



ISSN: 0975-766X
CODEN: IJPTFI
Research Article

Available Online through
www.ijptonline.com

SYNTHESIS, SPECTROSCOPIC AND MICROBIOLOGICAL STUDIES OF TRANSITION METAL COMPLEXES DERIVED FROM 3, 3'-DIAMINOBENZIDINE WITH O-PHTHALALDEHYDE AND 2, 3-DIAMINONAPHTHALENE

^ID. Sandhanamalar, ^{II}S.Vedanayaki and R. Rajavel*

^{1,*} Department of Chemistry, Periyar University, Salem-636 011, India.

² Department of Chemistry, Kandaswami Kandari's College, P. Velur, Namakkal-638 182, India.

Email: v.sanmalar@gmail.com

Received on 21-02-2012

Accepted on 12-03-2012

Abstract

A simple and efficient method has been developed for the synthesis of macrocyclic binuclear Schiff base transition metal complexes using template method. If the complexes has been synthesized by the condensation of 3,3'-diaminobenzidine with O-Phthalaldehyde, diaminonaphthalene and the corresponding metal salts in the ratio 1:4:2:2. The prepared macrocyclic binuclear metal complexes were structurally confirmed by analytical and spectral data and the bonding sites are the azomethine nitrogen atoms. The metal complexes exhibit different geometrical arrangements such as square planar and square pyramidal. The complexes were evaluated for their antimicrobial activities. The results showed that this skeletal framework exhibit marked potency as antimicrobial agents.

Key words: Macrocyclic, 3,3'-diaminobenzidine, ESR, NMR, squarepyramidal, skeletal.

1. Introduction

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different fields. Schiff bases are derived from aromatic carbonyl compounds and have been widely studied in connection with metalloprotein models and asymmetric catalysis, due to versatility of their steric and electronic properties[1]. Schiff bases and their biologically active complexes have been often used as chelating ligands in the coordination chemistry of transition metals, radiopharmaceuticals for cancer

R. Rajavel* et al. /International Journal Of Pharmacy&Technology
targeting[2], agrochemicals[3], model systems for biological macromolecules[4], catalysts[5] and as dioxygen carriers[6].

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 template for the ring formation[7,8].

The stability of macrocyclic metal complex depends upon a number of factors, including the number and type of donor atoms present in structure and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation.

In the present study the complexes was prepared by the template condensation of 3,3'- Diaminobenzidine with O-phthalaldehyde and diaminonaphthalene 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 invitro for their antibacterial and antifungal activities against human pathogenic bacteria [using disc diffusion method(DD)][9-11]. 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.

2. Materials and methods

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 were tested by TLC.

2.1. 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 760C. 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 0.1M tetra butyl ammonium perchloride(TBAP) as supporting electrolyte. The EPR spectra of Cu(II) complex were recorded on Bruker EMX Plus at room temperature. The antibacterial activity of the compounds were determined by using the disc diffusion method.

2.2. Antimicrobial activity

The standardized disk-diffusion method[12, 13] 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 fungi (*Aspergillus fumigatus*) *Streptomycin* was used as a standard reference in the case of bacteria while *Fluconazole* was used as a standard antifungal refrence.

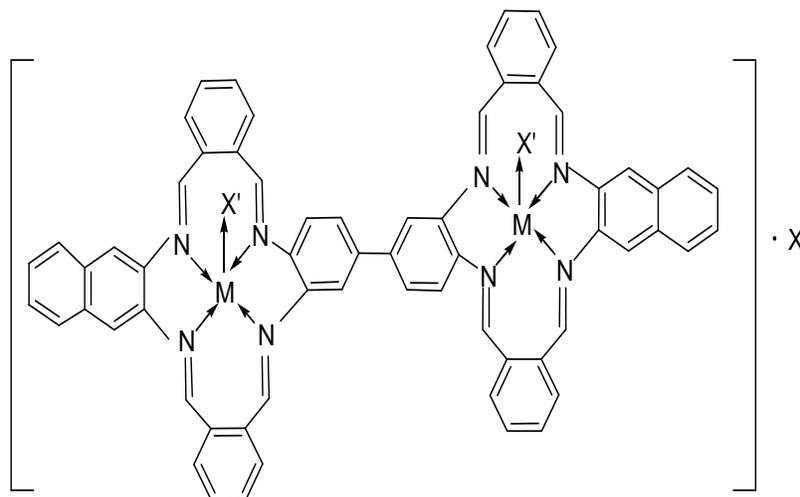
The tested compounds were dissolved in[DMSO which has no inhibition activity] to get concentration of 2 mg/mL. The test was performed on medium potato dextrose agar(PDA) which contains infusion of 200 g potatoes, 6 g dextrose and 15 g agar[14]. Uniform size filter paper disks(three disks per compound) 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.

