**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Thirumavalavan, M. , Akilan, P. and Kandaswamy, M.(2004) 'New Tetraaza Macrobicyclic Ditopic Receptors for Metal Ions: Synthesis, Redox Response and Kinetics of Phosphate Hydrolysis of Unsymmetrical Macrobicyclic Mono- and Binuclear Nickel(II) Complexes', Supramolecular Chemistry, 16: 7, 495 — 504

**To link to this Article: DOI:** 10.1080/10610270410001722349

**URL:** http://dx.doi.org/10.1080/10610270410001722349

*Supramolecular Chemistry*, October–November 2004, Vol. 16 (7), pp. 495–504

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# New Tetraaza Macrobicyclic Ditopic Receptors for Metal Ions: Synthesis, Redox Response and Kinetics of Phosphate Hydrolysis of Unsymmetrical Macrobicyclic Mono- and Binuclear Nickel(II) Complexes

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*Received in (Austin, USA) 18 November 2003; Accepted 5 May 2004*

**A new series of macrobicyclic ditopic receptors is derived from the precursor compound 3,4:10,11-dibenzo-1,13[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)-benzyl}di-aza]-5,9-dioxocyclohexadecane. Using this precursor, mono- and binuclear nickel(II) complexes of type [NiL]($ClO_4$) and [$Ni_2L$]$(ClO_4)_2$ have been synthesized to undertake electrochemical and catalytic studies on the basis of macrocyclic ring size. The receptor is a tricompartmental macrocycle consisting of ether oxygen, tertiary nitrogen and imine nitrogen atoms. The redox studies of these systems show that the nickel(II) complexes undergo quasi-reversible one-electron reduction and oxidation. All the nickel(II) complexes have square planar geometry and are EPR silent. Examination of the kinetics of the hydrolysis of 4-nitrophenyl phosphate shows that the catalytic activities of the complexes increase with the macrocyclic ring size of the complexes. As the macrocyclic ring size of the complexes increases, the spectral, electrochemical and catalytic studies of the complexes show considerable variation due to distortion in the geometry around the nickel(II) centre.**

*Keywords*: Ditopic ligands; Macrobicyclic nickel(II) complexes; Redox behaviour; Translocation; Phosphate hydrolysis; Macrocyclic ring size

## INTRODUCTION

The aggregation of molecular building blocks through self-assembly has recently been of wide interest because the potential of the ordered network directed by either metal ions or hydrogen bonds offers opportunities to develop new approaches to the synthesis of functional materials [1–4]. The design and synthesis of organic substrates that preferentially interact with particular metal ions is of fundamental importance to many areas of chemistry. Metal complex stability is highly influenced by a range of factors [5,6], including the number and nature of the donor atoms and their spatial arrangement, the backbone structure of the ligand and its ability to accommodate the preferred coordination geometries of the respective metal ions, and the number and size of the chelate rings formed on complexation. Investigation of molecules containing two or more metals focuses attention on various synergistic interactions in these metallobiomolecules, and catalytic and electron transfer processes [7]. The quest for rational routes leading to bi- and polymetallic complexes with low nuclearities has been stimulated by the potential relevance of these compounds to bioinorganic chemistry [8]. Several synthetic approaches have been used to design discrete bi- and polynuclear complexes. One of them consists in the ingenious use of compartmental ligands, which are organic molecules able to hold together two or more metal ions [9]. These ligands are capable of forming symmetrical or dissymmetrical homo- and heterobinuclear complexes. Several macroyclic complexes of ligands containing ether oxygen and tertiary nitrogen, tertiary nitrogen and phenolic oxygen as coordinating atoms have been reported in the literature [10] but only a few bicyclic systems have been studied so far [11]. In the field of supramolecular

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ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270410001722349

chemistry [11,12], unsymmetrical compartmental metal ions together with ligands contain a variety of structural information that has drawn attention to the self-assembly and translocation processes. During pH- and redox-driven translocation (the metal ion with variable oxidation states) the metal ion is translocated from one compartment to another.

This paper focuses on the synthesis of phenol-based macrobicyclic ligands having dissimilar metal binding sites sharing two phenolic oxygens for the study of di-μ-phenolato mono- and binuclear nickel(II) complexes. This work also brings out some interesting chemistry observed in the electrochemical and kinetic studies. Studies on the hydrolysis of 4-nitrophenyl phosphate (NPP) using nickel(II) complexes as model systems have produced a wealth of information. The mechanism of phosphate hydrolysis involves the concerted binding of the substrate on one metal centre and the nucleophilic attack of water or hydroxide ion at the other metal centre [13,14].

## RESULTS AND DISCUSSION

Schiff's base condensation of the precursor compounds with diamines in the presence of metal ions by the template method results in macrobicyclic mono- and binuclear nickel(II) complexes. Scheme 1 represents the synthetic pathway of these mono- and binuclear complexes. In all cases we could obtain only microcrystals and attempts to obtain crystals suitable for X-ray analysis were unsuccessful. All the complexes showed a single d–d transition in the UV–vis spectra. Hence, it is proposed that the geometry around the nickel(II) ion is distorted square planar. In mononuclear complexes, one of the tertiary nitrogen atoms is protonated. Conductivity measurements indicate that the mono- and binuclear nickel(II) complexes are of the 1:1 and 1:2 electrolyte type, respectively. Spectral, electrochemical and kinetic studies of the complexes were carried out.

### Spectral Studies

The IR spectra of the complexes show a $\nu$(C═N) peak [15] at 1620–1628 $cm^{-1}$. The effective Schiff's base condensation is evidenced by the formation of this new peak and the disappearance of the $\nu$(C═O) peak at 1674 $cm^{-1}$ in the complexes. The peaks appearing near 1100 and 620 $cm^{-1}$ are characteristic of the uncoordinated perchlorate ion. Three main transitions were observed in the electronic spectra of the complexes. A weak band was observed in the range 580–655 nm due to the d–d transition of the metal ion. On moving from the complexes of ligand $L^1$ to $L^3$ and $L^4$ to $L^5$, an increase in $\lambda_{max}$ (red shift) [16] of the d–d transition of Ni(II) ion in the complexes was observed for both mono- and binuclear copper(II) complexes. A moderately intense band observed at 375–390 nm is due to a ligand-to-metal charge-transfer transition and the strong band observed at 255–294 nm is due to an intraligand charge-transfer transition [17]. Apart from these, additional peaks are observed for the complexes of ligands $L^4$ to $L^5$ due to the presence of the aromatic ring in the imine nitrogen compartment. All the nickel(II) complexes are diamagnetic and ESR silent.

