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Coordination chemistry of a new tetranucleating 26-membered polyaza macropolycyclic ligand and a novel phenolate/phthalazine-bridged copper(II) and zinc(II) complexes

M.P. Sathisha^a, Naveen V. Kulkarni^a, Srinivasa Budagumpi^a, B.N. Kirasur^b and Vidyanand K. Revankar^{a*}

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The novel phenol and phthalazine-based symmetric compartmental 26-membered polyaza macropolycyclic ligand LH₂, was synthesised, incorporating 2,6-diformyl-*p*-cresol and 1,4-dihydrazinophthalazine via 1:1 condensation. Its coordination behaviour with Cu^{II} and Zn^{II} ions was investigated. The tetranuclear complexes [M₄μ(Cl₂)(L)Cl₄]·2H₂O exhibited a remarkably high stability, suggesting that, along with the large number of nitrogen donors available for metal binding, deprotonated phenolic functions were also involved in binding the metal ion. Incorporation of the bridging units into the macrocyclic cavity influenced electronic communications between the metal ions.

Keywords: macrocyclic; polyaza; symmetric compartmental; antiferromagnetism

1. Introduction

Schiff base macrocycles have fetched a massive significance in macrocyclic and supramolecular chemistry. The functionally substituted Schiff bases bearing additional donor groups represent the most important class of heteropolydentate ligands capable of forming mono-, bi- and polynuclear complexes with transition and non-transition metals (1, 2). Interest in exploring metal ion complexes with macrocyclic ligands has been continuously increasing owing to the recognition of the role played by these structures in metalloproteins (3–5).

In 1970, Travis and Busch (6) reported a macrocyclic ligand which circumscribes completely two metal ions. Following this, in 1971, Rosen (7) have reported a second example in which two nickel atoms are encompassed by a single macrocycle, formed by a metal template-promoted reaction of acetone with 1,4-dihydrazinophthalazine (dhph). On the other hand, Pilkington and Robson (8) have initiated the area of bimetallic Schiff base macrocycles in which two metal centres are bridged by the phenoxide group. Since then, many others have been involved in the synthesis of large macrocycles. McCrea et al. (4) have reported macrocyclic systems which can hold the four metal centres in close proximity. Similarly, Mercier et al. (9), Lozan et al. (10), Akine et al. (11), Brooker et al. (12), Nanda et al. (13) and Gerbeleu et al. (14) have contributed in this area by constructing various macrocycles with versatility in the number and nature of the donor atoms, cavity size and stereochemical arrangements. Recently, a review by Meyer's group (15) has given a

brief note on macrocyclic Schiff base ligand systems (Figures 1–3).

Brooker et al. (12) have reported many 2 + 2 macrocycles which provide a double pyridazine bridge between the two copper(II) ions. The diazine bridge between the coordinated copper(II) centres has been shown to mediate significant antiferromagnetic exchange. Tandon et al. (16, 17) have reported a number of dicopper complexes of analogous phenolate macrocycles with different thioether linkages.

So, for the last two decades, considerable efforts have been made for developing metal-free methods for furnishing macrocycles starting from various dicarbonyl compounds and diamines in addition to standard metal-templated protocols. Expansion of our fundamental understanding of the macrocyclisation processes allows diversity of ligands to be synthesised as artificial cationic, anionic and neutral guest receptors (5, 15). The macrocyclic ligand systems capable of accommodating two or more metal centres in close proximity and in predetermined spatial arrangements are an active area of research. In particular, polynuclear complexes, in which cation–cation interactions can be tuned via variation of functionality in the ligand structure, find applications as models for important metallobiosites (18–21), as catalysts (22), and in the investigation of the mutual influence of proximal metal centres on the electronic, magnetic and redox properties of such systems (23, 24).

Brooker et al. (12) reported a Schiff base macrocycle derived from 3,6-diformylpyridazine and 1,3-diaminopropane with copper(II) which resulted in 2 + 2 macrocycle.

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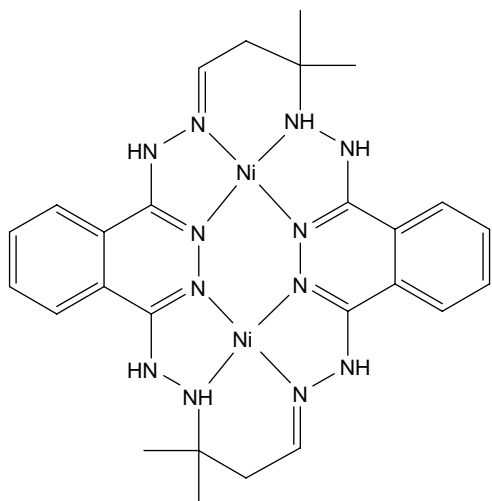


Figure 1. Dinickel complex prepared by Rosen.