2.3. Synthesis of the complexes

The complexes were synthesized using template method by condensing 3,3'-diaminobenzidine with O-phthalaldehyde and diaminonaphthalene in the presence of respective metal salt. To a hot stirring methanolic solution of (20ml) of 3,3'-diaminobenzidine was added to the metals like Cu, Ni and VO salt(0.2mmol) dissolved in the minimum quantity of methanol (~20ml). The resulting solution was boiled under reflux for ½ hr. Then the methanolic solution of O-phthalaldehyde(0. 4mmol) was added after that added a methanol solution of diaminonaphthalene(0.2mmol) in the same mixture and refluxing was continued for 8hrs. 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 Fig.I.

Fig-1: Proposed structure of the complex.



Where, M= Cu(II), Ni(II) and VO(II)

X' = CH₃COO⁻ ; X = 2ClO₄ ; 2SO₄

3. 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 complexes were characterized by elemental analysis, molar conductivity, IR, UV, EPR, electrochemical and thermal 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.

3.1. 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 for the perchlorate complexes are in the range characteristic of 1:2 electrolytes for all complexes. Whereas the acetate complexes of copper and nickel are non electrolytic in nature.

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

S. No	Compounds	Colour	Λ_m ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	μ_{eff} (BM)	Elemental analysis: calcd.(Found)%			
					C	H	N	Metal
1.	[Cu ₂ (C ₆₈ H ₄₀ N ₈ O ₄)]	Dark green		1.56	70.34(70.3)	3.44(3.42)	9.65(9.65)	11.0(11.0)
2.	[Ni ₂ (C ₆₈ H ₄₀ N ₈ O ₄)]	Pale green		-	71.08(71.0)	3.48(3.46)	9.75(9.74)	10.10(10.1)
3.	[Cu ₂ (C ₆₄ H ₃₄ N ₈)] . 4ClO ₄ ⁻	Brown	232	1.66	53.40(53.4)	2.36(2.34)	7.78(7.76)	8.90(8.92)
4.	[Ni ₂ (C ₆₄ H ₃₄ N ₈)] . 4ClO ₄ ⁻	Pale green	120	-	53.85(53.8)	2.38(2.36)	7.85(7.83)	8.13(8.13)
5.	[VO ₂ (C ₆₄ H ₃₄ N ₈)] . 2SO ₄	Green	142	1.67	67.14(67.1)	2.97(2.96)	9.79(9.77)	8.90(8.90)

3.2. 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., 1.56-1.66.B.M. The lower value of magnetic moment at room temperature is consistent with square planar geometry around the metal ions[15]. Whereas

the Ni(II) complexes are diamagnetic in nature. The room temperature value of VO(II) ion for the complex is 1.67.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.

3.3. Electronic absorption spectra: The electronic absorption spectra of the synthesized 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 $n \rightarrow \pi^*$ [16]. The position and intensity of this band show dependence on the nature of the substituents within the carbonyl imine moiety of the tetradentate structure.

Table-2: Significant bands in the IR and electronic spectra of the Macrocyclic binuclear Schiff base metal complexes

S.No	Compound	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{V}=\text{O})$ cm^{-1}	ClO_4^- $/\text{SO}_4^{2-} \text{cm}^{-1}$	$\nu(\text{M}-\text{N})$ cm^{-1}	λ_{max}
1.	$[\text{Cu}_2(\text{C}_{68}\text{H}_{34}\text{N}_8\text{O}_4)]$	1592			460	540
2.	$[\text{Ni}_2(\text{C}_{68}\text{H}_{34}\text{N}_8\text{O}_4)]$	1598			478	510
3.	$[\text{Cu}_2(\text{C}_{64}\text{H}_{34}\text{N}_8)].4\text{ClO}_4^-$	1600		1085	482	544
4.	$[\text{Ni}_2(\text{C}_{64}\text{H}_{34}\text{N}_8)].4\text{ClO}_4^-$	1588		1109	490	489
5.	$[\text{VO}_2(\text{C}_{64}\text{H}_{34}\text{N}_8)].2\text{SO}_4$	1586	980		501	508