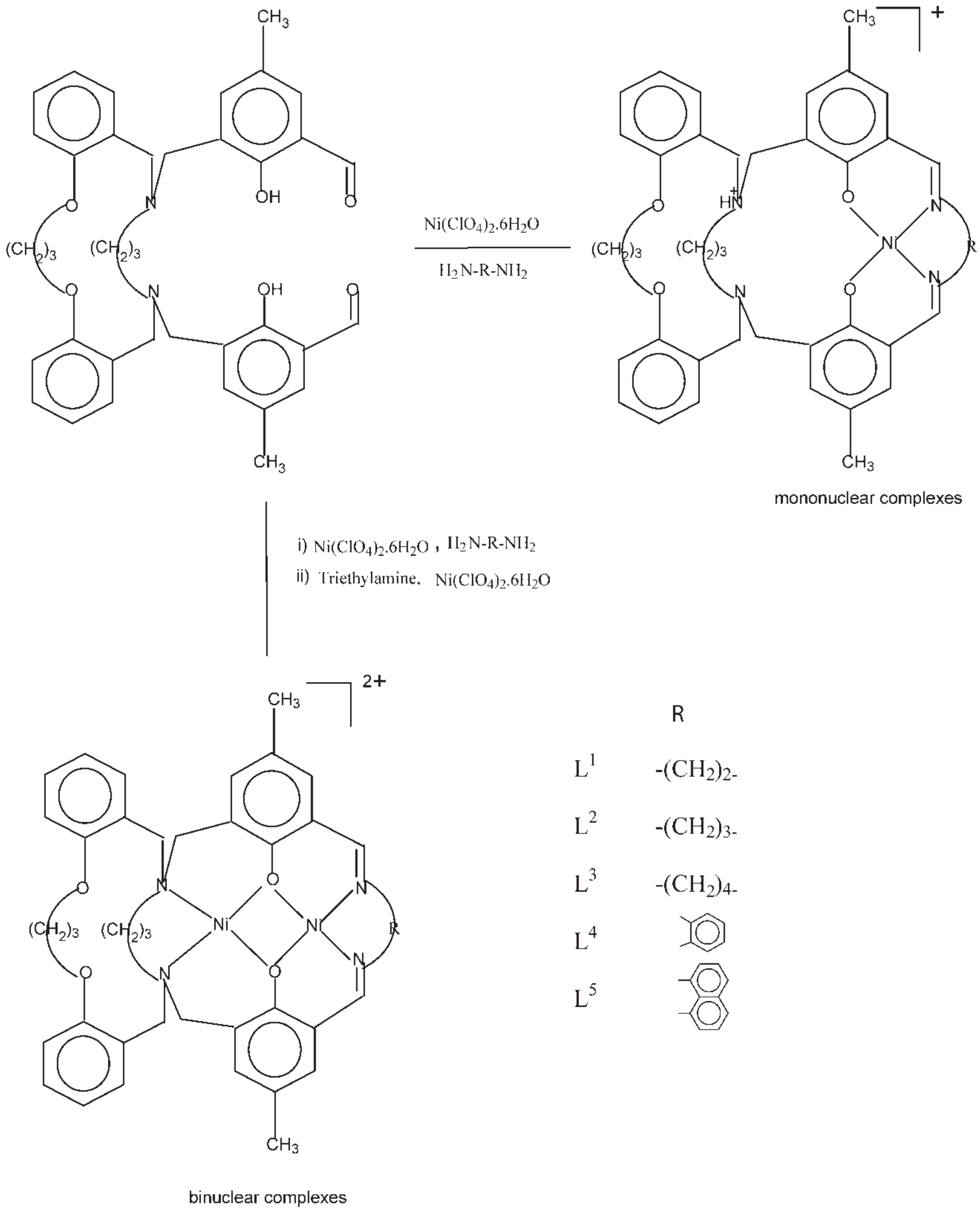
### Electrochemistry

The conductivity measurements [18] of the complexes in acetonitrile indicate that the mononuclear nickel(II) complexes are of the 1:1 (133–152 $\Lambda_m$/S $cm^2$ $mol^{-1}$) electrolyte type and the binuclear nickel(II) complexes are the 1:2 (275–313 $\Lambda_m$/S $cm^2$ $mol^{-1}$) electrolyte type. Electrochemical properties of the complexes reported in the present work were studied by cyclic voltammetry in the potential ranges 0 to $-1.6$ V and 0 to $+1.6$ V in dimethylformamide containing $10^{-1}$ M tetra(*n*-butyl)ammonium perchlorate. All the nickel(II) complexes undergo both reduction and oxidation in cathodic and anodic potentials, respectively. As the macrobicyclic complexes of ditopic ligands contain non-equivalent compartments, the translocation process has also been studied electrochemically using a redox-driven mechanism.

### *Reduction at the Cathode*

The cyclic voltammograms for the mononuclear complexes are shown in Fig. 1. Each voltammogram shows one quasi-reversible reduction wave at negative potential in the range $-0.83$ to $-1.07$ V. Controlled potential electrolysis carried out at 100 mV more negative than the reduction wave reveals the consumption of one electron per molecule ($n = 0.94$) and the study shows that the couple corresponds to a one-electron transfer process. Figure 2 shows the cyclic voltammograms of the binuclear complexes, which exhibit two quasi-reversible reduction waves. The first reduction potential ranges from $-0.95$ to $-1.29$ V and the second reduction potential falls in the range $-1.32$ to $-1.67$ V. Tables I and II present the electrochemical data for the nickel(II) complexes in the cathodic and anodic potentials, respectively. Controlled potential electrolysis was also carried out and our study shows that the each couple corresponds to a one-electron transfer process. Thus, the two redox processes are assigned as follows:

$$Ni^{II}Ni^{II} \leftrightarrow Ni^{II}Ni^{I} \leftrightarrow Ni^{I}Ni^{I}$$



SCHEME 1 Synthesis of macrocyclic mono- and binuclear nickel(II) complexes.

