

# Synthesis, electrochemical, magnetic, catalytic and antimicrobial studies of N-functionalized cyclam based trinuclear copper(II) and nickel(II) complexes

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**Abstract** Trinuclear copper(II) and nickel(II) complexes have been prepared by using Schiff base ligands derived from 1,8-[bis(3-formyl-2-hydroxy-5-methyl) benzyl]-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane, and 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane with aliphatic and aromatic diamines. All the complexes were characterized by elemental and spectroscopic analysis. Electrochemical studies of the copper(II) complexes in DMF solution show three irreversible one electron reduction process around  $E_{pc}^1 = -0.59$  to  $-0.80$  V,  $E_{pc}^2 = -0.89$  to  $-1.14$  V and  $E_{pc}^3 = -1.17$  to  $-1.29$  V, and for nickel(II) complexes it is around  $E_{pc}^1 = -0.63$  to  $-0.77$  V,  $E_{pc}^2 = -1.20$  to  $-1.35$  V and  $E_{pc}^3 = -1.60$  to  $-1.74$  V. ESR spectra and magnetic moments of the trinuclear Cu(II) complexes show the presence of antiferromagnetic coupling. Cryomagnetic investigation of the trinuclear copper(II) complexes show that the observed  $-2J$  values are in the range of  $116$ – $178$   $\text{cm}^{-1}$ . The rate constants for hydrolysis of 4-nitrophenylphosphate by the complexes are in the range of  $2.68 \times 10^{-2}$  to  $9.81 \times 10^{-2}$   $\text{min}^{-1}$ . The rate constants values for the catecholase activity of the copper(II) complexes fall in the range of  $3.03 \times 10^{-2}$  to  $9.32 \times 10^{-2}$   $\text{min}^{-1}$ . All the complexes.

**Keywords** Tricompartamental ligand · Cyclam · Copper(II) complexes · Catecholase · Cyclicvoltammetry · Antifungal activity

## Introduction

Polyamine macrocyclic ligands with one or more pendant arms containing a potentially coordinating group such as carboxylate, pyridine, amine, etc. have been prepared but they generally have been found not to bind a second metal ion [1]. N-functionalized derivatives of these ligands continue to be explored in a variety of contexts such as molecular recognition of DNA and RNA [2] depending upon their coordination properties of the pendant donor groups. In recent years, there has been a considerable interest in the synthesis of polyamine ligands able to bind two or more metal ions in close proximity. Special attention has been devoted to macrocyclic ligands, because of their ability to enforce a high degree of reorganization on metal coordination [3–5]. In particular, polyamine macrocyclic ligands with a large number of donors, appropriate cavity size, shape and dimension may be able to hold two or more metal centers at short distances, mimicking the multinuclear metal arrays at the active sites of several metalloenzymes. Asymmetric nature of a number of homotrimeric transition metal-derived metallobiosite and the ability of the individual metal ions to have quite distinct roles in functioning of metalloenzymes has led to a search for newly designed unsymmetrical ligands which will give trinuclear complexes capable of acting as models for the metallobiosite [6]. The presence of multinuclear copper centers at the active sites of copper oxidases and oxygen-transport proteins continues to stimulate interest in model

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compounds which closely mimic the structure, properties and function of these biosites [7, 8].

The present work describes the synthesis and characterization of trinuclear copper(II) and nickel(II) complexes derived from *N*-functionalized cyclam based tricompartmental ligands. These ligands are capable of binding upto three metal centers in close proximity.

## Experimental

### Materials and methods

5-methyl salicylaldehyde [9], 3-chloromethyl-5-bromo salicylaldehyde [10], 1,4,8,11-tetraazatricyclo[9.3.1.1<sup>4,8</sup>]hexadecane [11], 1,8-[bis(3-formyl-2-hydroxy-5-methyl)benzyl]-4,11 diazaniatricyclo[9.3.1.1<sup>4,8</sup>]hexadecane dichloride [12], 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-4,11 diazaniatricyclo[9.3.1.1<sup>4,8</sup>]hexadecane dichloride were prepared by the literature method [12] using 5-bromo salicylaldehyde instead 5-methyl salicylaldehyde. Analytical grade methanol, acetonitrile and dimethylformamide were purchased from Qualigens and used as such. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallised 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 were used as received.

### Synthesis of macrocyclic tricompartmental ligands (Scheme 1)

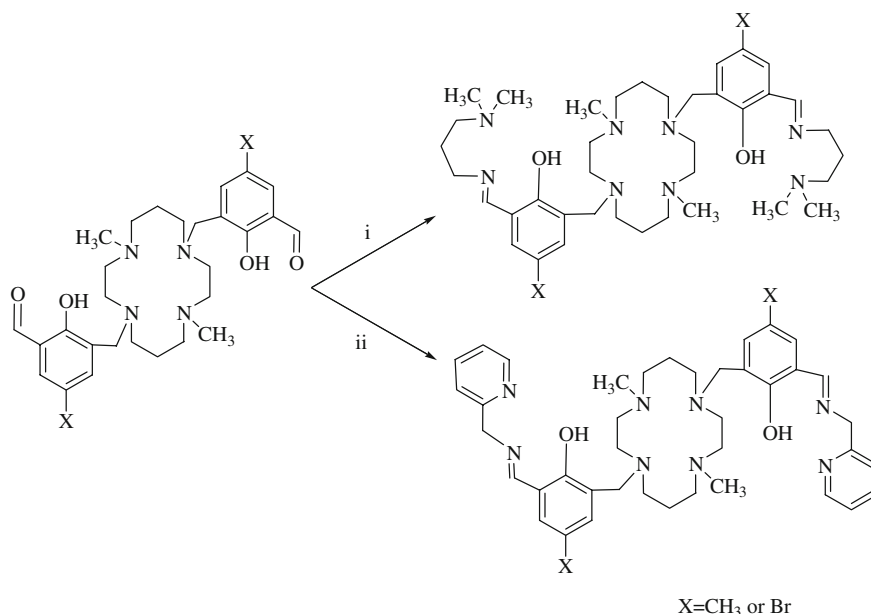
#### Synthesis of ligand *L*<sup>1</sup>

