

Synthesis and Characterization of New *trans N,N′*-Disubstituted Macrocyclic "tet *a*" Ligands and Their Copper(II) and Nickel(II) Complexes: Structural, Electrochemical, Magnetic, and Catalytic Studies

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New trans-disubstituted macrocyclic ligands (L^1), *trans*-1,8-[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}]-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane, and (L^2), 1,8-[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)-benzyl}]-4,11-dimethyl-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane, were synthesized. The ligands were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectral analyses. The ligand L^1 crystallized as monoclinic in the space group $P2_1/n$, and the final *R*-value was found to be 0.062. Copper(II) and nickel(II) complexes of these ligands were prepared and characterized by elemental analysis, IR, UV–visible, FAB-mass spectral studies. Electrochemical studies of the nickel(II) complexes show one-electron quasireversible reduction around −1.00 to −1.13 V and one-electron quasireversible oxidation around 1.00 to 1.14 V. The copper(II) complexes show one-electron quasireversible reduction around −0.93 to −1.10 V. ESR spectral studies of the copper(II) complexes show hyperfine splitting with a $g_\parallel$ value of 2.31, a $g_\perp$ value of around 2.02 and an *A* value of 160 G. The magnetic moment values (μ_{eff}) of the Cu(II) complexes fall in the range of 1.71 to 1.72 B.M. at room temperature (298 K). The rate-constant values of the catalytic hydrolysis of *p*-nitrophenyl phosphate for the copper(II) complexes were in the range 6.3×10^{-3} to 12.2×10^{-3} min^{-1} and for the nickel(II) complexes in the range 10×10^{-3} to 14×10^{-3} min^{-1}. The rate-constant values of the catalytic oxidation of catechol to *o*-quinone were in the range 9.4×10^{-3} to 13.4×10^{-3} min^{-1} for the copper(II) complexes. The copper(II) and nickel(II) complexes of ligand L^2 have higher catalytic activity than that of ligand L^1.

The chemistry of macrocyclic ligands with coordinating side arms[1–7] has been the subject of growing interest during the past few years. Synthetic macrocycles have been, and still are, a rapidly growing class of compounds having different molecular topologies,[8,9] a different set of donor atoms and thus a great variety of ligational properties towards protons,[10–12] metal cations and anions.[13] This variegated chemistry, which arose from the endless fantasy of synthetic chemists, has led to macrocycles and their complexes being used as catalysts, selective metal ion binders, NMR contrast agents, molecular recognition,[14] photochemical devices, selective extractants, analytical reagents, etc.[15,16] The copper-catalysed oxidation of phenols to catechols and subsequent oxidation of diphenols to quinones (tyrosinase) are important chemical processes in biological systems.[17,18] Hydrolysis is found to be the key process in the active sites of a number of enzymes, namely urease and carbon monoxide dehydrogenase mediated by nickel ions.[19] Hence, here we report on the synthesis of new tetraaza macrocyclic ligands (L^1) and (L^2) with coordinating side arms. Both of the ligands contain two side arms with phenolic oxygen as an additional coordinating site and formyl groups for further extension. This may be used as a spacer in long-chain molecules or dendrons to prepare dendrimers.[20] The structure of ligand L^1 has been solved by the X-ray crystallographic method. The ligands can be used to prepare mono-, di-, and tri-nuclear metal complexes.[21,22] The cavity size and the shape of the host molecule can be easily tuned in order to study the coordination properties of the ligands. Synthesis and electrochemical studies of ferrocene attached macrocycle are also in progress. Here, we report on the synthesis of mononuclear copper(II) and nickel(II) complexes of these ligands. The spectral, electrochemical, magnetic, and catalytic studies of these complexes are also discussed.

Experimental

An elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. The Nuclear magnetic resonance spectra were measured at 400.13 (^{1}H) and 100.40 (^{13}C) on a Jeol GSX400 spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer in the range of 200–850 nm. IR spectra were recorded on a Hitachi 270-50 spectrophotometer on KBr disks in the range of 4000–400 cm^{-1}. FAB mass spectra of the complexes were obtained on a JEOL SX 102/DA-6000; *m*-nitrobenzyl alcohol (NBA) was used as the matrix. The molar conductivity of a freshly prepared solution of the complex in DMF was measured using an Elico Model SX80 conductivity bridge. Cyclic Voltammograms were obtained on a CHI600A electrochemical analyzer. The measurements were carried out under an oxygen-free condition using a three-electrode cell in which a glassy carbon electrode was a working electrode, a saturated Ag/AgCl electrode was a reference electrode and a platinum wire was used as an auxiliary electrode. The concentration of the complexes was 10^{-3} M. Tetrabutylammonium perchlorate (10^{-1} M) was used as a

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supporting electrolyte. 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 was 470 mV in DMF, and ΔE_p for Fc/Fc^+ was 70 mV. The room-temperature magnetic moment was measured on a PAR vibrating sample magnetometer (Model-155). X-band ESR spectra of Cu(II) complexes were recorded using DMF as a solvent at liquid-nitrogen temperature on a Varian EPR-E 112 spectrometer with diphenylpicrylhydrazine (DPPH) as a reference. The catalytic oxidation of catechol to *o*-quinone and the hydrolysis of 4-nitrophenyl phosphate by the complexes (10^{-3} M, DMF solution) were studied. The catechol oxidation reaction was followed spectrophotometrically by choosing the strongest absorbance at 390 nm (*o*-quinone), and the phosphate hydrolysis reaction was followed at 420 nm (nitrophenolate anion). The increase in the absorbance at these wavelengths was monitored as a function of time. A plot of $\log(A_\infty/A_\infty - A_t)$ vs time was made for each complex and the initial rate constant was calculated.

