

Synthesis, Characterization, Electrochemical and Antimicrobial Activity of Macrocyclic Binuclear Cu(II), Ni(II) and VO(II) Schiff Base Complexes

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Abstract: A template condensation of 3,3'-diaminobenzidine with benzil and dimethyl ortho-phenylenediamine in the presence of Cu(II), Ni(II) and VO(II) resulted in the formation of tetradentate macrocyclic Schiff base binuclear complexes of the type $[M_2 L.X]$ and $[M_2 L]$. X_2 (where, $X = 2ClO_4^-$, CH_3COO^- and $2SO_4^{2-}$). Structural characterization of the complexes were achieved by several physicochemical methods, namely elemental analysis, electronic spectra, infrared, EPR, cyclic voltammetry, molar conductivity and magnetic susceptibility measurements. A square planar binuclear structure was proposed for the perchlorate anions in Cu(II) and Ni(II) complexes. Whereas the square pyramidal environment around the VO(II) center. The Schiff base complexes were investigated for antibacterial and antifungal properties of gram-positive bacteria (*staphylococcus aureus*), gram-negative bacteria (*pseudomonas fluorescens*) and fungi (*Aspergillus fumigatus*) were used in this study to assess their antimicrobial properties. The results showed that this skeletal framework exhibit marked potency as antimicrobial agents.

Keywords: Tetradentate macrocyclic Schiff base, EPR, Cyclic voltametry, Square-pyramidal, *Aspergillus fumigatus*

Introduction

The great interest in synthetic macrocycles and their corresponding metal complexes is related to the fact that they can mimic naturally-occurring macrocyclic molecules in their structural features. The formation of macrocyclic complexes depends significantly on the dimension of the internal cavity, on the rigidity of the macrocycle, on the nature of its donor atoms and on the complexing properties of the counter ion. The syntheses of the macrocyclic ligands are generally carried out in the presence of a suitable salt, the cation of which is assumed to act as a template for the ring formation^{1,2}. Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different fields. Schiff bases and their biologically active complexes have been often used as chelating ligands in

the coordination chemistry of transition metals, radiopharmaceuticals for cancer targeting³, agrochemicals⁴, model systems for biological macro molecules⁵, catalysts⁶ and as dioxygen carriers⁷.

In the present study the complexes was prepared by the template condensation of 3,3'-diaminobenzidine with benzil and dimethyl-orthophenylenediamine and the transition metals like Cu(II), Ni(II) acetate and perchlorate salts and VO(II) to afford the corresponding binuclear macrocyclic Schiff base complexes. These complexes were characterized with the help of various physicochemical techniques like IR, magnetic susceptibilities, elemental analysis and conductance measurements. Recently, a wide varieties of the Cu(II), Ni(II) and VO(II) complexes of Schiff base derivatives including compartmental and macrocyclic complexes was tested *in vitro* for their antibacterial and antifungal activities against human pathogenic bacteria [using disc diffusion method(DD)]⁸⁻¹⁰. The structure has been dibasic with four nitrogen atoms and can coordinate with two metal ions to form binuclear Cu(II), Ni(II) and VO(II) complexes.

The binuclear macrocyclic Schiff base metal complexes are investigated for antibacterial and antifungal properties. Gram-positive bacteria (*staphylococcus auerus*), gram-negative bacteria (*pseudomonas fluorescens*) and two fungi (*Aspergillus fumigatus*) were used in this study to assess their antimicrobial properties. The copper and vanadium complexes have more effective whereas the nickel complex exhibit mild antibacterial and antifungal activities against these organisms.

Experimental

All the chemicals used were purchased from Aldrich. Solvents used were of analytical grade and purchased commercially and used such as. The purity of metal complexes was tested by TLC.

