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Pyrrolidinedione based macrocyclic schiff base complexes: synthesis, PXRD, antimicrobial and DNA binding studies

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A collection of five macrocyclic complexes of Cd(II), Zn(II), Ni(II), Cu(II) and Co(II) have been synthesized through metal ion template [2+2] cyclocondensation of 1,8-diaminonaphthalene and pyrrolidine-2,5-dione. The newly designed metal complexes have been analyzed by various spectroscopic and physico-analytical techniques like UV-visible, elemental analysis, IR, molar conductance, ESI-MS, EPR, ^{1}H-NMR and PXRD. The synthesized macrcocyclic metal complexes have been evaluated for their biocidal effects against some strains of pathogenic microbes. The stoichiometry of the macrocyclic complexes has been confirmed with the assistance of molar conductance, ESI-MS and elemental analysis (CHN). DNA interaction studies have been carried out for the elucidation of type and mode of binding of the complexes with the Herring fish sperm DNA. The geometry optimization has been carried out with the help of molecular mechanics using Chem 3D Ultra Software.

Keywords: Template methodology, Macrocycle, DNA binding, Antimicrobial, PXRD

Macrocyclic complexes of divalent transition metal ions have enticed pronounced attentiveness in the field of supramolecular and coordination chemistry[1]. There are a large number of factors that play a significant role in their formation like the size of the cavity, rigidity, number and nature of donor atoms present in the macrocycle, and the potentiality of metal ions for promoting the template synthesis of macrocyclic complexes[2,3]. The macrocyclic complexes of Ni(II) and Cu(II) find use in oxidation, DNA recognition, cleavage and DNA binding activities[4]. These complexes are also very well known for their antimicrobial properties[5,6]. Most of the complexes of transition metal ions have been considered for a wide range of applications as DNA structure probes, mediating agents for the strand scission of DNA duplex and as chemotherapeutic agents[7-9]. The Cd(II) complexes exhibit better antimicrobial properties than the standard antibiotics as reported in literature[10]. The favourable applicability of a number of transition metal compounds having an organic moiety against several diseases especially in case of cancer, have increased the interest in designing of organometallic compounds based on pharmaceuticals[11]. Prompted from the above facts we have synthesized macrocyclic complex of divalent transition metal ions and screened them for various biological activities.

Materials and Methods

Synthesis of all the macrocyclic complexes was carried out under normal atmospheric conditions of temperature and pressure. Diamines and diketones used for the synthesis were obtained from Sigma Aldrich, while salts of metals were procured from E. Merck and Ranbaxy, India. Solvents used for the synthesis purpose and for washing were of reagent grade and used as received. Herring fish sperm DNA was purchased from SRL, India. Optimisation of the synthesized complexes was carried out using the assistance of Chem 3D Ultra Software.