Materials. 5-methylsalicylaldehyde,[23] 3-chloromethyl-5-methylsalicylaldehyde,[24] and 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane[25] were prepared by following literature methods. All of other chemicals were of analytical grade and were used as received.

Synthesis of Precursor Compound (P.C.-1). The compound 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane (1 g, 0.03 mol) was dissolved in acetonitrile (30 mL) and two equivalents of 3-chloromethyl-5-methylsalicylaldehyde (1.2 g, 0.066 mol) in acetonitrile (30 mL) were rapidly added. This solution was stirred at room temperature (25 °C) for three days and the white precipitate formed was filtered, washed with a small quantity of CH_3CN, and dried under a vacuum. This crude compound, 1,8-[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl]-4,11-diazaniatricyclo[9.3.1.1^{4,8}]-5,5,7,12,12,14-hexamethylhexadecane dichloride, was recrystallized from water to give white crystals.

Yield: 89%. mp: 275 °C (dec). Analytical data for $C_{36}H_{54}O_4N_4$: Calcd: C, 71.25; H, 8.97; N, 9.23%. Found: C, 71.36; H, 9.11; N, 9.41%. Selected IR (KBr): 3450 (br), 1668 (s) cm^{-1}. ^1H NMR Spectra: δ (ppm in D_2O) 0.72 to 1.30 (s, 18H, C–CH_3), 1.64 (s, 4H, CH_2), 2.36 (s, 6H, Ar–CH_3), 2.48 (m, 2H, CH), 2.94 (m, 4H, α-CH_2), 3.27 (m, 4H, β-CH_2), 3.96 (d, 4H, N–CH_2–Ar), 5.06 (d, 4H, N–CH_2–N), 7.26 (d, 4H, Ar–H), 10.50 (s, 2H, Ar–CHO), 12.94 (br. s, 2H, Ar–OH).

Synthesis of Ligand (L^1). The compound P.C.-1 (0.5 g, 0.08 mmol) was dissolved in 100 mL of an aqueous NaOH solution (3 M) with stirring. After stirring for 4 h, the solution was extracted with $CHCl_3$ (5 × 30 mL). The combined $CHCl_3$ extracts were dried with anhydrous $MgSO_4$, and concentrated under a vacuum to give a yellow compound. Light-yellow crystals of the ligand 1,8-[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}]-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane (L^1) were obtained upon recrystallization from chloroform.

Yield: 67%. mp: 318 °C (dec). Analytical data for $C_{34}H_{52}O_4N_4$: Calcd: C, 70.31; H, 9.02; N, 9.65%. Found: C, 70.02; H, 9.55; N, 9.92%. Selected IR (KBr): 3445 (br), 3289 (s), 1666 (s) cm^{-1}. ^1H NMR Spectra: (L^1) δ (ppm in $CDCl_3$) 0.63 to 1.10 (s, 18H, C–CH_3), 1.64 (s, 4H, CH_2), 2.19 (s, 6H, Ar–CH_3), 2.48 (m, 2H, CH), 2.65 (br. s, 2H, NH), 2.94 (m, 4H, α-CH_2), 3.27 (m, 4H, β-CH_2), 3.97 (d, 4H, N–CH_2–Ar, $J = 1.05$ Hz), 7.26 (d, 4H, Ar–H, $J = 1.78$ Hz), 10.40 (s, 2H, Ar–CHO), 12.94 (br. s, 2H, Ar–OH). ^{13}C NMR Spectra: (L^1) δ (ppm in $CDCl_3$) 19.3, 20.3, 31.2, 38.3, 46.2, 49.17, 51.2, 53.4, 55.2, 119.8, 124.5, 127.4, 133.4, 138.8, 158.2, 195.6.

Synthesis of Tetrasubstituted Ligand (L^2). The compound P.C.-1 (1 g, 1.6 mmol) was dissolved in an $EtOH/H_2O$ (95:5) mixture. Ten equivalents of $NaBH_4$ (1.3 g, 16 mmol) were then added, and the mixture was refluxed for 3 h. After cooling to room temperature, 10 mL of HCl (3 M in water) was added. The mixture was concentrated to dryness on a rotary evaporator, and the residue was then dissolved in 100 mL of water and KOH (1 M) was added until the solution attained a pH of 12. After extraction with $CHCl_3$ (5 × 30 mL), the organic phase was dried with anhydrous $MgSO_4$ and concentrated to give a yellow compound.[26–28] Light-yellow microcrystals of the ligand 1,8-[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl}benzyl)]-4,11-dimethyl-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane (L^2) were obtained upon recrystallization from chloroform.

