

Bi- and tetranuclear ligational deeds of a polyaza macrocycle having four diazine (N₂) bridging components headed for Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ions: An emphasis on electrochemistry of non-innocent ligand system

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Abstract Novel bi- and tetranuclear Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes having diazine bridging units have been prepared and characterised on the basis of analytical and spectroscopic techniques. With the help of electronic spectra and magnetic moment measurements, it is predicted that the Co^{II} and Ni^{II} complexes have octahedral geometry while Cu^{II} and Zn^{II} complexes found to be square pyramidal. Present Zn^{II} and Cu^{II} complexes are binuclear in nature, whereas Co^{II} and Ni^{II} complexes are tetranuclear with feeble antiferromagnetic exchange interactions. UV–visible spectral studies, in the range 275–425 nm, evidence the significant blue shift in $\pi \rightarrow \pi^*$ transition which provide the ease of stabilization of bonding molecular orbitals in the complexes. All complexes are monomeric in nature. Ligand and all complexes were found to be electrochemically active compounds. One electron transfer process is observed in ligand similarly, there is no significant change in the cyclic voltammograms of Co^{II} and Zn^{II} complexes, while Cu^{II} and Ni^{II} complexes show one and two electron transfer redox behaviours, respectively in the present macrocyclic ligand field.

Keywords Tetranuclear · Blue shift · Antiferromagnetic · Phthalazine · Pyrazole

Introduction

Cyclic ligands, which are able to encapsulate two or more metal centres, offer the prospect of generating unusual

electronic and magnetic properties that reflect the nature of guest as well as the host. Polynuclear metal complexes, in which a single ligand holds multiple identical metal centers have been of immense and escalating interest because of their importance in biology through the total delocalization of the metal valencies over the cluster, which makes them capable in electron-transfer processes [1–3]. Many of these complexes and their use as photosynthetic mimics, molecular devices and electrocatalysts have been reviewed [4–6].

Macrocyclic transition metal complexes are of immense interest because of their structural description and stability. A characteristic feature of d-group transition metals is their ability to form complexes with a variety of neutral molecules such as carbon monoxide, isocyanides and various ligands with delocalized π orbitals in addition to lone-pairs of electrons; they have vacant π orbitals that are available for occupation. Typically, π -acceptor orbitals are antibonding orbitals in ligands such as carbon monoxide, phosphines and diazines. These lie above the metal d orbitals in energy. Diazines are heterocyclic dinitrogen aromatic rings and better π -acceptor ligands than pyridine, function as bridging ligands, and this gives added stability through chelating effect [7].

On the other hand, ligands derived from 1,4-dihydra-zinophthalazine are found to be redox active systems. These compounds can undergo oxidation and form two new imine functionalities at 1- and 4-positions hence act as strong reducing agents and called “non-innocent ligands”. Further, the ligand part, in complexes may/may not be redox active. While formation of complexes, if the ligand system has undergone oxidation and then complexation, then ligand part is electrochemically inactive. This property of ligands is decided by the nature of metal ions. At the same time, another interesting objective is the formation of imidol functionality by the amide group of carbonylhydrazide unit.

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One of the objects of studying the multinuclear macrocyclic transition metal complexes of dicarbohydrazides is to investigate whether coordination to metal ion occurs through the oxygen or advantage is taken only by the available nitrogen donors to form polyaza macrocyclic complexes. Hence it is an interesting target to study the structure, magnetic and electrochemical aspects of macrocyclic complexes of a polyaza macrocyclic ligand composed of μ -1,2 diazine bridging units. In the present article we wish to report the synthesis, characterization and electrochemistry of novel bi- and tetranuclear Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes having diazine bridging units.

