FULL PAPER



Preparation, characterization, biological activity, density functional theory calculations and molecular docking of chelates of diazo ligand derived from *m*-phenylenediamine and *p*-chlorophenol

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ligand, 2,2'-(1,3-phenylenebis(diazene-2,1-diyl))bis(4novel dye А azo chlorophenol), was synthesized from the diazotization of *m*-phenelyenediamine and coupling with *p*-chlorophenol in alkaline medium. Mononuclear Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of the azo ligand (H₂L) were prepared and characterized using elemental analyses, infrared spectroscopy, electron spin resonance, magnetic susceptibility, conductance measurements and thermal analyses. The UV-visible, ¹H NMR and mass spectra of the ligand and its chelates were also recorded. The analytical data showed that the metal-to-ligand ratio in the mononuclear azo complexes was 1:1. Diffuse reflectance and magnetic moment measurements revealed the complexes to have octahedral geometry. The infrared spectral data showed that the chelation behaviour of the ligand towards transition metal ions was through phenolic oxygen and azo nitrogen atoms. The electronic spectral results indicated the existence of $\pi \rightarrow \pi^*$ (phenyl rings) and $n \rightarrow \pi^*$ (-N=N) and confirmed the mentioned structure. Molar conductivity revealed the non-electrolytic nature of all chelates. The presence of water molecules in all complexes was supported by thermal studies. Molecular docking was used to predict the binding between H₂L and the receptors of breast cancer mutant 3hb5oxidoreductase, crystal structure of Escherichia coli (3 t88) and crystal structure of Staphylococcus aureus (3q8u). The molecular and electronic structure of H₂L was optimized theoretically and the quantum chemical parameters were calculated. In addition, the effects of the H₂L azo ligand and its complexes on the inhibition of bacterial or fungal growth were evaluated. The prepared complexes had enhanced activity against bacterial or fungal growth compared to the H₂L azo ligand.

KEYWORDS

azo ligand, biological activity, molecular docking, *m*-phenelyenediamine, *p*-chlorophenol, quantum chemical parameters, spectral studies

2 of 19 WILEY-Organometallic Chemistry 1 INTRODUCTION

Coordination chemistry is essentially the chemistry of the electron-accepting behaviour of metal ions surrounded by ligands. The wide spectrum of colour exhibited by coordination compounds, and the puzzle of their structures which are manifestations of the coordination number of the metal ion and the ligational behaviour of the complexing agents, make their investigation very challenging and at the same time interesting. Coordination compounds find wide applications in the fields of medicine, analytical chemistry and industry. Azo compounds are versatile molecules and have received much attention in research, both fundamental and applied.^[1] Regarding the industrial importance of metalized azo dyes relative to their structures, they can be classified into two main types: those in which the azo group participates in coordination to the metal ion with formation of a chelate ring and those in which it does not.^[2] Azo compounds are known to be involved in a number of biological reactions, such as inhibition of DNA and RNA, protein synthesis, nitrogen fixation and carcinogenesis.^[3]

The present article focuses on the synthesis and characterization of a novel azo dye ligand and its Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes. The structures were confirmed using elemental analysis, and infrared (IR), UV–visible, electron spin resonance (ESR), ¹H NMR and diffuse reflectance spectral data. X-ray diffraction (XRD), molar conductance measurements and thermal analyses were utilized for the characterization of the synthesized ligand and its complexes. The molecular and electronic structure of the azo dye ligand was optimized theoretically and the quantum chemical parameters were calculated. Molecular docking was used to predict the binding between the azo dye ligand and the receptors of breast cancer mutant 3hb5oxidoreductase, crystal structure of *Escherichia coli* (3 t88) and crystal structure of *Staphylococcus aureus* (3q8u).

2 | EXPERIMENTAL

2.1 | Materials and measurements

2.1.1 | Materials and reagents

All chemicals used in this study were of pure grade and of highest purity available and used without further purification. The chemicals used included *m*-phenylenediamine (Sigma), *p*-chlorophenol (Sigma), CrCl₃·6H₂O (Sigma), MnCl₂·2H₂O (Sigma), NiCl₂·6H₂O (BDH), FeCl₃·6H₂O (Prolabo), CoCl₂·6H₂O (Aldrich), CuCl₂·2H₂O (Merck), ZnCl₂ (Strem Chemicals) and CdCl₂ (Aldrich). Organic solvents were spectroscopically pure from BDH and included ethanol and dimethylformamide (DMF). Hydrochloric acid, sodium nitrite and sodium acetate (AR) were used.

2.1.2 | Solutions

Stock solutions of metal complexes $(1 \times 10^{-3} \text{ M})$ were prepared by dissolving an accurately weighed amount of complex in DMF for measuring conductivity. Solutions of the azo ligand and metal complexes ranging from 1×10^{-4} to 1×10^{-5} M were prepared by accurate dilution of the prepared stock solutions to measure UV–visible spectra.

2.1.3 | Measurements

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Egypt, using a CHNS-932 (LECO) Vario elemental analyser. Analyses of metals followed the dissolution of the solid complexes in concentrated HNO₃, neutralizing the diluted aqueous solutions with ammonia and titrating the metal solutions with EDTA.

¹H NMR spectra, with samples as solutions in deuterated dimethylsulfoxide (DMSO- d_6), were recorded with a 300 MHz Varian-Oxford Mercury at room temperature using tetramethylsilane (TMS) as an internal standard. ESR spectra were recorded with a JES-FE2XG ESR spectrophotometer at the Microanalytical Center, Tanta University. Powder XRD analyses were carried out using a Philips Analytical X-ray BV diffractometer type PW 1840. Radiation was provided by a copper target (Cu anode 2000 W) high-intensity X-ray tube operated at 40 kV and 25 mA. Divergence and receiving slits were 1 and 0.2, respectively. Mass spectra were recorded using the EI technique at 70 eV with an MS-5988 GS-MS Hewlett-Packard instrument at the Microanalytical Center, National Center for Research, Egypt. IR spectra were recorded with a PerkinElmer 1650 spectrometer (400-4000 cm⁻¹) in KBr pellets. Electronic spectra were recorded in DMSO at room temperature with a Shimadzu UV-visible mini-1240 spectrophotometer. Molar magnetic susceptibility was measured with powdered samples using the Faraday method. Diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)₄] was used as a calibrant. Molar conductivities of 10^{-3} M solutions of the solid complexes in DMF were measured using a Jenway 4010 conductivity meter. Thermogravimetric (TG) and differential TG (DTG) analyses of the solid complexes were carried out from room temperature to 1000 °C using a Shimadzu TG-50H thermal analyser. Diffused reflectance spectral analyses were carried out at the Microanalytical Center, Cairo University, Egypt.

In the study simulating the actual docking process, the ligand–protein pairwise interaction energies were calculated using Docking Server.^[4] The MMFF94 force field was used for energy minimization of ligand molecule using Docking Server. Gasteiger partial charges were added to the (L) atoms. Docking calculations were carried out on (L) protein

model. Essential hydrogen atoms, Kollman united atom type charges and solvation parameters were added with the aid of AutoDock tools.^[5] AutoDock parameter set- and distance-dependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively. The molecular structures of the compounds were optimized using the HF method with 3-21G basis set. The molecules were built with PerkinElmer ChemBio Draw and optimized using PerkinElmer ChemBio3D software.^[6–8] Quantum chemical parameters such as the highest occupied molecular orbital energy ($E_{\rm LUMO}$), lowest unoccupied molecular orbital energy ($E_{\rm LUMO}$) and HOMO–LUMO energy gap (ΔE) for the investigated molecules were calculated.

The antimicrobial activities were determined at the Microanalytical Center, Cairo University, Egypt.

