

Synthesis, spectral characterization and antimicrobial activity of manganese (II) and copper (II) complexes of Salicylaldehydephenylhydrazone

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ABSTRACT

The metal complexes of Mn(II) and Cu(II) having composition $[M(\text{SPH})_2]X_2$ where $[\text{SPH} = \text{Salicylaldehydephenylhydrazone}; M = \text{Mn(II) and Cu(II)}; X = \text{Cl}^- \text{ and } 1/2\text{SO}_4^{2-}]$ have been prepared and characterized by elemental analysis, molar conductance, infrared and electronic spectral studies. Infrared spectral data suggests the involvement of azomethine nitrogen of the hydrazone moiety and phenolic oxygen of salicylaldehyde in coordination with the central metal ion. On the basis of electronic spectral data studies, Mn(II) have been assigned tetrahedral geometry and Cu(II) complex adopt square planar geometry. These synthesized complexes were tested for antimicrobial effectiveness on *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* (bacteria) *Candida albican* and *Aspergillus niger*. The ligand and metal(II) complexes exhibited significant inhibitory activity against these microbes and Cu(II) complex seem to be the most active compound

Keywords: Salicylaldehydephenylhydrazone, Bidentate ligand, Mn(II) and Cu(II) complexes, antimicrobial activity.

INTRODUCTION

Hydrazones and derivatives are potential multifunctional ligands in coordination chemistry. They can adopt a variety of coordination modes depending on tautomerism, reaction condition, number and the nature of the substituent on the hydrazone skeleton ^[1-3].

Interest in design, synthesis and characterization of metals complexes with hydrazone ligand has been stimulated because their biological activities which are often enhanced on complexation.

In fact hydrazones and their metal complexes have been reported to possess antimicrobial, anticonvulsant, anti-tubercular, analgesic, anti-inflammatory and antitumor properties^[4-9].

Salicylaldehyde-derivatives of hydrazone have also received considerable attention in spectrophotometric determination of trace ions such as cobalt^[10], gallium and indium^[11], enzymatic inhibition^[12], DNA synthesis and cell growth activities^[13].

The present work reports the synthesis, characterization and antimicrobial activities of manganese(II) and copper(II) complexes of salicylaldehydephenylhydrazone (SPH).

Materials and Methods

All chemicals used were of analytical grade and were used as supplied. The C, H. and N were analyzed on Perkin Elmer PE 2400 automatic elemental analyzer. The metallic ions were determined complexometrically. The IR spectra (KBr) were recorded on Perkin Elmer FT-IR spectrum XB spectrophotometer and the electronic spectra were determined in DMSO using Perkin Elmer spectro. UV-VIS double beam PC scanning spectrophotometer (UVD-2960) 3.3 software version. Molar conductance was measured on Jenway 4510 Conductivity Bridge with a conventional dip-type black electrode. All melting points were taken on Gallenkemp melting point apparatus.

Synthesis of ligand

Methanolic solutions of salicylaldehyde (0.610g, 0.005mol) and phenylhydrazine (0.541g, 0.005mol) were mixed in the presence of few drops of glacial acetic acid with constant stirring. This mixture was boiled under reflux for 2 hours, after which was left to stand overnight. Maroon coloured precipitate was filtered out, washed with ethanol and dried in a desiccator. The yield was 65%.

Synthesis of metal complexes

Methanolic solution (20ml) of the ligand (0.004mol), salicylaldehydephenylhydrazone and methanolic solution (20ml) of the respective metal salts (0.002mol) were mixed together while stirring until the solution becomes homogenous. The mixture was finally boiled under reflux for 1 hour, after which was left to cool overnight. The formed precipitate was filtered out, washed with methanol and dried in a desiccator over fused calcium chloride.