The conproportionation constant for the equilibrium

$$\mathrm{Ni^{II}Ni^{II}} + \mathrm{Ni^{I}Ni^{I}} \overset{K_{\mathrm{con}}}{\leftrightarrow} 2\mathrm{Ni^{II}Ni^{I}}$$

was calculated using the relationship $\log K_{\mathrm{con}} = \Delta E/0.0591$.

The electrochemical behaviour of the complexes was compared on the basis of the macrocyclic ring size. The reduction potential of the mononuclear nickel(II) complexes of ligands $L^1$ to $L^3$ and $L^4$ to $L^5$ shifts anodically from $-0.92$ to $-0.83$ V and from $-1.07$ V to $-0.97$ V, respectively, as the macrocyclic ring size increases due to the increase in chain length between the two imine nitrogen atoms. This imparts more flexibility to the macrocycle [19–22] and tries to stabilize nickel(I) complex. In this case, the $\Delta E$ values for the quasi-reversible waves are generally larger and this may be due to the occurrence of electrochemical interconversion (translocation) [23] of the reduced cation Ni(I) from the rigid imine nitrogen

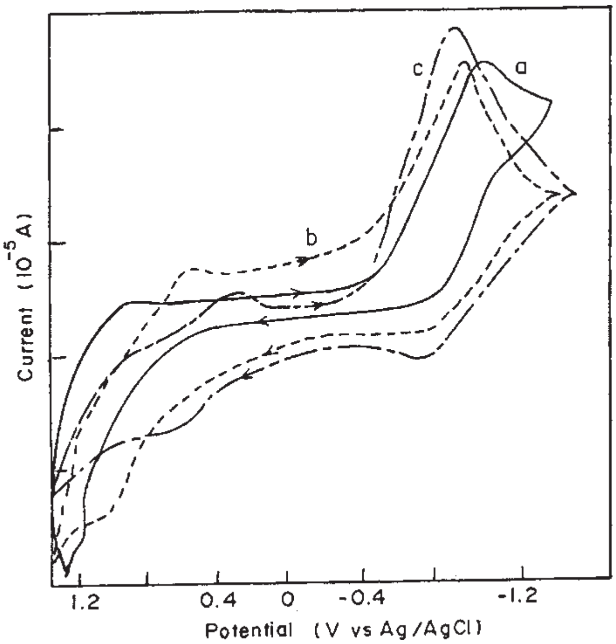


FIGURE 1 Cyclic voltammograms of the mononuclear nickel(II) complexes ($1\times10^{-3}$ M): (a) [$NiL^1$]($ClO_4$); (b) [$NiL^2$]($ClO_4$); (c) [$NiL^3$]($ClO_4$).

compartment ($N_2O_2$) to the flexible tertiary nitrogen compartment ($N_2O_2$), which favours the tetrahedral geometry. The translocation is explained in Scheme 2. The calculated larger $\Delta E$ values indicate that the reduction process is associated with an ECE mechanism. The decrease in $\Delta E$ values is observed as the chain length between the two imine nitrogens increases and this eases the translocation process [12,23–28] moving from the complexes of ligands $L^1$ to $L^3$ and $L^4$ to $L^5$.

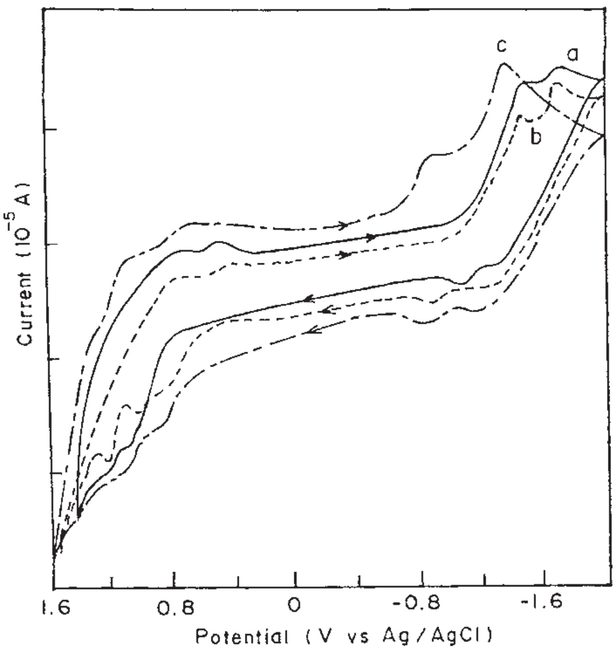


FIGURE 2 Cyclic votammograms of the binuclear nickel(II) complexes ($1\times10^{-3}$ M): (a) [$Ni_2L^1$]($ClO_4$)$_2$; (b) [$Ni_2L^2$]($ClO_4$)$_2$; (c) [$Ni_2L^3$]($ClO_4$)$_2$.

As the size of macrocycle is increased, shifting of both first and second reduction potentials towards anodic is observed for the binuclear nickel(II) complexes. For example, the complex [$Ni_2L^1$]($ClO_4$)$_2$ has $E^1_{pc} = -1.26$ V and $E^2_{pc} = -1.67$ V, that is more negative than for the complex [$Ni_2L^2$]($ClO_4$)$_2$ ($E^1_{pc} = -1.23$ V, $E^2_{pc} = -1.54$ V) and the same observation is inferred for the complexes of ligand $L^4$ and $L^5$. Thus, because of the increase in chain length in the imine nitrogen compartment, the whole macrocyclic ring becomes more flexible and hence undergoes easy reduction. Thus the large size of the cavity easily holds the reduced cation and stabilizes the formation of Ni(I) in both compartments. Concern in the calculation of $K_{con}$ values of binuclear Ni(II) complexes leads to another interesting feature, namely that the variation of $K_{con}$ is random and not uniform as the macrocyclic ring size increases, which has no explanation.

From the cyclic voltammetric studies it can be stated that the complexes containing aromatic diimines get reduced at higher negative potential than that of the complexes containing aliphatic diimines. The reason for this may be the increased stability of the systems due to their aromatic nature and less deviation from planarity.