Further the d-d transition showed a strong band at 540-544nm for Cu(II) complexes. This is due to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition. The spectra of Ni(II) complexes in the visible region at about 489-510nm and 480-488nm is assigned to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$, ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ transitions, suggesting an pseudo square planar geometry of the complex around the metal ions[17]. The intense charge transfer band at 508nm in VO(II) complex assigned to ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ transitions. This suggesting the square pyramidal environment[18]. Based on these data, a square planar geometry has been assigned to the complexes except VO(II) complex which has square pyramidal geometry.

3.4. IR-spectra

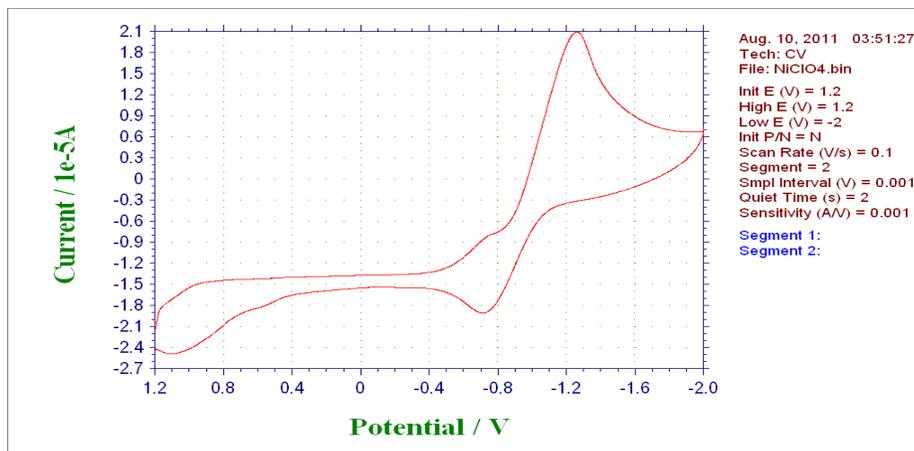
The IR spectra of the reported compounds were measured as KBr disk and the important IR-spectral feature along with their tentative assignments are given in Table-II. In the spectrum of the complexes the absence of band in the region $\sim 3400\text{cm}^{-1}$ corresponding to free primary amine suggests that complete condensation of amino group with diketone group. The disappearance of these band and the appearance of a new strong absorption band near $1586\text{-}1600\text{cm}^{-1}$ confirms the formation of the Schiff base, as this band assigned to $\nu(\text{C}=\text{N})$ stretching vibration[19]. The data in 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[20, 21], indicating that the coordination takes place through the nitrogen atom of the (C=N) group. Thus, it appears that each diketone molecule has reacted with the amino groups of the 3,3'-diaminobenzidine with phthalaldehyde forming the Schiff base and the diamionaphthalene 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 ion[22, 23, 24]. All of the perchlorate salts show a medium band near $1145\text{-}1190\text{ cm}^{-1}$ and a strong band at $1085\text{-}1109\text{ cm}^{-1}$ and sharp band at $621\text{-}626\text{ cm}^{-1}$, indicative of uncoordinated perchlorate anions[25- 28]. For vanadyl complexes, a strong band observed at 980 cm^{-1} is assigned to $\nu(\text{V}=\text{O})$ which rules out the possibility of a dimeric structure[29]. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR- spectra of the metal complexes appear at $460\text{-}501\text{ cm}^{-1}$ assigned to $\nu(\text{M-N})$ stretching vibrations[30]. Thus from the IR- spectra it is clear that the compounds may be bonded to the metal ions through the imine nitrogen.

3.5. 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 Fig.II.

Fig. II. Cyclic voltagram of Ni(II) Macrocylic Schiff complex(4).