2.2 | Synthesis of 2,2'-(1,3-phenylenebis (diazene-2,1-diyl))bis(4-chlorophenol) (H₂L)

m-Phenylenediamine (2 g, 0.01 mol) was dissolved in 50 ml of ethanol. Concentrated hydrochloric acid (10 ml) was diluted with about 60 g of crushed ice and then dropwise addition of the *m*-phenylenediamine solution to the crushed ice was carried out. To this cold solution was added sodium nitrite (5 g in 20 ml of water) and stirred for about 1 h until a dark reddish coloured solution was obtained. The coupling agent *p*-chlorophenol (4.7 g, 0.02 mol) dissolved in 50 ml of ethanol was then added to the cold mixture. The resulting solution was stirred well and sodium acetate (3 g) was added for neutralization. The dye was washed with ethanol and collected by vacuum filtration. The compound had a high melting point and it was found to be air stable.^[9] The preparation is shown in Scheme 1.

Yield 94%; m.p. > 300 °C; reddish brown solid. Anal. Calcd for $C_{18}H_{12}N_4Cl_2O_2$ (%): C, 55.80; H, 3.10; N, 14.47; Cl, 18.34. Found (%): C, 55.24; H, 3.39; N, 14.78; Cl, 18.33. IR (ν , cm⁻¹): 3432br (OH), 1596sh (N=N), 1230s (C–O phenolic). ¹H NMR (300 MHz, DMSO- d_6 , δ , ppm): 6.84–6.98 (m, 10H, Ar-H) and the proton of phenolic-OH disappeared due to the phenol acidic character. UV–visible (λ_{max} , nm): 398 (π – π^*), 284 (n– π^*).

2.3 | Synthesis of metal complexes

Azo ligand H_2L (0.5 g, 1.29 mmol) was dissolved in a mixture of 30 ml (2:1 ν/ν) of DMF and ethanol. Then the metal chloride salts (1.29 mmol) were each dissolved in 10 ml of ethanol and added to the clear solution of the ligand. The precipitated complexes were filtered and collected. The synthesis route is shown in Scheme 2.

$2.3.1 \mid [CrLCl(H_2O)]H_2O$

Yield 88%; orange solid; m.p. > 300 °C. Anal. Calcd for Cr (C₁₈H₁₄Cl₃N₄O₄) (%): C, 42.48; H, 2.75; N, 11.01; Cl, 20.94; Cr, 10.23. Found (%): C, 42.75; H, 2.81; N, 11.32; Cl,21.01; Cr, 10.27. IR (*ν*, cm⁻¹): 3425br (OH), 1653 m (N=N), 1274s (C–O phenolic), 510w (M–O coordinated water), 423w (M–N). UV–visible (*λ*_{max}, nm): 288 (*π*–*π**), 391 (n–*π**). Diffuse reflectance: 28 330, 26 710 and 13 688 cm⁻¹ for ⁴A_{2g}(F) → ⁴T_{2g}(F), ⁴A_{2g}(F) → ⁴T_{2g}(F) and ⁴A_{2g}(F) → ⁴T_{2g}(P) transitions.

2.3.2 | [MnL(H₂O)₂]

Yield 85%; grey solid; m.p. > 300 °C. Anal. Calcd for Mn (C₁₈H₁₄Cl₂N₄O₄) (%): C, 45.38; H, 2.94; N, 11.76; Cl, 14.92; Mn, 11.55. Found (%): C, 45.72; H, 3.05; N, 11.75; Cl, 14.99; Mn, 11.77. IR (ν , cm⁻¹): 3422br (OH), 1630 m (N=N), 1250s (C–O phenolic), 528w (M–O coordinated water), 408w (M–N). UV–visible (λ_{max} , nm): 261 (π – π *), 384 (n– π *). Diffuse reflectance: 27 670, 20 955 and 15 220 cm⁻¹ for ⁴T_{1g} \rightarrow ⁶A_{1g}, ⁴T_{2g}(G) \rightarrow ⁶A_{1g} and ⁴T_{1g} (D) \rightarrow ⁶A_{1g} transitions.

2.3.3 | [FeLCl(H₂O)]

Yield 86%; dark brown solid; m.p. > 300 °C. Anal. Calcd for Fe(C₁₈H₁₂Cl₃N₄O₃) (%): C, 43.68; H, 2.43; N, 11.32; Cl, 21.54; Fe, 11.32. Found (%): C, 43.45; H, 2.82; N, 11.22; Cl, 21.42; Fe, 11.04. IR (*ν*, cm⁻¹): 3418br (OH), 1652sh (N=N), 1263s (C–O phenolic), 537w (M–O coordinated water), 436w (M–N). UV–visible (*λ*_{max}, nm): 276 (*π*–*π**), 375 (*n*–*π**). Diffuse reflectance: 19 950, 21 260 and 25 478 cm⁻¹ for ${}^{6}A_{1g} \rightarrow T_{2g}$ (G), ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$ and charge transfer, respectively.



SCHEME 1 Preparation of azo ligand (H₂L)



SCHEME 2 Preparation of metal complexes

$2.3.4 + [CoL(H_2O)_2]$

Yield 90%; pale orange solid; m.p. > 300 °C. Anal. Calcd for Co(C₁₈H₁₄Cl₂N₄O₄) (%): C, 45.18; H, 2.93; N, 11.72; Cl, 21.54;Co, 12.01. Found (%): C, 45.94; H, 2.94; N, 11.87; Cl, 15.01; Co, 12.23. IR (ν , cm⁻¹): 3433br (OH), 1657sh (N=N), 1255s (C–O phenolic), 513w (M–O coordinated water), 421w (M–N). UV–visible (λ_{max} , nm): 268 (π – π^*), 353 (n– π^*). Diffuse reflectance: 21 811, 15 630 and 12 715 cm⁻¹ for ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions.

$2.3.5 \mid [NiL(H_2O)_2]2H_2O$

Yield 87%; pale brown solid; m.p. > 300 °C. Anal. Calcd for Ni(C₁₈H₁₈Cl₂N₄O₆) (%): C, 41.94; H, 3.49; N, 10.87; Cl, 13.79; Ni, 11.26. Found (%): C, 42.04; H, 3.94; N, 10.87; Cl, 13.57; Ni, 11.40. IR (ν , cm⁻¹): 3349br (OH), 1611 m (N=N), 1253s (C–O phenolic), 550w (M–O coordinated water), 463w (M–N). UV–visible (λ_{max} , nm): 288 (π – π *), 375 (n– π *). Diffuse reflectance: 26 440, 20 360, 14 360 and 13 340 cm⁻¹ for ligand–metal charge transfer (LMCT), ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}$ transitions.

$2.3.6 \mid [CuL(H_2O)_2]$

Yield 89%; brown solid; m.p. > 300 °C. Anal. Calcd for Cu(C₁₈H₁₄Cl₂N₄O₄) (%): C, 44.81; H, 2.90; N, 11.62; Cl, 14.3; Cu, 13.12. Found (%): C, 44.57; H, 2.92; N, 11.77; Cl, 14.33; Cu, 13.22. IR (ν , cm⁻¹): 3331br (OH), 1606 m (N=N), 1255s (C–O phenolic), 598w (M–O coordinated water), 513w (M–N). UV–visible (λ_{max} , nm): 272 (π – π *), 340 (n– π *). Diffuse reflectance: 24 813 and 13 441 cm⁻¹ for ²B_{1g} \rightarrow ²B_{2g}, ²B_{1g} \rightarrow ²E_g and ²B_{1g} \rightarrow ²A_{1g} transitions and 27 915 cm⁻¹ for LMCT.

$2.3.7 \mid [ZnL(H_2O)_2]$

Yield 92%; orange solid; m.p. > 300 °C. Anal. Calcd for Zn(C₁₈H₁₄Cl₂N₄O₄) (%): C, 44.63; H, 2.89; N, 11.57; Cl, 14.66; Zn, 13.02. Found (%): C, 44.45; H, 2.91; N, 11.72; Cl, 15.05; Zn, 13.11. IR (ν , cm⁻¹): 3440br (OH), 1623 m (N=N), 1230s (C–O phenolic), 543w (M–O coordinated

water), 465w (M–N). UV-visible (λ_{max} , nm): 276 (π – π^*), 375 (n– π^*).