Methods

Elemental analysis (C, H N) was obtained using Perkin Elmer elemental analyzer. The infrared spectra were recorded in Perkin-Elmer-283 spectrophotometer in the range of 4000-200 cm^{-1} and electronic spectra in DMF were obtained using Shimadzu UV-265 spectrometer. Conductivity measurements were carried out at room temperature on freshly prepared 10^{-3} M DMF solutions using a coronation digital conductivity meter. The magnetic studies were carried out at room temperature on a Gouy balance calibrated with $\text{Hg}[\text{Co}(\text{SCN})_4]$. The cyclic voltammetry studies were carried out in digital CHI 760 C. The electrochemical behavior of the complexes was examined by employing a platinum electrode as working electrode, Ag/AgCl as a reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMF containing 0.1 M tetra butyl ammonium perchlorate(TBAP) as supporting electrolyte. The EPR spectra of Cu(II) complex were recorded on Bruker EMX Plus at room temperature. The antibacterial activities of the compounds were determined by using the disc diffusion method.

Antimicrobial activity

The standardized disk-diffusion method^{11,12} was followed to determine the activity of the synthesized compounds against the sensitive organisms Gram-positive (*staphylococcus auerus*) and Gram-negative bacteria (*pseudomonas fluorescens*) and (*Aspergillus fumigatus*) *Streptomycin* was used as a standard reference in the case of bacteria while *Fluconazole* was used as a standard antifungal reference.

The tested compounds were dissolved in (DMSO which has no inhibition activity) to get concentration of 2 mg/mL. The test was performed on medium potato dextrose agar(PDA) which contains infusion of 200 g potatoes, 6 g dextrose and 15 g agar¹³. Uniform size filter paper disks (three disks per compound) were impregnated by equal volume (10 μ L) from the specific concentration of dissolved test compounds and carefully placed on incubated agar surface. After incubation for 36 h at 27 °C in the case of bacteria and for 48 h at 24 °C in the case of fungi.

Synthesis of the complexes

The complexes were synthesized using template method by condensing 3,3'-diaminobenzidine with benzil and dimethyl-OPD in the presence of respective metal salt. To a hot stirring methanolic solution of (20 mL) of 3,3'-diaminobenzidine was added to the metals like Cu, Ni and VO salt (0.2 mmol) dissolved in the minimum quantity of methanol (~20 mL). The resulting solution was boiled under reflux for ½ h. Then the methanolic solution of benzyl (0.4 mmol) was added after that added a methanol solution of dimethyl-OPD (0.2 mmol) in the same mixture and refluxing was continued for 8 h. The mixture was concentrated to half of its volume and kept in a desiccator overnight. The complexes obtained as solid were then filtered, washed with methanol and diethylether, dried in vacuum. The complexes are soluble in DMF and DMSO, but are insoluble in common organic solvents and water. The complexes were found thermally stable up to ~240-260 °C and then decomposed. The proposed structure of the complexes has been shown in Figure 1.

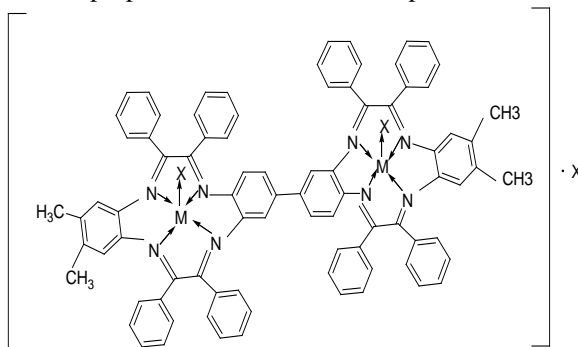


Figure 1. Proposed structure of the synthesized complexes
Where X= CH_3COO^- ; 2ClO_4 ; 2SO_4 ; M= Cu(II), Ni(II) and VO(II)

Results and Discussion

All the complexes were have the corresponding colored solids and are soluble in DMF and stable at room temperature. The macrocyclic binuclear Schiff base metal complexes were characterized by elemental analysis, molar conductivity, IR, UV, EPR and electrochemical studies are gives satisfactory results. The *in vitro* antibacterial screening effects of the investigated compounds were tested against the gram (+ve) and gram (-ve) bacteria and antifungal activities using disc diffusion method.

Molar conductance measurements

Conductivity measurements were carried out in 10^{-3} mol dm^{-3} in DMF solution at 25 °C. The room temperature molar conductivity values of the complexes are given in Table 1. The molar conductance values are in the range characteristic of 1:2 electrolytes for all the complexes, whereas, the acetate complexes of copper and nickel are non electrolytic in nature.

