



**ISSN: 0975-766X**  
**Research Article**

**Available Online through**  
**www.ijptonline.com**

**SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF  
NEW SYMMETRICAL MACROCYCLIC BINUCLEAR SCHIFF BASE COMPLEXES**

**K.Anuradha and R. Rajavel\***

Department of Chemistry, Periyar University, Salem-11, Tamilnadu, India.

Email: anuradhaboopathi@gmail.com

*Received on 10-03-2011*

*Accepted on 24-03-2011*

**Abstract**

A new series of macrocyclic binuclear metal complexes Cu(II), Ni(II) and VO(IV) having the general composition  $[ML]X_2$ . The binucleating schiff base ligand has been synthesized from freshly prepared o-aminobenzaldehyde and benzidine. This synthesised ligand reacts with 2,3-pentanedione and metal salts to form a macrocyclic binuclear schiff base complexes. Both ligand and complexes were characterized by elemental analysis, IR, UV-Vis spectral data, conductivity, magnetic moment, H-NMR and ESR spectra. The parent schiff base and its complexes are assayed against gram negative bacteria like *Klebsiella pneumoniae*, *Escherichia coli* and gram positive bacteria like *staphylococcus aureus* at 37°C by disc diffusion technique. The inhibition of bacterial growth high at copper(II) complex.

**Keywords:** Macrocyclic; o-aminobenzaldehyde; IR; Antibacterial

**Introduction**

The chemistry of multi metallic species has grown steady because they are considered useful model to understand the various fundamental biological functions including, transport of oxygen in mammals and photo synthesis [1], Homogeneous catalysis, magnetic exchange between paramagnetic centres, optically induced intrasystem charge transfer and bioinorganic chemistry [2,3]. For that considerable effort has been directed towards the synthesis of ligands, that can generate polynuclear systems, particularly capable of holding two similar or dissimilar metal ions, subject to control by appropriate modification of molecular topology [4,5]. The ligands

especialy Schiff base are important class of compounds in medicinal and pharmaceutical field. They show biological application including antibacterial, antifungal and antitumor activity. Microbes encounter a variety of metal ion in the environment and interact with them, which is sometimes beneficial or determinatal depending on the chemical/physical nature and oxidation state of the metal ions present in the external environmental the cell surface and transport them into the cell for various intracellular functions [6, 7].

Condensation between carbonyl and amine has played an important role in the development of synthesis macrocyclic ligands. Usually such synthesis are carried out in the presence of suitable metal ion, which serves to direct the steric course of the reaction preferentially towards cyclic rather than oligomeric or polymeric product [8-11]. Burn wound infections are a major source of marbidity and mortality to burn patients. The injury distrupts both the normal skin barrier and many of the systemic host defense mechanisms that prevent infection. When skin is burned, it is susceptible to colonization by microbial pathogens induding *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella* species [12]. From the above information we are interest in synthesis of new binuclear macrocyclic complexes. The ligand was synthesised by freshly prepared o-aminobenzaldehyde reflux with benzidine. This ligand undergoes template condensation with corresponding metal salts and 2, 3-pentanedione.

## **Experimental**

### **Materials and Experimental protocols**

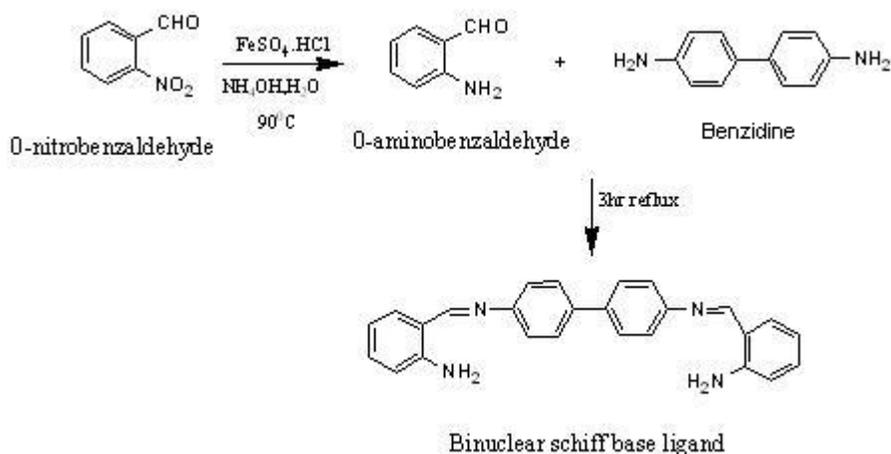
All the starting materials were pure and commercially available,0-nitrobenzaldehyde, benzidine, 2,3-pentanedione (Aldrich) were purchased. Metal salts were purchased from S.D.Fine, Merck and were used as received. Analytical grade solvents purchased were used as such. The microanalysis of C, H and N were estimated by elemental analyser Carlo-Eraba 1106 instrument. Melting points were determined by using capillaries in electrical melting point apparatus. The conductivity was measured in DMF with ELICO CM185 Conductivity Bridge. The IR spectra were recorded on a FT-IR spectrophotometer Perkin Elmer-8300 using KBr pellet. Electronic spectra (in DMSO) were recorderd on a Perkin Elemer Lambda 25 spectrophotometer (200-800 nm).<sup>1</sup>H-NMR spectra was recorded on a Bruker 300 MHz FT-NMR spectrometer using tetramethylsilane as an internal

