Synthesis, Spectroscopic studies and Biological Activity of Copper Schiff base complex

[a]K.Anna sudheer,[b]M.Jagadeesh Babu,[a]G.Raju,[a]M.S.N.A.Prasad and [a]Dr.B.KishoreBabu*
[a]. Department of Engineering Chemistry
AU College of Engineering, Andhra University
Visakhapatnam 530003, Andhra Pradesh, India

[b]. Department Of PNCO, School Of Chemistry
Andhra University,Visakhapatnam-530003,
Andhra Pradesh, India.

Abstract

Metal (II) complexe of Cu with Schiff base derived from ortho vanillin and ortho phenelyne diamine (L) were synthesized and characterized by standard physico-chemical procedures i.e. (metal analysis A.A, elemental chemical analysis C.H.N.S, FTIR, UV–vis, LC-MS and powder XRD measurements). On the basis of these studies, a six coordinated octahedral geometry for these complexe has been proposed. The Schiff base ligand and its complexes were also tested for their antibacterial activity to assess their inhibiting potential against ,Escherichia.coli (as gram negative bacteria) and Staphylococcus aureus (as gram positive bacteria) using two different concentrations (5 and 10 mM). The results showed the Cu(II) complex have the better rate in anti-bacterial activity with ampicillin as standard drug.

Key words
schiffs base, copper, azide, ,Escherichia.coli, Staphylococcus aureus

1. Introduction

Schiff bases and their bio-active complexes have been studied extensively over the past decade. Schiff bases provide potential sites for bio-chemically active compounds. Various transition and inner-transition metal complexes with bi, tri and tetraden-tate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems[1] Copper with chelating ligands forms coordination compounds. Copper (II) exists as $[Cu(H_2O)_6]^{2+}$ in aqueous solution. Cu (II) complex exhibits the fastest water exchange rate for any transition metal aqua complex. In recent years, a lot of research had been carried out to study the applications of copper containing coordination complexes in various fields like medicinal, bioinorganic chemistry, catalyst, analytical chemistry and many other industries[2-3]. Cu(II) complex of Schiff's base ligand had been synthesized, which was derived from *o*- hydroxy benzaldehyde and 2-amino pyridine. The ligand and the complex were The ligand and metal complexes had been screened for microbiological activity [4].

2.1.Experimental

2.1.1. Reagents

Chemicals are procured from renowned companies like sigma Aldrich, moly chem. and used without further purification. Ethanol, methanol used for amalgamation of metal complexes are A.R. grade and used as received for synthetic work.

$Cu(ClO_4)_2.6H_2O$ is procured from Alfa aesar.

Caution: Azides and per chlorates are explosive, handle with care.

2.1.3. Synthesis of [(Cu) (O-VAN)$_2$(OPD(N$_3$) (Clo$_4$)].(Clo$_4$)$_2$ 7H$_2$O

A solution of Schiff's base (0.5mmol, 0.188gms) is dissolved in 10ml of hot methanol is added to a solution of copper per chlorate (0.5mmol, 0.185gms) is dissolved in 10ml of water, instantaneously a pale green colored solution is appears. To this, a solution of sodium azide (0.5mmol, 0.032gms) is dissolved in 10ml of water is added, a green colored precipitate is obtained after one hour on constant stirring at room temperature Anal. Exptal. $C_{22}H_{18}$ Cu Cl O_8N_5 (M.Wt. 578) C, 45.62; H, 3.18; N, 12.46; O, 22.26; Found: C, 44.43 O, 21.28; H, 2.85; N, 11.28. Important IR absorptions (KBr disk,cm^{-1}): 3307, 1180, 1192, 1602, 2050, 1109, 424,533,.Mass peaks (m/z): 783,652,468,407,212.

M.P; 321^0 C

Yield; 0.203gm (57%)

