

Transition metal complexes of pyrazole head 24-membered polyazamacrocyclic bimetal cores: synthesis, characterization, electrochemistry and spectral study

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Abstract A series of new 24-membered macrocyclic Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes of the ligands L^1H_2 and L^2H_2 were prepared by the non-template and template methods respectively. The ligand L^1H_2 was formed by the condensation of pyrazole-3,5-dicarbohydrazide and glyoxal and all attempts to isolate the ligand L^2H_2 were unsuccessful. These, ligand and transition metal complexes were characterized on the basis of elemental analysis, IR, ^1H NMR, UV–Visible, magnetic susceptibility measurements, ESR, conductivity measurements, FAB-mass and thermal analysis. The redox behavior of metal ions in the polyazamacrocyclic ligand field is also studied. Electroreduction of carbon dioxide to carbon monoxide is mainly focused on using polydentate azamacrocyclic ligands with amine and imine functionalities, based on the electrochemical behavior of nickel (II) ion in the macrocyclic territory.

Keywords Polyazamacrocyclic · Template · Pyrazole-3 · 5-Dicarbohydrazide · Glyoxal · Electroreduction

Introduction

Transition metal chemistry of macrocyclic and acyclic polydentate ligands is an interesting area of recent research due to their applicability as catalysts as a part and bioinorganic mimics as whole [1, 2]. In particular, nitrogen-donor macrocycles are found to be more specific towards

the size of the guest and show high binding affinity with the same [3–5]. Macrocyclic organic ligands of 3,5-disubstituted pyrazole derivatives show the remarkable ability to form the stable transition metal complexes by involving their diazine group (μ -NN) as endogenous bridge. However very few number of diazine bridged pyrazole ligands are known, perhaps polypyrazolic macrocycles are known for their photophysical and photochemical properties [6]. Apart from this, a dicopper (I) complex of polypyrazolic ligand of imidazole analogue binds 1 equivalent of dioxygen between two copper ions inside the 22-membered cavity [7]. An antiferromagnetic interaction is expected between both the metal centers since the two nitrogen atoms in pyrazole ring are 1.44 Å units apart from each other, which would be able to hold two metal centers in close proximity. In addition to this, other important objective for the study of coordination compounds derived from carbonylhydrazones was to investigate the possibility of involvement of amide carbonyl in the coordination, or else the advantage was taken only by the hydrazide nitrogens for coordination to form azamacrocycles. Coordination diversity of amine and imine functionalities explores the architectural changes in the metal complexes to behave distinctly in their physico-chemical properties though the chelating atoms were same in the macrocycles. Hence it is an interesting target to study the magnetic, electrochemical and structural aspects of macrocyclic complexes derived from 3,5-disubstituted pyrazole. In our laboratory, we have developed a series of polyaza and polyoxaaza macrocyclic ligands, which have the unique binding abilities towards transition metal ions due to macrocyclic effect. In the present article we wish to report the synthesis, characterization and electrochemistry of new 24-membered polyaza macrocyclic transition metal complexes of 3,5-disubstituted pyrazole derivative.

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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. Pyrazole-3,5-dicarbohydrazide was prepared according to the earlier reports with slight modifications [8]. The metal chlorides used were in the hydrated form. Estimation of the metal(II) ions were done according to the standard methods. 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 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 4,000–400 cm^{-1} range. The electronic spectra of the complexes were recorded on a Hitachi 150-20 spectrophotometer in the range of 1,000–200 nm. The cyclic voltametric 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. TG and DTA measurements of the complexes were recorded in nitrogen atmosphere on Universal V2.4F TA instrument keeping final temperature at 800 °C and heating rate was 10 °C/min. 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.

Syntheses

Preparation of the ligand (L^1H_2)

Pyrazole-3,5-dicarbohydrazide (0.1 mol) was taken in 50 ml of absolute ethanol, to which glyoxal (0.1 mol) was added, and the mixture was stirred at room temperature for 15 min. Then catalytic amount of glacial acetic acid was added, and the reaction mixture was refluxed on water bath temperature for 4 h. The white solid that formed, upon cooling the reaction mixture at 0 °C, was filtered off and recrystallized from hot ethanol. M. P.: 285 °C, Yield: 67%.

All our attempts to isolate the ligand (L^2H_2) formed between the reaction of pyrazole-3,5-dicarbohydrazide with 1,2-dichloroethane were unsuccessful. Hence the complexes were prepared in situ.