Yield: 73%. mp: 290 °C (dec). Analytical data for $C_{36}H_{56}O_4N_4$: Calcd: C, 71.02; H, 9.27; N, 9.20%. Found: C, 71.32; H, 9.53; N, 9.54%. Selected IR (KBr): 3442 (br), 1658 (s), 1345 (s) cm^{-1}. ^1H NMR Spectra: δ (ppm in $CDCl_3$) 1.01 to 1.10 (s, 18H, C–CH_3), 1.64 (s, 4H, CH_2), 2.21 (s, 6H, Ar–CH_3), 2.27 (s, 6H, N–CH_3), 2.68 (m, 2H, CH), 2.80 (m, 4H, α-CH_2), 3.27 (m, 4H, β-CH_2), 3.96 (d, 4H, N–CH_2–Ar, $J = 1.04$ Hz), 7.26 (d, 4H, Ar–H, $J = 1.78$ Hz), 10.50 (s, 2H, Ar–CHO), 12.94 (br. s, 2H, Ar–OH). ^{13}C NMR Spectra: δ (ppm in $CDCl_3$) 18.50, 20.43, 27.30, 36.05, 37.45, 47.17, 51.80, 55.20, 117.82, 124.04, 126.3, 132.4, 138.6, 156.2, 193.7.

Synthesis of Macrocyclic Mononuclear Complexes. [CuL^1](PF_6)$_2$: A methanolic solution of copper(II) perchlorate hexahydrate (0.63 g, 1.7 mmol) was added to a hot solution of L^1 (1.0 g, 1.7 mmol) in methanol. The solution was refluxed on a water bath for 24 h, and filtered while hot. Then, KPF_6 (0.3 g, 1.7 mmol) in 10 mL of methanol was added to the solution. The resulting solution was stirred overnight at 25 °C. The crude product was precipitated by slow evaporation of the solvent at room temperature (25 °C). The complex was obtained as a green powder upon recrystallization of the crude product from CH_3CN.

Yield: 81%. Analytical data for $C_{34}H_{52}O_4N_4Cu(PF_6)_2$: Calcd: C, 43.71; H, 5.61; N, 6.00; Cu, 6.80%. Found: C, 43.68; H, 5.23; N, 6.38; Cu, 6.55%. Selected IR (KBr): 3428 (br), 3241 (m), 1659 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH_3CN: 125. λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_3CN: 547 (171), 388 (14800), 300 (38600). $g_\parallel = 2.31$, $g_\perp = 2.02$; μ_{eff}: 1.72 B.M.

[CuL^2](PF_6)$_2$: Complex [CuL^2](PF_6)$_2$ was synthesized by following the above procedure using ligand L^2 instead of ligand L^1. The complex was obtained as a dark-green powder upon recrystallization of the crude product from CH_3CN. Yield: 76%. Analytical data for $C_{36}H_{56}O_4N_4Cu(PF_6)_2$: Calcd: C, 44.93; H, 5.87; N, 5.82; Cu, 6.60%. Found: C, 44.68; H, 5.62; N, 6.02; Cu, 6.43%. Selected IR (KBr): 3436 (br), 1672 (s), 1342 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH_3CN: 143. λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_3CN: 562 (176), 395 (11300), 304 (47400). $g_\parallel = 2.32$, $g_\perp = 2.05$; μ_{eff}: 1.71 B.M.

[NiL^1](PF_6)$_2$: The complex was prepared by the procedure used for copper(II) complex by using $Ni(ClO_4)_2 \cdot 6H_2O$ (1 g, 1.7 mmol) instead of $Cu(ClO_4)_2 \cdot 6H_2O$. The complex was obtained as a dark-green powder upon recrystallization of the crude product from CH_3CN. Yield: 77%. Analytical data for $C_{34}H_{52}O_4N_4Ni(PF_6)_2$: Calcd: C, 43.94; H, 5.64; N, 6.03; Ni, 6.32%. Found: C, 43.79, H, 5.78; N, 6.34; Ni, 6.12%. MS (EI) $m/z = 926$ (m^+). Selected IR (KBr): 3452 (br), 3254 (m), 1667 (s), 1345 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH_3CN: 137. λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_3CN: 480 (181), 384 (15800), 302 (31600). ^1H NMR Spectra: δ (ppm in $CDCl_3$) 0.55 to 1.51 (s, 18H, C–CH_3), 1.64 to 1.9 (s, 4H, CH_2), 2.24 (s, 6H, Ar–CH_3), 2.55 (br s, 2H, NH), 2.68 (m, 2H, CH), 2.80 (m, 4H, α-CH_2), 3.27 (m, 4H,

β-CH_2), 3.61 (d, 4H, N–CH_2–Ar), 7.64 (d, 4H, Ar–H), 9.65 (s, 2H, Ar–CHO). ^{13}C NMR Spectra: δ (ppm in $CDCl_3$) 19.05, 20.17, 34.5, 41.95, 44.93, 48.42, 49.84, 51.89, 66.06, 118.2, 126.21, 128.9, 130.9, 152.17, 184.37.

