



Research Article

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Antimicrobial and electrochemical studies of Schiff base of Mn (II) and Ni (II) tetraazamacrocyclic complexes

Sweety*, Anuj Kumar, Prashant Tevatia and Randhir Singh

Department of Chemistry, Gurukula Kangri Vishwavidyalaya, Haridwar 249404, India

ABSTRACT

Tetraazamacrocyclic complexes have been synthesized by the condensation of 2, 3-diamino naphthalene, diethyl 2,6-pyridinedicarboxylate and metal ion salts of Mn (II), Ni (II). These synthesized complexes were characterized by elemental analysis, molar conductivity measurements, UV/Vis, IR and cyclic voltammetric technique. These complexes were also screened against antimicrobial activity. These complexes were found to be distorted octahedral geometry on the basis of electronic spectra. The electrochemical behavior of these complexes suggested that metal centers were distinguished by their intrinsic redox systems.

Keywords: Macrocylic complexes, antimicrobial activity, cyclic voltammetry

INTRODUCTION

The development of bioinorganic field is an important factor in the growth of interest in macrocyclic complexes [1-2]. The coordination chemistry of Polyazamacrocyclic complexes are extensively studied from the viewpoint of molecular recognition, supramolecular structures and artificial catalyst [3-4]. Macrocyclic complexes much studied because of their application in various scientific areas. The design and synthesis of macrocyclic complexes have a great attention because they can be used as supramolecular devices, MRI contrast agent, antimicrobial, anticancer and antitumor activity [5-8]. The chemistry of macrocyclic complexes are also important due to their use as dyes, pigments as well as NMR shift reagents [9-12]. The activity and stability of tetraaza macrocyclic complexes depends on the number of heteroatoms, the ring size and nature of the axial substituents on macrocyclic framework [13]. Electrochemistry of macrocyclic complexes have been a great interest as their usages in various areas such as photosensitization, photovoltaic cell, and electrochromic display. Their fundamental usages of these complexes are arises from their electron transfer capacities [14-16]. Condensation between dicarbonyl and diamine play a vital role in the development of synthetic macrocyclic complexes. In the present studies, we have synthesized Schiff base tetraazamacrocyclic complexes by template method using 2,3-diamino naphthalene, diethyl 2,6-pyridinedicarboxylate with Ni(II) and Mn(II) metal ion salts and their spectral, redox behavior and antimicrobial activities have been taken into account.

EXPERIMENTAL SECTION

All the chemicals used were of AR grade. Microanalyses were carried out at CIL SAIF, Punjab University, Chandigarh (Eager Xperience and TOF MS ES+6018e3). IR spectra were recorded on the Shimadzu 8400S spectrometer using KBr DRS system (4,000–400 cm^{-1} region). UV/Vis spectra were taken with Shimadzu 2450 spectrophotometer (800–400 cm^{-1}). The conductivity values were observed by Auto ranging Conductivity/TDS Meter

(TCM⁺). The CV measurements were carried out on PGSTAT101 Metrohm Model 663VA Stand using the NOVA software and utilizing a three-electrode system at 25°C. The working electrode was a Pt disc with an area of 0.03 cm². The working electrode surface was polished with a H₂O suspended Al₂O₃ before each run. A Pt wire served as the counter electrode and Ag/AgCl (saturated KCl) was employed as the reference electrode. Macrocylic complex to be analyzed are of 10⁻³ M with tetraethylammoniumperchlorate (TEAP) as the supporting electrolyte (0.1M) in AR grade methanol. High-purity N₂ was used for declaration before running the experiment.