The cyclic voltammogram of the complexes in 10^{-3} M solution was recorded at room temperature in the potential range 0.1 to 2.0 V with a scan rate 0.1vs^{-1} and the electrochemical data are summarized in Table.III and IIIa. The Cu(II) complexes 1&3 shows a redox potential corresponding to one electron transfer couple at $E_{pc} = -1.3\text{V}$ and associated anodic peak at $E_{pa} = -0.8\text{V}$ and the complex 3 at $E_{pc} = -1.45\text{V}$ and $E_{pa} = -1.10\text{V}$. 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 [30, 31]. On comparing the cyclic voltammograms, we observed that the variation in oxidation and reduction potential may be due to distortion in the geometry of the complex which arises due to different anions such as acetate(CH_3COO^-) and perchlorate to the metal ions[32].

Table-III: Reduction potential values for cyclic voltammetry studies of the Macrocylic binuclear Schiff base complexes.

Complexes	E_{pc}	E_{pa}	$E_{1/2}$	ΔE
1.	-1.3	-0.8	-1.05	-210
2.	-1.2	-0.72	-0.96	-192
3.	-1.45	-1.10	-1.27	-255

4.	-1.3	-0.75	-1.02	-205
5.	-1.59	-1.4	-1.49	-299

Table-IIIa: Oxidation potential values for cyclic voltammetry studies of the Macrocyclic binuclear Schiff base complexes.

Complexes	Epc	Epa	E _{1/2}	ΔE
1.	0.31	0.6	0.45	-290
2.	0.51	0.62	0.56	-110
3.	0.4	0.6	0.5	-200
4.	0.4	0.6	0.5	-200
5.	0.4	0.61	0.50	-210

Whereas, the Ni(II) complexes 2&4 shows a redox process corresponding to the Ni(II)→Ni(I) couple at E_{pa}= -0.72 V and associated cathodic peak at E_{pc}= -1.2 V and the complex- 4 at E_{pa}= -0.75 V and E_{pc}= -1.3 V. This couple is found to be quasi reversible as the peak separation between the anodic and cathodic potential is very high. On anodic scanning only one oxidation response is observed for the Cu(II) and Ni(II) complexes. The process is tentatively assigned to the oxidation of the coordinated ligand. The result suggests that the Cu and Ni complexes is unstable and undergoes rapid decomposition upon reduction. If the redox property of the VO^{II} complex shows two waves for vanadium(IV)→ vanadium(V) and vanadium(IV)→ vanadium(III) couples.

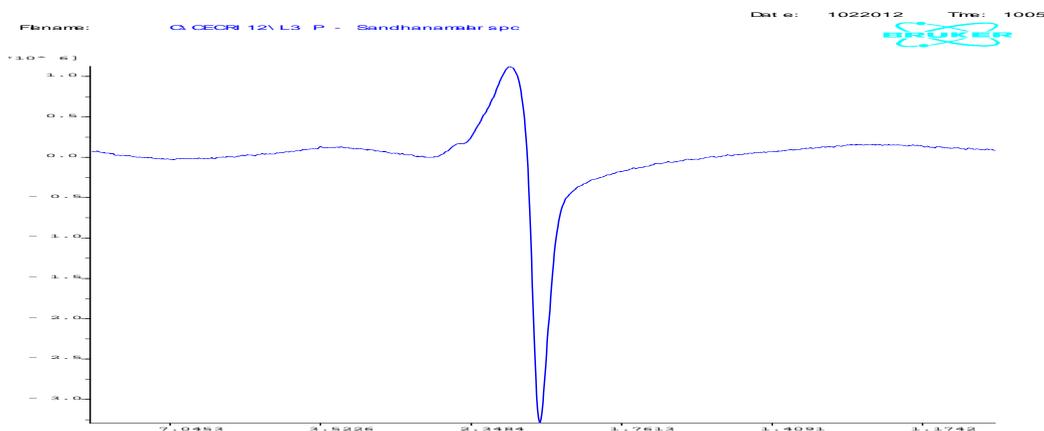
From the electrochemical studies it can be stated that the complexes containing aromatic diimines get reduced at higher negative potential. The higher reduction potential can be attributed due to the greater planarity and electronic properties those are associated with aromatic rings[34].