standard. ESR spectra of the complexes were recorder as powder samples of room temperature on a E4-EPR spectrometer using DPPH as the g-marks. Magnetic data were collected on powdered sample of the compounds at room temperature with PAR155 vibrating sample magnetometer.

Caution: Although no problem was encountered during this work with the perchlorate salts, it should be regards as potentially explosive.

### Synthesis of Ligand

The starting material o-aminobenzaldehyde was prepared according to the literature procedure [12]. An ethanolic solution of this freshly prepared o-aminobenzaldehyde mixed slowly with stirred ethanolic solution of benzidine. The mixture was refluxed at  $\approx 70^{\circ}\text{C}$  for 3 hrs. On cooling greenishyellow coloured precipitate is separated out, which was filtered, washed with EtOH, diethylether and dried in air Figure 1 Yield 74% melting point  $248^{\circ}\text{C}$ . Elemental analysis  $\text{C}_{20}\text{H}_{18}\text{N}_4$  Calculated C, 79.93, H, 5.64, N, 14.35% Found C, 80.03, H, 5.54, N, 14.09%  $\nu(\text{C}=\text{N})$ ,  $1615\text{ cm}^{-1}$ ,  $\nu(\text{NH}_2)$ ,  $3442\text{ cm}^{-1}$ , UV-vis ( $\lambda_{\text{max}}$ ) DMSO:  $\pi\text{-}\pi^*$ -223 nm, 275 nm,  $n\text{-}\pi^*$ -393 nm.

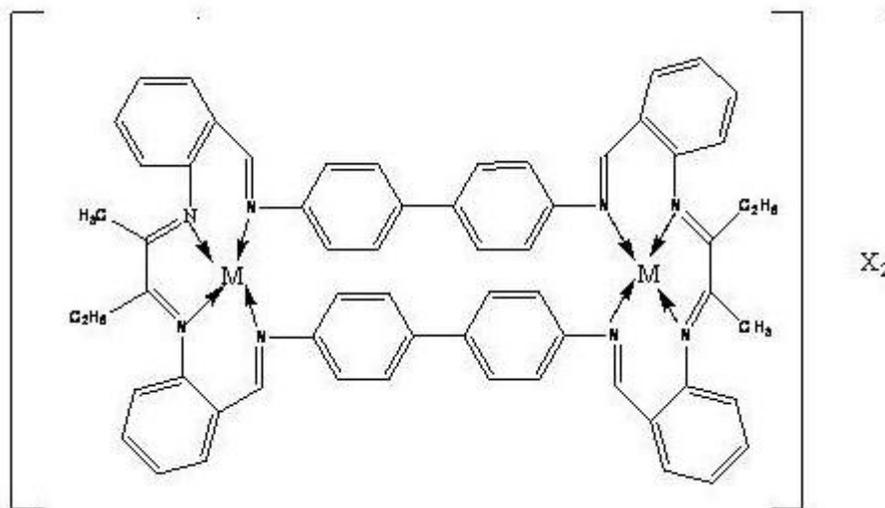


**Figure-1: Synthesis of binucleating schiff base ligand.**

### Synthesis of copper(II) complex

The copper(II) complex was prepared by methanolic solution of  $[\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$  salt were slowly added with stirred hot methanolic solution of ligand. To the same solution 2,3-pentanedione was added dropwise. The

