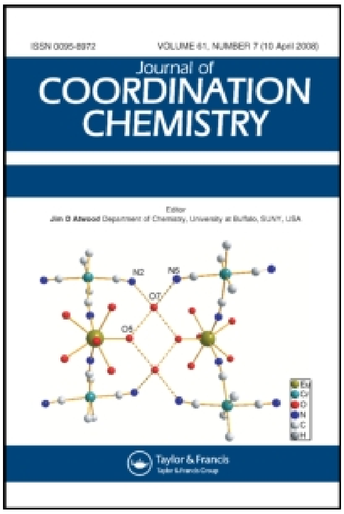

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Synthesis, spectral, magnetic, electrochemical and kinetic studies of copper(II), nickel(II) and zinc(II) complexes derived from a phenol-based unsymmetrical "end-off" ligand

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Synthesis, spectral, magnetic, electrochemical and kinetic studies of copper(II), nickel(II) and zinc(II) complexes derived from a phenol-based unsymmetrical "end-off" ligand

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A new unsymmetrical end-off, aminomethylated *N*-methylpiperazine and aminomethylated diethanolamine armed binucleating ligand, 2-[bis(2-hydroxyethyl)aminomethyl]-6-[(4-methylpiperazin-1-yl)methyl]-4-formylphenol (HL), was synthesized by following sequential aromatic Mannich reactions. Mononuclear and binuclear Cu(II), Ni(II) and Zn(II) complexes were synthesized and characterized by elemental and spectral analysis. The EPR spectrum of the mononuclear copper complex shows four hyperfine splittings and the binuclear complex shows a broad signal due to anti-ferromagnetic interaction. The room temperature magnetic moment of the mono and binuclear copper complexes are 1.72 and 2.68 BM, respectively. Variable temperature magnetic moment study of the binuclear copper(II) complex shows weak antiferromagnetic coupling ($-2J$ value, 21 cm^{-1}). The mononuclear Ni(II) complex is square planar and diamagnetic. The six-coordinate binuclear Ni(II) complex shows a magnetic moment of 3.06 BM. Electrochemical studies of the complexes reveal that all mononuclear complexes show a single irreversible one-electron reduction wave and the binuclear complexes show two irreversible one-electron reduction waves in the cathodic region. Catecholase activity of copper(II) complexes using pyrocatechol as a model substrate and the hydrolysis of 4-nitrophenylphosphate using copper(II), nickel(II) and zinc(II) complexes as catalysts showed that binuclear complexes have higher rate constants than corresponding mononuclear complexes.

Keywords: Unsymmetrical "end-off" ligands; Magnetic properties; Electrochemistry; Catalytic activity; Mono and binuclear metal complexes

1. Introduction

Organic ligands containing a variety of donor groups have potential applications in bioinorganic chemistry [1–3], magneto chemistry [4–6], redox chemistry [7, 8] and catalysis [9–12].

Although large numbers of dinuclear metalloenzymes have different coordination or geometric environments, most enzyme mimics reported so far are based on symmetric dinucleating ligands. In general, these ligands result in formation of dinuclear complexes with identical coordination and geometric environments for the two metal centers.

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There are only a limited number of unsymmetrical binuclear complexes due to practical difficulties in the synthesis of unsymmetrical ligands [13–17] and synthesis of ligands other than Schiff bases are sparse [18, 19].

One type, diaminomethylated phenols, have proven to be excellent mimics for the active site of a number of enzymes such as hemerythrin [20], methane monooxygenase [21], or ribonucleotide reductase [22] as dinuclear iron complexes. Further, a number of related dinuclear manganese complexes [23, 24] and various dinuclear copper complexes [25, 26] to mimic hemocyanin and tyrosinase activities were investigated earlier.

In this article, a new unsymmetrical diaminomethylated phenol-based end-off ligand, 2-[*bis*(2-hydroxyethyl)aminomethyl]-6-[(4-methylpiperazin-1-yl)methyl]-4-formylphenol, has been synthesized from sequential aromatic Mannich reactions. The ligand contains a highly reactive aldehyde group, which may lead to extension of the structure into a supramolecular moiety. Synthesis and electrochemical studies of such supramolecular moieties are in progress. The ligand (HL) has been used to prepare copper(II), nickel(II) and zinc(II) mononuclear and homo binuclear complexes. The spectral, electrochemical, magnetic and catalytic studies of these complexes are also discussed.

2. Experimental

2.1. *Physical measurements*

Elemental analysis of the complexes was obtained using a Haereus C, H, N rapid analyzer. ^{1}H NMR spectra were recorded using a JEOL GSX 400 MHZ NMR spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer in the range 200–1100 nm. IR spectra were recorded on a Shimadzu FT-IR 8300 series spectrophotometer as KBr disks in the range 4000 to 400 cm^{-1}. Mass spectra were obtained on a JEOL DX-303 mass spectrometer. Molar conductivity was measured by an Elico digital conductivity bridge model CM-88 using freshly prepared solution of the complex in dimethylformamide. Cyclic voltammograms were obtained on a CHI-600A electrochemical analyzer. The measurements were carried out under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode and platinum wire was used as the auxiliary electrode. A ferrocene/ferrocenium (1+) couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc$^+$) couple under the experimental condition is 470 mV. Tetra(n-butyl)ammonium perchlorate (TBAP) was used as the supporting electrolyte. Room temperature magnetic moments were measured on a PAR vibrating sample magnetometer model-155. Variable temperature magnetic moments were measured on an EG & G Princeton Applied Research VSM model 4500. X-band ESR spectra were recorded at 25°C on a Varian EPR-E 112 spectrometer using diphenylpicrylhydrazine (DPPH) as the reference. The atomic absorption spectral data were recorded using a Varian Spectra AA-200 model atomic absorption spectrophotometer. The catalytic oxidation of catechol to *o*-quinone by the copper complexes and the hydrolysis of 4-nitrophenylphosphate by copper, nickel and zinc complexes were studied in a 10^{-3} M DMF solution. The reaction was followed spectrophotometrically by choosing the strongest absorbance of *o*-quinone at 390 nm and monitoring the increase in the absorbance; hydrolysis of *p*-nitrophenyl phosphate was monitored by following the UV absorbance change at 420 nm (assigned to the 4-nitrophenolate anion) as a function of time. A plot of $\log(A\alpha/A\alpha - A_t)$ *versus* time was made for each complex and the rate constant for the catalytic oxidation or hydrolysis of 4-nitrophenyl phosphate was calculated.