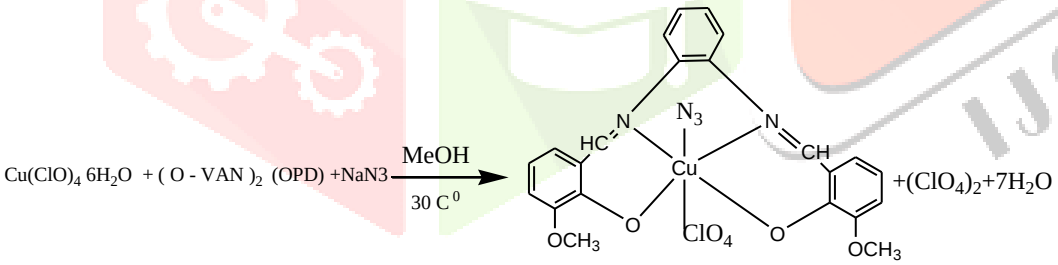


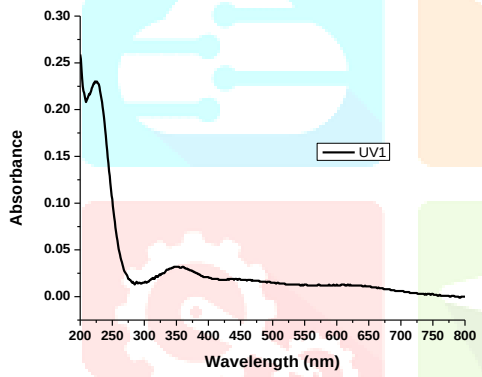
Fig: proposed structure of [(Cu) (O-VAN)$_2$(OPD(N$_3$) (Clo$_4$)].(Clo$_4$)$_2$ 7H$_2$O

2.2.Physical Measurements

An IR spectrum is obtained with a Bruker-alpha-T FT-IR spectrophotometer. UV spectra is recorded on systronics2700R UV spectrophotometer.LC-MS Spectra is recorded on AGILANT-Triple Quard (LC-MS/MS) mass spectrometer. XRD in Andhra university

2.2.2 Electronic spectrum of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O

The electronic absorption spectra of metal complexes are recorded in DMF in the range 200 – 800 nm. The electronic spectrum of free Schiff base revealed three bands around 240, 350 and 450 nm characteristic of π-π* and n-π* transitions. In the metal complexes, this band is shifted to a longer wave length with increasing intensity. This shift may be attributed to the donation of lone pair of electrons of oxygen of Schiff base to metal ion. The copper complexes exhibits bands around 255-300 nm, 350- 355 nm and 477-498 nm. The broad intense and poorly resolved bands around 350-355 nm may be assigned to LMCT or MLCT. The high intensity band around 250 nm is of ligand cause assignable to n-π*or π-π* transition n [5]The complexe exposed shoulder broad bands in the range of 300-325 nm may be assigned to the d–d transition.



2.2.5. IR Spectrum of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O

The weak broad bands in the region 3300 -3423 cm^{-1} due to hydrogen bonded OH group. This indicates that the phenolic oxygen atoms present in the Schiff bases are coordinated to the metal centers. The strong m(C=N) bands occurring in the range of 1624 cm^{-1} are shifted slightly toward lower frequency 1602cm^{-1} compared to the free Schiff bases indicating the Co-ordinated azomethine nitrogen atom to the metal center. The presence band at 1109 cm^{-1} corresponding to (ClO_4) and at 594 cm^{-1} assignable to (ClO_4) in above complex which proposes that per chlorate ion is in the coordination sphere of the complex[6]. The presence band 1078 cm^{-1} corresponding to (ClO_4) at outside the coordination sphere[7],The s (CN) absorption at 2050 cm^{-1}as a single peak suggests the presence of N-coordinated terminal azide group. (NNN) appears at 2050 cm^{-1} as a single peak indicating the presence of terminal azide ion coordination to the metal center.

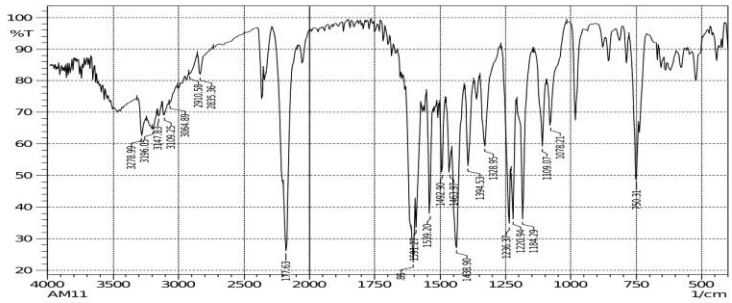


Fig: FTIR of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O

2.2.7. LC-MS Spectrum of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O

The peak at 891(m/z) is complex bound to two Ortho vanillin, one OPD, one copper and two azide, three per chlorates,and four water molecules[(Cu)(O-VAN)$_2$(OPD)(N_3) (Clo_4)].(Clo_4)$_2$7H_2O, peak at 654(m/z) refers to the two Ortho vanillin, one OPD, one copper and two per chlorate, and one water molecules[(Cu)(O-VAN)$_2$(OPD)] 2Clo_4. H_2O, The peak 437(m/z) refers to the two ortho vanillin,one OPD,and one copper molecule [(Cu)(O-VAN)$_2$(OPD)]. The peak at 303(m/z) is complex destined to one Ortho vanillin, one OPD,and one azide fragments embodied as [(O-VAN)(OPD)(N_3)]. Moreover, peak at 149(m/z) is indicates [(O-VAN)].