### *Oxidation at Anode*

The cyclic voltammograms of the nickel(II) complexes obtained at positive potential region show one-electron transfer waves. The oxidation process is also quasi-reversible. It is clear that the increase in macrocyclic ring size influences the oxidation potential to a less extent and no uniform variation is observed. Hence, the influence of the macrocyclic ring size is unpredictable. The oxidation process can be described as follows:

$$\mathrm{Ni^{II}Ni^{II}} \leftrightarrow \mathrm{Ni^{II}Ni^{III}} \leftrightarrow \mathrm{Ni^{III}Ni^{III}}$$

### Kinetic Studies of Hydrolysis of 4-Nitrophenyl Phosphate

Kinetic studies of the nickel(II) complexes indicate that they can act as a model for phosphate hydrolase. The kinetics of the hydrolysis of 4-nitrophenyl phosphate was carried out using equal concentration of the complex catalyst and tetramethylammonium hydroxide ($10^{-3}$ M) and 4-nitrophenyl phosphate ($10^{-1}$ M). The chromophore-leaving group 4-nitrophenolate, which is the hydrolysis product of the substrate, was monitored at 420 nm. The course of the reaction was followed at 420 nm for nearly 45 min at regular time intervals. The slope was determined

TABLE I Electrochemical data* of mono- and binuclear nickel(II) complexes in DMF medium (reduction)

| Complexes | $E^1_{pc}$(V) | $E^1_{pa}$(V) | $E^1_{1/2}$(V) | $\Delta E$ (mV) | $E^2_{pc}$(V) | $E^2_{pa}$(V) | $E^2_{1/2}$(V) | $\Delta E$ (mV) | $K_{con}$ |
|---|---|---|---|---|---|---|---|---|---|
| $[NiL^1](ClO_4)$ | −0.92 | −0.74 | −0.83 | 180 | – | – | – | – | – |
| $[NiL^2](ClO_4)$ | −0.87 | −0.70 | −0.79 | 170 | – | – | – | – | – |
| $[NiL^3](ClO_4)$ | −0.83 | −0.67 | −0.79 | 160 | – | – | – | – | – |
| $[NiL^4](ClO_4)$ | −1.07 | −0.96 | −1.02 | 110 | – | – | – | – | – |
| $[NiL^5](ClO_4)$ | −0.97 | −0.86 | −1.02 | 110 | | | | | |
| $[Ni_2L^1](ClO_4)_2$ | −1.26 | −1.14 | −1.20 | 120 | −1.67 | −1.55 | −1.61 | 120 | $8.65 \times 10^6$ |
| $[Ni_2L^2](ClO_4)_2$ | −1.23 | −0.99 | −1.11 | 240 | −1.54 | −1.32 | −1.43 | 220 | $2.59 \times 10^5$ |
| $[Ni_2L^3](ClO_4)_2$ | −0.95 | −0.86 | −0.91 | 90 | −1.48 | −1.28 | −1.38 | 200 | $8.97 \times 10^7$ |
| $[Ni_2L^4](ClO_4)_2$ | −1.29 | −1.13 | −1.21 | 160 | −1.45 | −1.32 | −1.39 | 130 | $1.11 \times 10^3$ |
| $[Ni_2L^5](ClO_4)_2$ | −1.19 | −1.10 | −1.14 | 90 | −1.32 | −1.20 | −1.26 | 120 | $1.07 \times 10^2$ |

*Measured by CV at 25 mV s$^{-1}$. *E vs* 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.

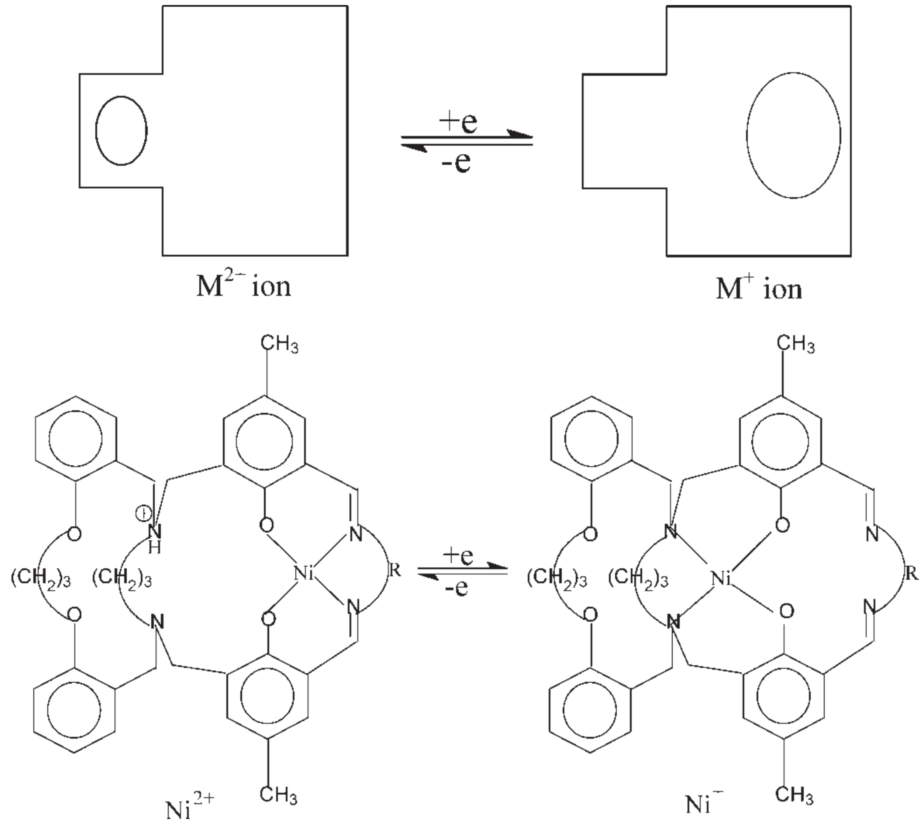
by the method of initial rates by monitoring the growth of the 420 nm band of the product 4-nitrophenolate ion. All the kinetic studies were carried out in DMF solvent at room temperature (25°C). A constant ionic strength (0.1 M) was maintained through out the kinetic studies by using tetraethylammonium perchlorate (TEAP). The pH of the solution was checked (10.8) and the pH values are within ± 0.05 pH units throughout the course of the reaction monitored.

