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The structure of the metal complexes



Synthesis, structural, spectroscopic and biological studies of Schiff base complexes

M.A. Diab^{a,*}, A.Z. El-Sonbati^a, A.F. Shoair^a, A.M. Eldesoky^b, N.M. El-Far^a

^a Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt
 ^b Engineering Chemistry Department, High Institute of Engineering &Technology (New Damietta), Egypt
 and Al-Qunfudah Center for Scientific Research (QCSR), Chemistry Department, Al-Qunfudah University College, Umm Al-Qura University, KSA

Abstract

Schiff base ligand 4-((pyridin-2- yl)methyleneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one (PDMP) and its complexes were prepared and characterized on the basis of elemental analysis, IR, mass spectra and thermogravimetric analysis. All results confirm that the complexes have 1:1 (M: PMDP) stoichiometric formula $[M(PMDP)Cl_2H_2O]$ (M= Cu(II), Co(II), Ni(II) and Mn(II)), $[Cd(PMDP)Cl_2]$ and the ligand behaves as a bi/tridentate forming five-membered chelating ring towards the metal ions, bonding through azomethine nitrogen/exocyclic carbonyl oxygen, azomethine pyridine nitrogen and exocyclic carbonyl oxygen. The shift in the band positions of the groups involved in coordination has been utilized to estimate the metal-nitrogen and/or oxygen bond lengths. The complexes of Co(II), Ni(II) and Cu(II) are paramagnetic and the magnetic as well as spectral data suggest octahedral geometry, whereas the Cd(II) complex is tetrahedral. The XRD studies show that both the ligand and its metal complexes (1 and 3) show polycrystalline with crystal structure. Molecular docking was used to predict the binding between PMDP ligand and the receptors. The corrosion inhibition of mild steel in 2 M HCl solution by PDMP was explored utilizing potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and (EFM) electrochemical frequency modulation method. Potentiodynamic polarization demonstrated that PDMP compound is mixed-type inhibitor. EIS spectra exhibit one capacitive loop and confirm the protective ability. The percentage of inhibition efficiency was found to increase with increasing the inhibitor concentration.

Keywords: Schiff base; Molecular structures; X-ray diffraction; Quantum chemical parameters; Molecular docking; Inhibition efficiency.

^{*}Corresponding author: E-mail address: m.adiab@yahoo.com (M.A. Diab).

1. Introduction

Over the past few years, transition metal complexes have been given a great attention of inorganic, metallo-organic as well as bio-organic chemists because of their extensive applications in wide ranging area [1,2] such as biology including antibacterial, antifungal, anticancer, antioxidant, antimalarial, antiviral activity and also as oxidation of organic compounds, reduction reaction of ketones [3] and epoxidation of alkenes. Schiff bases are widely used as pigments and dyes, catalysts, intermediates inorganic synthesis and as polymer stabilizers [4].

Transition metal complexes of Schiff bases derived from 2-pyridine carboxaldehyde and different amines have reported considerable attention for their synthetic and catalytic activities [5]. 2-Pyridine carboxaldehyde Schiff base complexes have also been examined for their catalytic properties for different chemical reactions like amination of aryl halides [6], olefin cyclopropanation [7] and olefin epoxidation [8]. Catalytic epoxidation of carbon–carbon double bonds is importance in organic chemistry due to the wide range applications.

Moreover, It has been found that the tridentate Schiff base ligands with a flexible atom in comparison with the bidentate ligands are more suitable ligand for stabilizing organo-metal complexes because of the coordination of the additional donor atom. It has been found that heterocyclic compounds such as pyridine (Py), 2,2'-bipyridine (bipy) and related molecules are good ligands due to the presence of at least one ring nitrogen atom due to their bioinorganic applications and thermal stability [9]. 4-Aminoantipyrine compounds are considered to be excellent corrosion inhibitors in combating acidic corrosion due to high inhibition efficiency, good thermal stability and lack of irritating odor for many metals and alloys in various aggressive media [10-12].

Mild steel is the major structural material in industry, the insurance of steel against corrosion has pulled in much consideration. As most steels are for the most part stable in neutral and alkaline media, acidic environments are the real concern [13]. Inhibitors are utilized as a part of this procedure to control metal dissolution. The majority of the notable corrosive inhibitors are organic compounds in acidic solutions containing O, S, and/or N atoms [14-16]. In spite of the fact that there are a several studies on the corrosion inhibition effects of organic compounds in acidic solutions

[17,18]. The inhibitive activity is associated with a several factors including the structure and the charge distribution on the molecule, the number and the sorts of adsorption sites, and the way of interaction between the atom and the metal surface [19]. Corrosion inhibition happens by means of adsorption of the organic molecule on the corroding metal surface following some known adsorption isotherms with the polar groups going about as active centers in the molecules.

In this study a novel Schiff base with NO/N₂O donor set of atoms has been synthesized with condensation reaction of 4-aminoantipyrine with pyridine-2-carbaldehyde. The molecular and electronic structure of the Schiff base ligand (PDMP) was optimized theoretically and the quantum chemical parameters were calculated. Molecular docking was used to predict the binding between (PDMP) and the receptors of 3hb5-oxidoreductase (breast cancer mutant 3hb5) and 2q7k-hormone (prostate cancer mutant 2q7k). The nature of bonding of the Schiff base and structural composition of complexes were confirmed and characterized by elemental analyses, spectroscopic, magnetic susceptibility, molar conductance, electron spin resonance, conductivity measurements, thermogravimetric analyses and powder x-ray diffraction.

2. Procedure

2.1. Materials

Pure grade chemicals were used for the preparation of the ligand and the metal complexes. The used chemicals including metals of CuCl₂.2H₂O, CoCl₂.6H₂O, NiCl₂.2H₂O, MnCl₂.4H₂O and CdCl₂.2H₂O were purchased from Sigma without any further purification. Other materials such as organic solvents (e.g., ethanol, methanol and acetone) were purchased in the highest possible purity as received. Materials used for the corrosion study were mild steel sheet of composition (wt %) 0.20 C, 0.029 Si, 0.018 S, 0.0067 P, 0.397 Mn, 0.025 Ni, 0.0076 Cr, 0.0020 Mo, 0.0010 V, 0.036 Cu, 0.0010 Sn, 0.0057 Co, 0.126 Al, 0.023 Zn, 0.0020 Mg, 0.0046 Nb, 0.0025 Bi and the rest Fe.

2.2. Synthesis of Schiff base

The Schiff base ligand (PMDP) (Fig. 1) was prepared by adapting a reported method [4, 20]. Pyridine-2-carbaldehyde (start) (1 mmol) and 4-aminoantipyrine (1 mmol), each dissolved in 20 ml ethanol were mixed with constant stirring. The mixture was refluxed

and the obtained precipitate was filtered out and washed by methanol then dried in air. The purity of the synthesized compound was tested by the TLC method.

2.3. Preparation of metal complexes

Complexes (1-5) were prepared by the direct reaction of the appropriate hydrated metal(II) chloride with the ligand (PMDP) (Fig. 2). A boiling solution of the Schiff base (1 mmol) in ethanol was added to a solution of hydrated metal(II) chloride (1 mmol) in hot ethanol (20 ml). The mixture was gently heated on water bath for 1-3 h and then left to stand overnight. The resulting solution yielded shinning deep colored crystals which wee filtered and washed with ether and dried over P_4O_{10} in vacuum.

2.4. DNA binding experiments

The binding properties of the ligand and complexes (1–5) 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 a ratio of UV absorbance at 260 and 280 nm (A260/A280) of ca. 1.8–1.9, indicating that the DNA was sufficiently free of protein and the concentration was determined by UV absorbance at 260 nm ($\mathcal{E} = 6600 \text{ M}^{-1} \text{ cm}^{-1}$) [21].

2.5. Biological activity investigation

For this investigation the agar well diffusion method was applied [21]. The antibacterial activities of the investigated compounds were tested against three local Gram positive bacterial species (*Bacillus cereus*, *Staphylococcus aureus* and *Enterococcus faecalis*) and three local Gram negative bacterial species (*Escherichia coli*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*) on nutrient agar medium. Also, the antifungal activities were tested against three local fungal species (*Aspergillus niger*, *Fusarium oxysporum* and the yeast *Candida albicans*) on DOX agar medium. The concentrations of each solution were 50, 100 and 150 μ g/mL in dimethyl formamide (DMF). By using a sterile cork borer (10 mm diameter), wells were made in agar medium plates previously seeded with the test microorganism. 200 μ l 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 °C or 30 °C for bacteria and fungi, respectively. The diameters of inhibition zone were determined after 24 h and 7 days for bacteria and fungi, respectively, taking the consideration of the control values (DMF). Penicillin and miconazole were used as standard drugs against bacteria and fungi, respectively.

2.6. Analytical, physical and computational measurements

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Egypt, using a CHNS-932 (LECO) Vario elemental analyzer. Analyses of the 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 in a solution in DMSO- d_6 were recorded with a 330 MHz Varian-Oxford Mercury at room temperature using tetramethylsilane as an internal standard. ESR spectra were recorded with a JES-FE2XG ESR spectrophotometer at the Microanalytical Center, Tanta University. The molecular structures of the compounds were optimized using the Hartree-Fock method with 3-21G basis set. The molecules were built with Perkins Elmer ChemBio3D software [22,23]. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1340 spectrophotometer. Mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard. Ultraviolet-visible spectra of the compounds were recorded in nujol mull using a Unicom SP 8800 spectrophotometer. The magnetic moment of the 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, $\mu_{eff.} = 2.84 [Tc_M^{coor.}]^{1/2}$. The conductance was achieved using Sergeant Welch scientific Co., Skokie, IL, USA. Thermal studies were computed on Simultaneous Thermal Analyzer (STA) 6000 system using thermogravimetric analysis (TGA) method. Thermal properties of the samples were analyzed in the temperature range from 30 to 800 °C at the heating rate of 10 °C/min under dynamic nitrogen atmosphere. X-ray diffraction analysis of compounds powder forms was recorded on X-ray diffractometer analysis in the range of diffraction angle $2\theta^{\circ} = 4-80^{\circ}$ and carried out using CuK_a radiation ($\lambda =$ 1.540598 Å). The applied voltage and the tube current are 40 kV and 30 mA, respectively.

Docking calculations were carried out on receptor of prostate cancer mutant 2q7khormone and receptor of breast cancer mutant 3hb5-oxidoreductase proteins models. The MMFF94 Force field was used for energy minimization of ligand molecule using Docking Server. Affinity (grid) maps of $20 \times 20 \times 20$ Å grid points and 0.375 Å spacing were generated using the Autogrid program [23]. Auto Dock parameter set- and distance-dependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively.

2.7. Corrosion inhibition of mild steel

The experiments were completed potentiodynamically in a thermostated three electrode cell. Platinum foil was utilized as counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode was in the form mild steel under scrutiny and was embedded in a Teflon bar with an exposed area of 1 cm². The electrode was immersed in 100 ml of a test solution for 30 min until a steady state open-circuit potential (E_{ocp}) was accomplished. Potentiodynamic polarization was conducted in an electrochemical system (Gamry framework instruments version 3.20) which contains a PCI/300 potentiostat, controlled by a computer recorded and stored the data. Potentiodynamic curves were recorded by changing the electrode potential from - 1.0 to 0.0 V *vs.* SCE with scan rate of 5 mV/s. All experiments were completed in freshly prepared solution at constant temperature (25 ±1 °C) utilizing a thermostat. Inhibition efficiency (%IE) and the degree of surface coverage (θ) were characterized as [19]:

% IE =
$$[(i_{corr} - i_{corr(inh)}) / i_{corr}] \ge 100$$
 (1)

$$\theta = [(i_{corr} - i_{corr(inh)}) / i_{corr}]$$
(2)

where i_{corr} and $i_{corr(inh)}$ are the uninhibited and inhibited corrosion current density values, respectively, determined by extrapolation of Tafel lines.

Electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) experiments carried out using the same instrument as before with a Gamry framework system based on ESA400. Gamry applications involve software EIS300 for EIS measurements and EFM140 for EFM measurements; computer was used

for collecting data. EchemAnalyst 5.5 software was used for plotting, graphing and fitting data. EIS measurements were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential. EFM carried out using two frequencies 2 and 5 Hz. The base frequency was 1 Hz. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 2 and 5 Hz.

