



SYNTHESIS, SPECTRAL CHARACTERISATION AND BIOLOGICAL APPLICATIONS OF COPPER (II) COMPLEXES WITH TERNARY SCHIFF BASE

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Abstract:

Two different Mononuclear copper (II) complexes containing 1, 10-Phenanthroline of the composition $[CuL(OOC-C_6H_5-P-X)(phen)]$ (L =Ternary Schiff base) [$Phen$ =Phenanthroline] [where $X = CH_3(1), OMe(2)$] have been prepared by the reaction of their corresponding dinuclear copper(II) arylcarboxylate precursor complex with phenanthroline, L-Valine and o-hydroxy acetophenone. The synthesized complexes were characterized by UV-Visible, Infra-red spectroscopy and Molar Conductivity studies. The synthesized complexes have been screened for antimicrobial studies.

Key Words: Ternary Schiff Base, 1, 10-Phenanthroline, UV-Vis, IR & Antimicrobial Studies

1. Introduction:

Schiff bases are one of the most prevalent and important of the mixed donor systems in the field of coordination chemistry¹. The first preparation of imines was reported in the 19th century by Schiff (1984), which are prepared by condensing primary amines with an aldehyde or a ketone under specific conditions. Because of the relative easiness of preparation, synthetic flexibility and special property of $C=N$ group, Schiff bases are considered as an excellent chelating agents²⁻⁵. Schiff bases and its metal complexes have been found to exhibit biological activities including antifungal, antibacterial, antimalarial, antipyretic, larvicidal, antiviral and antitubercular activities. Besides the biological activities, the metal complexes of Schiff bases are widely used as catalyst in the reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis, corrosion inhibitor and as polymers⁶⁻¹⁰.

2. Experimental Methods:

2.1 Materials and Measurements:

All common laboratory chemicals and reagents were from Aldrich and have been used without further purifications. FT-IR spectra of ligand and complexes were obtained on a Shimadzu IR-Affinity-I spectrometer with samples prepared using KBr pellets. UV-Visible spectra were recorded using Systronics spectrophotometer operating in the range of 200–800 nm with quartz cell.

2.2 Synthesis of Copper (II) Precursors:

The copper (II) precursors were synthesized using organic compounds like p-chloro and p-hydroxy benzoic acids with NaOH and stirred well for 15 minutes using magnetic stirrer, then $CuSO_4 \cdot 5H_2O$ was added with the above mixture and stirred well for half an hour. The ratio of the organic acid, base and metal was taken in the ratio of 2:2:1 for the synthesis of copper (II) precursors. The crude blue copper (II) precursors obtained was washed thoroughly with water and ethanol and dried well. The copper (II) precursors obtained was used for the synthesis of Copper (II) complexes as such.

2.2 Synthesis of Copper (II) Complexes:

The synthesis of complex-I was achieved by taking to a stirred mixture of L-valine (1mmol) and potassium hydroxide (1mmol) in hot methanol (10mL) was added o-hydroxy acetophenone (1mmol) in 5mL of methanol. The yellow solution was then stirred at 323K for 2hours. Subsequently, an aqueous solution of copper (II) precursors (1mmol) was added dropwise and the mixture was stirred for 2hours. Finally, a methanol solution (5ml) of 1,10-phenanthroline (1mmol) was then added dropwise and the mixture was stirred continuously for 4hours. The resultant solution was filtered and dried.

3. Results and Discussion:

3.1 UV-Visible Spectra: The UV-Visible spectra of the ligand and its complexes were recorded in the DMF solution in the wavelength range 200-800nm. The band observed at 236-237 nm is due to $\pi-\pi^*$ transition¹¹ of the benzene ring present in the ligand and it was shifted to lower wavelength upon complexation. The band at 473-495 nm is due to $n-\pi^*$ transition of the azomethine group present in the ligand and it was shifted to lower wavelength this shows the coordination of metal with the azomethine nitrogen. The weak band at 574 and 581 nm is due to d-d transition. Generally d-d transition of the copper (II) complex exhibit a band at 570-590nm.