Preparation of complexes of the ligand (L^1H_2)

To a stirred ethanolic solution (50 ml) of respective metal chlorides, viz, Cu(II), Ni(II), Co(II) and Zn(II) chloride (0.005 mol), ligand (L^1H_2) (0.005 mol) was added and stirred further for about 15 min and then the reaction mixture was refluxed on water bath 4 h. In case of zinc and copper complexes, few drops of ammonia was added to get the complexes in solid form. So obtained solids were filtered off, washed with hot ethanol and dried over fused CaCl_2 .

Preparation of complexes of the ligand (L^2H_2)

[in situ method]

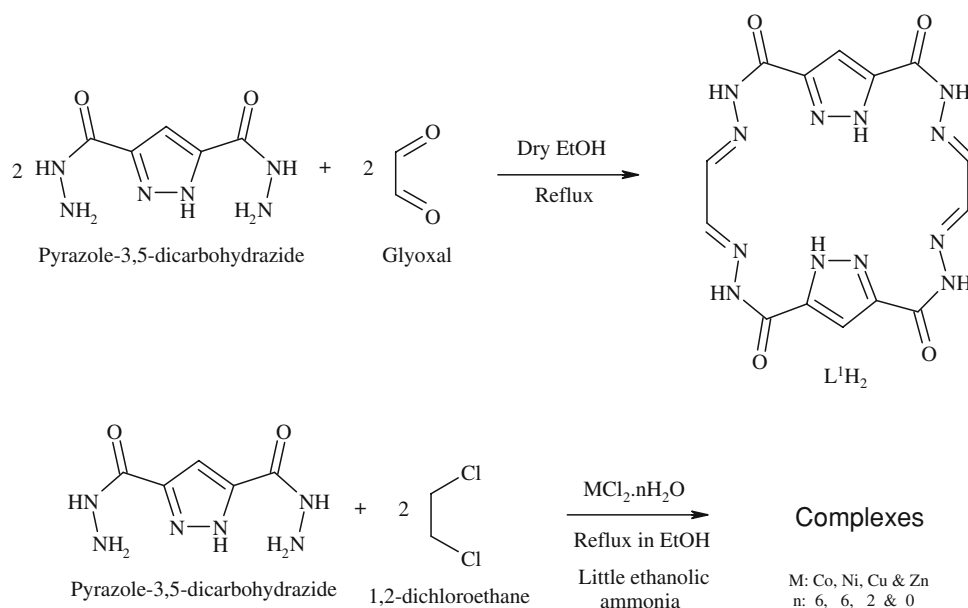
To a stirred ethanolic solution (50 ml) of metal chloride, viz, Cu(II), Ni(II), Co(II) and Zn(II) chloride (0.005 mol), 1,2-dichloroethane (0.005 mol) was added followed by the addition of pyrazole-3,5-dicarbohydrazide (0.005 mol) and further stirred for about 30 minutes, then the reaction mixture was refluxed on water bath for 4 hours, during this little ammonia was added to separate the complexes in solid form. So obtained solids were filtered off, washed with hot ethanol and dried over fused CaCl_2 . (Scheme 1)

Results and discussion

The analytical and physicochemical data of the complexes are summarized in Table 1. All complexes are soluble in organic solvents like DMF, DMSO and acetonitrile.

Infrared spectral studies

Infrared frequencies for the ligands and complexes along with their assignments are presented in Table 2. Ligand L^1H_2 shows characteristic strong bands at 3,202 and 3,314 cm^{-1} which are assigned to the pyrazole N–H and amide N–H stretching frequencies, respectively. A sharp band with splitting at 1,658 and 1,630 cm^{-1} are assigned to the amide carbonyl. The bands at 2,923 and 1,600 cm^{-1} are due to the stretching frequencies of C–H of glyoxal and azomethine group respectively. All the complexes (except $[\text{Ni}_2\text{L}^1\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ complex) of ligand L^1H_2 show a strong band in the range 1,663–1,655 cm^{-1} that confirms the non-involvement of amide carbonyl in the coordination to the metal centers. Azomethine group suffered a negative shift, of 25–55 cm^{-1} , after coordination. The band due to N–H of pyrazole is disappeared and nonligand band around 1,500 cm^{-1} collectively supports involvement of the pyrazole nitrogens through deprotonation. Only in nickel complex, all amide groups are converted in to imidol