2.2. *Materials and safety note*

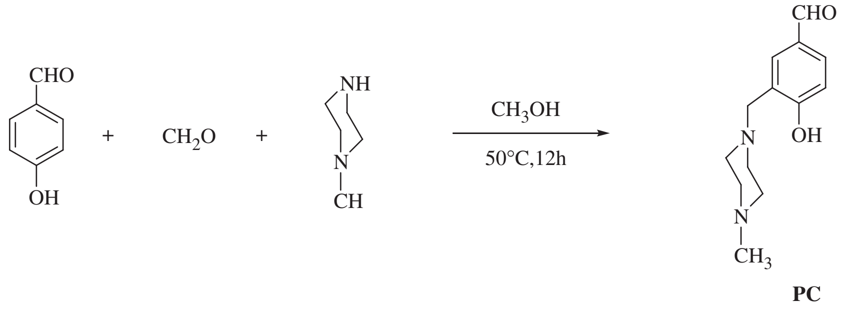
Formaldehyde solution, *N*-methylpiperazine, diethanolamine and *p*-hydroxybenzaldehyde were purchased from Qualigens and used as received. Methanol, acetonitrile and dimethylformamide were purchased from Qualigens and distilled before use. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallized from hot methanol. (**Caution!** TBAP is potentially explosive; hence, care should be taken in handling the compound.) All other chemicals and solvents were of analytical grade and used as received.

2.3. *Synthesis of 2-[(4-methylpiperazin-1-yl)methyl]-4-formyl phenol (Precursor Compound, PC)*

A mixture of 4-formylphenol (6.11 g, 0.05 mol), *N*-methylpiperazine (5.54 mL, 0.05 mol) and formaldehyde solution (37%) (3.77 mL, 0.05 mol) in methanol (50 mL) were reacted at 50°C for 12 h. One 3 mL portion of formaldehyde was added after 6 h (scheme 1). Methanol was evaporated under vacuum and the resulting compound was extracted with chloroform. Then the crude compound was purified by column chromatography using chloroform–methanol mixture (98 : 2) as eluent. A colorless compound was obtained. Yield: 6.21 g (53%), m. pt.: 66°C. Mass (EI) *m*/*z*: 235.73. Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.73; H, 7.62; N, 12.11%. ^{1}H NMR (δ ppm in $CDCl_3$) ~2.29 (s, 3H), ~2.60 (br s, 8H), ~3.77 (s, 2H), 6.87–7.75 (m, 3H), ~9.77 (s, 1H).

2.4. *Synthesis of 2-[bis(2-hydroxyethyl)aminomethyl]-6-[(4-methylpiperazin-1-yl) methyl]-4-formylphenol (Ligand, HL)*

Ligand (HL) was synthesized by taking PC (4.69 g, 0.02 mol) in methanol (100 mL) mixed with diethanolamine (1.92 mL, 0.02 mol) and formaldehyde solution (37%)



Scheme 1. Synthesis of precursor compound (PC).

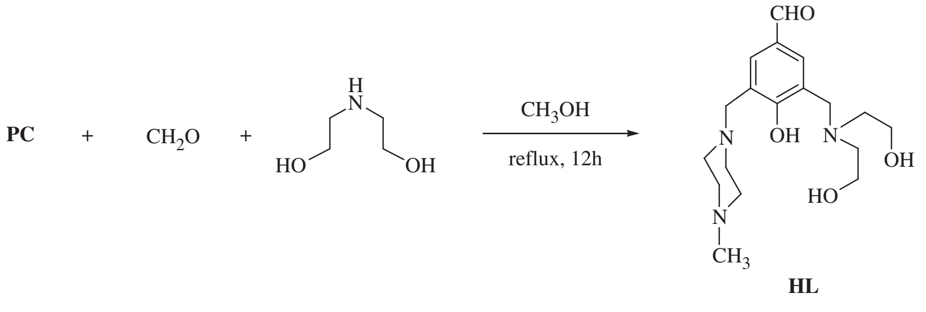
(1.51 mL, 0.02 mol), and the solution was refluxed for 12 h. One 2 mL portion of formaldehyde was added at 6 h. Methanol was evaporated under vacuum and the resulting oil was extracted with chloroform. The crude compound was purified by column chromatography using chloroform-methanol mixture (96 : 4) as eluent (scheme 2). A light brown oily compound was obtained. Yield: 4.22 g (60%). Mass (EI) *m*/*z*: 351.65. Anal. Calcd for $C_{18}H_{29}N_3O_4$: C, 61.52; H, 8.32; N, 11.96. Found: C, 61.54; H, 8.37; N, 11.89%. Selected IR data (KBr disc, ν/cm^{-1}): 3200–3500, 2941, 2810, 1676. ^{1}H NMR (δ ppm in $CDCl_3$) ~2.17 (s, 2H), ~2.30 (s, 3H), ~2.58 (m, 12H), ~3.75 (m, 8H), 6.91 and 7.75 (s, 2H), ~9.76 (s, 1H). UV-Vis [λ_{max}(nm) (ε, $M^{-1}\,cm^{-1}$)] in MeOH: 282 (22 300).