A solution of 1,8-[bis(3-formyl-2-hydroxy-5-methyl)benzyl]-4,11-dimethyl-1,4,8,11 tetraazacyclotetradecane (PC 1) (1.05 g, 0.002) in methanol (60 mL) was refluxed with 2 equivalents of *N,N*-dimethyl-1,3-propanediamine (0.02 g, 0.002 mol) for 8 h at 70 °C. Then the solvent was evaporated under reduced pressure. The crude compound was purified by column chromatography using chloroform:methanol (98:2) as eluent. Yield: 0.96 g (69%); M.p.: 292 °C (dec); Selected IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3397  $\nu(\text{OH})$ , 1625 [s,  $\nu(\text{C}=\text{N})$ ]; <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 1.70–1.74 (m, 8H,  $\beta\text{-CH}_2$ ), 2.28 (s, 6H Ar-CH<sub>3</sub>), 2.41–2.49 (m, 20H, N-CH<sub>2</sub>), 2.65 (m, 18H, N-CH<sub>3</sub>), 3.65 (m, 4H), 4.13 (s, 4H, N-CH<sub>2</sub>-Ar), 7.13 (d, 4H, Ar-H), 8.45 (s, 2H, Ar-CH=N), 13.76 (s, Ar-OH); <sup>13</sup>CNMR:  $\delta$  (ppm in DMSO-D<sub>6</sub>): 20.3, 20.6, 28.4, 29.0, 32.1, 35.3, 46.9, 49.1, 50.1, 51.6, 52.0, 53, 57.4, 118.5, 124.6, 127.0, 131.3, 135.7, 158.1, 163.0;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) in DMF: 274 (20,220).

#### Synthesis of ligand *L*<sup>2</sup>

H<sub>2</sub>L<sup>2</sup> was prepared following the previous method using 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane (PC-2) (1.31 g, 0.002) and *N,N*-dimethyl-1,3-propanediamine (0.02 g, 0.002 mol)

**Scheme 1** Synthesis of tricompartmental ligands



(i) *N,N*-dimethyl-1,3-propanediamine, CH<sub>3</sub>OH (ii) 2-(aminomethyl)pyridine, CH<sub>3</sub>OH

instead of (PC-1). Yield: 1.1 g (67%); M.p.: 290 °C (dec); Selected IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3407  $\nu(\text{OH})$ , 1630 [s,  $\nu(\text{C}=\text{N})$ ];  $^1\text{H NMR } \delta$  (ppm in  $\text{CDCl}_3$ ): 1.50–1.57 (m, 8H,  $\beta\text{-CH}_2$ ), 2.53–2.58 (m, 20H, N- $\text{CH}_2$ ), 2.73 (m, 18H, N- $\text{CH}_3$ ), 3.60 (m, 4H), 4.1 (s, 4H, N- $\text{CH}_2\text{-Ar}$ ), 7.43 (d, 4H, Ar-H), 8.29 (s, 2H, Ar- $\text{CH}=\text{N}$ ), 12.78 (s, Ar-OH);  $^{13}\text{CNMR}:\delta$  (ppm in  $\text{DMSO-D}_6$ ): 27, 30.1, 49.7, 54.7, 55.2, 55.8, 60.2, 124.1, 124.8, 126.5, 133.0, 136.4, 157.9, 160.0;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) in DMF: 278 (21,340).

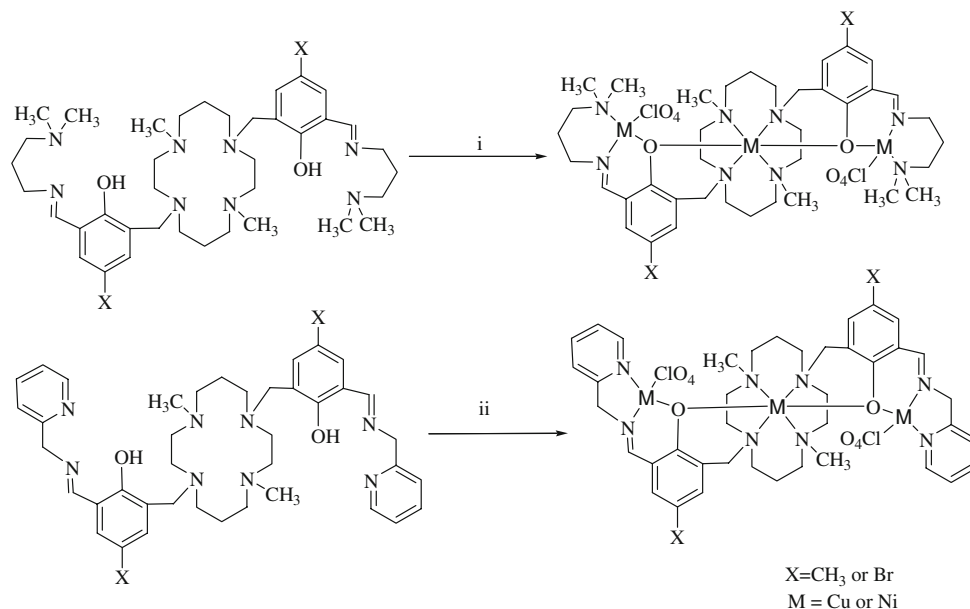
#### Synthesis of ligand $L^3$

$\text{H}_2\text{L}^3$  was prepared by following the above method, using the (PC-1) (1.05 g, 0.002) and 2-(aminomethyl)pyridine (0.22 g, 0.002 mol). Yield: 0.95 g (67%); M.p.: 289 °C (dec); Selected IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3405  $\nu(\text{OH})$ , 1610 [s,  $\nu(\text{C}=\text{N})$ ];  $^1\text{H NMR } \delta$  (ppm in  $\text{CDCl}_3$ ): 1.87–1.95 (m, 4H,  $\beta\text{-CH}_2$ ), 2.41 (s, 6H Ar- $\text{CH}_3$ ), 2.45–2.53 (m, 16H, N- $\text{CH}_2$ ), 3.31 (s, 4H), 3.37 (s, 6H, N- $\text{CH}_3$ ), 3.57 (s, 4H, N- $\text{CH}_2\text{-Ar}$ ), 6.79–6.85 (m, 8H Ar-H), 7.13 (d, 4H, Ar-H), 8.65 (s, 2H, Ar- $\text{CH}=\text{N}$ ), 11.49 (s, Ar-OH);  $^{13}\text{CNMR}:\delta$  (ppm in  $\text{DMSO-D}_6$ ): 24.2, 24.2, 34.3, 38.1, 46.7, 53.3, 58.5, 118.6, 119.2, 122.8, 123.3, 124.7, 125.2, 126.4, 130.0, 157.1, 159.2, 161.5;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) in DMF: 270 (21,340).