3. Results and discussion

On the basis of elemental analysis, the complexes were assigned the composition as shown in Table 1. The molar conductance values of the complexes (1-5) in 10^{-3} molar solution in DMF are found to be less than $18 \ \Omega^{-1} \ \text{mol}^{-1} \ \text{cm}^{-1}$, indicating that they are non-electrolytic [21] which prove that the anion and the ligand are coordinated to the central metal.

3.1. ¹H NMR spectra

In the proton magnetic resonance spectrum of the ligand and complex (5) recorded in DMSO-d₆. The ¹H NMR spectrum of the ligand does not give any signal corresponding to primary amine protons. The azomethinyl proton, (HC=), seems to be greatly affected by the isomer(s) or bulkiness present. Azomethine proton of the ligand is observed as singlets in a different integral ratio in ~ 8.35 ppm. This undergoes downfield shift in their corresponding complex (5). The spectrum of the ligand show pyridine ring protons signal at ~ δ 7.30-7.45 ppm as singlet and exhibit downfield shift in the complex to show the involvement of pyridine nitrogen in coordination with metal ions. The =C-CH₃ and -N-CH₃ protons were observed as singlet at δ 2.12-2.48 ppm, respectively, and equivalent to three protons each.

3.2. Mass spectra

The electron impact mass spectra of ligand and its complexes are recorded and investigated at 70 eV of electron energy. The mass spectrum fragmentation mode of PMDP ligand shows the exact mass of 292 corresponding to the formula $C_{17}H_{16}N_4O$. This ion undergoes fragmentation to a stable peak at m/z = 157 by losing $C_8H_{11}N_2$ atoms (structure I) as shown in Scheme 1.The loss of carbon atom leads to the fragmentation

with m/z = 145 (structure II). The loss of CO atoms leads to the fragmentation with m/z=117 (structure III). The loss of C₂HN atoms leads to the fragmentation with m/z = 78 (structure IV).

The electron impact mass spectra of complexes (**1-3**) are shown in Schemes 2 and 3. The ion of m/z = 444.546 undergoes fragmentation to a stable peak at m/z = 292, 184, 141 and 78 by losing Cl₂H₂OCu, C₇H₈O, CH₃N₂ and C₄HN atoms, respectively, (structures I-IV) for Cu(II) complex (**1**) (Scheme 2). The ion of m/z = 439.933 undergoes fragmentation to a stable peak at m/z = 292, 200, 117 and 78 by losing Cl₂H₂OCo, C₇H₈, C₃H₃N₂O and C₂HN, respectively, (structures I-IV) for Co(II) complex (**2**) (Scheme 3). The ion of m/z = 439.69 undergoes fragmentation to a stable peak at m/z = 292, 200, 172, 117, 90 and 78 by losing Cl₂H₂ONi, C₇H₈, N₂, C₃H₃O, CHN and C atoms, respectively, (structures I-VI) for Ni(II) complex (**3**) (Scheme 4).

3.3. X-ray diffraction analysis of Schiff base and its metal complexes

The X-ray diffraction (XRD) patterns powder forms of Schiff base ligand (PMDP), complex (1) and complex (3) are presented in Fig. 3. The XRD of PMDP ligand and complexes (1) and (3) show many diffraction peaks which indicate the polycrystalline phases. The values of inter-planar spacing (d) and Miller indices (hkl) for Schiff base ligand (PMDP), complex (1) and complex (3) are determined by using CHEKCELL program [25]. The values of d and hkl for Schiff base ligand (PMDP), complex (1) and complex (3) are tabled in Tables 2-4, respectively. The results show that each Schiff base ligand (PMDP), complex (1) and complex (3) are polycrystalline with crystal system and structure with space group P21, P21/a and P21, responsively. The lattice parameters are estimated as: 23.5905 Å, 5.7890 Å, 6. 13.7263 Å, 90.00 °, 124.57 ° and 90.00 ° for a, b, c, α , β and γ , respectively, for ligand (PMDP). 24.4595 Å, 7.6978 Å, 8.5211 Å, 90.00 °, 99.28 ° and 90.00 ° for a, b, c, α , β and γ , respectively, for ligand γ , respectively, for complex (1) and 23.9043 Å, 5.7986 Å, 10.4241 Å, 90.00 °, 94.68 ° and 90.00 ° for a, b, c, α , β and γ , respectively, for complex (3).

The average crystallite size (ξ) can be calculated from the XRD pattern according to Debye–Scherrer Eq. [26]:

$$\xi = \frac{K\lambda}{\beta_{1/2}\cos\theta} \tag{3}$$

The equation uses the reference peak width at angle (θ), where λ is wavelength of X-ray radiation (1.541874 Å), K is constant taken as 0.95 for organic compounds [26] 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 [26]:

$$\delta = \frac{1}{\xi^2}$$

The value of ξ is calculated and found to be 73, 48 and 54 nm and the value of δ is 1.85 × 10^{-4} , 4.27×10^{-4} and 3.47×10^{-4} nm⁻² for ligand (PMDP), complex (1) and complex (3), responsively.

(4)

3.4. Molecular docking

In this context, we used molecular docking between start and Schiff base ligand (PMDP) with receptors of 3hb5-oxidoreductase (breast cancer mutant 3hb5) and 2q7k-hormone (prostate cancer mutant 2q7k). The results showed a possible arrangement between start and Schiff base ligand (PMDP) with receptors (3hb5 and 2q7k). The docking study showed a favorable interaction between start and Schiff base ligand (PMDP) with receptors (3hb5 and 2q7k). The docking study showed a favorable interaction between start and Schiff base ligand (PMDP) with the receptors (3hb5 and 2q7k) as shown in Figs. 4 and 5 and the calculated energy is listed in Table 5. According to the results obtained in this study, HB plot curve indicates that the start binds to the proteins with hydrogen bond interactions and decomposed interaction energies in kcal/mol were exist between the start and Schiff base ligand (PMDP) with receptors (3hb5 and 2q7k) as shown in Figs. 6 and 7. 2D plot curves of docking with start and Schiff base ligand (PMDP) are shown in Figs. 8 and 9.

3.5. Geometrical structures of Schiff base and its metal complexes

The geometrical structures of the Schiff base (PMDP) and its complexes (1-5) are shown in Fig. 10. The bond lengths and bond angles for PMDP and its metal complexes (1-5) are listed in Tables 6-11. 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. The HOMO and LUMO of the Schiff base ligand (PMDP) and its complexes (1-5) are shown in Fig. 11. The parameters of quantum chemical are listed in Table 12. Additional parameters such as ΔE , absolute electro negativities, 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 [22,23]:



The value of ΔE for Schiff base ligand (PMDP) and its metal complexes (1-5) was found to be 5.400, 0.935, 0.664, 1.405, 0.070 and 2.958 eV, respectively, therefore the complex (4) is more stable than the other complexes (Table 12). As shown in Fig. 12, it is

clear that the value of ΔE increase with decreasing the ionic radii of metal complexes and the complex (3) is higher than the other complexes, due to the lower ionic radius.

3.6. Infrared spectra

IR spectrum of the ligand does not exhibit any band corresponding for the free primary amine and aldehydic groups [27]. New bands appear in the spectrum of the free ligand in ~ 1644 (C=O) and ~ 1562 cm⁻¹ (>C=N) groups. These two bands shifted towards lower side (~ 20-30 cm⁻¹) in the complexes (1-5) (Table 13) indicating that the coordination takes place through the oxygen of v(C=O) and nitrogen of azomethine group v(>C=N) [28]. There are new bands at 515-535 (M-O) and 410-430 cm⁻¹ (M-N) which are not present in the spectrum of the free ligand.

The pyridine ring vibrations, most affected by nitrogen of pyridine in coordination with a metal atom are pyridine ring deformation in plane ring deformation and outof-plane deformation [29]. These vibrations in the complexes (**1-4**) (Table 13) exhibit medium to strong bands at 1496-1492 and 1466-1424 cm⁻¹ as expected for the highest pyridine ring vibration. The low frequency pyridine mode lies in the range 637-620 and 445-432 cm⁻¹. This suggests the involvement of pyridine ring in coordination [30].

Based on the above spectral evidences, it is confirmed that the ligand is neutral tridentate, coordinating *via* the carbonyl oxygen of 4-aminoantipyrine, azomethine nitrogen and the pyridine nitrogen atom for all complexes (1-4), except complex (5) bidentate neutral through carbonyl oxygen of 4-aminoantipyrine, and azomethine nitrogen atoms.

The results and discussion on metal chelate of Schiff base (PDMP) denote that the CO and CN bands, suffer some changes in their position. However, it is of interest to mention that the magnitude of frequency shifts is dependent on the nature of both metal ion and ligand. This was essentially ascribed to the change in the strength of the electrostatic field of the metal ion and the position of the vibrating dipole [31]. For the metal ions which have the same charge, the distance between the metal ion and the coordinated groups is the main factor affecting band shifts. The magnitude of frequency shifts was utilized by Issa et al. [31] in detreming the distance between the metal ion and coordinated of the coordination bond. According to Karagounis and Peter [32], the shifts in the

IR spectrum of Schiff base, on coordination to metal ions, are comparable to those due to adsorption on salt substrate. The Scheme given by Issa et al. [31] can be treated in more or less the same manner.

The value of the coordination bond length (r) can be determined from the relation:

$$\Delta v = (32\pi/a^2)[\alpha (v_{x=y} - v_{x-y})e^{-2\pi\sqrt{2}r/a}/l]$$
(13)

where, $\alpha = \text{bond polarisability}$, $\Delta v = \text{shift in the oscillator frequency } (v_{\text{ligand}} - v_{\text{complex}})$, a = lattice constant of the metal salt used, $v_{x-y} = \text{frequency of the oscillator with single}$ bond, $v_{x=y}=$ frequency of the oscillator with double bond and l = length of the oscillatorcoordinated to metal ion.

The relation denotes that $\log \Delta v$ would be a linear function of (r). The value of (r) can be directly calculated for determined graphically. The values of (r) for Schiff base (PDMP) is given in Table (14). The length of the coordination bond for CO group is not much different from the CN, indicating a more or less symmetrical arrangement of the the ligand about the metal ion.

3.7. Thermal analysis

3.7.1. Thermogravimetric analysis of ligand (PMDP)

The TGA curve for ligand is shown in Fig. 13 and Table 15. Ligand shows two decomposition steps, the first stage occur in the temperature range 40-475 °C corresponding to loss of $C_{11}H_{11}N_2O$ with a practical weight loss of 64.48 % (calc. 64.04 %). The second stage in the temperature range 475-800 °C corresponding to loss of $C_6H_5N_2$ with a practical weight loss of 35.52 % (calc. 35.96 %).

3.7.2 Thermal analysis of complexes (1–5)

The TGA curves for complexes are shown in Fig. 13 and thermal analysis data of complexes (1-5) are listed in Table 15. The thermogram of the complexes (1-4) underwent degradation in three stages. The first stage of decomposition in the range ~126-295 °C for M(II) complexes can be attributed to loss of coordinated water molecule. The second stage of decomposition corresponds to the loss of Cl₂ molecule and decomposition

of a part of the ligand. The third stage is attributed to loss of a part of the ligand. The remaining final product is metal oxide residue.

The TGA curves of compound (5) showed that the complex underwent degradation in two successive stages. The first stage of decomposition is due to loss of $C_7H_5N_2Cl_2$ at the temperature range 285-460 °C. The second stage of decomposition is due to loss of $C_{10}H_{11}N_2$ at the temperature range 460-650 °C. The residue corresponds to cadmium oxide.

3.8. Kinetic studies

The kinetic parameters such as activation energy (E_a), Gibbs free energy change of the decomposition (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) were evaluated graphically by employing the Coast-Redfern [33] and Horowitz-Metzger [34] methods.

The thermal activation energy for decomposition (\mathbf{E}_a) and entropy ($\Delta \mathbf{S}^*$) were calculated [21]. The enthalpy ($\Delta \mathbf{H}^*$) and Gibbs free energy of decomposition ($\Delta \mathbf{G}^*$) were calculated from $\Delta \mathbf{H}^* = E_a - RT$ and $\Delta \mathbf{G}^* = \Delta \mathbf{H}^* - T \Delta \mathbf{S}^*$, respectively.

The thermodynamic data obtained with the two methods for M(II) complexes (1-5) are listed in Table 16 and Figures 14 and 15. The thermodynamic results obtained from the Coats-Redfern and Horowitz-Metzger methods are comparable and can be considered in good agreement with each other [21].

