

**CHARACTRISATION OF SYNTHESIZED NI (II), CU (II) METAL COMPLEXES AND ANTIOXIDANT, ANTIMICROBIAL STUDY****Shyam R. Annapure***

P.G. Department of Chemistry, Milind College of Science, Aurangabad-431002,
Maharashtra, India.

Article Received on
22 May 2017,

Revised on 12 June 2017,
Accepted on 03 July 2017,

DOI: 10.20959/wjpps20178-9668

Corresponding Author*Dr. Shyam R. Annapure**

P.G. Department of
Chemistry, Milind College
of Science, Aurangabad-
431002, Maharashtra,
India.

ABSTRACT

Solid complexes of Ni (II), and Cu (II) of asymmetrical Schiff bases are synthesized from 4-methylbenzen-1, 2-diamine, 3-Acetyl-6-methyl-pyran-2, 4-dione (DHA) and 5-bromo Salicylaldehyde. The structures of ligands and complexes are characterized by elemental analysis, UV-visible spectra, ¹H-NMR, mass, IR, thermal analysis, X-ray diffraction, magnetic susceptibility, and conductometry. Thermal behavior (TG-DSC) of the complexes were studied. The ligand field parameters have been characterized for Ni (II), Cu (II) complexes, which approve square planar geometry. The x-ray diffraction data suggests monoclinic crystal system for both complexes. The ligand and their metal complexes were subjected for fungicidal activity against

Trichoderma and Aspergillus Niger and antibacterial activity against Escherichia coli and Staphylococcus aureus. Antioxidant property is investigated by DPPH, among two, Cu (II) complex is found more potent.

KEYWORDS: Antioxidant, Antimicrobial activity, X-ray, Thermal analysis, Dehydroacetic acid.

INTRODUCTION

The Organometallic chemistry with Schiff base ligands containing oxygen and nitrogen as donor atoms plays important role in biological system in nature.^[1] Ligands coordinate to metal atom in different ways in different media. This fact had been result in infinite publication in coordination chemistry. So researcher infatuated to use it as medicinal power house, as anti-cancer, antibacterial, antiviral, DNA-cleavage, antitumor, anti-oxidant,^[2-7] In continuation of our earlier work^[8] in this study we synthesized complexes of Ni(II), and Cu

(II) with tetradentate ligands formed by the condensation of 3-Acetyl-4-hydroxy-6-methyl-2H-pyran-2-one(DHA),4-methylbenzen-1,2-diamine, and 5-bromoSalicylaldehyde [**Fig.1(a)**], and characterized by different spectral methods, also evaluated for antioxidant and microbial activity.

MATERIALS AND METHODS

Reagents and solvents purchased from sigma Aldrich are used without purification. DHA, 4-methylbenzen-1, 2-diamine, and 5-bromo Salicylaldehyde of Analytical grade were used for synthesis of ligand. AR grade metal chlorides were also used for the preparation of the complexes. DPPH is purchased from sigma Aldrich.

Instrumentation

All electronic absorption spectra of the complexes and ligand were chronicled on Shimadzu 1800 spectrometer. The CHN analysis was carried out on Thermo Scientific (FLASH 2000) CHN elemental analyzer. IR study has been carried out on Perkin Elmer-Spectrum RX-I FTIR spectrometer using KBr pellets. ¹H-NMR spectra of ligand were recorded on FT NMR spectrometer (400MHz) model Advance-II (Bruker) in CDCl₃ as a solvent using tetramethylsilane as internal standard. XRD were recorded on Pananalytical X'Pert Pro at USIC Kolhapur, The TGA/DSC recorded on TA Inc. SDT-2790 at SAIF Chandigarh.

Synthesis of ligand

It's a two- step synthesis; in the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of (10 mmol) of DHA and (10mmol) 4-methylbenzen-1, 2-diamine, in absolute ethanol for about 4 hr. The development of reaction was checked by thin layer chromatography. The resulting mono-Schiff base thus formed was then refluxed with 10mmol of 5-bromo Salicylaldehyde to synthesis final product. Product was then cooled at room temperature and collected by pouring on crushed ice and filtration, followed by recrystallization in super dry ethanol. (Yield: 87%).