#### Synthesis of ligand $L^4$

$\text{H}_2\text{L}^4$  was prepared by following the above method using (PC-2) (1.31 g, 0.002) and 2-(aminomethyl)pyridine (0.22 g, 0.002 mol). Yield: 0.91 g (55%); M.p.: 292 °C

**Scheme 2** Synthesis of trinuclear copper(II) and nickel(II) complexes



i,ii) 1.  $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{Et}_3\text{N}$ . 2.  $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

(dec); Selected IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3398  $\nu(\text{OH})$ , 1618 [s,  $\nu(\text{C}=\text{N})$ ];  $^1\text{H NMR } \delta$  (ppm in  $\text{CDCl}_3$ ): 1.65–1.70 (m, 4H,  $\beta\text{-CH}_2$ ), 2.38–2.41 (m, 16H, N- $\text{CH}_2$ ), 3.31 (s, 4H), 3.39 (s, 6H, N- $\text{CH}_3$ ), 3.61 (s, 4H, N- $\text{CH}_2\text{-Ar}$ ), 6.95–6.98 (m, 8H Ar-H), 7.23 (d, 4H, Ar-H), 8.67 (s, 2H, Ar- $\text{CH}=\text{N}$ ), 12.35 (s, Ar-OH);  $^{13}\text{CNMR}:\delta$  (ppm in  $\text{DMSO-D}_6$ ): 21.7, 24.6, 34.0, 38.3, 45.0, 46.7, 53.2, 58.5, 117.4, 118.3, 122.8, 123.8, 124.7, 125.2, 128.0, 130.5, 157.0, 157.8, 165.1;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) in DMF: 278 (21,340).

Synthesis of trinuclear copper(II) and nickel(II) complexes (Scheme 2)

#### General procedure:

A solution of copper(II) perchlorate hexahydrate or nickel(II) perchlorate hexahydrate (0.002 mol) in methanol (50 mL) was added to a hot solution of the ligand (0.0015 mol) in methanol (50 mL). The mixture was refluxed for 1 h. After 1 h, another 2 equivalents of corresponding metal(II) perchlorate (0.002 mol) in methanol and triethylamine (0.003 mol) in methanol (50 mL) was added and the solution was refluxed for 24 h. The resulting solution was filtered whilst hot and allowed to stand at room temperature. After slow evaporation of the solvent at 25 °C, dark green compound was collected by filtration, which was recrystallised from acetonitrile, and dried in vacuum.

$[\text{Cu}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$ : Dark green compound; Yield: 0.89 g (50%); FAB mass ( $m/z$ ) (%):  $[\text{Cu}_3\text{L}^1(\text{ClO}_4)]\text{ClO}_4^+$  1180. Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1628 [s,  $\nu(\text{C}=\text{N})$ ],

1093, 1087 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1103 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 632 (s);  $g = 2.10$ ,  $\mu_{\text{eff}}$ : 1.47.

**[Ni<sub>3</sub>L<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 0.93 g (53%); Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1633 [s,  $\nu(\text{C}=\text{N})$ ], 1093, 1085 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1105 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 630 (s).

**[Cu<sub>3</sub>L<sup>2</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 0.93 g (55%); Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1623 [s,  $\nu(\text{C}=\text{N})$ ], 1093, 1085 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1100 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 624 (s);  $g = 2.11$ ,  $\mu_{\text{eff}}$ : 1.51.

**[Ni<sub>3</sub>L<sup>2</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 0.97 g (58%); FAB mass (m/z) (%): [Ni<sub>3</sub>L<sup>2</sup>(ClO<sub>4</sub>)<sup>+</sup> 1195. Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1610 [s,  $\nu(\text{C}=\text{N})$ ], 1105, 1091 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1107 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 634 (s).

**[Cu<sub>3</sub>L<sup>3</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 0.95 g (53%); FAB mass (m/z) (%): [Cu<sub>3</sub>L<sup>3</sup>(ClO<sub>4</sub>)<sup>+</sup> 1092. Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1643 [s,  $\nu(\text{C}=\text{N})$ ], 1092, 1098 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1105 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 630 (s);  $g = 2.10$ ,  $\mu_{\text{eff}}$ : 1.49.

**[Ni<sub>3</sub>L<sup>3</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 1.00 g (56%); Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1628 [s,  $\nu(\text{C}=\text{N})$ ], 1097, 1085 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 1103 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 629 (s).

**[Cu<sub>3</sub>L<sup>4</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 0.95 g (56%); Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 3290  $\nu(\text{NH})$ , 1632 [s,  $\nu(\text{C}=\text{N})$ ], 1093, 1087 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1101 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 625 (s);  $g = 2.10$ ,  $\mu_{\text{eff}}$ : 1.47.

**[Ni<sub>3</sub>L<sup>4</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Dark green compound; Yield: 0.98 g (58%); Selected IR data (KBr) ( $\nu/\text{cm}^{-1}$ ): 1627 [s,  $\nu(\text{C}=\text{N})$ ], 1090, 1084 (w) [ $\nu(\text{ClO}_4^-)$  coordinated], 1100 (w) [ $\nu(\text{ClO}_4^-)$  uncoordinated], 626 (s).