The calculated values of E_a , A, ΔS^* , ΔH^* and ΔG^* for the decomposition steps for Schiff base ligand (PMDP) and its metal complexes (1-5) are summarized in Table 16. The kinetic data obtained from the two methods are comparable and can be considered in good agreement with each other. From the results obtained, the following remarks can be pointed out:

(1) The high values of the energy of activation, E_a of the complexes reveal the high stability of such chelates due to their covalent bond character [21].

- (2) The positive sign of ΔG^* for the investigated complexes reveals that the free energy of the final residue is higher than that of the initial compound, and all the decomposition steps are non spontaneous processes.
- (3) The negative ΔS^* values for the decomposition steps indicate that all studied complexes are more ordered in their activated state.

3.9. Magnetic moment and electronic spectra

The room temperature magnetic moment of Co(II) complex (2) is 4.92 B.M. The electronic spectrum in solid state shows three absorption bands 8300 [${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$], 17600 [${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$] and 20800 cm⁻¹ [${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$], in an octahedral field [35]. The octahedral geometry of cobalt(II) complex is further supported by the value of the v_{3}/v_{2} ratio, which is 1.18. Racah parameters of Co(II) complex (2) are calculated. The values of the ligand field parameters $10Dq = 9300 \text{ cm}^{-1}$ and B = 900 cm⁻¹ are in good agreement with the predicted values for octahedral complexes of Co(II) [36]. The nephlauxetic ratio (β) = 0.804 suggesting an ionic character of cobalt (II)-ligand bonds [37]. The ligand field stabilization energy (LFSE = 26.63 kcal mol⁻¹) and the percentage lowering of energy in free gaseous ion ($\beta^{\circ} = 20$ %) has been calculated.

The electronic spectrum of Ni(II) complex exhibits three bands 8500 [${}^{3}A_{1g}(F) \rightarrow {}^{3}T_{2g}(F)$], 14500 [${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$] and 25000 cm⁻¹ [${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$] transition. The Racah parameter of interelectronic ratio for Ni(II) complex is calculated . The v_3/v_1 , v_3/v_2 and v_2/v_1 transition ratios are 2.941, 1.724 and 1.706 respectively. Also the values of Dq, B, Dq/B and β are 850, 933, 0.911 cm⁻¹ and 0.899, respectively, and ligand field stabilization energy (LFSE = 29.21 kcal mol⁻¹), supporting the octahedral structure [38]. The effective magnetic moment data of Ni(II) complex is 3.32 BM. within the high spin octahedral (3.00-3.50 BM.). The high spin data are due to arise from the spin orbit coupling which causes an orbital contribution to the quenched ${}^{3}A_{2g}$ ground state of Ni(II) ion in an octahedral structure [39].

The value of Dq is found to be in the range, indicating the intermediate ligand field position of the ligands in the nerphelauxetic series. The interelectronic repulsion parameter value is lower than that for the free Ni(II) ion, which attributed to the deloca-

tion of the electrons over the molecular orbitals that encompass both the metal and the ligand. Furthermore, the value of B showed that the e_g electrons are σ -antibonding and spend some of their time on the ligand. The t_{2g} electrons may become π -bonding or antibonding and spend some of their time on the ligand. The nephelauxetic ratio β for the Ni(II) complex indicate the presence of electron delocalization over all the molecular orbitals and therefore a covalent character of nickel(II)-ligand bonding. The percentage lowering of energy in free gaseous ion ($\beta^{\circ} = 10$ %) has been calculated.

The electronic spectrum of Mn(II) complex shows three bands between 15770 and 16120 cm⁻¹ due to ${}^{4}T_{1g} \rightarrow {}^{6}A_{1g}$, ${}^{4}T_{2g}(G) \rightarrow {}^{6}A_{1g}$ and ${}^{4}T_{1g}(D) \rightarrow {}^{6}A_{1g}$ transition [40]. The magnetic moment is found to be 5.31 B.M., which indicates the presence of Mn(II) complex in octahedral geometry.

Cu(II) complex has one unpaired electron and magnetic moment 1.96 B.M. The reflectance spectrum exhibits a broad band 14100 cm⁻¹ assignable to the transition ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ of an octahedral Cu(II) ion [41]. The broadening of the band may be due to Jahn-Teller effect, since the state ${}^{2}E_{g}$ is susceptible to distortion.

3.10. ESR spectrum

The room temperature solid state ESR spectrum of copper complex exhibits axially symmetric g-tensor parameters with $g_{11} > g_{\perp} > 2.0023$. The g-values reflect that the Cu(II) center has a tetragonal distorted octahedral geometry with dx^2-y^2 orbital as a ground state [42]. The observation of g_{11} and g_{\perp} for copper suggest that the system is axially symmetric [27]. In the axial spectrum the g-values are related by the expression [42], $G = g_{11}-2.0023/g_{\perp}-2.0023 = 5.33$ suggest, that local tetragonal axes are aligned parallel with unpaired electron in d_{x2-y2} orbital [43]. The f value also indicate the stereochemistry of the Cu(II) complex (1). Reported range for square planar complexes is 105-135 cm⁻¹ and for tetragonal distorted complexes is > 135 cm⁻¹ [27]. For the present Cu(II) complex f value is > 135 cm⁻¹, indicates the tetragonal distortion.

In hexa-coordinated complex, tetragonal distortion from octahedral symmetry due to the Jahn-Teller distortion is very common. The low g-value obviously corresponds to regular octahedral Cu(II) complex. Super hyperfine structure for this complex is not seen at higher field excluding any interaction of the nuclear spins of nitrogen with the unpaired electron density on Cu(II).

The ESR parameters g_{II} , g_{\perp} , g_{av} , A_{II} and energy d-d of transition was used to evaluated the bonding parameters α^2 , β^2 and γ^2 (Table 17). The extent of departure of these coefficients from unity measures the extent of delocalization of the metal electrons due to metal-ligand bonding. α^2 measure σ -bonding [44], β^2 measures out-of-plane π bonding and γ^2 measure in-plane π -bonding. In the present case, the α^2 value indicates the slight ionic nature of the metal-ligand σ -bonding is more covalent than in-plane π bonding. The deviation from unity in β^2 and γ^2 values indicates the presence of considerable out-of-plane and in-plane π -bonding contribution in metal ligand π -bonding. These data are well in accordance with other reported values [45]. Based on these observations, a distorted octahedral geometry is proposed for the complex (1). The ESR study of the copper(II) complex (1) has provided supportive evidence to the conclusion obtained on the basis of electronic spectrum and magnetic moment value.

3.11. Corrosion inhibition of mild steel using PDMP

3.11.1. Potentiodynamic polarization measurements

The potentiodynamic polarization curves for mild steel in 2 M HCl without and with various concentrations of PDMP at 25 ± 1 °C are shown in Fig. 16. The electrochemical parameters; cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion potential (E_{corr}), and corrosion current density (i_{corr}), were acquired and recorded in Table 18. It was found that i_{corr} decreases by adding the PDMP and by increasing concentration. Fig. 16 clearly demonstrates that both anodic and cathodic reactions are inhibited, which shows that investigated compound go about as mixed-type inhibitor [19,27]. Likewise, the consequences of θ and %IE where calculated utilizing values of i_{corr} . The rate inhibition efficiencies (%IE) calculated from i_{corr} of PDMP is given in Table 18. A review of the outcomes acquired from this Table reveals that, the presence of various concentrations of the added substance decreases the anodic and cathodic current densities and the polarization resistance. This shows the inhibiting effects of the investigated compound.

3.11.2. Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 2 M HCl within the presence of the researched compound was examined by EIS strategy at 25 \pm 1 °C after 30 min immersion. Nyquist plots in the absence and presence of PDMP is exhibited in Fig. 17. It is clear that Nyquist plots demonstrate a single capacitive circle, both in uninhibited and inhibited solutions. The impedance data of mild steel in 2 M HCl are examined as far as an equivalent circuit model Fig. 18 which include the solution resistance R_s and the double layer capacitance C_{dl} which is put in parallel to the charge transfer resistance R_{ct} [19] because of the charge transfer reaction The capacity of double layer (C_{dl}) can be calculated from the accompanying equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$
(14)

where f_{max} is the maximum frequency. The parameters got from impedance values are given in Table 19. It can see from Table 19 that the values of charge transfer resistance R_{ct} increases with inhibitor concentration [27]. On account of impedance studies, %IE increases with inhibitor concentration within the presence of researched inhibitor.

The inhibition efficiency (% IE) and the surface coverage (θ) of the used inhibitor obtained from the impedance measurements were calculated by applying the following relations:

$$\% \mathbf{IE} = \left(1 - \frac{\mathbf{R}_{ct}^{o}}{\mathbf{R}_{ct}}\right) \times 100 \tag{15}$$
$$\theta = \left(1 - \frac{\mathbf{R}_{ct}^{o}}{\mathbf{R}_{ct}}\right) \tag{16}$$

where, R_{ct}^{o} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively.

It is additionally noticed that the (C_{dl}) values tend to decrease when the concentration of these compound increases. This decrease in (C_{dl}) , which can come about because of a decrease in local dielectric consistent and/or an increase in the thickness of the electrical double layer, proposes that this compound molecule function by adsorption at the metal/ solution interface [19]. The inhibiting effect of this compound can be attributed to their parallel adsorption at the metal solution interface.

3.11.3. Electrochemical frequency modulation technique (EFM)

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current values without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [46]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Fig. 19 shows the EFM Intermodulation spectrums of mild steel in 2 M HCl solution containing different concentrations of PDMP compound. The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 200 µA, are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 nA). The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the "activation" model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode [47]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were listed in Table 20. It was found that the addition of tested compound at a given concentration to the acidic solution decreases the corrosion current density, indicating that this compound inhibit the corrosion of mild steel in 2 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality. The inhibition efficiencies% IE_{EFM} increase by increasing the inhibitor concentrations and was calculated as from equation (17):

$$% IE_{EFM} = [1 - (i_{corr} / i_{corr}^{o})] x \ 100$$
 (17)

where i_{corr}^{o} and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

3.12. DNA binding studies

DNA usually exhibits hypochromic as a consequence of the intercalation mode, which involves a strong stacking interaction between an aromatic chromophore and the base pairs of DNA. The intrinsic binding constant to CT-DNA by monitoring the absorption intensity of the charge transfer spectral bands near 346 nm for the ligand (PMDP) and 344, 345, 345, 344 and 345 nm for complexes (1-5), respectively, was determined. The intrinsic binding constant (K_b) of the compound with CT-DNA was determined using the following equation [21]:

$$\frac{[DNA]}{(\varepsilon_a - \varepsilon_f)} = \frac{[DNA]}{(\varepsilon_b - \varepsilon_f)} + \frac{1}{K_b(\varepsilon_a - \varepsilon_f)}$$
(18)

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 bond 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.

DNA interaction study by UV–Visible spectroscopy electronic absorption spectra was initially used to examine the interaction between ligand and CT-DNA. After interaction with increasing amount of DNA, the absorption spectra of ligand (PMDP) and complexes (1–5) display clear hypochromism with slight red shift (~1 nm). These interactions result in the observed hypochromic [48]. The intrinsic binding constant (K_b) values obtained from the absorption spectral technique (Fig. 20) were calculated as 2.61×10^4 M⁻¹ for ligand (PMDP) and 4×10^4 M⁻¹, 2.31×10^4 M⁻¹, 2.81×10^4 M⁻¹, 2.64×10^4 M⁻¹, and 1.99×10^4 M⁻¹ for complexes (1-5), respectively.

3.13. Antimicrobial studies

The antimicrobial Schiff 4-((pyridin-2activity of base ligand yl)methyleneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one (PDMP) and metal complexes (1–5) are tested against three positive and three negative bacteria, two fungi and one yeast using agar well diffusion method [21]. The antibacterial activities were recorded in the present investigations against Bacillus cereus, Staphylococcus aureus, Enterococcus faecalis, Escherichia coli, Klebsiella pneumoniae and Pseudomonas aeruginosa. The zone of inhibition was measured in mm and was compared with a standard drug as listed in Table 21. DMSO was used as a blank and penicillin was used as the antibacterial standard. The results indicated that, these compounds at the prepared concentrations (50, 100 and 150 µg/mL) are inactive against Bacillus cereus, Staphylococcus aureus, Enterococcus faecalis, Escherichia coli, Klebsiella pneumonia except compound PMDP showed low activity against Escherichia coli (1.0 mm at 150 µg/mL only). Complex (4) showed little activities against Pseudomonas aeruginosa at 150 μ g/mL only (0.4 mm). Complexes 2, 3 and 5 have moderate antibacterial activities (0.6, 0.8 and 1.0 mm for complex 2 at 50, 100 and 150 µg/mL respectively, and 0.93, 1.0 and 1.4 mm for complex 3 at 50, 100 and 150 µg/mL respectively, and 0.5, 0.4 and 0.4 mm for complex 5 at 50, 100 and 150 µg/mL respectively) against Pseudomonas aeruginosa when compared with penicillin (Table 21).