Magnetic properties

The magnetic moment values of binuclear metal complexes were carried out by room temperature. The magnetic moment of Cu(II) complexes lies below the spin only values *i.e.*, 1.56-1.64.B.M. The lower value of magnetic moment at room temperature is consistent with square planar geometry around the metal ions¹⁴. Whereas the Nickel(II) complexes shows diamagnetic in nature and the geometry of the complexes is square planar environment around the central metal atom and there is no metal- metal interaction in Ni(II) centers. The room temperature value of VO(II) ion for the complex is 1.69.B.M. It has been observed that the μ_{eff} values indicate a single unpaired electron and is consistent with non-interacting metal centers or the absence of any strong magnetic interaction between the two VO(II) centers of the molecules.

Table 1. Physical properties and elemental analysis of the macrocyclic binuclear Schiff base complexes

S.No	Compounds	Colour	λ_{max} \AA	ϵ $\text{cm}^2 \text{mol}^{-1}$	μ_{eff} (BM)	Elemental analysis: calcd.(Found)%			
						C	H	N	Metal
1.	[Cu ₂ (C ₈₄ H ₆₆ N ₈ O ₄)]	Dark green			1.58	80.12(80.2)	5.24(5.24)	4.45(4.44)	10.17(10.16)
2.	[Ni ₂ (C ₈₄ H ₆₆ N ₈ O ₄)]	Pale green	234	-	77.41(77.4)	5.06(5.13)	8.60(8.60)	8.90(8.91)	
3.	[Cu ₂ (C ₈₄ H ₆₆ N ₈)] . 2ClO ₄ ⁻	Brown	122	1.64	58.94(58.8)	3.85(3.84)	6.54(6.52)	7.48(7.46)	
4.	[Ni ₂ (C ₈₄ H ₆₆ N ₈)] . 2ClO ₄ ⁻	Pale green	140	-	59.36(59.3)	3.88(3.87)	6.59(6.58)	6.83(6.82)	
5.	[VO ₂ (C ₈₄ H ₆₆ N ₈)] . 2SO ₄	Green			1.69	71.19(71.1)	4.66(4.64)	7.91(7.90)	7.19(7.17)

Electronic absorption spectra

The electronic absorption spectra of the reported compounds were measured at room temperature and the spectral data are given in Table 2. The strong absorption band in the 27,027-37,035 cm^{-1} range of all complexes originating from the azomethine linkage of the Schiff base moiety and it is assignable $n \rightarrow \pi^*$ ¹⁵. The position and intensity of this band show dependence on the nature of the substituents within the carbonyl imine moiety of the tetradentate ligands. An examination of λ_{max} values Table 2 for $n \rightarrow \pi^*$ indicates that an electron donating group *eg.* CH₃ decreases the λ_{max} value while an electron withdrawing group *eg.* Phenyl ring increases it. This is obvious as the presence of electron donating group and the reverse is true when an electron withdrawing group is present. As a result of this, the charge transfer $n \rightarrow \pi^*$ transition requires higher energy for the former and lower energy for the latter.

Further the d-d transition showed a strong band at 540-546 nm for Cu(II) complexes. This is due to $^2B_{1g} \rightarrow ^2A_{1g}$ transition. The spectra of Ni(II) complexes in the visible region at about 510-516 nm and 482-488 nm is assigned to $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{1g}$ transitions, suggesting an pseudo square planar geometry of the ligand around the metal ions¹⁶. The intense charge transfer band at 502 and 528 nm in VO(II) complex assigned to $^2B_2 \rightarrow ^2E$ transitions. This suggesting the square pyramidal environment¹⁷. Based on these data, a square planar geometry has been assigned to the complexes except VO(II) complex which has square pyramidal geometry.