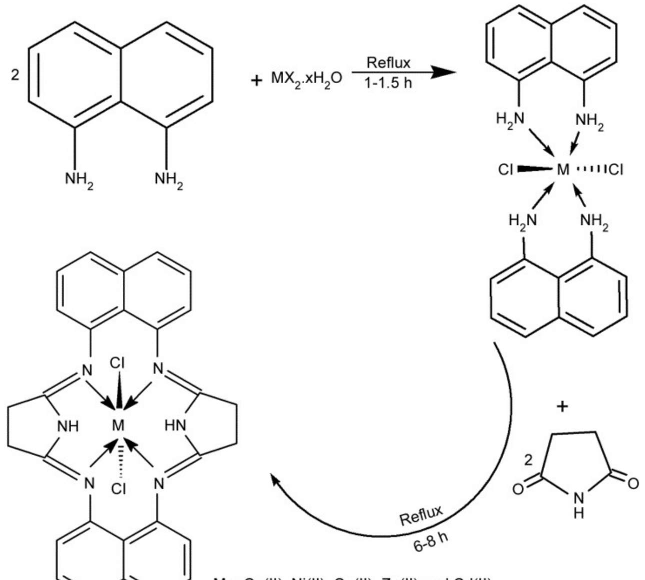
Physical measurements

The Fourier transform infrared (FTIR) measurements were carried out on IR-Schimadzu (IRA Affinity-1S) instrument using KBr pellets at NIT, Kurukshetra in the range of (4000–400 cm^{-1}). The EPR studies of the copper complexes were performed on ESR, Varian, USA, at SAIF, IIT-Bombay. Electronic spectra were obtained on Thermo Scientific Evolution 201 spectrophotometer. Elemental analysis was done at Euro Elemental Analyzer at SAIF, PU Chandigarh. NMR spectral measurements were carried out on 400 MHz instrument at GJUST, Hisar. PXRD was recorded on Pan-Analytical XPERT-PRO instrument at the Department of Electronic Science, Kurukshetra University, Kurukshetra.

Synthesis of the complexes

For the synthesis of all the metal complexes, the template methodology was adopted. The solution of 1,8-diaminonaphthalene (10 mmol, 1.58 g) and divalent metal salts (5 mmol) in methanol as reaction medium was refluxed for about 30–40 min. During reflux, the color of the reaction mixture changed rapidly showing the complexation of metal with an amine. After the change in the color, a methanolic solution of pyrrolidine-2,5-dione (10 mmol, 0.99 g) was added and the refluxing was continued for 6–7 h. A single spot on the TLC confirmed the completion of reaction (Scheme 1). Thereafter, the entire reaction mixture was kept at room temperature in desiccators overnight. The colored precipitates obtained were washed and filtered with acetone, methanol and diethyl ether.

***[Co($C_{28}H_{22}N_6$)Cl_2] complex*:** For the synthesis of Co(II) complex, 1,8-diaminonaphthalene (10 mmol, 1.58 g) and $CoCl_2$ (5 mmol, 0.496 g) were taken and refluxed for 30–40 min. Thereafter, pyrrolidine-2,5-dione (10 mmol, 0.99 g) was added dropwise and the contents refluxed for 6–8 h. A black colored powder was obtained as the product. Yield: 65%, Anal. Found: C, 58.20; H, 3.47; N, 14.44; M, 10.12% Calc.: C, 58.76; H, 3.87; N, 14.68; M, 10.30. IR (cm^{-1}): $\nu_{C=N}$, 1598s, $\nu_{N\text{-}H}$, 3190w, $\nu_{C\text{-}H}$, 820 m. Molar conductivity (Ω^{-1} $mol^{-1}cm^2$) in DMSO 21. Magnetic moment μ_{eff} (BM): 4.69. UV-visible [dmso, λ (nm), ε ($L\text{-}mol^{-1}$ cm^{-1})]: 925 ($\varepsilon = 3.7\times10^2$), 756 ($\varepsilon = 2.1\times10^2$), 610 ($\varepsilon = 6.1\times10^2$).



M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)
X = Cl⁻
Synthetic pathway of the complexes

Scheme 1

***[Ni($C_{28}H_{22}N_6$)Cl_2] complex*:** The same procedure was adopted for the synthesis with $NiCl_2$ (5 mmol, 0.648 g) as the metal salt. The product was obtained as a black powder. Yield: 72%, Anal. Found: C, 58.29; H, 3.27; N, 14.33; M, 10.11% Calc.: C, 58.78; H, 3.88; N, 14.69; M, 10.26. IR (cm^{-1}): $\nu_{C=N}$, 1605s, $\nu_{N\text{-}H}$, 3040w, $\nu_{C\text{-}H}$, 827 m. Molar conductivity (Ω^{-1} $mol^{-1}cm^2$) in DMSO 19. Magnetic moment μ_{eff} (BM): 3.01. UV-visible [dmso, λ (nm), ε ($L\text{-}mol^{-1}$ cm^{-1})]: 930($\varepsilon = 2.8\times10^3$) , 800 ($\varepsilon = 3.9\times10^2$), 440 ($\varepsilon = 6.1\times10^2$) and 270 ($\varepsilon = 9.0\times10^2$).