$2.3.8 \mid [CdL(H_2O)_2]H_2O$

Yield 95%; red solid; m.p. > 300 °C. Anal. Calcd for Cd(C₁₈H₁₆Cl₂N₄O₅) (%): C, 39.20; H, 2.90; N, 10.16; Cl, 12.89; Cd, 20.32. Found (%): C, 38.92; H, 2.76; N, 9.85; Cl, 13.00; Cd, 20.71. IR (ν , cm⁻¹): 3342br (OH), 1616 m (N=N), 1207s (C–O phenolic), 554w (M–O coordinated water), 451w (M–N). UV–visible (λ_{max} , nm): 283, 339 (π – π *), 410 (n– π *).

2.4 | Spectrophotometric studies

Absorption spectra were recorded for 1×10^{-4} and 5×10^{-5} M solutions of the free azo ligand and its metal complexes dissolved in DMF. The spectra were scanned within the wavelength range from 200 to 700 nm.

2.5 | Antimicrobial activity

Filter paper discs (5 mm) were transferred into 250 ml flasks containing 20 ml of working volume of test solution (100 mg ml⁻¹). All flasks were autoclaved for 20 min at 121 °C. LB agar media surfaces were inoculated with four investigated bacteria (Gram-positive bacteria: Bacillus subtilis and Staphylococcus aureus; Gram-negative bacteria: Neisseria gonorrhoeae and Escherichia coli) and one strain of fungus (Candida albicans) using the diffusion agar technique, then transferred to a saturated disc with a test solution in the centre of Petri dishes (agar plates). All compounds were placed at four equidistant places at a distance of 2 cm from the centre in the inoculated Petri plates. DMSO served as control. Finally, all these Petri dishes were incubated at 25 °C for 48 h where clear or inhibition zones were detected around each disc. A control flask of the experiment was designed to perform under the same conditions as described previously for each microorganism but with DMF solution only. By subtracting the diameter of the inhibition zone resulting from DMF from that obtained in each case, the antibacterial activity could be calculated.^[10,11] Amikacin and ketokonazole were used as reference compounds for antibacterial and antifungal activities, respectively. All experiments were performed in triplicate and data plotted were the mean values.

2.6 | Computational methodology

The electronic structure calculations of H_2L were carried out using the Gaussian 03 suite of programs.^[12] They were fully optimized employing density functional theory (DFT)-based B3LYP method along with the LANL2DZ basis set. In order to incorporate the effect of the solvent around the molecule, the time-dependent DFT (TD-DFT) method (along with LANL2DZ basic set) was used to calculate the electronic absorption spectra of the ligand. The contributions of molecular orbitals on HOMO and LUMO were also calculated.

2.7 | Molecular docking

In the study simulating the actual docking process, the ligand–protein pairwise interaction energies were calculated using Docking Server.^[13] The MMFF94 force field was used for energy minimization of ligand molecule using Docking Server. Gasteiger partial charges were added to the H₂L atoms. Docking calculations were carried out on H₂L protein model. Essential hydrogen atoms, Kollman united atom type charges and solvation parameters were added with the aid of AutoDock tools.^[14] AutoDock parameter set- and distance-dependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization of free Azo ligand (H_2L)

The results of elemental analyses (C, H and N) were compared with the molecular formula. The prepared ligand (Figure 1) was stable at room temperature and possessed good keeping qualities. It was a non-hygroscopic solid and insoluble in ethanol and water but soluble in DMF and DMSO. H₂L and its metal complexes have high melting points. From the elemental analyses data, it was found that the theoretical values were in agreement with the found values. Also, it was confirmed that the metal-to-ligand ratio was 1:1. The IR spectrum of the free azo ligand was recorded in the range 400–4000 cm⁻¹. The strong band observed at 1596 cm⁻¹ was assigned to the ν (N=N) stretching vibration.^[15] The broad band at 3436 cm⁻¹ was attributed to





 ν (O–H) stretching vibration. Another band observed at 1230 cm⁻¹ for the diazo ligand was attributed to ν (C–O).

The ¹H NMR spectrum of H₂L in DMSO- d_6 exhibited signals at 6.84–6.98 ppm (m, 10H, Ar-H)^[13] that can be assigned to protons of aromatic rings. Unfortunately, the proton of (OH) disappeared in the spectrum of the azo ligand due to the phenol acidic character. Phenol was sufficiently acidic to have recognizably acidic properties even if it was still a very weak acid. A hydrogen ion can break away from the –OH group and transfer to a base. Phenol is a very weak acid and the position of equilibrium lies well to the left, for example, in water solution as shown in Scheme 3.^[16]

The mass spectrum of H_2L showed accurate parent molecular ion peak at m/z 387 amu, matching with the theoretical molecular weight. Also, the mass spectrum displayed multiple peaks corresponding to successive degradation of the ligand.

3.2 | Characterization of metal complexes

3.2.1 | Elemental analyses

Composition and structures of the ligand and metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions were subjected to elemental analyses (C, H, N and metal content), IR, magnetic moment studies, molar conductance and thermal analyses (TG and DTG), to identify their tentative formulae in a trial to elucidate their molecular structures. The results of elemental analyses suggested the formulae [M(L)Cl(H₂O)]·*n*H₂O (M = Cr(III) and Fe(III)) and [M(L)(H₂O)₂]·*n*H₂O (M = Co(II), Ni(II), Cu(II), Mn(II), Zn(II) and Cd(II)). Based on the elemental analyses, all complexes were of stoichiometric ratio 1:1 and of ML type. The diazo ligand and its metal complexes were stable at room temperature and soluble in common organic solvents such as DMSO and DMF, but insoluble in ethanol and water.

3.2.2 | Molar conductance measurements

By using the relation ($A_{\rm m} = K/C$), the molar conductance of the complexes ($A_{\rm m}$) can calculated, where *C* is the molar concentration of the metal complex solutions. The chelates were dissolved in DMF and the molar conductivities of 10^{-3} M solutions at 25 ± 2 °C were measured using the recommended procedure. It is concluded from the results that the molar conductance values fall in the range $11-30 \ \Omega^{-1} \ \text{mol}^{-1} \ \text{cm}^2$ indicative of their non-electrolytic nature.^[17–19] The interpretation concerning decreasing of conductivity values

$$\begin{array}{c} \mathsf{OH} \\ \\ \\ \\ \\ \\ \\ \end{array} + \mathsf{H}_2\mathsf{O} \end{array} \xrightarrow{\mathsf{O}^-} + \mathsf{H}_3\mathsf{O}^+$$



6 of 19 | WILEY-Organometallic Chemistry

can comes back to the deprotonation of phenolic OH group for p-chlorophenol.

3.2.3 | IR spectral studies

In the absence of a powerful technique such as X-ray crystallography, IR spectroscopy has proven to be the most suitable technique to give enough information to elucidate the nature of bonding of ligand to metal ion. As mentioned, the ligand had different coordinating sites. IR spectroscopy has proven to be, in this particular case, a suitable technique to give enough information to elucidate the way of bonding of the ligand to the metal ions. There were some guide peaks in the spectrum of the free ligand which were of great help for achieving this goal. The positions and/or the intensities of these peaks were expected to change upon complex formation.^[20] The characteristic peaks of the free ligand and its metal complexes are detailed in Section 1, where the band assignments of the guide bands (those affected by coordination) are given. Thus a detailed interpretation of IR spectra of these and the effect of binding of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions on the vibration frequencies of the free ligand are discussed.

The band due to ν (OH) was broadened in the spectra of all the complexes indicating coordination through the phenolic OH group which was confirmed from the shift in the position of in-plane ν (OH) of the ligand (3432 cm⁻¹) which was found to be shifted into the range 3331–3440 cm⁻¹ in the spectra of the complexes. Also, it was evidenced from the phenolic ν (C–O) stretching band^[20–24] which was found to be shifted into the range 1207–1274 cm⁻¹ for the complexes (1230 cm⁻¹ for the free ligand). This suggested the weakening of ν (C–O) and formation of stronger M–O bond.^[18–21] All complexes displayed bands in the region 510–598 cm⁻¹ which were assigned to ν (M–O) stretching vibration.