3.6. EPR-studies

The EPR-spectra of Cu(II) complex were measured at X-band frequencies at 9.829475 GHZ. EPR-spectra of Cu(II) complex provides information about the coordination environment around Cu(II) ion[35, 36]. The EPR-spectra of the copper(II) complex showed a sharp band, centered around $g = 2.10883$. Isotropic lines are usually the results of either intermolecular spin exchange, which can broaden the lines or occupancy of the unpaired electron in a

degenerate orbital in square planar geometry shown in Fig.III. This indicates that the two paramagnetic centers are equivalent and there is no super exchange interaction between the two metal centers[37].

Fig. III. EPR-spectrum of Copper (II) Complex.



3.7. Biological activity

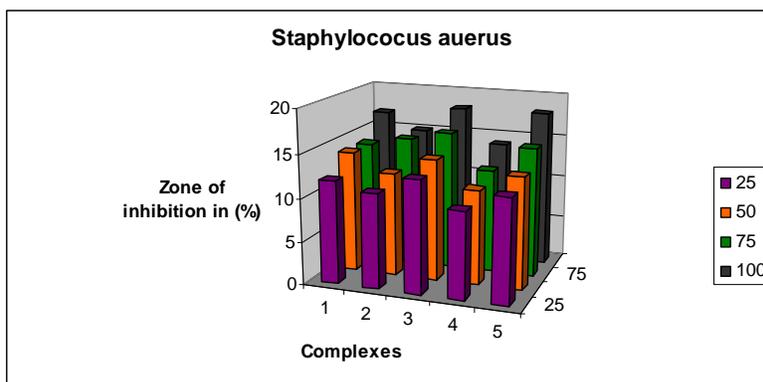
In the present study we synthesized new binuclear macrocyclic Schiff base complexes. Generally the macrocyclic compounds have more active than the open chain derivatives. Here, the synthesized compounds were evaluated against Gram-positive(*Staphylococcus auerus*), Gram-negative(*Pseudomonas fluorescens*) 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 membrane and can be explained by Tweedy's chelation theory[38]. Chelation will enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layers of the cell membrane[39] and blocking the metal binding sites on enzymes of microorganisms. *Streptomycine* were used as a standard antibiotics and were used to compare the synthesized complexes with the standard shown by Table-IV. All the compounds of the tested series were the copper and vanadium complexes possessed good antibacterial activity shown in Fig.IV & IVa. The antifungal activities of all the complexes were carried out against fungal strains ie., (*Aspergillus fumigatus*) and then compared with standard antifungal drug *Fluconazole*. The antifungal activities are given in Table-IV. If the copper complexes 1&3 shows high antifungal activity. The increase in antifungal activity is due to the faster diffusion

R. Rajavel* et al. /International Journal Of Pharmacy&Technology
of metal complexes as a whole shown in Fig.V. Such increased activity of metal complexes can be explained by the
chelation theory[40].

Table-IV: Antimicrobial activity data of macrocyclic binuclear Schiff base metal Complexes.

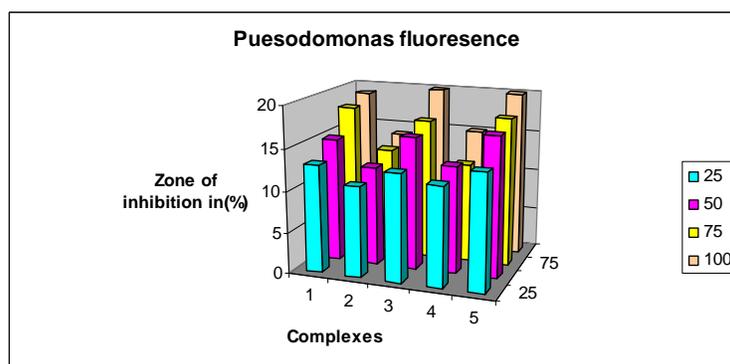
Complexes	Diameter of growth of inhibition in (%)											
	Gram(+Ve)				Gram(-Ve)				Fungi			
	S.auerus				P.fluorescens				A.fumigatus			
	25	50	75	100	25	50	75	100	25	50	75	100
[Cu ₂ (C ₆₈ H ₃₄ N ₈ O ₄)]	12	14	14	17	13	15	18	19	11	14	18	20
[Ni ₂ (C ₆₈ H ₃₄ N ₈ O ₄)]	11	12	15	15	11	12	13	14	10	12	14	15
[Cu ₂ (C ₆₄ H ₃₄ N ₈)].4ClO ⁻	13	14	16	18	13	16	17	20	13	15	18	21
[Ni ₂ (C ₆₄ H ₃₄ N ₈)].4ClO ⁻	10	11	12	14	12	13	12	15	10	12	13	17
[VO ₂ (C ₆₄ H ₃₄ N ₈)].2SO ₄	12	13	15	18	14	17	18	20	12	16	16	19