#### Analytical and physical measurements

Elemental analysis of the complexes was obtained using a Haereus CHN rapid analyzer. <sup>1</sup>H NMR spectra were recorded using a JEOL GSX 400 MHz NMR spectrometer. Electronic spectra studies were obtained on a Hitachi 320 spectrophotometer in the range 200–1,100 nm. IR spectra were recorded on a Shimadzu FTIR 8300 series spectrophotometer on KBr disks in the range 4,000–400  $\text{cm}^{-1}$ . Molar conductivities were measured using an Elico digital conductivity bridge model CM-88 using freshly prepared solutions of the complex in DMF. Atomic absorption spectra were recorded using a Varian spectra AA-200 model atomic absorption spectrophotometer. Mass spectra were obtained on a JEOL SX-102 (FAB) mass spectrometer. 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 a Pt wire was used as the auxiliary electrode. The ferrocene/ferrocenium (1+) couple was used as an internal standard with E<sub>1/2</sub> couple under the experimental conditions of 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 studies were performed on a PAR model 155 vibrating sample magnetometer in the temperature range 77–300 K, and the instrument was calibrated using metallic Ni as supplied with the instrument. X-band ESR spectra were recorded using DMF as a solvent at liquid nitrogen temperature on a Varian EPR-E 112 spectrometer with diphenylpicrylhydrazine (DPPH) as the reference. The catalytic oxidation of catechol to o-quinone and the hydrolysis of 4-nitrophenylphosphate by the copper(II) complexes were studied in a 10<sup>-3</sup> M dimethylformamide solution. The reaction was followed spectrophotometrically by choosing the strongest absorption band of o-quinone at 390 nm and monitoring the increase in the absorbance and the hydrolysis of 4-nitrophenylphosphate 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  $\log(A_x/A_x - A_t)$  versus time was made for each complex and the rate constants for the catalytic oxidation and the hydrolysis of 4-nitrophenylphosphate were calculated.

#### Results and discussion

The analytical data of the ligands and the complexes are given in Table 1. The coordination geometries of the complexes were deduced from their spectra. Conductivity measurements of ( $\Lambda_m$ , 87–97  $\text{S cm}^2 \text{mol}^{-1}$ ) all the complexes show that they are 1:2 electrolytes in DMF solution. A broad spectrum with no hyperfine splitting was obtained for the trinuclear copper(II) complexes with  $g = 2.05$ – $2.11$  indicating the presence of an antiferromagnetic interaction [2.8] between the three copper ions.

#### FTIR spectral studies

The FTIR spectra of free macrocycles show a band in the region 3,395–3,407  $\text{cm}^{-1}$ , assigned to the phenolic  $\nu(\text{OH})$  group. The absence of a peak around 3,400  $\text{cm}^{-1}$  in all the complexes indicates the absence of phenolic  $\nu(\text{OH})$  due to deprotonation followed by complexation [13]. The FTIR spectra of the ligands H<sub>2</sub>L<sup>1</sup>–H<sub>2</sub>L<sup>4</sup> show a sharp band in the region 1,610–1,643  $\text{cm}^{-1}$  due to the presence of  $\nu(\text{C}=\text{N})$  group [14–16]. All the complexes showed two sharp peaks near 1,100  $\text{cm}^{-1}$ , perchlorate ions [14–16]. Only one

**Table 1** Analytical and conductance data of the ligands and the complexes

No.	Compound	Cald (found) %				$(\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
		M	C	H	N	
1	L <sup>1</sup>		69.3 (69.3)	9.9 (9.8)	16.2 (16.1)	
2	L <sup>2</sup>		55.5 (55.4)	7.6 (7.6)	13.6 (13.5)	
3	L <sup>3</sup>		71.6 (71.5)	8.0 (7.9)	15.9 (15.9)	
4	L <sup>4</sup>		57.6 (57.5)	6.0 (6.0)	13.4 (13.4)	
5	[Cu <sub>3</sub> L <sup>1</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	14.9 (14.8)	37.5 (37.5)	5.2 (5.1)	8.8 (8.8)	95
6	[Cu <sub>3</sub> L <sup>2</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	13.5 (13.5)	32.4 (32.4)	4.3 (4.2)	7.9 (7.9)	77
7	[Cu <sub>3</sub> L <sup>3</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	14.8 (14.7)	39.1 (39.0)	4.2 (4.2)	8.7 (8.6)	98
8	[Cu <sub>3</sub> L <sup>4</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	13.4 (13.4)	33.8 (33.8)	3.4 (3.3)	7.9 (7.9)	89
9	[Ni <sub>3</sub> L <sup>1</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	13.9 (13.9)	37.9 (37.9)	5.3 (5.2)	8.9 (8.9)	93
10	[Ni <sub>3</sub> L <sup>2</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	12.6 (12.6)	32.7 (32.7)	4.4 (4.4)	8.0 (8.0)	89
11	[Ni <sub>3</sub> L <sup>3</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	13.8 (13.7)	39.5 (39.4)	4.3 (4.2)	8.8 (8.7)	87
12	Ni <sub>3</sub> L <sup>4</sup> (ClO <sub>4</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	12.5 (12.5)	34.2 (34.1)	3.4 (3.4)	8.0 (7.9)	93

**Table 2** Electronic spectral data of the trinuclear copper(II) and nickel(II) complexes

Complexes	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	
	d-d	Charge transfer
[Cu <sub>3</sub> L <sup>1</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	779 (96)	395 (12,200), 273 (21,000)
[Cu <sub>3</sub> L <sup>2</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	817 (102)	397 (11,240), 301 (18,200)
[Cu <sub>3</sub> L <sup>3</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	848 (110)	391 (12,200), 276 (20,100)
[Cu <sub>3</sub> L <sup>4</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	875 (130)	403 (11,300) 278 (20,800)
[Ni <sub>3</sub> L <sup>1</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1,075 (28), 884 (56), 628 (135)	398 (12,300), 340 (19,700)
[Ni <sub>3</sub> L <sup>2</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1,084 (28), 870 (76), 604 (153)	397 (12,100), 338 (18,700)
[Ni <sub>3</sub> L <sup>3</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1,015 (42), 718 (68), 654 (127)	415 (10,600), 324 (19,700)
[Ni <sub>3</sub> L <sup>4</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1,058 (30), 721 (76), 660 (167)	410 (12,300), 312 (18,600)

among these two peaks shows splitting consistent with the presence of both coordinate and uncoordinated perchlorate [14–17]. Apart from this an additional peak is observed in the range of 624–630 cm<sup>-1</sup> is assigned to a perchlorate bending vibration. The appearance of bands in the region of 1,530–1,545 cm<sup>-1</sup> in all the complexes suggests phenoxide bridging with the metal ions [14–16].