string was continued for 1hr, after it undergo reflux at  $\approx 70^{\circ}\text{C}$  until a dark greenishbrown precipitate was formed. It was filtered, washed several times with methanol, diethylether and dried in air Figure 2 Yield 62%. The complex show melting point  $>250^{\circ}\text{C}$ .  $\text{C}_{58}\text{H}_{52}\text{N}_8\text{Cu}_2\text{Cl}_4\text{O}_{16}$  Calcd; C, 50.28, H, 3.75, N, 8.92, Cu, 9.24% Found: C, 50.68, H, 3.95, N, 8.08, Cu, 9.19%  $\Lambda_m$ , 276 ( $\Omega^{-1}\text{cm}^2\text{m}^{-1}$ ),  $\nu(\text{C}=\text{N})$ , 1610  $\text{cm}^{-1}$ ,  $\nu(\text{M}-\text{N})$ , 510  $\text{cm}^{-1}$ ,  $\nu(\text{ClO}_4)$  1086  $\text{cm}^{-1}$  & 624 $\text{cm}^{-1}$ , UV-vis ( $\lambda_{\text{max}}$ ) DMSO:  $d \leftrightarrow d$ , 540 nm.



Where  $\text{M}=\text{Cu}$  &  $\text{Ni}$   $\text{X}=\text{ClO}_4^-$ ;  $\text{M}=\text{VO}$   $\text{X}=\text{SO}_4^{2-}$

**Figure-2: Proposed structure of the metal complexes.**

### Synthesis of Nickel(II) complex

The same procedure was adopted for nickel  $[\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}]$  complex. It undergo reflux until it form greenishblue colour precipitate. Yield 63% melting point  $> 250^{\circ}\text{C}$ .  $\text{C}_{58}\text{H}_{52}\text{N}_8\text{Ni}_2\text{Cl}_4\text{O}_{16}$  Calcd: C, 50.65, H, 3.78, N, 8.15, Ni, 8.58% Found: C, 51.03, H, 3.69, N, 8.45, Ni, 8.39%  $\Lambda_m$  240 ( $\Omega^{-1}\text{cm}^2\text{m}^{-1}$ ), IR (KBr pellet)  $\nu(\text{C}=\text{N})$ , 1610  $\text{cm}^{-1}$ ,  $\nu(\text{M}-\text{N})$ , 550  $\text{cm}^{-1}$ ,  $\nu(\text{ClO}_4)$  1088,  $\text{cm}^{-1}$  & 625  $\text{cm}^{-1}$ , UV-vis ( $\lambda_{\text{max}}$ ) DMSO:  $d \leftrightarrow d$ , 506 nm, 795 nm.

### Synthesis of Oxovanadium(IV) complex

The same procedure was adopted for vanadyl  $[\text{VOSO}_4 \cdot \text{H}_2\text{O}]$  complex. It gave dark blue colour precipitate. Yield 60% melting point  $> 250^{\circ}\text{C}$   $\text{C}_{58}\text{H}_{52}\text{N}_8\text{V}_2\text{S}_2\text{O}_{10}$  Calcd: C, 58.68, H, 4.38, N, 9.44,  $(\text{VO})_2$ , 11.29% Found C, 56.68, H, 4.29, N, 9.29,  $(\text{VO})_2$ , 11.03%  $\Lambda_m$ , 146 ( $\Omega^{-1}\text{cm}^2\text{m}^{-1}$ ),  $\nu(\text{C}=\text{N})$ , 1608  $\text{cm}^{-1}$ ,  $\nu(\text{M}-\text{N})$ , 520  $\text{cm}^{-1}$ ,  $\nu(\text{SO}_4)$  1112

$\text{cm}^{-1}$ ,  $\nu(\text{V}=\text{O})$   $943 \text{ cm}^{-1}$ , UV-vis ( $\lambda_{\text{max}}$ ) DMSO:  $d \leftrightarrow d$ , 539 nm.