Plots of $\log(A_\infty/A_\infty - A_t)$ *vs* time for catalytic activity of the mono- and binuclear complexes hydrolysis for 4-nitrophenyl phosphate are shown in Figs. 3 and 4, respectively. The rate constant values are also reported in Table III. The first apparent result was that the reactivities of the complexes differed significantly, as the size of the macrocycle increased. The binuclear complexes have higher activities than the mononuclear complexes [29–33]. For example, the binuclear complexes $[Ni_2L^1](ClO_4)_2$, $[Ni_2L^2](ClO_4)_2$, $[Ni_2L^3](ClO_4)_2$, $[Ni_2L^4](ClO_4)_2$ and $[Ni_2L^4](ClO_4)_2$ have the rate constant values $1.80 \times 10^{-2}$, $2.79 \times 10^{-2}$, $3.79 \times 10^{-2}$, $1.65 \times 10^{-2}$ and $2.40 \times 10^{-2}$ min$^{-1}$, respectively, whereas the mononuclear complexes $[NiL^1](ClO_4)$, $[NiL^2](ClO_4)$, $[NiL^3](ClO_4)$, $[NiL^4](ClO_4)$ and $[NiL^5](ClO_4)$ have the rate constant values $1.68 \times 10^{-3}$, $1.93 \times 10^{-3}$, $2.26 \times 10^{-3}$, $1.13 \times 10^{-3}$ and $1.22 \times 10^{-3}$ min$^{-1}$, respectively. This shows that the catalysis requires the presence of two metal ions in close proximity and hence the rate constant values of binuclear complexes are comparatively high. This is inconsistent with previously reported systems [34–36]. The mononuclear complexes proceed via an $S_N1$-type of reaction mechanism in which the external hydroxide ion is coordinated to the metal ion, followed by deprotonation of OH and formation of an intermediate with the phosphate group and then cleavage of the bond to form the phenolate anion, along with the hydroxylation of the phosphate group. The binuclear nickel(II) complexes follow a concerted $S_N2$-type of mechanism in which the nucleophile $OH^-$ adds to one of the Ni ions and the phosphate is bound to the other metal ion. Here, bond formation and bond breakage occur at the same time. The mechanism are shown in Scheme 3. The catalytic activities of both the mono- and binuclear complexes are found to increase as the macrocyclic ring size increases (from $L^1$ to $L^3$) due to the intrinsic flexibility. The study indicates that for mononuclear complexes the observed variation in the value of the rate constant is very small when compared to the binuclear complexes. The catalytic activity of the complexes containing aromatic diimines is found to

TABLE II Electrochemical data* of mono- and binuclear nickel(II) complexes in DMF medium (oxidation)

| Complexes | $E^1_{pa}$(V) | $E^1_{pc}$(V) | $E^1_{1/2}$(V) | $\Delta E$ (mV) | $E^2_{pa}$(V) | $E^2_{pc}$(V) | $E^2_{1/2}$(V) | $\Delta E$ (mV) |
|---|---|---|---|---|---|---|---|---|
| $[NiL^1](ClO_4)$ | 1.12 | 0.98 | 1.05 | 140 | – | – | – | – |
| $[NiL^2](ClO_4)$ | 0.91 | 0.78 | 0.85 | 130 | – | – | – | – |
| $[NiL^3](ClO_4)$ | 0.61 | 0.50 | 0.56 | 110 | – | – | – | – |
| $[NiL^4](ClO_4)$ | 1.12 | 0.99 | 1.06 | 130 | – | – | – | – |
| $[NiL^5](ClO_4)$ | 0.98 | 0.87 | 0.93 | 110 | | | | |
| $[Ni_2L^1](ClO_4)_2$ | 0.94 | 0.85 | 0.89 | 90 | 1.13 | 1.00 | 1.07 | 130 |
| $[Ni_2L^2](ClO_4)_2$ | 0.84 | 0.76 | 0.80 | 80 | 1.18 | 1.06 | 1.12 | 120 |
| $[Ni_2L^3](ClO_4)_2$ | 0.93 | 0.80 | 0.87 | 130 | 1.19 | 1.07 | 1.13 | 120 |
| $[Ni_2L^4](ClO_4)_2$ | 0.89 | 0.78 | 0.84 | 110 | 1.02 | 0.91 | 0.97 | 110 |
| $[Ni_2L^4](ClO_4)_2$ | 0.86 | 0.75 | 0.80 | 110 | 1.14 | 1.04 | 1.09 | 100 |

*Measured by CV at 25 mV s$^{-1}$. E *vs* 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.



SCHEME 2 Schematic representation of the redox-driven translocation of the metal ion.

be less than that of the complexes containing aliphatic diimines. This can be explained by the fact that the planarity, which is associated with the aromatic ring, imparts less catalytic efficiency due to the rigidity of the systems as observed in the case of electrochemical reduction of the complexes.

## CONCLUSION

Various mono- and binuclear nickel(II) complexes of macrocyclic ditopic receptors were synthesized and studies on their spectral, electrochemical and catalytic properties carried out. These studies show that a small variation in macrocyclic ring size and in

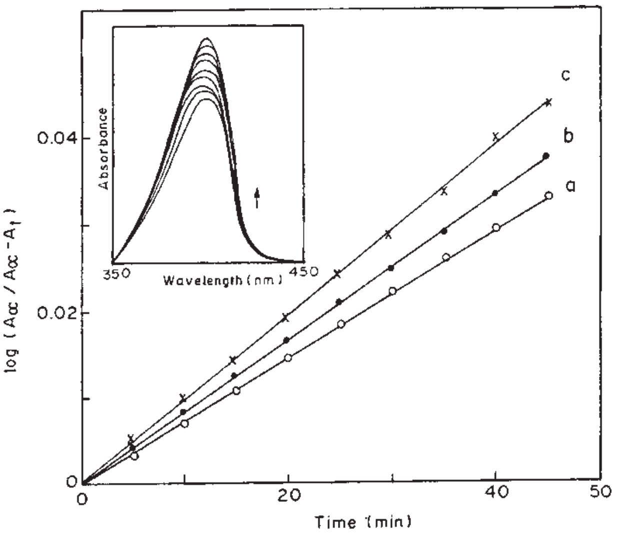


FIGURE 3 Catalytic activity of mononuclear nickel(II) complexes for hydrolysis of 4-nitrophenyl phosphate: (a) $[NiL^1](ClO_4)$; (b) $[NiL^2](ClO_4)$; (c) $[NiL^3](ClO_4)$.