Experimental

Reagents and apparatus

All the chemicals used were of reagent grade and the solvents were dried and distilled before use according to the standard procedures. 1,4-dihydrazinophthalazine was prepared according to the earlier reports with slight modifications [8]. Pyrazole-3,5-dicarboxylic acid was purchased. The metal chlorides used were in the hydrated form. Estimation of the metal(II) ions were carried out according to the standard methods. C, H and N analysis was carried out using Thermo quest analyzer. The molar conductivity measurements were made on ELICO-CM-82 conductivity bridge. The magnetic susceptibility measurements were made on Faraday balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The ^1H NMR spectra were recorded in $\text{DMSO}-d_6$ solvent on Bruker-300 MHz spectrometer at room temperature using TMS as internal reference. IR spectra were recorded in a KBr matrix using an Impact-410 Nicolet (USA) FT-IR spectrometer in $4000\text{--}400\text{ cm}^{-1}$ range. The electronic spectra of the complexes were recorded on a Hitachi 150-20 spectrophotometer in the range of 1000--

200 nm . The cyclic voltammetric studies were performed at room temperature in DMSO under O_2 free condition using CH instruments Electrochemical analyzer, CHI-1110A (USA). The ESR spectra of the copper complexes were scanned on a Varian E-4X-band EPR spectrometer, using TCNE as the g-marker. The FAB mass spectra were drawn from JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB gas. TG and DTA measurements of the complexes were recorded in nitrogen atmosphere on Universal V2.4FTA instrument keeping final temperature at $800\text{ }^\circ\text{C}$ and heating rate was $10\text{ }^\circ\text{C}/\text{min}$.

Syntheses

Preparation of the ligand (LH_2)

0.02 mol of pyrazole-3,5-dicarboxylic acid was refluxed with 10 mL of thionyl chloride for about 4 h at $110\text{--}115\text{ }^\circ\text{C}$ under anhydrous conditions. Excess thionyl chloride was removed under reduced pressure. The resultant white pasty solid was cooled in an ice bath for about additional 15 min. Then the hot ethanolic solution of 1,4-dihydrazinophthalazine (0.02 mol) was added and further refluxed for about 4 h where upon a clear pale orange solution was produced. The resultant solution was then cooled to get the pale orange coloured ligand (LH_2) which was then separated by filtration under suction. The ligand is recrystallized from hot ethanol and dried under lamp. (The reaction involved in the synthesis of the ligand is shown in Fig. 1). M.P.: $>300\text{ }^\circ\text{C}$. Yield: 62.5%.

Preparation of the complexes

Later first row transition metal complexes of the ligand were prepared by the addition of an ethanolic solution

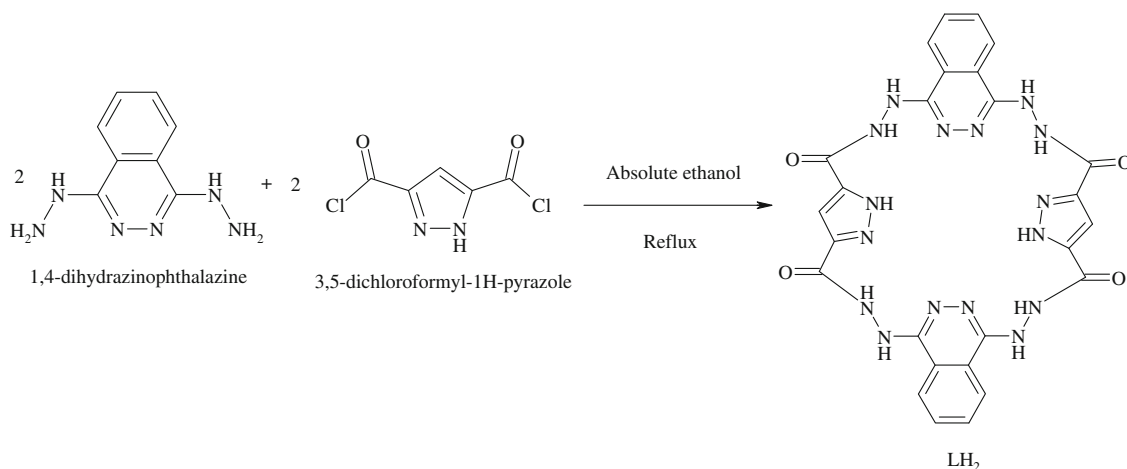


Fig. 1 Preparation of the macrocyclic ligand LH_2

(50 mL) of the respective metal chlorides, viz, Cu(II), Ni(II), Co(II) and Zn(II) chloride (0.004 mol), to the ligand (LH₂) (0.001 mol) and stirred for about 15 min. Then the reaction mixture was refluxed on water bath for about 4–5 h. In case of zinc and copper complexes, little ammonia was added to raise the pH for complexation. So obtained complexes were filtered off under suction, washed with hot ethanol and dried over fused CaCl₂.