#### <sup>1</sup>H NMR spectral analysis

The <sup>1</sup>H NMR spectra of all the free macrocycles show a singlet at  $\delta$  11.49–13.76 assigned to phenolic OH protons. A singlet in the region of  $\delta$  8.29–8.67 due to CH=N– (imine) protons. A peak in the region of  $\delta$  3.57–4.13 for all the macrocycle is assigned to the benzylic proton (Ar–CH<sub>2</sub>) in addition to other aliphatic and aromatic protons.

#### Mass spectral analysis

The FAB mass spectra were obtained for the complexes [Cu<sub>3</sub>L<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Ni<sub>3</sub>L<sup>2</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Cu<sub>3</sub>L<sup>3</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. The spectra show the presence of three

copper atoms in the complexes with the molecular ion peak at  $m/z = 1180$ , 1195 and 1092 respectively, which are assigned to the {[Cu<sub>3</sub>L<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>}<sup>+</sup>, {[Ni<sub>3</sub>L<sup>2</sup>(ClO<sub>4</sub>)<sub>2</sub>]}<sup>+</sup> and {[Cu<sub>3</sub>L<sup>3</sup>(ClO<sub>4</sub>)<sub>2</sub>]}<sup>+</sup> ions.

#### Electronic spectral analysis

The electronic spectra data of the complexes were given in Table 2. Electronic spectra of the complexes were obtained in DMF. The electronic spectra of all the complexes exhibit three main features. One or two peaks in the range of 250–320 nm is assigned to the intra ligand transition ( $\pi-\pi^*$ ). An intense peak in the range of 350–412 nm is due to ligand-to-metal charge transfer. All the copper(II) complexes show the d–d transition in the range of 779–875 nm, which are characteristic of Cu<sup>2+</sup> in the 6/4 coordination environment [18]. Even though the metal ions are present in two different compartments (N<sub>4</sub>O<sub>2</sub> and N<sub>2</sub>O), we observed a broad d–d band that could not be further resolved. The d–d transition for the nickel(II) complexes show three main bands in the region of 604–1,084 nm, which is characteristic of Ni<sup>2+</sup> in the 6/4 coordination environment [19]. The

appearance of the spectra bear similarities with those for octahedrally coordinated Ni(II) ions, with the assignment of the three most intense bands  ${}^3A_{2g} \rightarrow {}^3T_{2g}(P)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  to the spin allowed transitions from the ground state of an octahedrally coordinated  $d^8$  ion. The charge transfer and the visible absorption spectra of the present complexes (tetra *N*-substituted cyclam) falls into higher wavelength region than the complexes derived from 1,8-disubstituted cyclam ligands [14c].

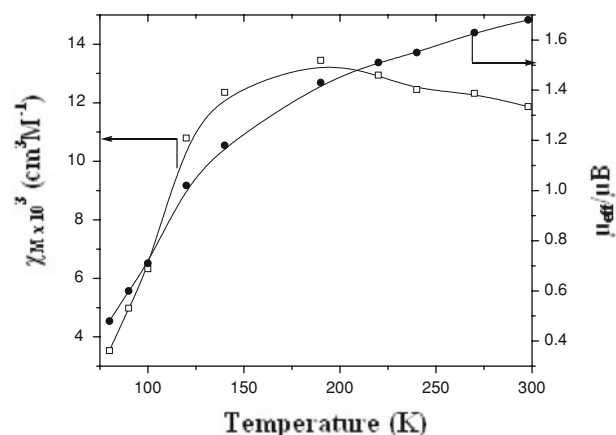
### Magnetic studies

All the copper(II) complexes show magnetic moments in the range of 1.51 to 1.54 B.M., which are less than the total spin-only values. The lowering of these magnetic moments is due to antiferromagnetic coupling by superexchange through the phenolic oxygen atoms [20]. To evaluate the singlet–triplet energy separation ( $-2J$ ), variable temperature magnetic studies for the trinuclear copper(II) complexes were performed in the temperature range 78–298 K, and the experimental magnetic susceptibility values were fitted to the modified Bleaney–Bowers equation [21, 22].

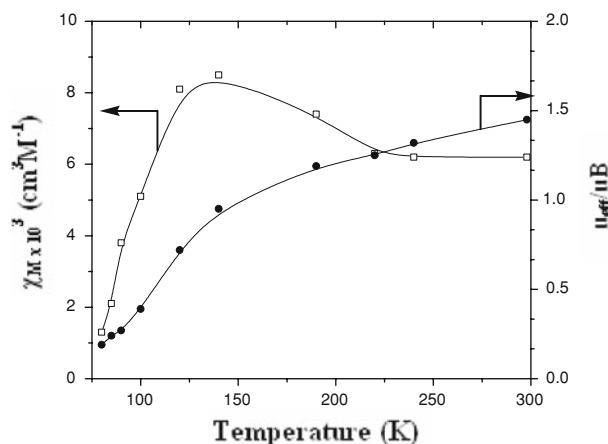
$$\chi_m = \left\{ Ng^2 \beta^2 / 3kT \right\} \left[ 3 + \exp(-2J/kT) \right]^{-1} (1 - P) + (0.45P/T) + N_A$$

The temperature dependence of magnetic properties for the copper(II) complexes of  $L^1$  and  $L^3$  are shown in Figs. 1 and 2.

