

Synthesis and structure of transition metal complexes derived from a novel polynucleating oxaza macrocycle having diazine and phenoxo bridging components

Anupama Kamath · Vidyanand K. Revankar

Received: 13 August 2010 / Accepted: 18 March 2011 / Published online: 21 April 2011
© Springer Science+Business Media B.V. 2011

Abstract Novel Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes of the polynucleating oxaza macrocyclic ligand (LH_4) derived from the 2:2 condensation of pyrazole-3,5-dicarbohydrazide and 2,6-diformyl-4-methylphenol have been synthesized. Ligand and complexes were characterized on the basis of elemental analysis, IR, ^1H NMR, UV–Visible, magnetic susceptibility, ESR and conductivity measurements, FAB-mass and thermal analysis. Present Zn^{II} and Cu^{II} complexes are binuclear in nature with octahedral geometry, where as Co^{II} and Ni^{II} complexes are tetranuclear with square-planar geometry. Cu^{II} and Co^{II} complexes are paramagnetic whereas Zn^{II} and Ni^{II} complexes are diamagnetic. Only the copper complex has shown redox property in the applied potential range while the ligand and other complexes are found to be electrochemically innocent.

Keywords Tetranuclear · Pyrazole-3,5-dicarbohydrazide · 2,6-diformyl-4-methylphenol · Square-planar

Introduction

Considerable recent attention has been given to coordination compounds prepared from ligand systems capable of binding multiple metal ions in the immediate proximity to each other. Complexes of this type are of importance in studies of electron transfer, magnetic interactions, optical phenomena, excited-state reactivity, biomimetic chemistry, mixed valency and ionophoric activity. One strategy for the

design of multimetallic systems has involved the use of polynucleating macrocyclic ligands [1–9]. 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 p orbitals in addition to lone-pairs of electrons; they have vacant p orbitals that are available for occupation.

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 [10–13]. 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 as endogenous bridge.

Ligands derived from 2,6-diformyl-4-substituted phenols have attracted a lot of attention, mainly because they can act as good precursors for macrocyclic systems. An important aspect of these ligands is that the phenolic oxygen of the 4-substituted phenol has a tendency to simultaneously coordinate to two metal atoms acting as a bridge. The donor groups of these ligands provide a significant diversification of the coordination sites making them good candidates for metal ion complexation and for mimicking biological systems. The study of their stereochemical, electronic, magnetic, catalytic and spectroscopic properties have allowed the proposal of probes for some important applications. It has been studied the biological activity of related compounds with interesting results [14–21].

It is an interesting target to study the magnetic, electrochemical and structural aspects of macrocyclic complexes derived from 3,5-disubstituted pyrazole since

A. Kamath · V. K. Revankar (✉)
Department of Studies in Chemistry, Karnatak University,
Pavatenagar, Dharwad 580 003, Karnataka, India
e-mail: vkrevankar@rediffmail.com

coordination diversity of amine and imine functionalities explores the architectural changes in the metal complexes to behave distinctly in their physico-chemical properties even though the chelating atoms present are same. It is also fascinating to investigate whether coordination has occurred through the oxygen, or advantage is taken only by the available nitrogen donors to form macrocyclic complexes. In the present article we wish to report the synthesis, characterization and electrochemistry of a novel macrocyclic ligand obtained by “2 + 2” condensation of 2,6-diformyl-4-methylphenol with pyrazole-3,5-dicarbohydrazide and its bi- and tetranuclear Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes.

Experimental

Materials and methods

All chemicals used were of reagent grade. Solvents were dried and distilled before use according to standard procedures [22]. 2,6-Diformyl-4-methylphenol was prepared according to the method reported by Denton and Suschitzky with slight modification [23]. Pyrazole-3,5-dicarbohydrazide was prepared according to the earlier reports with slight modifications [24]. The metal salts used were in hydrated form, i.e., $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 .

Preparation of the ligand (LH_4)

Pyrazole-3,5-dicarbohydrazide (0.2 mol) was taken in 50 ml of absolute ethanol, to which 2,6-diformyl-4-methylphenol (0.2 mol) was added slowly with stirring. Further the mixture was stirred at room temperature for 15 min. The reaction mixture was refluxed on water bath for 4 h. The orange solid that formed was filtered off and washed with hot ethanol (MP: 317 °C, Yield: 68%) (Fig. 1).

Preparation of complexes

To the stirred ethanolic solution (50 ml) of respective metal chlorides (0.02 mol), ligand (0.005 mol) was added and stirred further for about 15 min and then the reaction mixture was refluxed on water bath for 4 h. So obtained solid was filtered off, washed with hot ethanol and dried over fused CaCl_2 .