Results and discussion

Analytical, Magnetic and conductivity data for the complexes are given in Table 1. All the complexes are insoluble in water, sparingly soluble in common organic solvents and completely soluble in DMF, DMSO and acetonitrile.

FTIR spectral studies

Infrared frequencies along with their assignments for the ligand and complexes are presented in Table 2. In the ligand LH₂, possibility of imidol formation is ruled out, since there is no sharp band around 3400 cm⁻¹ and the same is supported by the appearance of a distinguished amide carbonyl band at 1660 cm⁻¹. $\nu(\text{C}=\text{N})$ of phthalazine and pyrazole were found at 1602 and 1585 cm⁻¹ as stronger bands, respectively. Further ligand shows prominent peak at 3322 cm⁻¹ which is assignable to the N–H absorption [9]. Amide carbonyl absorption in Cu^{II} and Zn^{II}

complexes was totally disappeared and suggests the coordination of oxygen after deprotonation in both the cases and the same is further supported by the appearance of non-ligand band at around 1600 cm⁻¹ attributed to the new azomethine fragment. $>\text{C}=\text{N}-$ absorption of phthalazine was shifted to 1623 and 1628 cm⁻¹, respectively, in both the complexes which supports the bridging of diazine (N₂) group, but pyrazole absorption remained unchanged, suggesting the non involvement of pyrazole 1,2-diazine component in the coordination. In case of Co^{II} and Ni^{II} complexes, amide carbonyl absorption remained unchanged, being at 1660 cm⁻¹, indicating the non-involvement of amide carbonyls in the coordination. Further, the absorption due to $>\text{C}=\text{N}-$ of phthalazine and pyrazole were shifted to 1630, 1580 cm⁻¹ and 1629, 1516 cm⁻¹, respectively, confirms the bridging of all four diazine components to the metal centres.

In case of only 1,4-dihydrazinophthalazine as ligand, the coordination of transition metal ions show increase in the C=N frequency for about 9–20 cm⁻¹, as the delocalisable lone pair is involved in the coordination, due to which, the increase in N–N bond length after donating their lone pair to metal orbitals [10–12]. In the same way, ligand (LH₂) displays sharp and distinguishable bands at 1169 and 1019 cm⁻¹, which are attributed to the stretching frequency of phthalazine and pyrazole ring N–N bonds, respectively. After coordination, in all complexes phthalazine N–N band shifts to the lesser energy and pyrazole N–N band remains unchanged (only in case of Cu^{II} and Zn^{II} complexes), supports the possibility of increase in diazine ring N–N bond distance. All complexes have lattice celled water molecules

Table 1 Analytical, magnetic moment and conductance data of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes^a

Sl. No	Complex	Metal	Carbon	Hydrogen	Nitrogen	Chloride	μ_{eff} in BM	Molar conductance mho cm ² mole ⁻¹
1	LH ²	–	50.32 (50.57)	3.51 (3.22)	37.01 (36.52)	–	–	–
2	[Co ₄ LCl ₆ (H ₂ O) ₄]	20.79 (20.73)	27.03 (27.41)	2.29 (2.21)	19.68 (19.33)	18.46 (18.45)	4.13	3.9
3	[Ni ₄ LCl ₆ (H ₂ O) ₄]	19.97 (20.59)	27.03 (27.46)	2.32 (2.12)	19.86 (19.71)	18.40 (18.48)	2.73	4.2
4	[Cu ₂ LH ₂ (H ₂ O) ₂].H ₂ O	15.93 (15.89)	39.38 (39.04)	2.07 (2.25)	28.03 (28.03)	–	1.69	3.3
5	[Zn ₂ LH ₂ (H ₂ O) ₂].H ₂ O	16.98 (16.31)	38.33 (38.85)	2.24 (2.24)	27.80 (27.89)	–	–	2.2