The participation of N=N group in bonding was confirmed from the shift in the position of the in-plane N=N of the ligand (1596 cm⁻¹) which was found to be shifted into the range 1606–1657 cm⁻¹. Also the IR spectra of the complexes showed other new bands at 408–465 cm⁻¹, assignable to ν (M–N) stretching vibrations. Therefore, from the IR spectra it was concluded that the H₂L ligand behaves as a bi-negative tetradentate ligand coordinated to the metal ions via two deprotonated phenolic oxygens and two azo nitrogens.

3.2.4 | ¹H NMR spectral studies

A survey of the literature revealed that NMR spectroscopy has proved useful in establishing the nature and structure of H_2L as well as its complexes in solution. The ¹H NMR spectrum of H_2L was recorded in DMSO- d_6 solution using TMS as internal standard. The spectra of the complexes were examined in comparison with that of the parent ligand. The ¹H NMR spectral data for the azo ligand and its Zn(II) metal chelate are discussed. Upon examination it was found that uncoordinated H₂L had the peak positions and corresponding assignments of multiplet signals at 6.84–6.98 ppm (m, 10H, Ar-H)which can assigned to protons of aromatic rings and the proton of (OH) which disappeared due to the phenol acidic character (Scheme 3).^[17] On comparing the peaks of the free azo dye ligand and its Zn(II) complex, it was observed that aromatic protons exhibited a shift at 7.43–7.96 ppm leading to the observation that H₂L coordinated to the metal ions through the azo nitrogen. The signal of the –OH proton in phenolic group of *p*-chlorophenol disappeared due to coordination to metal ions.^[17]

3.2.5 | Spectrophotometric studies

UV-visible spectrum provides the most detailed information about the electronic structure of a compound. The UVvisible spectra of the ligand and its complexes were recorded in DMF and ethanol (2:1 v/v) at room temperature. The UVvisible spectrum of diazo ligand exhibited a band at 284 nm which was attributed to π - π * transition within the ligand.^[25] In the spectra of the complexes, $\pi - \pi^*$ transition band was found at 260-285 nm. On the other hand, the absorption band at 398 nm for the H₂L ligand can be attributed to $n-\pi^*$ transition between lone pair of electrons. The $n-\pi^*$ transition band was shifted to 340-410 nm in the spectra of the metal complexes. The absorption shift and intensity change in the spectra of the metal complexes most likely originate from metalation which increases the conjugation and delocalization of the whole electronic system and results in an energy change of the π - π ^{*} and n- π ^{*} transitions of the conjugated chromospheres.^[26-31]

The results clearly indicated that the ligand coordinated to Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions, which was in accordance with the results of the other spectral investigations. Furthermore, according to modern molecular orbital theory,^[28] any factors that can influence the electronic density of a conjugated system must result in a bathochromic or hypsochromic shift of absorption bands. Here, in the case of the metal complexes with the same ligand, the main reason for the shifts was generally related to the electronegativity of the different metal ions.^[27,31]

3.2.6 | Magnetic susceptibility and electronic spectral studies

The magnetic moment value of 4.81 BM for the Cr(III) complex suggested an octahedral geometry. The predominant electronic spectral bands at 28 330, 26 710 and 13 688 cm⁻¹ for ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ and

 ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(P)$ transitions, respectively, also pointed to an octahedral geometry. The magnetic moment of the Mn(II) complex was 5.31 BM, in the range of octahedral geometry.^[32–37] The spectrum of the Mn(II) complex showed three medium intensity bands at 27 670, 20 955 and 15 220 cm⁻¹ which can be assigned to ${}^{4}T_{1g} \rightarrow {}^{6}A_{1g}$, ${}^{4}T_{2g}(G) \rightarrow {}^{6}A_{1g}$ and ${}^{4}T_{1g}(D) \rightarrow {}^{6}A_{1g}$ transitions, respectively, indicative of Mn(II) ion in an octahedral field.^[36,37]

The electronic absorption spectrum of the Fe(III) complex showed three weak bands at 19 950, 21 260 and 25 478 cm⁻¹, which may be assigned to the ${}^{6}A_{1g} \rightarrow T_{2g}(G)$ and ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$ transitions and charge transfer, respectively. The electronic transitions together with the magnetic moment value of 5.51 BM for the Fe(III) complex suggested an octahedral geometry.^[32–37]

The three bands in the electronic spectrum of the Co(II) complex at 21 811, 15 630 and 12 715 cm⁻¹ were assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions, respectively.^[37] Also, the Ni(II) complex exhibited four electronic spectral bands at 26 440, 20 360, 14 360 and 13 340 cm⁻¹ which may be assigned to LMCT, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}$ transitions, respectively. The positions of these bands suggested an octahedral geometry around the Co(II) and Ni(II) ions.^[32-36]

The Cu(II) complex showed broad bands at 24 813 and 13 441 cm⁻¹ which may be assigned to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions, and indicative of an octahedral geometry around the Cu(II) ion.^[36,37] Furthermore, it showed a broad band at 27 915 cm⁻¹ which was assigned to LMCT excitation. The Co(II), Ni(II) and Cu(II) complexes were found to have magnetic moment values of 5.43, 3.14 and 1.82 BM, respectively, indicating octahedral geometry. The Zn(II) and Cd(II) complexes were diamagnetic. According to the empirical formulae, an octahedral geometry was proposed for these chelates.

3.2.7 | ESR studies of Cu(II) complex

ESR studies of paramagnetic transition metal(II) complexes give information about the distribution of unpaired electrons and hence about the nature of the bonding between metal ion and ligand. The ESR spectrum of the Cu(II) complex was recorded in the solid state at room temperature to obtain further information about its stereochemistry. The *g*-tensor values of the Cu(II) complex ($g_{\parallel} = 1.95$, $g_{\perp} = 1.79$) can be used to derive the ground state. In octahedral geometry of the Cu(II) complex, ${}^{2}B_{1g}$ was considered as the ground state where the unpaired electron lies in $d_{x^2-y^2}$ orbital with g_{\parallel} (1.95) > g_{\perp} (1.79) > g_{e} (2.0023) which was characteristic of octahedral geometry around the Cu(II) ion.^[35–37] The geometric parameter *G* was evaluated using the relation $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between the metal centres. If *G* is greater than 4, the exchange interaction is negligible; *G* less than 4 indicates considerable exchange interaction in solid complexes.^[38]

Kivelson and Neiman showed that, for an ionic environment, g_{\parallel} is normally 2.3 or larger, but for a covalent environment g_{\parallel} is less than 2.3. The g_{\parallel} value for the Cu(II) complex was 1.95; consequently the environment is essentially covalent. In order to quantify the degree of distortion of the Cu(II) complex, the *f* factor ($g_{\parallel}/A_{\parallel}$) obtained from the ESR spectra was selected. Although the *f* factor was considered as an empirical index of tetrahedral distortion,^[39–42] its value ranges between 105 and 135 for square planar complexes, depending on the nature of the coordinated atoms. In the presence of a tetrahedrally distorted structure, the values can be much larger. The g/A value was 142, evidence in support of an octahedral structure for the Cu(II) complex.

The ESR spectrum is shown in Figure 2 of only the Cu(II) complex. The ESR spectra of the solid Fe(III), Co(II) and Ni(II) complexes at room temperature did not show a signal, because of the rapid spin lattice relaxation of the Fe(III), Co(II) and Ni(II) complexes which broadness the lines at higher temperatures.^[43,44] The ESR spectra only showed signals that may be accounted for by the presence of free radicals that can result from the cleavage of any double bond and distribution of the charge on two neighbour atoms.

3.2.8 | TG and DTG analyses

TG and DTG analyses of the ligand and its chelates were used to (i) get information about the thermal stability of these new complexes, (ii) decide whether the water molecules (if present) are inside or outside the inner coordination sphere of the central metal ion and (iii) suggest a general scheme for thermal decomposition of these chelates.