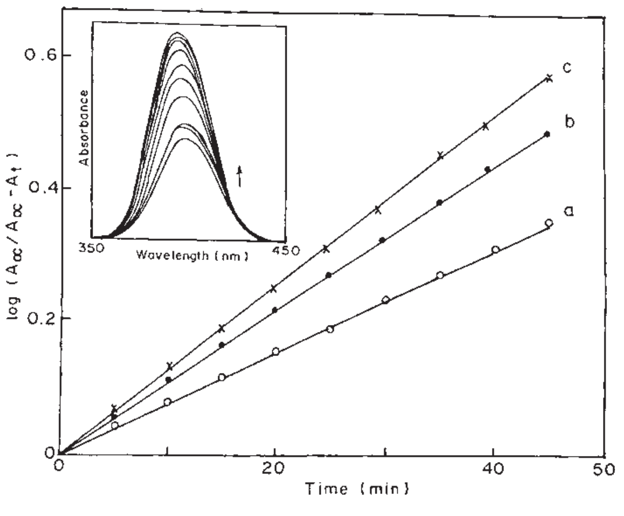


FIGURE 4 Catalytic activity of binuclear nickel(II) complexes for hydrolysis of 4-nitrophenylphosphate: (a) $[Ni_2L^1](ClO_4)_2$; (b) $[Ni_2L^2](ClO_4)_2$; (c) $[Ni_2L^3](ClO_4)_2$.

TABLE III Catalytic activity* of mono- and binuclear nickel(II) complexes for hydrolysis of 4-nitrophenyl phosphate

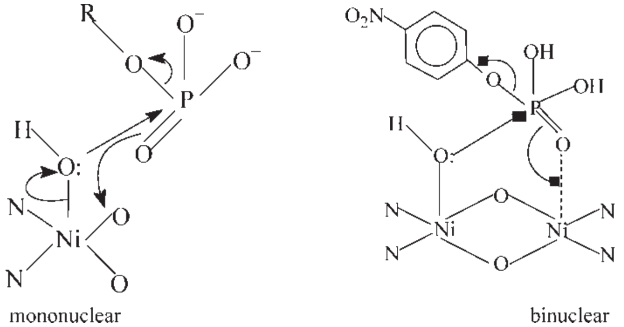
| Complexes | Rate constant ($min^{-1}$) |
|---|---|
| $[NiL^1](ClO_4)$ | $1.68 \times 10^{-3}$ |
| $[NiL^2](ClO_4)$ | $1.93 \times 10^{-3}$ |
| $[NiL^3](ClO_4)$ | $2.26 \times 10^{-3}$ |
| $[NiL^4](ClO_4)$ | $1.13 \times 10^{-3}$ |
| $[NiL^5](ClO_4)$ | $1.22 \times 10^{-3}$ |
| $[Ni_2L^1](ClO_4)_2$ | $1.80 \times 10^{-2}$ |
| $[Ni_2L^2](ClO_4)_2$ | $2.79 \times 10^{-2}$ |
| $[Ni_2L^3](ClO_4)_2$ | $3.79 \times 10^{-2}$ |
| $[Ni_2L^4](ClO_4)_2$ | $1.65 \times 10^{-2}$ |
| $[Ni_2L^4](ClO_4)_2$ | $2.40 \times 10^{-2}$ |

*Measured spectrophotometrically in DMF medium. Concentration of the complexes and tetramethylammonium hydroxide: $1 \times 10^{-3}$ M. Concentration of 4-nitrophenyl phosphate: $1 \times 10^{-1}$ M.

the nature of the diamines in the ligand framework influences the spectral, electrochemical and catalytic properties of the complexes.

## EXPERIMENTAL

Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. $^1H$ NMR spectra were recorded using FX-80-Q Fourier transition NMR spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer in the range 200–800 nm. IR spectra were recorded on a Hitachi 270-50 spectrophotometer on KBr disks in the range 4000–250 $cm^{-1}$. Mass spectra were obtained on a Jeol DX-303 mass spectrometer. Molar conductivity was measured by using an Elico model SX 80 conductivity bridge using freshly prepared solution of the complex in $CH_3CN$. Cyclic Voltammograms were obtained on a CHI600A 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 internal standard and $E_{1/2}$ of the ferrocene/ferrocenium ($Fc/Fc^+$) couple under the experimental condition is 470 mV in DMF and $\Delta E_p$ for $Fc/Fc^+$ is 70 mV. Tetra($n$-butyl)ammonium perchlorate was used as the supporting electrolyte. The kinetic investigation of hydrolysis of 4-nitrophenyl phosphate was carried out spectrophotometrically by choosing the strongest absorbance at 420 nm and monitoring the increase in the absorbance at this wavelength as a function of time. A plot of $\log(A_\propto/A_\propto - A_t)$ $vs$ time was made for each complex and the initial rate constant of hydrolysis of 4-nitrophenyl phosphate was calculated.



SCHEME 3 Mechanism for hydrolysis of 4-nitrophenyl phosphate.

### Materials

5-Methylsalicylaldehyde [37], 3-chloromethyl-5-methylsalicylaldehyde [38] and 3,4:9,10-dibenzo-1,13-diaza-5,9-dioxacyclohexadecane [39,40] were prepared from the literature methods. TBAP, used as supporting electrolyte in the electrochemical measurements, was purchased from Fluka and recrystallized from hot methanol. (Caution! TBAP is potentially explosive; hence care should be taken in handling the compound). DMF and $CH_3CN$ were obtained from E. Merck. All other chemicals and solvents were of analytical grade and were used as received without any further purification.

