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SYNTHESIS, SPECTRAL CHARACTERIZATION, ELECTROCHEMICAL AND ANTIMICROBIAL ACTIVITY OF MACROCYCLIC SCHIFF BASE VANADYL COMPLEXES

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ABSTRACT

The new macrocyclic Schiff base ligands were synthesized by the condensation reaction between 9,10-phenanthrenequinone and *o*-phenylenediamine derivatives in 1:1 molar ratio. The ligands react with vanadylsulphate in 1:1 molar ratio to give square pyramidal geometry for VO(IV) complexes. All the complexes are non–hygroscopic in nature and stable to the atmosphere. The synthesized macrocyclic ligands and the isolated Schiff base complexes have been characterized by elemental analysis, molar conductivity, IR, electronic spectroscopy and cyclic voltammetric studies. Further the complexes have been subjected to antimicrobial activity. The results obtained from these studies and their interpretation to solve the structure of the complexes.

Keywords: Macrocyclic, 9,10-phenanthrenequinone, Schiff base, Antimicrobial activity.

INTRODUCTION

Macrocyclic Schiff base nitrogen donor ligands have received special attention because of their mixed hard–soft donor character and versatile coordination behavior[1], and for their biological activities, i.e., toxicity against bacterial growth[2], anticancerous[3] and other biochemical properties[4]. Macrocyclic Schiff base ligands are known to play a very important and vital role in the stability of the metal complexes. They differ from other noncyclic ligands due to the structural factors such as the cavity size, stereochemical rigidity, flexibility and ability to coordinate in either neutral or deprotonated form[5]. On concerning the metal ions the macrocyclic Schiff bases have selective chelation to certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of metal ion and coordinating properties of counter ions[6]. They also contain –N=CH–CH=N– structure unit, which forms a strong chelate ring giving possible electron delocalization associated with extended conjugation that may affect the nature of the complex formed[7].

The present work aims to synthesis, characterize the chemical structure and to study the antimicrobial activity of the synthesized tetraazamacrocyclic Schiff base oxovanadium(IV) complexes. The oxovanadium(IV) forms greenish brown coloured complexes with the tetraazamacrocyclic Schiff bases obtained by the condensation of 9,10-phenanthrenequinone and *o*-phenylenediamine derivatives. The synthesized complexes were characterized by elemental analysis, molar conductivity, eletrochemical and spectral studies. The metal complexes were also evaluated for their antibacterial activity against several bacterial strains, such as Staphylococcus aureus, Salmonella.thypi and Escherichia coli.

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade. $VOSO_4.H_2O$, 9,10-phenanthrenequinone, 4,5-dichloro-*o*-phenylenediamine and 4,5-dimethyl-1,2-phenylenediamine were purchased from Aldrich and p-phenylenediamine was purchased from Loba Chemie and were used without further purification. Ethanol, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were used as solvents. Ethanol was distilled with a good fractionating column.

The elemental analyses were performed using a Carlo–Eraba 1106 instrument. Molar conductances of the complexes in DMF solution were measured with ELICO CM 185 conductivity Bridge. The infrared spectra were recorded on the Perkin Elmer FT-IR-8300 model spectrometer using KBr disc in the region 4000–400 cm^{-1}. Electronic absorption spectra in the ultraviolet(UV)–Visible range were recorded on Perkin Elmer Lambda-25 between 200 and 800 nm by using DMF as the solvent.

All voltammetric experiments were performed with a CHI 760 electrochemical analyzer, in single compartmental cells using tetrabutylammonium perchlorate as a supporting electrolyte. The redox behavior of the complexes has been examined at a scan rate of 0.1 Vs^{-1} in the potential range +2.0 to –2.0 V. A three-electrode configuration was used, comprising a glassy carbon electrode as the working electrode, a Pt-wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. The electrochemical data such as cathodic peak potential (Epc) and anodic peak potential (Epa) were measured.

The antibacterial activity of the complexes of Cu(II), Ni(II) and Mn(II) were checked by the disc diffusion technique[8]. This was done on Staphylococcus aureus, Salmonella thypi and Escherichia coli at 37°C. The disc of Whatmann no.4 filter paper having the diameter 8.00 mm were soaked in the solution of compounds in DMSO (1.0 mg cm^{-1}). After drying it was placed on nutrient agar plates. The inhibition areas were observed after 36 hours. DMSO was used as a control and Streptomycin as a standard.