Synthesis of Schiff base tetraazamacrocyclic complexes:

Synthesis of these tetraazamacrocyclic complexes were carried out according to the literature [17]. A methanolic solution of 2, 3-diamino naphthalene (0.316 g, 0.002 mol) was added slowly to the methanolic solution of diethyl 2,6-pyridinedicarboxylate (0.390g, 0.002mol) in a round bottom flask then the mixture were added to a methanolic solution of metal salt (MnCl₂.4H₂O.0.197g, 0.001 mol and NiCl₂.6H₂O 0.237 g, 0.001mol). The reaction mixture was refluxed under heating for 8 hours. The mixture was cooled at room temperature and dry over a rotary evaporator. Colored crystals were obtained and crystallized by methanol solvent.

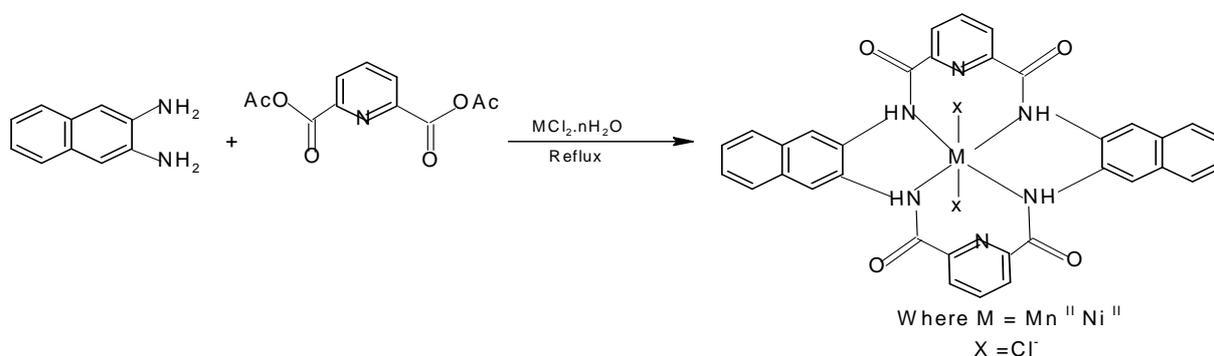


Fig.1: Synthesis scheme for Schiff base tetraazamacrocyclic complexes of Mn(II) and Ni(II)

RESULTS AND DISCUSSION

Physical properties: These synthesized Schiff base tetraazamacrocyclic complexes are colored and soluble in methanol, dimethylformamide, dichloromethane and acetonitrile solvent. They are stable at room temperature and non hygroscopic in nature. These complexes are found monomeric in nature by molecular weight determination. The molar conductance data showed non electrolytic in nature of these macrocyclic complexes. Thus, these complexes may be formulated as [M(L)X₂] where M = Mn(II), Ni(II) and X = Cl⁻ [18-20]. Physical and analytical data are given in **table1**.

Table 1: Physical and analytical data of Mn (II) and Ni (II) Schiff base tetraazamacrocyclic complexes

Complex	Yield (%)	M.P. (°C)	Color	M.W Found (calc.)	Elemental analysis; found (calc.) in %			Molar cond.
					C	H	N	
[C ₃₄ H ₂₂ N ₆ O ₄ Mn]Cl ₂	75.28	190	Green	688 (704)	56.88 (57.59)	3.01 (3.12)	11.90 (11.93)	32
[C ₃₄ H ₂₂ N ₆ O ₄ Ni]Cl ₂	90.80	180	Brown	701 (707)	57.65 (57.70)	3.10 (3.11)	11.86 (11.88)	40

Spectral Studies

UV/Vis Spectra:

The electronic spectra of these tetraazamacrocyclic complexes were observed in dichloromethane (10⁻⁴ M) at room temperature. The spectra of Mn (II) complex showed three adsorption bands at 30120, 26178 and 24875 cm⁻¹ that may be assigned to ⁶A_{1g} → ⁴A_{1g} (4G), ⁶A_{1g} → ⁴E_g (4G), ⁶A_{1g} → ⁴E_g (4D) transitions, respectively. The electronic spectra Ni (II) macrocyclic complex exhibit four absorption bands in similar conditions (**fig.2**) that showed two bands at 40000 and 31746 cm⁻¹ that assigned to n → π* and π → π* transitions whereas other two bands of lower energy at 24691 and 17361 cm⁻¹ indicated as ³A_{2g}(F) → ³T_{2g}(F) and ³A_{2g}(F) → ³T_{1g}(P) transitions[21-22].

