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Synthesis and characterization of n-functionalized Macrocyclic binuclear Cu(ii),Ni(ii) and Vo(ii) Schiff base complexes and their antimicrobial activity

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ABSTRACT

A simple and efficient method has been developed for the synthesis of macrocyclic binuclear Schiff base ligand and their transition metal complexes of the type $[M_2(L)X]$ where M= Ni(II), Cu(II), $X=CH_3COO^-$ and $[M_2(L)].X$ where M=Ni(II), Cu(II) and VO(II), $X=4ClO_4^-$, $2SO_4^{2-}$. If the ligand have been synthesized by the condensation of 3,3'-diaminobenzidine with Phthaldehyde and O-phenylenediamine in the ratio 1:4:2. The prepared macrocyclic ligand and their 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 ligand and the complexes were evaluated for their antimicrobial activities. The results showed that this skeletal framework exhibit marked potency as antimicrobial agents.

Introduction

The design and study of well arranged metal containing macrocyclic is an interesting field of chemistry[1]. The chemistry of marocyclic complexes has attracted the interest of inorganic chemists in recent years[2]. Macrocyclic compounds and their derivatives are interesting ligand system because they are good hosts for metal anions, neutral molecules and organic cation guests[3]. Currently a considerable effort is being in the development of new chelating ligand, particularly the binucleating imino ligand is versatile and they exhibit very rich in coordination chemistry, such species occupy an important position in modern inorganic chemistry[4, 5, 6]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number & size of the chelate rings formed on complexation[7]. In the present study the ligand were prepared by the condensation of 3,3'- Diaminobenzidine with phthaldehyde and O-phenylenediamine to afford the corresponding ligand. The reactions of these ligand with some transition metal in the molar ratio(1: 2 ligand : metal) were studied. The newly prepared metal complexes of these ligands were confirmed by different physicochemical and spectroscopic techniques. Here, we have noticed that tetramine with several potential donor atoms could be a good choice to condense with O-phthalaldehyde to develop binucleating Schiff- base ligand. A description on characterization data using analytical spectroscopic, thermal and magnetic data has been systematically presented. Furthermore, the application of these metal complexes as potential antibacterial agents has also been demonstrated.

Recently, a wide varieties of the Cu(II), Ni(II) and VO(II) complexes of Schiff base derivatives including compartmental and macrocyclic ligand were tested invitro for their antibacterial and antifungal activities against human pathogenic bacteria [using disc diffusion method(DD)][8-10], where the metal complexes have higher antimicrobial activities than the free ligand. The ligand act as a dibasic with four nitrogen atoms and can coordinate with two metal ions to form binuclear Cu(II), Ni(II) and VO(II) complexes.

The Schiff base, ligand and its metal complexes were investigated for antibacterial and antifungal properties. Two Gram-positive bacteria(staphylococcus auerus and streptococcus pyogenes), two Gram-negative bacteria (pseudomonas fluorescens and pseudomonas phaseolicola) and two fungi (Fusarium oxysporum and Aspergillus fumigatus) were used in this study to assess their antimicrobial properties. Most of the complexes exhibit mild antibacterial and antifungal activities against these organisms and some of them were more effective than the free ligand.

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 ligand and metal complexes were 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. ^1H-NMR spectra in DMSO were recorded on a Brucker WH 300 (200 MHZ). 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 $Hg[Co(SCN)_4]$. The cyclic voltammetry studies were carried out in digital CHI 760C.

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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 TG-DTG thermograms of the complexes were recorded on Mettler Toledo star system. The antibacterial activity 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 Two Gram-positive(*staphylococcus auerus, streptococcus pyogenes*) and Gram-negative bacteria (*pseudomonas fluorescens, pseudomonas phaseolicola*) and two fungi (*Fusarium oxysporum, 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[13]. Uniform size filter paper disks(three disks per compound) were impregnated by equal volume (10μL) 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 macrocyclic Schiff-base ligand(L)

The macrocyclic binuclear Schiff base ligand were synthesized by the condensation of 3,3'-diaminobenzidine with Phthalaldehyde and O-phenylenediamine in 1:4:2 mole ratio. A methanolic solution of 3,3'-diaminobenzidine (0.0214 g), a stirred solution of phthalaldehyde (0.0736 g) in methanol(10ml) to add dropwise. After 1hr add a methanolic solution of O-phenylenediamine(0.0216 g) drop wise with constant stirring. After the addition was completed, the stirring was continued for 2 hrs. A yellow color precipitate was filtered out and washed with methanol. Then the precipitate was dried under desiccator over $CaCl_2$.