The antifungal activities were recorded in the present investigations against *Aspergillus niger*, *Fusarium oxysporum* and the yeast *Candida albicans*. DMSO was used as a blank and miconazole was used as standard antifungal drug and the results were recorded in Table 22. Unfortunately, all the tested compounds in the different prepared concentration did not show any antifungal or anticandidal activities.

Conclusion

In this study, we have synthesized and characterized ligand and complexes by combined study of spectroscopic, magnetic susceptibility and thermal analysis. The ligand behaves tridentate forming five-membered chelating ring towards the metal ions, bonding through azomethine nitrogen, azomethine pyridine nitrogen and exocyclic carbonyl oxygen. Apart from this, XRD studies show that both the ligand and its metal complexes (1 and 3) show polycrystalline with crystal structure. Furthermore, the detailed thermal study played an important role to confirm the number and nature of water molecules in coordination. Double layer capacitances decrease with respect to blank solution when the inhibitor added. This fact may explained by adsorption of the inhibitor molecule on the mild steel surface. EFM can be used as a rapid and nondestructive technique for corrosion measurements without prior knowledge of Tafel slopes. The hetero atoms N and O are the active sites of the PDMP ligand. It can adsorb on Fe surface firmly by donating electrons to Fe atoms and accepting electrons from 3d orbital of Fe atoms.

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Compound ^a	M.p.	$\mu_{eff.}$		Exp. (calco	d.)%	
	(°C)		С	Н	Ν	Μ
		(B.M.)				
PMDP	146	-	69.66	5.63	18.89	-
			(69.86)	(5.48)	(19.18)	
			()			
$[C_{11}(PMDP)C]_{2}H_{2}O](1)$	232	196	45.66	3.92	12.39	14 20
	252	1.70	(45.80)	(4.05)	(12.5)	(14.20)
			(43.69)	(4.03)	(12.00)	(14.29)
$[Co(PMDP)Cl_2 H_2O]$ (2)	> 300	4.92	46.25	3.89	12.55	13.44
			(46.37)	(4.09)	(12.73)	(13.40)
$[Ni(PMDP)Cl_2 H_2O]$ (3)	> 300	3 32	46.26	4 87	12 54	13.04
	2 300	5.52	(46.40)	(4.00)	(12.54)	(12.25)
			(40.40)	(4.09)	(12.74)	(13.33)
	200	5.01			10.55	10.05
$[Mn(PMDP)Cl_2 H_2O] (4)$	> 300	5.31	46.69	4.01	12.66	12.97
			(46.80)	(4.13)	(12.85)	(12.60)
$[Cd(PMDP)Cl_2]$ (5)	> 300	dia.	42.84	3.29	11.53	23.73
			(42.91)	(3.37)	(11.78)	(23.64)
			(,)1)	(0.07)	(111/0)	()

Table	1.	Elemental	analyses	and	physical	properties	of	PMDP	and	its	metal
complexes											

^aThe identification test for the chloride ions inside the coordination sphere was performed using $AgNO_3$ reagent after decomposition of Schiff base complexes by adding 1 mL of concentrated HNO₃. This result proves that two chlorine atoms are attached to metal ion to complete the coordination sphere.

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Peak no.	$2\theta_{\rm obs.}$ (°)	d _{obs.} (Å)	$2\theta_{\text{calc.}}$ (°)	d _{calc.} (Å)	h k l
1	7.9055	11.1831	7.9525	11.1172	201
2	11.0808	7.9846	11.0668	7.9947	101
3	13.5953	6.5130	13.6094	6.4662	<u>102</u>
4	17.2128	5.1514	17.2092	5.1288	011
5	17.8475	4.9697	17.8364	4.9727	210
6	19.4340	4.5674	19.4028	4.5688	303
7	19.8400	4.4748	19.8597	4.4704	203
8	21.3330	4.1649	21.3226	4.1669	<u>1</u> 03
9	22.2188	4.0008	22.1702	4.0095	4 12
10	25.1578	3.5397	25.1685	3.5382	213
11	28.1990	3.1645	28.2077	3.1635	501
12	32.2770	2.7734	32.2569	2.7751	700
13	41.4653	2.1776	41.4904	2.1763	723
14	42.2612	2.1384	42.2709	2.1379	801

Table 2.	Crystallograp	nic data of Schi	iff base ligand	(PMDP).
	2 0 1		U	· /

Peak no.	$2\theta_{obs.}$ (°)	d _{obs.} (Å)	$2\theta_{calc.}$ (°)	d _{calc.} (Å)	h k l
1	7.3115	12.0809	7.3183	12.0697	200
2	10.5892	8.3477	10.5111	8.4095	0 0 1
3	11.7045	7.5546	11.8067	7.4894	201
4	13.8011	6.4113	13.7593	6.4307	2 0 1
5	17.8551	4.9637	17.9591	4.935	211
6	19.4387	4.5627	19.4220	4.5666	4 0 1
7	20.1080	4.4123	20.0809	4.4182	311
8	21.1098	4.2052	21.1119	4.2047	002
9	21.7370	4.0852	21.7113	4.0900	510
10	22.8392	3.8905	22.8235	3.8931	511
11	23.8689	3.7249	23.8531	3.7274	ī 1 2
12	25.4994	3.4903	25.4642	3.4951	511
13	26.2269	3.3951	26.2120	3.3977	212
14	27.6680	3.2215	27.7221	3.2153	402
15	28.5973	3.1189	28.5899	3.1197	4 4 2 1
16	30.3456	2.9430	30.3463	2.9430	421
17	31.7876	2.8128	31.7658	2.8146	711
18	32.7226	2.7345	32.7429	2.7328	6 2 1
19	33.6840	2.6586	33.6835	2.6586	213
20	35.3047	2.5402	35.2625	2.5431	721
21	35.9901	2.4934	35.9534	2.4958	213
22	42.2152	2.1390	42.2099	2.1392	10 1 1
23	45.4007	1.9960	45.4194	1.9952	114
24	47.0556	1.9296	47.1089	1.9275	10 2 1

Table 3.	Crystall	ographic	data of	complex	(1).
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Peak no.	2θ _{obs.} (°)	d _{obs.} (Å)	$2\theta_{\text{calc.}}$ (°)	d _{calc.} (Å)	h k l
1	7.4105	11.9197	7.4152	11.9122	200
2	8.4852	10.4123	8.5041	10.3892	0 0 1
3	9.5564	9.2474	9.5533	9.2504	101
4	10.8258	8.1658	10.8241	8.1670	201
5	15.7132	5.6352	15.7162	5.6341	Ī 1 0
6	17.0627	5.1924	17.0554	5.1946	0 0 2
7	18.9383	4.6822	18.9347	4.6830	<u>3</u> 10

 Table 4. Crystallographic data of complex (3).

Table 5. Energy values obtained in docking calculations of start and Schiff base ligand (PMDP) with receptors of 3hb5-oxidoreductase (breast cancer mutant 3hb5) and 2q7k-hormone (prostate cancer mutant 2q7k).

Compound	Receptors	Est. Free Energy of Binding (kcal/mol)	Est. inhi- bition constant (K _i) (µM)	vdW+ bond+ desolv energy (kcal/mol)	Electrostatic Energy (kcal/mol)	Total in- tercooled Energy (kcal/mol)	Interact surface
Start	3hb5	-4.01	1.15	-4.25	-0.05	-4.31	359.508
	2q7k	-3.58	2.37	-3.79	-0.09	-3.88	280.291
Schiff base	3hb5	-6.68	12.67	-7.73	-0.16	-7.89	732.285
(PMDP)	2q7k	-5.97	41.81	-7.05	+0.03	-7.03	568.364

Bond lengt	ths (Å)	Bond angles (°)			
C(21)-H(38)	1 103	H(37)-C(20)-C(21)	120 173		
C(20)-H(37)	1.103	H(37)-C(20)-C(19)	119.783		
C(19)-H(36)	1.103	C(21)-C(20)-C(19)	120.041		
C(18)-H(35)	1 103	H(36)-C(19)-C(20)	120.492		
C(17)-H(34)	1.101	H(36)-C(19)-C(18)	120.513		
C(15)-H(33)	1.112	C(20)-C(19)-C(18)	118.995		
C(15)-H(32)	1.113	H(35)-C(18)-C(19)	119.575		
C(15)-H(31)	1.112	H(35)-C(18)-C(17)	120.109		
C(13)-H(30)	1.113	C(19)-C(18)-C(17)	120.315		
C(13)-H(29)	1.114	H(38)-C(21)-C(16)	120.86		
C(13)-H(28)	1.112	H(38)-C(21)-C(20)	116.846		
C(7)-H(27)	1.097	C(16)-C(21)-C(20)	122.264		
C(6)-H(26)	1.102	H(34)-C(17)-C(18)	116.063		
C(5)-H(25)	1.103	H(34)-C(17)-C(16)	121.948		
C(2)-H(24)	1.103	C(18)-C(17)-C(16)	121.956		
C(1)-H(23)	1.102	C(21)-C(16)-C(17)	116.421		
C(16)-C(21)	1.349	C(21)-C(16)-N(11)	119.478		
C(20)-C(21)	1.342	C(17)-C(16)-N(11)	124.085		
C(19)-C(20)	1.34	H(30)-C(13)-H(29)	109.096		
C(18)-C(19)	1.34	H(30)-C(13)-H(28)	103.773		
C(17)-C(18)	1.343	H(30)-C(13)-N(12)	112.574		
C(16)-C(17)	1.349	H(29)-C(13)-H(28)	109.301		
C(5)-C(4)	1.348	H(29)-C(13)-N(12)	110.736		
N(3)-C(4)	1.271	H(28)-C(13)-N(12)	111.11		
C(2)-N(3)	1.265	C(9)-N(11)-N(12)	102.377		
C(1)-C(2)	1.341	C(9)-N(11)-C(16)	130.413		
C(6)-C(1)	1.34	N(12)-N(11)-C(16)	122.969		
C(5)-C(6)	1.342	H(33)-C(15)-H(32)	107.721		
N(12)-C(14)	1.277	H(33)-C(15)-H(31)	103.309		
C(8)-C(14)	1.348	H(33)-C(15)-C(14)	112.313		
C(9)-C(8)	1.367	H(32)-C(15)-H(31)	110.77		
N(11)-C(9)	1.274	H(32)-C(15)-C(14)	111.004		
N(12)-N(11)	1.362	H(31)-C(15)-C(14)	111.429		
C(7)-N(22)	1.264	C(14)-N(12)-N(11)	114.2		
C(8)-N(22)	1.267	C(14)-N(12)-C(13)	116.117		
N(11)-C(16)	1.279	N(11)-N(12)-C(13)	129.121		
C(14)-C(15)	1.509	N(12)-C(14)-C(8)	104.51		
N(12)-C(13)	1.485	N(12)-C(14)-C(15)	127.747		
C(9)-O(10)	1.215	C(8)-C(14)-C(15)	127.523		
C(4)-C(/)	1.35	C(8)-C(9)-N(11)	111.358		
		U(8) - U(9) - U(10)	124.109		
		N(11)-C(9)-O(10)	124.389		
		C(14) - C(8) - C(9)	100.338		
		C(14)-C(8)-IN(22)	134.208		
		\cup	117.420		

Table 6. The selected geometric parameters for Schiff base ligand (PMDP).