In all cases, the (2 + 2) macrocycle provides a double pyridazine bridge between the two copper(II) ions. Magnetic studies show that the double pyridazine bridge mediates strong antiferromagnetic exchange between the copper(II) ions in all of these complexes. The macrocyclic nickel complex of dhph, which is reported by Rosen (7), is also consistent with the expected antiferromagnetism. Electrochemical studies of pyridazine or phenol-based macrocycles reveal that reduction of the dicopper(II) complexes occurs in two one-electron steps, via stable mixed valent intermediates in marked contrast to phthalazine-based macrocycles, where ligand redox behaviour is dominated. A tetranucleating macrocyclic ligand derived from [2 + 2] Schiff base condensation of 2,6-diformyl-4-methylphenol and 1,5-diaminopentan-3-ol by McCrea et al. (4) accounts for the transmission of geometric constraints from one metal ion to the next through the ligand framework, providing a basis for cooperative control of redox processes.

Our interest in macrocyclic complexes has led us to explore reliable routes for the synthesis of a polynucleating macrocyclic ligand which contain donor groups having special affinity for metal ions, phthalazine and phenol. Our approach to prepare a polynucleating macrocyclic ligand has been based on the 1:1 condensation synthesis. In this

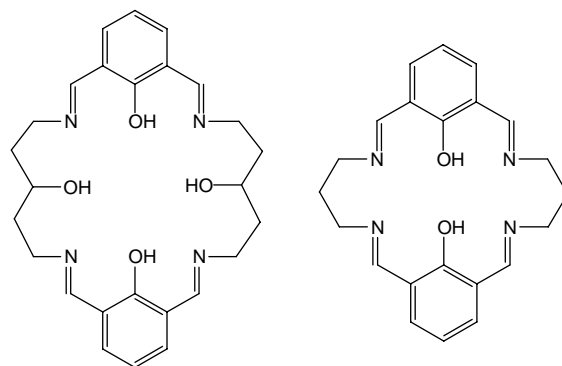


Figure 2. Robson-type macrocyclic ligand systems synthesised by Brooker and McKee.

respect, great attention has been focused on the use of phenol and phthalazine-based compartmental macrocycles (25, 26), since they can provide different types of bridging environment holding two metal ions bound and situated in close proximity through the bridging phenolic oxygen or bridging phthalazine, or both.

We were interested in discovering the nature of local coordination behaviour, bridging, whether anionic exogenous bridging will be across the atom (phenolic oxygen) bridge or atom bond (phthalazine) bridge. We report herein the coordinative properties of a tetranucleating macrocyclic ligand towards a series of Cu^{II} and Zn^{II} metal ions which are characterised by different spectrochemical and analytical methods.

2. Experimental

The reagents and solvents employed were used as received without further purification. The precursors 2,6-diformyl-*p*-cresol (27) and dhph (28) were prepared following the literature procedures. Elemental analyses (C, H, N) were determined with a thermo quest elemental analyser at STIC Cochin University of Science and Technology, Cochin. The percentage of copper and zinc were estimated after decomposition with a mixture of HCl and HClO_4 by gravimetric and EDTA titration methods, respectively. The FT-IR spectra were recorded from KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$ on a Nicolet 170 SX FT-IR spectrometer.

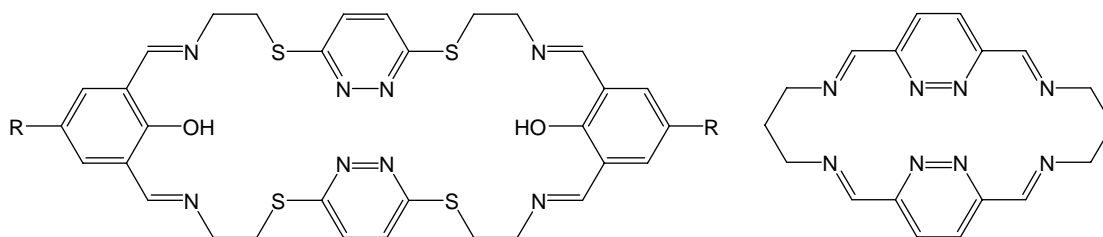


Figure 3. Macrocyclic ligands constructed by Thompson and Brooker.

The low-frequency region, far IR from 400 to 200 cm^{-1} , was recorded in polyethylene discs on a Bruker Vector 22 spectrometer. The ^1H NMR spectra of the ligand and its zinc(II) complex were recorded in DMSO- d_6 on a Bruker 300 MHz spectrometer using TMS as an internal standard. Magnetic susceptibility of complexes was measured at room temperature on a Faraday balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. Electronic spectra were recorded using a Varian Cary 50 Bio UV-vis spectrophotometer in DMSO. The EPR spectra of copper(II) complexes were recorded at room temperature on a Varian E-4 X-band spectrometer using TCNE as the g -marker. Conductivity measurements were made on 10^{-3}M solutions of complexes in DMSO using an ELICOCM82 conductivity bridge provided with a cell whose cell constant is 0.51. Thermogravimetric analyses of the metal complexes were carried out in nitrogen atmosphere on a Rigaku Thermoflex instrument using a limiting temperature of 800°C and a heating rate of 10°C/min. The FAB mass spectra were recorded on a Jeol EX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas at Central Drug Research Institute, Lucknow. The cyclic voltammetric experiments were carried out with a three-electrode apparatus using a CHI1110A electrochemical analyser (CH Instruments, Inc. Austin, TX USA). Cyclic voltammetric data were recorded using a glassy carbon working electrode (0.082 cm^2), a platinum counter electrode and an Ag/Ag^+ reference electrode. Glassy carbon electrode surfaces were polished with 0.05 mm alumina, rinsed in water and air-dried immediately before use. The electrochemical experiments were carried out and the positions of the waves were compared to the potential of the ferrocene/ferrocenium couple. The DMSO solution