^a Calculated values are given in the parenthesis

Table 2 Infrared spectral data of ligand and its complexes

Compounds	N–H (Hydrazide)	N–H (Pyrazole)	>C=O (Amide)	>C=N (Phthalazine)	>C=N (Pyrazole)	M–N
LH ₂	3320	3089	1660	1602	1585	–
[Co ₄ LCl ₆ (H ₂ O) ₄]	3300	–	1658	1630	1580	469
[Ni ₄ LCl ₆ (H ₂ O) ₄]	3292	–	1653	1629	1516	474
[Cu ₂ LH ₂ (H ₂ O) ₂].H ₂ O	3185	3080	–	1623, ~1600 ^a	1525	463
[Zn ₂ LH ₂ (H ₂ O) ₂].H ₂ O	3168	3062	~1600	1628, ~1600 ^a	1524	496

^a New azomethine formation because of the imidol functionality of carbohydrazide units

Table 3 ^1H NMR^a spectral data of the compounds in DMSO- d_6

Compounds	–NH pyrazole (ring)	–NH Phthalazine (1- and 4-position)	–NH amide	Aromatic region
LH ₂	14.22	12.09	10.26	7.13–8.50
[Zn ₂ LH ₂ (H ₂ O) ₂]·H ₂ O	12.02	11.28	–	7.23–7.78

^a Chemical shift values of the protons were measured with respect to TMS

which were confirmed by the appearance of a broad band at around 3400 cm^{-1} . Finally, metal to nitrogen bands were observed in the region 463–496 cm^{-1} .

^1H NMR spectral studies

The polyaza macrocyclic ligand and its Zn^{II} complex were scanned in the range 0–16 δ ppm for proton NMR studies and the data obtained is tabulated in Table 3. Within this array ligand put on view the singlet and broad peaks at 14.22 and 12.09, 10.26 δ ppm which can be assigned to pyrazole N–H [13] and phthalazine N–H (at 1 and 4 position), amide protons [14], respectively. Spectrum shows aromatic protons in the range 7.13–8.50 δ ppm.

^1H NMR spectrum of Zn^{II} complex, is different when compared with ligand spectrum, shows only two singlets at 12.02 and 11.28 δ ppm were assigned to pyrazole N–H and phthalazine N–H (at 1 and 4 position), respectively, which supports the non-involvement of pyrazole diazine group in the coordination. Aromatic region was appeared in the range 7.23–7.78 δ ppm. Amide singlet is absent in this spectrum indicates the coordination of oxygen atom via deprotonation.

Molar conductivity measurements

The molar conductance values of complexes were obtained at room temperature in DMF solution at 10^{-3} mol/dm³ concentration. The molar conductivity values of all the complexes fall in the range 2.2–4.2 ohm $\text{cm}^2 \text{mol}^{-1}$, which is in agreement with non-electrolytic nature of the complexes [15].

Electronic spectral studies

Electronic absorption spectra of all the compounds were recorded in DMSO solution over the range 200–1000 nm and the spectral data are listed in Table 4. Ligand exhibits absorption bands at 327 and 340 nm, which are due to the intra ligand $\pi \rightarrow \pi^*$ transition of μ -diazine units present in phthalazine and pyrazole rings and $n \rightarrow \pi^*$ of filled lone

Table 4 UV–visible spectral data of ligand and its complexes

Compounds	Peak values (in nm) (λ_{max} in cm^{-1})
LH ₂	336 (29761), 327 (30581)
[Co ₄ LCl ₆ (H ₂ O) ₄]	540–560 (18518–17857), 341 (29325), 299 (33444)
[Ni ₄ LCl ₆ (H ₂ O) ₄]	949 (10537), 608 (16447), 518 (19305), 350 (28571), 343 (29154), 300 (33333)
[Cu ₂ LH ₂ (H ₂ O) ₂]·H ₂ O	410–450 (24390–22222), 343 (29154), 294 (34013)
[Zn ₂ LH ₂ (H ₂ O) ₂] H ₂ O	350–360 (28571–27777), 331 (30211), 329 (30395)