Scheme 1 Synthesis of the ligand L^1H_2 and complexes of L^2H_2 **Table 1** Analytical, magnetic moment and conductance data of Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes

Sl. No.	Complex	Metal	Carbon	Hydrogen	Nitrogen	Chloride	μ_{eff} in BM	Molar conductance (mho $\text{cm}^2 \text{mole}^{-1}$)
1	$[Co_2L^1Cl_2(H_2O)_2] \cdot 2H_2O$	17.36 (17.89)	25.15 (25.77)	2.69 (2.23)	25.15 (25.07)	10.48 (9.75)	5.08	4.5
2	$[Ni_2L^1Cl_2(H_2O)_2] \cdot H_2O$	17.84 (16.91)	25.84 (24.89)	2.46 (2.92)	25.84 (25.09)	10.76 (9.67)	3.05	2.8
3	$[Cu_2L^1Cl_2(H_2O)_2]$	18.82 (18.43)	24.70 (24.61)	2.64 (2.54)	24.70 (24.22)	10.29 (9.70)	1.77	3.3
4	$[Zn_2L^1Cl_2(H_2O)_2] \cdot 4H_2O$	18.21 (17.65)	23.39 (23.87)	3.06 (3.71)	23.39 (24.18)	9.74 (10.52)	–	2.4
5	$[Co_2L^2Cl_2(H_2O)_2] \cdot 3H_2O$	16.92 (16.04)	24.01 (24.94)	4.01 (3.57)	24.01 (23.07)	10.18 (9.66)	5.24	6.8
6	$[Ni_2L^2(H_2O)_4]Cl_2$	23.15 (24.67)	33.13 (34.20)	3.94 (4.36)	33.13 (33.03)	14.00 (14.92)	3.31	76
7	$[Cu_2L^2Cl_2(H_2O)_2]$	17.88 (17.09)	23.82 (23.88)	3.97 (4.09)	23.82 (23.88)	10.07 (10.31)	1.89	2.0
8	$[Zn_2L^2Cl_2(H_2O)_2] \cdot H_2O$	19.42 (20.01)	24.96 (24.90)	3.56 (3.59)	24.96 (24.29)	10.54 (10.45)	–	4.9

Calculated values are given the parenthesis

functionalities and the same is further supported by the appearance of new azomethine band at $1,633 \text{ cm}^{-1}$. This imidol group is present outside the coordination sphere and the peak due to the imidol hydroxyl group is merged with the hydroxyl stretching frequencies of coordinated/lattice celled water molecules. Apart from this, remaining bands are same as in case of above discussed complexes.

All the complexes (except $[Ni_2L^2(H_2O)_4]Cl_2$) of the ligand L^2H_2 show a strong band in the range $1,667$ – $1,645 \text{ cm}^{-1}$ which is assigned to the stretching frequency of non-involved amide carbonyl group. The band in the range $1,586$ – $1,561 \text{ cm}^{-1}$ and non-ligand band in the range $1,515$ – $1,535 \text{ cm}^{-1}$ are attributed to the azomethine group and pyrazole moiety respectively. All these complexes have a distinguished band in the range $3,240$ – $3,300 \text{ cm}^{-1}$ assigned to the stretching of carbohydrazide N–H. As in case of above discussed Ni(II) complex, $[Ni_2L^2(H_2O)_4]Cl_2$ complex also has imidol groups and they are present

outside the coordination sphere. Apart from this, a non-ligand band at $1,603 \text{ cm}^{-1}$ is observed due to the formation of new azomethine fragments and imidol stretching frequency is not exactly observed due to the presence of coordinated as well as lattice celled water molecules. Finally the remaining bands are same as in case of above discussed complexes.