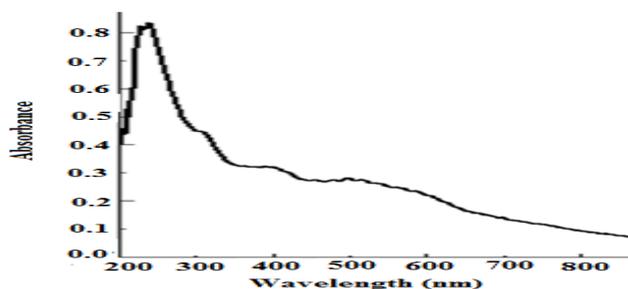


Fig. 2: UV-Vis spectra of Ni (II) Schiff base tetraazamacrocyclic complex

IR Spectra:

The primary identification regarding formation of macrocyclic complexes were carried out by IR spectral studies. The presence of medium intensity bands in the region $3200-3310\text{ cm}^{-1}$ are due to N-H stretching indicate of imine-enol tautomeric form of amide in the complexes. The IR absorption bands in the region $1600-1630\text{ cm}^{-1}$ showed the C=N stretching vibration that prove the complete condensation of carbonyl and diamines. The medium intensity bands in the region $2820-2950\text{ cm}^{-1}$ are due to C-H stretching vibration. The bands in the range $430-480\text{ cm}^{-1}$ are due to M-N stretching vibration that also proves the complexation of macrocyclic complexes [23-25]. IR spectra of Mn (II) complex showed in **fig.3** and the electronic data are given in **table 2**. These spectral studies suggest distorted octahedral geometry for both the complexes.

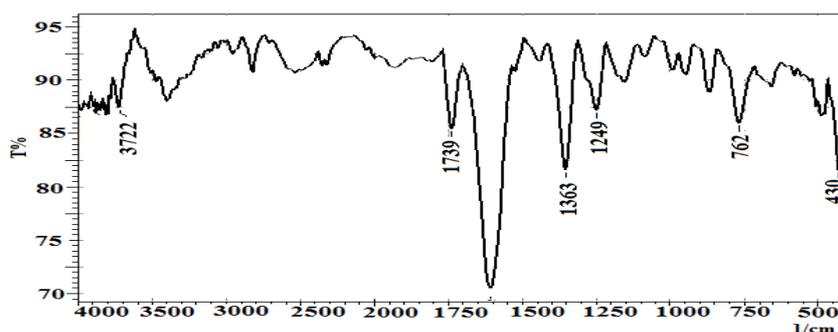


Fig.3: IR spectra of Mn (II) Schiff base tetraazamacrocyclic complex

Table 2: Spectral data of Schiff base tetraazamacrocyclic complexes of Mn (II) and Ni (II)

Complexes	λ_{max} (cm^{-1})	Assignments	IR bands (cm^{-1})	Assignments
$\text{C}_{34}\text{H}_{22}\text{N}_6\text{O}_4\text{Mn}$	30,120	${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}(\text{G})$	430	M-N str.vib.
	26,178	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$	767	C-H bend. vib.
	24,875	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{D})$	1239,1363	C-H str. vib. in CH_2
			1650,1739	C=O vib. of amide
			3722	N-H str.vib of amide
$\text{C}_{34}\text{H}_{22}\text{N}_6\text{O}_4\text{Ni}$	40,000	$n \rightarrow \pi^*$	460	M-N str.vib.
	31746	$\pi \rightarrow \pi^*$	720	C-H bend. vib.
	24691	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$	1250,1352	C-H str. vib in CH_2
	17361	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{P})$	1680,1745	C=O vib. of amide
			3718	N-Hstr.vib. of amide