Antimicrobial Activity Test

The method adopted for the antimicrobial tests is the general and widely reported procedure in many literatures such as^[24,25] etc.,. The antimicrobial activities of salicylaldehyde-phenylhydrazone and its Mn(II) and Cu(II) complexes dissolved in DMF was tested *in vitro* by paper disc method and broth dilution method for the fungi. The microbes used were *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* (bacteria), *Candida albicans* and *Aspergillus niger* (fungi). These were obtained from stock culture. They were kept in agar medium (2% Difco 15/l, Bushell and Hass salt mixture and glucose 1%w/v). All the materials used

were sterilized. The preparation of inoculum from agar nutrient was done by the treatment of the media with 3ml suspension of the respective cells. Each colony of the microbes was subcultured and incubated for about 8 hours before pouring into agar plates. The discs (7mm diameter) were soaked in different synthesized compounds, (concentration 1000 μ g/ml), drained and then placed in agar plates using sterilized forceps. The plates were incubated at 37 $^{\circ}$ C for 24hours. At the end of this period, the zones of inhibition were measured in mm. The minimum inhibitory concentrations (MIC) of the synthesized compounds were also carried out using double serial dilution of 500,250,125,62.5,31.25,15.62,7.81,3.91 and 1.92 μ g/ml. Ampicillin was used as the standard.

Result and Discussion

The ligand SPH was synthesized as described above. The Mn(II) and Cu(II) complexes were synthesized by refluxing the metal salts with ligand in a 1:2 metal:ligand molar ratio. The structure and 3-dimensional view of metal complexes were established with the help of their elemental analysis, infrared, UV-VIS and conductivity measurement. (figure 1a and b). The physical properties of the complexes are presented in Table 1. The complexes showed various shade of colours ranging from maroon, brown and dark brown. The % yield of the ligand was in the range of 65-49%. The metal complexes show sharp melting points of 177 and 195 $^{\circ}$ C respectively. Molar conductance of the complexes in DMSO is in the range of 3.85-5.35 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that the complexes are non-electrolyte. Micro-analytical data correspond to expected molecular formula $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$ for SPH and revealed the metal complexes analyzed as $[\text{M}(\text{SPH})_2]\text{X}_2$ the general equation leading to the formation of metal complexes is given below.

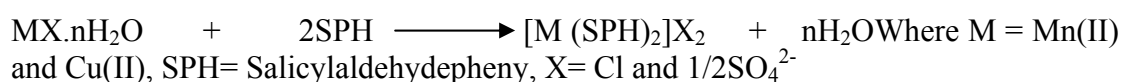


Table 1 Physical characteristics and analytical data of the ligand and its metal complexes

Compounds	Molecular Formular/atomic Mass (g)	% yield	M.p. ($^{\circ}$ C)	Colour	Observed (Calculated)%				Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
					C	H	N	M	
SPH	$\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$ 212.26	65	158.7	Maroon	73.50 (73.45)	5.65 (5.44)	13.19 (13.04)	-	-
$[\text{Mn}(\text{SPH})_2]\text{Cl}_2$	$\text{MnC}_{26}\text{H}_{24}\text{N}_4\text{O}_2\text{Cl}_2$ 550.46	54	177.1	Brown	56.68 (56.49)	4.36 (4.59)	10.17 (10.05)	9.98 (9.62)	3.87
$[\text{Cu}(\text{SPH})_2]\text{SO}_4$	$\text{CuC}_{26}\text{H}_{24}\text{N}_4\text{O}_6\text{S}$ 584.06	48.6	194.0	Dark brown	53.42 (53.38)	4.12 (4.03)	9.59 (9.96)	10.88 (10.97)	5.32

Table 2 Important infrared spectral bands (cm^{-1}) and their assignments, where s=strong; m=medium; w=weak; b=broad; v=very.