Analyses and physical measurements

Estimation of the metal(II) ions was 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 $4000\text{--}400\text{ cm}^{-1}$ range. The electronic spectra of the complexes were recorded on a Hitachi 150-20 spectrophotometer in the range of $1000\text{--}200\text{ nm}$. 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 (at room temperature and liquid nitrogen temperature) 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 $1000\text{ }^\circ\text{C}$ and heating rate $10\text{ }^\circ\text{C}/\text{min}$. 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.

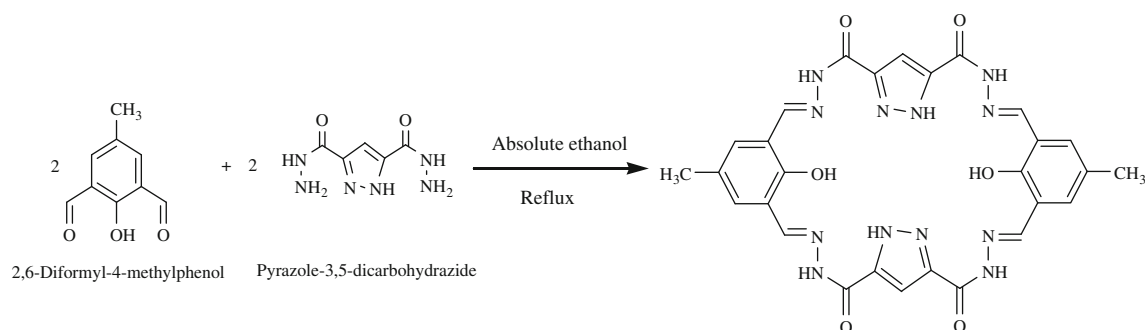


Fig. 1 Preparation of the macrocyclic ligand LH_4

Results and discussion

The analytical and physicochemical data of the complexes are summarized in Table 1. All complexes are stable in air at room temperature, non-hygroscopic in nature, insoluble in common organic solvents and partially soluble in solvents like DMF, DMSO and acetonitrile.

FTIR spectral studies

The FTIR spectra give some important information regarding the skeleton of the complexes. The spectrum of the macrocyclic Schiff base was compared with that of its starting material which does not show any band corresponding to amino and aldehyde groups, confirming the condensation of these groups [25]. The spectrum of free macrocycle shows bands at 3314, 3100, 1663, 1626 and 1250 cm^{-1} which can be assigned to the hydrazide $\nu(\text{NH})$, pyrazole $\nu(\text{NH})$, amide $\nu(\text{C}=\text{O})$, azomethine $\nu(\text{C}=\text{N})$ and phenolic $\nu(\text{C}-\text{O})$ respectively [26]. The $\nu(\text{C}=\text{N})$ has shifted to lower frequency region in all complexes due to coordination through nitrogen. In case of Cu and Zn complexes amide $>\text{C}=\text{O}$ shifted to 1622 and 1626 cm^{-1} respectively indicating the coordination of oxygen. Further pyrazole $\nu(\text{NH})$ absorption remained unchanged, suggesting the non-involvement of pyrazole diazine component in the coordination. The absence of amide $>\text{C}=\text{O}$ in Ni and Co complexes suggests that the complexes are in imidol form. Disappearance of pyrazole $\nu(\text{NH})$ in Ni and Co complex shows involvement of pyrazole diazine component in the coordination through deprotonation. $\nu(\text{C}-\text{O})$ for phenolic

group has shifted to higher frequency in all complexes due to the coordination of $-\text{OH}$ upon deprotonation [27]. The appearance of bands in the region of 1530–1545 cm^{-1} in all the complexes suggests phenoxide bridging with the metal ions [28, 29]. Further, the bands in the region 520–570 and 400–480 cm^{-1} are due to the formation of M–O and M–N bonds respectively [24] (Table 2).

^1H NMR spectral studies

The macrocyclic ligand and its Zn^{II} complex were scanned in the range 0–16 δ ppm for proton NMR studies. Within this range N–H of pyrazole [26], N–H amide, C–H azomethine and O–H phenolic protons resonate at 14.22, 9.85, 9.03 and 12.30 δ ppm respectively. ^1H NMR spectrum of Zn^{II} complex differs from ligand spectrum, shows three signals at 11.99, 10.36 and 9.12 δ ppm which are assigned to pyrazole N–H, amide $-\text{NH}$ and C–H azomethine respectively. It is again emphasized the non-involvement of pyrazole diazine group in the coordination. Aromatic protons are found in the range 6.90–8.77 δ ppm. The shift of amide signal to 10.36 δ ppm and absence of phenolic $-\text{OH}$ peak suggests the coordination via deprotonation. The spectrum of Ni^{II} complex shows signals at 12.28 and 8.80 δ ppm, which can be assigned to imidol $-\text{OH}$ and azomethine $-\text{CH}$ respectively. The aromatic protons are resonated in the region 6.90–7.90 δ ppm. The absence of peak corresponds to pyrazole N–H suggests the involvement of pyrazole ring in coordination via deprotonation. Ar- CH_3 protons are observed at 2.33 δ ppm for ligand and complexes (Table 3).