IR-spectra

The IR spectra of the reported compounds were measured as KBr disk and the important IR-spectral feature along with their tentative assignments are given in Table 2. In the spectrum

of the complexes the absence of band in the region $\sim 3400\text{ cm}^{-1}$ corresponding to free primary amine suggests that complete condensation of amino group with diketone group. The disappearance of these band and the appearance of a new strong absorption band near $1597\text{-}1589\text{ cm}^{-1}$ confirms the formation of the Schiff base, as this band assigned to $\nu(\text{C}=\text{N})$ stretching vibration¹⁸ (Table 2). display that frequency value of the $\nu(\text{C}=\text{N})$ is lower value of $\nu(\text{C}=\text{N})$ stretching energy may explained on the basis of a drift of the lone pair density of the azomethine nitrogen towards the central metal atoms^{19,20}, indicating that the coordination takes place through the nitrogen atom of the $(\text{C}=\text{N})$ group. This contention finds support in the presence of new band in the spectra of the complexes at $2932\text{-}2924\text{ cm}^{-1}$ assignable to $\nu(\text{CH}_3)$ and ring ring deformations respectively. The spectra of all complexes reveal an absorption band in the region $1200\text{-}1220\text{ cm}^{-1}$ characteristic to the diimine moiety of the metal chelates²¹. This finding has observed in several diimine containing tetraaza macrocyclic Schiff base complexes²². Thus, it appears that each diketone molecule has reacted with the amino groups of the 3,3'-diaminobenzidine with benzil forming the Schiff base and the dimethyl-orthophenylenediamine is used for ring closure and giving rise to macrocyclic metal complex molecule. The presence of acetate in complexes 1&2 is evidenced by two medium absorption features centered at 1610 cm^{-1} for $\nu_{\text{as}}(\text{COO})$ and 1450 cm^{-1} for $\nu_{\text{sy}}(\text{COO})$. The difference between $(\nu_{\text{as}}-\nu_{\text{sy}})$ is around 160 cm^{-1} agrees with the coordination mode for the acetate ion with the central metal ion²³⁻²⁵. All of the perchlorate salts show a medium band near $1145\text{-}1190\text{ cm}^{-1}$ and a strong band at $1083\text{-}1109\text{ cm}^{-1}$ and sharp band at $621\text{-}626\text{ cm}^{-1}$, indicative of uncoordinated perchlorate anions²⁶⁻²⁹. For vanadyl complexes, a strong band observed at 982 cm^{-1} is assigned to $\nu(\text{V}=\text{O})$ which rules out the possibility of a dimeric structure³⁰. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR- spectra of the metal complexes appear at $490\text{-}470\text{ cm}^{-1}$ assigned to $\nu(\text{M-N})$ stretching vibrations³¹. Thus from the IR- spectra it is clear that the compounds may be bonded to the metal ions through the imine nitrogen.

Table 2. Significant bands in the IR and electronic spectra of the macrocyclic binuclear Schiff base ligand and their metal complexes

S. No	Compound	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{CH}_3)$ cm^{-1}	$\nu(\text{V}=\text{O})$ cm^{-1}	$\text{ClO}_4^-/\text{SO}_4^{2-}$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	λ_{max}
1.	$[\text{Cu}_2(\text{C}_{84}\text{H}_{66}\text{N}_8\text{O}_4)]$	1590	2934			462	542
2.	$[\text{Ni}_2(\text{C}_{84}\text{H}_{66}\text{N}_8\text{O}_4)]$	1596	2928			468	512
3.	$[\text{Cu}_2(\text{C}_{84}\text{H}_{66}\text{N}_8)].2\text{ClO}_4^-$	1598	2932		1083	480	546
4.	$[\text{Ni}_2(\text{C}_{84}\text{H}_{66}\text{N}_8)].2\text{ClO}_4^-$	1580	2930		1110	467	487
5.	$[\text{VO}_2(\text{C}_{84}\text{H}_{66}\text{N}_8)].2\text{SO}_4$	1584	2924	982		489	502

Cyclic voltammetry studies

The electrochemical behavior of the complexes was examined by employing a platinum electrode as working electrode, Ag/AgCl as a reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMF containing 0.1 M tetra butyl ammonium perchloride (TBAP) as supporting electrolyte. The electrochemical properties of the complexes reported in the present work were studied by cyclic voltammetry shown in Figure 2 & 2a.