Compound	$\nu(\text{OH})$ phenolic	$\nu(\text{C-O})$ phenolic	$\nu(\text{C=N})$	$\nu(\text{N-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
SPH	3406w,b	1251m	1601m	1496m	-	-
$[\text{Mn}(\text{SPH})_2]\text{Cl}_2$	3371w,b	1245s	1595m	1501m	607w	518w
$[\text{Cu}(\text{SPH})_2]\text{SO}_4$	3451w,b	1243v,w	1596m	1498w	695v,w	592v,w

Table 3 Electronic spectral bands (cm^{-1}) of the ligand and its metal complexes

Compound	Band (cm^{-1})	$\epsilon(\text{Lmol}^{-1} \text{cm}^{-1})$	Assignment	Geometry
SPH	42,553 38,461 35,088	18,210 17,170 15,210	$n - \sigma^*$ $\pi - \pi^*$ $\pi - \pi^*$	-
$[\text{Mn}(\text{SPH})_2]\text{Cl}_2$	41,667 37,736 28,571 21,505 19,802	18,480 17,160 15,290 210 223	$n - \sigma^*$ $\pi - \pi^*$ $\pi - \pi^*$ ${}^6\text{A}_1 \xrightarrow{4\text{P}} {}^4\text{P}, {}^2\text{D}$ ${}^6\text{A}_1 \xrightarrow{4\text{F}} {}^4\text{G}$	Tetrahedral
$[\text{Cu}(\text{SPH})_2]\text{SO}_4$	42,553 32,787 30,303 22,727 20,619 19,608	18,400 15,700 15,330 231 236 223	$n - \sigma^*$ $\pi - \pi^*$ $\pi - \pi^*$ CT ${}^2\text{B}_{1g} \xrightarrow{2\text{E}_g} {}^2\text{E}_g$ ${}^2\text{B}_{1g} \xrightarrow{2\text{A}_g} {}^2\text{A}_g$	Square planar

Table 4 Zone of inhibition 1000 $\mu\text{g}/\text{ml}$ (minimum inhibitory concentration μg)

<i>E.coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>C.albican,</i>	<i>A. nigers</i>	
SPH	12.3 (250)	12.2 (125)	9.0 (500)	10.4 (250)	8.5 (125)
MnSPH	24.0 (31.25)	16.2 (7.81)	12.8 (3.09)	12.2 (31.5)	13.5 (31.8)
CuSPH	15.45 (125)	21.11 (7.91)	12.5 (125)	14.8 (31.25)	18.5 (31.25)
Ampicilin	18.5 (14.5)	16.8 (62.5)	14.4 (62.5)	13.5 (125)	14.3 (31.25)

Infrared Spectra

The infrared spectra of the complexes, in comparison with that of free SPH ligand, displayed certain changes, which indicated the type of coordination and their

structures as presented in table 2. The IR spectra of the ligand and its metal (II) complexes showed bands in the range of $375\text{--}3760\text{cm}^{-1}$ which are attributable to $(\text{OH})_{\text{phenolic}}$, $(\text{C-O})_{\text{phenolic}}$, C=O , N-N and M-L bands respectively. The vibration frequency generated by phenolic OH group, appearing in the IR spectrum of the ligand at 3406cm^{-1} , is shifted to lower frequency of 3371cm^{-1} for the Mn(II) complex and higher value of 3440cm^{-1} in the spectra of Cu(II) complexes. These indicate the coordination of phenolic OH to the metallic ions^[14,15]. The shift of C-O band to lower vibrational frequency in the spectra of the complexes as compared to the free SPH, also give an evidence for the deprotonation and coordination of phenolic oxygen to metal ions^[16,17].