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 $\text{mho cm}^2 \text{mol}^{-1}$ |
|--------|--|---------------|---------------|-------------|---------------|---------------|--------------------------|---|
| 1) | $[\text{Co}_4\text{LCl}_2]\text{Cl}_2$ | 24.19 (23.64) | 33.17 (33.70) | 2.28 (2.00) | 16.64 (16.85) | 15.54 (14.22) | 2.15 | 106.7 |
| 2) | $[\text{Ni}_4\text{LCl}_2]\text{Cl}_2$ | 23.69 (23.59) | 33.89 (33.76) | 2.07 (2.01) | 17.26 (16.88) | 15.61 (14.25) | – | 113.2 |
| 3) | $[\text{Cu}_2\text{LH}_2]\text{Cl}_2$ | 15.93 (15.49) | 40.32 (40.97) | 2.89 (2.68) | 20.59 (20.48) | 9.42 (8.64) | 1.79 | 102.4 |
| 4) | $[\text{Zn}_2\text{LH}_2]\text{Cl}_2$ | 16.12 (15.87) | 41.06 (40.77) | 2.54 (2.67) | 20.64 (20.38) | 9.35 (8.60) | – | 103.6 |

Calculated values are given in the parenthesis

Table 2 Infrared spectral data of ligand and its complexes

| Compounds | N–H (Hydrazide) | N–H (Pyrazole) | $>\text{C}=\text{O}$ (Amide) | $>\text{C}=\text{N}$ (Azomethine) | C–O (Phenolic) |
|--|-----------------|----------------|------------------------------|-----------------------------------|----------------|
| LH_2 | 3314 | ~3100 | 1663 | 1626 | 1250 |
| $[\text{Co}_4\text{LCl}_2]\text{Cl}_2$ | – | – | – | 1624 | ~1260 |
| $[\text{Ni}_4\text{LCl}_2]\text{Cl}_2$ | – | – | – | 1625 | ~1270 |
| $[\text{Cu}_2\text{LH}_2]\text{Cl}_2$ | 3207 | 3080 | 1622 | 1590 | 1264 |
| $[\text{Zn}_2\text{LH}_2]\text{Cl}_2$ | 3292 | 3062 | 1626 | 1573 | ~1270 |

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

| Compounds | –NH Pyrazole (ring) | –OH Phenolic | –OH Imidol | =CH Azomethine | Aromatic region |
|--|---------------------|--------------|------------|----------------|-----------------|
| LH_4 | 14.22 | 12.30 | – | 9.03 | 7.05–8.99 |
| $[\text{Zn}_2\text{LH}_2]\text{Cl}_2$ | 11.99 | – | – | 9.12 | 6.90–8.77 |
| $[\text{Ni}_4\text{LCl}_2]\text{Cl}_2$ | – | – | 12.28 | 8.80 | 6.90–7.90 |

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

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

| Compounds | Peak values (in nm) (λ_{max} in cm^{-1}) |
|--|--|
| LH_2 | 303 (33003), 372 (26881) |
| $[\text{Co}_4\text{LCl}_2]\text{Cl}_2$ | 771(12970), 500–410 (20000–24390), 300(33333) |
| $[\text{Ni}_4\text{LCl}_2]\text{Cl}_2$ | 736(13586), 510–420 (19607–23809), 303 (33003) |
| $[\text{Cu}_2\text{LH}_2]\text{Cl}_2$ | 710–640 (14084–15625), ~440 (22727), 397 (25188), 307 (32573) |
| $[\text{Zn}_2\text{LH}_2]\text{Cl}_2$ | 387 (25839), 308 (32467) |

Molar conductivity measurements

The molar conductance values of complexes were obtained at room temperature in DMSO solution at 10^{-3} mol/dm³ concentration. The molar conductivity values of all the complexes fall in the range 103.6–113.2 mho cm² mol⁻¹, which is in agreement with 1:2 electrolytic nature of the complexes [30].