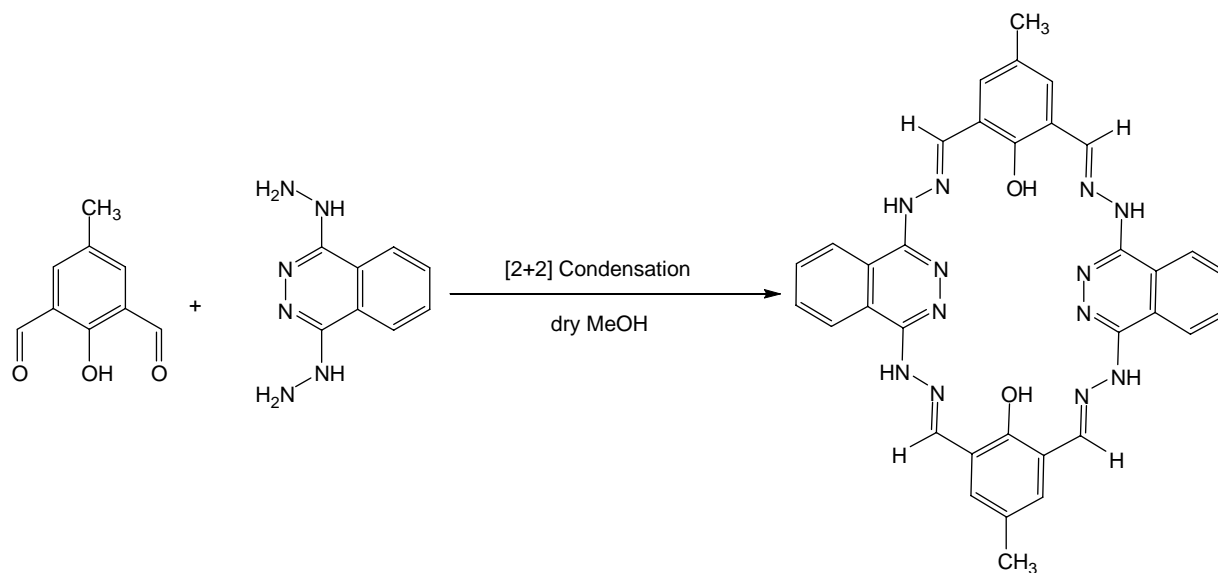
(containing 0.1 M tetrabutylammonium perchlorate, as the supporting electrolyte, 10^{-3} molar concentration of the ligand and each of the complexes) was placed in a single-compartment electrochemical cell and degassed by bubbling with $\text{N}_2(\text{g})$. A N_2 atmosphere was continuously maintained while the experiments were in progress.

2.1 Synthesis of a tetranucleating ligand, LH_2

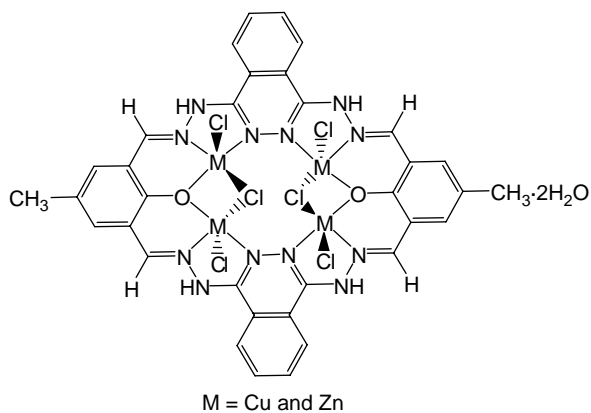
To a dry deaerated methanolic (80 ml) solution of dhph (5.00 g, 0.025 mol) was added dropwise a 2,6-diformyl- p -cresol (4.32 g, 0.025 mol) in methanol (50 ml) over a period of 25–30 min with constant stirring at room temperature. The reaction mixture shows a dark-brownish coloration and solid starts separating immediately as the dropwise addition commenced. The mixture was refluxed for 1 h and the separated brownish solid is filtered off, washed with dry methanol and dried. Yield: 80%. Mp: 181–183°C (dec). Elemental analysis: Calcd (found) for $\text{C}_{33}\text{H}_{26}\text{N}_{12}\text{O}_2$: C, 63.66 (63.32); H, 4.18 (4.01); N, 27.00 (26.48); O, 5.14 (4.85). FT-IR (KBr) cm^{-1} : 3408 (br s) (H-bonded phenolic OH stretching), 3230 (br m) ν (NH) (secondary amine), 1650 (vs) ν (C=N) (open-chain azomethine), 1610–1620 (m) (NH deformation), 1510 (m) (phthalazine ring). ^1H NMR (300 MHz, DMSO) δ : 11.03 (s, 4H, phthalazine N–H (D_2O exchangeable)), 9.85 (s, 2H, phenolic O–H (D_2O exchangeable)), 8.94 (s, 4H, formyl C–H), 7.73–7.96 (m, 12H, Ar–H), 2.27 (s, 6H, methyl protons of p -cresol (Scheme 1)).