2.5. *Synthesis of mono and binuclear complexes*

2.5.1. Synthesis of mononuclear complexes of HL

2.5.1.1. *Synthesis of [CuL(OAc)]* $\cdot H_2O$. To a 40 mL methanol solution of the ligand (HL) (1.05 g, 0.003 mol) was added $Cu(OAc)_2 \cdot H_2O$ (0.60 g, 0.003 mol) dissolved in 20 mL of methanol and refluxed for 12 h. The solution was filtered when hot and allowed to stand at room temperature. After slow evaporation of the solvent at 25°C, a dark green compound was obtained. The compound was recrystallized from acetonitrile. Yield: 0.96 g (65%). Anal. Calcd for $[C_{20}H_{31}N_3O_6Cu] \cdot H_2O$: C, 48.92; H, 6.77; N, 8.56; Cu, 12.94. Found: C, 48.91; H, 6.85; N, 8.52; Cu, 12.98%. Selected IR data (KBr disc, ν/cm^{-1}): 3300–3600, 2911, 2848, 1450. UV-Vis [λ_{max}(nm) (ε, $M^{-1}\,cm^{-1}$)] in MeOH: 592 (155), 350 (15 400), 283 (23 100), $g_{\parallel} = 2.25$, $g_{\perp} = 2.04$ and $A_{\parallel} = 182$. $\mu_{eff} = 1.72$ BM.

2.5.1.2. *Synthesis of [NiL(OAc)]* $\cdot H_2O$. The Ni(II) complex was prepared by following the above procedure using the ligand (HL) (1.05 g, 0.003 mol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.75 g, 0.003 mol). A brown compound was obtained on recrystallization from acetonitrile. Yield: 1.01 g (69%). Anal. Calcd for $[C_{20}H_{31}N_3O_6Ni] \cdot H_2O$: C, 49.41; H, 6.84; N, 8.64; Cu, 12.07. Found: C, 49.47; H, 6.78; N, 8.69; Cu, 12.05%. Selected IR data (KBr disc, ν/cm^{-1}): 3300–3600, 2925, 2843, 1452. UV-Vis [λ_{max}(nm) (ε, $M^{-1}\,cm^{-1}$)] in MeOH: 568 (132), 354 (15 600), 286 (22 800).



Scheme 2. Synthesis of unsymmetrical end-off ligand (HL).

2.5.1.3. *Synthesis of [ZnL(OAc)(H$_2$O)$_2$].* The Zn(II) complex was prepared by following the above procedure using HL (1.05 g, 0.003 mol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.66 g, 0.003 mol). A colorless compound was obtained on recrystallization from acetonitrile. Yield: 0.93 g (61%). Anal. Calcd for $[C_{20}H_{31}N_3O_6Zn(H_2O)_2]$: C, 47.02; H, 6.90; N, 8.22; Zn, 12.80. Found: C, 47.08; H, 6.82; N, 8.14; Zn, 12.83%. Selected IR data (KBr disc, ν/cm^{-1}): 3300–3600, 2928, 2842, 1453. ^{1}H NMR (δ ppm in $CDCl_3$) ~2.02 (s, 3H), 2.23–2.66 (m, 21H), 3.80–3.91 (m, 8H), 7.57–7.72 (m, 2H), ~9.80 (s, 1H). UV-Vis [λ_{max}(nm) (ε, M^{-1} cm^{-1})] in MeOH: 285 (22 100).

2.5.2. Synthesis of binuclear complexes of HL

2.5.2.1. *Synthesis of [Cu$_2$L(OAc)(H$_2$O)](ClO$_4$)$_2$.* A solution of HL (0.70 g, 0.002 mol) in MeOH (40 mL) was added to $Cu(OAc)_2 \cdot H_2O$ (0.80 g, 0.004 mol) in MeOH (20 mL) and refluxed for 23 h. The mixture was then reacted with two equivalents of $NaClO_4$ dissolved in 10 mL of methanol and further refluxed for an hour. A dark green precipitate was collected on evaporation of the resulting solution to half the volume and then allowing to cool by standing at room temperature (25°C). A dark green colored compound was obtained on recrystallization from acetonitrile. Yield: 1.15 g (76%). FAB mass (m/z): 752. Anal. Calcd data for $[C_{20}H_{31}N_3O_6Cu_2(H_2O)](ClO_4)_2$: C, 31.88; H, 4.41; N, 5.58; Cu, 16.87. Found: C, 31.85; H, 4.49; N, 5.67; Cu, 16.75%. Selected IR data (KBr disc, ν/cm^{-1}): 3300–3600, 2924, 2848, 1603, 1455, 1102, 650. Conductance (Λ_m S^{-1} cm^2 mol^{-1}) in DMF 156. UV-Vis [λ_{max}(nm) (ε, M^{-1} cm^{-1})] in MeOH: 666 (392), 355 (15 200), 284 (24 300). $g = 2.11$. $\mu_{eff} = 2.68$ BM.

2.5.2.2. *Synthesis of [Ni$_2$L(OAc)(H$_2$O)$_3$](ClO$_4$)$_2$.* The Ni(II) complex was prepared by following the above procedure by using HL (0.70 g, 0.002 mol) and $Ni(OAc)_2 \cdot 4H_2O$ (1.00 g, 0.004 mol). A brown compound was obtained on recrystallization from acetonitrile. Yield: 1.14 g (73%). Anal. Calcd data for $[C_{20}H_{31}N_3O_6Ni_2(H_2O)_3](ClO_4)_2$: C, 30.80; H, 4.78; N, 5.39; Ni, 15.05. Found: C, 30.74; H, 4.84; N, 5.32; Ni, 15.11%. Selected IR data (KBr disc, ν/cm^{-1}): 3300–3600, 2928, 2850, 1606, 1452, 1100, 651. Conductance (Λ_m S^{-1} cm^2 mol^{-1}) in DMF 161. UV-Vis [λ_{max}(nm) (ε, M^{-1} cm^{-1})] in MeOH: 990 (112), 790 (130), 628 (265), 359 (15 800), 287 (24 200).