Electronic spectral studies

The electronic absorption spectra of the complexes 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 303 and 372 nm, which are due to the intra ligand $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transitions respectively. In Co^{II} and Ni^{II} complexes, band at 372 nm has disappeared (Fig. 2) which internally supports the enolisation of carbohydrazide unit [26, 31] and coordination of the diazine unit. The UV–visible spectra exhibit a

medium intensity broad band at around 390 nm in Cu^{II} , Zn^{II} complexes and 450 nm in Co^{II} , Ni^{II} complexes due to charge transfer transitions. The $^2\text{B}_{2g} \rightarrow ^2\text{E}_g$ transition of cobalt complex and $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ transition of nickel complex are obscured into their broad charge transfer transitions. In addition to the above observations, present Co^{II} complex shows band at 771 nm, because of the $^2\text{B}_{2g} \rightarrow ^2\text{A}_{1g}$ transition and Ni^{II} complex shows low intensity band at 736 nm due to $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition concordant with square-planar geometry of both the complexes [32, 33]. The geometry of nickel complex is further supported by diamagnetic nature of the complex. Electronic spectrum of the copper complex exhibits the broad band in the range 640–710 nm corresponds to the d–d transitions which is in agreement with the octahedral geometry [34]. The electronic spectrum of the Zn^{II} complex does not show d–d transition bands as expected.

Magnetic moment measurements

The room temperature magnetic moment data are summarized in Table 1. Zn^{II} and Ni^{II} complexes are diamagnetic whereas Cu^{II} and Co^{II} complexes are paramagnetic in nature with effective magnetic moment 1.79 and 2.15 BM respectively. Comparatively high magnetic moments rule out the existence of antiferromagnetic exchange interaction. The higher magnetic moment of copper complex is due to spin–orbit coupling. In the doubly bridged metal(II) complexes having counter-complementarily bridging groups, the overall magnetic interaction is very weakly antiferromagnetic [15]. Naturally, as a result of bond bridge (diazine bridging) and atom bridge (phenoxide bridging), the metal centers are in close proximity and super exchange interactions are expected in cobalt

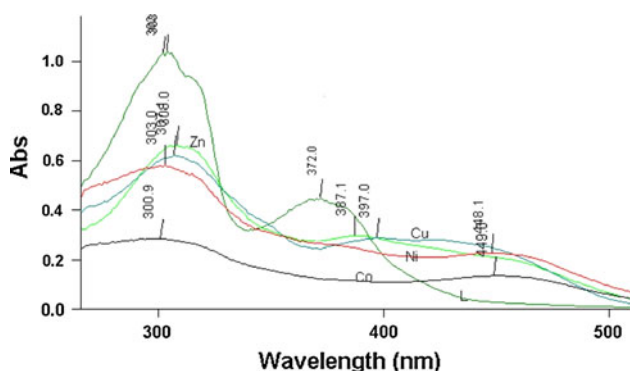


Fig. 2 UV–Visible spectra of ligand, Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes in the range 275–500 nm

complex. But the contrary results of magnetic susceptibility measurements are due to the more electronegative bridged chloro ligands [13, 32]. The drop in electron density on the metal centers caused by the electron withdrawing effect of bridging atoms is the probable reason for less effective spin exchange interactions.

Electron spin resonance spectral study

The X-band ESR spectrum of copper(II) complex in solid form scanned in the region of 9000 MHz with corresponding field intensity at ~ 3000 Gauss. The spectra exhibit isotropic intense broad signal with g_{iso} 2.0793 and 2.0727 at room temperature and liquid nitrogen temperature respectively with no hyperfine splitting. This suggests that both copper ions are in similar chemical environment. No half field absorption which is an index of metal–metal interaction was observed. These types of spectra were reported earlier for the complexes bearing large organic ligand substituents having considerable covalent character for metal–ligand bonds [35]. The broadening in ESR signal is found to be because of the dipolar interaction [36]. Similar nature of ESR spectra at room temperature and liquid nitrogen temperature shows no considerable change in the geometry of ligand field around the metal ion when temperature is lowered.

FAB-mass spectral studies

The elemental and analytical data of the complexes are supported by the FAB mass spectrum. FAB mass spectrum of Cu^{II} and Ni^{II} complexes show peak at 820 and 997 respectively corresponding to the mass of the entire complex [37]. Apart from this, spectra show some other peaks, which are due to molecular ions of various fragments of the complexes. The information got from FAB mass data agrees well with binuclear nature of Cu^{II} and Zn^{II} complexes and tetranuclear nature of Co^{II} and Ni^{II} complexes. Important conclusion drawn from FAB mass data along with analytical and spectral data of all the complexes is that the complexes are monomeric.