Fig-IV: Antibacterial activity of Gram(+ve) bacteria with macrocyclic Schiff base Complexes.



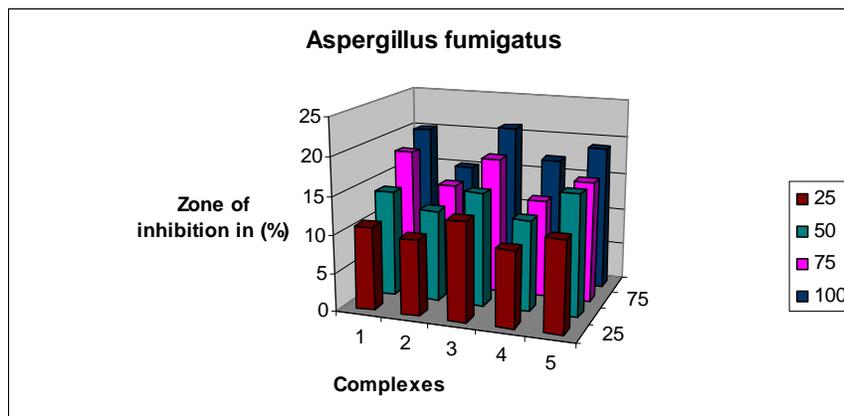
Where, 1.Cu(II) acetate; 2. Ni(II) acetate; 3. Cu(II) pechloride 4. Ni(II) perchloride; 5.VO(II) complexes

Fig-Iva: 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.

Fig.V. 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

4. Conclusion

In the present study the coordination chemistry of macrocyclic binuclear Schiff base complexes, derived from the reaction of 4,4'-diaminobenzidine, O-Phthalaldehyde and diaminonaphthalene is discussed. The macrocyclic binuclear Schiff base complexes of Cu(II), Ni(II) acetate, perchloride 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. From the analytical data and ESR- spectra of Cu(II) complex there is no exchange interaction between the two copper centers of the macrocyclic unit. Fig.I. depicts the proposed structures of the metal complexes. The 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.

Reference:

1. M. H. Habibi, M. Montazerzohori, A. Lalegani, R. W. Harrington, W. Clegg, J. Fluorine Chem. 6 (2006) 7691.
2. G.H Hamor, D. Watson, J. Pharma. Sci., 60, 2006, 925.