***[Cu($C_{28}H_{22}N_6$)Cl_2]complex*:** The same pathway was adopted for the synthesis with the use of $CuCl_2$ (5 mmol, 0.678 g). The product was obtained as a brown powder. Yield: 78%, Anal. Found: C, 58.10; H, 3.77; N, 15.13; M, 10.92% Calc.: C, 58.29; H, 3.84; N, 15.57; M, 11.01. IR (cm^{-1}): $\nu_{C=N}$, 1618s, $\nu_{N\text{-}H}$, 3236w, $\nu_{C\text{-}H}$, 820.3 m. Molar conductivity (Ω^{-1} $mol^{-1}cm^2$) in DMSO 24. Magnetic moment μ_{eff} (BM): 1.81. UV-visible [dmso, λ_{max} (nm), ε ($L\text{-}mol^{-1}$ cm^{-1})]: 585 ($\varepsilon = 4.1\times10^2$) and 270 ($\varepsilon = 7.4\times10^2$).

***[Zn($C_{28}H_{22}N_6$)Cl_2]complex*:** Similar procedure was used for the synthesis with $ZnCl_2$ (5 mmol, 0.681 g). The product was obtained as a silver brown powder. Yield: 70%, Anal. Found: C, 58.01; H, 3.52; N, 14.43; M, 11.21% Calc.: C, 58.10; H, 3.83; N, 14.52; M, 11.30. IR (cm^{-1}): $\nu_{C=N}$, 1590.3s, $\nu_{N\text{-}H}$, 3138.7w, $\nu_{C\text{-}H}$, 814.3 m. Molar conductivity (Ω^{-1} $mol^{-1}cm^2$) in DMSO 22. Magnetic moment μ_{eff} (BM): 0 diamagnetic. UV-visible: 325 and 274 nm. ^{1}H NMR (δ in ppm in DMSO-d_6) 6.4–7.2 (m, aromatic protons), for CH_2, 1.5 (s) and 6.1 (s, N-H proton).

***[Cd($C_{28}H_{22}N_6$)Cl_2]complex*:** Similarly, $CdCl_2$ (5 mmol, 0.916 g) salt was used in this case. The product was obtained as a silver brown powder. Yield: 64%, Anal. Found: C, 53.49; H, 3.43; N, 13.31; M, 17.83% Calc.: C, 53.74; H, 3.54; N, 13.43; M, 17.96. IR (cm^{-1}): $\nu_{C=N}$, 1591.5s, $\nu_{N\text{-}H}$, 3138.7w, $\nu_{C\text{-}H}$, 814.3 m. Molar conductivity (Ω^{-1} $mol^{-1}cm^2$) in DMSO 23.2. Magnetic moment μ_{eff} (BM): 0 diamagnetic. UV-visible: 323 and 274 nm. ^{1}H NMR (δ in ppm in DMSO-d_6) 6.6–7.2 (m, aromatic protons), for CH_2, 1.5 (s) and 6.2 (s, N-H proton).

Test microorganisms and methodology

The bacterial and fungal strains used in the current study are *Staphylococcus aureus*, *Candida albicans*, *Bacillus cereus* and *Aspergillus niger*. All the experiments were carried out in triplicate. MIC and zone of inhibition were calculated from the experiment given below.

MIC determination

MIC of the synthesized macrocyclic complexes against pathogenic strains of bacteria and yeast strains was determined by the assistance of modified agar well diffusion method[12]. In this, a two-fold serial dilution of each newly synthesized compound was carried out by first dissolving the compound in DMSO, followed by its dilution with the help of sterile distilled water in order to achieve a concentration range of 256 to 8.0 µg/mL. A 100 µL volume of each dilution was introduced into wells (in triplicate) in the agar plates already seeded with 100 µL of standardized inoculums (106 cfu/mL) of the test microbial strain. All test plates were incubated aerobically at 37 °C for 24 h and the inhibition zones were observed. MIC is taken as the lowest concentration of the chemical compound that completely inhibits the growth of the microbe, which is indicated by a clear zone of inhibition and recorded for each test organism. Ciprofloxacin and amphotericin B were used as positive controls while DMSO as a negative control.