2.5.2.3. *Synthesis of [Zn$_2$L(OAc)(H$_2$O)$_3$](ClO$_4$)$_2$.* The Zn(II) complex was prepared by following the above procedure using HL (0.70 g, 0.002 mol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.88 g, 0.004 mol). A colorless compound was obtained on recrystallization from acetonitrile. Yield: 1.09 g (69%). FAB mass (m/z): 791. Anal. Calcd for $[C_{20}H_{31}N_3O_6Zn_2(H_2O)_3](ClO_4)_2$: C, 30.28; H, 4.70; N, 5.30; Zn, 16.49. Found: C, 30.35; H, 4.64; N, 5.24; Zn, 16.52%. Selected IR data (KBr disc, ν/cm^{-1}): 3300–3600, 2925, 2814, 1605, 1460, 1100, 652. ^{1}H NMR (δ ppm in $CDCl_3$) ~2.03 (s, 3H), 2.23–2.67 (m, 23H), 3.80–3.91 (m, 8H), 7.57–7.72 (m, 2H), ~9.80 (s, 1H). Conductance (Λ_m S^{-1} cm^2 mol^{-1}) in DMF 165. UV-Vis [λ_{max}(nm) (ε, M^{-1} cm^{-1})] in MeOH: 285 (22 900).

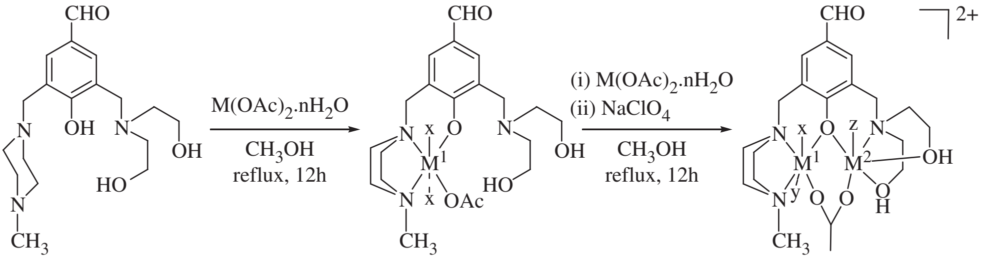
3. Results and discussion

A new unsymmetrical end-off type ligand having two different aminomethylated side arms has been synthesized by sequential aromatic Mannich reactions (schemes 1 and 2) and characterized. The mononuclear and homo binuclear Cu(II), Ni(II) and Zn(II) complexes of the ligand were prepared as shown in scheme 3. Their spectral, magnetic, electrochemical and catalytic behaviors are discussed.

3.1. *Spectral studies*

The IR spectrum of the ligand shows a broad band at 3200–3500 cm^{-1} characteristic of phenolic OH and aliphatic OH stretching frequencies. The sharp band around 1676 cm^{-1} for HL shows the aromatic carbonyl in the ligand and it remains unchanged in all the complexes, indicating that the carbonyl is not involved in complex formation. The band around 3300–3600 in all the complexes is due to alcoholic OH and water. The strong $\nu(CO_2)$ bands at 1450 cm^{-1} in mononuclear complexes indicates the presence of acetate. The binuclear complexes show the antisymmetric and symmetric $\nu(CO_2)$ vibrations of the acetate group at 1600–1610 and 1450–1460 cm^{-1}, respectively. A $\Delta\nu$ value $[\Delta\nu = \nu_{as}(CO_2) - \nu_s(CO_2)]$ smaller than 200 cm^{-1} is typical of bridging carboxylate [27]. The presence of uncoordinated perchlorate anions in all the binuclear complexes are inferred from a single broad band around 1100 cm^{-1} (ν_3-antisymmetric stretching), not split, and a band around 650 cm^{-1} (ν_4-antisymmetric bending). The band around 930 cm^{-1} (ν_2-symmetric stretching) due to coordinated perchlorate is not observed, clearly indicating that perchlorate is not coordinated in the complexes [28].

The electronic spectra of the mono and binuclear Cu(II) complexes and the mononuclear Ni(II) complex exhibit three main transitions. The moderately intense peak in the range 280–290 nm is probably due to intra-ligand charge transfer [29]. A peak or shoulder in the range 350–360 nm is due to phenolato to copper(II) charge transfer [30]. The mononuclear Cu(II) complex shows a λ_{max} at 592 nm due to the d-d



Complexes	M	n	x
1	Cu	1	-
2	Ni	4	-
3	Zn	2	H_2O

Complexes	M^1	M^2	x	y	z
4	Cu	Cu	H_2O	-	-
5	Ni	Ni	H_2O	H_2O	H_2O
6	Zn	Zn	H_2O	H_2O	H_2O

Scheme 3. Synthesis of unsymmetrical end-off complexes.

transition which is characteristic of square planar geometry, and the d-d transition for the binuclear Cu(II) complex at 666 nm is indicative of distorted square-pyramidal geometry [31, 32]. The mononuclear Ni(II) complex shows a single weak d-d band at 568 nm due to an $^1A_{1g} \rightarrow {}^1A_{2g}$ transition for square planar geometry [32]. The binuclear Ni(II) complex shows three d-d transitions at 990 nm, 790 nm and 628 nm assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, characteristic of octahedral Ni^{2+} [32, 33]. The mono and binuclear Zn(II) complexes display only ligand centered, charge-transfer transitions in the UV region [34].

3.2. *ESR spectra*

The solid state ESR spectra of the copper(II) complexes were recorded in the X-band region at room temperature. The ESR spectra of $[CuL(OAc)] \cdot H_2O$ and $[Cu_2L(OAc)(H_2O)](ClO_4)_2$ are shown in figure 1. The mononuclear copper(II) complex shows four lines [35] with nuclear hyperfine spin 3/2 due to hyperfine splitting. The observed $g_{\|}$ value is 2.25, $g_{\perp} = 2.04$ and $A_{\|}$ is 182. A broad [36] spectrum with no hyperfine splitting for dicopper complex with $g = 2.1$ indicates the presence of an antiferromagnetic interaction between copper ions. Owing to the favorable relative orientation of the magnetic orbitals due to phenoxide bridge and in spite of the Cu-Cu separation, an antiferromagnetic interaction is observed.