C(7)-N(22)-C(8)	128.685
H(26)-C(6)-C(1)	120.767
H(26)-C(6)-C(5)	121.098
C(1)-C(6)-C(5)	118.134
H(27)-C(7)-N(22)	118.763
H(27)-C(7)-C(4)	116.417
N(22)-C(7)-C(4)	124.806
H(25)-C(5)-C(4)	121.923
H(25)-C(5)-C(6)	117.909
C(4)-C(5)-C(6)	120.168
C(5)-C(4)-N(3)	120.353
C(5)-C(4)-C(7)	122.158
N(3)-C(4)-C(7)	117.488
C(4)-N(3)-C(2)	120.096
H(24)-C(2)-N(3)	116.224
H(24)-C(2)-C(1)	119.827
N(3)-C(2)-C(1)	123.949
H(23)-C(1)-C(2)	121.385
H(23)-C(1)-C(6)	121.315
C(2)-C(1)-C(6)	117.299

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Bond lengths	Bond angles (Bond angles (°)		
O(26)-H(44)	1.016	H(41)-C(20)-C(21)	120.178	
O(26)-H(43)	1.024	H(41)-C(20)-C(19)	119.713	
C(21)-H(42)	1.101	C(21)-C(20)-C(19)	120.102	
C(20)-H(41)	1.103	H(40)-C(19)-C(20)	120.536	
C(19)-H(40)	1.103	H(40)-C(19)-C(18)	120.541	
C(18)-H(39)	1.103	C(20)-C(19)-C(18)	118.917	
C(17)-H(38)	1.101	H(39)-C(18)-C(19)	119.593	
C(15)-H(37)	1.112	H(39)-C(18)-C(17)	120.134	
C(15)-H(36)	1.113	C(19)-C(18)-C(17)	120.274	
C(15)-H(35)	1.113	H(42)-C(21)-C(16)	121.215	
C(13)-H(34)	1.113	H(42)-C(21)-C(20)	116.436	
C(13)-H(33)	1.111	C(16)-C(21)-C(20)	122.315	
C(13)-H(32)	1.113	H(38)-C(17)-C(18)	115.883	
C(7)-H(31)	1.104	H(38)-C(17)-C(16)	122.004	
C(6)-H(30)	1.107	C(18)-C(17)-C(16)	122.1	
C(3)-H(29)	1.101	C(21)-C(16)-C(17)	116.261	
C(2)-H(28)	1.102	C(21)-C(16)-N(11)	120.903	
C(1)-H(27)	1.103	C(17)-C(16)-N(11)	122.794	
C(16)-C(21)	1.349	H(34)-C(13)-H(33)	104.349	
C(20)-C(21)	1.342	H(34)-C(13)-H(32)	110.019	
C(19)-C(20)	1.34	H(34)-C(13)-N(12)	110.691	
C(18)-C(19)	1.34	H(33)-C(13)-H(32)	107.714	
C(17)-C(18)	1.343	H(33)-C(13)-N(12)	113.506	
C(16)-C(17)	1.349	H(32)-C(13)-N(12)	110.358	
O(10)-Cu(23)	1.841	H(37)-C(15)-H(36)	107.383	
N(5)-Cu(23)	1.383	H(37)-C(15)-H(35)	106.92	
N(22)-Cu(23)	1.391	H(37)-C(15)-C(14)	111.854	
O(26)-Cu(23)	1.862	H(36)-C(15)-H(35)	109.351	
Cu(23)-Cl(25)	2.187	H(36)-C(15)-C(14)	110.556	
Cu(23)-Cl(24)	2.186	H(35)-C(15)-C(14)	110.644	
C(7)-N(22)	1.272	C(14)-N(12)-C(13)	115.287	
C(8)-N(22)	1.278	C(14)-N(12)-N(11)	115.32	
N(11)-C(16)	1.277	C(13)-N(12)-N(11)	129.081	
C(8)-C(14)	1.34	C(8)-C(14)-C(15)	123.894	
C(14)-C(15)	1.504	C(8)-C(14)-N(12)	104.331	
N(12)-C(14)	1.283	C(15)-C(14)-N(12)	131.758	
N(12)-C(13)	1.484	C(16)-N(11)-N(12)	127.287	
N(11)-N(12)	1.367	C(16)-N(11)-C(9)	129.92	
C(9)-N(11)	1.266	N(12)-N(11)-C(9)	99.515	
V(9) - U(10)	1.215	N(11)-C(9)-O(10)	138.73	
C(8)-C(9)	1.348	N(11)-C(9)-C(8)	114.778	
C(4)-C(7)	1.535	U(10)-U(9)-U(8)	106.485	
U(0)-U(1)	1.548	H(44)-U(26)-H(43) $H(44)-O(26)-G_{}(22)$	/0.952	
N(3) - U(0) C(4) N(5)	1.281	$\Pi(44) - O(20) - O(23)$ $\Pi(42) O(25) Cu(23)$	90.708 127 100	

 Table 7. The selected geometric parameters for complex (1).

C(3)-C(4)	1.342	N(22)-C(8)-C(14)	137.394
C(2)-C(3)	1.341	N(22)-C(8)-C(9)	117.36
C(1)-C(2)	1.342	C(14)-C(8)-C(9)	105.123
		Cu(23)-N(22)-C(7)	107.896
		Cu(23)-N(22)-C(8)	114.867
		C(7)-N(22)-C(8)	107.001
		Cu(23)-O(10)-C(9)	109.084
		O(10)-Cu(23)-N(5)	92.219
		O(10)-Cu(23)-N(22)	88.747
		O(10)-Cu(23)-O(26)	93.475
		O(10)-Cu(23)-Cl(25)	86.752
		O(10)-Cu(23)-Cl(24)	172.496
		N(5)-Cu(23)-N(22)	102.892
		N(5)-Cu(23)-O(26)	89.606
		N(5)-Cu(23)-Cl(25)	166.066
		N(5)-Cu(23)-Cl(24)	94.54
		N(22)-Cu(23)-O(26)	167.222
		N(22)-Cu(23)-Cl(25)	90.983
		N(22)-Cu(23)-Cl(24)	92.912
		O(26)-Cu(23)-Cl(25)	76.599
		O(26)-Cu(23)-Cl(24)	83.329
		Cl(25)-Cu(23)-Cl(24)	85.904
		H(30)-C(6)-C(1)	113.55
		H(30)-C(6)-N(5)	123.79
		C(1)-C(6)-N(5)	122.64
		H(31)-C(7)-N(22)	124.745
		H(31)-C(7)-C(4)	124.77
		N(22)-C(7)-C(4)	110.377
		Cu(23)-N(5)-C(6)	130.187
		Cu(23)-N(5)-C(4)	110.015
		C(6)-N(5)-C(4)	112.849
		C(7)-C(4)-N(5)	107.837
		C(7)-C(4)-C(3)	126.498
		N(5)-C(4)-C(3)	125.646
		H(29)-C(3)-C(4)	121.943
		H(29)-C(3)-C(2)	120.911
		C(4)-C(3)-C(2)	116.866
		H(28)-C(2)-C(3)	121.1
		H(28)-C(2)-C(1)	121.164
		C(3)-C(2)-C(1)	116.618
		H(27)-C(1)-C(6)	120.903
		H(27)-C(1)-C(2)	119.721
		C(6)-C(1)-C(2)	119.217
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Bond lengths (Å)		Bond angles (°)	
O(26)-H(44)	1.11	H(41)-C(20)-C(21)	120.195
O(26)-H(43)	1.134	H(41)-C(20)-C(19)	119.748
C(21)-H(42)	1.102	C(21)-C(20)-C(19)	120.051
C(20)-H(41)	1.103	H(40)-C(19)-C(20)	120.552
C(19)-H(40)	1.103	H(40)-C(19)-C(18)	120.554
C(18)-H(39)	1.103	C(20)-C(19)-C(18)	118.892
C(17)-H(38)	1.1	H(39)-C(18)-C(19)	119.553
C(15)-H(37)	1.113	H(39)-C(18)-C(17)	120.121
C(15)-H(36)	1.113	C(19)-C(18)-C(17)	120.326
C(15)-H(35)	1.113	H(42)-C(21)-C(16)	120.964
C(13)-H(34)	1.113	H(42)-C(21)-C(20)	116.557
C(13)-H(33)	1.112	C(16)-C(21)-C(20)	122.441
C(13)-H(32)	1.113	H(38)-C(17)-C(18)	115.525
C(7)-H(31)	1.104	H(38)-C(17)-C(16)	122.308
C(6)-H(30)	1.104	C(18)-C(17)-C(16)	122.135
C(3)-H(29)	1.102	C(21)-C(16)-C(17)	116.138
C(2)-H(28)	1.102	C(21)-C(16)-N(11)	119.619
C(1)-H(27)	1.102	C(17)-C(16)-N(11)	124.215
C(16)-C(21)	1.349	H(34)-C(13)-H(33)	104.524
C(20)-C(21)	1.342	H(34)-C(13)-H(32)	109.828
C(19)-C(20)	1.34	H(34)-C(13)-N(12)	110.912
C(18)-C(19)	1.34	H(33)-C(13)-H(32)	107.795
C(17)-C(18)	1.343	H(33)-C(13)-N(12)	113.122
C(16)-C(17)	1.349	H(32)-C(13)-N(12)	110.45
O(10)-Co(23)	0.999	H(37)-C(15)-H(36)	107.21
N(5)-Co(23)	1.884	H(37)-C(15)-H(35)	109.22
N(22)-Co(23)	1.872	H(37)-C(15)-C(14)	110.682
O(26)-Co(23)	1.184	H(36)-C(15)-H(35)	107.602
Co(23)-Cl(25)	2.193	H(36)-C(15)-C(14)	111.519
Co(23)-Cl(24)	2.192	H(35)-C(15)-C(14)	110.489
C(7)-N(22)	1.269	C(14)-N(12)-C(13)	114.961
C(8)-N(22)	1.256	C(14)-N(12)-N(11)	114.944
N(11)-C(16)	1.279	C(13)-N(12)-N(11)	129.792
C(8)-C(14)	1.333	C(8)-C(14)-C(15)	125.333
C(14)-C(15)	1.501	C(8)-C(14)-N(12)	101.683
N(12)-C(14)	1.279	C(15)-C(14)-N(12)	132.929
N(12)-C(13)	1.484	C(16)-N(11)-N(12)	123.372
N(11)-N(12)	1.368	C(16)-N(11)-C(9)	129.836
C(9)-N(11)	1.281	N(12)-N(11)-C(9)	102.892
$\mathbf{C}(9)$ - $\mathbf{O}(10)$	1.252	N(11)-C(9)-O(10)	130.384
C(8)-C(9)	1.345	N(11)-C(9)-C(8)	108.301
C(4)-C(7)	1.341	U(10)-U(9)-U(8)	121.187
U(0) - U(1)	1.345	H(44)-O(26)-H(43)	62.652
N(3)-U(0)	1.278	$\Pi(44)-\Pi(26)-\Pi(23)$ $\Pi(42)=\Omega(26)-\Pi(23)$	127.099
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 Table 8. The selected geometric parameters for complex (2).