### **Antibacterial Studies**

All the complexes have been screened for their invitro antimicrobial activity against human pathogenic bacteria were checked by the disc diffusion technique. This was done on Gram negative bacteria like *Klebsiella pneumoniae*, *Escherichia coli* and Gram positive bacteria *Staphylococcus aureus* at  $37^{\circ}\text{C}$ . The disc of Whatmann no.4 filter paper having the diameter 8.00 mm were soaked in the solution of compounds in DMSO ( $1.0 \text{ mg cm}^{-1}$ ). After drying, it was placed on nutrient agar plates. The inhibition areas were observed after 36 hrs. DMSO was used as a control and Streptomycin as a standard [14].

### **Results and Discussion**

A new macrocyclic binuclear Cu(II), Ni(II) and VO(IV) Schiff base complexes have been synthesized by condensation of benzidine with freshly prepared o-aminobenzaldehyde, with this ligand 2,3 pentanedione and respective metal salts were added. All the complexes were crystalline in nature stable at room temperature. All macrocyclic complexes are dark coloured solids and are soluble in DMF, DMSO. All the complexes gave satisfactory elemental analysis results, with the proposed structure of the macrocyclic binuclear Schiff base complexes. The formation of the macrocyclic binuclear Schiff base complexes and their geometry were further confirmed by IR, UV-Vis, magnetic moment and EPR spectral studies. The complexes are also screened for their biological activity against several bacterial species.

### **Molar conductivity measurements**

The molar Conductivities of  $10^{-3} \text{ M}$  solutions of the dissolved chelates in DMF are  $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  indicating that, these chelates are gave high conductivity value confirms the electrolyte in nature [15]. Further the chemical analysis data and IR spectra reveals that  $\text{ClO}_4^-$  or  $\text{SO}_4^{2-}$  ions are present outside the coordination sphere.

### **IR spectral studies**

The ir spectra show a band  $3442 \text{ cm}^{-1}$  indicates a primary amine present in a Schiff base ligand. For a ligand and a complexes have no bands assignable to carbonyl group in the region of  $1700 \text{ cm}^{-1}$  confirms the

condensation occurring in a both cause. The band in a region  $1615\text{ cm}^{-1}$  conform the azomethine group present in a ligand and shift in a frequency further confirm the azomethine group coordinate with metal ion. The presence of bands in the region  $500\text{-}550\text{ cm}^{-1}$  due to the (M-N) [16,17]. The IR spectra of macrocyclic binuclear VO(IV) complex display a strong band at  $943\text{ cm}^{-1}$  this band is typical of oxometal species and is assigned to the V=O stretching of the vanadyl group [18]. In addition, spectra of the complexes show perchlorate and sulphate bands at  $1080\text{-}1115\text{ cm}^{-1}$ . The observation of the bands ascribable to the perchlorate or sulphate ions, is in confirmative with the elemental analysis and molar conductivity [19].

### **<sup>1</sup>H-NMR spectral studies**

The formation of Schiff base ligand was confirmed by the <sup>1</sup>H-NMR spectra. <sup>1</sup>H-NMR spectra of the ligand was taken in DMSO-d<sub>6</sub> solvent. The aromatic region was a set of multiplets in the range 6.5–7.3 ppm for the Schiff base ligand, while the azomethine protons were observed in the range 8.6 ppm. The total number of protons present in the Schiff base exhibited signals of the protons in their expected regions. It was also observed that DMSO did not show any coordinating effect on the ligand.

### **Magnetic properties**

The magnetic moment values are useful in the evaluation of result provided by the other techniques of the structural investigation. The geometry assessment of the complexes around Cu(II) and VO(IV) ions was supported further from the results of the magnetic moment. The lower values of magnetic moment at room temperature are 1.68 and 1.76 B.M is consistent with square planar geometry and square pyramidal geometry around the metal ion. Generally the low magnetic moment values of binuclear complexes are attributed to the weak anti-ferromagnetic interaction between two central metal ions, this indication was the formation binuclear complexes [20].

### **Electronic spectral studies**

Electronic spectra of the ligand and the complexes have been measured in DMSO. The ligand shows 221 nm, 275 nm and 393 nm assigned to  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transition within the molecules [21]. The d-d transition at low

energy absorption band at 540 nm  ${}^2B_{1g} \leftarrow {}^2E_g$  for copper and intense band at 510 nm  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  for nickel confirms the square planar geometry [22,23]. It also exhibits a weak band at 795 nm which is assigned to a spin forbidden  ${}^1A_{1g} \rightarrow {}^3A_{2g}$  transition. The band due to charge transfer around 539 nm in oxovanadium(IV) complex show Figure 2 it has square –pyramidal geometry [23].