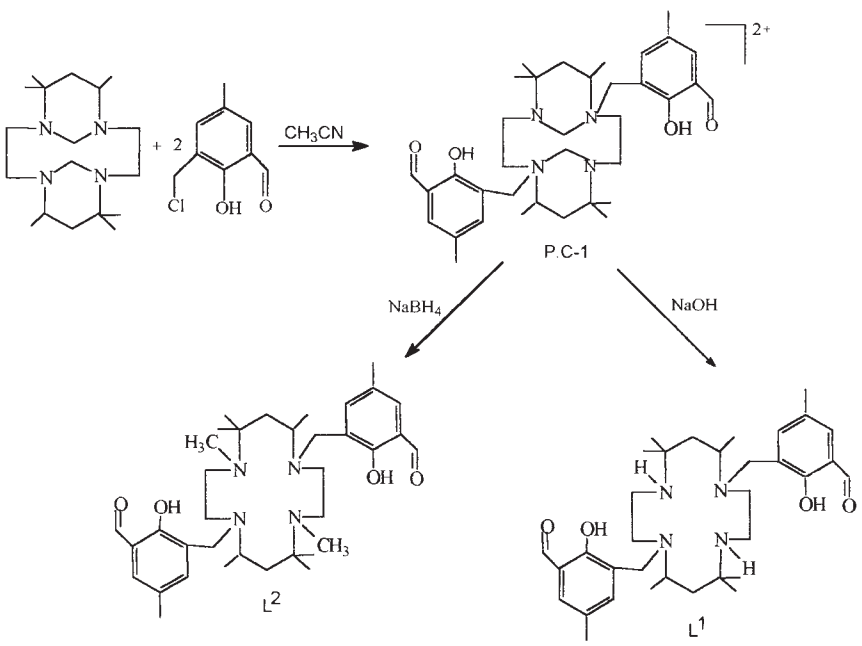
$[NiL^2](PF_6)_2$: Complex $[NiL^2](PF_6)_2$ was synthesized by following the above procedure using ligand L^2 instead of ligand L^1. The complex was obtained as a green powder upon recrystallization of the crude product from CH_3CN. Yield: 72%. Analytical data for $C_{36}H_{56}O_4N_4Ni(PF_6)_2$: Calcd: C, 45.15; H, 5.90; N, 5.85; Ni, 6.13%. Found: C, 45.45; H, 5.62; N, 5.51; Ni, 6.42%. MS (EI) $m/z = 956$ (m^+). Selected IR (KBr): 3433 (br), 1664 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH_3CN: 136. λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_3CN: 492 (193), 392 (13300), 305 (58400). ^{1}H NMR Spectra: δ (ppm in $CDCl_3$) 0.52 to 1.58 (s, 18H, C–CH_3), 1.65 to 1.80 (s, 4H, CH_2), 2.47 (s, 6H, Ar–CH_3), 2.38 (s, 6H, N–CH_3), 2.60 (m, 4H, α,β-CH_2), 3.05 (m, 2H, CH), 4.04 (d, 4H, N–CH_2–Ar), 7.64 (d, 4H, Ar–H, $J = 2.42$ Hz), 9.45 (s, 2H, Ar–CHO). ^{13}C NMR Spectra: δ (ppm in $CDCl_3$) 18.15, 21.17, 33.59, 40.97, 45.53, 47.32, 48.64, 50.89, 67.16, 115.26, 124.20, 127.5, 130.6, 151.15, 182.57.

Results and Discussion

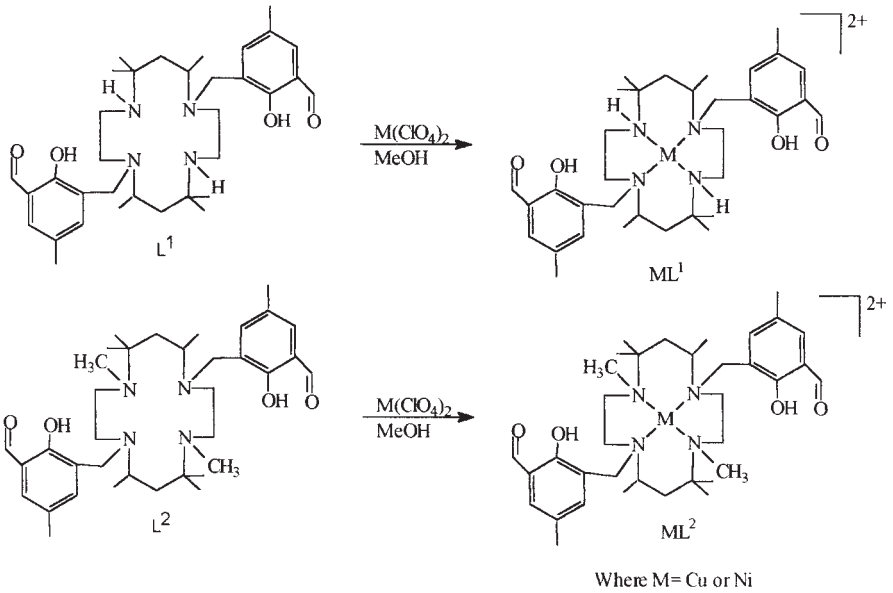
The precursor compound-1 (P.C.-1) was prepared from a reaction of hexamethylated 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]-hexadecane with two equivalents of 3-chloromethyl-5-methylsalicylaldehyde in acetonitrile. Compound P.C.-1 hydrolyzed with aqueous NaOH to yield the macrocycle ligand L^1. The ligand L^1 crystallized as a yellow crystal, which was suitable for single crystal X-ray analysis. The ligand L^2 was prepared by the reduction of P.C.-1 with sodium borohydride in ethanol. Mononuclear copper(II) and nickel(II) complexes were prepared by mixing an equimolar amount of the ligand and metal(II) perchlorate salts in a methanol medium. The synthetic routes for the preparation of ligands and their complexes are shown in Schemes 1 and 2, respectively.