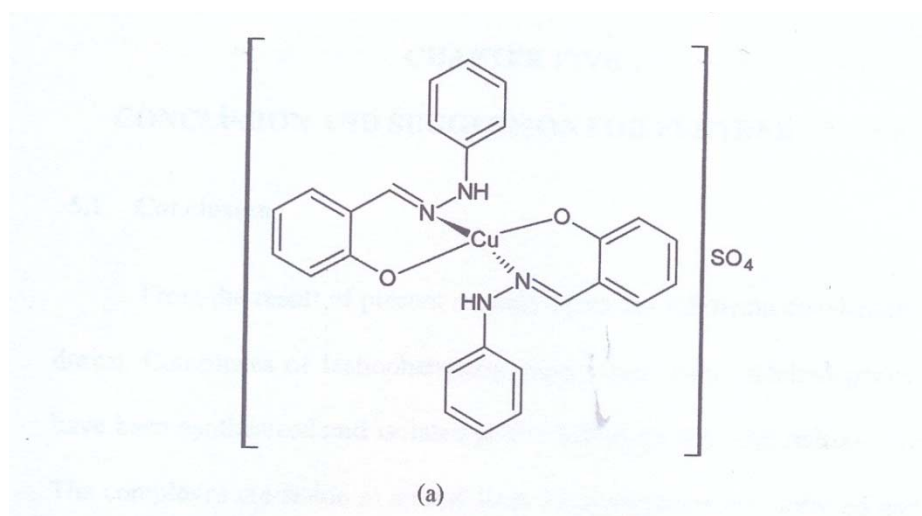
The band appearing at 1601cm^{-1} is attributed to azomethine vibration mode in the spectrum of the ligand and is shifted to lower values in the spectra of complexes, suggesting that the azomethine nitrogen is involved in the coordination with the metal ions^[18,19].

The coordination via the nitrogen atom of the azomethine group is further supported by the shift of N-N bands to higher vibrational frequency values in the spectra of complexes as compared to the free ligand^[20]. The bands at $605\text{--}695\text{cm}^{-1}$ and $515\text{--}592\text{cm}^{-1}$ in the spectra are attributed to M-O and M-N bonds in the complexes.

In each complex, salicylaldehydephenylhydrazoneligand coordinate to the central metal ion through azomethine N atom and phenolic O atom. Thus, it is concluded that salicylaldehydephenylhydrazone ligand acts as a bidentate chelating agent.

Electronic Spectra

The observed absorption bands in the electronic spectra of SPH ligand and its metal complexes in DMSO are shown in Table 3. Three bands at $42,553$; $38,461$ and $35,088\text{cm}^{-1}$ are observed in the ultraviolet region for the free SPH. These bands are attributed to intraligand transition due to the unsaturated nature of SPH system as shown in FIG. 1(a) and (b).