### Synthesis of Precursor Compound

#### *3,4:9,10-Dibenzo-1,13[N,N′-bis{(3-formyl-2-hydroxy-5-methyl}benzyl)diaza]-5,9-dioxacyclohexadecane (PC)*

A mixture of 3,4:9,10-dibenzo-1,13-diaza-5,9-dioxacyclohexadecane (1.043 g, 3.2 mmol) and triethylamine (1.32 g, 6.4 mmol) in THF was added slowly to a stirred solution of 3-chloromethyl-5-methyl salicylaldehyde (1.16 g, 6.4 mmol) in THF. After the addition was over the stirring was continued for 1 h. The whole solution was then refluxed under water bath for 3 h and was allowed to cool on standing at room temperature. Copious quantities of water were added to this solution to dissolve any salt obtained. Then the required compound was extracted in organic medium using chloroform. The extraction was repeated for two to three times. A pale yellow compound was obtained on evaporation of the solvent at room temperature (25°C), and light yellow microcrystals were obtained on recrystallization from chloroform. Yield: 1.59 g (80%), mp: 78°C. Anal. Calcd. for $C_{38}H_{42}O_6N_2$: C, 73.31; H, 6.75; N, 4.50, Found (%): C, 73.51; H, 6.87; N, 4.68. IR data ($\nu cm^{-1}$): 1672 ($\nu C{=}O$, s), 3440 ($\nu OH$, br). $^1H$ NMR ($\delta$ ppm in $CDCl_3$): 10.0 (s, 2H, CHO protons), 7.1 (m, 12H, aromatic protons), 4.6 (m, 4H, methylene protons attached to oxygen atom), 3.6 (m, 8H, benzylic protons), 3.2 (s, 4H, methylene protons attached to nitrogen atom), 2.3 (s, 6H, aromatic $CH_3$ protons), 2.1 (s, 4H, $CH_2$ protons attached to alkyl chain. Mass (EI) $m/z$: 622 ($m^+$).

## Synthesis of Macrobicyclic Mononuclear Nickel(II) Complexes

### [NiL$^1$](ClO$_4$)

A methanolic solution of nickel(II)perchlorate hexahydrate (0.694 g, 1.9 mmol) was added to the hot solution of PC (1.182 g, 1.9 mmol) in $CHCl_3$ followed by the addition of 1,2-diaminoethane (0.128 g, 1.9 mmol) in methanol. The solution was refluxed on a water bath for 24 h. After the reaction was over, the solution was filtered under hot conditions and then allowed to stand at room temperature. After slow evaporation of the solvent at 25°C, the product obtained was an orange–red compound, which washed with methanol and dried in vacuum. Yield: 1.33 g (75%). Anal. Calcd. for $C_{42}H_{48}O_8N_5ClNi$(%): C, 59.71; H, 5.68; N, 8.29, Found: C, 59.88; H, 5.79; N, 8.32. Selected IR (KBr): 1627 (s), 1088 (s), 627 (s) $cm^{-1}$. Conductance ($\Lambda_m/S\,cm^2\,mol^{-1}$) in $CH_3CN$: 140. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 580 (177), 375 (13 300), 255 (35 800).

### [NiL$^2$](ClO$_4$)

[NiL$^2$](ClO$_4$) was synthesized by following the procedure described previously for [NiL$^1$](ClO$_4$), using 1,3-diaminopropane instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.29 g (79%). Anal. Calcd. for $C_{43}H_{50}O_8N_5ClNi$(%): C, 60.13; H, 5.82; N, 8.15. Found: C, 60.21; H, 5.98; N, 8.26. Selected IR (KBr): 1628 (s), 1099 (s), 625 (s) $cm^{-1}$. $^1$H NMR ($\delta$ ppm in $CH_3CN$): 8.1 (s, 2H, protons in CH═N), 6.5–7.0 (m, 12H, aromatic protons), 3.8 (m, 4H, methylene protons attached to oxygen atom), 2.2 (m, 2H, methylene protons attached to $CH_2$—O), 4.4 (s, 4H, benzylic protons attached to $^+$NH in the amine compartment), 3.7 (s, 4H, benzylic protons attached to N in the amine compartment), 3.2 (s, 2H, methylene protons attached to $^+$NH in the amine compartment), 3.2 (s, 2H, methylene protons attached to $^+NH—CH_2$ in the amine compartment), 2.3 (s, 2H, methylene protons attached to N in the amine compartment), 2.3 (s, 6H, aromatic $CH_3$ protons), 3.5 (s, 4H, $CH_2$ protons attached to imine nitrogen), 1.6 (s, 2H, $CH_2$ protons attached to $CH_2$—N═). $^{13}$C NMR ($\delta$ ppm in $CH_3CN$): 162 (s, carbon in CH═N), 118, 124, 128 and 130 and 136 (m, aromatic carbons in imine compartment), 114, 120, 123, 126, 129, 159 (m, aromatic carbons in the ether oxygen compartment), 68 (m, 2C, carbons in $CH_2$—O), 30 (m, 1C, carbon in $CH_2$—$CH_2$-—O), 48 (s, 4C, benzylic carbons attached to $^+$NH and N in the amine compartment), 51 (s, 1C, methylene carbon in $CH_2$—$^+$NH and carbon in $CH_2$—N), 25 (s, 1C, methylene carbon in $CH_2$—$CH_2$—N), 21 (s, 2C, carbons in Ar—$CH_3$), 163 (s, 2C, carbons in Ar—CH═N), 34 (s, 2C, carbons in ═N—$CH_2$—$CH_2$—N═), 21 (s, 1C, carbon in $CH_2$—$CH_2$—N═). Conductance ($\Lambda_m/S\,cm^2\,mol^{-1}$) in $CH_3CN$: 152. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 602 (129), 382 (18 100), 260 (32 600).

### [NiL$^3$](ClO$_4$)

[NiL$^3$](ClO$_4$) was synthesized by following the procedure described previously for [NiL$^1$](ClO$_4$), using 1,4-diaminobutane instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.28 g (77%). Anal. Calcd. for $C_{44}H_{52}O_8N_5ClNi$(%): C, 60.55; H, 5.96; N, 8.02, Found: C, 60.66; H, 5.99; N, 8.11. Selected IR (KBr): 1621 (s), 1086 (s), 620 (s) $cm^{-1}$. Conductance ($\Lambda_m/S\,cm^2\,mol^{-1}$) in $CH_3CN$: 133. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 625 (136), 390 (12200), 280 (35200).

### [NiL$^4$](ClO$_4$)

[NiL$^4$](ClO$_4$) was synthesized by following procedure described previously for [NiL$^1$](ClO$_4$), using *o*-phenylenediamine instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.35 g (80%). Anal. Calcd. for $C_{46}H_{48}O_8N_5ClNi$(%): C, 61.88; H, 5.38; N, 7.84, Found: C, 61.96; H, 5.41; N, 7.92. Selected IR (KBr): 1623 (s), 1100 (s), 629 (s) $cm^{-1}$. Conductance ($\Lambda_m/S\,cm^2\,mol^{-1}$) in $CH_3CN$: 141. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 620 (132), 466 (sh), 382 (12 400), 276 (33 200), 245 (32 600).