3.3. *Magnetic studies*

The magnetic moment values of mono and binuclear complexes were calculated at room temperature. The magnetic moment value for $[CuL(OAc)] \cdot H_2O$ is 1.72 BM, very close to the spin only value (1.73 BM) expected for complexes having one copper(II) ion with a single unpaired electron in an essentially $d_{x^2-y^2}$ orbital. The values of the magnetic moments observed at room temperature for $[Cu_2L(OAc)(H_2O)](ClO_4)_2$ is 2.68 BM, confirming the presence of anti-ferromagnetic interaction between the

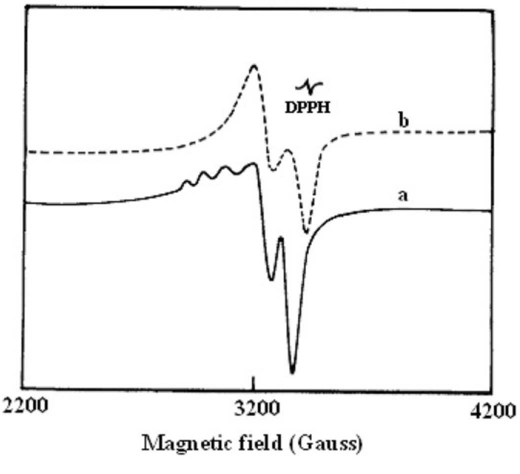


Figure 1. ESR spectra of (a) $[CuL(OAc)] \cdot H_2O$ and (b) $[Cu_2L(OAc)(H_2O)](ClO_4)_2$.

copper(II) ions. To evaluate the singlet–triplet energy separation ($-2J$), variable-temperature magnetic study of the binuclear copper complex was carried out from 77–300 K and the experimental magnetic susceptibility values were fitted to the modified Bleany-Bowers equation [37].

$$\chi_m = \{Ng^2\beta^2/3kT\}[3 + \exp(-2J/kT)]^{-1}(1 - P) + (0.45P/T) + N_\alpha$$

where χ_m is the paramagnetic susceptibility per metal atom after correction for diamagnetism, N is Avogadro's number, g is the average gyromagnetic ratio and P is the fraction of monomeric copper(II) impurities, $-2J$ is the singlet–triplet energy separation, N_α is the temperature independent fraction, usually assumed to be 120×10^{-6} cgs units for copper(II) compounds. The temperature dependence of the magnetic properties is shown in figure 2. The value of the exchange integral $-2J$ for the binuclear copper complex is $21\ \mathrm{cm}^{-1}$, indicative of weak antiferromagnetic coupling between the copper(II) ions. Poor exchange interaction is generally observed in unsymmetrical binuclear copper(II) complexes due to different geometries or different coordination environments around the coppers [38], resulting in larger dihedral angle between the copper magnetic orbitals [39]. In accord with these results, the observed coupling constants are low.

A significantly smaller $-2J$ value is observed for the unsymmetrical HL than for the complex of the symmetrical 2,6-*bis*(4-methyl piperazin-1-yl-methyl)-4-formyl phenol published in our earlier report [40]. There is a change of one aminomethylated diethanolamine side arm in the unsymmetrical ligand HL instead of one of the two aminomethylated piperazinylmethyl side arms in the symmetrical ligand. In the complex with the unsymmetrical ligand, the flexibility of diethanolamine side arm is larger than the piperazinyl side arm in the symmetrical ligand. The larger flexibility of the side arms in the unsymmetrical ligand leads to low $-2J$ value [41].

The mononuclear Ni(II) complex has a square planar geometry and is diamagnetic [35]. The binuclear Ni(II) complex has a magnetic moment value of 3.06 BM, characteristic of octahedral Ni^{2+} [42].

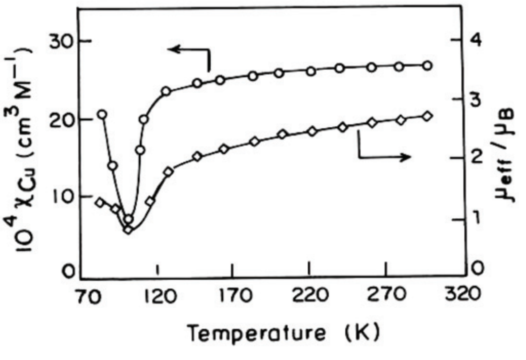


Figure 2. Temperature-dependent magnetic properties for $[Cu_2L(OAc)(H_2O)](ClO_4)_2$ (◇ is $\mu_{eff}\mu_B{}^{-1}$, ○ is χ).

3.4. *Electrochemical studies*

Conductance measurement of all complexes were carried out in DMF. For the mononuclear complexes, the conductance was in the range 10–15 (Λ_m S^{-1} cm^2 mol^{-1}), indicating that the complexes are neutral. Conductance values of the binuclear complexes are in the range 150–170 (Λ_m S^{-1} cm^2 mol^{-1}), indicating that they are 1 : 2 electrolytes [43].