X-ray Structural Study of the Ligand (L^1). The ligand L^1 was crystallized from a chloroform–methanol solution in the space group $P2_1/n$ with two molecules in a unit cell. The crystal structure of the ligand along with the atomic labeling is given in Fig. 1. The crystal data and structure refinement for the ligand (L^1) is given in Table 1. The crystal structure[29] reveals that the ligand has a center of inversion due to the 3-chloromethyl-5-methyl salicylaldehyde group attached to the trans nitrogen atoms. The cyclam unit is more buckled compared to the unsubstituted cyclam due to the attachment of a bulkier group in the ring. The overall C–C distance varies between 1.363(4) and 1.538(4) Å. The overall C–N distance varies between 1.448(4) and 1.515(3) Å. No anomalous bond distances or bond angles were found in the structure, and all of the bond distances and bond angles agree well with the reported literature.[30]

Spectral Studies. The ligand L^1 shows ν(C=O), ν(N–H), and ν(OH) peaks at 1666, 3289, and 3445 cm^{-1}, respectively. Ligand L^2 shows ν(C=O) and ν(OH) peaks at 1658 and 3442 cm^{-1}, respectively. The infrared spectra of all the complexes show a sharp band in the range 1650–1674 cm^{-1}, corresponding to ν(C=O) stretching. Complexes of ligand L^1 exhibit a peak due to ν(N–H) stretching at 3256 cm^{-1}. The FAB mass spectrum of the complex $[NiL^1](PF_6)_2$ shows a molecular ion peak at 926. The electronic spectra of all the complexes exhibit three main peaks. One peak below 300 nm ($\varepsilon \sim 31400$ M^{-1} cm^{-1}) is assigned to the intraligand transitions (π–π^*); a moderately intense peak in the range 380–400 nm ($\varepsilon \sim 12300$ M^{-1} cm^{-1}) is due to ligand-to-metal charge transfer transitions, and a broad peak in the region 480–562 nm is due to d–d transitions. The copper(II) complexes show λ_{max} value in the region 545–562 nm ($\varepsilon \sim 170$ M^{-1} cm^{-1}), which are consistent with reported tetraaza macrocyclic Cu^{2+} complexes.[31] The nickel(II) complexes show a single band in the region 480–495 nm ($\varepsilon \sim 181$ M^{-1} cm^{-1}), which indicates a square-plannar geometry of the complexes[32] with N_4 coordina-



Scheme 1.



Scheme 2.

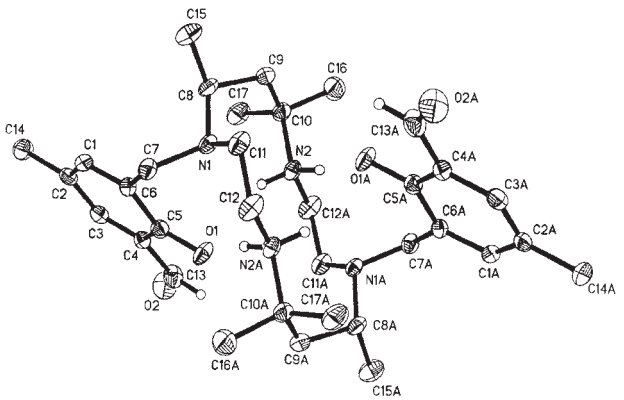


Fig. 1. ORTEP diagram of ligand (L^1) with atom labels and numbering scheme. (Hydrogen atoms are omitted for clarity.)

Table 1. Crystal Data and Structure Refinement for (L^1)

Compound	Ligand-L^1
Empirical formula	$C_{34}H_{52}N_4O_4$
Formula weight	580.78
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a	10.1862(6) Å
b	12.2663(8) Å
c	13.4698(8) Å
α	90.00°
β	107.13(1)°
γ	90.00°
Volume	1608.4(2) Å^3
Z	2
Density (calculated)	1.183 Mg m^{-3}
Absorption coefficient	0.075 mm^{-1}
$F(000)$	620
Crystal size	0.34 × 0.20 × 0.20 mm
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 9$, $-14 \le l \le 14$
Reflections collected	7400
Independent reflections	2298 [R(int) = 0.1164]
Completeness to 2θ	99.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2298/0/195
Goodness-of-fit on F^2	0.93
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.062$, $wR2 = 0.146$
R indices (all data)	$R1 = 0.097$, $wR2 = 0.172$
Largest diff. peak and holes	0.33 and −0.32 e Å^{-3}

tion.