Synthesis of metal complexes

Metal complexes were synthesized by mixing a stoichiometric fraction (1:1) by dissolving in methanol. The ligand (0.01 mol) and metal chloride (0.01 mol) are mixed in hot condition with nonstop stirring. The mixture was heated at reflux for about 3-4 h. On cooling, the volume of reaction mixture is reduced to half, then colored solid metal complex is appeared.

Thus achieved solid metal complex was purified by petroleum ether and dried over vacuum desiccator (yield: 78%).

RESULTS AND DISCUSSION

CHN analysis, MP, Color, Mol.Wt, and molar conductance data of ligand and metal complexes is represented in **Table 1**. The data shows equimolar stoichiometry (metal: ligand) and adequate general formula [ML] [where M = Ni (II), Cu (II)].

¹H-NMR spectra of ligand

The ¹H NMR spectra of free ligand in CDCl₃ at room temperature shows the following signals. 2.09 δ (s, 3H, C₆-CH₃), 2.11 δ (s, 3H, N=C-CH₃), 2.25 δ (s, 3H, C₄-CH₃ hydrogen of phenyl ring), 5.77 δ (s, 1H, C₅-H), 6.73-7.03 δ (m, aromatic protons), 8.88 δ (s, 1H, N=C-H), 9.76 δ (phenolic (-OH) hydrogen of phenyl ring) and 15.88 δ (s, 1H, enolic OH of DHA moiety). [9] [Fig. 2].

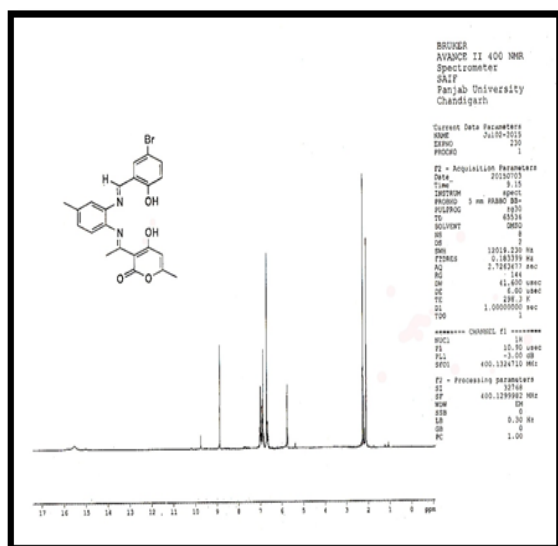


Figure 2

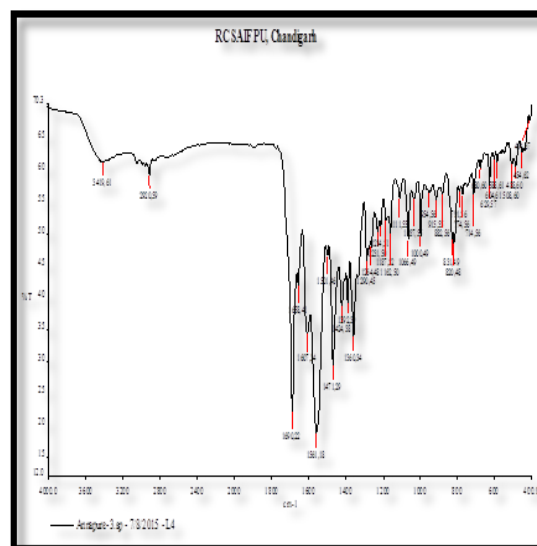


Figure 3

Table-1 Physical characterization, analytical and molar conductance data of compounds