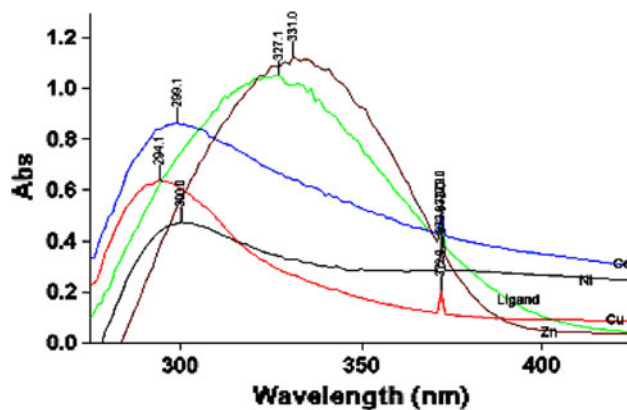


Fig. 2 UV–visible spectra of Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes in the range 275–425 nm

pair electron transitions, respectively. In all complexes (except Zn^{II} complex), $\pi \rightarrow \pi^*$ transition has suffered blue shift (Fig. 2) which internally supports the enolisation of carbohydrazone unit in the solution [16, 17] and confirms the enough stability of bonding molecular orbitals and indicating the coordination of diazine unit.

Apart from above two observations, present Co^{II} complex shows a medium intensity band at 550 nm, because of the $^4\text{T}_{1\text{g}}(\text{F}) \rightarrow ^4\text{T}_{1\text{g}}(\text{P})$ transition, which is a characteristic transition in octahedral Co^{II} complexes [18–21]. Ni^{II} complex exhibits three distinct bands at 949, 608 and 581 nm which are in consistent with the three spin allowed transitions for octahedral Ni^{II} complexes [18–20]. These

spin allowed transition bands in spectrum may thus be assigned as ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The UV–visible spectrum of Cu^{II} complex exhibits a medium intensity broad band at around 450 nm probably due to overlap with other charge transfer transitions. Magnetic moment and the UV–visible parameters confirms the square pyramidal geometry around the Cu^{II} ion. Finally Zn^{II} complex shows two charge transfer transitions at 450 and 345 nm with little red shift.

Electron spin resonance spectral study

The powder state X-band ESR spectrum of copper complex was operated in the region of 9000 MHz with corresponding field intensity at ~ 3000 Gauss. ESR spectrum of Cu^{II} complex exhibit isotropic intense broad signal with $g_{iso} = 2.016$ without any hyperfine splitting. This kind of spectrum have been reported earlier for complexes having large organic ligands [22, 23], and also the broad ESR signal indicates the presence of chloro coordinated binuclear copper(II) complexes [24]. This broadening is because of the dipolar interaction.

Magnetic moment measurements

The room temperature magnetic moment data are summarized in Table 1. For planar complexes derived from phthalazine or pyrazole, exhibits antiferromagnetic interactions have usually been reported. However, in several cases, especially for complexes with asymmetric ligands of distorted geometry, only weak/moderate antiferromagnetic interactions were observed.

The magnetic moment value (1.69 BM) of Cu^{II} complex is found to be little less than the spin only value emphasises the weak antiferromagnetic exchange interaction between copper centers via μ -diazine component of phthalazine ring. By comparing the electronic absorption behaviour and magnetic susceptibility value, the present Cu^{II} complex has square pyramidal geometry [25]. Similarly, Ni^{II} complex also show lesser magnetic moment value (2.73 BM), which is below the spin only value indicating a weak antiferromagnetic interaction between the metal centers. By comparing electronic absorption spectral data and magnetic moment measurements, present Ni^{II} complex has distorted octahedral geometry [26]. In case of Co^{II} complex, the magnetic moment value is found to be 4.13 BM, which shows the moderate exchange interaction between metal centers through the diazine units. Magnetic susceptibility value along with electronic spectral data supports the octahedral geometry for Co^{II} complex.

FAB-mass spectral studies

The FAB mass spectra of Cu^{II} and Ni^{II} complexes were recorded by using *m*-NO₂ benzyl alcohol as matrix. FAB mass spectrum of Cu^{II} and Ni^{II} complexes show molecular ion peak corresponding to *m/z* at 643 and 1137, respectively. Apart from this, spectra show some other peaks, which are due to molecular ions of various fragments of the complexes. The important conclusion drawn from this data is the complexes are monomeric in nature. By comparing all the analytical and spectral data of Co^{II} and Zn^{II} complexes, it is evident that, these are also monomeric in nature.