Thermal study

All prepared complexes were studied for their thermal behavior over the temperature range of 30–1000 °C under nitrogen atmosphere. All complexes decompose in same fashion. TG-DTA curves show weight losses in two considerable steps for all complexes. In the first step about 9%, in the temperature range 90–160 °C attributed to the weight loss of two counter chloride ions. In the next step, the ligand part of the complex decompose completely and the corresponding DTA signal is observed at 382.12 °C.

The final decomposition products were found to be metal oxides. The thermal data is in well agreement with the proposed structure of complexes.

Electrochemistry

The cyclic voltammograms of all ligand and complexes were recorded in the potential range of +1.0 to –1.0 V with different scan rates (0.15, 0.1 and 0.05 V/s). Only the copper complex exhibits redox property. Whereas ligand and other complexes are found to be electrochemically innocent in the working potential domain indicating that the electrochemical activity of copper complex is purely metal based. The voltammogram of Cu complex shows a single oxidation peak in the range 0.49–0.53 V in the anodic potential scan. The cathodic scan, exhibits a single peak in the range 0.18–0.22 V due to the reduction of metal species. The high value of ΔE_p , separation between the cathodic and anodic peak potentials ($E_{pa} - E_{pc}$) which is greater than 60 mV indicates quasi-reversible redox process [38, 39] assignable to the Cu(III)/Cu(II) couple with $E_{1/2} [(E_{pc} + E_{pa})/2]$ value ~ 0.61 V. The appearance of Cu(III)/Cu(II) and absence of Cu(II)/Cu(I) couple can be rationalized in terms of flexibility and the size of the coordination cavity in the complexes and the geometric requirements and the size of the metal ions in the different oxidation states. The voltammogram of complex scanned after keeping the solution overnight and at slower rates have shown decrease in ΔE_p value indicating the reversibility of reaction with slow rate (Fig. 3).

Conclusion

It is concluded from the above investigation that, the novel oxaza macrocycle is binucleating towards copper and zinc, and tetranucleating towards cobalt and nickel. Magnetic susceptibility measurements and electronic spectral studies witnessed the presence of octahedral and square planar ligand field around the Cu^{II} , Zn^{II} and Ni^{II} , Co^{II} metal ions, respectively. In cobalt and nickel complexes bridging occurred through diazene of pyrazole ring by deprotonation, leaving carbonylhydrazide unit in its enol form. However, in case of copper and zinc complexes pyrazole ring remained intact and coordination has occurred through carbonyl groups of pyrazole-3,5-dicarbonylhydrazide. Phenoxide bridging between two metal ions has found in all complexes. Symmetric environment around the copper ions has shown by the isotropic nature ESR spectra. Copper and cobalt complexes have shown higher magnetic moments with no antiferromagnetic exchange interactions whereas zinc and nickel complexes are diamagnetic. Cu^{II} complex has shown one electron transfer redox property, while the

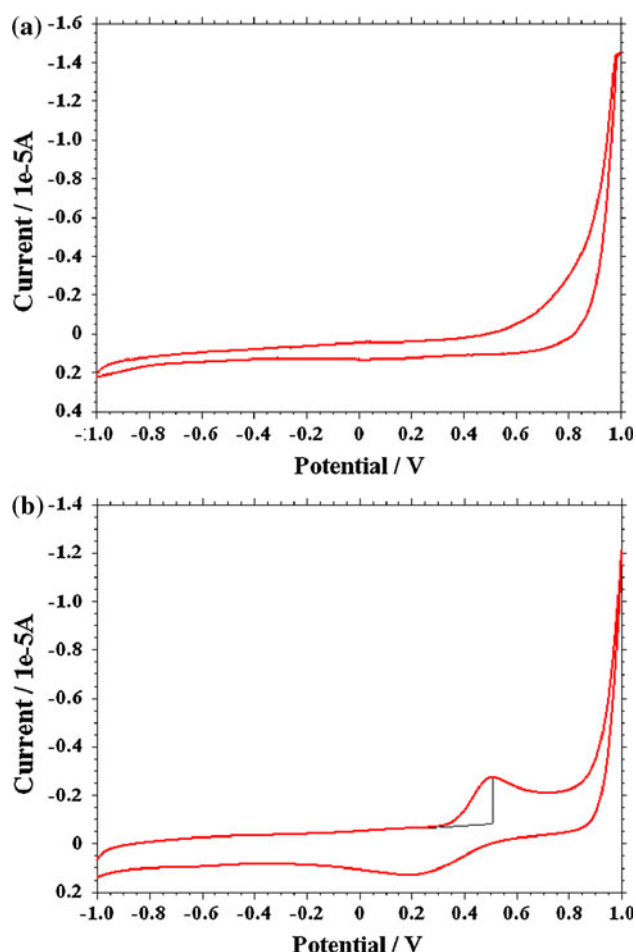


Fig. 3 **a** Cyclic voltammogram of ligand at the scan rate of 0.05 Vs^{-1} . **b** Cyclic voltammogram of Cu^{II} complex at the scan rate of 0.05 Vs^{-1}