Compound Molecular formula	Mol.Wt.	M.P/Decomp Temp. °C	Color	Molar conduc. Mho cm ² mol ⁻¹	Found (calculated)			
					C	H	N	M
(H ₂ L) C ₂₂ H ₁₉ N ₂ O ₄ Br	454.30	173	Dark Yellow	----	58.02 (58.04)	4.26 (4.21)	6.21 (6.15)	----
[LNi]	513.99	255	Red	28.60	60.96 (51.41)	4.45 (2.73)	8.49 (5.45)	11.86 (11.42)
[LCu]	518.85	234	Green	49.13	60.36 (50.93)	4.31 (2.70)	8.39 (5.40)	12.68 (12.25)

Table: 2 IR data of ligand and metal complexes

Compound	IR band frequency (cm ⁻¹)							
	$\nu(\text{OH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	C=C	C-N	C-O	M-O	M-N
L	3419	1690	1658	1561.1	1360	1214	-	-
Ni-L	3075	1685	1631	1560.7	1351	1212	510	460
Cu-L	3072	1685	1629	1558	1350	1210	535	459

IR spectra

The IR data of ligand (H₂L) and its metal complexes are listed in (Table 2). It depicts prominent bands at 3419, 1690, 1658, 1360 and 1214 cm⁻¹ assignable to ν OH, ν C=O (lactone carbonyl), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively (Fig.3).^[10] The presence of a strong broad band in the 3419 cm⁻¹ region, in the spectra of the ligand, which is not observed in complexes elucidates coordination of phenolic oxygen to the metal ion by deprotonation.^[11] Chelation by nitrogen of azomethine (C=N) is confirmed by observing band at 1647 cm⁻¹ in the spectra of ligand, which finds at lower frequency 1629-1631 cm⁻¹ when complex formed. This change can be supported by transfer of electrons from nitrogen to the vacant d-orbitals of the metal. Finding new bands in the 510-535 and 459-460 cm⁻¹ regions confirms the M-O and M-N bonding respectively.^[12] No any change in skeletal vibrations (C=C) upon complexation.

Powder x-ray diffraction

Scanning of x-ray diffractogram of Ni (II), Cu (II) metal complexes of L is done at wavelength 1.543 Å in the range 5-100°. The x-ray diffraction pattern of these complexes compared with major peaks of relative intensity greater than 10% has been indexed to their hkl value by using computer program.^[13] The diffractogram of Ni (II) complex of L had thirteen reflections with maxima at $2\theta = 10.798^\circ$ corresponding to d value 6.4587 Å. The unit cell of Ni (II) complex of L yielded values of lattice constants, $a=13.98756\text{Å}$, $b=8.54987\text{Å}$, $c = 6.785694\text{Å}$, $\beta = 116.544^\circ$ and unit cell volume $V=876.456982\text{Å}^3$. The diffractogram of Cu (II) complex of L had twelve reflections with maxima at $2\theta = 15.032^\circ$ corresponding to d value 5.8889 Å. The unit cell of Cu (II) complex of L yielded values of lattice constants, $a=10.3243\text{Å}$, $b=7.3001\text{Å}$, $c = 8.1047\text{Å}$, $\beta = 104.504^\circ$ and unit cell volume $V=591.378\text{Å}^3$.

In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that Ni (II), Cu (II), complex of L has monoclinic crystal system.

Magnetic susceptibility and electronic absorption spectra

The electronic absorption spectra of Ni (II) complex consists of two bands at about 556 nm and 377 nm assignable to $1A_{1g} \rightarrow 1T_{2g}$ and charge transfer transitions respectively. Observed electronic transitions, the diamagnetic nature and red color of the complex suggests square planar geometry for Ni (II) complex. Cu (II) show three bands at 613, 358 and 308 nm assignable to the transitions $2B_{1g} \rightarrow 2A_{1g}$ and two intra ligand charge transfer bands. These electronic transitions and observed 1.80 B.M magnetic moment value suggests square-planar geometry around Cu (II).^[14]

Thermal analysis

The TG/DSC analysis of Ni (II), and Cu (II) complexes was done from ambient temperature to 1000°C in nitrogen atmosphere using α -Al₂O₃ as reference.