DNA binding studies

UV-visible spectra were recorded at room temperature for determining the binding of DNA with the synthesized complexes. The purity of DNA free from proteins is indicated by the ratio of absorbance at 260 and 280 nm, which lies within the range of 1.8–1.9. DMSO was used as a solvent for making the stock solution of metal complexes (conc. 10^{-3} M). The concentration of DNA varied from 0.00 to 17×10^{-9} mol L^{-1}. In the current study, the total volume of the solution is adjusted to 2600–2900 µL by taking 2500 µL buffer, and 50 µL DMSO, 50 µL of complex, changing the amount of DNA at each subsequent addition.

Results and Discussion

All the macrocyclic complexes were synthesized by template condensation by taking the metal ion as a template. The ratio of the amine, metal and carbonyl compound used for synthesis is 2:1:2. The newly prepared complexes exibited good solubility in DMSO and were insoluble in common organic solvents. The stoichiometry of the complexes was confirmed by CHN (elemental analysis) data**.** Lower values (10–25 Ω^{-1} mol^{-1}cm^{2}) of molar conductance, reveals about their non-electrolytic behavior. Most of the complexes have good antimicrobial and DNA binding activity as evaluated by biological assay.

Infra-red spectra

The formation of the macrocyclic complex was evaluated by FTIR spectral data. The absence of characteristic bands of -NH_2 and C=O group provides a strong indication about the complete condensation. In addition to this, the spectrum of all the complexes showed peaks in the range of 1585–1630 cm^{-1} which confirms the formation of azomethine group[13] from the condensation of amine and carbonyl compound. The band near 3000–3300 cm^{-1} are because of N-H group of Pyrrolidine-2,5-dione which show its non coordinating behavior. The absorption frequency of the azomethine group is slightly drifted towards the lower side due to the coordination from nitrogen to the central metal ion. Far IR data reveals band near 300–350 cm^{-1} showing ν of M-Cl bond (Supplementary Data Figs. S1-S5).

Electronic spectra

***Cobalt complex*:** The magnetic moment of the macrocyclic complexes of Cobalt(II) was measured at room temperature with a value of 4.69 B.M. which indicate the presence of three unpaired electrons . Electronic spectrum of the complexes displayed three absorption bands at 925 nm, 756 nm and 610 nm corresponding to three transitions i.e., $^4T_{1g} \rightarrow {}^4T_{2g}$ (F) (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) (ν_2) and $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_3) respectively (Supplmentary Data Fig. S6). Higher energy band below 300 nm may be due to π→π* transition[14]. These absorption maxima are in accordance with distorted octahedral geometry and D_{4h} symmetry.

Nickel complex: Nickel(II) complex was found to have an effective magnetic moment (μ_{eff}) of 3.01 B.M. at room temperature Fig. 1. Complexes exhibits bands at 930 nm, 800 nm, 440 nm and 270 nm that are due to $^3A_{2g} \rightarrow {}^3T_{2g}$ (F), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), while higher energy band may be because of π→π*.

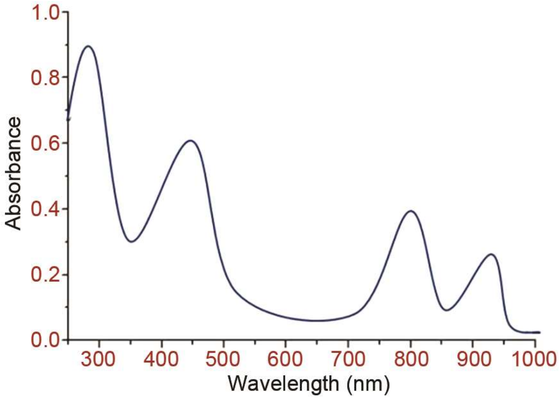


Fig. 1 — Electronic spectrum of [$Ni(C_{28}H_{22}N_6)Cl_2$]

D_{4h} symmetry was suggested by these complexes as the data is consistent with the structure which is confirmed by X-ray crystallography[15-17].

Copper complexes: The value of magnetic moment for Cu(II) complex was 1.81 B.M. showing the presence of single unpaired electron. Absorption spectrum displayed two bands at 585 nm and 270 nm which may be due to *d-d* transition and $\pi \rightarrow \pi^*$ transition of azomethine group present in the complex[18] (Supplementary Data Fig. S7).