The cyclic voltammogram of the complexes in 10^{-3} M solution was recorded at room temperature in the potential range 2.0 to -2.0 V with a scan rate 0.1Vs^{-1} . The Cu(II) complex-3 shows a redox potential corresponding to one electron transfer couple at $E_{pc}= 0.6\text{V}$ and associated anodic peak at $E_{pa}= 0.1\text{V}$. This couple is found to be quasi-reversible as the peak separation between the anodic and cathodic potential is very high. But the ratio between the anodic and cathodic current suggests that the process is simple one electron process^{32,33}. The cyclic voltammogram for oxovanadium complex 5 displays one reduction peak at $E_{pc}= 0.9\text{V}$ with a corresponding oxidation peak at $E_{pa}= -0.3\text{V}$. The peak separation peak (ΔE_p) is 30V at 100 mV/s . The most significant feature of the VO(IV) complex is the one electron transfer redox process corresponding to the VO(IV)/VO(III) couple shown in the voltgram Figure 2a.

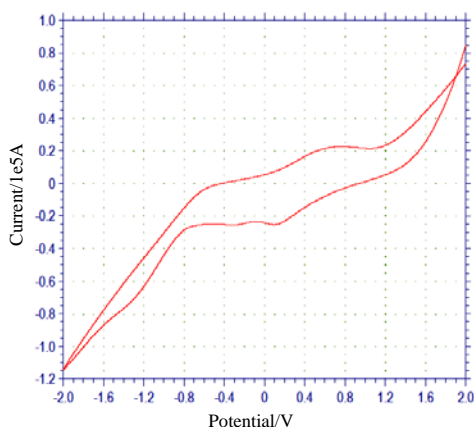


Figure 2. Cyclic voltammogram of Cu(II) macrocyclic Schiff complex (2)

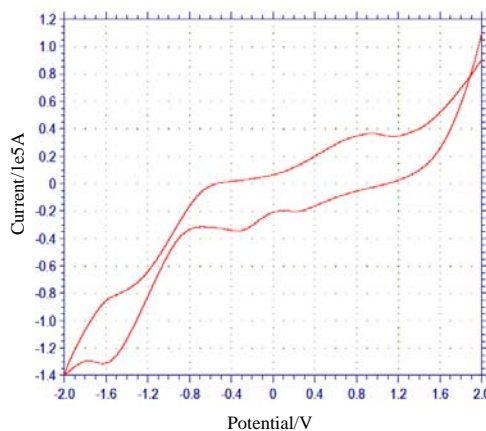


Figure 2a. Cyclic voltammogram of VO(II) macrocyclic Schiff complex (5)

Biological activity

In the present study we synthesized new binuclear macrocyclic Schiff base complexes. Generally the macrocyclic compounds have more active than the open chain derivatives. Here, the synthesized compounds were evaluated against gram-positive (*Staphylococcus aureus*), gram-negative (*Pseudomonas fluorescens*) bacteria. The obtained results indicate that the complexes were more effective against some microbes under identical experimental conditions. This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane³⁴ and can be explained by Tweedy's chelation theory³⁵. Chelation will enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layers of the cell membrane³⁶ and blocking the metal binding sites on enzymes of microorganisms. *Streptomycin* were used as standard antibiotics and were used to compare the synthesized complexes with the standard shown by Table 3. All the compounds of the tested series were the copper complexes 1 & 3 possessed good antibacterial activity shown in Figure 3 & 3a. The antifungal activities of all the complexes were carried out against fungal strains i.e., (*Aspergillus fumigatus*) and then compared with standard antifungal drug *Fluconazole*. The antifungal activities are given in Table 3. If the copper complexes 1 & 3 shows high antifungal activity. The increase in antifungal activity is due to the faster diffusion of metal complexes as a whole shown in Figure 4. Such increased activity of metal complexes can be explained by the chelation theory³⁷.