ligand and other complexes are found to be electrochemically innocent. All complexes are 1:2 electrolytes (Fig. 4).

Acknowledgments The authors thank the USIC and Department of chemistry, Karnatak University, Dharwad for providing spectral facility. Recording of FAB mass spectra (CDRI Lucknow) and ESR spectra (IIT Bombay) are gratefully acknowledged. The author(AK) thanks UGC for providing Research Fellowship in Science for Meritorious Students.

References

- Feiters, M.C.: X-ray absorption spectroscopic studies of metal coordination in zinc and copper proteins. *Comments Inorg. Chem.* **11**, 131–174 (1990)
- Solomon, E.I., Baldwin, M.J., Lowery, M.D.: Electronic structures of active sites in copper proteins: contributions to reactivity. *Chem. Rev.* **92**, 521–542 (1992)
- Blondin, G., Girerd, J.J.: Interplay of electron exchange and electron transfer in metal polynuclear complexes in proteins or chemical models. *Chem. Rev.* **90**, 1359–1376 (1990)

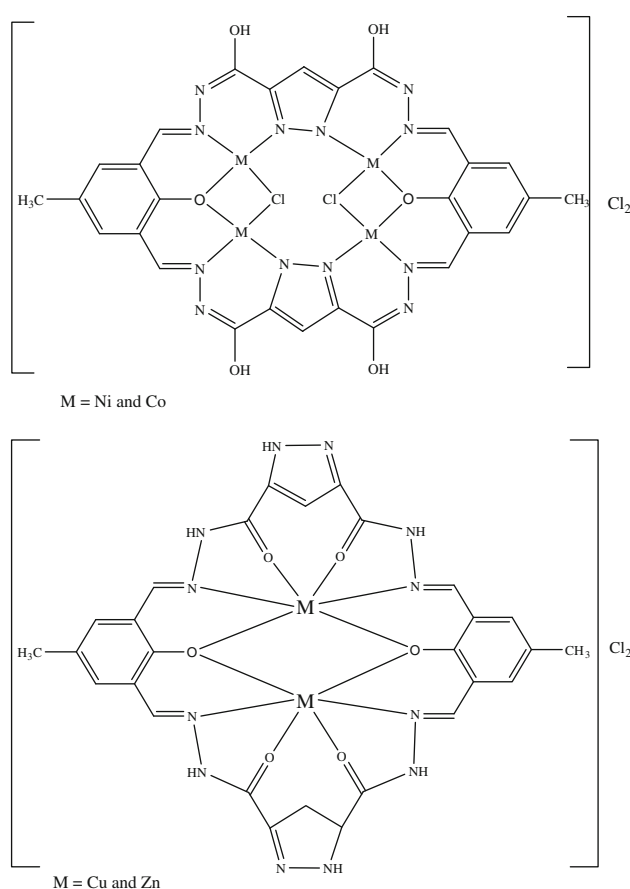


Fig. 4 Proposed structures of the complexes

- Kalyanasundaram, K., Nazeeruddin, K.: Free radical-mediated electron transfer in organometallic complexes: homolysis and alkyl group crossover reactions for alkyliron(II) porphyrins. *Inorg. Chim. Acta* **226**, 213–230 (1994)
- Balzani, V., Juris, A.: Photochemistry and photophysics of Ru(II)—polypyridine complexes in the Bologna group. From early studies to recent developments. *Coord. Chem. Rev.* **211**, 97–115 (2001)
- Cola, L.D., Belster, P.: Photo-induced energy and electron transfer processes in rigidly bridged dinuclear Ru/Os complexes. *Coord. Chem. Rev.* **177**, 301–346 (1998)
- Gibney, B.R., Kessissoglou, D.P.: Copper(II) 12-metallacrown-4: synthesis, structure, ligand variability, and solution dynamics in the 12-MC-4 structural motif. *Inorg. Chem.* **33**, 4840–4849 (1994)
- Nakamura, Y., Yonemura, M.: Tetranuclear mixed-metal $\text{M}_2^{\text{II}}\text{Cu}_2^{\text{II}}$ complexes derived from a phenol-based macrocyclic ligand having two N(amine)₂O₂ and two N(imine)₂O₂ metal-binding sites. *Inorg. Chem.* **40**, 3739–3744 (2001)
- Baumann, T.F., Nasir, M.S.: Solitaire-porphyrazines: synthetic, structural, and spectroscopic investigation of complexes of the novel binucleating norphthalocyanine-2, 3-dithiolato ligand. *J. Am. Chem. Soc.* **118**, 10479–10486 (1996)
- Richard, H.B., Johan, E.B., Willem, L.D., Frans, B.H., Jan, R., Anthony, L.S.: Formation of dinuclear copper (II) complexes from a macrocycle with built-in pyrazole groups. *Inorg. Chem.* **38**, 1239–1243 (1999)
- Naik, A.D., Annigeri, S.M., Gangadharmath, U.B., Revankar, V.K., Mahale, V.B.: Thiocarbonylhydrazide as “Diamine” to