In the present investigation, heating rates were suitably controlled at 10 °C min⁻¹ under nitrogen atmosphere and the weight loss was measured from ambient temperature up to *ca* 1000 °C. The data are listed in Table 1. The weight



FIGURE 2 ESR spectrum of [Cu(L)(H₂O)₂] complex

TABLE 1 Thermoanalytical results (TG and DTG) for H₂L ligand and its metal complexes

Complex	TG range (°C)	DTG max. (°C)	n ^a	Mass loss, estim. (calcd) (%)	Total mass loss, estim. (calcd) (%)	Assignment	Residue
H_2L	30–310 310–1000	207 368, 504	1 2	64.35 (63.30) 35.65 (36.60)	100 (99.90)	Loss of $4C_2H_2$, CO_2 and Cl_2 Loss of $C_9H_4N_4$	_
[Cr(L)Cl(H ₂ O)].H ₂ O	45–140 140–390 390–990	92 226, 344 481	1 2 1	2.00 (2.43) 32.33 (33.10) 46.62 (46.13)	80.95 (81.66)	Loss of H ₂ O Loss of Cl ₂ , H ₂ O and C ₄ H ₄ N ₂ Loss of C ₁₃ H ₈ ClN ₂ O _{0.5}	$C + \frac{1}{2}Cr_2O_3$
$[Mn(L)(H_2O)_2]$	30–260 260–890	177 360, 639	1 2	12.23 (12.97) 66.64 (67.14)	78.87 (80.11)	Loss of 2H ₂ O and C ₂ H ₂ Loss of C ₁₄ H ₁₀ Cl ₂ N ₄ O	2C + MnO
[Fe(L)Cl(H ₂ O)]	45–230 230–990	150 384, 472 633	1 3	8.47 (8.86) 67.48 (68.53)	75.95 (77.39)	Loss of H_2O and C_2H_2 Loss of Cl_2 and $C_{14}H_{10}ClN_2$	$2C + \frac{1}{2}Fe_2O_3$
[Co(L) (H ₂ O) ₂]	30-1000	215, 425	2	81.37 (81.94)	81.37 (81.94)	Loss of 2H ₂ O, Cl ₂ and C ₁₇ H ₁₂ N ₄ O	C + CoO
[Ni(L)(H ₂ O) ₂].2H ₂ O	45–180 185–1000	127 216, 282 454, 891	1 4	20.96 (20.65) 58.20 (57.90)	79.16 (78.55)	Loss of 2H ₂ O, 2H ₂ O and $\frac{1}{2}Cl_2$ Loss of C ₁₅ H ₁₂ ClN ₄ O ₃	3C + NiO
[Cu(L)(H ₂ O) ₂]	30–200 200–500	176 265	1 1	7.42 (7.39) 71.09 (71.94)	78.51 (79.33)	Loss of 2H ₂ O Loss of C ₁₆ H ₁₂ Cl ₂ N ₄ O	2C + CuO
$[Zn(L)(H_2O)_2]$	45–205 205–830	184 426	1 1	7.36 (7.72) 75.62 (75.94)	82.98 (83.66)	Loss of 2H ₂ O. Loss of C ₁₈ H ₁₂ Cl ₂ N ₄ O	ZnO
[Cd(L)(H ₂ O) ₂].H ₂ O	30–220 220–1000	115 437, 655	1 2	5.10 (5.78) 78.39 (77.54)	83.49 (83.32)	Loss of H ₂ O and NH ₃ Loss of C ₁₉ H ₁₃ Cl ₂ N ₃ O ₃	CdO

^aNumber of decomposition steps.

losses for each chelate were calculated within the corresponding temperature ranges.

The thermal decomposition process of the free H₂L azo ligand involved three decomposition steps. Decomposition of the H₂L ligand started at 30 °C and finished at 1000 °C. The first stage of decomposition involved the removal of four molecules of C₂H₂, carbon dioxide gas and chlorine gas in the 30–310 °C range, and was accompanied by a weight loss of 64.35% (calcd 64.56%). The second and third stages of decomposition occurred in the 310–1000 °C range, corresponding to the loss of C₉H₄N₄ molecule. They were accompanied by a weight loss of 35.65% (calcd 35.39%).

TG analysis was used as a probe to investigate whether the associated water or solvent molecules to be in the coordination sphere or in the crystalline form.^[45] TG analyses were carried out for the complexes. The stages of decomposition, temperature ranges, decomposition product loss as well as the found and calculated weight loss percentages of the complexes are given in Table 1.

TG curve of the $[Cr(L)Cl(H_2O)]H_2O$ complex showed four steps of decomposition. The first stage of decomposition occurred in the 45–140 °C range, corresponding to the loss of uncoordinated H₂O molecule, and was accompanied by a weight loss of 2.0% (calcd 2.43%). The second and third stages of decomposition involved the removal of water, $C_4H_4N_2$ and chlorine molecules in the 140–390 °C range, and were accompanied by weight loss of 32.33% (calcd 33.10%). While the fourth stage involved the removal of $C_{13}H_8ClN_2O_{0.5}$ molecule in the 390–990 °C range, and was accompanied by a weight loss of 46.62% (calcd 46.13%). The total weight loss amounted to 81.13% (calcd 82.20%) and chromium oxide contaminated with carbon remained as a residue.

TG curve of the $[Mn(L)(H_2O)_2]$ complex indicated that the decomposition of the complex started at 30 °C and finished at 890 °C with three stages. The first stage of decomposition occurred in the 30–260 °C range, corresponding to the loss of two coordinated H₂O molecules and C₂H₂ molecule, and was accompanied by a weight loss of 12.23% (calcd 12.97%). The last two steps of decomposition involved the removal of C₁₄H₁₀Cl₂N₄O molecule in the 260–890 °C range, accompanied by a weight loss of 66.64% (calcd 67.14%).

TG thermogram of the [Fe(L)Cl(H₂O)] complex indicated that decomposition started at 45 °C and finished at 990 °C with four stages. The first stage of decomposition occurred within the range 45–230 °C, corresponding to the loss of coordinated H₂O and C₂H₂ molecules, and was accompanied by a weight loss of 8.47% (calcd 8.86%). The second, third and fourth stages of decomposition involved the removal of Cl₂ gas and C₁₄H₁₀ClN₂ molecule in the 230–990 °C range, accompanied by a weight loss of 67.48% (calcd 68.53%). The total weight loss amounted to 76.07% (calcd 77.30%) leaving ferric oxide contaminated with carbon as a residue.

The thermal decomposition process of the $[Co(L)(H_2O)_2]$ complex involved two decomposition steps. Decomposition

of the complex started at 30 °C and finished at 1000 °C with two stages. The stages of decomposition involved the loss of two coordinated H₂O molecules, $C_{17}H_{12}N_2O$ molecule and Cl_2 gas in the 30–1000 °C range, accompanied by a weight loss of 81.37% (calcd 81.94%).

TG thermogram of the $[Ni(L)(H_2O)_2] \cdot 2H_2O$ complex showed five steps of decomposition. The first stage of decomposition occurred in the 45–180 °C range, corresponding to the loss of two uncoordinated H₂O molecules, two coordinated H₂O molecules and $\frac{1}{2}Cl_2$ gas and was accompanied by a weight loss of 20.96% (calcd 20.65%). The subsequent steps of decomposition involved the removal of the azo dye ligand as carbon and nitrogen oxide gases in the 185–1000 °C range, accompanied by a weight loss of 58.20% (calcd 57.90%). NiO contaminated with carbon was the residue of decomposition of the complex.

The thermal decomposition process of the $[Cu(L)(H_2O)_2]$ complex started at 30 °C and finished at 500 °C with two stages. The first stage of decomposition involved the removal of two coordinated H₂O molecules within the range 30– 200 °C, accompanied by a weight loss of 7.42% (calcd 7.39%). The second stage of decomposition occurred in the 200–500 °C range, corresponding to the loss of C₁₆H₁₂Cl₂N₄O molecule and was accompanied by a weight loss of 70.49% (calcd 70.70%).