Synthesis of Ligands

To a stirring solution of *o*-phenylenediamine and substituted *o*-phenylenediamine (4,5-dichloro-*o*-phenylenediamine, 4,5-dimethyl-1,2-phenylenediamine) in methanol (25 ml), hydrochloric acid (2 ml; 2M) and 9,10-phenanthrenequinone in methanol (25 ml) was added drop wise with constant stirring and the mixture was boiled under reflux for 5 hrs[9]. The product was filtered off, washed with methanol, and dried in vacuum. Synthesis pathway is shown in Figure 1.

Synthesis of Complexes

A solution of ligand [9,10-phenanthrenequinone, *o*-phenylenediamine] (0.01 mol) in acetonitrile (25 ml) were separately added dropwise to a stirred acetonitrile solution (25 ml) of vanadyl sulphate (0.01 mol; 0.163g) at 50°C, giving colored product. The product was filtered off, washed with acetonitrile, and dried under vacuum at room temperature. The same procedure was adopted for the synthesis of other two complexes. Synthesis pathway is shown in Figure 2.

RESULTS AND DISCUSSION

The synthesized macrocyclic ligands and their complexes were checked by comparing the TLC with the starting materials, which results a single spot different from the starting materials, confirms the formation and the purity of the ligands and their complexes. Solubility of the ligands and their complexes were studied in various organic solvents. The ligands were soluble in non polar organic solvents and partially soluble in methanol. The complexes were soluble in DMF and DMSO. The sharp melting points show the purity of the ligands and their complexes.

The elemental analyses data were presented in Table 1. From the presented data the 1:1 ligand to metal stiochiometric for the complexes is concerned. The elemental analysis data was compared with that of such a formulation, which is expected to give rise to neutral complexes. Further the analytical data of the complexes are also in good agreement with the formula proposed.

The conductivity measurements were performed to establish the charge type of the complexes. The molar conductance of the metal complexes ($1x10^{-3}$M) in DMF at room temperature. The observed molar conductance values are presented in Table 1. The complexes of oxovanadium(IV) presently reported are electrolytes, confirming the ionic structure proposed. The results were compared with the literature values in arriving at this conclusion[10].

IR spectra are useful to assign the structure of the ligands and the mode of coordination. The IR spectrum of the free ligands shows absorption bands in the frequency range 1613–1588 cm^{-1} assigned to C=N stretching mode[11]. This band is shifted to lower wave numbers in the complexes indicating the participation of the azomethine nitrogen in coordination[12] (M–N). New band was found in the spectra of the complexes in the region 431–442 cm^{-1} which was assigned to υ(M–N) stretching vibrations. A further

examination of the IR spectra of the complexes reveals a band in the 950–960 cm^{-1} region. This band is typical of oxometal species and is assigned to the V=O stretching of the vanadyl group[13]. The absence of band characteristic of ν(C=O), aromatic primary amine bands ν(N–H) expected to appear in free 9,10-phenanthrenequinone and phenylenediamines, respectively, confirms the formation of the proposed macrocyclic framework. The absorption bands in the frequency range 1064–1107 cm^{-1} assigned to the SO_4^{2-} ion as counter ion[14].The spectral data are listed in Table 2.

The electronic spectrum of the ligands in DMSO shows absorption bands at 295 and 385 nm (Table 3). The bands are indicative of benzene and other chromophore moieties present in the ligands. The absorption bands of the complexes are shifted to longer wave length compared to that of the ligand as expected[15]. The d–d transitions[16] for the complexes were observed at 535–550 nm indicate that the complexes are square pyramidal geometry. A moderately intensive band observed in the range of 350–385 nm is due to n–π* transition, and the strong band observed in the range of 265–290 nm is due to π–π* for these complexes[17].