Synthesis of macrocyclic complexes

A hot methanolic (20ml) solution of ligand (0.02035 g) and a methanolic(20 ml) solution of Cu(II) salt(0.02mol) were mixed together with constant stirring. The mixture was refluxed for 3 hrs at 75-80°C. On cooling, the green color precipitate was filtered out and washed with cold methanol and dried under desiccator over $CaCl_2$. The same procedure was carried out for the other complexes such as Ni(II) and VO(II) metal salts.

Results and Discussion

All the complexes were have the corresponding colored solids and are soluble in DMF and stable at room temperature. The macrocyclic ligand and its metal complexes were characterized by elemental analysis, molar conductivity, IR, UV, ^{1}H NMR , 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.

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.

^{1}H NMR Spectra

The ^{1}H- NMR spectra of the free ligand was recorded in DMSO-d_6. The chemical shifts are expressed in ppm downfield from TMS. Signal for the methine proton of the azomethine group –N=C(H)– was observed at 7.9 ppm. In the region of 7.7–7.2 ppm were assigned to chemical shifts for protons of the aromatic ring. The total number of protons present in the Schiff base exhibited signals of the protons in their expected regions and these data are in good agreement with that of the formation of Schiff base ligand of the expected compounds shown in Fig.1.

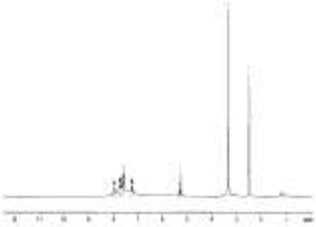

Fig. 1.^{1}H NMR- spectra of macrocyclic binuclear Schiff base ligand

Electronic Spectrum

The electronic spectra of ligand and its metal complexes have been recorded in DMF between 200-800nm. The Schiff base ligand exhibit two absorption bands at 252 and 320 nm. These bands are due to the transition such as $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ of –C=N group in the ligand structure[14, 15]. Another intense band in higher energy region of the spectra of the free ligand was related to $\pi\rightarrow\pi^*$ transitions of benzene rings. These transitions are also found in the spectra of the complexes but they shifted towards lower frequencies, confirming the coordination of the ligand to the metal ions. Further the d-d transition showed a strong band at 540-546nm 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 510-516nm and 482- 488nm 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 ions[16]. The intense charge transfer band at 502 and 528nm in VO(II) complex assigned to $^2B_2\rightarrow{}^2A_1$, $^2B_2\rightarrow{}^2E$ transitions. The data shown in Table.2. This suggesting the square pyramidal environment[17]. Based on these data, a square planar geometry has been assigned to the complexes except VO(II) complex which has square pyramidal geometry.

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., 1.56-1.62.B.M. The lower value of magnetic moment at room temperature is consistent with square planar geometry around the metal ions[18]. The magnetic moment of the Ni(II) complexes in the range of 2.0-2.6.B.M. These values are in tune with the low spin configuration and show the presence of square planar environment around the 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 1.68.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.