TG curve of the $[Zn(L)(H_2O)_2]$ complex showed two steps of decomposition. The first stage of decomposition occurred in the 45–205 °C range, corresponding to the loss of two coordinated water molecules, and was accompanied by a weight loss of 7.36% (calcd 7.72%). The second stage of decomposition involved the removal of $C_{18}H_{12}Cl_2N_4O$ molecules in the 205–830 °C range, and was accompanied by a weight loss of 75.62% (calcd 75.94%).

TG curve of the $[Cd(L)(H_2O)_2]\cdot H_2O$ complex indicated that the complex was thermally decomposed in three steps within the range 30–1000 °C. The first stage of decomposition occurred in the 30–220 °C range, corresponding to the loss of uncoordinated H₂O and NH₃ molecules, and was accompanied by a weight loss of 5.10% (calcd 5.78%). The second and third stages of decomposition involved the removal of ligand molecule as carbon and nitrogen oxide gases in the 220–1000 °C range, and was accompanied by a weight loss of 78.39% (calcd 77.54%). The total weight loss amounted to 83.49% (calcd 83.32%) and CdO was left as the residue of decomposition.

3.2.9 | Powder XRD

The powder XRD patterns of the azo dye ligand and its metal complexes were obtained in the $0^{\circ} < 2\theta < 60^{\circ}$ range in order to give an insight about the lattice dynamics of these compounds. The powder XRD patterns reflected the fact that

each solid represents a definite compound of a definite structure which was not contaminated with starting materials.

Crystalline peaks were not seen in the powder XRD patterns of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes, indicating the amorphous nature of all the complexes.^[46,47]

3.2.10 | Geometry optimization

The fully optimized geometries of the ligand H_2L were obtained without any constraint in the gaseous state at the same level of theory. The optimized structures were checked as minima on the potential energy surfaces by frequency calculations. A view of the optimized structure and its atom numbering is shown in Figure 1. Selected bond distances and angles are listed in Table 2.^[48]

 TABLE 2
 Selected geometric parameters for H₂L

Bond length (Å)		Bond angle (°)	
O(24)–H(38)	0.966	C(21)-C(20)-C(19)	119.278
O(23)–H(37)	0.971	C(21)-C(20)-Cl(25)	120.592
C(21)-H(36)	1.105	C(19)-C(20)-Cl(25)	120.13
C(19)-H(35)	1.103	H(35)-C(19)-C(20)	121.234
C(18)-H(34)	1.104	H(35)-C(19)-C(18)	119.908
C(14)–H(33)	1.103	C(20)-C(19)-C(18)	118.859
C(13)-H(32)	1.103	H(38)-O(24)-C(17)	113.398
C(11)–H(31)	1.103	H(34)-C(18)-C(19)	118.362
C(6)–H(30)	1.103	H(34)-C(18)-C(17)	118.846
C(5)–H(29)	1.103	C(19)-C(18)-C(17)	122.791
C(3)–H(28)	1.104	H(36)-C(21)-C(22)	119.868
C(1)-H(27)	1.104	H(36)-C(21)-C(20)	118.06
C(17)–C(22)	1.355	C(22)-C(21)-C(20)	122.073
C(21)–C(22)	1.351	C(22)-C(17)-C(18)	118.202
C(20)–C(21)	1.341	C(22)-C(17)-O(24)	124.525
C(19)–C(20)	1.339	C(18)-C(17)-O(24)	117.27
C(18)–C(19)	1.34	H(37)–O(23)–C(15)	109.945
C(17)–C(18)	1.347	H(33)-C(14)-C(15)	119.138
C(11)–C(16)	1.348	H(33)-C(14)-C(13)	119.181
C(15)–C(16)	1.351	C(15)-C(14)-C(13)	121.681
C(14)–C(15)	1.345	H(32)-C(13)-C(14)	119.645
C(13)–C(14)	1.34	H(32)-C(13)-C(12)	121.131
C(12)–C(13)	1.34	C(14)-C(13)-C(12)	119.224
C(11)–C(12)	1.343	C(13)-C(12)-C(11)	119.818
C(1)–C(6)	1.341	C(13)-C(12)-Cl(26)	119.846
C(5)–C(6)	1.341	C(11)-C(12)-Cl(26)	120.337

10 of 19 | Applied WILEY-Organometallic Chemistry

TABLE 2 (Continued)

Bond length (Å)		Bond angle (°)	
C(4)–C(5)	1.346	C(16)-C(15)-C(14)	118.978
C(3)–C(4)	1.349	C(16)-C(15)-O(23)	121.092
C(2)–C(3)	1.349	C(14)-C(15)-O(23)	119.929
C(1)–C(2)	1.346	H(31)-C(11)-C(16)	121.208
N(9)-C(16)	1.268	H(31)-C(11)-C(12)	117.807
N(10)-C(22)	1.27	C(16)-C(11)-C(12)	120.984
C(12)–Cl(26)	1.728	C(17)–C(22)–C(21)	118.797
C(20)–Cl(25)	1.727	C(17)-C(22)-N(10)	127.717
C(17)–O(24)	1.364	C(21)-C(22)-N(10)	113.486
C(15)–O(23)	1.364	C(22)-N(10)-N(7)	121.003
N(7)-N(10)	1.249	C(11)-C(16)-C(15)	119.315
N(8)-N(9)	1.251	C(11)-C(16)-N(9)	125.363
C(2)–N(8)	1.269	C(15)-C(16)-N(9)	115.322
C(4)–N(7)	1.268	C(16)-N(9)-N(8)	120.368
		H(30)–C(6)–C(1)	119.787
		H(30)–C(6)–C(5)	119.921
		C(1)-C(6)-C(5)	120.292
		N(10)-N(7)-C(4)	120.563
		H(29)-C(5)-C(6)	117.402
		H(29)-C(5)-C(4)	122.156
		C(6)-C(5)-C(4)	120.443
		C(5)-C(4)-C(3)	118.138
		C(5)-C(4)-N(7)	125.443
		C(3)-C(4)-N(7)	116.419
		N(9)-N(8)-C(2)	119.514
		H(28)-C(3)-C(4)	117.366
		H(28)-C(3)-C(2)	120.116
		C(4)-C(3)-C(2)	122.517
		C(3)-C(2)-C(1)	117.669
		C(3)-C(2)-N(8)	125.96
		C(1)-C(2)-N(8)	116.371
		H(27)-C(1)-C(6)	118.431
		H(27)–C(1)–C(2)	120.628
		C(6)-C(1)-C(2)	120.941

3.2.10.1 | Molecular electrostatic potential (MEP)

MEP provides a visual method to understand the relative polarity of the molecule. MEP is a valuable tool for predicting and analysing the molecular interactions such as drug–receptor and enzyme–substrate interactions. MEP is very helpful for the qualitative elucidation of electrophilic and nucleophilic reactions for the study of biological discovery process and hydrogen bonding interactions.^[49] An electron density iso-surface mapped with electrostatic potential surface depicts the size, shape, charge density and site of chemical reactivity of a molecule. The different values of the electrostatic potential at the surface are represented by different colours: red-coloured surfaces with negative MEP represent high electron density; blue-coloured surfaces represent lowest electron density. MEP map with electron contour graph of H₂L is shown in Figure 3. The MEP showed that the negative potential site was situated over phenolic oxygens and nitrogen atoms and the positive potential site was present around the hydrogen atoms. The regions over the rings were neutral, represented by green colour. These sites gave information about the regions that can be considered as sites of electrophilic attack by metal ions during the complextion process.^[48,49]

3.2.10.2 | Mulliken charge analyses

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems.^[48,49] The total atomic charge values were obtained by Mulliken population analysis with optimized geometry and the data are listed in the table in the supporting information and shown in Figure 4. As can be seen, the C26 and C6 atoms had higher positive atomic charges than the other carbon atoms. This was due to the electronegative atoms such as oxygen and nitrogen attached to carbon atoms. Results from the table in the supporting information indicated that oxygen and nitrogen atoms in H₂L had more negative charges than the other atoms. The Mulliken method was used for predicting suitable sites of coordination to the metal ions present in azo ligand H₂L, which was also supported by MEP analysis.