2.2 Synthesis of $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$

The CuCl_2 (0.002 mol, 0.0341 g) in dry deaerated methanol was added to the ligand (0.001 mol, 0.031 g) in



Scheme 1. Synthesis of the tetranucleating macrocyclic ligand.



Scheme 2. Proposed structures for tetranuclear macrocyclic complexes.

50 ml of dry deaerated boiling methanol. The mixture was cooled and then stirred at room temperature for 2 h, when the solid complex precipitates, then the separated solid was filtered off, washed with dry methanol followed by anhydrous ether and dried *in vacuo*. Yield: 85%. Mp: 384–386°C (dec). Elemental analysis: Calcd (found) for $[\text{Cu}_4(\text{C}_{33}\text{H}_{24}\text{N}_{12}\text{O}_2)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$: C, 35.29 (35.15); H, 2.49 (2.35); N, 14.97 (14.82); O, 5.70 (5.64); Cu, 22.65 (22.56); Cl, 18.95 (18.87). FT-IR (KBr) cm^{-1} : 3425 (br s) ν (OH) (lattice water), 3218 (br m) ν (NH) (secondary amine), 1620 (vs) ν (C=N) (coordinated azomethine). Molar conductance: 22 $\text{S cm}^2 \text{mol}^{-1}$.

2.3 Synthesis of $[\text{Zn}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$

The same procedure as in the case of $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ is used with ZnCl_2 (0.002 mol, 0.0271 g) and LH_2 (0.001 mol, 0.031 g). Yield: 75%. Mp: 360–364°C (dec). Elemental analysis: Calcd (found) for $[\text{Zn}_4(\text{C}_{33}\text{H}_{24}\text{N}_{12}\text{O}_2)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$: C, 35.10 (35.02); H, 2.48 (2.37); N, 14.89 (14.78); O, 5.67 (5.59); Zn, 23.18 (23.09); Cl, 18.85 (18.78). FT-IR (KBr) cm^{-1} : 3403 (br s) ν (OH) (lattice water), 3216 (br m) ν (NH) (secondary amine), 1616 (vs) ν (C=N) (coordinated azomethine). ^1H NMR (DMSO) δ : 11.06 (s, 4H, phthalazine N–H (D_2O exchangeable)), 9.16 (s, 4H, formyl C–H), 7.48–7.59 (m, 12H, Ar–H), 2.27 (s, 6H, methyl protons of *p*-cresol). Molar conductance: 18 $\text{S cm}^2 \text{mol}^{-1}$ (Scheme 2).

3. Results and discussion

The direct 1:1 Schiff base condensation of 1 molar equivalent of 2,6-diformyl-*p*-cresol with 1 molar equivalent of dhph in dry MeOH affords the ligand LH_2 in 80% yield as demonstrated by ^1H NMR, FT-IR and FAB mass spectroscopy. Copper and zinc complexes of the macrocyclic ligand were synthesised in deaerated methanol and both the complexes were precipitated out in room temperature.

The ligand precursor dhph is a fairly air stable compound as a solid, but is extremely air sensitive in solution. Exposure of a solution of dhph to oxygen results in a rapid change in the colour of the solution from the yellowish orange to cherry red, followed by a slower bleaching of the red colour to a pale yellow. The ligand system with the dhph precursor when exposed to air undergoes oxidation, which is attributed to the conversion of dhph to the diimine form, a process that involves the phthalazine ring and the two proximal nitrogens from the hydrazine substituents. Therefore, all experimental manipulations were carried out in nitrogen atmosphere using dry solvents.

The complexes are sparingly soluble in methanol and ethanol, and completely soluble in DMF, DMSO and MeCN. The attempts made to grow the crystals for the X-ray diffraction studies by various methods, such as slow cooling, slow evaporation and liquid diffusion, were unsuccessful. The conductance data (18–49 $\text{S cm}^2 \text{mol}^{-1}$) are also consistent with the formulated structures (Scheme 2), and thus complexes are non-electrolytes.