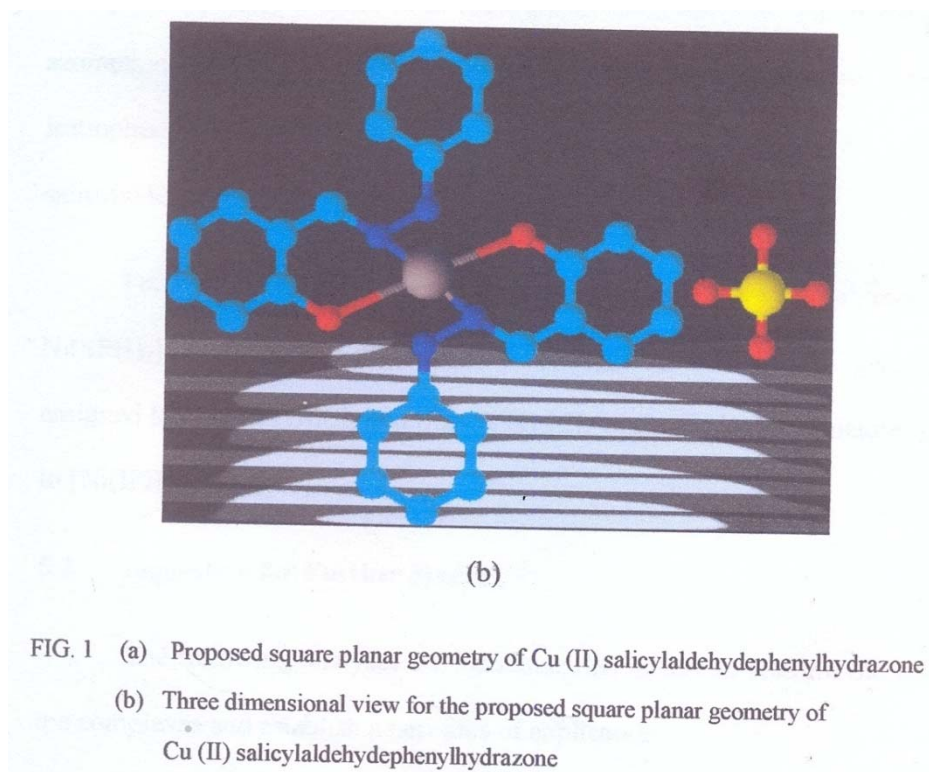


FIG. 1 (a) Proposed square planar geometry of Cu (II) salicylaldehydephenylhydrazone
(b) Three dimensional view for the proposed square planar geometry of Cu (II) salicylaldehydephenylhydrazone

These bands were shifted to lower wave numbers (bathochromic shift) in the spectra of the complexes, indicating the coordination of the metal ions to SPH. Bands in the region $28,000\text{--}30,000\text{cm}^{-1}$ in $[\text{Mn}(\text{SPH})_2]\text{Cl}_2$ and $[\text{Cu}(\text{SPH})_2]\text{SO}_4$ were attributed to $n \rightarrow \sigma^*$ transition due to the lone pair of electron on the heteroatom in the structure of SPH.

The metal complexes also exhibited d-d transition but with $[\text{Cu}(\text{SPH})_2]\text{SO}_4$ showing charge transfer transition in the visible region of the spectrum. In the visible region of the spectrum of $[\text{Mn}(\text{SPH})_2]\text{Cl}_2$, several bands due to forbidden transition were observed. The band at $21,505$ and $19,802\text{cm}^{-1}$ are assigned to ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2({}^4\text{P}, {}^4\text{D})$ and $\text{A}_1 \rightarrow {}^4\text{E}({}^4\text{G})$ respectively and are typical of tetrahedral manganese (II) complexes^[22].

Bands observed at $20,619$ and $19,688\text{cm}^{-1}$ in the visible spectrum of $[\text{Cu}(\text{SPH})_2]\text{SO}_4$ were attributed to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transitions respectively. The observed bands were typical of square planar copper(II) complexes being above $10,000\text{cm}^{-1}$ wave number and having molar absorptivity (ϵ) greater than $100\text{Lmol}^{-1}\text{cm}^{-1}$ ^[23].

Additional band at $21,023\text{cm}^{-1}$ is due to charge transfer transitions. The proposed structure and 3-dimensional view of the metal (II) complexes formulated as $[\text{M}(\text{SPH})_2]\text{X}_2$ is shown in FIG.1: (a) Proposed structure of the metal (II) complexes. (b) Three dimensional view of the proposed structure of the metal (II) complexes.

Where $\text{M}=\text{Mn}(\text{II})$ and $\text{Cu}(\text{II})$ and $\text{X}=\text{Cl}$ and $1/2\text{SO}_4^{2-}$

Antimicrobial Activity

The result as presented in Table 4 indicates that the ligand and the metal complexes significantly affect the life and growth of the above named microbes.. They were found to be very active both at high and low concentrations.

The Cu(II) complex displaced a good inhibiting effect on all the micro – organisms. This is evident in the diameters of zones of inhibition ranging from 21.11mm for *S aureus*, to 15.45mm for *E.coli* to 12.5mm for *B.subtili* to 18.5mm for *A. nigers* and to 14.45mm for *C. albican* and minimum inhibitory concentration (MIC) of 7.92g particularly over *S. aureus*