3.2.10.3 | Molecular parameters

The analysis of the wave function indicated that the electron absorption corresponded to the transition from the ground state to the first excited state, mainly described by one-electron excitation from the HOMO to the LUMO.^[50] LUMO as an electron acceptor represented the ability to obtain an electron and HOMO as an electron donor represented the



FIGURE 3 Molecular electrostatic potential map of H₂L.The electron density iso-surface is 0.004 a.U



FIGURE 4 Mulliken charges for free H₂L

TABLE 3 Calculated quantum chemical parameters for H₂L ligand

E _{HOMO} (eV)	E _{LUMO} (eV)	<i>Ε</i> Δ (eV)	χ (eV)	η (eV)	$\sigma m eV^{-1}$	Pi (eV)	S eV ⁻¹	ω (eV)	$\Delta N_{\rm max}$	E (a.u.)	Dipole moment (D)
-4.244	-2.199	2.045	3.222	1.023	0.978	-3.222	0.489	5.075	3.150	1092.199	3.239

ability to donate electron. The energy gap between the HOMO and LUMO determines the chemical stability and electrical transport properties of a molecule. The green and red colours of the molecular orbital plot represented positive and negative phase, respectively. Additional parameters such as absolute electronegativities, χ , chemical potentials, Pi, absolute hardness, η , absolute softness, σ , global electrophilicity, ω , global softness, S, and additional electronic charge, $\Delta N_{\rm max}$, have been estimated for the H₂L free ligand and are listed in Table 3. Electrophilicity index (ω) is one of the most important quantum chemical descriptors in describing toxicity and the reactivity of various selective sites. The electrophilicity may quantify the biological activity of drug-receptor interaction. Also, this index measures the stabilization energy when the system acquires extra negative charge from the environment. Parameters η and σ are measures of the molecular stability and reactivity, and their concepts are related to each other. The softness index is the converse of global hardness. These parameters were useful in order to support the suggested structures. The mentioned quantum chemical parameters were calculated with the help of the following equations:^[50–52]

 $\Delta E = E_{\rm LUMO} - E_{\rm HOMO} \tag{1}$

11 of 19

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

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \tag{3}$$

$$\sigma = \frac{1}{\eta} \tag{4}$$

$$Pi = -\chi \tag{5}$$

$$S = \frac{1}{2\eta} \tag{6}$$

$$\omega = \frac{Pi^2}{2\eta} \tag{7}$$

TABLE 4 Main calculated optical transitions with composite ion in terms of molecular orbitals

Compound	Transition	Excitation energy (eV)	λ_{\max} calcd (nm)	λ _{max} exp. (nm)	Oscillator strength
H ₂ L	Homo \rightarrow LUMO	3.35	370	_	0.03
	Homo-1 \rightarrow LUMO + 1	3.75	330	_	0.02
	Homo-4 \rightarrow LUMO	4.13	379	398	0.15
	Homo-5 \rightarrow LUMO + 1	4.52	272	284	0.09

$$\frac{12 \text{ of } 19}{\text{WILEY}} WILEY - \frac{\text{Applied}}{\text{Chemistry}} \Delta N_{\text{max}} = -\frac{Pi}{\eta}$$
(8)

The calculated data are presented in Table 3 and the following considerations can be noted:

- (i) The data for H_2L indicate a great possibility for biological activity based on high ω value.
- (ii) S and ω are softness indexes while η is hardness indication; a hard molecule has a high stability due to its high energy difference between E_{HOMO} and E_{LUMO} compared to a soft molecule. So, a soft molecule is a reactive one having flexible donation towards metal ions.



FIGURE 5 Theoretical electronic absorption transitions for H_2L in DMF solvent

ILEY-Organometallic Chemistry 13 of 19

Accordingly, the investigated H_2L molecule was soft towards coordination.

- (iii) The positive electrophilicity index (χ) value and the negative electronic chemical potential (μ) value indicated that the H₂L molecule is capable of accepting electrons from the environment and its energy must decrease upon accepting electronic charge. Therefore, the electronic chemical potential must be negative.^[53]
- (iv) The total energy of the free ligand was small, which indicated the stability of the isolated azo ligand.
- (v) The small energy gap can be associated with a high chemical reactivity, low kinetic stability and reflects efficient electronic charge transfer interaction making the molecule highly polarizable.



FIGURE 6 IR spectra of H_2L : (a) theoretical spectrum; (b) experimental spectrum

3.2.10.4 | Relation between theoretical and experimental UV-visible spectral data

Due to high accuracy and low computational cost of TD-DFT, it has been popularized for theoretical investigation of electronic spectra of molecules. The present investigation for low-lying excited state on optimized ground state structure was performed at TD-DFT/B3LYP/LANL2DZ level of theory for 30 singlet states. The experimental and theoretical electronic spectral data are presented in Table 4.

The TD-DFT calculations have been evaluated in DMF solvent background and compared with the experimental data. The transitions between inter-frontier orbitals for wavelengths corresponding to maximum oscillator strength of simulated results with corresponding experimental observations are presented in Table 4. Figure 5 shows the inter-frontier orbitals obtained from TD-DFT calculations at the contour value of 0.02 which were used to analyse the electronic transition behaviour for reported peaks (Table 4). The electronic transition calculated for 379 nm corresponds to experimental peak at 398 nm. This transition is mainly contributed from HOMO-4 to LUMO transition which is primarily $n-\pi^*$ in nature. The observed transition at 284 nm was calculated at 272 nm and the transfer of electronic charge from π -bonding orbital to aromatic benzene belongs to π^* .

The different transitions and experimental counterparts for the free ligand are summarized in Table 4 and shown in Figure 5.

3.2.10.5 | Vibrational properties

Theoretical harmonic vibrational analysis was also performed based on the optimized geometry. It is well known that the vibrational frequencies computed using quantum chemical methods such as DFT levels contain well-known systematic

(a) In case of Cr(III) and Fe(III) complexes (where y = 1 for Cr(III) complex and y = 0 for Fe(III) complex)



(b) In case of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes (where y = 1 for Cd(II) complex, y = 2 for Ni(II) complex and y = 0 for Mn(II), Co(II), Cu(II) and Zn(II))

FIGURE 7 Structures of metal complexes. (a) Cr(III) and Fe(III) complexes (where y = 1 for Cr(III) complex and y = 0for Fe(III) complex). (b) Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes (where y = 1 for Cd(II) complex, y = 2 for Ni(II) complex and y = 0 for Mn(II), Co(II), Cu(II) and Zn(II) complexes)



14 of 19 WILEY-Organometallic Chemistry

errors. The scaling factor of 0.96 for LanL2DZ level was used to correct the effects of anharmonicity and neglected part of electron correlation.^[51,52,54] The IR and corresponding theoretical spectra for H₂L are shown in Figure 6. The stretching vibration of a free or non-hydrogen bonded OH group appeared in the range 3550–3700 cm⁻¹.^[54] The OH stretching mode of H₂L was calculated theoretically at 3569 cm⁻¹. The stretching vibration of N=N group was found at 1611 cm⁻¹. It was noted that the calculated values were very close to the experimental data.

3.2.11 | Structural interpretation

On the basis of various physicochemical and spectral data presented and discussed above, the structures of the complexes of H_2L azo ligand with Cr(III), Mn(II), Fe(III),



 $FIGURE \ 8 \quad \ \ Biological \ activity \ of \ H_2L \ ligand \ and \ its \ complexes$

TABLE 5 Biological activity of H ₂ L ligand and its metal co	omplexes
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Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions were confirmed from the results of elemental, IR, ¹H NMR, molar conductance, magnetic moment, solid reflectance, ESR, UV-visible, XRD, TG and DTG analyses. From all of the above observations, the structure of these complexes may be interpreted in accordance with complexes of H₂L azo ligand with a similar distribution of coordinating sites. The structural information from previously reported complexes was in agreement with the data reported in this paper based on the IR, ¹H NMR, mass, molar conductance, ESR, magnetic and electronic spectra measurements. Consequently, the structures proposed are based on octahedral complexes. H₂L always coordinated via two deprotonated phenolic oxygen and two azo nitrogen atoms forming four binding chelating sites. The proposed structural formulas of the complexes are shown in Figure 7.