3.1 Infrared spectral studies

The ligand shows very characteristic peaks corresponding to a phenolic OH stretching band around 3408 cm^{-1} , a secondary amine stretching band at 3230 cm^{-1} and a intense sharp band at 1650 cm^{-1} due to ν (C=N) of the azomethine group. In both the complexes, the phenolic OH stretching band disappears, indicating the coordination of oxygen via deprotonation. A new broad band that appeared around 3425 cm^{-1} is due to lattice held water molecules, which is confirmed by thermal decomposition studies. Secondary amine, ν (N–H), shows a slight shift in its position due to the coordination of an adjacent azomethine nitrogen. Further, the ν (C=N) frequency shows a marked decrease in its position ($30\text{--}40 \text{ cm}^{-1}$) as compared to its position in the ligand indicating its coordination. The low frequency bands in complexes in the region 500–470 and 400–325 cm^{-1} are assigned to ν (M–N) and ν (M–O), respectively. The presence of a chloro-bridge is evident from the far-IR bands in the region 280–260 cm^{-1} .

3.2 ^1H NMR spectral studies

The ligand spectrum shows two signals in the region 11.03 and 9.85 ppm (D_2O exchangeable) due to phthalazine NH and phenolic OH proton resonances. In the zinc complex, the resonance peak due to phenolic OH disappears, indicating the coordination of the oxygen atom via deprotonation. The phthalazine NH (D_2O , exchangeable) resonance peak shifts slightly downfield, ca. 11.06 ppm. The sharp singlet resonance peak in the ligand at 8.94 ppm was assigned to the azomethine proton, which shifts downfield (9.16 ppm) in the complex as it is attached to a

strongly coordinating azomethine nitrogen atom. A sharp resonance peak due to methyl protons appears at a shielding region, 2.27 ppm, which remains almost unchanged in the zinc complex.

3.3 Electronic spectral studies

The UV-vis spectra of the macrocyclic ligand exhibit the bands around the regions 260, 280, 330 and 370 nm, which have molar absorptivity in the range $1800\text{--}4200\text{ dm}^3\text{ M}^{-1}\text{ cm}^{-1}$. All the absorption peaks observed in the region 260–370 nm were assigned to intraligand, ligand $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions. The ligand band around 453 nm is assigned to the $n\text{--}\pi^*$ transition from the phenoxide to an aromatic π -system. If an electron is excited into the extended π^* chromophore, the atom from which it was removed becomes electron deficient, while the π -system of the aromatic ring acquires an extra electron. This causes a separation of charge in the molecule and is generally represented as regular resonance. Such an excited state is often called a charge transfer or an electron-transfer excited state and transition as charge-transfer transition. The absorption peaks running into the visible region with $\epsilon = 500\text{--}1000\text{ dm}^3\text{ M}^{-1}\text{ cm}^{-1}$ were assigned to the oxidised form of the precursor dhph in the ligand system. These bands almost remain in the spectra of both the complexes with slight shifts. Further, the copper complex shows additional medium intensity absorption bands in the region 485–530 nm with relatively lower molar extinction coefficients, ca. $140\text{--}220\text{ dm}^3\text{ M}^{-1}\text{ cm}^{-1}$, which are assigned to the d–d transitions (Figure 4).

3.4 Magnetic moment studies

The experimental magnetic moment data for the $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ complex is 1.35 BM. The most obvious generalisation for this low value is that the complex in which two or more copper(II) ions are bridged by a phenolic oxygen or phthalazine system shows a spin–spin interaction resulting in a weak antiferromagnetic coupling between copper(II) ions.

Ball and Blake (29) have made an attempt to put the various bridging moieties in the order of their ability to facilitate spin–spin interaction between metal (II) ions. The order observed is phthalazine > pyridazine > pyrazole > oxalate > azine. A variety of different structural and electronic factors (bond lengths and angles, ligand basicity, metal–ligand covalency, etc.) could contribute to this variation. The only trend here is to show a marked trend in the nitrogen ligands, which can establish an electron overlap between the π -MOs of the bridging system.

Further antiferromagnetic spin exchange can also be evident from the atom bridge through phenoxide. Antiferromagnetism will predominate if the bridge consists of at least two atoms with considerable π -delocalisation (30).

The observed antiferromagnetism for copper(II) complexes was in agreement with the earlier reports on pyridazine-based macrocyclic systems reported by Brooker et al. (12), Tandon et al. (16, 17) and Rosen (7). Magnetic studies show that the double pyridazine bridge mediates strong antiferromagnetic exchange between the copper(II) ions in all of these complexes.

3.5 ESR studies

The X-band (9.75 GHz, 3000 G) powder EPR spectra of the $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ complex was recorded at room temperature. The EPR signals for $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ (with $g_z = 2.13$, $g_y = 2.04$) is typical for ‘rhombic stereochemistry’. The g_z values for the copper(II) complex, being a very sensitive parameter of covalence, indicate a very low covalent character of the metal–ligand bond ($g_z < 2.3$) in the complex, as expected for nitrogen donor atoms (Figure 5).