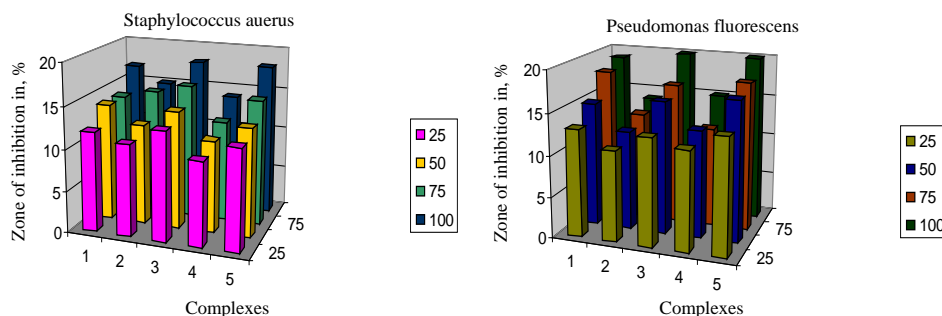


Figure 3. Antibacterial activity of Gram(+ve) bacteria with macrocyclic Schiff base Complexes

Where, 1.Cu(II) acetate; 2. Ni(II) acetate; 3. Cu(II) pechloride 4. Ni(II) perchloride; 5.VO(II) complexes

Figure 3a. Antibacterial activity of Gram(-ve) bacteria with macrocyclic Schiff base Complexes

Where, 1.Cu(II) acetate; 2. Ni(II) acetate; 3. Cu(II) pechloride 4. Ni(II) perchloride; 5.VO(II) complexes

Table 3. Antimicrobial activity data of macrocyclic binuclear Schiff base metal complexes

Complexes	Diameter of growth of inhibition in, %											
	Gram(+Ve)				Gram(-Ve)				Fungi			
	<i>S.aureus</i>				<i>P.fluorescens</i>				<i>A.fumigatus</i>			
	25	50	75	100	25	50	75	100	25	50	75	100
[Cu ₂ (C ₈₄ H ₆₆ N ₈ O ₄)]	12	14	14	17	13	15	18	19	11	14	18	20
[Ni ₂ (C ₈₄ H ₆₆ N ₈ O ₄)]	11	12	15	15	11	12	13	14	10	12	14	15
[Cu ₂ (C ₈₄ H ₆₆ N ₈).2ClO ₄ ⁻	13	14	16	18	13	16	17	20	13	15	18	21
[Ni ₂ (C ₈₄ H ₆₆ N ₈).2ClO ₄ ⁻	10	11	12	14	12	13	12	15	10	12	13	17
[VO ₂ (C ₈₄ H ₆₆ N ₈).2SO ₄	12	13	15	18	14	17	18	20	12	16	16	19

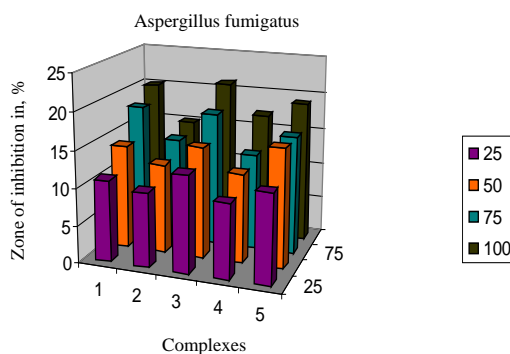


Figure 4. Antifungal activity of macrocyclic Schiff base Complexes.

Where, 1. Cu(II) acetate; 2. Ni(II) acetate; 3. Cu(II) pechloride 4. Ni(II) perchloride; 5. VO(II) complexes

Conclusion

In the present study the coordination chemistry of macrocyclic binuclear Schiff base derived from the reaction of 4,4'-diaminobenzidine, benzil and dimethyl-*O*-phenylenediamine is discussed. The macrocyclic binuclear Schiff base complexes of Cu(II), Ni(II) acetate,

perchlorate and VO(II) metal salts have been synthesized and characterized by spectral and analytical data. Structural characterization also reveals both square planar and distorted square planar geometry of Cu(II) and Ni(II) centers within the symmetric unit. For VO(II) complex has square pyramidal geometry. The macrocyclic binuclear Schiff base metal complexes enhanced a significant antimicrobial activity compared with standard antifungal and antibacterial agents. Keeping in view the rising problems of antimicrobial resistance, these chemical compounds may be used for formulating novel chemotherapeutic agents and further investigation will be necessary to identify the active principle.

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