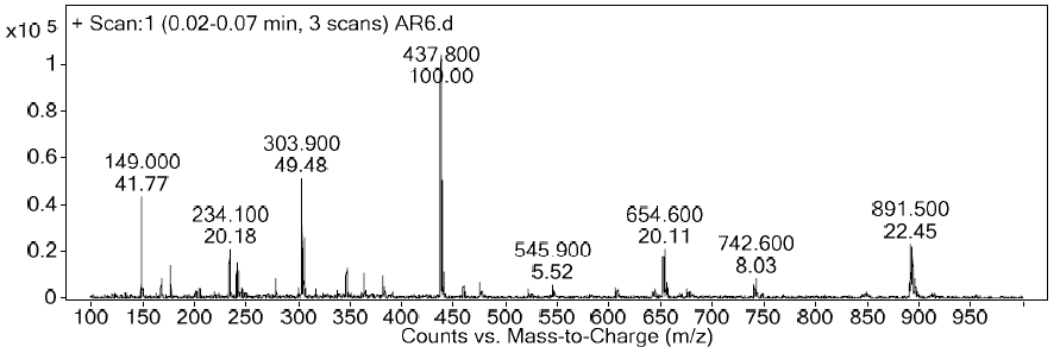


Fig: *LC-MS Spectrum of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O*

2.2.15. Powder X-Ray Diffractogram of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O

Crystallite size is obtained using Scherer's equation, D = Kλ/ (β cosθ), where D is he particle size in nm of the crystal gain has been calculated using maximum intensity peak; K is the Scherrer's constant; λ is the wavelength of target used; β is the full width at half maximum reflection height in terms of radian and θ is the Bragg diffraction angle at peak position in degree.

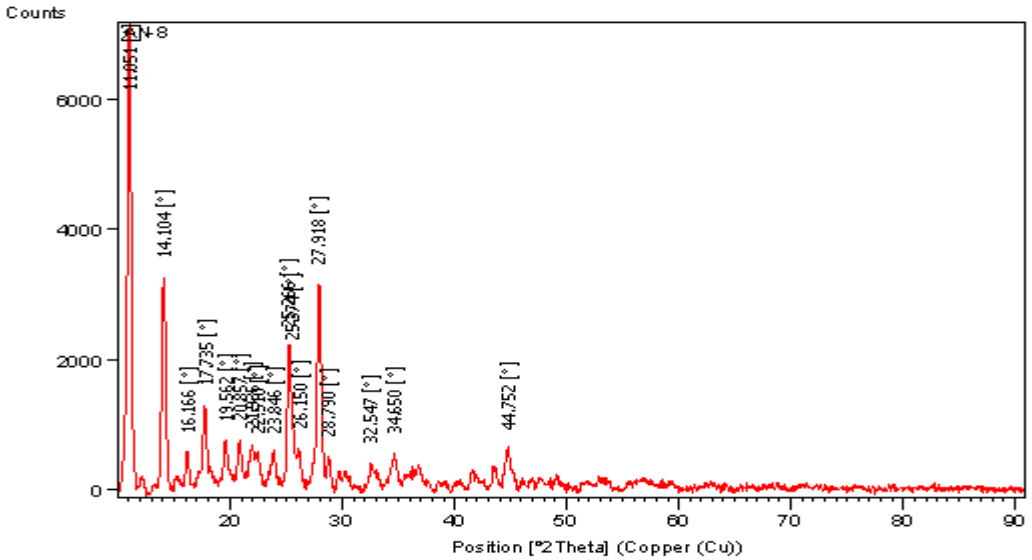


Fig.. Powder X-Ray Diffractogram of complex

COMPLEX	**2θ**	**Crystallite size**
[(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O	**11.051**	**79.52nm**

Table.5. crystllitesize of schiff's base Complex

2.2.12. Antimicrobial Screening of [(Cu) (O-VAN)$_2$(OPD) (N_3))(Clo_4)].(Clo_4)$_2$ 7H_2O

The complex is screened in vitro for antibacterial activity against E.coli, S.aureus and anti-fungal activity against C.albicans by Agar-well diffusion method[8]. the anti-bacterial and anti-fungal activities of complex are listed in table

Fig.3 Inhibition zones for complex against.S.aureusE.coli

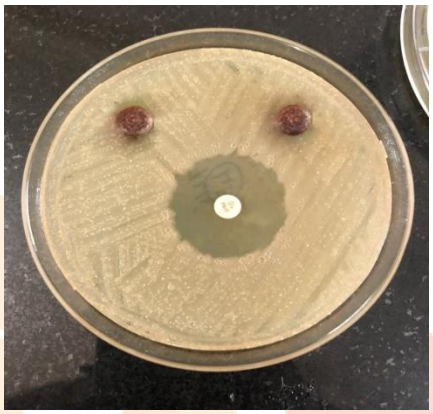


Fig.4Inhibition zones for complex against.C.albicans

Bacteria	**Inhibition zone (mm)**
S.aureus	9
E.coli	12
Fungi	**Inhibition zone (mm)**
C.albicans	Nil

Table. ***2antimicrobial activities of schiff's base complex***

The Schiff's base complex showed good antibacterial activity against E.coli andB.subtilis but didn't show anti fungalactivity against fungal organisms.