3.4.1. Reduction at negative potential. Electrochemical properties of the complexes were studied by cyclic voltammetry in the potential range 0 to −1.8 V in DMF containing 0.1 M TBAP as supporting electrolyte (table 1). The hard nature of the phenoxide influence the electrochemical properties of the complexes [44]. Cyclic voltammograms with different scan rates show no corresponding anodic peak in the reverse direction, which indicates that the electrode process is irreversible. The mononuclear copper(II), nickel(II) and zinc(II) complexes show an irreversible one-electron reduction in the cathodic region, while the binuclear complexes show two step irreversible one-electron reductions. Controlled potential electrolysis was also carried out for the complexes at 100 mV s^{-1} negative to the cathodic peak, consuming one electron per molecule ($n = 0.95$), indicating that each wave corresponds to a one-electron process. The two reduction processes are assigned,

$$M^{II}M^{II} \longrightarrow M^{II}M^{I} \longrightarrow M^{I}M^{I}.$$

According to HSAB concept, soft acid will prefer soft base to form stable complex and vice versa. In this case, as the transition metals copper, nickel and zinc are soft acids, they will favor coordination with soft base nitrogen when compared to oxygen. Hence, in the complexation of the binucleating ligand, the first metal prefers to coordinate to the nitrogen rich arm possessing N_2O coordination sites rather than NO_3 coordination sites. On reduction, the metal in NO_3 coordination sites will reduce first. Oxygen is more electronegative than nitrogen and hence, NO_3 compartment can hold the reduced metal ion in preference to the N_2O compartment. This is also supported by the flexibility of the diethanolamine arm possessing NO_3 coordination sites which can make the compartment to hold the reduced cation, stabilizing formation of Cu(I) [41]. This is emphasized from the lowering of the first reduction potential (table 1) of the binuclear complexes compared to that of the corresponding mononuclear complexes.

Table 1. Electrochemical data* for the complexes (reduction at cathodic potential).

Complexes	E^1_{pc}(V)	E^2_{pc}(V)
$[CuL(OAc)] \cdot H_2O$	−0.77	–
$[NiL(OAc)] \cdot H_2O$	−0.86	–
$[ZnL(OAc)(H_2O)_2]$	−0.88	–
$[Cu_2L(OAc)(H_2O)](ClO_4)_2$	−0.70	−1.15
$[Ni_2L(OAc)(H_2O)_3](ClO_4)_2$	−0.76	−1.26
$[Zn_2L(OAc)(H_2O)_3](ClO_4)_2$	−0.78	−1.49

*Measured by CV at 50 mV s^{-1}. *E vs.* Ag/AgCl conditions: GC working and Ag/AgCl reference electrodes; supporting electrolyte: TBAP; concentration of complex: 1×10^{-3} M, concentration of TBAP: 1×10^{-1} M.

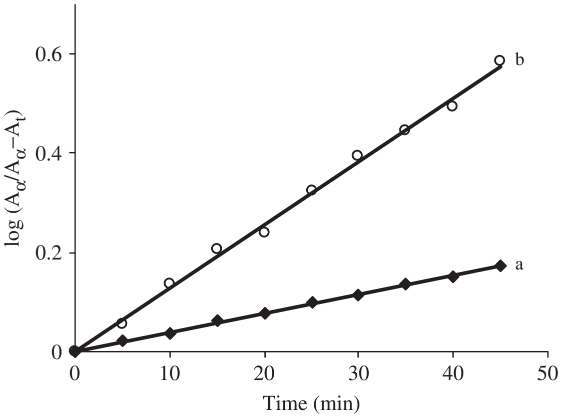


Figure 3. Catecholase activity of (a) $[CuL(OAc)]\cdot H_2O$ and (b) $[Cu_2L(OAc)(H_2O)](ClO_4)_2$.

3.4.2. Oxidation process at anodic potential. Cyclic voltammogram of the mononuclear Ni(II) complex shows an irreversible oxidation wave at +0.87 V. The binuclear Ni(II) complex shows two irreversible one-electron processes in the potential range +0.92 V and +1.40 V. The two oxidation processes for the binuclear Ni(II) complexes are assigned,

$$Ni^{II}Ni^{II} \longrightarrow Ni^{III}Ni^{II} \longrightarrow Ni^{III}Ni^{III}$$

3.5. *Kinetic studies*

3.5.1. Oxidation of pyrocatechol. *Catecholase activity*. The catecholase activity of both mono and binuclear copper(II) complexes synthesized in the present work was carried out using pyrocatechol as model substrate [45]. For this purpose, 10^{-3} mol dm^{-3} solutions of complexes in DMF were treated with 100 equivalents of pyrocatechol in the presence of air. The reaction was followed spectrophotometrically at 390 nm for 45 min at intervals of 5 min. The slope was determined by the method of initial rates by monitoring the growth of the 390 nm band of the product *o*-quinone. A linear relationship for initial rate and the complex concentration obtained for both copper(II) complexes shows a first-order dependence on the complex concentration.

Plots of $\log(A_\alpha/A_\alpha - A_t)$ *versus* time for catecholase activity of the mononuclear and binuclear complexes are obtained as shown in figure 3. The observed initial rate constants for mononuclear and binuclear copper(II) complexes are given in table 2. The binuclear copper(II) complex shows higher reactivity, due to the fact that oxidation of pyrocatechol to *o*-quinone is enhanced by two metal ions in proximity [46].

3.5.2. Kinetic studies of hydrolysis of 4-nitrophenylphosphate. The catalytic activity of the mono and binuclear copper(II), nickel(II) and zinc(II) complexes on the hydrolysis of 4-nitrophenylphosphate was determined spectrophotometrically by monitoring the increase of the 4-nitrophenolate anion characteristic absorption at 420 nm over the time in DMF at 25°C. For this purpose, 10^{-3} mol dm^{-3} solutions of complexes in DMF with

Table 2. Hydrolysis of 4-nitrophenylphosphate* and catecholase activity*.

	Rate constant (k) ($\times10^{-3}$) min^{-1}	
Complexes	NPP	Catecholase
$[CuL(OAc)]\cdot H_2O$	5.9	8.9
$[NiL(OAc)]\cdot H_2O$	6.8	–
$[ZnL(OAc)(H_2O)_2]$	5.6	–
$[Cu_2L(OAc)(H_2O)](ClO_4)_2$	23.7	29.5
$[Ni_2L(OAc)(H_2O)_3](ClO_4)_2$	31.4	–
$[Zn_2L(OAc)(H_2O)_3](ClO_4)_2$	21.3	–

*Measured spectrophotometrically in DMF.
Concentration of the complexes: 1×10^{-3} M.
Concentration of 4-nitrophenylphosphate: 1×10^{-1} M.
Concentration of pyrocatechol: 1×10^{-1} M.
The error limit in the rate contant values: ±0.2.