1H NMR spectral studies

The macrocyclic ligand is scanned in the range 0 – 16δ ppm for proton n.m.r. studies, within this range it display the singlets at 14.5 , 11.1 , 9.0 and 6.9δ ppm, which are attributed to N–H of pyrazole [9], amide proton (4H), azomethine proton (4H) and pyrazole aromatic proton (2H) respectively. Unlike ligand, its zinc complex shows azomethine protons at 9.4δ ppm and amide protons at 9.8δ ppm

Table 2 Infrared spectral data of ligand and complexes

Compound	ν (OH)	ν (NH) amide	ν (NH) Carbo-hydrazide	ν (C=O) Amide	ν (C=N) Azomethine	ν (C=N) Pyrazole	ν (M–N)
Ligand	–	3,314	–	1658, 1630	~1,600	1,537	–
[Co ₂ L ¹ Cl ₂ (H ₂ O) ₂] \cdot 2H ₂ O	3,424	~3,200	–	1660, 1629	1,585	1,550	471
[Ni ₂ L ¹ Cl ₂ (H ₂ O) ₂] \cdot H ₂ O	3,399	~3,200	–	–	1631 [#] , ~1590	1,545	471
[Cu ₂ L ¹ Cl ₂ (H ₂ O) ₂]	3,422	3,230	–	1661, 1632	1,575	~1,550	472
Zn ₂ L ¹ Cl ₂ (H ₂ O) ₂ \cdot 4H ₂ O	3,400	3,210	–	1660, 1630	~1,590	1,540	470
[Co ₂ L ² Cl ₂ (H ₂ O) ₂] \cdot 3H ₂ O	3,393	3,240	3,291	1650, ~1630	–	1,586	607
[Ni ₂ L ² (H ₂ O) ₄]Cl ₂	3,405	3,281	~3200	–	–	~1,515	467
[Cu ₂ L ² Cl ₂ (H ₂ O) ₂]	3,412	~3,300	3,150	1647, 1633	–	1,517	471
[Zn ₂ L ² Cl ₂ (H ₂ O) ₂] \cdot H ₂ O	3,452	3,326	3,251	1655, ~1625	–	1,558	630

[#] Azomethine fragment of new imidol functionality

confirms the coordination occurred through azomethine nitrogens. The peak due to N–H of pyrazole is disappeared and supports the coordination of diazine bridge through deprotonation. A broad peak was observed at 3.5 δ ppm was assigned to the coordinated water molecules.

The ¹H NMR Spectrum of [ZnL²H₂Cl₂] complex shows amide protons (4H) at 10.6 δ ppm and N–H protons (4H) of carbohydrazide group shows doublets in the range 8.1–8.9 δ ppm which confirms the coordination of carbohydrazide nitrogen atoms. Finally the usual peak due to N–H of pyrazole in the range 13–15 δ ppm is absent, which supports the coordination of diazine bridge after deprotonation. A broad peak was observed at 3.5 δ ppm was assigned to the coordinated water molecules.

Electronic spectral studies

Electronic absorption spectra of all the compounds were recorded in DMF solution over the range 200–1,000 nm. Ligand L¹H₂ shows two distinct bands at 313 and 345 nm which correspond to the intraligand, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and these bands have suffered red shift of 35–55 nm upon complexation indicating the coordination of azomethine group. Electronic spectrum of [Co₂L¹Cl₂(H₂O)₂] \cdot 2H₂O complex show d–d transitions at 911 and 630 nm, and a sharp charge transfer band at 550 nm and [Co₂L²Cl₂(H₂O)₂] \cdot 3H₂O complex shows two d–d transfer bands at 623 and 684 nm and a charge transfer band around 390 nm, which are in consistent with the octahedral structure [10]. [Ni₂L¹Cl₂(H₂O)₂] \cdot H₂O complex exhibits two bands at 896 and 600 nm which are of d–d transitions and charge transfer transition is observed at 420 nm and [Ni₂L²(H₂O)₄]Cl₂ complex displays two distinct bands at 437 and 477 nm which correspond to d–d transitions and sharp charge transfer transition occurred at 340 nm, collectively all these offers the octahedral geometry for both

the nickel complexes [11–14]. Electronic spectra of both the copper complexes exhibit the broad band in the range 550–600 nm corresponds the d–d transitions which is in agreement with the copper complexes of octahedral geometry [15]. Finally, zinc complexes show no d–d transition band as expected and all complexes show bands at the wavelength less than 320 nm, which are due to the intra ligand transitions. The ultimate conclusion drawn from the electronic spectral studies is that, the complexes of L¹H₂ have shown all expected transitions at higher wavelengths due to the extended conjugation of imine functionality, which are absent in the complexes derived from L²H₂ though the coordinating sites were same in both the macrocycles.

Molar conductivity measurements

The molar conductance values of the complexes in DMF at the concentration of 10^{−3} M are listed in Table 1. The molar conductance values for all the complexes are much less than that for 1:1 electrolyte [16] and hence all the complexes are treated as non-electrolytes, except [Ni₂L²(H₂O)₄]Cl₂ where it was found to be 86 mho cm² mol^{−1} which correspond to the nature of 1:2 electrolyte.