EPR studies

ESR spectra of the macrocyclic complex of Cu(II) was recorded at both room and low temperature in the solid state at a frequency of 9.1 GHz under the magnetic field strength of 3,000 G using TCNE as a reference (Fig. 2 and Supplementary Data Fig. S8). The spectra provided information regarding the coordination environment around the central Cu(II) ion. The copper complexes showed a broad isotropic signal at room temperature but good splitting of the signal is observed at low temperature. Thus, the $g_{\|}$ & $g_{\perp}$ values were obtained as 2.25 and 2.12, respectively. The condition of octahedral distortion holds good because g (tensor) follows the order of $g_{\|} > g_{\perp} > 2.0023$. The axial symmetry parameter G is found to have value of 2.08 showing considerable amount of exchange interaction in Cu-Cu in solid state. The g_{iso} value of 2.10 showed the presence of slightly distorted geometry[19]. With the assistance of g-value, magnetic moment can also be calculated by using the following equation[20].

$$\mu_{eff} = \tfrac{1}{2}\sqrt{(g_{\|}^2 + 2g_{\perp}^2)} \quad \text{... (1)}$$

From the obtained g-value the calculated magnetic moment was found to have a value of 1.85 B.M. that is in close proximity with the experimental obtained valued of magnetic moment that is 1.81 B.M.

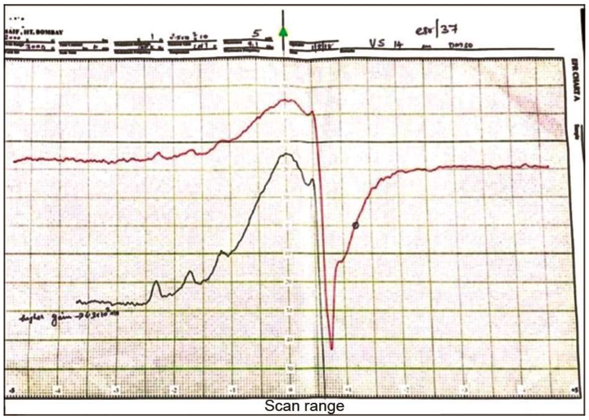


Fig. 2 — ESR spectrum of $Cu(C_{28}H_{22}N_6)Cl_2$ complex at low temperature

ESI-MS

The mass spectra of two representative complexes were recorded because this helps in providing structural information of the species under analyses. The ESI-MS of $[Zn(C_{28}H_{22}N_6)Cl_2]$ and $[Cu(C_{28}H_{22}N_6)Cl_2]$ showed molecular ion peak at 574 and 576 corresponding to the $[M-4H]^+$ and $[M]^+$ ions, respectively. The fragmentation of the complexes and mass spectra are shown in Supplementary Data Figs S9-S11.

PXRD studies

The growth of the single crystal of the synthesized macrocyclic complexes was not successful after much trials, so in order to interpret the nature of the complexes (crystalline or amorphous) powder XRD analysis was carried out in the range of 5–90° (2θ). The presence of very sharp and distinct peaks in the diffractogram (Supplementary Data Figs S12-S13 and Fig. 3) indicate the crystalline behavior of all the complexes. Various parameters associated with the crystalline nature were calculated by the assistance of Full proof suite software. The complexes of Zn(II) and Cd(II) crystallize in the monoclinic system, whereas the complex of Cu(II) possess the orthorhombic type of crystal system. The diffractogram of Ni(II) and Co(II) complexes shows the absence of crystalline nature. The interspacing (*d*) values and the calculated *h,k,l* (miller indices) are given in (Table 1 and Supplementary Data Tables S1-S2). The cell parameter is agreeable with the condition of respective crystal. The cell parameters (unit) values for complexes are given in Supplementary Data Table S3.