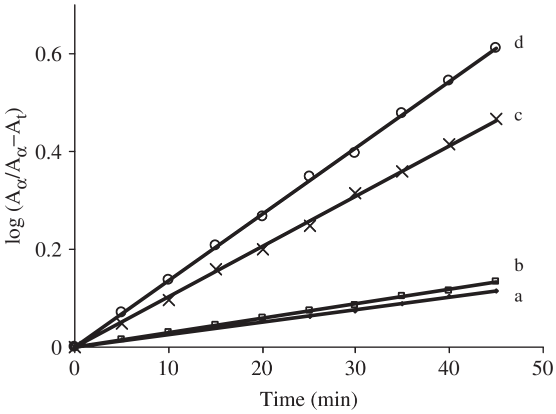


Figure 4. Hydrolysis of 4-nitrophenylphosphate by copper(II) and nickel(II) complexes: (a) $[CuL(OAc)]\cdot H_2O$; (b) $[NiL(OAc)]\cdot H_2O$; (c) $[Cu_2L(OAc)(H_2O)](ClO_4)_2$; (d) $[Ni_2L(OAc)(H_2O)_3](ClO_4)_2$.

2.5×10^{-3} M solution of tetramethylammonium hydroxide were treated with 100 equivalents of nitrophenyl phosphate in air.

The reaction was followed at 420 nm for 45 min at intervals of 5 min. The slope was determined by the method of initial rates by monitoring growth of the 420 nm band of 4-nitrophenolate. A linear relationship for all the complexes shows a first-order dependence on the complex concentration. Plots of $\log(A_\alpha/A_\alpha - A_t)$ *versus* time for hydrolysis of 4-nitrophenylphosphate activity of the complexes are obtained (figure 4). The observed initial rate constant values for all the mono and binuclear complexes are given in table 2. Binuclear complexes show higher reactivity than the corresponding mononuclear complexes due to the mechanism requiring two metal ions in proximity. The mechanism of action has already been explained with the help of model complexes [47].

Nickel(II) complexes have a higher rate constant than the copper(II) and zinc(II) complexes, similar to the higher catalytic activity of Ni(II)(tren) than copper(II)(tren) and zinc(II)(tren) reported by Trogler *et al.* [48]. The catalytic activity of copper(II) complexes towards oxidation of pyrocatechol is more than that for phosphate hydrolysis. The rate constants of both the hydrolysis of nitrophenylphosphate and catecholase activity of the complexes of HL are larger than those of the complexes of 2,6-*bis*(4-methylpiperazin-1-yl-methyl)-4-formyl phenol [40].

4. Summary

A new phenol-based unsymmetrical "end-off" ligand and mono and binuclear Cu(II), Ni(II) and Zn(II) complexes have been prepared and characterized. Variable temperature magnetic and ESR spectral studies of the binuclear Cu(II) complexes exhibit the presence of magnetic exchange interaction between coppers. The magnetic and catalytic properties of the complexes of the unsymmetrical ligand were compared with complexes of a similar symmetrical ligand.

Supplementary material

The cyclic voltammograms for binuclear copper(II) and nickel(II) complexes are given as supplementary material.

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References

[1] K. Wieghardt. *Angew. Chem., Int. Ed. Engl.*, **28**, 1153 (1989).
[2] R. Krämer, I.O. Fritsky, H. Pritzkow, L.A. Kovbasyuk. *J. Chem. Soc., Dalton Trans.*, 1307 (2002).
[3] S.L. Jain, P. Bhattacharyya, H.L. Milton, A.M.Z. Slawin, J.A. Crayston, J.D. Woollins. *J. Chem. Soc., Dalton Trans.*, 862 (2004).
[4] T. Chattopadhyay, K.S. Banu, A. Banerjee, J. Ribas, A. Majee, M. Nethaji, D. Das. *J. Mol. Struct.*, **833**, 13 (2007).
[5] M.H. Klingele, B. Moubaraki, J.D. Cashion, K.S. Murray, S. Brooker. *Chem. Commun.*, 987 (2005).
[6] B.A. Leita, B. Moubaraki, K.S. Murray, J.P. Smith, J.D. Cashion. *Chem. Commun.*, 156 (2004).
[7] R.R. Gagne, R.P. Kreh, J.A. Dodge. *J. Am. Chem. Soc.*, **101**, 6917 (1979).
[8] S. Brooker. *Coord. Chem. Rev.*, **222**, 33 (2001).
[9] D.E. Wilcox. *Chem. Rev.*, **96**, 1647 (1996).
[10] N. Strater, W.N. Lipscomb, T. Klabunde, B. Krebs. *Angew. Chem. Int. Ed. Engl.*, **35**, 2024 (1996).
[11] T. Gadja, R. Kramer, A. Jancso. *Eur. J. Inorg. Chem.*, 1635 (2000).
[12] S.O. Kang, M. Kim. *J. Am. Chem. Soc.*, **125**, 4684 (2003).
[13] S.L. Roderick, B.W. Matthews. *Biochemistry*, **32**, 3907 (1993).
[14] M. Lanznaster, A. Neves, A.J. Bortoluzzi, B. Szpoganicz, E. Schwingel. *Inorg. Chem.*, **41**, 5641 (2002).

[15] S. Uozumi, H. Furutachi, M. Ohba, H. Okawa, D.E. Fenton, K. Shindo, S. Murata, D.J. Kitko. *Inorg. Chem.*, **37**, 6281 (1998).