CONCLUSION

The SPH ligand and its manganese(II) and Copper(II) complexes have been synthesized and structurally characterized. The analytical data show that metal: ligand ratio in all these complexes was 1:2. All the complexes were non-electrolyte in DMSO solvent. The spectra data show that the ligand acted as a bidentate coordinating through nitrogen atom of azomethine group and oxygen atom of the hydroxyl group of salicylaldehyde respectively. Molar conductance, infrared and electronic spectra data of Mn(II) and Cu(II) complexes led to the assignment of tetrahedral and square planar geometries respectively. These compounds were also found to exhibit significant antimicrobial effects on the growth and proliferation of the named microbes; and these activities were enhanced on complexation of the ligand with manganese(II) and copper(II) ions. The copper(II) complex was found to be most active.

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REFERENCES

1. Saleem, H. S. (2010). Transition metal complexes of an Isatinicquinolhydrazone. *Chemistry Central Journal*, 5(35):1-8.
2. Koh, L. L., Kon, O. L., Lon, K. W., Long, Y. C., Ranford, J. O., Tan, A. I. C. & Tjan, Y. Y. (1998). Complexes of salicylaldehyde sacylhydrazones: cytotoxicity, QSAR and Crystal structure of the sterically hindered t-butyl dimmer. *Journal of Organic Biochemistry*, 72:155-162)
3. Kuriakose, M., Prathapachandra Kurup, M. R. & Suresh, E. (2007). Synthesis, spectroscopic studies and crystals structures of new vanadium complexes of 2-benzoylpyridine containing hydrazone ligands. *Polyhedron*, 26(12): 2713-2718.

4. Babaham, I. Coban, P. E., Ozmen, A., Biyik, H. & Isman, B. (2011). Synthesis, characteristics and biological activity of vic-diomme derivatives containing benzaldehydhydrazone groups and their metal complexes. *African Journal of Microbiology Research*, 5(3); 271-283.
5. Sridhar, S. K., Pandeya, S. N., stable, J. P. & Ramesh, A. (2002). Anticonvulsant activity of hydrazone Schiff and Mannich bases derivatives of Isatin. *Eur. J. Pharm. Sci.*, 16(13):129-132.
6. Salvem, T. P. & Kumar, P. V. (2010). Synthesis and antitubercular activity of novel 6, 7, 8, 9- tetrahydro4H-5-(2'-Hydroxyphenyl)-2-(4'-substituted benzylidene) thiazolo (2,3,-6) quinazolin-3-phenylhydrazones. *Malaysian Journal of Pharmaceutical Science*, 8(1): 45-55.
7. Sondhi, S. M., Dimodia, M., & Kumar, A. (2006). Synthesis, anti-inflammatory and analysis activity evaluation of some amidine and hydrazoien derivatives. *Bioorganic and Medicinal Chemistry*, 14(13): 4657-4663.
8. Despaigne, A. A. R., Da Silva, J. G., De Carino, A. C. Sives, F., Piro, O. E., Castellano, E. E. & Berolido, H. (2009). Cu(II) and Zn(II) complexes with 2-benzoylpridine –derived hydrazones. *J. mol. struct.*, 920:97-102.
9. Sathisha, M. P., Revankar, V. K. & Pia. S. R. (2007). Synthesis, structure, electrochemistry and spectral characterization of Bis-IsatinThiocarbonhydrazone Metal complexes and their Antitumoral Activity against Ehrlich Ascites Carcinoma in Swiss Albino Mice. *Hindawi Publishing Corporation Metal-Based Drug*, Vol. 2008, Articles ID3262105, 11 pages.
10. Park, C. J. & Cha, K. W. (1998). Spectrophotometric determination trace amounts of cobalt with 2-hydroxybenzenidehyde-5-nitro-pyridylhydrazine in presence of surfactant after separation with amberlite IRC -178 resin. *Talanta*, 46(6): 1515-1523.
11. Katiya, T. S. & Tandon, S. N. (1964). 1-Isonicotinyl-2-salicylidene hydrazone as a new chelatometric reagent. *Talanta*, 11:892-894.
12. Xu, G. C., Zhang, L., Liu, G. F. & Jia, D. Z. (2008). Synthesis, characterization and crystal have structures of mixed-ligand Cu(II), Ni(II) and Mn(II) complexes of N-(1-phenyl-3-methyl-4-propenylidene-5-pyrazovono)-salicylidenehydrazide containing ethanol or pyridine so a co-ligand. *Polyhedron*, 27(1):12-24.
13. Sreeja, P. B., PrathapachndraKurup, M. R., Kishore, A. & Jasmin, C. (2004). Spectral Characterization, X-ray structure and biological investigation of copper(II) ternary complexes of 2-hydroxy acetophenone-4-hydroxybenzoic acid hydrazone and heterocyclic bases. *Polythedron*. 24:575-581.
14. Mounika, K., Pragthia, A. & Cyanakurani, C. (2010). Synthesis and biological activity of some Schiff base derived from 3-ethoxy salicylaldehyde and 2-amino benzoic acid and its transition metal complexes. *Journal of Scientific Research*, 2(3): 513-524.
15. Pourlimardan, O., Chamayou, A. C., Janiak, C. & Monfred, H. H. (2007). Hydrazone Schiff base-manganese (II) complexes: synthesis, crystal structure and catalytic reactivity. *Inorganic chimicaacta*, 360:1599-1608.