Infrared spectra

The IR- spectra of the complexes were recorded to confirm their structures. The vibrational frequencies and their tentative assignments for the ligand and their transition metal complexes are listed in Table.2. The assignments were aided by comparison with the vibrational frequencies of the free ligand and their related complexes[19]. In the spectrum of ligand the absence of band in the region ~3400 cm^{-1} corresponding to free primary amine suggests that complete condensation of amino group with aldehyde group. Appearance of a new strong absorption band at 1620 cm^{-1} attributable to the characteristic stretching frequency of the imino linkage ν(C=N)[20]. In all the complexes this band is shifted to lower frequencies in the range 1592-1589 cm^{-1} provides strong evidence for the presence of cyclic product. The absorption in the range of 732-768 cm^{-1} and 1415-1592 cm^{-1} due to the presence of phenyl group. The presence of acetate in complexes 1&2 is evidenced by two medium absorption features centered at 1610 cm^{-1} for ν_{as}(COO) and 1450 cm^{-1} for ν_{sy}(COO). The difference between (ν_{as}-ν_{sy}) is around 160 cm^{-1} agrees with the coordination mode for the acetate ion with the central metal ion[21, 22, 23]. All of the perchlorate salts show a medium band near 1145-1190 cm^{-1} and a strong band at 1083-1109 cm^{-1} and sharp band at 621-626 cm^{-1}, indicative of uncoordinated perchlorate anions[24-27]. For vanadyl complexes, a strong band observed at 982 cm^{-1} is assigned to ν(V=O) which rules out the possibility of a dimeric structure[28]. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR- spectra of the metal complexes appear at 490-470 cm^{-1} assigned to ν(M-N) stretching vibrations[29]. Thus from the IR- spectra it is clear that the compounds may be bonded to the metal ions through the imine nitrogen.

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.2.

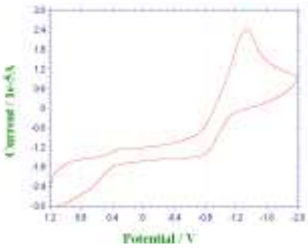

Fig. 2. Cyclic voltagram of Cu(II) complex

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.3 and 3a. The Cu(II) complexes 1&3 shows a redox potential corresponding to one electron transfer couple at Epc= -1.3V and associated anodic peak at Epa= -0.8V and the complex 3 at Epc= -1.45V and Epa= -1.10V. This couple is found to be quasi-reverrsible as the peak separation between the anodic and cathodic potential is verry 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 perchloride to the metal ions[32].

Whereas, the Ni(II) complexes 2&4 shows a redox process corresponding to the Ni(II)→Ni(I) couple at Epa= -0.72 V and associated cathodic peak at Epc= -1.2 V and the complex- 4 at Epa= -0.75 V and Epc= -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 shown in the voltagram Fig. 2a.

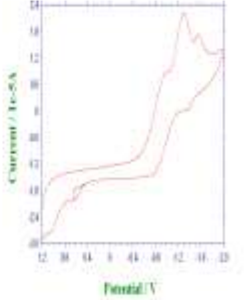

Fig. 2a. Cyclic voltagram of VO(II) complex

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[33].

Thermal analysis

The thermal behaviours of all the complexes were almost the same. Therefore, the two binuclear perchloride complexes such as Cu(II) and Ni(II) are discussed here in detail. TG and DTG analyses for the metal complexes were carried out within the temperature range from ambient temperature upto 900°C. The correlations between the different decomposition steps of the compounds with the corresponding weight losses are discussed in terms of the proposed formula of the compounds. The thermal behaviour of the complexes is summarized in Table.4.

The thermal decomposition of the complex with the molecular formula $[Cu_2(C_{56}H_{38}N_8)]\cdot 4ClO_4$ proceeds with two main degradation steps. The first estimated mass loss of 29.3% (Calcd.29.45%) within the temperature range 198-262°C could be attributed to the liberation of perchloride unit. The DTG curve gives a peak at 230°C. The second step occurs within the temperature range 262-605°C with an estimated mass loss 47.4%(Calcd.47.23%), which is reasonably accounted for loss of phenyl group with four nitrogen atoms, three aldehydic groups with four nitrogen atoms and one aromatic ring respectively, Fig.3. The last step probably accounted for the decomposition of remainingpart of the ligand molecule. But decomposition did not finish at 900°C. Therefore, last decomposition residue did not determine.