3.6 Mass spectral studies

Mass spectral results clearly give a proof for structural assignments supplementing other spectral observations. The macrocyclic ligand shows a molecular ion peak at

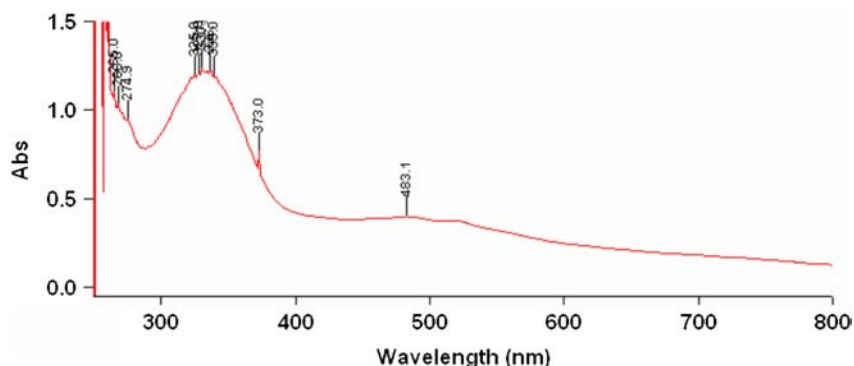


Figure 4. UV spectrum of $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ in DMSO.

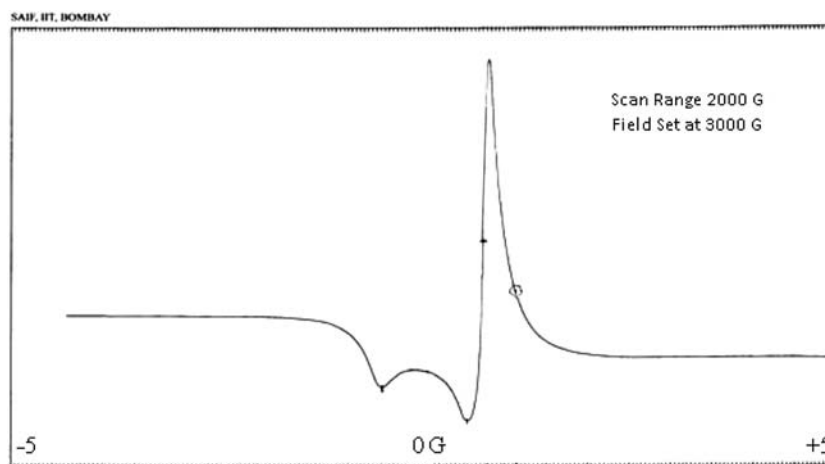


Figure 5. Powder EPR spectrum of $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ at 25°C .

620, supporting the formation of targeted macrocycles. The other key peaks are observed at 580, 386, 324 and 198 corresponding to the ligand fragmentations. FAB mass spectroscopic data for the complexes clearly suggest that tetranuclear macrocyclic complexes have formed, showing an m/z ion peak corresponding to the molecular weight of the complexes. The FAB mass spectra of the complexes show the characteristic isotope patterns corresponding to the ^{35}Cl and ^{37}Cl isotopes of chlorine. For example, the complex $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ shows the isotope pattern at 1120 and 1132 that represent the M and $M + 2$ ion peaks nearly in a 3:1 ratio. The loss of six ^{35}Cl from 1120 or six ^{37}Cl from 1132 gives the base peak at $m/z = 910$, corresponding to the loss of all the chloride ions. These experimental observations well matches with theoretical calculations and clearly indicate the formation of proposed complexes. The molecular ion peak observed in the particular case corresponds to the mass of the entire complex including bridging chloride, lattice held water

molecules. The spectra also contain peaks due to molecular cations. The spectra show some prominent peaks at 609, 596, 436, 326 and 240 corresponding to the various fragments of the complex. (The mass spectra of the ligand and copper complex are shown in Figures 8 and 9.)

3.7 Thermogravimetric analyses

Both the macrocyclic complexes, $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$ and $[\text{Zn}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$, show initial weight loss up to 235°C , which corresponds to the combined loss of lattice water molecules and chlorides. Then, a partially decomposed, rearranged, intermediate complex continues to lose weight up to 580°C . The plateau is obtained beyond 580°C , indicating the formation of the corresponding metal oxide. In all cases, the residual weight of stable metal oxides well agrees with the preliminary metal estimation studies. The weight loss from the thermal studies agrees well with theoretical calculations and supports our stereochemical assignments to metal complexes.

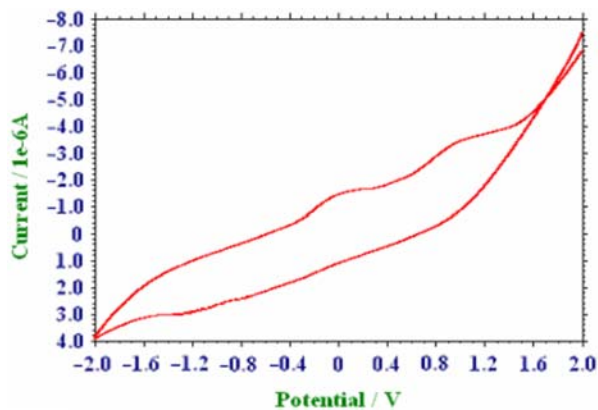


Figure 6. Cyclic voltammogram of the macrocyclic ligand.