2.2.13. Cytotoxic studies of [(Cu) (O-VAN)$_2$(OPD) (N_3) (Clo_4)].(Clo_4)$_2$ 7H_2O

The synthesized complex is screened for their cytotoxicity (MCF-7, cell lines).from the data, it is observed that the complex displayed their cytotoxic activities as IC_{50} (μg/mL) against breast cancer MCF-7,The IC_{50}values of the complex are listed in table

Conc(µg/ml)	**% cell survival**	**% cell inhibition**
0.1	89.40216955	10.597830454
1	84.45560466	15.544395339
10	77.47930896	32.52069104
100	24.6870229	75.3129771

Table.3 Dose response of complex on MCF-7 cell line

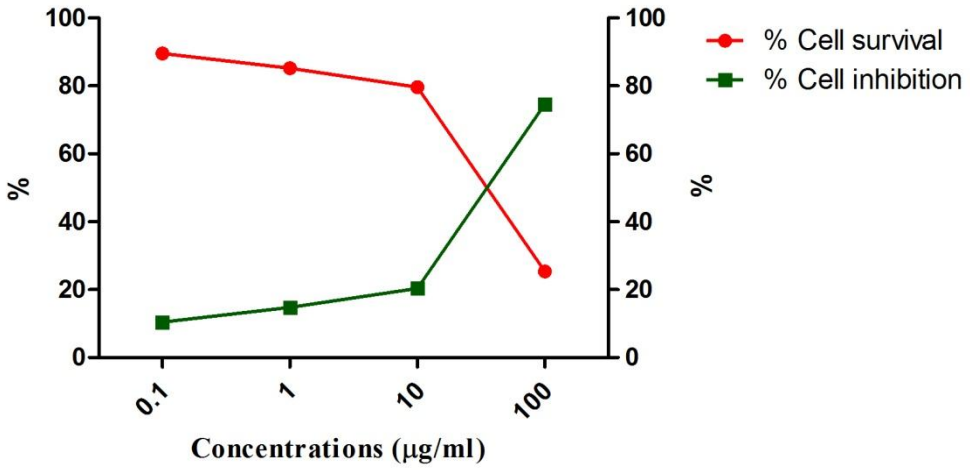


Fig.5. Effect of complex on MCF-7 Cell Viability for 24 h Incubation Time.

IC50	**44.59µg/mL**

5. Conclusions

In the present research study, we synthesized new complexe of Cu(II) these complexes are characterized by various physicochemical and spectral analyses. The results exhibit that the synthesized ligand binds with metal ions in tetra-dentate through N donor sites of orho phenelyne diamineas well as O atom of the ortho vanillin group. IR,,LC-MS.XRD studies of the complexes also helped to characterize the complexes. The antibacterial data show that the metal complexes have biological activity.the complex shows cytotoxic properties.

6. Acknowledgement

The Authors Expresses their deep sense of gratitude to Andhra University College of Engineering for providing equipment and laboratory facilities and Advanced Analytical Laboratory for carrying out Characterization (UV,LCMS,XRD and FTIR).

Refrences

1. Malik, S., Ghosh, S., Mitu, L., 2011.. J. Serb. Chem. Soc. 76 (10), 1387–1394
2. V. V. Gandin, M. Porchia, F.Tisato, A.Zanella, E.Severin, A.Dolmella, and C. Marzano, Journal of Medicinal Chemistry, 2013, 56, 7416.
3. M. Gonzalez-Alvarez, A. Pascual-Alvarez, L. C. Agudo, A. Castineiras, M. Liu-Gonzalez, J. Borras and G. Alzuet-Pina, Dalton Transactions, 2013, 42, 10244.
4. A. Kumar, S. Gupta and V. D. Barhate, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 2012, **3**, 1013.
5. Kalia, S.B.,Lumba, K.,Kaushal, G., Sharma, M.Ind. J. Chem, 46 A, 1233- 1239 ,2007.
6. C. preti & G.Tosi,J .Canad.53,177 (1975)

7. . B.J. Hathway & A.E.Underhill.,J chem..soc.3091(1961)

8. Cappucino, J.G., Sherman N., 'Microbiology' A Laboratory Mannual. 6th Ed., Pearson Education (Singapore) Ltd., 2004.