C(3)-C(4)	1.345	N(22)-C(8)-C(14)	142.345
C(2)-C(3)	1.341	N(22)-C(8)-C(9)	106.659
C(1)-C(2)	1.341	C(14)-C(8)-C(9)	110.894
		Co(23)-N(22)-C(7)	113.726
		Co(23)-N(22)-C(8)	92.8
		C(7)-N(22)-C(8)	107.544
		Co(23)-O(10)-C(9)	109.63
		O(10)-Co(23)-N(5)	90.111
		O(10)-Co(23)-N(22)	106.437
		O(10)-Co(23)-O(26)	109.768
		O(10)-Co(23)-Cl(25)	165.29
		O(10)-Co(23)-Cl(24)	90.271
		N(5)-Co(23)-N(22)	80.665
		N(5)-Co(23)-O(26)	159.757
		N(5)-Co(23)-Cl(25)	78.814
		N(5)-Co(23)-Cl(24)	92.91
		N(22)-Co(23)-O(26)	89.748
		N(22)-Co(23)-Cl(25)	81.503
		N(22)-Co(23)-Cl(24)	161.999
		O(26)-Co(23)-Cl(25)	82.175
		O(26)-Co(23)-Cl(24)	90.838
		Cl(25)-Co(23)-Cl(24)	80.756
		H(30)-C(6)-C(1)	115.184
		H(30)-C(6)-N(5)	121.248
		C(1)-C(6)-N(5)	123.523
		H(31)-C(7)-N(22)	120.346
		H(31)-C(7)-C(4)	123.186
		N(22)-C(7)-C(4)	116.399
		Co(23)-N(5)-C(6)	124.58
		Co(23)-N(5)-C(4)	114.492
		C(6)-N(5)-C(4)	114.779
		C(7)-C(4)-N(5)	113.973
		C(7)-C(4)-C(3)	122.417
		N(5)-C(4)-C(3)	123.58
		H(29)-C(3)-C(4)	121.637
		H(29)-C(3)-C(2)	119.791
		C(4)-C(3)-C(2)	118.402
		H(28)-C(2)-C(3)	121.225
		H(28)-C(2)-C(1)	121.182
		C(3)-C(2)-C(1)	116.951
		H(27)-C(1)-C(6)	121.082
		H(27)-C(1)-C(2)	120.317

Bond lengths (Å)			
		Bond angles (°)	
O(26)-H(44)	1.033	H(41)-C(20)-C(21)	120.147
O(26)-H(43)	1.038	H(41)-C(20)-C(19)	119.608
C(21)-H(42)	1.102	C(21)-C(20)-C(19)	120.245
C(20)-H(41)	1.103	H(40)-C(19)-C(20)	120.548
C(19)-H(40)	1.103	H(40)-C(19)-C(18)	120.549
C(18)-H(39)	1.103	C(20)-C(19)-C(18)	118.9
C(17)-H(38)	1.101	H(39)-C(18)-C(19)	119.684
C(15)-H(37)	1.113	H(39)-C(18)-C(17)	120.176
C(15)-H(36)	1.113	C(19)-C(18)-C(17)	120.133
C(15)-H(35)	1.113	H(42)-C(21)-C(16)	121.899
C(13)-H(34)	1.113	H(42)-C(21)-C(20)	115.901
C(13)-H(33)	1.112	C(16)-C(21)-C(20)	122.179
C(13)-H(32)	1.113	H(38)-C(17)-C(18)	116.287
C(7)-H(31)	1.105	H(38)-C(17)-C(16)	121.327
C(6)-H(30)	1.1	C(18)-C(17)-C(16)	122.343
C(3)-H(29)	1.102	C(21)-C(16)-C(17)	116.183
C(2)-H(28)	1.102	C(21)-C(16)-N(11)	122.349
C(1)-H(27)	1.102	C(17)-C(16)-N(11)	121.44
C(16)-C(21)	1.35	H(34)-C(13)-H(33)	107.643
C(20)-C(21)	1.343	H(34)-C(13)-H(32)	110.215
C(19)-C(20)	1.34	H(34)-C(13)-N(12)	110.433
C(18)-C(19)	1.34	H(33)-C(13)-H(32)	104.347
C(17)-C(18)	1.342	H(33)-C(13)-N(12)	113.388
C(16)-C(17)	1.348	H(32)-C(13)-N(12)	110.617
O(10)-Ni(23)	1.815	H(37)-C(15)-H(36)	107.195
N(5)-Ni(23)	1.839	H(37)-C(15)-H(35)	109.332
N(22)-Ni(23)	1.846	H(37)-C(15)-C(14)	110.635
O(26)-Ni(23)	1.836	H(36)-C(15)-H(35)	107.443
Ni(23)-Cl(25)	2.152	H(36)-C(15)-C(14)	111.478
Ni(23)-Cl(24)	2.152	H(35)-C(15)-C(14)	110.634
C(7)-N(22)	1.275	C(14)-N(12)-C(13)	115.384
C(8)-N(22)	1.268	C(14)-N(12)-N(11)	114.66
N(11)-C(16)	1.278	C(13)-N(12)-N(11)	129.85
C(8)-C(14)	1.338	C(8)-C(14)-C(15)	123.981
C(14)-C(15)	1.503	C(8)-C(14)-N(12)	103.867
N(12)-C(14)	1.28	C(15)-C(14)-N(12)	132.137
N(12)-C(13)	1.483	C(16)-N(11)-N(12)	127.289
N(11)-N(12)	1.366	C(16)-N(11)-C(9)	128.551
C(9)-N(11)	1.271	N(12)-N(11)-C(9)	101.697
C(9) - O(10)	1.227	N(11)-C(9)-O(10)	131.268
C(8) - C(9)	1.35	N(11)-C(9)-C(8)	112.215
C(4)-C(7)	1.341	U(10)-U(9)-U(8)	115.409
C(6)-C(1)	1.343	H(44)-O(26)-H(43)	168.59
N(3)-C(6)	1.268	H(44)-U(26)-N1(23)	97.856
U(4) - N(5)	1 268	$\Pi(4.5) - U(20) - N(2.5)$	95.54

 Table 9. The selected geometric parameters for complex (3).
$\begin{array}{l} N(22) \cdot O(3) \cdot O(11) \\ N(22) \cdot O(8) \cdot O(9) \\ C(14) \cdot O(8) \cdot O(9) \\ Ni(23) \cdot N(22) \cdot O(7) \\ Ni(23) \cdot N(22) \cdot O(8) \\ C(7) \cdot N(22) \cdot O(8) \\ C(7) \cdot N(22) \cdot O(8) \\ O(10) \cdot Ni(23) \cdot N(5) \\ O(10) \cdot Ni(23) \cdot N(5) \\ O(10) \cdot Ni(23) \cdot O(26) \\ N(5) \cdot Ni(23) \cdot O(26) \\ N(22) \cdot Ni(23)$	116.288 107.215 109.939 105.403 105.896 109.625 97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.562
C(14)-C(8)-C(9) Ni(23)-N(22)-C(7) Ni(23)-N(22)-C(8) C(7)-N(22)-C(8) Ni(23)-O(10)-C(9) O(10)-Ni(23)-N(5) O(10)-Ni(23)-N(22) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25)	107.215 109.939 105.403 105.896 109.625 97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
Ni(23)-N(22)-C(7) Ni(23)-N(22)-C(8) C(7)-N(22)-C(8) Ni(23)-O(10)-C(9) O(10)-Ni(23)-N(5) O(10)-Ni(23)-N(22) O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	109.939 105.403 105.896 109.625 97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
Ni(23)-N(22)-C(8) C(7)-N(22)-C(8) Ni(23)-O(10)-C(9) O(10)-Ni(23)-N(5) O(10)-Ni(23)-N(22) O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	105.403 105.896 109.625 97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
C(7)-N(22)-C(8) Ni(23)-O(10)-C(9) O(10)-Ni(23)-N(5) O(10)-Ni(23)-N(22) O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(24) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	105.896 109.625 97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.562
Ni(23)-O(10)-C(9) O(10)-Ni(23)-N(5) O(10)-Ni(23)-N(22) O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	109.625 97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
O(10)-Ni(23)-N(5) O(10)-Ni(23)-N(22) O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	97.645 83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
O(10)-Ni(23)-N(22) O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-N(22) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	83.647 82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
O(10)-Ni(23)-O(26) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-N(22) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	82.064 169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.562
O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(25) O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	169.51 89.009 82.86 172.083 91.56 103.683 89.251 92.563
O(10)-Ni(23)-Cl(24) N(5)-Ni(23)-N(22) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-O(26) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	89.009 82.86 172.083 91.56 103.683 89.251 92.563
N(5)-Ni(23)-N(22) N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-O(26) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	82.86 172.083 91.56 103.683 89.251 02.563
N(5)-Ni(23)-O(26) N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-O(26) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	172.083 91.56 103.683 89.251
N(5)-Ni(23)-Cl(25) N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-O(26) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	91.56 103.683 89.251 02.562
N(5)-Ni(23)-Cl(24) N(22)-Ni(23)-O(26) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	103.683 89.251
N(22)-Ni(23)-O(26) N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	89.251
N(22)-Ni(23)-Cl(25) N(22)-Ni(23)-Cl(24)	02 562
N(22)-Ni(23)-Cl(24)	רחנ ∠ע
	170 795
O(26)-Ni(23)-Cl(25)	88 124
O(26) - Ni(23) - Cl(24)	84.23
Cl(25)-Ni(23)-Cl(24)	93 709
H(30)-C(6)-C(1)	118.693
H(30)-C(6)-N(5)	117.613
C(1)-C(6)-N(5)	123 629
H(31)-C(7)-N(22)	120.102
H(31)-C(7)-C(4)	121.637
N(22)-C(7)-C(4)	117.492
Ni(23)-N(5)-C(6)	121.721
Ni(23)-N(5)-C(4)	111.094
C(6)-N(5)-C(4)	118.128
C(7)-C(4)-N(5)	112.302
C(7)-C(4)-C(3)	124.421
N(5)-C(4)-C(3)	123.265
H(29)-C(3)-C(4)	121.324
H(29)-C(3)-C(2)	120.17
C(4)-C(3)-C(2)	118.485
H(28)-C(2)-C(3)	121.011
H(28)-C(2)-C(1)	120.962
C(3)-C(2)-C(1)	118.001
H(27)-C(1)-C(6)	120.969
H(27)-C(1)-C(2)	120.834
C(6)-C(1)-C(2)	118.197
	N(22)-N(23)-Cl(23) $N(22)-Ni(23)-Cl(24)$ $O(26)-Ni(23)-Cl(24)$ $Cl(25)-Ni(23)-Cl(24)$ $H(30)-C(6)-N(5)$ $C(1)-C(6)-N(5)$ $H(31)-C(7)-N(22)$ $H(31)-C(7)-N(22)$ $H(31)-C(7)-C(4)$ $N(22)-C(7)-C(4)$ $N(22)-C(7)-C(4)$ $N(23)-N(5)-C(6)$ $Ni(23)-N(5)-C(4)$ $C(7)-C(4)-N(5)$ $C(7)-C(4)-C(3)$ $H(29)-C(3)-C(4)$ $H(29)-C(3)-C(4)$ $H(29)-C(3)-C(2)$ $C(4)-C(3)$ $H(28)-C(2)-C(1)$ $H(28)-C(2)-C(1)$ $H(27)-C(1)-C(2)$ $C(6)-C(1)-C(2)$

Bond length	ns (Å)	Bond angles (°)
O(26)-H(44)	1.046	H(41)-C(20)-C(21)	120.142
O(26)-H(43)	1.05	H(41)-C(20)-C(19)	119.612
C(21)-H(42)	1.102	C(21)-C(20)-C(19)	120.247
C(20)-H(41)	1.103	H(40)-C(19)-C(20)	120.553
C(19)-H(40)	1.103	H(40)-C(19)-C(18)	120.548
C(18)-H(39)	1.103	C(20)-C(19)-C(18)	118.895
C(17)-H(38)	1.1	H(39)-C(18)-C(19)	119.687
C(15)-H(37)	1.113	H(39)-C(18)-C(17)	120.173
C(15)-H(36)	1.113	C(19)-C(18)-C(17)	120.132
C(15)-H(35)	1.113	H(42)-C(21)-C(16)	121.905
C(13)-H(34)	1.113	H(42)-C(21)-C(20)	115.89
C(13)-H(33)	1.112	C(16)-C(21)-C(20)	122.185
C(13)-H(32)	1.113	H(38)-C(17)-C(18)	116.281
C(7)-H(31)	1.107	H(38)-C(17)-C(16)	121.325
C(6)-H(30)	1.106	C(18)-C(17)-C(16)	122.351
C(3)-H(29)	1.102	C(21)-C(16)-C(17)	116.171
C(2)-H(28)	1.102	C(21)-C(16)-N(11)	122.387
C(1)-H(27)	1.102	C(17)-C(16)-N(11)	121.413
C(16)-C(21)	1.35	H(34)-C(13)-H(33)	107.656
C(20)-C(21)	1.343	H(34)-C(13)-H(32)	110.215
C(19)-C(20)	1.34	H(34)-C(13)-N(12)	110.439
C(18)-C(19)	1.34	H(33)-C(13)-H(32)	104.349
C(17)-C(18)	1.342	H(33)-C(13)-N(12)	113.358
C(16)-C(17)	1.348	H(32)-C(13)-N(12)	110.623
O(10)-Mn(23)	1.835	H(37)-C(15)-H(36)	107.214
N(5)-Mn(23)	1.86	H(37)-C(15)-H(35)	109.34
N(22)-Mn(23)	1.864	H(37)-C(15)-C(14)	110.624
O(26)-Mn(23)	1.864	H(36)-C(15)-H(35)	107.43
Mn(23)-Cl(25)	2.17	H(36)-C(15)-C(14)	111.477
Mn(23)-Cl(24)	2.17	H(35)-C(15)-C(14)	110.633
C(7)-N(22)	1.275	C(14)-N(12)-C(13)	115.347
C(8)-N(22)	1.268	C(14)-N(12)-N(11)	114.666
N(11)-C(16)	1.278	C(13)-N(12)-N(11)	129.869
C(8)-C(14)	1.338	C(8)-C(14)-C(15)	123.984
C(14)-C(15)	1.503	C(8)-C(14)-N(12)	103.826
N(12)-C(14)	1.28	C(15)-C(14)-N(12)	132.177
N(12)-C(13)	1.483	C(16)-N(11)-N(12)	127.281
N(11)-N(12)	1.366	C(16)-N(11)-C(9)	128.602
C(9)-N(11)	1.271	N(12)-N(11)-C(9)	101.741
C(9)-O(10)	1.228	N(11)-C(9)-O(10)	131.306
C(8)-C(9)	1.35	N(11)-C(9)-C(8)	112.114
C(4)-C(7)	1.343	O(10)-C(9)-C(8)	115.489
C(6)-C(1)	1.345	H(44)-O(26)-H(43)	160.469
N(5)-C(6)	1.273	H(44)-O(26)-Mn(23)	102.292
('(4) - N(5))	1.27	H(43)-O(26)-Mn(23)	97 223

 Table 10. The selected geometric parameters for complex (4).