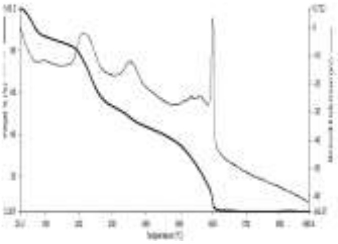

Fig. 3. TG – DTG curves of macrocyclic binuclear Schiff base Cu(II) complex

The thermal decomposition of the complex with the molecular formula $[Ni_2(C_{56}H_{38}N_8)]\cdot 4ClO_4$ proceeds with single degradation step. In the estimated mass loss of 83.6%(Calcd.83.62%) within the temperature range 266-562°C could be attributed to the loss of perchloride unit, phenyl group with four nitrogen atoms, two aldehydic group with two nitrogen atoms and two aromatic ring respectively, Fig.3a. The DTG curve gives a peak at 298, 440 and 498°C. The temperature range 562-900°C the mass loss is in progress. The decomposition is in progress.

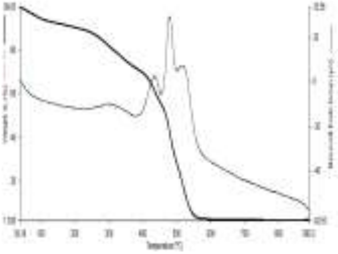

Fig. 3a. TG – DTG curves of macrocyclic binuclear Schiff base Ni(II) complex

EPR-studies

The EPR-spectra of Cu(II) complex were measured at X-band frequencies at 9.862117 GHZ. EPR-spectra of Cu(II) complex provides information about the coordination environment around Cu(II) ion[34, 35]. The EPR-spectra of the copper(II) complex showed a sharp band, centered around g = 2.12883. 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.4. This indicates that the two paramagnetic centers are equivalent and there is no super exchange interaction between the two metal centers[36].

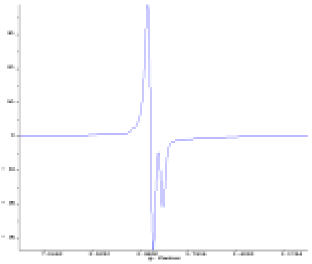

Fig. 4. EPR- Spectra of macrocyclic binuclear Schiff base Cu(II) complex

Biological activity

In the present study we synthesized new binuclear macrocyclic Schiff base ligand and their complexes. Generally the macrocyclic compounds have more active than the open chain derivatives. Here, the synthesized compounds were evaluated against two Gram-positive(*Staphylococcus auerus and streptococcus pyogenes*), two Gram-negative(*Pseudomonas fluorescens and Pseudomonas phascolicola*) bacteria. The obtained results indicate that the complexes were more effective than the free ligands 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[37] 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 ligand and complexes with the standard shown by Table.6. All the compounds of the tested series were the copper complexes 1&3 possessed good antibacterial activity. The antifungal activities of all the complexes were carried out against two fungal strains ie., (*Fusarium oxysporum and Aspergillus fumigatus*) and then compared with standard antifungal drug *Fluconazole*. The antifungal activities are given in Table.6. If the copper complexes 1&3 shows high antifungal activity.

Conclusion

In the present study the coordination chemistry of macrocyclic binuclear Schiff base ligand, derived from the reaction of 4,4'- diaminobenzidine, Phthalaldehyde and O-phenylenediamine 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 and TGA for Ni(II) and Cu(II) complexes it is possible to draw up the tentative structures of the transition metal complexes. Fig. 5. depicts the proposed structures of the metal complexes. The ligand and its 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.

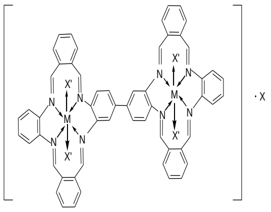

Fig. 5. Proposed structure of the complexes

Where,

X'= CH3COO- ; X= 4ClO4 – and 2SO4 – ; M = Cu(II), Ni(II) and VO(II)