Particle size of the crystallite

For the analysis and interpretation of the size of a particle of the synthesized macrocyclic complexes,

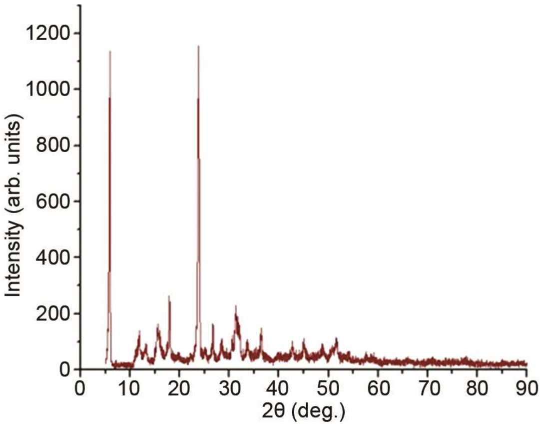


Fig. 3 — Diffractogram of $[Zn(C_{28}H_{22}N_6)Cl_2]$

Table 1 — Interplanar spacing and miller indices of $[Zn(C_{28}H_{22}N_6)Cl_2]$

h	*k*	*l*	D_{OBS}	D_{CAL}	D_{OBS}-D_{CAL}	2TH.OBS	2TH.CAL	DIF.2TH.
0	1	0	14.96465	14.92294	0.04171	5.901	5.918	- 0.017
0	2	0	7.44571	7.46086	-0.01515	11.876	11.852	0.024
1	0	0	4.93868	4.93873	-0.00005	17.946	17.946	0.000
0	4	0	3.73148	3.73028	0.00120	23.827	23.835	-0.008
0	1	1	3.33951	3.33954	-0.00003	26.672	26.672	0.000
1	2	-1	2.84536	2.84535	0.00001	31.414	31.414	0.000
1	2	1	2.46357	2.46356	0.00001	36.441	36.441	0.000

the Debye-Scherrer formula[21-23] was used, which can be mathematically represented as:

$$D = 0.94\ \lambda / \beta \cos\theta \qquad \dots (2)$$

where D = apparent particle size
λ = incident X-ray wavelength
β = full width at half maximum (FWHM) of the given XRD peak (characteristic)
cosθ = position of the particular diffraction peak.

From the diffractogram data, the value λ was found to be 1.54 (Å) and the value of β (radians) is different for the different complexes. The value of cosθ is obtained from diffractogram. From the above calculations, we find that the size of particle ranges in between 10–12.5 nm and lattice strain lies in the range of 0.0100–0.0170 nm as shown in Supplementary Data Table S4.

^{1}H-NMR of Zn(II) and Cd(II) complexes: The NMR spectrum of the complexes was taken in d_6 (DMSO) at room temperature. Both the complexes exhibit signal in the range of 6.4–7.5 ppm (m) due to the aromatic protons of the 1,8-diaminonaphthalene[24]. Signals due to methylene protons of the succinimide moiety appeared in the range of 1.5 ppm**.**

DNA binding studies

The binding of all the synthesized complexes was evaluated by UV absorption studies, because of its wide importance in studying the mode of binding of DNA with the metal complexes[25]. The absorption spectra of the complexes are shown in (Supplementary Data Fig. S14 i-v). All the complexes give a sharp peak around 260 nm due to п→п* transition. From the spectra it has been observed that there is hyperchromism in the spectra with some redshift. According to reported literature, hyperchromism is observed due to external binding or may be because of binding with the major or minor groove. In addition to this concept, hyperchromism may also be explained based on the two phenomena: Firstly due to the large surface area of the macrocyclic ligand as well as presence of planar aromatic benzene rings that can facilitate a very strong binding interaction of the metal complexes with Herring fish sperm DNA, on the condition that there are various possibilities for the complexes to bind with the DNA through the partial penetration of the aromatic ring moiety in between the stacking base pair[26]. Secondly, the presence of transition metal ion in the complexes can also be responsible for the somewhat higher extent of binding of the complexes with herring fish sperm DNA in comparison to the free ligand. There would be uncoiling of the helical structure of DNA which would expose the base pairs that are embedded to the helix exterior ultimately leading to an effective binding with transition metal ions. The K_b i.e., intrinsic binding constant was calculated by the following equation:

$$[DNA]/\varepsilon_a\text{-}\ \varepsilon_f = [DNA]/\ \varepsilon_b\text{-}\ \varepsilon_f + 1/K_b/\ \varepsilon_b\text{-}\ \varepsilon_f \qquad \dots (3)$$