C(3)-C(4)	1.344	N(22)-C(8)-C(14)	136.446
C(2)-C(3)	1.341	N(22)-C(8)-C(9)	116.108
C(1)-C(2)	1.341	C(14)-C(8)-C(9)	107.296
		Mn(23)-N(22)-C(7)	108.889
		Mn(23)-N(22)-C(8)	105.594
		C(7)-N(22)-C(8)	106.896
		Mn(23)-O(10)-C(9)	109.621
		O(10)-Mn(23)-N(5)	100.851
		O(10)-Mn(23)-N(22)	82.526
		O(10)-Mn(23)-O(26)	80.339
		O(10)-Mn(23)-Cl(25)	165.716
		O(10)-Mn(23)-Cl(24)	88.481
		N(5)-Mn(23)-N(22)	82.853
		N(5)-Mn(23)-O(26)	174.622
		N(5)-Mn(23)-Cl(25)	91.929
		N(5)-Mn(23)-Cl(24)	101.531
		N(22)-Mn(23)-O(26)	92.135
		N(22)-Mn(23)-Cl(25)	92.868
		N(22)-Mn(23)-Cl(24)	170.625
		O(26)-Mn(23)-Cl(25)	86.356
		O(26)-Mn(23)-Cl(24)	83.712
		Cl(25)-Mn(23)-Cl(24)	95.244
		H(30)-C(6)-C(1)	115.781
		H(30)-C(6)-N(5)	120.776
		C(1)-C(6)-N(5)	123.309
		H(31)-C(7)-N(22)	120.033
		H(31)-C(7)-C(4)	121.504
		N(22)-C(7)-C(4)	117.68
		Mn(23)-N(5)-C(6)	123.173
		Mn(23)-N(5)-C(4)	108.843
		C(6)-N(5)-C(4)	118.121
		C(7)-C(4)-N(5)	113.239
		C(7)-C(4)-C(3)	123.364
	· Y	N(5)-C(4)-C(3)	123.385
		H(29)-C(3)-C(4)	121.391
		H(29)-C(3)-C(2)	119.998
		C(4)-C(3)-C(2)	118.602
		H(28)-C(2)-C(3)	121.078
		H(28)-C(2)-C(1)	121.053
		C(3)-C(2)-C(1)	117.866
		H(27)-C(1)-C(6)	120.942
		H(27)-C(1)-C(2)	120.436

Bond length	s (Å)	Bond angles (°)	
C(21)-H(41)	1.1	H(40)-C(20)-C(21)	120.129
C(20)-H(40)	1.103	H(40)-C(20)-C(19)	119.524
C(19)-H(39)	1.103	C(21)-C(20)-C(19)	120.347
C(18)-H(38)	1.103	H(39)-C(19)-C(20)	120.57
C(17)-H(37)	1.102	H(39)-C(19)-C(18)	120.548
C(15)-H(36)	1.11	C(20)-C(19)-C(18)	118.879
C(15)-H(35)	1.113	H(38)-C(18)-C(19)	119.754
C(15)-H(34)	1.113	H(38)-C(18)-C(17)	120.199
C(13)-H(33)	1.114	C(19)-C(18)-C(17)	120.041
C(13)-H(32)	1.112	H(41)-C(21)-C(16)	122.23
C(13)-H(31)	1.113	H(41)-C(21)-C(20)	115.613
C(7)-H(30)	1.114	C(16)-C(21)-C(20)	122.132
C(6)-H(29)	1.102	H(37)-C(17)-C(18)	116.489
C(5)-H(28)	1.097	H(37)-C(17)-C(16)	121.004
C(2)-H(27)	1.103	C(18)-C(17)-C(16)	122.472
C(1)-H(26)	1.102	C(21)-C(16)-C(17)	116.107
C(16)-C(21)	1.349	C(21)-C(16)-N(11)	124.28
C(20)-C(21)	1.343	C(17)-C(16)-N(11)	119.576
C(19)-C(20)	1.34	H(33)-C(13)-H(32)	108.198
C(18)-C(19)	1.34	H(33)-C(13)-H(31)	109.695
C(17)-C(18)	1.342	H(33)-C(13)-N(12)	110.546
C(16)-C(17)	1.35	H(32)-C(13)-H(31)	104.156
C(5)-C(4)	1.348	H(32)-C(13)-N(12)	113.045
N(3)-C(4)	1.273	H(31)-C(13)-N(12)	110.973
C(2)-N(3)	1.265	C(16)-N(11)-N(12)	124.112
C(1)-C(2)	1.34	C(16)-N(11)-C(9)	130.771
C(6)-C(1)	1.339	N(12)-N(11)-C(9)	101.542
C(5)-C(6)	1.342	Cd(23)-O(10)-C(9)	108.984
N(22)-Cd(23)	2.173	H(36)-C(15)-H(35)	106.615
O(10)-Cd(23)	2.132	H(36)-C(15)-H(34)	106.672
Cd(23)-Cl(25)	2.475	H(36)-C(15)-C(14)	113.433
Cd(23)-Cl(24)	2.475	H(35)-C(15)-H(34)	109.096
C(7)-N(22)	1.277	H(35)-C(15)-C(14)	110.44
C(8)-N(22)	1.287	H(34)-C(15)-C(14)	110.397
N(11)-C(16)	1.279	C(14)-N(12)-C(13)	115.812
C(8)-C(14)	1.346	C(14)-N(12)-N(11)	114.333
C(14)-C(15)	1.508	C(13)-N(12)-N(11)	129.529
N(12)-C(14)	1.277	C(8)-C(14)-C(15)	125.214
N(12)-C(13)	1.485	C(8)-C(14)-N(12)	105.37
N(11)-N(12)	1.363	C(15)-C(14)-N(12)	129.387
C(9)-N(11)	1.273	N(11)-C(9)-O(10)	128.704
C(9)-O(10)	1.229	N(11)-C(9)-C(8)	112.058
C(8)-C(9)	1.379	O(10)-C(9)-C(8)	119.139
C(4)-C(7)	1.354	N(22)-Cd(23)-O(10)	81.077
		N(22)-Cd(23)-Cl(25)	114.51

Table 11. The selected geometric parameters for complex (5).

N(22)-Cd(23)-Cl(24)	114.722
O(10)-Cd(23)-Cl(25)	114.652
O(10)-Cd(23)-Cl(24)	114.729
Cl(25)-Cd(23)-Cl(24)	113.42
N(22)-C(8)-C(14)	125.434
N(22)-C(8)-C(9)	129.522
C(14)-C(8)-C(9)	104.885
Cd(23)-N(22)-C(7)	111.139
Cd(23)-N(22)-C(8)	100.52
C(7)-N(22)-C(8)	113.764
H(29)-C(6)-C(1)	120.651
H(29)-C(6)-C(5)	121.121
C(1)-C(6)-C(5)	118.228
H(30)-C(7)-N(22)	109.727
H(30)-C(7)-C(4)	114.115
N(22)-C(7)-C(4)	136.158
H(28)-C(5)-C(4)	122.7
H(28)-C(5)-C(6)	116.315
C(4)-C(5)-C(6)	120.985
C(5)-C(4)-N(3)	118.937
C(5)-C(4)-C(7)	125.505
N(3)-C(4)-C(7)	115.557
C(4)-N(3)-C(2)	121.051
H(27)-C(2)-N(3)	116.261
H(27)-C(2)-C(1)	119.817
N(3)-C(2)-C(1)	123.922
H(26)-C(1)-C(2)	121.597
H(26)-C(1)-C(6)	121.526
C(2)-C(1)-C(6)	116.877

Compound [*]	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	σ $(eV)^{-1}$	Pi (eV)	S (eV) ⁻¹	ω (eV)	ΔN_{max}
PMDP	-7.188	-1.788	5.400	4.488	2.700	0.370	-4.488	0.185	3.730	1.662
(1)	-3.27	-2.335	0.935	2.803	0.468	2.139	-2.803	1.070	8.400	5.995
(2)	-4.013	-3.349	0.664	3.681	0.332	3.012	-3.681	1.506	20.406	11.087
(3)	-7.528	-6.123	1.405	6.826	0.703	1.423	-6.826	0.712	33.158	9.716
(4)	-7.976	-7.906	0.070	7.941	0.035	28.571	-7.941	14.286	900.850	226.886
(5)	-6.287	-3.329	2.958	4.808	1.479	0.676	-4.808	0.338	7.815	3.251

Table 12. The calculated quantum chemical parameters for PMDP and its complexes

*Numbers as given in Table 1

 Table 13. IR spectra data (cm⁻¹) of PMDP and its metal complexes

Compound ^a	υ(C=O)	υ(C=N)	Pyridine C-C stretching vibrations	υ(M-O) υ(M-N)	C=C	υCH;CH ₃
PMDP	1644	1562	1490 1465 1416 620 437		1590	3082,3032,2922
1	1609	1529	1492 1460 1426 627 440	528 416	1602	3082,3032,2922
2	1619	1539	1492 1458 1427 637 445	519 410	1595	3030,2924,2854
						, ,
3	1614	1540	1493 1464 1445 632 432	520 412	1609	3087.3056.3022.2921
-						
4	1610	1520	1493 1466 1442 630 432	535 430	1608	3022,2924
	1010	1020		000 100	1000	
5	1606	1524	1496 1466 1424 620	530 /20	1605	3055 2925
5	1000	1527	1470 1400 1424 020	550 720	1005	5055,4745

Metal ion*		C=O			C=N	
_						
	Δυ	logΔυ	r(Å)	Δυ	logΔυ	r(Å)
(1)	35	1.5441	2.53	33	1.5185	2.643
(1)						
(2)	25	1.3979	2,57	22	1.3424	3.083
(3)	30	1.4770	2.66	23	1.3617	2.994

Table 14. Band shift and coordination bond-length Schiff base-metal complexes

Compound ^a	TG range	Mass loss	Total mass loss Exp.	Assignment	Residue
	(°C)	Exp. (Calcd.) %	(Calcd.) %		
PMDP	40-475	64.48 (64.04)	100	$C_{11}H_{11}N_2O$	
	475-800	35.52 (35.96)	(100)	C ₆ H ₅ N ₂	-
(1)	130-206	4.16 (4.05)		H ₂ O	
	206-342	16.62 (15.97)	82.23	Cl ₂	CuO
	342-638	61.45 (62.09)	(82.80)	$C_{17}H_{16}N_4$	
(2)	160-288	3.96 (4.09)		H ₂ O	
	288-335	16.34 (16.14)	82.91	Cl ₂	CoO
	335-639	62.61 (62.74)	(82.97)	$C_{17}H_{16}N_4$	
(3)	126-295	3.56 (4.09)		H ₂ O	
	295-422	33.45 (33.66)	83.40	$Cl_2 + C_6H_5$	NiO
	422-540	46.39 (45.26)	(83.01)	$C_{11}H_{11}N_4$	
(4)	220-450	32.65 (32.35)		$H_2O+Cl_2+C_4H_4$	
	450-627	23.50 (24.32)	83.16	C ₆ H ₆ N ₂	MnO
	627-800	27.01 (27.07)	(83.74)	$C_7H_6N_2$	
(5)	285-460	38.98 (39.54)	72.89	$C_7H_5N_2Cl_2$	CdO
	460-650	33.91 (33.45)	(73.08)	$C_{10}H_{11}N_2$	