3.3 | Antimicrobial activity of metal complexes

The preliminary fungal toxicity screening of the complexes was performed *in vitro* against the photopathogenic fungus *C. albicans* by the diffusion technique.^[55] The inhibition of fungal growths expressed in percentage terms was determined for the growth in test plates compared to the respective control plates:

Inhibition (%) =
$$100 \times \frac{C-T}{C}$$

where C is the diameter of fungal growth for the control and T the diameter of fungal growth for the test sample. The azo ligand and its complexes showed fungal growth inhibition

	Inhibition zone diameter (mm mg ⁻¹ sample)						
Sample	B. subtilis	E. coli	N. gonorrhoeae	S. aureus	C. albicans		
Control: DMSO	0.0	0.0	0.0	0.0	0.0		
Ligand (H ₂ L)	0.0	0.0	0.0	0.0	0.0		
$[Cr(L)Cl(H_2O)].H_2O$	9	9	0.0	9	0.0		
$[Mn(L)(H_2O)_2]$	10	10	9	11	0.0		
[Fe(L)Cl(H ₂ O)]	10	0.0	9	9	0.0		
[Co(L)(H ₂ O) ₂]	10	18	10	15	9		
[Ni(L)(H ₂ O) ₂].2H ₂ O	16	13	14	25	17		
$[Cu(L)(H_2O)_2]$	10	11	11	11	10		
$[Zn(L)(H_2O)_2]$	15	12	15	15	9		
$[Cd(L)(H_2O)_2].H_2O$	30	30	29	31	17		
Amikacin	6	9	7	6	_		
Ketokonazole	—	—	—	—	9		



3hb5



(a)



15 of 19

(b)







(b)



FIGURE 9 Interaction of H_2L (green in (a) and blue in (b)) with receptors of breast cancer mutant 3hb5-oxidoreductase, crystal structure of *E. coli* (3 t88) and crystal structure of *S. aureus* (3q8u). (for interpretation of the references to colour in this figure caption, the reader is referred to the online version of this article)



FIGURE 10 HB plots of interaction between H_2L and receptors: (a) breast cancer mutant 3hb5-oxidoreductase; (b) crystal structure of *E. coli* (3 t88); (c) crystal structure of *S. aureus* (3q8u)

following the order: Cd(II) = Ni(II) > Cu(II) > ketokonazole= $Zn(II) = Co(II) > H_2L = Fe(III) = Cr(III) = Mn(II).$

The antibacterial activity of the free azo ligand and its metal(II)/(III) complexes was determined using the disc diffusion method.^[56] This was done using the bacterial species B. subtilis, S. aureus, N. gonorrhoeae and E. coli. All the compounds were positioned at four equidistant places at a distance of 2 cm from the centre in inoculated Petri plates. DMSO served as control and amikacin as standard drug. All determinations were made in duplicate for each of the compounds. An average of two independent readings for each compound was recorded. The Petri plates were kept in a refrigerator for 24 h for prediffusion. Finally the plates were incubated at 30 °C for 24 h. The bacterial growth inhibitory capacity of the ligand and its complexes follows the order Cd(II) > Ni(II) > Zn(II) > Fe(III) = Co(II) = Cu(II) = Mn(II) > Cr(III) > amikacin > H_2L (for *B. subtilis*); Cd(II) > Ni (II) > Zn(II) = Co(II) > Cu(II) = Mn(II) > Fe(III) = Cr(III) > amikacin > H_2L (for *S. aureus*); Cd(II) > Zn(II) > Ni (II) > Cu(II) > Co(II) = Cu(II) > Fe(III) = Mn(II) > amikacin> $H_2L = Cr(III)$ (for *N. gonorrhoeae*); and Cd(II) > Co (II) > Ni(II) > Zn(II) > Cu(II) > Mn(II) > amikacin = Cr(III) > H_2L (for *E. coli*) (Figure 8).

From the observed results (Table 5). metal complexes showed enhanced antimicrobial activity in many cases over the free azo ligand and standards. Such increased activity of the metal complexes can be explained on the basis of chelation theory.^[57–59] According to the theory, on chelation the polarity of the metal ion will be reduced as a result of the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups.^[60,61] In addition, it increases the delocalization of π -electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes with blocking of the metal binding sites inside the enzymes of microorganisms. Also, these complexes disturb the respiration process of cells and thus block the synthesis of proteins, which restricts further growth of the microorganisms.^[62,63] The complexes were more active towards the Gram-negative bacteria due to their thin peptidoglycan layer, which makes their cells more permeable to the complexes.^[9,64]

3.4 | Molecular docking

Molecular docking is a key tool in computer drug design.^[65–67] The focus of molecular docking is to simulate the molecular recognition process. Molecular docking aims to achieve an optimized conformation for both protein and drug with relative orientation between them such that the free energy of the overall system is minimized. In this context, we used molecular docking between H₂L and breast cancer mutant 3hb5-oxidoreductase, crystal structure of *E. coli* (3 t88) and crystal structure of *S. aureus* (3q8u). The results



FIGURE 11 Two-dimensional plots of interaction between H_2L and receptors: (a) breast cancer mutant 3hb5-oxidoreductase; (b) crystal structure of *E. coli* (3 t88); (c) crystal structure of *S. aureus* (3q8u)

18 of 19		
	Chemistry	

TABLE 6	Energy values obtained in docking calculations of H ₂ L	with receptors of breast	cancer mutant 3h	b5-oxidoreductase,	crystal s	structure o	f
E. coli (3 t88	B) and crystal structure of S. aureus (3q8u)						

Receptor	Est. free energy of binding (kcal Mol ⁻¹)	Est. inhibition constant, K_i (μ M)	vdW + bond + desolv. Energy (kcal Mol ⁻¹)	Electrostatic energy (kcal Mol ⁻¹)	Total intercooled energy (kcal Mol ⁻¹)	Interaction surface
3hb5	-6.75	11.34	-8.19	-0.02	-8.22	994.272
3 t88	-4.62	412.64	-6.61	-0.02	-6.63	645.974
3q8u	-6.41	20.19	-9.28	-0.04	-9.32	921.559

showed a possible arrangement between H_2L and 3hb5, 3 t88 and 3q8u receptors. The docking study showed a favourable interaction between H_2L and the receptors (3hb5, 3 t88 and 3q8u) as shown in Figures 9–11. The calculated energies are listed in Table 6. According to the results obtained in this study, hydrogen bonding interaction (HB) plots indicated that the free azo dye ligand binds to the proteins with hydrogen bond interactions and decomposed interaction energies existed between free azo dye ligand with 3hb5, 3 t88 and 3q8u receptors as shown in Figure 10. Two-dimensional plots of docking with free azo dye ligand are shown in Figure 11.

4 | **CONCLUSIONS**

A novel azo ligand was synthesized from the reaction of *m*phenylenediamine with *p*-chlorophenol and its mononuclear Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were prepared. The possible structures of the ligand and its metal complexes based on elemental analyses suggested the formulae $[M(L)Cl(H_2O)] \cdot nH_2O$ (M = Cr(III) and Fe(III)) and $[M(L)(H_2O)_2] \cdot nH_2O$ (M = Co(II), Ni(II), Cu(II), Mn(II), Zn(II) and Cd(II)). Also, UV-visible and IR spectral data and thermogravimetric analyses supported the suggested formulae. The magnetic and solid reflectance measurements confirmed octahedral geometry of the complexes. XRD results showed that the free ligand and metal complexes have an amorphous nature. ESR spectra of the solid Cu(II) complex at room temperature showed axial type $(d_{x^2-v^2})$ with covalent bond character in an octahedral environment. In addition, the antimicrobial activity study indicated that the complexes showed greater biological activity than the ligand against the same microorganisms under identical experimental conditions.

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