[16] J. Chen, X. Wang, Y. Zhu, J. Lin, X. Yang, Y. Li, Y. Lu, Z. Guo. *Inorg. Chem.*, **44**, 3422 (2005).

[17] P. Nordlund, B.M. Sjoberg, H. Eklund. *Nature*, **345**, 593 (1990).

[18] M. Lubben, B.L. Feringa. *J. Org. Chem.*, **59**, 2227 (1994).

[19] R. Mahalakshmy, R. Venkatesan, P. Sambasiva Rao, R. Kannappan, T.M. Rajendiran. *Transition Met. Chem.*, **29**, 623 (2004).

[20] A.S. Borovik, M.P. Hendrich, T.R. Holman, E. Munck, V. Papaefthymiou, L. Que Jr. *J. Am. Chem. Soc.*, **112**, 6031 (1990).

[21] B.P. Murch, F.C. Bradley, L. Que Jr. *J. Am. Chem. Soc.*, **108**, 5027 (1986).

[22] Y. Nishida, T. Akamatsu, M. Nasu. *Chem. Lett.*, **20**, 1703 (1991).

[23] H. Drill, H.R. Chang, M.J. Nilges, X. Zhang, J.A. Potenza, H.J. Schugar, S.S. Isied, D.N. Hendrickson. *J. Am. Chem. Soc.*, **111**, 5102 (1989).

[24] Y. Guitneh, A. Farooq, S. Liu, K.D. Karlin, J. Zubieta. *Inorg. Chem.*, **31**, 3607 (1992).

[25] K.J. Oberhausen, J.F. Richardson, R.M. Buchanan, J.K. McCusker, D.N. Hendrickson, J.M. Latour. *Inorg. Chem.*, **30**, 1357 (1991).

[26] O.J. Gelling, B.L. Feringa. *J. Am. Chem. Soc.*, **112**, 7599 (1990).

[27] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **32**, 227 (1980).

[28] M. Lachkar, R. Guilard, A. Atmani, A. DeCian, J. Fischer, R. Weiss. *Inorg. Chem.*, **37**, 1575 (1998).

[29] J. Manonmani, M. Kandaswamy, V. Narayanan, R. Thirumurugan, S. Shanmuga Sundara Raj, G. Shanmugam, M.N. Ponnuswamy, H.K. Fun. *Polyhedron*, **20**, 3039 (2001).

[30] (a) M. Thirumavalavan, P. Akilan, M. Kandaswamy. *Inorg. Chem. Commun.*, **5**, 422 (2002); (b) K.J. Oberhausen, J.F. Richardson, R.M. Buchnan, J.K. McCusker, D.N. Hendrickson, J.M. Latour. *Inorg. Chem.*, **30**, 1357 (1991).

[31] (a) D. Reinen, C. Friebel. *Inorg. Chem.*, **23**, 791 (1984); (b) K. Bertoncello, G.D. Fallon, J.H. Hodgkin, K.S. Murray. *Inorg. Chem.*, **27**, 4750 (1988).

[32] (a) A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, Amsterdam (1984); (b) S. Bhattacharya, T.J.R. Weakley, M. Chaudhury. *Inorg. Chem.*, **38**, 633 (1999).

[33] (a) T.C. Higgs, C.J. Carrano. *Inorg. Chem.*, **36**, 298 (1997); (b) M.F. Cabral, B. Murphy, J. Nelson. *Inorg. Chim. Acta*, **90**, 169 (1984).

[34] F. Yilmaz, V.T. Yilmaz, S. Topcu, N. Menek. *J. Coord. Chem.*, **56**, 903 (2003).

[35] A. Bottcher, H. Elias, E.G. Jager, H. Langfelderova, M. Mazur, L. Muller, H. Paulus, P. Pelikan, M. Rudolph, M. Valko. *Inorg. Chem.*, **32**, 4131 (1993).

[36] M. Thirumavalavan, P. Akilan, M. Kandaswamy, K. Chinnakali, G. Senthilkumar, H.K. Fun. *Inorg. Chem.*, **42**, 3308 (2003).

[37] B. Bleaney, K.D. Bowers. *Proc. R. Soc. Lond. Ser. A*, **214**, 451 (1952).

[38] M. Lubben, R. Hage, A. Meetsma, K. Byma, B.L. Fermga. *Inorg. Chem.*, **34**, 2217 (1995).

[39] A. Benzekri, P. Dubourdeaux, J.M. Latour, J. Laugier, P. Rey. *J. Chem. Soc., Dalton Trans.*, 3359 (1991).

[40] K. Shanmuga Bharathi, A. Kalilur Rahiman, K. Rajesh, S. Sreedaran, P.G. Aravindan, D. Velmurugan, V. Narayanan. *Polyhedron*, **25**, 2859 (2006).

[41] A. Benzekri, P. Dubourdeaux, J.M. Latour, J. Laugier, P. Rey. *Inorg. Chem.*, **27**, 3710 (1988).

[42] M.P. Suh, B.Y. Shim, T.S. Yoon. *Inorg. Chem.*, **33**, 5509 (1994).

[43] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[44] F. Azevedo, C.T. Carrondo, B. Caseto, M. Convery, D. Domingues, C. Freire, T. Durate, K. Neilson, C. Santos. *Inorg. Chim. Acta*, **219**, 43 (1994).

[45] A. Neves, L.M. Rossi, I. Vencato, V. Drago, W. Hasse, R. Werner. *Inorg. Chim. Acta*, **281**, 111 (1998).

[46] A. Neves, L.M. Rossi, A.J. Bortoluzzi, B. Szpoganicz, C. Wiezbicki, E. Schwingel, W. Haase, S. Ostrovsky. *Inorg. Chem.*, **41**, 1788 (2002).

[47] R.G. Clewley, H. Slebocka-Tilk, R.S. Brown. *Inorg. Chim. Acta*, **157**, 233 (1989).

[48] M.A. De Rosch, W.C. Trogler. *Inorg. Chem.*, **29**, 2409 (1990).