Table 1: UV-Visible spectral data of Schiff base copper (II) complexes

Complex	$\pi-\pi^*$ (nm) (benzene)	$\pi-\pi^*$ (nm) (-HC=N)	n- π^* (nm)	d-d (nm)
I	236	376	495	574
II	237	380	473	581

3.2 FT-IR Spectra:

The characteristic FTIR bands of the synthesized complexes are given in Table 2. All the complexes exhibited an intense band around 1598-1602 cm^{-1} due to the coordinated imine group with the metal ions¹². FT-IR spectra is an important tool in investigating the coordination mode of the carboxylate anion with the metal ions. In the present case the difference between asymmetric and symmetric stretching frequencies of the carboxylate group lies above the free carboxylate anion which is 192 cm^{-1} . This confirms the monodentate coordination nature of the carboxylate ion with the metal ions¹³. The bands observed around 500 cm^{-1} and 400 cm^{-1} confirms the M-N and M-O linkages in the coordination complexes.

Table 2: IR Spectral data of Schiff Base Copper (II) Complexes

Compound	$\nu(\text{-OH})$	$\nu(\text{C=O})$	$\nu(\text{CH=N})$	$\nu(\text{Cu-N})$	$\nu(\text{Cu-O})$
Complex-I	3406	1689	1598	540	468
Complex-II	3352	1712	1602	624	476

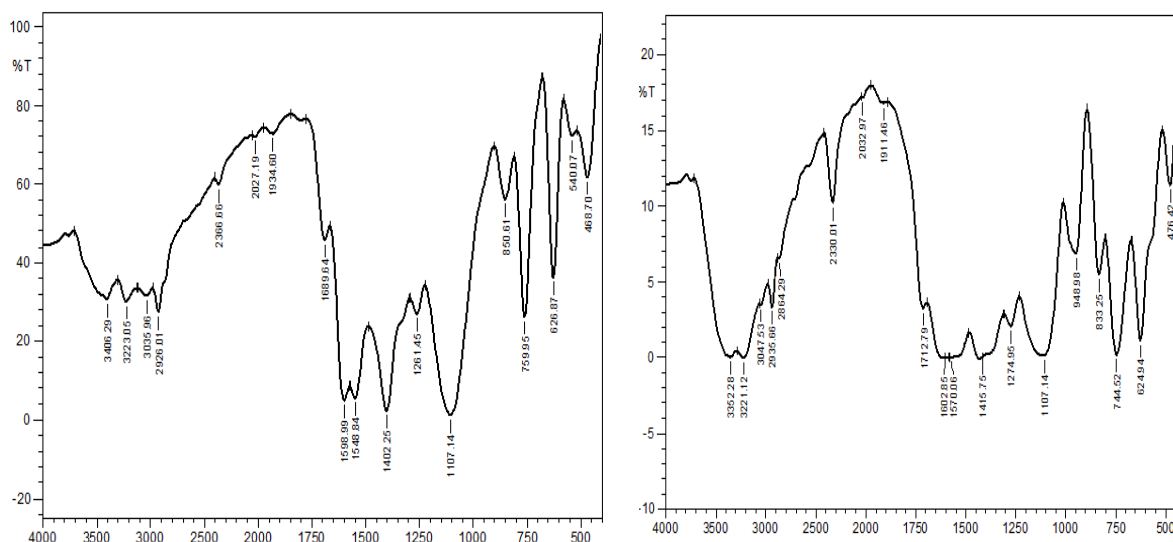


Figure 1: FT-IR spectra of copper (II) complexes – I & II

3.3 Molar Conductance Measurement:

The molar conductance of the complexes-I & II was measured in 10^{-3}M DMF solution and data are summarized in Table-3. The molar conductance values indicate the non-electrolytic nature of the complexes.