Thermal studies

All prepared complexes were studied for their thermal behavior over the temperature range of 30–800 °C under nitrogen atmosphere. In representative explanation the copper(II) complex is explained in detail. TG-DTA curves of copper(II) complex shows weight losses in two considerable steps. In the first step 8.6%, in the temperature range 60–130 °C attributed to the combined weight loss of one lattice celled and two coordinated water molecules. Loss of water molecule from the complex is an endothermic process which is evident from the DTA curve. The weight loss at second step is 32.33% observed in the temperature range of 180–480 °C is attributed to the elimination ligand part, the corresponding DTA signal is observed at 236.15 and 344.66 °C. And thereafter the graph became plateau due to the formation of stable CuO. The thermograms obtained for the remaining complexes are in well agreement with the proposed structure of the complexes.

Electrochemistry

Electrochemical behavior of metal complexes having two or more chemically equivalent electroactive sites has been the subject of number of studies. The ligands derived from 1,4-dihydrazinophthalazine were found to be electroactive, hence are called “non-innocent” ligands. After oxidation these ligands form two added azomethine functionalities at 1 and 4 positions of the phthalazine ring. The reported compounds were scanned for the cyclic voltammetric studies in the range -1 to $+1$ V with 0.05, 0.1 and 0.15 Vs⁻¹ scan rates. Ligand is potentially active and shows one electron transfer process in the working potential range, demonstrates an oxidation peak at -0.64 , -0.62 and -0.59 V with above mentioned scan rates, respectively. During reverse scan, ligand exhibits a reduction peak at -0.48 , -0.49 and -0.50 V with the same scan

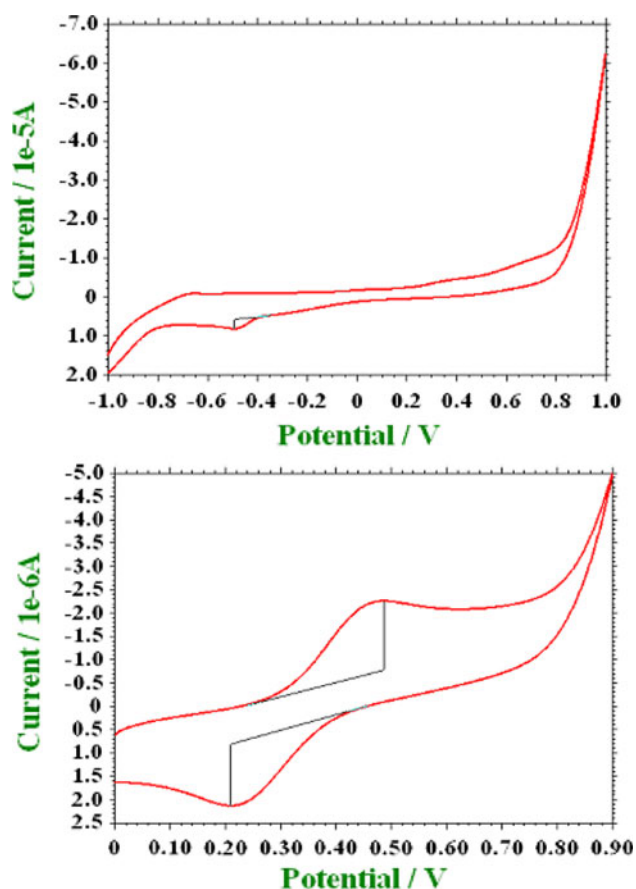
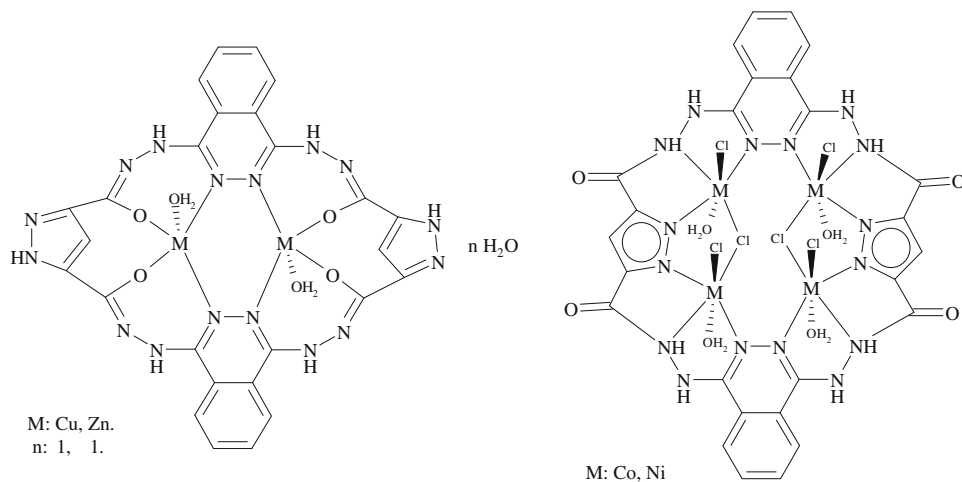