Electrochemical Properties of the Complexes. The molar conductance values of the complexes in DMF are in the range 125 to 143 Λ_m/S cm^2 mol^{-1}, which indicates that the complexes are 1:2 electrolyte.[33] The electrochemical properties of the copper(II) and nickel(II) complexes reported in the present work were studied by cyclic voltammetry in dimethylformamide containing 10^{-1} M tetra(*n*-butyl)ammonium perchlorate (TBAP) (Caution! TBAP is potentially an explosive; hence, care should be taken in handling the compound); the electrochemical data are summarized in Table 2. Cyclic voltammograms of copper(II) complexes are shown in Fig. 2 and for nickel(II) complexes are shown in Fig. 3.

Reduction Process at Negative Potential. The cyclic voltammograms of the copper(II) and nickel(II) complexes were recorded in the potential range 0 to −1.4 V. Each voltammogram shows one quasireversible reduction wave at a negative potential in the range −0.92 to −1.13 V. The reduction process for the complexes is quasireversible in nature, as is evident from the following criteria: ΔE increases with increasing scan rate, and is always greater than 60 mV. The peak currents, I_{pc} and I_{pa}, were not equal. That a controlled potential electrolysis carried out at 100 mV more negative than the reduction wave conveys the consumption of one electron per molecule

Table 2. Electrochemical Data of Copper(II) and Nickel(II) Complexes

Complexes	Reduction [M(II) ⇌ M(I)]				Oxidation [M(II) ⇌ M(III)]			
	E_{pc} /V	E_{pa} /V	$E_{1/2}$ /V	ΔE /mV	E_{pa} /V	E_{pc} /V	$E_{1/2}$ /V	ΔE /mV
$[NiL^1](PF_6)_2$	−1.13	−0.99	−1.06	140	1.05	0.98	1.02	70
$[NiL^2](PF_6)_2$	−1.06	−0.94	−1.00	120	1.14	0.90	1.02	240
$[CuL^1](PF_6)_2$	−1.04	−0.76	−0.90	280	—	—	—	—
$[CuL^2](PF_6)_2$	−0.92	−0.72	−0.82	200	—	—	—	—

Measured by cyclic voltammetry at 50 mV/s in DMF. 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.

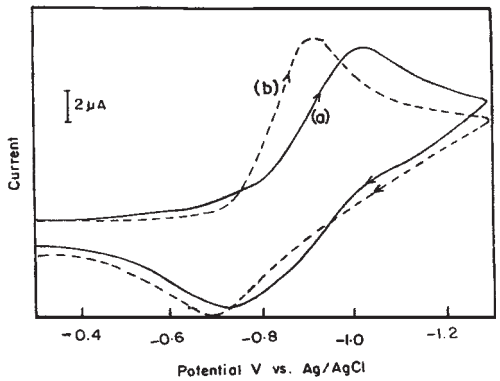


Fig. 2. Cyclic voltammograms of the copper(II) complexes. (a) $[CuL^1](PF_6)_2$; (b) $[CuL^2](PF_6)_2$.

($n = 0.92$).

The reduction potential of the copper(II) complexes shifts towards anodically from ligand L^1 ($E^1_{pc} = -1.04$) to ligand L^2 ($E^1_{pc} = -0.92$). This may be due to steric effects of the methyl group present in two trans-nitrogen atoms of the macrocycle, which causes a distortion of the geometry of the Cu(II) complexes (due to macrocyclic ring distortion); also, the number of tertiary nitrogen atoms increases in L^2, which stabilize the low valent metal Cu(I).[34] The same trend was also observed for the nickel(II) complexes. Thus, the N-methylation of the macrocyclic frame was shown to stabilize the monovalent metal ions by increasing the cavity size of the macrocyclic ligand and by decreasing the ligand field strength imparted by the nitrogen donor atoms.[35]

Oxidation Process at Positive Potential. The cyclic voltammograms for the nickel(II) complexes at positive potential were recorded in the potential range 0 to 1.3 V. Cyclic voltammograms of nickel(II) complexes at a positive potential show a single redox wave in the potential range +1.05 to +1.14 V. The oxidation process for the complexes is quasireversible in nature. Controlled potential electrolysis indicates that the waves correspond to a one-electron transfer process. The oxidation potential of nickel(II) complexes shifts towards a positive value[36] ($E_{pa} = 1.05$ to 1.14 V) as the N-methylation of ligand L^1 to L^2. Since the ligand L^2 stabilize the lower oxidation state, as mentioned above, the oxidation of NiL^2 complex is more difficult than the NiL^1 complex.