### **ESR spectral studies**

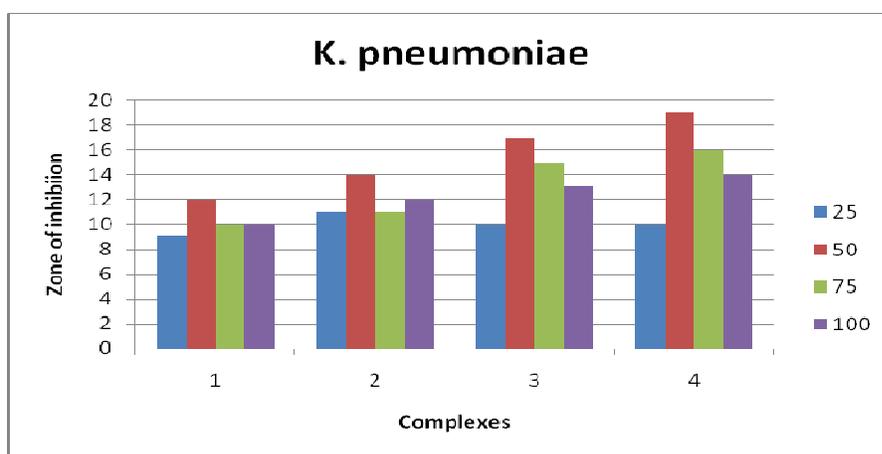
ESR spectra was used to identify coordination number, geometry of the complexes and also used to determine metal-ligand environment covalency. ESR spectra of the macrocyclic binuclear schiff base Cu(II) complex at room temperature show a  $g_{iso}=2.24$  and  $2.22$  respectively, these values indicate square planar geometry of the complex. The Cu(II) complex show an axial type of  $d_{x^2-y^2}$  ground state with considerable covalent bond character. In the macrocyclic binuclear Cu(II) complex,  $g_{||} > g_{\perp} > 2.0023$ , indicating square planar geometry around the Cu(II) ions [25]. Vanadyl complexes shows 8 broad splitting peaks with  $g_{||}=2.12$ ,  $g_{\perp}=2.02$ . This indicates the covalent character of the metal-ligand bond [26].

### **Antibacterial studies**

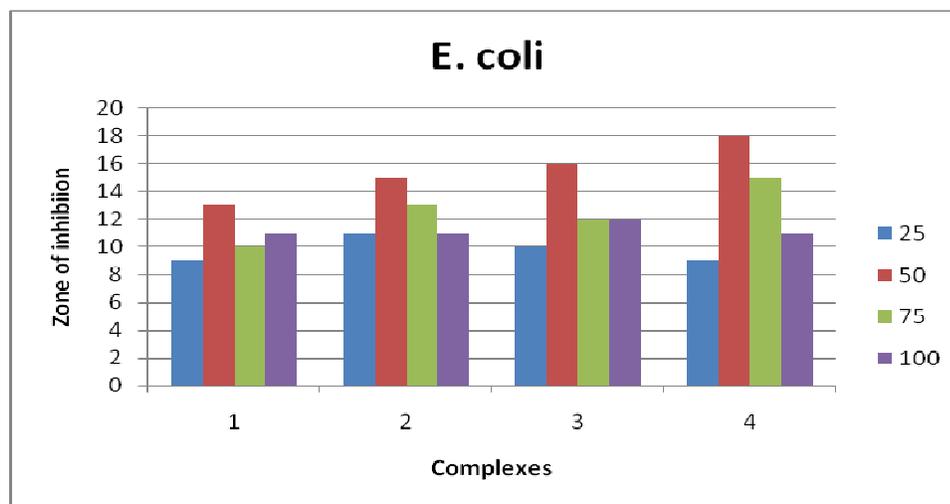
The antibacterial activity of the ligand and their metal complexes are given in Table 1. The metal complexes are more active than that of the standard. It has been suggested that chelation reduces the polarity of the metal ion. Chelation thus increase the lipophilic nature of the central metal atom, which in turn favors its permeation through the lipid layer of the membrane thus causing the metal complex to cross the bacterial membrane more efficiently increase the activity of the complexes [27]. Greater activity of these complexes can be explained on the bases of their particle size, concentration of metal and size of metal ion. It also has been observed that some moieties, such as azomethine linkage exhibit extensive biological activities [28]. The bacterial growth inhibition capacity of the macrocyclic binuclear Schiff base complexes in Figure 3a, 3b, 3c follows the order  $Cu(II) > Ni(II) > VO(IV)$  [29].