Since, the nature of the donor atoms and phenoxide bridging groups in all the complexes are same, a comparison of the magnetic properties based on the side arm of the imine compartment would be useful in discovering the possible effects on spin exchange interactions in the complexes. The antiferromagnetic exchange interaction ( $-2J$ ) for the trinuclear copper(II) complexes of  $L^1$  ( $-2J = 116 \text{ cm}^{-1}$ ) is lower than that of  $L^3$  ( $-2J = 178 \text{ cm}^{-1}$ ). The coordination



**Fig. 1** Temperature-dependent magnetic properties for  $[Cu_3L^1(CIO_4)_2](CIO_4)_2$  where filled circle is  $\mu_{\text{eff}}/\mu_B$  and open square is  $\chi_M$



**Fig. 2** Temperature-dependent magnetic properties for  $[Cu_3L^3(CIO_4)_2](CIO_4)_2$  where filled circle is  $\mu_{\text{eff}}/\mu_B$  and open square is  $\chi_M$

geometry around the copper atom of the  $[Cu_3L^1(CIO_4)_2](CIO_4)_2$  complex is perhaps more distorted due to more flexible nature [21–24] of the *N,N*-dimethyl-1,3-propanediamine side arm, when compared with the 2-(aminomethyl)pyridine side arm. This distortion in geometry around the metal ion increases the dihedral angle between the copper magnetic orbitals, which results lower  $-2J$  values. The most probable reason for the strong antiferromagnetic exchange interaction in the complex of  $L^3$  may be the greater planarity induced by the aromatic 2-(aminomethyl) pyridine group.

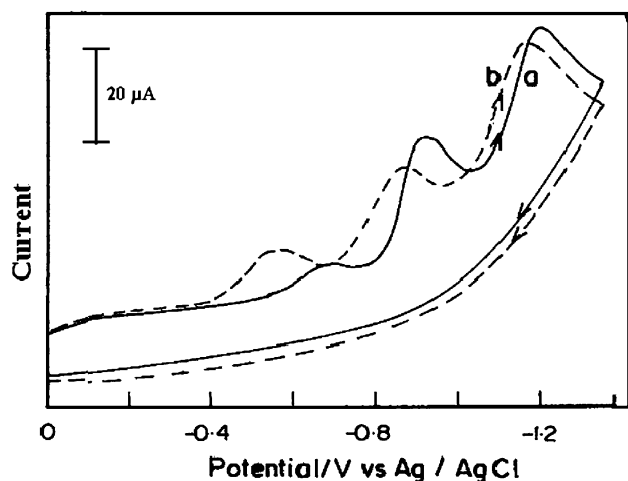
The lower  $-2J$  value for the copper(II) complexes of  $L^2$  ( $-2J = 96 \text{ cm}^{-1}$ ) compared to  $L^1$  complex may be due to the electron withdrawing group (Br). The electron withdrawing group (Br) in the para position of the phenolic ring in the complex of  $L^2$  decreases the electron density on the copper centers and weakens the Cu–O bond and reduces the spin exchange interaction [23, 24].

### Electrochemical properties

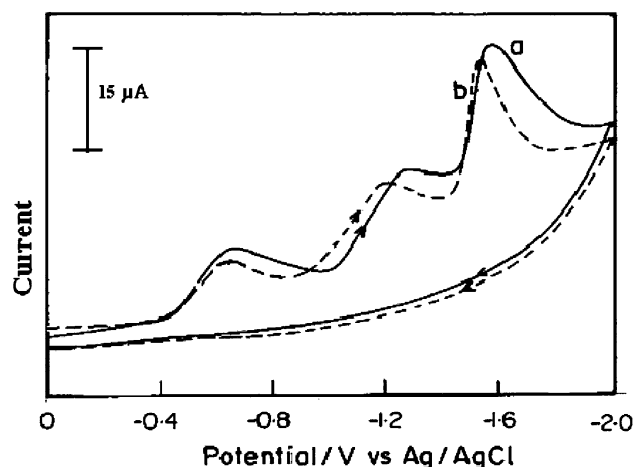
Electrochemical behavior of the complexes was studied by cyclic voltammetry in DMF containing  $10^{-1} \text{ M}$  tetra(*n*-butyl)ammonium perchlorate over the range of 0 to  $-1.4 \text{ V}$ . Cyclic voltammograms for copper(II) complexes are shown in Figs. 3 and 4. The electrochemical data of the complexes were given in Table 3.

#### Reduction process at negative potential

All the copper(II) complexes show three irreversible reduction waves in the cathodic potential region in the range of  $-0.59$  to  $-0.80 \text{ V}$ ,  $-0.89$  to  $-1.14$  and  $-1.17$  to  $-1.29 \text{ V}$ . Controlled potential electrolysis was also carried out at  $100 \text{ mV}$  more negative to the cathodic peak, and the

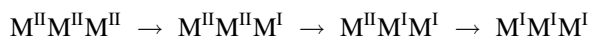


**Fig. 3** Cyclic voltammogram of the copper(II) complexes: (reduction process) (a)  $[\text{Cu}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$  (b)  $[\text{Cu}_3\text{L}^2(\text{ClO}_4)_2](\text{ClO}_4)_2$



**Fig. 4** Cyclic voltammogram of the nickel(II) complexes: (reduction process) (a)  $[\text{Ni}_3\text{L}^3(\text{ClO}_4)_2](\text{ClO}_4)_2$  (b)  $[\text{Ni}_3\text{L}^4(\text{ClO}_4)_2](\text{ClO}_4)_2$

results show that each wave corresponds to one-electron transfer process, as follows:



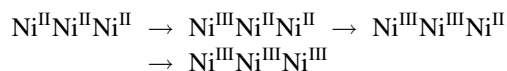
The first and second reduction potential in the range of ( $E_{\text{pc}}^1 - 0.59$  to  $-0.80$ ; and  $E_{\text{pc}}^2 - 0.89$  to  $-1.14$  V) are attributed to the reduction of copper(II) in the imine compartment. The third reduction wave in the range of  $-1.17$  to  $-1.29$  V, is attributed to the reduction of copper(II) in the amine (cyclam) compartment. From the results it is observed that the complex of the ligand  $\text{L}^3$  and  $\text{L}^4$  get reduced at high negative potential due to greater planarity [25, 26] of the complexes induced by the 2-(aminomethyl)pyridine group and conjugation [27, 28]. The reduction potential of the complexes is less negative ( $-0.59$  to  $-0.89$  V) when compared to the di-N-substituted cyclam complexes ( $-0.73$  to  $-0.98$  V) [14c]. This may be

due to the presence of two trans nitrogen's in the cyclam ring, causing more distortion of the geometry of the complexes which ease reduction.