The cyclicvoltammetry studies were done by using DMSO as solvent with TBAP as supporting electrolyte and an Ag / AgCl as reference. The working electrode was a platinum electrode. A platinum wire served as the counter electrode. The electrochemical data such as cathodic peak potential (Ep_c), anodic peak potential (Ep_a) are given in Table 3. The cyclicvoltammogram of the ligands may contain two peaks. One peak at Ep_c and another peak at Ep_a. The above peaks may be due to the reduction of the azomethine group and oxidation of the organic moiety. Vanadyl complexes are expected to undergo reduction to V(III), V(II) and oxidation to vanadium (V). The examination of the cyclicvoltammogram over the whole range reveals that the vanadyl complexes in the present study underwent an almost reversible oxidation to vanadium(V).

Antibacterial activities of the complexes have been carried out against bacteria like Staphylococcus aureus, Salmonella.thypi and Escherichia coli using nutrient agar medium by the well diffusion method[18]. The biological activity of the complexes was described in Table 4 and Figure 3.

The above values clearly indicate that the zone of inhibition area is greater for the metal complexes than the standard. The increase in antibacterial activity is due to faster diffusion of metal complexes as hole through the cell membrane or due to the combined activity effect of the metal and ligand. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and Chelation theory[19].

The oxovanadium(IV) complexes have been screened for the evaluation of antibacterial activities. The complexes exhibited higher activities than the standard. Out of the three complexes, $[VO(C_{42}H_{28}N_4)]SO_4$ has the higher activity, because of electron donating nature of the methyl group in the ligand environment. Some of the other oxovanadium(IV) complexes also showed higher antibacterial effects than those of the standard antibiotic. This phenomenon was explained based on chelation theory[20].

The antibacterial activity is also dependent on the molecular structure of the compound, the employed solvent and the bacterial strain under consideration. Such screening of various organic compounds and identifying the active agents is essential because the successful prediction of a molecule and drug-like properties at the onset of drug design will pay off later in drug development.

CONCLUSION

The ligands and the mononuclear macrocyclic complexes were characterized by Physico-chemical methods. The stoichiometric of the complexes have been proposed based on elemental analysis and molar conduction data. The coordination behavior of the ligands and its complexes has been determined with help of infrared spectra. The higher values of conductivity indicates the electrolytic nature of the mononuclear macrocyclic complexes, which was, supported IR spectra showing the presence of sulphate ions as the counter ions, in addition to the presence of V=O group. Electronic spectral studies indicate that the d-d transition of oxovanadium(IV) ion was responsible for the appearance of a band in the visible region. Vanadyl complexes are expected to undergo reduction to V(III) , V(II) and oxidation to vanadium(V). The ligands and the oxovanadium(IV) complexes have been screened for the evaluation of antibacterial activities. The complexes exhibited higher activities compare to that exhibited by the

standard. Out of the three complexes, $[VO(C_{42}H_{28}N_4)]$ SO_4 is the higher activity, because of electron donating nature of the methyl group in the ligand environment.

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Table-1: Elemental analysis and molar conductance data of the ligands and their vanadyl complexes

Ligands/ Complexes	Calculated (Found)				Color	Λ_M (Ohm^{-1} cm^2 mol^{-1}
	C	H	N	Metal		
$C_{40}H_{24}N_4$	86.33 (86.29)	03.59 (03.54)	10.07 (10.03)	-	Greenish yellow	-
$[VO(C_{40}H_{24}N_4)]SO_4$	66.75 (66.72)	02.78 (02.74)	07.78 (07.77)	09.31 (09.27)	Greenish Brown	85
$C_{40}H_{20}N_4Cl_4$	69.36 (69.32)	02.31 (02.27)	08.09 (08.02)	-	Yellow	-
$[VO(C_{40}H_{20}N_4Cl_4)]SO_4$	56.14 (56.11)	01.87 (01.82)	06.54 (06.48)	07.83 (07.86)	Dark Brown	82
$C_{44}H_{28}N_4$	86.27 (86.25)	04.57 (04.53)	09.15 (09.12)	-	Pale yellow	-
$[VO(C_{44}H_{32}N_4)]$ SO_4	68.12 (68.10)	03.61 (03.54)	07.22 (07.16)	08.64 (08.61)	Dark Green	89

Table-2:Infrared spectral data for macrocyclic Schiff ligands and their vanadyl complexes