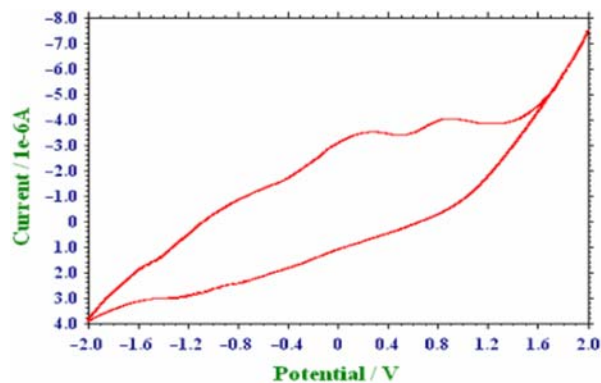


Figure 7. Cyclic voltammogram of $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$.

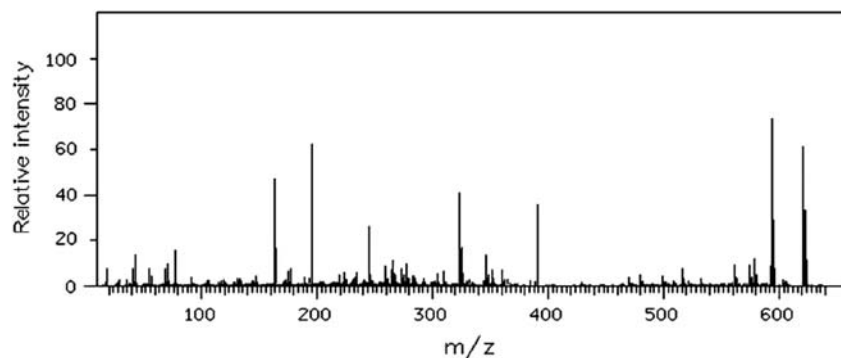


Figure 8. Mass spectrum of the macrocyclic ligand.

3.8 Cyclic voltammetric studies

Thompson et al. (31) reported the electrochemical characterisation of the hydroxyl-bridged binuclear copper (II) complex of the mono-deprotonated ligand (Figure 5). The authors state that the copper complex in DMF exhibits a quasi-reversible cyclic voltammetry wave at $E_{1/2} = 0.50$ V vs. SCE with a peak separation $\Delta E_p = 110$ mV at a 200 mV/s scan rate (glassy carbon working electrode, platinum counter electrode). From these results, they conclude that the observed process corresponds to a two-electron oxidation of the binuclear copper(II) complex to a binuclear copper(III) species.

The assignment of the observed redox process to the oxidation of Cu(II) to Cu(III) for this complex is questionable. This conclusion contradicts extensive work by Bossu et al. (32) and Levason and Spicer (33), which indicates that hard anionic donor groups are necessary to produce low potentials for the Cu(III)/Cu(II) couple. The relatively soft environment of the Cu(II) ions present in this complex is unlikely to allow oxidation to the Cu(III) state at the low potentials observed. In addition, because of

the presence of readily oxidisable functionalities within the ligand system, it is thought that a ligand-based redox process may be responsible for the observed electrochemical results.

In the following discussion, evidence that the redox behaviour of the tetranuclear copper(II) complex is localised on the Schiff base ligand is presented.

The electrochemical behaviour of the macrocyclic ligand, copper(II) and zinc(II) complexes in the potential range studied shows a similar type of responses. CV scans for the copper(II) complex in the positive direction using the Ag^+/AgCl reference electrode at a scan rate of 100 mV/s shows the evidence for two irreversible anodic waves at 190 and 810 mV corresponding to the oxidation process. The conclusion from this observation is that the redox activity for the binuclear copper complex occurs on the ligand and does not involve the copper ions. The study of the electrochemical behaviour of the zinc(II) complex of the same ligand provides additional support that the oxidation process seen for the binuclear copper(II) complex is ligand centred. Since the zinc(II) ion is redox