### [NiL$^5$](ClO$_4$)

[NiL$^5$](ClO$_4$) was synthesized by following the procedure described previously for [NiL$^1$](ClO$_4$), using 1,8-diaminonaphthalene instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.31 g (73%). Anal. Calcd. for $C_{50}H_{50}O_8N_5ClNi$(%): C, 63.69; H, 5.30; N, 7.43, Found: C, 63.80; H, 5.42; N, 7.58. Selected IR (KBr): 1622 (s), 1098 (s), 625 (s) $cm^{-1}$. Conductance ($\Lambda_m/S\,cm^2\,mol^{-1}$) in $CH_3CN$: 138. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 655 (126), 420 (15 400), 380 (17 600), 294 (33 000).

## Synthesis of Macrobicyclic Binuclear Nickel(II) Complexes

### [Ni$_2$L$^1$](ClO$_4$)$_2$

A methanolic solution of nickel(II)perchlorate hexahydrate (0.694 g, 1.9 mmol) was added to the hot solution of PC (1.182 g, 1.9 mmol) in $CHCl_3$ followed by the addition of 1,2-diaminoethane (0.128 g, 1.9 mmol) and triethylamine (0.265 g, 1.9 mmol) in methanol. After 1 h nickel(II)perchlorate (0.694 g, 1.9 mmol) was added and the reaction mixture was refluxed on a water bath for 24 h. After the reaction was over, the reaction mixture was filtered and allowed to stand at room temperature (25°C). After slow evaporation of the solvent at 25°C, the orange–red compound obtained was washed with methanol and dried in vacuum. Yield: 1.68 g (79%). Anal. Calcd. for $C_{44}H_{50}O_{12}N_6Cl_2Ni_2$(%): C, 50.67; H, 4.79; N, 8.06, Found: C, 50.79; H, 4.92; N, 8.21. Selected IR (KBr): 1628 (s), 1099 (m), 627 (s) $cm^{-1}$. Conductance $(\Lambda_\mathrm{m}/\mathrm{S\,cm^2\,mol^{-1}})$ in $CH_3CN$: 310. $\lambda_\mathrm{max}$ (nm) $(\varepsilon/\mathrm{M^{-1}\,cm^{-1}})$ in $CH_3CN$: 589 (231), 390 (17 100), 255 (36 000).

### *$[Ni_2L^2](ClO_4)_2$*

$[Ni_2L^2](ClO_4)_2$ was synthesized by following the procedure described previously for $[Ni_2L^1](ClO_4)_2$, using 1,3-diaminopropane instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.62 g (81%). Anal. Calcd. for $C_{45}H_{52}O_{12}N_6Cl_2Ni_{2:}$(%): C, 51.13; H, 4.92; N, 7.95, Found (%): C, 51.31; H, 5.04; N, 8.08. Selected IR (KBr): 1627 (s), 1098 (m), 627 (s) $cm^{-1}$. Conductance $(\Lambda_\mathrm{m}/\mathrm{S\,cm^2\,mol^{-1}})$ in $CH_3CN$: 288. $\lambda_\mathrm{max}$ (nm) $(\varepsilon/\mathrm{M^{-1}\,cm^{-1}})$ in $CH_3CN$: 605 (236), 372 (19 100), 267 (32 500).

### *$[Ni_2L^3](ClO_4)_2$*

$[Ni_2L^3](ClO_4)_2$ was synthesized by following the procedure described previously for $[Ni_2L^1](ClO_4)_2$, using 1,4-diaminobutane instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.68 g (83%). Anal. Calcd. for $C_{46}H_{54}O_{12}N_6Cl_2Ni_2$(%): C, 51.58; H, 5.04, N, 7.85, Found: C, 51.69; H, 5.18; N, 8.00. Selected IR (KBr): 1620 (s), 1100 (m), 628 (s) $cm^{-1}$. Conductance $(\Lambda_\mathrm{m}/\mathrm{S\,cm^2\,mol^{-1}})$ in $CH_3CN$: 313. $\lambda_\mathrm{max}$ (nm) $(\varepsilon/\mathrm{M^{-1}\,cm^{-1}})$ in $CH_3CN$: 622 (265), 376 (18 100), 270 (36 800).

### *$[Ni_2L^4](ClO_4)_2$*

$[Ni_2L^4](ClO_4)_2$ was synthesized by following the procedure described previously for $[Ni_2L^1](ClO_4)_2$, using *o*-phenylenediamine instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.59 g (77%). Anal. Calcd. for $C_{48}H_{50}O_{12}N_6Cl_2Ni_2$(%): C, 52.84; H, 4.58, N, 7.70, Found: C, 52.98; H, 4.66; N, 7.82. Selected IR (KBr): 1621 (s), 1099 (m), 625 (s) $cm^{-1}$. Conductance $(\Lambda_\mathrm{m}/\mathrm{S\,cm^2\,mol^{-1}})$ in $CH_3CN$: 275. $\lambda_\mathrm{max}$ (nm) $(\varepsilon/\mathrm{M^{-1}\,cm^{-1}})$ in $CH_3CN$: 625 (202), 378 (11 500), 312 (15 500), 274 (30 100).

### *$[Ni_2L^5](ClO_4)_2$*

$[Ni_2L^5](ClO_4)_2$ was synthesized by following the procedure described previously for $[Ni_2L^1](ClO_4)_2$, using 1,8-diaminonaphthalene instead of 1,2-diaminoethane. The compound obtained was orange–red. Yield: 1.62 g (75%). Anal. Calcd. for $C_{52}H_{54}O_{12}N_6Cl_2Ni_2$(%): C, 54.73; H, 4.56, N, 7.36, Found: C, 54.90; H, 4.56; N, 7.51. Selected IR (KBr): 1620 (s), 1100 (m), 620 (s) $cm^{-1}$. Conductance $(\Lambda_\mathrm{m}/\mathrm{S\,cm^2\,mol^{-1}})$ in $CH_3CN$: 278. $\lambda_\mathrm{max}$ (nm) $(\varepsilon/\mathrm{M^{-1}\,cm^{-1}})$ in $CH_3CN$: 655 (210), 425 (13 600), 380 (12 600), 290 (37 200).

## *Acknowledgements*

M.T gratefully appreciates the financial support received from CSIR and the UGC major project sanctioned to M.K., New Delhi.

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