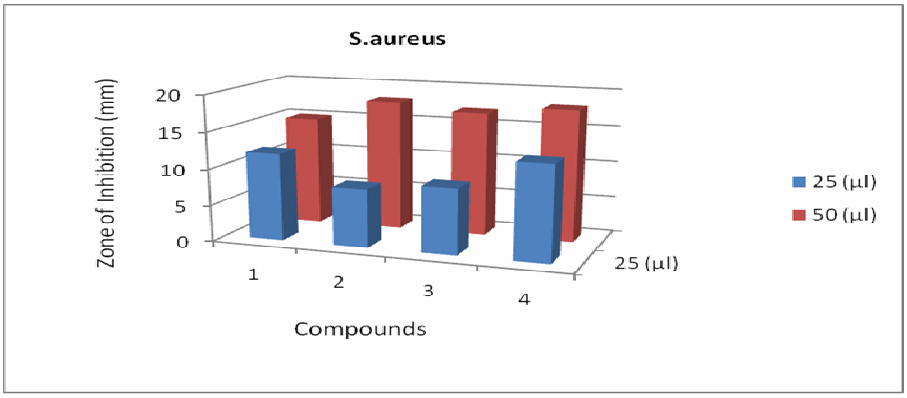
Ligands/Complexes	C = N (cm^{-1})	C – N (cm^{-1})	V=O (cm^{-1})	M–N (cm^{-1})	SO_4^{2-} (cm^{-1})
$C_{40}H_{24}N_4$	1606	1475	-	-	-
$[VO(C_{40}H_{24}N_4)]SO_4$	1566	1468	961	437	1064
$C_{40}H_{20}N_4Cl_4$	1588	1460	-	-	-
$[VO(C_{40}H_{20}N_4Cl_4)]SO_4$	1568	1456	957	431	1107
$C_{44}H_{28}N_4$	1613	1480	-	-	-
$[VO(C_{44}H_{32}N_4)]\ SO_4$	1570	1472	959	442	1095

Table-3:Electronic absorption spectral data and cyclic voltammetric data of the ligands and complexes

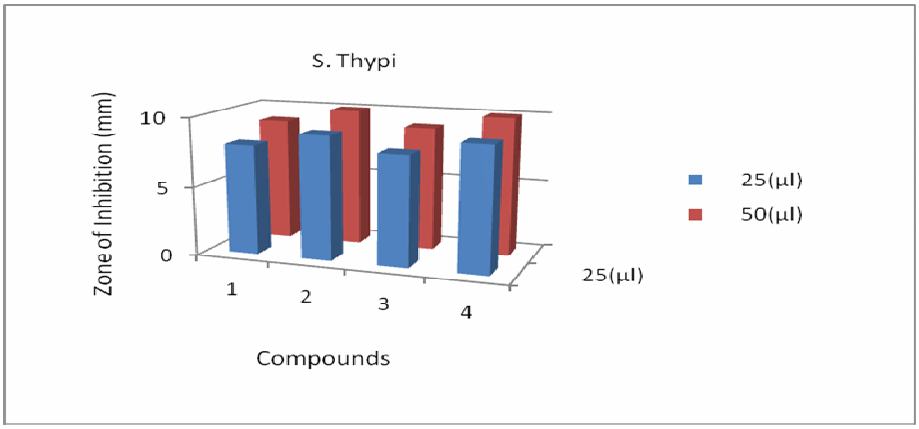
Ligands/ Complexes	$\pi\rightarrow\pi^*$ (nm)	$n\rightarrow\pi^*$ (nm)	L→M (CT) (nm)	d-d (nm)	Epc (V)	Epa (V)	ΔEp (V)
$C_{40}H_{24}N_4$	290	385	-	-	–1.29, 0.33	-	
$[VO(C_{40}H_{24}N_4)]SO_4$	245,285	360	455	550	–0.44, –1.8	–1.26	0.2
$C_{40}H_{20}N_4Cl_4$	290	380	-	-	–0.42, –1.49	–1.23	0.26
$[VO(C_{40}H_{20}N_4Cl_4)]SO_4$	280	375	470	535	–0.11, –0.63	–0.86, –1.00	0.37
$C_{44}H_{28}N_4$	265	350	-	-	–0.27, –1.3	-	
$[VO(C_{44}H_{32}N_4)]\ SO_4$	280	365	465	540	–0.8	–1.11, –1.26	0.31