- construct macrocyclic and side-off compartmental ligands. *J. Incl. Phenom. Macrocycl. Chem.* **43**, 291–297 (2002)
12. Kaniz, F.S., So, Y.L., Jai, Y.L., Ki-Min, P., Shim, S.L.: Discrete and soft metal complexes of O₂S₂ and NO₂S₂ macrocycles with endo- or exo-coordination mode. *Bull. Korean Chem. Soc.* **29**, 241–244 (2008)
 13. Budagumpi, S., Sathisha, M.P., Kulkarni, N.V., Kurdekar, G.S., Revankar, V.K.: Transition metal complexes of pyrazole head 24-membered polyazamacrocyclic bimetal cores: synthesis, characterization, electrochemistry and spectral study. *J. Incl. Phenom. Macrocycl. Chem.* **66**(3), 327–333 (2009)
 14. Illán-Cabeza, N.A., Francisco, H.-U.: Synthesis, characterization and antiproliferative activity of metal complexes with the Schiff base derived from the condensation 1:2 of 2, 6-diformyl-4-methylphenol and 5, 6-diamino-1, 3-dimethyluracil. *J. Inorg. Biochem.* **102**, 647–655 (2008)
 15. Annigeri, S.M., Naik, A.D., Gangadharmath, U.B., Revankar, V.K., Mahale, V.B.: Symmetric binuclear complexes with an ‘end-off’ compartmental Schiff base ligand. *Trans. Metal Chem* **27**, 316–320 (2002)
 16. Croucher, P.D., Klingele, M.H.: Tricopper(II) complexes of unsymmetrical macrocycles incorporating phenol and pyridine moieties: the development of two stepwise routes. *Dalton Trans.* 4000–4007 (2007)
 17. Wan, X.-B., Jin, C.-M.: Crystal structure of a tetranuclear nickel (II) complex of a 24-membered Schiff base macrocyclic ligand. *J. Chem. Crystallogr.* **34**(1), 57–60 (2004)
 18. Atkins, A.J., Black, D.: Synthesis and structure of mononuclear and binuclear zinc(II) compartmental macrocyclic complexes. *D Dalton Trans.* 1730–1737 (2003)
 19. Khanra, S., Weyhermuller, T.: Deliberate synthesis for magneto-structural study of linear tetranuclear complexes BI^{II}Mn^{II}Mn^{II}BI^{II}, Mn^{III}Mn^{II}Mn^{II}Mn^{III}, Mn^{IV}Mn^{II}Mn^{II}Mn^{IV}, Fe^{III}Mn^{II}Mn^{II}Fe^{III}, and Cr^{III}Mn^{II}Mn^{II}Cr^{III}. Influence of Terminal Ions on the Exchange Coupling. *Inorg. Chem.* **45**(15), 5911–5923 (2006)
 20. Dutta, B., Adhikary, B.: Organized assemblies of lead(II) complexes of a tetraaminodiphenol macrocyclic ligand: manifestation of weak metal–anion interactions and the directional influence of anions. *J. Chem. Soc., Dalton Trans.* 2760–2767 (2002)
 21. Leelavathy, L., Anbu, S.: Synthesis and characterization of a new series of unsymmetrical macrocyclic binuclear vanadyl(IV) complexes: electrochemical, antimicrobial, DNA binding and cleavage studies. *Polyhedron* **28**, 903–910 (2009)
 22. Vogel, Text book of practical organic chemistry, 5th ed., Longman, London, (1989)
 23. Denton, D.A., Suschitzky, H.: Synthetic uses of polyphosphoric acid. *J. Chem. Soc.*, 4741–4743 (1963)
 24. Subrata, K.D., Tareque, S.M.A., Louise, N.D., Santokh, S.T., Julie, L.C., Laurence, K.T., Andrei, V.P., Mohammad, S.A., Paul, M.: Supramolecular self-assembled polynuclear complexes from tritopic, tetratopic, and pentatopic ligands: structural, magnetic and surface studies. *Inorg. Chem.* **46**, 7767–7781 (2007)
 25. Nakamoto, K.: Infrared and raman spectra of inorganic and coordination compounds, 3rd edn. Wiley Interscience, New York (1997)