16. Abd-Elzahar, M. M. (2001). Spectroscopic characterization of some tetradentate Schiff base and their complexes with nickel copper and zinc. *J. Chin. Chem. Soc.*, 48: 153-158.
17. Lindoy, L., Moody, W. E. & Taylor, D. (1997). *Inorg. Chem.* 16, 1962.
18. Sece, J. M., Quiros, M. & Garmendia, M. J. G. (2000). *Polyheron*. 19. 1005.
19. Aranha, P. E., Do Santo, M. P., Romera, S. & Dockel, E. R. (2007). Synthesis, characterization and spectroscopic studies of tetradentate Schiff base chromium (III) complexes. *Polyhedron*, 26(7): 1373-1382.
20. Abdul Rahim, A. K., Jahfar, M. & Krishnankutty, K. (2009). Synthesis, characterization of metal chelates with 1, 5-diaryl-3-(2-hydroxyphenyl) formazans. *International Journal of Chemical Society*, 7(2): 646-654.
21. Nakamoto, K. (1997). Infrared and Raman spectra of inorganic and coordination compounds. 3rd edition, New York, NY, USA: Wiley interscience.
22. Osowole, A. A., Kempe, R., Schobert, R. & Balogun, S. A. (2010) Synthesis, characterization and in-vitro Biological activities of some Metal (II) complexes of 3-(1-4-methy 1-6- Chloro)-2-Pyrimidinylimino) methyl-2-Napothol. *Canadian Journal of pure and applied sciences*, 4(2): 1169-1178.
23. Woods, J. A. O. Omoregie, H. O. Retta, N., Chebedu, Y. & Capitelli, F. (2009). Synthesis and characterization of some nickel(II) and Copper(II) complexes of 2-substituted-4,4,4-trifluoro-(-2thyienyl) butane-1,3-dione(ITA) and their 2,2'-bipyridine and 1,10 phenanthroline adducts and X-ray structure of (2,2'-bipyridinebis(4,4,4-trifluoro-92-thieny) butane-1,3-dionate) Nickel(II). *Synthesis and Reactivity in Inorganic and Nano-Metal Chemistry*. 39: 704-717.
24. Offiong, O.E. and Martelli, S. (1992). Antifungal, and Antibacterial Activity of 2-acetylpyridine-(4-phenylthiosemicarbazone) and its metal(II) complexes. *IL Farmaco* 47(12)1543-1554
25. Raja, N.D. and Sakthivel, A. (2007). Synthesis, Spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity Studies. *Indian Academy of Science -J. Chem. Sci.* Vol. 119(4) 303-310