The TG curve of Ni (II) complex [Fig.4] show no mass loss up to 240 °C indicates absence of coordinated water,^[15] First mass loss 58.59 % (calcd.58.63%) in the range 240-370°C and an endothermic peak in this region $\Delta T_{min} = 250.31^\circ\text{C}$, indicate removal of non -coordinated part of ligand. The second step slow decomposition from 370-980 °C with 24.99 % mass loss, confirmed by exotherm $\Delta T_{max} = 411.73^\circ\text{C}$ indicate loss of coordinated part. The mass of the final residue corresponds to stable NiO, 16.52 % (calcd.16.41%).

The thermal profile of Cu (II) complex shows mass loss 42.56 % (calcd.42.65%) in the range 240-390°C and an endothermic peak in this region $\Delta T_{min} = 310^\circ\text{C}$ indicates loss of coordinated part of ligand. The complex show slow decomposition from 390-750°C with mass 26.85% (calcd.26.98%) loss and a broad exotherm $\Delta T_{max} = 425^\circ\text{C}$ in DSC may be attributed to removal of coordinated part of ligand. No mass loss observed after 800 °C indicates more thermal stability of complex.

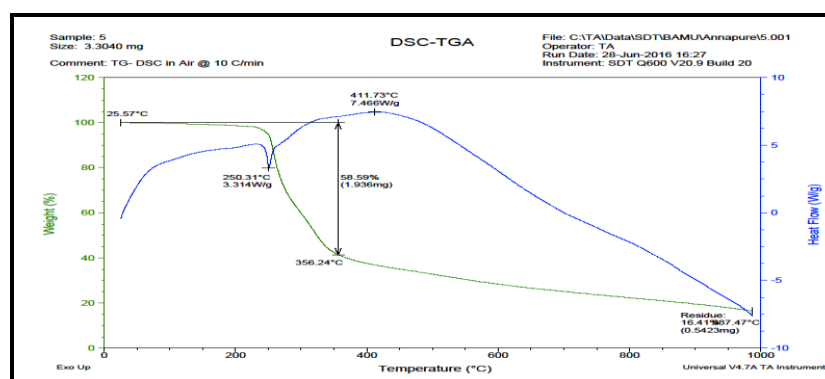


Figure 4

Kinetic Calculation

The kinetic and thermodynamic parameters viz ΔG (free energy change), ΔS (entropy of activation, z (pre-exponential factor), E_a (energy of activation) and n (order of reaction), together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method and Coats-Redfern Integral method.^[16] The data is arranged in (Table 3). The results show that the values obtained by two methods are comparable.

Table-3.The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	n	Method	E_a	Z	ΔS	ΔG	Correlation coefficient(r)
Ni(II)	I	1.83	HM	65.58	145029	-151.34	75.74	0.9993
			CR	69.97	295299	-150.74	74.58	0.9989
	II	1.12	HM	35.00	82124	-159.15	50.47	0.9984
			CR	32.02	111299	-156.74	46.16	0.9987
Cu(III)	I	1.17	HM	47.68	854765	-141.23	55.23	0.9984
			CR	45.96	24517232	-140.35	52.58	0.9979
	II	1.20	HM	32.78	154698	-138.45	44.89	0.9989
			CR	30.14	45879621	-134.98	41.67	0.9996

E_a in kJ mol^{-1} , Z in S^{-1} , ΔS in $\text{JK}^{-1}\text{mol}^{-1}$ and ΔG in kJ mol^{-1}

Antioxidant Activity

25, 50, 100,200 $\mu\text{g/ml}$ concentration of ligand, two complexes and ascorbic acid (standard) were prepared in methanol. 2 ml of 1, 1-Diphenyl-2-picrylhydrazyl solution (0.002%) was mixed with 2ml of all compounds separately in clean test tubes. After incubation for 30 min. in dark at room temperature optical density was measured at 517 nm using Shimadzu 1800 spectrometer. The scavenging activity was calculated by formula:

$$\text{Scavenging Activity (\%)} = [(A_{\text{DPPH}} - A_{\text{Sample}}) / A_{\text{DPPH}}] \times 100$$

Where A_{DPPH} – Absorbance of DPPH with ascorbic acid, A_{Sample} - Absorbance of DPPH with sample solution.