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

S. No	Compounds	Colour	$\wedge_m$ (Ω^{-1}cm^{2}mol^{-1}	μ_{eff} (BM)	Elemental analysis:calcd.(Found)%			
					C	H	N	Metal
1.	Ligand	Yellow			81.5(81.3)	4.62(4.60)	13.62(13.60)	11.98(11.86)
2.	$[Cu_2 (C_{60}H_{44}N_8O_4)]$	Dark green		1.56	67.41(67.4)	4.11(4.12)	10.48(10.44)	10.98(10.93)
3.	$[Ni_2 (C_{60}H_{44}N_8O_4)]$	Pale green		2.3	68.18(68.1)	4.16(4.13)	8.32(8.30)	9.50(9.49)
4.	$[Cu_2(C_{56}H_{38}N_8)].4ClO_4^-$	Brown	238	1.60	49.92(49.6)	2.82(2.80)	8.39(8.36)	19.19(19.10)
5.	$[Ni_2(C_{56}H_{38}N_8)].4ClO_4^-$	Pale green	126	2.6	50.37(50.3)	2.84(2.80)	11.33(11.32)	10.31(10.30)
6.	$[V_2 (C_{60}H_{44}N_8)].SO_4^{2-}$	Green	144	1.68	63.81(63.6)	3.54(3.82)	9.02(9.02)	8.13(8.15)

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

S.No	Compound	ν(C=N) cm^{-1}	ν(V=O) cm^{-1}	ClO_4^-/SO_4^{2-} cm^{-1}	ν (M-N) cm^{-1}	λ_{max}
1.	Ligand	1620	-	-	-	278, 252
2.	$[Cu_2 (C_{60}H_{44}N_8O_4)]$	1592			462	542,545
3.	$[Ni_2 (C_{60}H_{44}N_8O_4)]$	1598			468	512, 486
4.	$[Cu_2(C_{56}H_{38}N_8)].4ClO_4^-$	1596		1090	480	546, 544
5.	$[Ni_2(C_{56}H_{38}N_8)].4ClO_4^-$	1589		1110	467	516, 487
6.	$[V_2 (C_{60}H_{44}N_8)].SO_4^{2-}$	1586	982	1070	489	502, 528

Table. 3. Reduction potential values for cyclic voltammetry studies of the Macrocyclic binuclear Schiff base complexes

Complexes	Epc	Epa	$E_{1/2}$	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. 3a. 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

Table. 4. Thermogravimetric data of Ni(II) and Cu(II) macrocyclic binuclear Schiff base complexes

Complexes	TG range	DTG_{max}	Estimated(Calculated)		Assignments	Residue
			Mass loss	Total mass loss		
1.	198-262 262-605	230 355, 590	29.3(29.4) 47.4(47.23)	76.7(76.65)	Loss of perchloride unit Loss of phenyl group with four nitrogen atoms three aldehydic group with four nitrogen atoms and one aromatic ring.	Decomposition is in progress.
2.	286-562	298, 440, 498.	83.6(83.62)	83.6(83.62)	Loss of Perchloride ion and phenyl group with four nitrogen atoms, 2-aldehydic group with two nitrogen atoms and two aromatic ring.	Decomposition is in progress.

Table. 5. Antimicrobial activity data of macrocyclic binuclear schiff base ligand and its metal complexes

Compounds	Diameter of growth of inhibition Zones in(mm)																	
	Gram(+ve)						Gram(-ve)						Fungi					
	S.auerus			S.pyogenes			P.fluorescens			P.phaseolicola			F.oxysporum			A.fumigatus		
	25	50	75	25	50	75	25	50	75	25	50	75	25	50	75	25	50	75
Ligand	10	12	13	9	11	14	10	12	14	11	13	16	10	14	16	11	14	16
$[Cu_2 (C_{60}H_{44}N_8O_4)]$	12	14	18	11	14	17	14	17	17	14	16	19	12	16	18	12	16	18
$[Ni_2 (C_{60}H_{44}N_8O_4)]$	11	12	14	10	12	15	12	14	16	12	15	17	12	15	17	15	15	17
$[Cu_2(C_{56}H_{38}N_8)].4ClO_4^-$	13	16	19	13	17	19	14	18	20	15	16	22	13	17	20	12	18	21
$[Ni_2(C_{56}H_{38}N_8)].4ClO_4^-$	11	12	15	10	15	16	11	14	15	13	14	18	12	15	17	15	15	19
$[V_2 (C_{60}H_{44}N_8)].SO_4^{2-}$	12	13	16	12	13	18	13	15	16	14	16	19	11	16	17	14	17	20