Table-4: Antibacterial activities of macrocyclic Schiff base vanadyl complexes

Compound	Staphylococcus aureus (mm)		Salmonella thypi (mm)		Escherichia coli (mm)	
	25(µl)	50(µl)	25(µl)	50(µl)	25(µl)	50(µl)
Standard	12	15	8	9	12	18
$[VO(C_{40}H_{24}N_4)]SO_4$	8	18	9	10	19	20
$[VO(C_{40}H_{20}N_4Cl_4)]SO_4$	9	17	8	9	18	17
$[VO(C_{44}H_{32}N_4)]SO_4$	13	18	9	10	19	23



(A)



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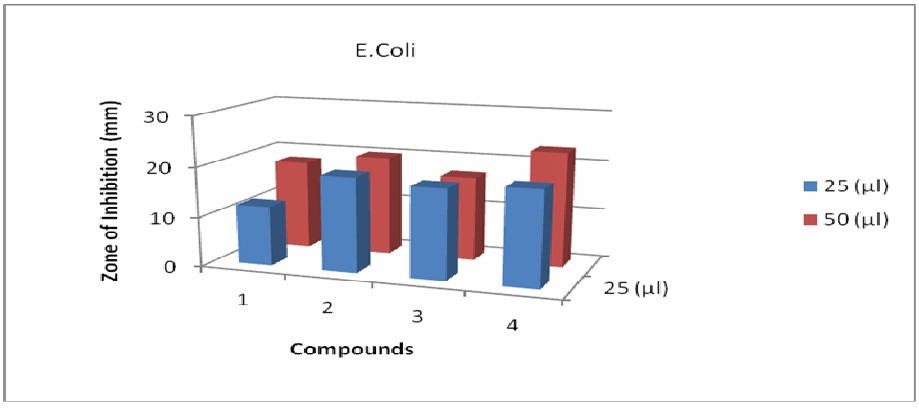

(C)

Fig.-3: Difference between the antimicrobial activities of the macrocyclic Schiff base metal complexes. 1.Standard, 2. $[VO(C_{40}H_{24}N_4)]SO_4$, 3. $[VO(C_{40}H_{20}N_4Cl_4)]SO_4$, 4. $[VO(C_{44}H_{32}N_4)]\ SO_4$.

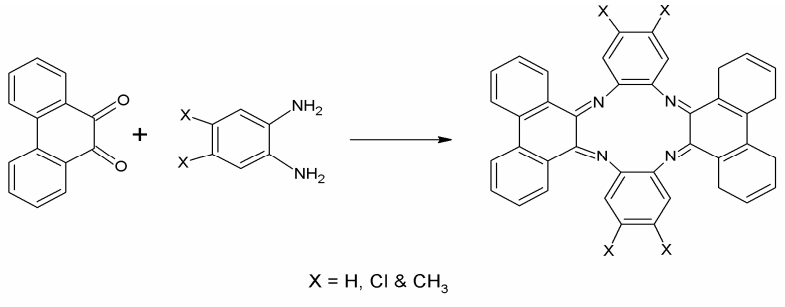

Fig.-1: Synthesis of macrocyclic Schiff base ligands.

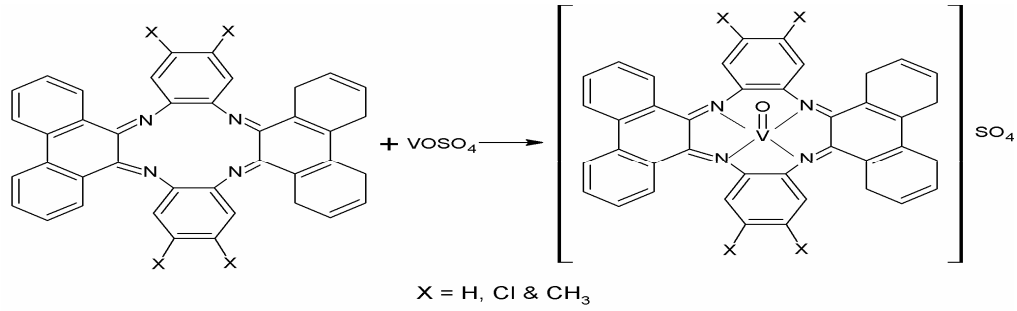

Fig.-2: Synthesis of macrocyclic Schiff base complexes

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