Cyclic voltammetric studies

Electrochemical studies of these tetraazamacrocyclic complexes have been carried out in DMSO and DMF containing 0.1M TEAP as supporting electrolyte. The cyclic voltammogram (**fig. 4a**) of Mn(II) Schiff base complex was recorded at 100 mVs^{-1} scan rate in DMSO solvent which exhibited two anodic peaks at -0.25 and -0.86 V corresponding to the cathodic peaks at +0.35 and -0.46 V. On the basis of peak separation $\Delta E = 0.10 - 0.40\text{ V}$ and peak current ratio ($i_{\text{pa}}/i_{\text{pc}}$) these redox couple found to be quasireversible and irreversible process which can be assigned to $\text{Mn}^{+3/+2}$ and $\text{Mn}^{+2/+1}$ redox process respectively. Another redox couple are also observed at E_{pa} and E_{pc} +0.79 and +1.25 V that suggested to $\text{L}^{0/+1}$ redox process. Further, the cyclic voltammogram (**fig. 4b**) of this complex was also recorded in DMF in similar conditions that showed interesting results with elimination of ligand redox

couple while other redox process were observed as similar too in DMSO with shifting of 0.12 V in negative potential region with decrease in peak height. The cyclic voltammogram of Ni (II) macrocyclic complex were also recorded in same solvents. In DMSO, this complex showed one redox process corresponding to $\text{Ni}^{2+/+}$ couple. This redox process is quassireversible with the peak separation $\Delta E = 0.14$ V and peak current ratio ($i_{pa}/i_{pc} \approx 1$). One separate cathodic peak is also observed in positive potential region which can be assigned to $\text{Ni}^{+2} \rightarrow \text{Ni}^+$ reduction process at +0.41 V while in DMF, this complex showed only one redox process same as in DMSO but the peak height is less than that of in DMSO solvent. Further, the plots of i_p against $v^{1/2}$ were found to be linear for the $\text{Mn}^+/\text{Mn}^{+2}$ and $\text{Ni}^{+2}/\text{Ni}^+$ redox processes in both solvents, indicating that these redox processes were diffusion controlled process.

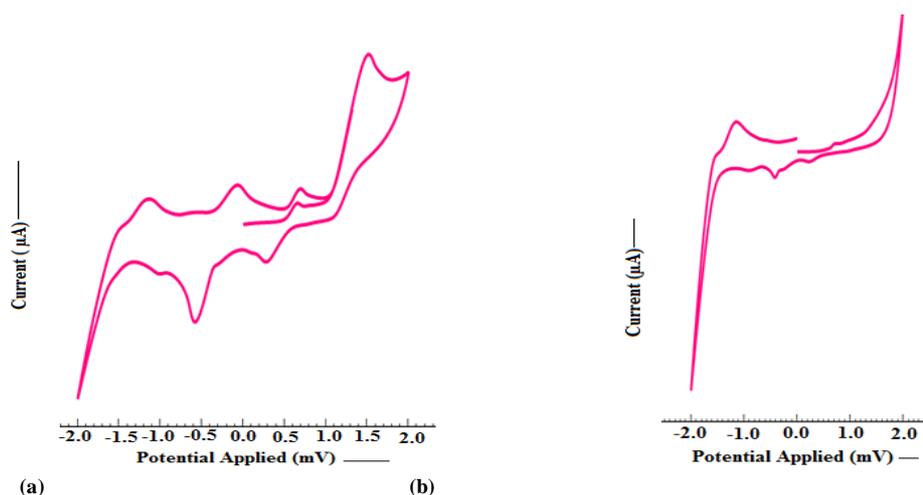


Fig 4: Cyclic voltammogram of Mn(II) Schiff base macrocyclic complexes (a) in DMSO and (b) in DMF containing 0.1 M TEAP and recorded at 100 mVs^{-1}

Biological activity:

The antimicrobial activities of these tetraazamacrocyclic complexes were studied by agar well diffusion method. DMSO solvent medium was used as a negative control while Gentamycin media was used as positive control. Antimicrobial activities of both the Schiff base tetraazamacrocyclic complexes were evaluated by measuring the zone of growth inhibition against the *E. coli*, *S. aureus*, *B. cereus*, *P. aeruginosa pathogens* and *C. albicans* with zone reader (Hi Antibiotic Zone Scale) [26]. The Mn(II) Schiff base tetraazamacrocyclic complex showed maximum zone of inhibition against *E. coli* (22 mm) while Ni(II) Schiff base tetraazamacrocyclic complex exhibit maximum zone of inhibition against *S. aureus* (19 mm). Against fungal pathogen *C. albicans*, Ni(II) Schiff base tetraazamacrocyclic complex was found most effective (18 mm) followed by the Mn(II) Schiff base tetraazamacrocyclic complex (17 mm) as showed in **fig. 5**.

Table 3: Antimicrobial activity of Mn (II) and Ni (II) Schiff base tetraazamacrocyclic complexes

Complex (100 mg/ml)	Diameter of inhibition zone (mm)				
	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>B. cereus</i>	<i>S. aureus</i>	<i>C. albicans</i>
$[\text{C}_{34}\text{H}_{22}\text{N}_6\text{O}_4\text{Mn}]\text{Cl}_2$	22	17	15	18	17
$[\text{C}_{34}\text{H}_{22}\text{N}_6\text{O}_4\text{Ni}]\text{Cl}_2$	16	16	18	19	18
Gentamycin	24	24	24	24	20

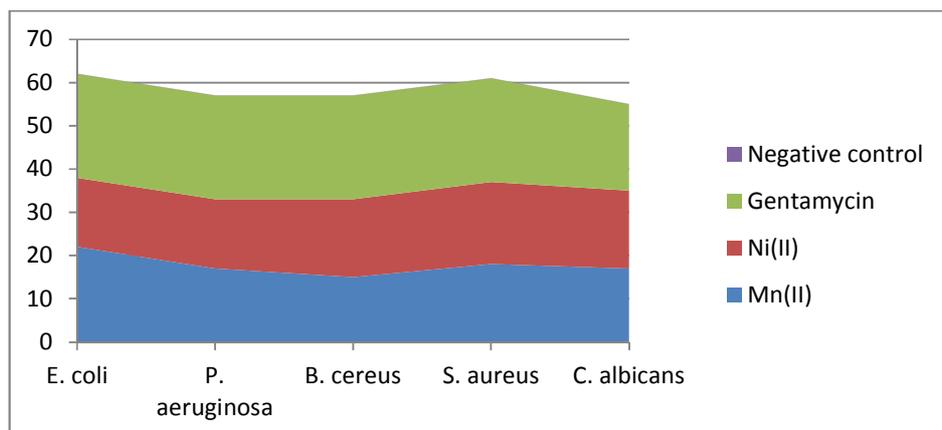


Fig. 5: Graphical representation of antimicrobial activity of Mn (II) and Ni (II) Schiff base tetraazamacrocyclic complexes

CONCLUSION

In these studies, Schiff base tetraazamacrocyclic complexes of Mn (II) and Ni (II) have been synthesized by the template method using 2,3-diaminonaphthalene, diethyl-2,6-pyridinedicarboxylate and corresponding metal ion salts. The electronic studies confirmed the octahedral geometry to these Schiff base tetraazamacrocyclic complexes. Cyclic voltammetric studies were carried out in the potential region -2.0 to +2.0 V vs Ag/AgCl at 100 mVs⁻¹ scan rate for both complexes that showed the stabilization of their unusual oxidation states. These synthesized Schiff base tetraazamacrocyclic complexes have shown good promise for antimicrobial activity against Gram +ve and Gram -ve bacteria and compared with the standard drug.

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