3. A. Gama, L. Z. Flores-lopez , G. Aguirre, M. ParraHake, R. Somanathan, P. Walsh, *J. Tetrahedron.*, 13, 2002, 149.
4. M. K. Taylor, K. D. Trotter, J. Reglinski, L. E. A. Berlouis, A. R. Kennedy, C. M. Spickett, R. J. Sowden, *Inorg. Chim. Acta.*, 361, 2008, 2851.
5. S. Rayati, N. Torabi, A. Chaemi, S. Mohebbi, A. Wojtczak, A. Kozakiewicz, *Inorg.Chim. Acta.*, 361, 2008, 1239.
6. J. Dai, Y. Chai, R. Yuan, X. Zhong, Y. Liu, D. Tang, *Anal. Sci.* 20 (2006)1661.
7. D. E. Fenton, P. A. Vigato, *Chem. Soc. Rev.*, 17, 1988, 69.
8. V. Alexander, *Chem. Rev.*, 95, 1995, 273. Z. Xinde, C. Wang, Z. Lu, Y. Dang, *Trans. Met. Chem.*, 22, 1997, 13.
9. Y. L. Sang, X.-S. Lin, *J. Coord. Chem.*, 63, 2010, 315.
10. M. Rajasekar, S. Sreedaran, R. Prabu, V. Narayanan, R. Jegadeesh,
11. N. Raaman, K. A. Rahiman, *J. Coord. Chem.*, 63, 2010, 136.
12. C. Demetgil, M. Karakaplan, S. Selahattin, M. Digrak, 62(2009) *J. Coord. Chem.*, 62, 2009, 3544.
13. E. O. Offiong, S. Martelli, *Iu Farmaco.*, 49, 1994, 513.
14. J. G. Collee, J. P. Duguid, A. G. Farser, Marmion(Eds.). *B D, Practical Medical Microbiology*, Churchill Livingstone, New York., 1989.
15. F. Feigl, *Chemistry of Specific Selective and Sensitiv Reactions* Academic Press., 1949.
16. (a) D. X. West, A. A. Nassar, F. A. El-Saied, M. I. Ayad, *Trans.*
 - a. *Met. Chem.*, 23, 1998, 423;
 - (b) D. X. West, D. L. Huffman, J. S. Saleda, A. E. Liberta, *Trans.*
 - b. *Met. Chem.*, 16, 1991, 565.
17. F. Karipcin and G. Baskale-Akdogan, *J. Incl. Phenom. Macrocycl. Chem.*, 183, 2009, 64.
18. B. T. Thaker and K. R. Surati, *J. Coord. Chem.*, 1191, 2006, 59.

19. R. M. Silverstein, G. C. Bassler, T. C. Morrill, Spectrometry Identification of Organic Compounds, 4th Ed., Wiley, New York, 1981, p, 126.
20. S. Ilham, H. Temel, I. Yilmaz, M. Sekerci, J Organometallic. Chem., 692, 2007, 3855.
21. J. J. Lopez-Carriga, G. T. Babcock, J. F. Harrison, J. Am. Chem. Soc., 108, 1986, 7241.
22. B. Jazowska, J. Lisowski, A. Vogt, P. Chmielewski, Polyhedron., 7, 1988, 337.
23. S. Chandra, L. K. Gupta, Trans. Met. Chem., 27, 2002, 732.
24. S. Chandra, L. K. Gupta, spectrochim. Acta., A(80), 2004, 1563.
25. H. Temel, U. Cakir, I. H. Ugras, synt.Reat.Inorg. Met. Org. Chem., 34(4), 2004, 819.
26. B.-H. Ye, L.-N Ji, F. Xue, T. C. W. Mak, polyhedron 17, 1998, 2687.
27. J. M. Rowland, M. M. Olmstead, P. K. Mascharak, Inorg. Chem., 39, 2000, 5326.
28. I. A. Koval, P. Games, U. Roubeau, W. L. Driessen, M. Lutz, A. L. Spek, Inorg. Chem., 42, 2003, 868.
29. M. Pasquali, F. Marchetti, C. Floriani and S. Merlino, 133 (1977) J. chem.. soc., Dalton Trans., 133, 1977.
30. B. J. Hathaway, A. E. Underhill, The infrared spectra of some transition-metal perchlorates, J. chem. Soc., 1961, 3091-3097.
31. K. Nakamoto, 1986 Infrared and Raman Spectra of Inorganic and coordination compounds, 4th ed., Wiley, New York.
32. M. R. Rosenthal, J. Michael, 50(1973) The myth of the non-coordinating anion, J. chem.. Edu. 331-335.
33. Z. Shirin, R. M. Mukherjee, 4(1958) Polyhedron 163.
34. S. Chandra, L. K. Gupta, Sangeetika, Synth. React. Inorg. Met.-Org. Chem. 34.
35. M. Thirumavalavan, P. Akilan, M. Kandaswamy, 16(2004) Supramol. Chem. 495-504.
36. M. J. Upadhyay, P. K. Bhattacharya, P. A. Ganeshpure, S. Satish, 73(1992) J. Mol. Catal. 277.
37. C. S. Allardyce, P. J. Dyson, D. J. Ellis, P. A. Salter, J. Organomet, Chem. 2003, (35), 668.

Corresponding Author:

R. Rajavel*

Email: v.sanmalar@gmail.com