Fig. 3 Cyclic voltammograms of ligand and Cu^{II} complex at the scan rate of 0.1 V/s

rates. This electrochemical potential of the ligand confirms one electron transfer redox process. This activeness is because of the loss of protons present at 1 and 4 position of the phthalazine moiety. Co^{II} and Zn^{II} complexes also exhibit the same cyclic voltammograms with negligible differences in the peak potentials and peak currents, hence the electrochemical behavior of these two metal complexes

Fig. 4 Proposed structures of the complexes



is attributed only to the ligand part and there is no participation of metal ions though they can be stable in variable oxidation states. The representative cyclic voltammograms of ligand and Cu^{II} complex are shown in Fig. 3.

Cu^{II} complex exhibits one electron transfer quasi-reversible redox process with oxidation peak at 0.47, 0.49 and 0.50 V and a reduction peak at 0.22, 0.20 and 0.19 V at above mentioned scan rates. In all these cases I_{p_c}/I_{p_a} is almost constant and but not unity, hence the process is designated as quasi-reversible one electron transfer redox process. Apart from these two peaks, there were no peaks corresponding to the ligand moiety, indicates the electroactive innocence of ligand part. Finally, Ni^{II} complex is also electroactive and displays one electron transfer oxidation peak at 0.50, 0.51 and 0.53 V and two electron transfer reduction peaks at 0.21, 0.23, 0.24 V and -0.46 , -0.44 and -0.43 V at above mentioned scan rates. The peak is attributed to the oxidation of $\text{Ni}^{\text{II}}-\text{Ni}^{\text{III}}$ and reverse scan represents the reduction of $\text{Ni}^{\text{III}}-\text{Ni}^{\text{II}}$ and $\text{Ni}^{\text{II}}-\text{Ni}^{\text{I}}$. As in Cu^{II} complex, there are no peaks corresponding to ligand moiety, confirms the redox processes were metal based.

Conclusion

It is concluded from the above investigation that, the reported novel ligand system is a polyaza macrocycle consists of pyrazole and phthalazine ring systems and provides the diazine units for bridging. The present polyaza macrocycle acts as tetra/binucleating ligand with Ni^{II} , Co^{II} / Cu^{II} , Zn^{II} metal ions by involving/non-involving the pyrazole 1,2-diazine bridge (Fig. 4). UV-visible studies especially in the range 275–425 nm confirms the blue shift of intra ligand transition of azomethine fragment present in the phthalazine and/or pyrazole ring which supports the enough stability of bonding molecular orbitals of the complexes. Magnetic susceptibility measurements and

electronic spectral studies witnessed the presence of octahedral and square pyramidal ligand field around the Ni^{II}, Co^{II} and Cu^{II}, Zn^{II} metal ions, respectively. All complexes are monomeric in nature, which is confirmed by the FAB-mass spectra. Ligand is electrochemically active and shows one electron transfer process and more or less similar cyclic voltammograms were obtained for Co^{II} and Zn^{II} complexes indicating the electrochemical activeness of ligand part. Whereas Cu^{II} and Ni^{II} complexes show one and two electron transfer redox properties, respectively.

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