**Table-1: Antimicrobial activity of the ligand and its Cu(II), Ni(II) and VO(IV) complexes.**

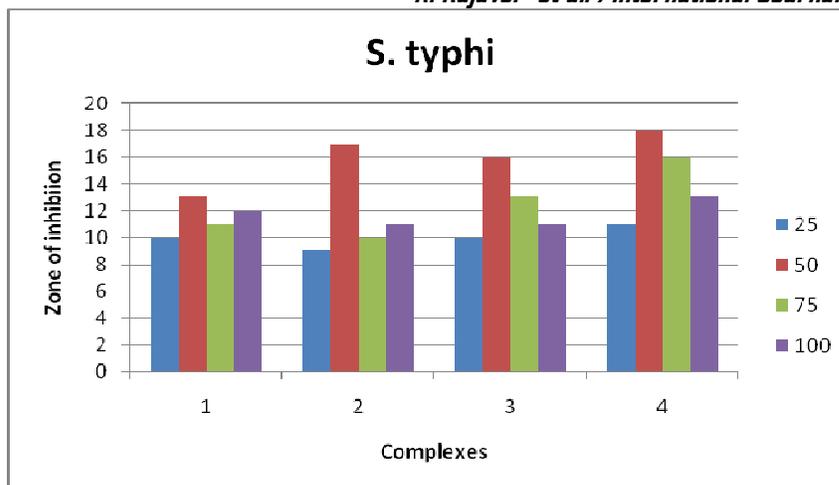
S.No	Ligand/complex	K.K.pneumoniae(mm)				E. coli (mm)				S. typhi(mm)			
		25	50	75	100	25	50	75	100	25	50	75	100
1	C <sub>20</sub> H <sub>18</sub> N <sub>4</sub>	9	11	10	10	9	11	10	9	10	9	10	11
2	C <sub>58</sub> H <sub>52</sub> N <sub>8</sub> Cu <sub>2</sub> Cl <sub>4</sub> O <sub>16</sub>	12	14	17	19	13	15	16	18	13	17	16	18
3	C <sub>58</sub> H <sub>52</sub> N <sub>8</sub> Ni <sub>2</sub> Cl <sub>4</sub> O <sub>16</sub>	10	11	15	16	10	13	12	15	11	10	13	16
4	C <sub>58</sub> H <sub>52</sub> N <sub>8</sub> V <sub>2</sub> S <sub>2</sub> O <sub>10</sub>	10	12	13	14	11	11	12	11	12	11	11	13



**Figure-3a: Klebsiella pneumoniae activities of the ligand and metal complexes.**



**Figure-3b: Escherichia coli activities of the ligand and metal complexes.**



**Figure-3c: Staphylococcus aureus activities of the ligand and metal complexes.**

## Conclusion

A novel macrocyclic binuclear Schiff base complexes have been synthesized by template method. The schiff base ligand can be prepared by fresh o-aminobenzaldehyde with benzidine. The ligand react with 2,3-pentanedione and respective metal salts. The metal-ligand ratio of 1:1 has been arrived at by estimating the nitrogen and metal contents. The complexes are electrolytic as indicated by the high molar conductivity values. The involvement of the azomethine nitrogen atoms of the ligand in binding with the metal has been inferred from the IR spectra. The lower value of magnetic moment of binuclear complexes are attributed to the weak anti-ferromagnetic interaction between two central metal ions, this indication was the formation of binuclear complexes. The presence of counter ion has been confirmed from the IR and high conductivity values. The antibacterial activity more pronounced in Cu(II) complex because of the Chelation theory.

## Acknowledgement

The authors thank to the Indian Institute of Technology Bombay for providing ESR spectra.