As DPPH is a good scavenger free radical, reduction capacity of all samples is estimated by degree of decolourisation, to convert it into 1, 1-Diphenyl-2-picrylhydrazine.^[17] L-Cu complex is found to be more potent compare to Ni (II) complexes. (Table 4).

Samples	Scavenging activity of different concentration ($\mu\text{g}/\text{ml}$) in %			
	25	50	100	200
L	67.56	59.45	51.25	44.35
L-Ni	73.48	65.48	56.49	44.98
L-Cu	94.78	85.56	73.47	66.78
Standard	81.14	86.32	90.21	92.14

Antimicrobial activity

Compounds were tested for antimicrobial activity against bacteria such as *Escherichia coli* and *Staphylococcus aureus* by paper disc plate method.^[18] The compounds were tested at the concentration 500ppm and 1000ppm in DMF, considering Ciproflaxin as standard (**Table-5**). Ligand and metal complexes are subjected for antifungal activity, by using Mycelia dry weight method compounds were tested against *Trichoderma* and *Aspergillus Niger*. The activity is tested at 250 and 500 ppm in DMF and depicted in (**Table-6**) by comparison with standard. Perceiving the values of Table-5 and 6, inference made that the inhibition by metal complexes is more than a ligand. Solubility of metal complexes in organic solvents increase its activity.

Table: 5 Antibacterial activity of compounds

Test Compound	Inhibition Zone (mm)			
	<i>E.Coli</i>		<i>Staphylococcus</i>	
	500 ppm	1000 ppm	500 ppm	1000 ppm
<i>Ciproflaxin</i>	29	32	31	35
(H ₂ L)	13	16	15	16
[LNi]	16	17	19	20
[LCu]	20	21	21	22

Table 6 Yield of Mycelial dry weight in mg (% inhibition)

Test Compound	<i>Aspergillus Niger</i>		<i>Trichoderma</i>	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
(H ₂ L)	43(46)	17(78)	24(66)	15(79)
[LNi]	28(65)	07(91)	10(86)	01(99)
[LCu]	24(70)	06(92)	09(87)	01(99)

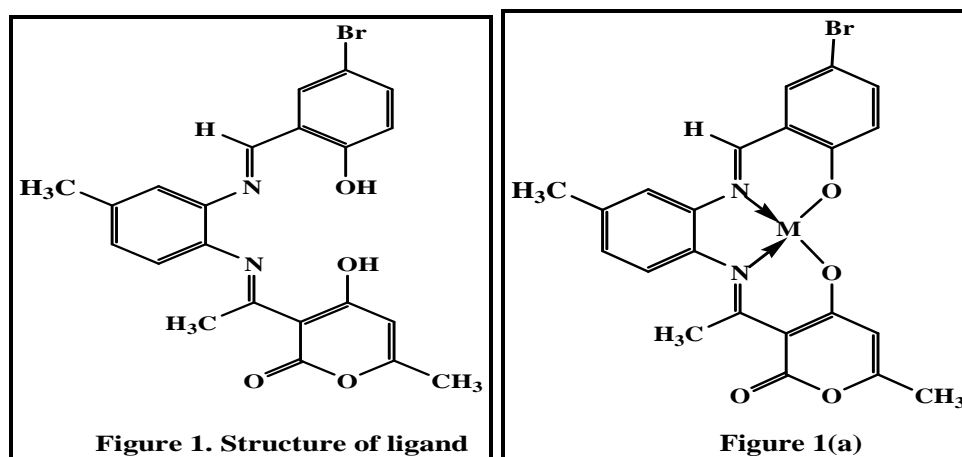


Figure: 1 a proposed structure of the complexes, Where M=Ni (II), Cu (II).