Further, the complexes of the ligands  $\text{L}^{2\&4}$  undergo reduction at less negative potential compared to the complexes of  $\text{L}^{1\&3}$ . The easy reduction of the complexes of  $\text{L}^{2\&4}$  may be due to the presence of electron-withdrawing substituent (Br) at the para position to the phenoxide oxygen [29, 30]. Literature reports, [29, 30] also suggest that the complexes containing electron withdrawing groups get reduced at less negative potential than complexes, which contain electron donating substituent.

#### Oxidation process at anodic potential

All the trinuclear nickel(II) complexes show three irreversible one electron oxidation processes in the range of 0 to  $+1.6$  V. The cyclic voltammogram of the trinuclear nickel(II) complexes in the anodic potential region are shown in Fig. 5. The electrochemical data were given in Table 3 The three oxidation processes for nickel(II) complexes as follows,



From the results it is observed that the para substitution and the side arm influence the oxidation potential to less extend only.

#### Kinetic studies

##### Hydrolysis of 4-nitrophenylphosphate

The catalytic activity of the trinuclear copper(II) and nickel(II) complexes with respect to hydrolysis of 4-nitrophenylphosphate was determined spectrophotometrically as described previously [14–16]. A linear relationship for all the complexes shows a first-order dependence on the complex concentration. Figure 6 shows the results hydrolysis of 4-nitrophenylphosphate by and  $[\text{Ni}_3\text{L}^{1\&2}(\text{ClO}_4)_2](\text{ClO}_4)_2$ . The observed initial rate constant values for the complexes are given in Table 3.

##### Oxidation of pyrocatechol (catecholase activity)

The catecholase activity of the copper(II) complexes was studied using pyrocatechol as model substrate by following our previous reports [31]. The observed kinetics shows a first-order dependence on the complex concentration. Figure 7 shows the plots of  $\log(A_\infty/A_\infty - A_t)$  versus time for catecholase activity of the  $[\text{Cu}_3\text{L}^{1\&2}(\text{ClO}_4)_2](\text{ClO}_4)_2$ . The initial rate constant values for the copper(II) complexes are given in Table 3. It is remarkable that the reactivity of the

**Table 3** Electrochemical<sup>a</sup> (reduction at cathodic potential), hydrolysis of 4-nitrophenylphosphate<sup>b</sup> and catecholase<sup>b</sup> activity data of the trinuclear copper(II) complexes

No.	Complexes	$E_{pc}^1$ (V)	$E_{pc}^2$ (V)	$E_{pc}^3$ (V)	Rate constant (k) ( $\times 10^{-2}$ ) $\text{min}^{-1}$	
					NPP	Catecholase
1	$[\text{Cu}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.69	-0.92	-1.20	7.58	8.15
2	$[\text{Cu}_3\text{L}^2(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.59	-0.89	-1.17	9.81	9.32
3	$[\text{Cu}_3\text{L}^3(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.80	-1.14	-1.29	3.98	3.03
4	$[\text{Cu}_3\text{L}^4(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.59	-0.93	-1.23	4.23	3.43
5	$[\text{Ni}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.89	-1.26	-1.72	7.44	–
6	$[\text{Ni}_3\text{L}^2(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.77	-1.20	-1.60	8.47	–
7	$[\text{Ni}_3\text{L}^3(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.77	-1.35	-1.74	2.68	–
8	$[\text{Ni}_3\text{L}^4(\text{ClO}_4)_2](\text{ClO}_4)_2$	-0.63	-1.22	-1.63	3.12	–

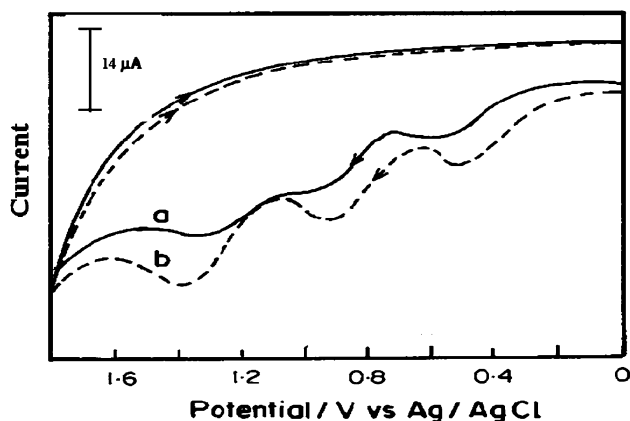
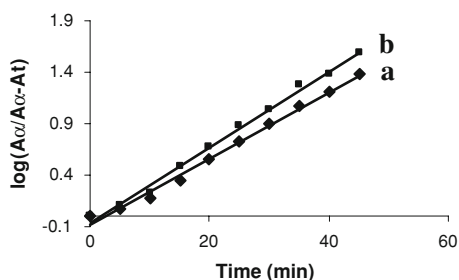
<sup>a</sup> Measured by CV at 50 mV/s. V versus Ag/AgCl conditions: GC working and Ag/AgCl reference electrodes; supporting electrolyte TBAP; concentration of complex  $1 \times 10^{-3}$  M, concentration of TBAP  $1 \times 10^{-1}$  M

<sup>b</sup> Measured spectrophotometrically in DMF

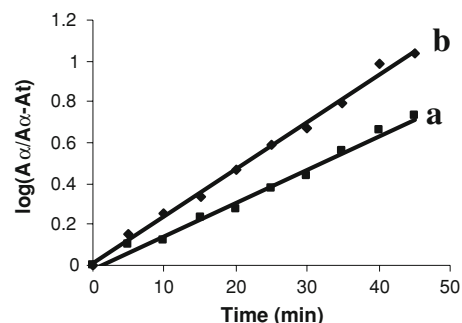
Concentration of the complexes:  $1 \times 10^{-3}$  M