## References

1. D. Lusscan, J.M.Saranauli, P.C. Cassou, J.P. Tuchanques, J. Chem. Soc. Dalton Trans, 1988, pp1225.
2. P. Zanello, S. Tambarini, P.A. Vigeto and G.A. Mazzocchin, Coord. Chem. Rev, 1987, Vol 77, pp165.
3. O. Kahn, J. Galy, Y. Journaux, J. Jaud, I.M. Badanan, J. Am. Chem. Soc, 1982, Vol 104, pp2165-2176.

4. V. Alexander, Chem. Rev, 1995, Vol 95, pp273-342.
5. H. Furutachi, H. Okawa, Inorg. Chem, 1997, Vol 36, pp3911-3918.
6. A.A.A. Abu-Hussen, J. Coord. Chem, 2006, Vol 59, pp157-176.
7. M.S. Karthikeyan, D.J. Parsad, B. Poojary, K.S. Bhat, B.S. Holla, N.S. Kumari, Bio Org. Med.Chem, 2006, Vol 14, pp7482-7489.
8. T-B. Lu, H. Xiang, R.L. Luck, L. Jiang, Z.W. Mao, L-N. Ji, New. J. Chem, 2002, Vol 26, pp969.
9. M. Salvatari-Niasari, A. Amiri, J. Mol. Catal. A, 2005, Vol 235, pp114-121.
10. S.V. Rosokha, Y.D. Lamperka, I.M. Maloshtan, J. Chem. Soc. Dalton Trans, 1993, pp631-636.
11. R.W. Hey, J.M. Armstrong, M.M. Hassan, Trans. Metal Chem, 1992, Vol 17, pp270.
12. G. Revathi, J. Puri, B.K. Jain, Bacteriology of burns. Burns, 1998, Vol 24, pp347-349.
13. Lee Irvin Smith and J.W. Opie, Org. synthesis, Coll. 1948, Vol 28, pp11.
14. S. Sreedaran, K.S. Bharathi, A.K. Rahiman, L. Jadadish, V. Kaviyaran, V. Narayanan, Polyhedron, 2008, Vol 27, pp2931-2938.
15. W.J. Geary, Coord. Chem. Rev, 1971, Vol 7, pp81-122.
16. G.G. Mohamed, M.M. Omar, Ahamed, M.M. Hindy, Turkish J. Chem, 2006, Vol 30, pp361-382.
17. V.B. Ran, D.P. Singh, M.P. Testia, Trans. Met. Chem, 1982, Vol 7, pp174.
18. N. Raman, A. Kulandaisamy, C. Thangaraja, Trans. Met. Chem, 2003, Vol 28, pp29-36.
19. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Wiley-Inter Science, New York 1997.
20. A.A. Ahmed, S.A. Benguzzi, Journal of science and its Application, 2008, Vol 2, pp83-90
21. Z.H. Wahab, M.M. Mashaly, Chem. Pap, 2005, Vol 59, pp25-36.
22. H.D. Bian, J.Y. Xu, W. Gu, S.P. Yan, P. Cheng, D.Z. Dao, Z.H. Jiang, Polyhedron, 2003, Vol 22, pp2927-2932.
23. B. Sarkar, M.S. Ray, M.G. Drew, A. Figuerola, C. Diaz, A. Ghosh, Polyhedron, 2006, Vol 25, pp3084-3094.
24. A.A. Osowole, E-Journal of Chemistry, 2008, Vol 5, pp130-135.

25. A.Hathaway, A.A.G. Tomlinson, Coord. Chem. Rev. 1970, Vol 5, pp1-43.
26. A.Veeraraj, P. Sami, N. Raman, Proc. Ind. Acad. Sci, 2000, Vol 112, pp515-521.
27. N.Padmapriya, S. Arunachalam, A. Manimaran, D. Muthupriya, C. Jayabalakrishnan, Spectrochim. Acta Part A, 2009, Vol 72, pp670-676.
28. N.Dharmaraj, P. Viswanthamurthi, K. Natarajan, Trans. Met. Chem 2001, Vol 26, pp105.
29. S. Prasad, P. Jayaseelan, R. Rajavel, IJPT, 2010, Vol 2, pp694-707.

**Corresponding Author**

**R. Rajavel\***

Assistant Professor,

Department of Chemistry,

Periyar University, Salem – 636 011

Tamil Nadu, India.

**E-mail:** [anuradhaboopathi@gmail.com](mailto:anuradhaboopathi@gmail.com)