Magnetic Properties of the Complexes. The ESR spectrum of copper(II) complexes shows four lines due to hyperfine splitting with nuclear hyperfine spin 3/2. For the $[CuL^1]$ complex, the observed $g_\parallel$ value (avg) is 2.31, the $g_\perp$ value is 2.02, and the $A_\parallel$ value is 160 G; for the $[CuL^2]$ complex, the $g_\parallel$ value (avg) is 2.32, the $g_\perp$ value is 2.05, and the $A_\parallel$ value is 165 G. The relation $g_\parallel > g_\perp$ is typical of Cu(II) having one unpaired electron in a $d_{x^2-y^2}$ orbital.[37] Figure 4 shows the ESR spectrum of the mononuclear copper(II) complex of L^1. Room-temperature (at 298 K) magnetic moment studies of the copper(II) complexes show a μ_{eff} value of 1.72 B.M. for $[CuL^1]$, and 1.71 B.M. for $[CuL^2]$, which is nearer to the spin-only value of the copper(II) ion.[38] The nickel(II) complexes are diamagnetic.

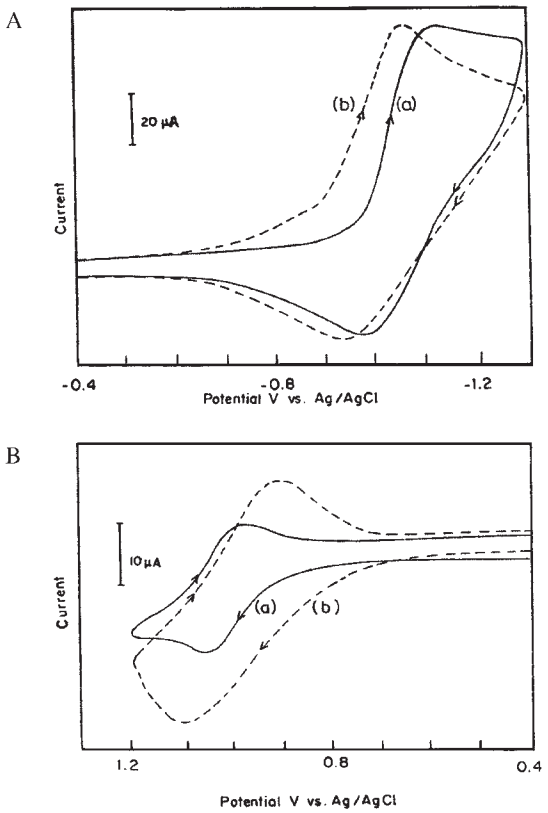


Fig. 3. A: Cyclic voltammograms of the nickel(II) complexes in the cathodic region. (a) $[NiL^1](PF_6)_2$; (b) $[NiL^2](PF_6)_2$. B: Cyclic voltammograms of the nickel(II) complexes in the anodic region. (a) $[NiL^1](PF_6)_2$; (b) $[NiL^2](PF_6)_2$.

Kinetic Studies. The catalytic reaction rate of the copper(II) and nickel(II) complexes towards the hydrolysis of 4-nitrophenyl phosphate is given in Table 3, and a plot of

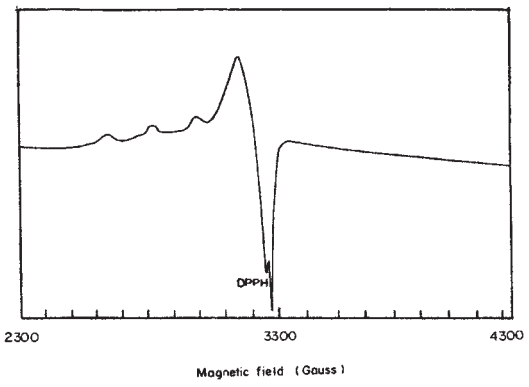


Fig. 4. ESR spectrum of $[CuL^1](PF_6)_2$.

Table 3. (a) Hydrolysis of 4-Nitrophenyl Phosphate by Copper(II) and Nickel(II) Complexes, (b) Catecholase Activity of Copper(II) Complexes

Complexes	(a) Rate constant (k) $k \times 10^3$ min^{-1}	(b) Rate constant (k) $k \times 10^3$ min^{-1}
$[NiL^1](PF_6)_2$	10.0	—
$[NiL^2](PF_6)_2$	14.0	—
$[CuL^1](PF_6)_2$	6.3	9.4
$[CuL^2](PF_6)_2$	12.2	13.4

Measured spectrophotometrically in DMF medium. Concentration of the complex 1×10^{-3} M, concentration of *p*-nitrophenyl phosphate 1×10^{-1} M, and concentration of pyrocatechol 1×10^{-1} M.

$\log(A_\infty/A_\infty - A_t)$ vs time for the complexes is shown in Fig. 5.