Concentration of 4-nitrophenylphosphate:  $1 \times 10^{-1}$  M

Concentration of catechol:  $1 \times 10^{-1}$  M

**Fig. 5** Cyclic voltammogram of the nickel(II) complexes: (oxidation process) (a)  $[\text{Ni}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$  (b)  $[\text{Ni}_3\text{L}^2(\text{ClO}_4)_2](\text{ClO}_4)_2$ **Fig. 6** Hydrolysis of 4-nitrophenylphosphate by trinuclear nickel(II) complexes: (a)  $[\text{Ni}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$  (b)  $[\text{Ni}_3\text{L}^2(\text{ClO}_4)_2](\text{ClO}_4)_2$ 

complexes differs significantly by varying side arm of the imine compartment and by the Para substituent of the phenyl ring. The rate constants of the copper(II) complexes

**Fig. 7** Catecholase activity of trinuclear copper(II) complexes: (a)  $[\text{Cu}_3\text{L}^1(\text{ClO}_4)_2](\text{ClO}_4)_2$  (b)  $[\text{Cu}_3\text{L}^2(\text{ClO}_4)_2](\text{ClO}_4)_2$ 

of  $\text{L}^{3\&4}$  are lower than the complexes of  $\text{L}^{1\&2}$  presence of 2-(aminomethyl)pyridine group [25–28].

Further, the rate constant values of the complexes are also higher  $2.68$  to  $9.81 \times 10^{-1} \text{ min}^{-1}$  than the trinuclear complexes derived from the di-N-substituted cyclam ligands ( $2.67$  to  $7.58 \times 10^{-1} \text{ min}^{-1}$ ). This shows, the rate of oxidation of catechol to *o*-quinone and the hydrolysis of 4-nitrophenyl phosphate is increases due to the increase of macrocyclic N-alkylation. The structural features and electrochemical properties are important factors in determining the catalytic activity of the complexes. The catalytic activity of the complexes of  $\text{L}^2$  is higher than that of the complexes of  $\text{L}^1$ . This may be due to the *para*-substituent of the phenoxide of the phenyl ring. The complexes containing electron-withdrawing substituent (Br) at the *para*-position to the phenyl ring  $\text{L}^2$  are reduced at less negative potential show higher catalytic activity than complexes with electron-donating substituent ( $\text{CH}_3$ ) [29,



**Table 4** Antibacterial and antifungal screening data of complexes

No.	Compound	Representation zone of inhibition (100 µg/mL)					Antifungal <i>C. a</i>
		Antibacterial					
		<i>S. a</i>	<i>B. c</i>	<i>K. p</i>	<i>P. a</i>	<i>E. c</i>	
1	Cu(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	1.5	–	2	2.5	–	3
2	H <sub>2</sub> L <sup>1</sup>	10	11	10	12	9	13
3	H <sub>2</sub> L <sup>2</sup>	12	10	12	11	11	9
4	H <sub>2</sub> L <sup>3</sup>	13	10	12	12	9	10
5	H <sub>2</sub> L <sup>4</sup>	12	13	11	13	11	9
6	[Cu <sub>3</sub> L <sup>1</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	17	16	19	16	15	19
7	[Cu <sub>3</sub> L <sup>2</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	21	19	12	14	18	20
8	[Cu <sub>3</sub> L <sup>3</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	19	18	16	16	19	16
9	[Cu <sub>3</sub> L <sup>4</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	18	20	22	18	12	22
10	[Ni <sub>3</sub> L <sup>1</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	27	16	20	14	17	23
11	[Ni <sub>3</sub> L <sup>2</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	20	19	20	17	17	26
12	[Ni <sub>3</sub> L <sup>3</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	23	21	19	23	16	21
13	[Ni <sub>3</sub> L <sup>4</sup> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	17	19	18	18	14	22

*S. a*—*Staphylococcus aureus*

*B. a*—*Bacillus subtilis*

*K. p*—*Klebsiella pneumonia*

*P. a*—*Pseudomonas aeruginosa*

*E. c*—*Escherichia coli*

*C. a*—*Candida albicans*

30]. The same trend was also observed for the complexes of L<sup>3&4</sup>.

#### Antimicrobial activities

Antifungal and antibacterial activities of the complexes were tested by following our earlier literature reports [31]. We have evaluated the antifungal activity of all the copper(II) and nickel(II) complexes against the human pathogenic fungus *Candida albicans*. The screening data were reported in the Table 4. All the tested complexes show some antifungal activity. The activity reported by the present complexes was comparable with the N-substituted tetraazamacrocycles [32].

The complexes have also been screened for their in vitro antimicrobial activity against the human pathogenic bacteria gram (–) *Escherichia coli* (ATCC 11775), *Pseudomonas aeruginosa* (ATCC 10145), *Bacillus subtilis* (ATCC 6633) *Klebsiella pneumonia* (ATCC 13883) and gram (+) *Staphylococcus aureus* (ATCC 12600) were using the agar dilution method. The screening results are given in Table 4.

All the trinuclear copper(II) and nickel(II) complexes are highly potent against *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Klebsiella pneumonia* and gram (+) *Staphylococcus aureus*. All the tested trinuclear copper(II)

complexes show moderate activity against gram (–) *Escherichia coli*. But trinuclear nickel(II) complexes show no inhibition against gram (–) *Escherichia coli*. All the complexes show superior activity than the ligands and the metal salts. The complexes are all highly potent against *P. aeruginosa*, *B. subtilis*, *K. pneumonia* and *S. aureus*, with moderate activity against *E. coli*. It is of interest to compare the electronic spectra results with antimicrobial activity. The trinuclear complexes which have maximum charge transfer show slightly higher antimicrobial activity than the other complexes. From the results it is observed that the copper(II) complexes of the ligands L<sup>2</sup> have higher charge transfer value and show higher antibacterial activity. The same is also true for the nickel(II) complexes.

#### Conclusion

In conclusion, it has been observed that the small variation in the side arm of the imine compartment and the para substituent of the phenoxide to the phenyl ring influences on electrochemical, magnetic and catalytic properties of the copper(II) and nickel(II) complexes.

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