Magnetic susceptibility measurements

The magnetic moments measured at room temperature are listed in Table 1. The magnetic susceptibility of metal ions, encapsulated by the organic ligand field, is one of the most important properties of coordination compounds, which focuses the electronic structure [17]. The observed room temperature magnetic moment value for [Cu₂L¹Cl₂(H₂O)₂] and [Cu₂L²Cl₂(H₂O)₂] complexes are 1.77 and 1.89 BM respectively, these values are slightly more than the spin

only value of free metal ion hence the existence of antiferromagnetic exchange interaction may transmit by the endogenous pyrazole bridge will be ruled out. These data quote the proposed geometry around both the copper ions [18] and the same were further supported by large isotropic signal in electron spin resonance spectrum. In case of nickel (3.05 and 3.31 BM) and cobalt complexes (5.08 and 5.24 BM) the magnetic moment values are found to be more than the spin only value, hence the possibility of antiferromagnetic interaction is ignored. The common entity measured for these ions from the magnetism point of view is that, they have surrounded by the octahedral macrocyclic ligand field [19, 20]. The higher magnetic moments in few cases are due to spin-orbit coupling.

Electron spin resonance spectral study

The powder state X-band ESR spectra of copper complexes were operated in the region of 9,000 MHz with corresponding field intensity at $\sim 3,000$ Gauss in powder state at room temperature. Both the spectra exhibit isotropic intense broad signal with g_{iso} 2.072 and 2.26 with no hyperfine splitting. ESR spectra of these kinds have been reported earlier for complexes having large organic ligands [21, 22], and also the broad ESR signal indicates the presence of chloro coordinated binuclear copper(II) complexes [23]. This broadening is because of the dipolar interaction.

Cyclic voltammetric studies

The study of electroreduction of CO_2 using metal complexes of azamacrocycles and redox behavior of metal ions in presence of CO_2 was our aim. In this connection, Ni^{II} complexes were selected for the electroreduction of CO_2 into CO finally to formalin. The reduction potential of $[\text{Ni}_2\text{L}^1\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ complex in N_2 atmosphere is found to be -1.8 V with $I_{\text{p}_c} = 120$ mA, which is in resemblance with the reported Ni^{II} polyazamacrocyclic complexes meant for such electroreduction [24, 25]. When the same reduction scan is done in CO_2 atmosphere the I_{p_c} value should increase to confirm the electroreduction of CO_2 to CO. Unfortunately, there was no reduction peak of the complex due to the effect of abundant CO_2 . All our attempts to achieve the target were unsuccessful. Apart from this, both the copper complexes were electrochemically active whereas remaining were not. $[\text{Cu}_2\text{L}^1\text{Cl}_2(\text{H}_2\text{O})_2]$ complex shows irreversible redox process with reduction potential at -0.58 V ($I_{\text{p}_c} = 191$ mA) and $[\text{Cu}_2\text{L}^2\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ complex shows quasireversible, one electron transfer

process with oxidation potential at 0.077 V ($I_{\text{p}_c} = 53$ mA) and reduction potential at -0.29 V ($I_{\text{p}_c} = 110$ mA).

FAB mass spectral studies

The FAB mass spectrum of copper complexes was recorded by using *m*- NO_2 benzyl alcohol as matrix. FAB mass spectra of $[\text{Cu}_2\text{L}^1\text{Cl}_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2\text{L}^2\text{Cl}_2(\text{H}_2\text{O})_2]$ complexes show molecular ion peak corresponding to m/z at 639 and 648 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 that, the complexes are monomeric in nature. By comparing all the analytical and spectral data of cobalt, nickel and zinc complexes, it is evident that, these are monomeric and binuclear complexes.