 26. Budagumpi, S., Kurdekar, G.S., Kulkarni, N.V., Revankar, V.K.: Bi- and tetranuclear ligational deeds of a polyaza macrocycle having four diazine (N₂) bridging components headed for CoII, NiII, CuII and ZnII ions: An emphasis on electrochemistry of non-innocent ligand system. *J. Incl. Phenom. Macrocycl. Chem.* **67**, 217–223 (2010)
 27. Naresh Kumar, K., Ramesh, R., Liu, Y.: Synthesis, structure and catalytic activity of cycloruthenated carbonyl complexes containing arylazo phenolate ligands. *J. Mol. Catal. A: Chem* **265**, 218–226 (2007)
 28. Sreedaran, S., Bharathi, K.S.: Synthesis, electrochemical, magnetic, catalytic and antimicrobial studies of N-functionalized cyclam based trinuclear copper(II) and nickel(II) complexes. *J. Incl. Phenom. Macrocycl. Chem.* **66**, 297–306 (2010)
 29. Srinivas, B., Arulsamy, N., Zacharias, P.S.: Catalytic and magnetic properties of a new series of binuclear copper(II) complexes. *Polyhedron* **10**, 731 (1991)
 30. Geary, W.J.: The use of conductivity measurements in organic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.* **7**, 81–122 (1971)
 31. Naik, A.D., Revankar, V.K.: Design, synthesis and physico-chemical investigation of a dinuclear zinc(II) complex with a novel ‘end-off’ compartmental ligand. *Proc. Indian Acad. Sci. (Chem. Sci.)* **113**, 285–290 (2001)
 32. Sallam, S.A., Orabi, A.S.: Copper, nickel and cobalt complexes of Schiff-bases derived from β-diketones Shehab A. *Transition. Met. Chem.* **27**, 447–453 (2002)
 33. Lever, A.B.P.: Inorganic electronic spectroscopy. Elsevier, New York (1968)
 34. Köse, D.A., Kaya, A.: Necefoglu, H.: Synthesis and characterization of bis(N,N-dimethyl nicotinamide) m-hydroxybenzoate complexes of Co(II), Ni(II), Cu(II) and Zn(II). *Russian J. Coord. Chem.* **33**, 422–427 (2007)
 35. Keshavalu, C., Naidu, R.S., Naidu, R.R.: Electron spin resonance and optical absorption studies of copper-oxime chelates in dimethyl formamide and pyridine. *Polyhedron* **4**, 761 (1985)
 36. Munakata, M., Wu, L.P., Yamamoto, M., Kuroda-Sowa, T., Maekawa, M., Kawata, S., Kitagawa, S.: Co-ordinative versatility of 3,5-bis(2-pyridyl)pyrazole in silver and copper compounds. *J. Chem. Soc. Dalton Trans.*, 4099–4106 (1995)
 37. Korupaju, S.R., Mangayarkarasi, N., Ameerunisha, S., Valente, E.J., Zacharis, P.S.: Formation of dinuclear macrocyclic and mononuclear acyclic complexes of a new trinucleating hexaaza triphenolic Schiff base macrocycle: structure and NLO properties. *J. Chem. Soc. Dalton Trans.*, 2845–2852 (2000)
 38. Bailey, C.L., Bereman, R.D., Paul Rillema, D.: Redox and spectral properties of cobalt (II) and copper(II) tetraazaannulene complexes: {H₂[Me₄(RBzo)₂][4]tetraeneN₄] (R=H, CO,CH). evidence for superoxide ligation and reduction. *Inorg. Chem.* **25**, 3149 (1986)
 39. Kulkarni, N.V., Hegde, G.S., Kurdekar, G.S., Budagumpi, S., Sathisha, M.P., Revankar, V.K.: Spectroscopy, electrochemistry, and structure of 3D-transition metal complexes of thiosemicarbazones with quinoline core: evaluation of antimicrobial property. *Spectroscopy Letters* **43**, 1–12 (2010)