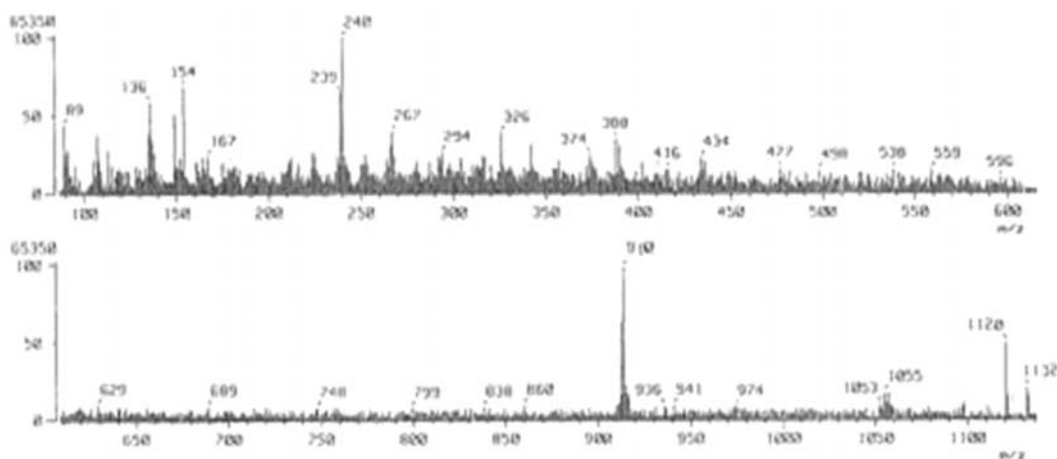
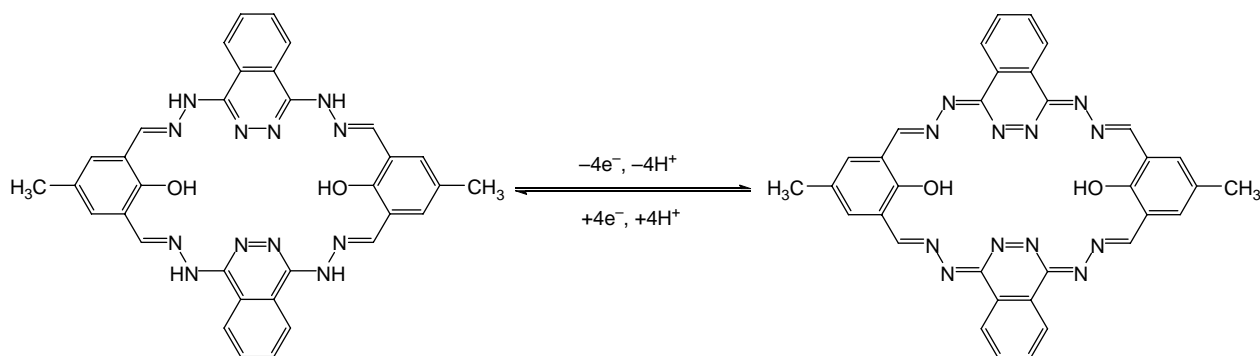


Figure 9. Mass spectrum of $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$.

inactive, any oxidations which are seen in CV scans must arise from ligand-based processes (Figures 6 and 7).



The proposed 4e-oxidation process of the macrocyclic ligand

With these proposed oxidation processes, the Schiff base macrocyclic ligand and complexes, it is possible to explain the cyclic voltammetry behaviour. The redox reaction involves a two-electron, two-proton process. In aprotic solvents, protons are not readily available for the return reduction, thereby causing the highly irreversible electrochemical behaviour observed. The electrochemical study clearly reveals that the two-electron oxidations of the binuclear copper(II) complex are ligand centred and does not produce a tetranuclear copper(III) species. The similarity observed for the two-electron oxidations of the copper complex, ligand and zinc complexes provides strong evidence for this conclusion. The oxidised species of the Schiff base macrocyclic compound appears to be the highly conjugated azine moiety. The intense coloration of the solutions under CV scans further supports the formation of this highly conjugated azine moiety (34–36). The similar type of observations were made in the past where the electrochemistry of bi- and tetranuclear Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes of a polyaza macrocycle having four diazine (N_2) bridging components was investigated (37).

4. Conclusion

The incorporation of the dhph precursor into macrocycles has resulted in a novel and rich coordination chemistry. We report here the [2 + 2] macrocyclic ligand and its copper and zinc complexes. A rich electrochemistry is a feature of these macrocycles. The macrocyclic framework leads to increased stability of the redox product over that generally observed for the acyclic complexes. Careful observations at the point and designing macrocyclic side arm wisely, one can design a shell-like architecture. A common feature of these shell-like architectures is their ability to encapsulate neutral and/or charged guests whose size, shape and chemical exteriors complement those of the host's inner surface. Their interiors can often be regarded as a new phase of matter, capable of controlling the flow of incoming

guests via electronic super exchange through bridging units and catalysing reactions of both chemical and biological

relevance. Incorporation of the bridging phthalazine and phenolate moiety into the macrocyclic framework has resulted in the marked spin exchange interaction resulting in a moderate antiferromagnetism in the copper complex $[\text{Cu}_4\mu(\text{Cl}_2)(\text{L})\text{Cl}_4]\cdot 2\text{H}_2\text{O}$. In the new phenol-based compartmental system, for the first time, the phthalazine bridge has been introduced as part of the lateral chains connecting the two *p*-cresol units to afford a 26-membered polyaza tetranucleating macropolycycle. The macrocyclic system establishes the particular binding properties of the phenol-based compartmental macrocycle combined with that of phthalazine to afford a ligand characterised by four adjacent chambers, each with a potential N_2O donor set capable of accommodating, in close proximity, four metal ions. Each compartment provides two sets of the phenoxide bridge between two sets of metal ions, which are each bound within an independent N_2O donor, across which exists an exogenous chloride bridge. Phthalazine provides an atom bond bridge between these two compartments to form tetranuclear complexes.

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