In the plots of $[DNA]/\ \varepsilon_a$- ε_f versus [DNA], K_b is calculated as the ratio of slope to intercept[27]. The binding constants are given in Supplementary Data, Table S5 and follows the order

$1.7\times10^4 > 1.28\times10^4 > 0.89\times10^4 > 0.76\times10^4 > 0.49\times10^4$ corresponding to Cu(II), Ni(II), Cd(II), Zn(II) and Co(II) complexes, respectively, which are in good accordance with the reported literature[28-31].

Antimicrobial assay

All the metal complexes were evaluated for their biocidal effects against the pathogenic strains of bacteria and fungus. (Supplementary Data Figs S15 (i-iv) and S16). All the complexes exhibit fair activity, whereby excellent activity was exhibited by $[Cu(C_{28}H_{22}N_6)Cl_2]$ against the *S aureus* and *C albicans* (Supplementary Data, Tables S6-S7). The potent activity against *B cereus* was shown by the complexes $[Ni(C_{28}H_{22}N_6)Cl_2]$, $[Zn(C_{28}H_{22}N_6)Cl_2]$ and $[Cd(C_{28}H_{22}N_6)Cl_2]$. Good activity of the complexes can be explained on the basis of Tweedy's chelation theory that demonstrates that chelation of the ligand with the central metal ion increases the lipophilic character of the complexes and hence it becomes

Table 2 — Quantum chemical parameters

Comp.	E_{min}.(Kcal/mol)	E_{HOMO}	E_{LUMO}	ΔE	χ	η	σ	Pi	S	ω	N_{max}
Zn(II)	468.29	-7.49	-0.57	6.92	4.03	3.46	0.28	-4.03	0.14	2.34	1.16
Cd(II)	448.38	-8.39	-0.543	7.84	4.46	3.92	0.25	-4.46	0.12	2.54	1.13
Co(II)	491.08	-7.02	-6.98	0.04	7	0.02	50	-7	25	1225	350
Ni(II)	536.2	-6.54	-5.8	0.74	6.17	0.37	2.70	-6.17	1.35	51.44	16.67
Cu(II)	743.47	-1.649	-1.448	0.201	1.54	0.10	9.95	-1.54	4.97	11.92	15.40

easier for the complexes to penetrate the lipoplasmic membrane of the microbes due to which lysis of the cell takes place.

Computational Studies

The optimization of the metal complexes was done by Hartree Fock (HF) method using the 3-21G basis set[32]. The structures were drawn with the help of Perkin-Elmer Chem BioDraw. Perkin-Elmer Chem Bio3D software was used to analyze the optimized geometries. The energy gap ΔE (HOMO-LUMO) is a key stability index and is widely applicable for the development of the theoretical models for predicting the conformational and structural barrier in various molecular systems. The reactivity of the compound can be easily evaluated on the basis of ΔE. The calculated quantum chemical parameters are given in Table 2. Several other parameters like absolute hardness (η), global softness (S), electronic charge, ΔN_{max}, global electrophilicity (ω), absolute electronegativity (χ) and separation energy (ΔE) were calculated using the standard equations.[33]

From the results of the above calculation, it is revealed that the Cd(II) complex possess the least energy value and higher ΔE value, showing its higher stability among all the synthesized complexes. The stability can be attributed to the fully filled *d* orbitals in case of Zn(II) and Cd(II) complex and symmetrically filled *d* orbitals in case of Ni(II) complex. The stability order can be represented as Cd(II)>Zn(II)>Ni(II)>Cu(II)>Co(II).

Conclusions

In the present research, Schiff base macrocyclic complexes were synthesized. Their antimicrobial and DNA binding efficacy were evaluated. Results show that the synthesized complexes can be used as good antimicrobial agents in pharmaceuticals. A distorted octahedral geometry has been proposed to all metal complexes.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(10)1235-1241_SupplData.pdf.

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