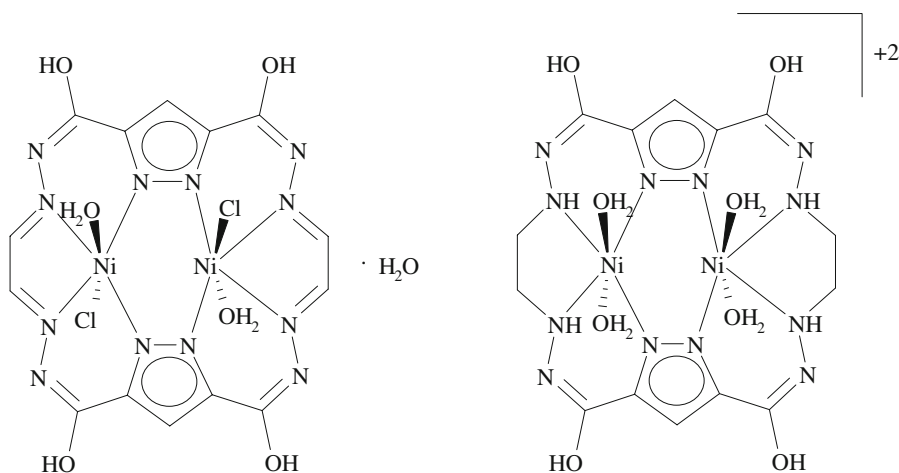
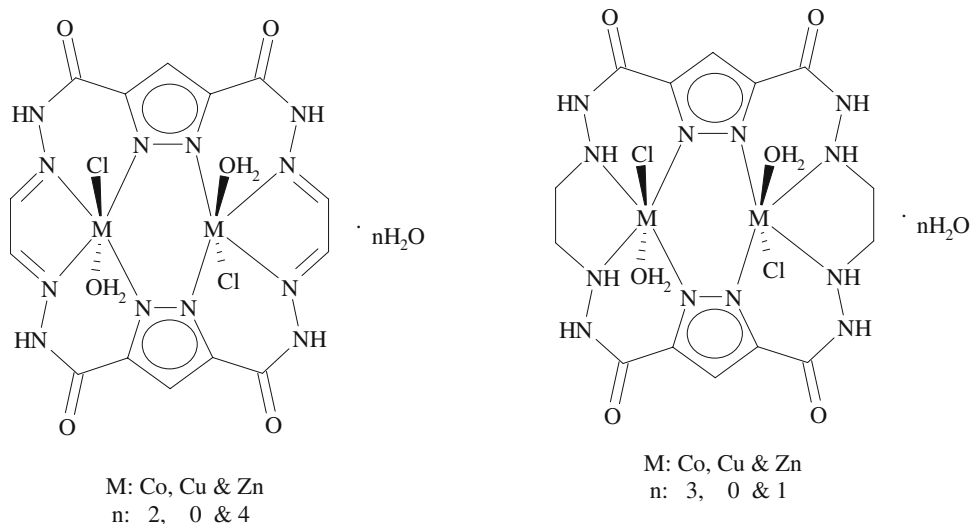
Thermal study

The thermogravimetric analysis of the Cu(II) complex has carried out in nitrogen environment. TG-DTA curves of $[\text{Cu}_2\text{L}^1\text{Cl}_2(\text{H}_2\text{O})_2]$ show weight losses in three considerable stages. In the first stage 5.5%, in the temperature range 55–120 °C is attributed to the weight loss of two coordinated water molecules, which is further supported by the DTA peak at 130 °C. Further weight loss is at 254 °C which indicates the presence of chloride. And last weight loss is due to ligand and finally the graph became plateau because of the formation of stable metal oxide. Similarly, TG-DTA graphs of cobalt and zinc complexes follow the same pattern with slight differences.

Conclusion

The present work has thus shown that the chelation occurred through N_8 donating sites. In all the complexes (except nickel complexes) coordination occurred through nitrogen atoms of both pyrazole rings and carbonyl nitrogens. In addition to this, in the Ni(II) complexes, imidol group is formed and as amide carbonyl, these imidol hydroxyl groups are also present outside the coordination sphere. Metal to ligand ratio is found to be 1:2 in all complexes. Magnetic moment and UV–visible studies reveal the presence of octahedral geometry around all the metal ions. Both copper complexes possess isotropic nature in ESR spectra, which show the symmetric environment around the copper ions (Proposed structures of the complexes are as shown in Fig. 1). The electroreduction of CO_2 to CO was carried out using nickel complex, but it ended with the negative result.

Fig. 1 Tentative structures of the complexes



The cyclic voltammograms of $[\text{Cu}_2\text{L}^1\text{Cl}_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2\text{L}^2\text{Cl}_2(\text{H}_2\text{O})_2]$ complexes show irreversible and quasi-reversible redox properties respectively.

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