Table 15. Thermal analysis data of PMDP and its metal complexes

	Temp.				Parameter			Correlation
Compound ^a	range (°C)	Method	E _a (kJ mol ⁻¹)	A (s ⁻¹)	ΔS* (J mol ⁻¹ K ⁻¹)	$\Delta \mathbf{H}^*$ (kJ mol ⁻¹)	$\Delta \mathbf{G}^{*}$ (kJ mol ⁻¹)	coefficient (r)
PMDP	200-475	CR	70.6	2.91E+3	-0.185	65.5	178	0.99492
		HM	90.1	2.47E+5	-0.148	85	175	0.96513
	492-690	CR	105	6.87E+3	-0.180	98	254	0.99289
		HM	119	5.01E+4	-0.164	112	254	0.98174
(1)	195-460	CR	39.0	5.63E+4	-0.313	39.3	184	0.99672
		HM	38.6	4.90E+01	-0.338	33.6	176	0.92243
	474-652	CR	140	1.54E+6	-0.135	133	246	0.97781
		HM	157	2.76E+7	-0.111	150	243	0.96667
(2)	40-288	CR	13.2	3.54E+02	-0.276	9.59	130	0.99699
		HM	16.9	8.21E+01	-0.250	17.8	127	0.99345
	288-361	CR	14.4	6.26E+02	-0.274	7.41	171	0.9983
		HM	19.9	6.13E+02	-0.274	14.9	179	0.9983
(3)	40-295	CR	31.4	5.54E+01	-0.234	27.7	131	0.99821
		HM	39.2	1.79E+02	-0.205	35.5	126	0.97471
	295-442	CR	117	3.11E+05	-0.146	93.0	187	0.98148
		HM	125	1.25E+05	-0.101	119	183	0.9489
(4)	220-500	CR	106	4.44E+05	-0.143	101	192	0.98865
		HM	114	1.56E+07	-0.113	109	181	0.99552
	500-625	CR	195	2.84E+09	-0.101	188	249	0.98865
		HM	211	8.44E+10	-0.098	204	241	0.98509
(5)	295-500	CR	130	4.31E+07	-0.105	124	195	0.97708
		HM	142	1.42E+05	-0.083	136	191	0.95836
	500-670	CR	184	3.13E+08	-0.091	176	255	0.99358
		HM	200	8.23E+09	-0.081	193	248	0.98806

Table 16. Thermodynamic data of PMDP and its metal complexes

 Table 17. ESR Spin Hamiltonian parameters of complex (1).

g _{ll}	gl	g _{av} .	G	α^2	$A_{ll}x 10^{-4}$	f	β^2	γ^2
2.31	2.06	2.143	5.33	0.599	169.7	136	1.09	0.819

Table 18. Effect of concentrations of PDMP on the free corrosion potential
(E _{corr.}), corrosion current density (i _{corr.}), Tafel slopes ($\beta_a \& \beta_c$), degree of surface
coverage (θ) and inhibition efficiency (% IE) for mild steel in 2M HCl at 25 ±1
°C.

Concentration (M)	-E _{corr.} , mV (vs SCE)	i _{corr} . μA cm ⁻²	βa, mV dec ⁻¹	βc , mV dec ⁻¹	θ	% IE
Blank	488	5.89	82	125		
1 x 10 ⁻⁶	474	1.77	41	67	0.6994	69.94
3 x 10 ⁻⁶	470	1.68	36	47	0.7147	71.47
5 x 10 ⁻⁶	490	1.65	66	95	0.7198	71.98
7 x 10 ⁻⁶	482	1.53	83	98	0.7402	74.02
9 x 10 ⁻⁶	488	1.49	84	103	0.7470	74.70
11 x 10 ⁻⁶	471	1.37	99	119	0.7674	76.74

Table 19. Electrochemical kinetic parameters obtained from EIS technique for the corro-
sion of mild steel in 2 M HCl in the absence and presence of various concentrations of
PDMP at 25 ± 1 °C.

Concentration (M)	R_s , $\Omega \text{ cm}^2$	$Y_{o}, x 10^{-3} \ \mu \Omega^{-1} s^{n}$	n	$R_{ct},$ $\Omega \text{ cm}^2$	$C_{dl},$ μFcm^{-2}	θ	%IE		
Blank	1.569	353	879	40.3	69.70	? `			
1 x 10 ⁻⁶	1.273	342	888	51.3	19.69	0.214	21.4		
3 x 10 ⁻⁶	1.570	220	898	55.9	17.40	0.279	27.9		
5 x 10 ⁻⁶	1.499	303	897	59.8	16.74	0.326	32.6		
7 x 10 ⁻⁶	1.813	397	852	61.0	16.60	0.339	33.9		
9 x 10 ⁻⁶	2.209	259	886	85.8	11.74	0.530	53.0		
11 x 10 ⁻⁶	2.449	109	869	267.7	37.80	84.9	84.9		

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Table 20. Electrochemical kinetic parameters obtained by EFM technique for the
corrosion of mild steel in 2 M HCl in the absence and presence of various con-
centrations of PDMP at 25 ± 1 °C.

Concentra- tion (M)	I _{corr} , μAcm ⁻²	$\beta_c,$ mV dec ⁻¹	$egin{array}{c} \beta_a, \ mV \ dec^{-1} \end{array}$	CF-2	CF-3	θ	%IE
Blank	907	122	163	1.99	3.02	-	-
1 x 10 ⁻⁶	233	39	40	2.01	2.94	0.743	74.3
3 x 10 ⁻⁶	180	52	54	1.98	2.97	0.801	80.1
5 x 10 ⁻⁶	174	49	52	1.90	2.88	0.808	80.8
7 x 10 ⁻⁶	169	47	49	2.04	3.06	0.813	81.3
9 x 10 ⁻⁶	113	46	51	1.99	2.98	0.875	87.5
11 x 10 ⁻⁶	53	76	78	2.02	3.00	0.941	94.1

Table 21. Antibacterial activity data of PMDP and its metal complexes. The results wererecorded as the average diameter of inhibition zone (mm) \pm standard deviation.

			Gram positive bac	cteria	Gram negative bacteria			
Compound ^a	Conc. (µg/mL)	Bacillus cereus	Staphylococcus aureus	Enterococcus faecalis	Escherichia coli	Klebsiella pneumoniae	Pseudomonas aeruginosa	
PMDP	50	-ve	-ve	-ve	-ve	-ve	-ve	
	100	-ve	-ve	-ve	-ve	-ve	-ve	
	150	-ve	-ve	-ve	1	-ve	-ve	
(1)	50	-ve	-ve	-ve	-ve	-ve	-ve	
	100	-ve	-ve	-ve	-ve	-ve	-ve	
	150	-ve	-ve	-ve	-ve	-ve	-ve	
(2)	50	-ve	-ve	-ve	-ve	-ve	0.6	
	100	-ve	-ve	-ve	-ve	-ve	0.8	
	150	-ve	-ve	-ve	-ve	-ve	1	
(3)	50	-ve	-ve	-ve	-ve	-ve	0.93±0.067*	
	100	-ve	-ve	-ve	-ve	-ve	1*	
	150	-ve	-ve	-ve	-ve	-ve	1.4*	
(4)	50	-ve	-ve	-ve	-ve	-ve	-ve	
	100	-ve	-ve	-ve	-ve	-ve	-ve	
	150	-ve	-ve	-ve	-ve	-ve	0.4	
(5)	50	-ve	-ve	-ve	-ve	-ve	0.5 ± 0.057	
	100	-ve	-ve	-ve	-ve	-ve	0.4	
	150	-ve	-ve	-ve	-ve	-ve	0.4	
Penicillin	50	1 ± 0.14	2 ± 0	1.46 ± 0.03	1 ± 0	-ve	0.87 ± 0.033	
	100	3 ± 0.28	2 ± 0.14	1.86 ± 0.03	3 ± 0	-ve	1.06 ± 0.033	
	150	3 ± 0.14	2 ± 0	2.2 ± 0	3 ± 0	-ve	1.4 ± 0.058	

^aNumbers as given in Table 1

* Indicate significant different value from that of penicillin.

Table 22.	Antifungal	activity c	lata of	PMDP	and its	metal	complexes.	The results	were
recorded a	s the averag	e diamete	er of in	hibition	zone (r	nm) ±	standard dev	viation.	

Complex ^a		Aspergillus	Fusarium	Candida	
	Conc. (µg/mL)	niger	oxysporum	albicans	
PMDP	50	-ve	-ve	-ve	
	100	-ve	-ve	-ve	
	150	-ve	-ve	-ve	
(1)	50	-ve	-ve	-ve	Q
	100	-ve	-ve	-ve	
	150	-ve	-ve	-ve	
(2)	50	-ve	-ve	-ve	
	100	-ve	-ve	-ve	
	150	-ve	-ve	-ve	
(3)	50	-ve	-ve	-ve	
	100	-ve	-ve	-ve	
	150	-ve	-ve	-ve	
(4)	50	-ve	-ve	-ve	
	100	-ve	-ve	-ve	
	150	-ve	-ve	-ve	
(5)	50	-ve	-ve	-ve	
	100	-ve	-ve	-ve	
	150	-ve	-ve	-ve	
Miconazole	50	1 ± 0	2 ± 0	1.1 ± 0	
X	100	3 ± 0.14	3 ± 0	1.3 ± 0	
,	150	4 ± 0	3 ± 0	1.7 ± 0.058	
		1	l		

^aNumbers as given in Table 1.

* Indicate significant different value from that of miconazole.







Scheme 2. Fragmentation patterns of Cu(II) complex (1).



Scheme 3. Fragmentation patterns of Co(II) complex (2).











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

(5)





Fig. 3. X-ray diffraction patterns of powder forms for a) ligand (PMDP),

b) Cu(II) complex (1) and (c) Ni(II) complex (3).



Fig. 4. The start (green in (a) and gray in (b)) in interaction with receptors of breast cancer mutant 3hb5-oxidoreductase and prostate cancer mutant 2q7k-hormone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).



Fig. 5. The Schiff base ligand (PMDP) (green in (a) and gray in (b)) in interaction with receptors of breast cancer mutant 3hb5-oxidoreductase and prostate cancer mutant 2q7k-hormone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).





Fig. 6. HB plot of interaction between start and receptors (a) breast cancer mutant 3hb5oxidoreductase and (b) prostate cancer mutant 2q7k-hormone.





Fig. 7. HB plot of interaction between Schiff base ligand (PMDP) and receptors (a) breast cancer mutant 3hb5-oxidoreductase and (b) prostate cancer mutant 2q7k-hormone.





Fig. 8. 2D plot of interaction between start and receptors (a) breast cancer mutant 3hb5oxidoreductase and (b) prostate cancer mutant 2q7k-hormone.





Fig. 9. 2D plot of interaction between Schiff base ligand (PMDP) and receptors (a) breast cancer mutant 3hb5-oxidoreductase and (b) prostate cancer mutant 2q7k-hormone.





Fig. 10. Optimized structures of Schiff base ligand (PMDP) and its complexes (1-5).











Fig. 11. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Schiff base ligand (PMDP) and its complexes

(1-5).


Fig. 12. The relation between of $\Delta E vs$. ionic radii of metal complexes.



Fig. 13. TGA curves of PMDP and its complexes (1-5)







Fig. 14. Coats–Redfern (CR) of PMDP and its complexes (1-5).





Fig. 15. Horowitz–Metzger (HM) of PMDP and its complexes (1-5).



Fig. 16. Potentiodynamic polarization curves for the corrosion of mild steel in 2 M HCl in the absence and presence of various concentrations of PDMP at 25 ± 1

°C.



Fig. 17. The Nyquist plots for the corrosion of mild steel in 2 M HCl in the absence and presence of various concentrations of PDMP at 25 ± 1 °C.



Fig. 18. Equivalent circuit model used to fit the impedance spectra.





Fig. 19. EFM spectra for the corrosion of mild steel in 2 M HCl in the absence and presence of various concentrations of PDMP at 25 ± 1 °C.

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Fig. 20. Plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ as function of DNA concentration as determined from the absorption spectral data of PMDP and its complexes (1-5).

- A series of M(II) complexes of Schiff base were prepared and characterized
- Molecular docking was used to predict the binding between Schiff base ligand and the receptors
- ESR calculations support the characterization of the structure of the complex geometry
- The molar conductivities show that all the complexes are non-electrolytes