μ g/mL (inhibition zone = 5 mm) and at 150 μ g/mL (inhibition zone = 4 mm); compound (3) has low antibacterial activities (inhibition zone = 2 mm); and compound (5) has higher antibacterial activities at 50,100, and 150 μ g/mL (inhibition zone = 20 mm). In the case of K. pneumonia, compound (1) has antibacterial activities at 50 and 150 μ g/mL (inhibition zone = 10 mm) and at $100 \ \mu g/mL$ (inhibition zone = 14 mm); compound (2) has antibacterial activities at 50 µg/mL (inhibition zone = 14 mm) and at 100 and 150 µg/mL (inhibition zone = 10 mm; compound (3) has good antibacterial activities at all concentrations (inhibition zone = 10 mm); and compound (5) has higher antibacterial activities at 50 μ g/mL (inhibition zone = 10 mm), and at 100 μ g/mL (inhibition zone = 14 mm) and at 150 µg/mL (inhibition zone = 20 mm).

The results of the antifungal activities of the synthesized compounds are recorded in Table 15. The Schiff base ligand (**HL**) has no antifungal activities. In the case of *A. alternaria*, compounds (1) and (3) have antifungal activities at all concentrations

Fig. 13 A 2-D plot of interaction between ligand HL and receptor **a** crystal structure of *E*. *coli* (3t88) and **b** crystal structure of *S*. *aureus* (3q8u)

Fig. 14 Absorption spectra of the Schiff base ligand (**HL**) and its metal complexes (1–5) in buffer at pH 7.2 at 25 °C in the presence of an increasing amount of CT-DNA. *Arrows* indicate the changes in absorbance upon increasing the CT-DNA concentration

(inhibition zone = 10 mm); compound (2) has antifungal activities at 50 and 100 μ g/mL (inhibition zone = 10 mm) and at 150 μ g/mL (inhibition zone = 14 mm); compound (4) has antifungal activities at 150 μ g/mL (inhibition zone = 6 mm); and compound (5) has higher antifungal activities at 100 and 150 μ g/mL (inhibition zone = 14 mm). Synthesized complexes were found to have no antifungal activities against *A. niger*, but compound (5) was found to have low

Fig. 15 Plot of $[DNA]/(\epsilon_a - \epsilon_f)$ as a function of DNA concentration as determined from the absorption spectral data of the Schiff base ligand (HL) and its metal complexes (1–5)

antifungal activities at all concentrations (inhibition zone = 3 mm), and compound (2) was found to have low antifungal activities at 50 μ g/mL (inhibition zone = 3 mm).

Molecular docking

The focus of molecular docking is to simulate the molecular recognition process. Molecular docking aims to achieve an optimized conformation for both the protein and drug with relative orientation between them such that the free energy of the overall system is minimized [63, 64]. In this context, we used molecular docking between ligand (**HL**) and crystal structure of *E. coli* (3t88) and crystal structure of *S. aureus* (3q8u). The results showed a possible arrangement between ligand (**HL**) and 3t88 and 3q8u receptors. The docking study showed a favorable interaction between the ligand (**HL**) and the receptors (3t88 and 3q8u) as shown in Fig. 11, and the calculated energy is listed in Table 16. According to the results obtained in this study, the HB plot curve indicates that the ligand **HL** binds to the proteins with hydrogen bond interactions and decomposed interaction energies in kcal mol⁻¹ that exist between ligand (**HL**) with 3t88 and 3q8u receptors as shown in Fig. 12. The 2-D plot curves of docking with ligand (**HL**) are shown in Fig. 13. The ligand (**HL**) shows best interaction with 3t88 receptor other than the 3q8u receptor.

DNA binding studies

The intrinsic binding constant to CT-DNA by monitoring the absorption intensity of the charge transfer spectral bands near 383 nm for the ligand (HL) was determined. It was determined to be near 384, 388, 385, 388, and 385 nm for complexes (1-5), respectively. The absorption spectra of the ligand with increasing concentration of CT-DNA in the range 340-460 nm are shown in Fig. 14. Upon the addition of an increasing amount of CT-DNA, a significant "hyperchromic" effect was observed accompanied by a moderate red shift of 2-3 nm, indicative of stabilization of the DNA helix. These spectral characteristics suggest that the ligand bind either to the external contact (electrostatic binding) or to the major and minor grooves of DNA. The intrinsic binding constants (K_b) of the ligand (HL) and its complexes (1–5) with CT-DNA were determined (Eq. 1) [65]. The $K_{\rm b}$ values obtained from the absorption spectral technique were calculated as 5.52×10^6 M⁻¹ for ligand (HL) and 2.38×10^4 , 1.7×10^4 , 1.05×10^4 , 1.10×10^4 and 1.07×10^4 M⁻¹ for complexes (1–5), respectively. Plot of [DNA]/ $(\varepsilon_a - \varepsilon f)$ as a function of DNA concentration as determined from the absorption spectral data is shown in Fig. 15. The results indicate that the high value of $K_{\rm b}$ for ligand supports the idea that intercalative π stacking interactions of the ligand with DNA are essential for their efficient electron transfer reaction, the low values of k_b for complexes indicate weak or moderate strength of binding [66]. Herein, the high K_b value in complex (1) indicates that a chloro substituent affects positively the ability of the complex to bind to CT-DNA, since it can increase the hydrophobic properties. In addition, the chloro atom leads to a slightly changed dipole of the complex, thus increasing dipole-dipole interactions in the binding site, and it may even operate as a hydrogen-bond acceptor [67].

Conclusions

The Schiff base ligand acts as a neutral/monobasic bidentate/tridentate forming a five/six-membered chelating ring towards the metal ions, bonding through azomethine nitrogen, exocyclic carbonyl oxygen and/or deprotonated phenolic

oxygen atoms. On the basis of all the spectral data and conductance measurements, it is observed that there is the presence of an anion, viz., CI^- , NO_3^- or SO_4^- in the coordination sphere. The XRD studies show that the ligand and Cu(II) complex (1) show a polycrystalline with monoclinic crystal structure. The thermal properties of the Schiff base ligand and its metal complexes were investigated by thermogravimetry. The molecular structures of the ligand (HL) and its complexes (1–5) have been discussed. It was found that the form (A) is more stable than other forms. Molecular docking was used to predict the binding between the HL ligand and the receptors of the crystal structure of *E. coli* (3T88) and the crystal structure of *S. aureus* (3q8u). It was found that the ligand (HL) shows best interaction with 3t88 receptor other than the 3q8u receptor.

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