Hydrolysis of Phosphate Ester. Copper(II) and nickel(II) complexes were subjected to hydrolysis of the phosphate ester. The rate of hydrolysis of 4-nitrophenyl phosphate for $[NiL^2]$ (14×10^{-3} min^{-1}) was slightly higher than $[NiL^1]$ (10×10^{-3} min^{-1}). The catalytic activities of the nickel(II) complexes were found to increase with an increase in N-alkylation, which causes a distortion of the geometry of the metal ion in the complexes and favors axial substrate coordination. A similar trend was also observed for copper(II) complexes. From the results, it is found that the Ni(II) complexes have a rate-constant value higher than that of the Cu(II) complexes for phosphate hydrolysis.

Oxidation of Catechol (Catecholase Activity). A plot of $\log(A_\infty/A_\infty - A_t)$ vs time for the oxidation of catechol to quinone by the copper(II) complexes is shown in Fig. 6. The rate-constant values are also reported in Table 3. The complex $[CuL^2](PF_6)_2$ has higher activities (13.4×10^{-3} min^{-1}) than complex $[CuL^1](PF_6)_2$ (9.4×10^{-3} min^{-1}). The oxidation of catechol to *o*-quinone by the complexes was found to increase as the macrocyclic N-methylation increases.[39,40] N-alkylation may cause a greater distortion of the geometry of the complexes. This geometry may favour substrate coordination in the axial position, which in turn increases the reaction rate. It is expected that the catalytic activity of complexes with side arms is suppose to be higher than that of complexes with no side arms due to the flexibility resulting from the distorted geometry.

The catecholase activity of non-substituted macrocyclic copper(II) complexes has a rate-constant value of 2.9×10^{-3} min^{-1}. The catecholase activity of the copper(II) complex reported in the present study is 9.4×10^{-3} min^{-1}, which is higher than that of the non-substituted macrocyclic complexes. This higher catalytic activity may be due to a greater distortion in the geometry of the substituted macrocyclic complexes than the non-substituted macrocyclic complexes. This distortion in geometry is inferred from the wavelength of the absorption of the d–d transition of the complexes. The side-arm substituted copper(II) complex (CuL^1) has a d–d band at 547 nm, and the non-substituted macrocyclic copper(II) has a d–d band at 517 nm. The side-arm substituted nickel(II) complex (NiL^1) has a d–d band at 480 nm and the non-substituted macrocyclic nickel(II) complex has a d–d band at 471 nm.[41] The red shift in the wavelength indicates that the coordination geometry in the side-arm substituted complexes is more distorted than that of the non-substituted complexes. It is evidenced from the literature,[42] that the rate constant for the more-distorted complexes is higher than that of the less-distorted complexes.

From these studies, it is well understood that substitution in the ring nitrogen atom deviates the planarity of the ring, which

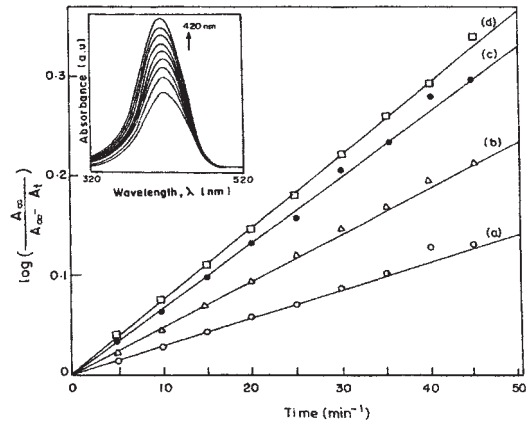


Fig. 5. Hydrolysis of 4-nitrophenyl phosphate by copper(II) and nickel(II) complexes. (Inset: Absorbance maximum at 420 nm.) (a) $[CuL^1](PF_6)_2$; (b) $[NiL^1](PF_6)_2$; (c) $[CuL^2](PF_6)_2$; (d) $[NiL^2](PF_6)_2$.

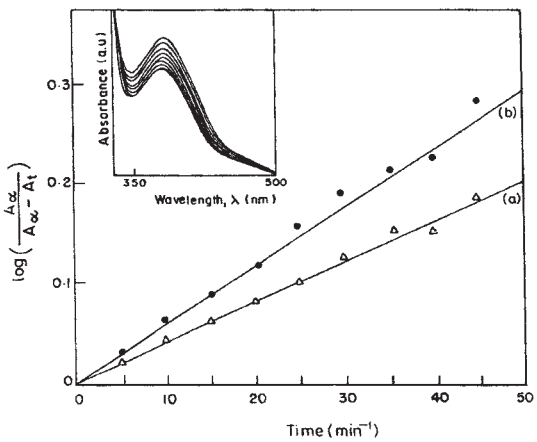


Fig. 6. Catecholase activity of the copper(II) complexes. (Inset: Absorbance maximum at 390 nm.) (a) $[CuL^1](PF_6)_2$; (b) $[CuL^2](PF_6)_2$.

causes a distortion in the geometry of the complex. This alters the electrochemical, magnetic and catalytic properties of the complexes.

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Supplementary Material. Full crystal data and structure refinement details of the atomic coordinates, equivalent isotropic displacement parameters, full interatomic distances and angles anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters for ligand L^1 CCDC No. 196207 are available from the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk [or] www.http//www.ccdc.cam.ac.uk.)

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