CONCLUSION

In this study we report synthesis of tetradentate ligand and its metal complexes of Ni(II) and Cu(II). Spectral study recommends that azomethine nitrogen and phenolic oxygen are involved in the co-ordination with metal ions (**fig.1 (a)**). Suggesting square planar geometry for Ni (II), and Cu (II), complexes. It is resolved that the ligand is dibasic in nature. Asymmetrical NOON donor metal complexes show good antioxidant activity, Cu (II) is found more potent than Ni (II). Complexes are biologically active and indicates heightened antimicrobial activities compared to its free ligand. Thermal study predicts thermal behavior and stability of complexes. The XRD reveals monoclinic crystal system for Ni (II), and Cu (II) complexes.

ACKNOWLEDGEMENTS

The Author convey his truthful thanks to SAIF Punjab University, Chandigarh for providing CHN, IR, ¹HNMR, Mass and XRD facility. Also grateful to USIC, Shivaji University, Kolhapur for providing TGA-DSC facility.

REFERENCES

1. Cleiton M.daSilva, DanielL.daSilva, LuziaV.Modolo, *Journal of Advanced Research*, 2011; 2: 1-8.
2. Amit P Singh, Nagendra K Kaushik, et al, *Indian Journal of chemistry*, 2011; 50(A): 474-483.
3. Anu Kajal, Suman Bala, et al, *Journal of Catalysts*, 2013; A893512: 14.
4. Eddie L.Chang, Christa Simmers, D. Andrew Knight, *pharmaceuticals*, 2010; 3: 1711-1728.

5. Marri Pradeep Kumar, Somapangu Tejaswi, et al, *Polyhedron*, 2015; 102: 111-120.
6. Regina M. S. Pereira, Norma E.D. Andrades, et al, *molecules*, 2007; 12: 1352-1366.
7. Enis Nadia Md Yusof, Thahira Begum S.A. Ravooof, et al, *International J. of Molecular Sciences*, 2015; 16: 11034-11054.
8. Shyam R Annapure, Shantilal D Rathod, *Inter.National.Journal of Chem Tech Research*, 2017; 10(3): 333-338.
9. Achut S. Munde, Amarnath N. Jagdale, Sarika M. Jadhav and Trimbak K. Chondhekar, *J. Serb.Chem.Soc*, 2010; 75(3): 349-359.
10. Shyam R Annapure, Achut S Munde, Shantilal D Rathod, *Der Chemica Sinica*, 2016; 7(4): 47-54.
11. Fasina, Tolulope M.and Ogundele Olorunfemi, *Der Pharma Chemica*, 2014; 6(4): 18-22.
12. Vinod A. Shelke, Sarika M. Jadhav, Sunil G. Shankarwar, T.K. Chondekar, *Journal of Chemical Science and Technology*, 2013; 2(2): 61-69.
13. J. R. Carvajal, T. Roisnel, Winplotr, 2004, A Graphic Tool for Powder Diffraction, Laboratoire Leon Brillouin (cea/enrs) 91191 gif suryvettedex, France.
14. Jadhav SM, Shelke VA, Munde AS, Shankarwar SG, Patharkar VR, Chondhekar TK., *Journal of Coordination Chemistry*, 2010; 63(23): 4153-4164.
15. A.S. Munde, A.N. Jagdale, S.M. Jadhav, and T.K. Chondhekar, *Journal of the Korean Chemical Society*, 2009; 53(4): 407-414.
16. V.M. Naik and et al, *Indian Journal of Chemistry*, 2008; 47: 1793-1797.
17. Nouredine Charef and et al, *Polyhedron*, 2015; 85: 450-456.
18. Cruickshank R, Duguid J P, Marion B P, Swain R H A, Twelfthed. *Medicinal Microbiology*, Churchill Livingstone, London, 1975; II: 196-202.