Table 3: Molar conductance of Schiff base copper (II) complexes

Complexes	Solvent	Conductance of solution (mho)	Molar Conductance ($\text{cm}^2 \text{ohm}^{-1} \text{mol}$)
I	DMF	0.048	48
II	DMF	0.049	49

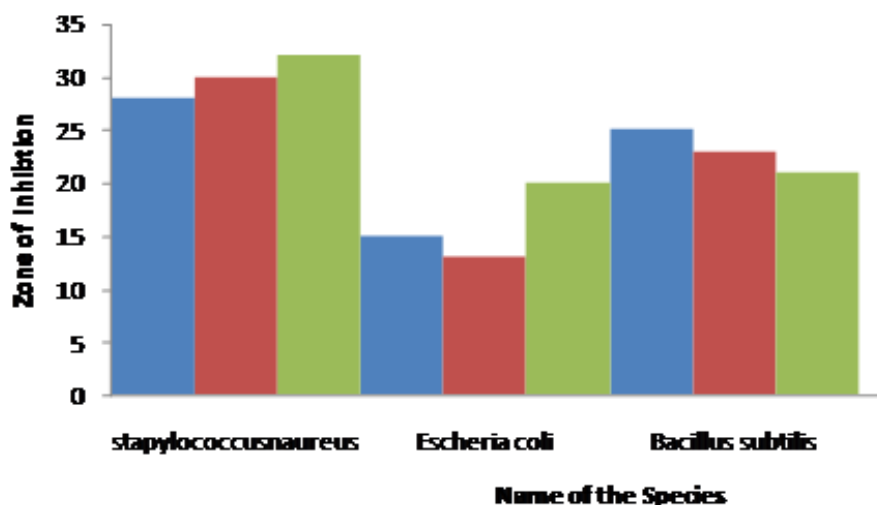
3.4 Antibacterial Activity:

In vitro antibacterial activity of the Schiff base ligand and its metal complexes were screened against Gram-positive bacteria such as *Staphylococcus aureus* and Gram-negative bacteria such as *Bacillus subtilis*, and *Escherichia coli* using well diffusion method. The zone of inhibition values against the growth of the selected bacteria were measured in mm. The standard ciprofloxacin was used as a positive control and DMSO was used as negative control. All the metal complexes exhibited very good zone of inhibition against the bacteria under study¹⁴. The antibacterial activities exhibited by synthesized compounds are summarized in table 4.

Table 4: Antibacterial activity of Schiff base copper(II) complexes

S.No	Micro organisms	C1	C2	Ciprofloxacin
1.	<i>Staphylococcus aureus</i>	28mm	30mm	32mm
2.	<i>Escherichia coli</i>	15mm	13mm	20mm
3.	<i>Bacillus subtilis</i>	25mm	23mm	21mm

Antibacterial activity



3.5 Antifungal Activity:

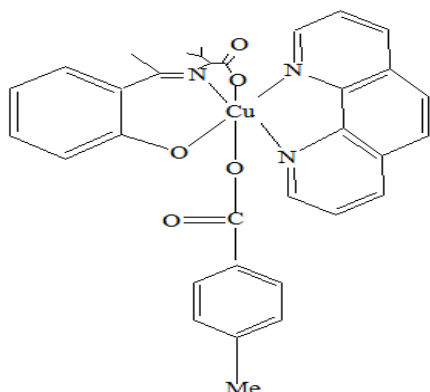
The Schiff base ligand and its metal complexes were assessed for their in vitro antifungal activity by well diffusion method against fungi such as *Aspergillus niger*, *Aspergillus flavus* and *Mucor indicus*. The standard amphotericin-B was used as positive control and DMSO was used as negative control. All the metal complexes exhibited very good zone of inhibition against the fungi under study¹⁵. The results with reference to in vitro antifungal activities of synthesized complexes are summarized in table 5.

Table 5: Antifungal activity of Schiff base copper(II) complexes

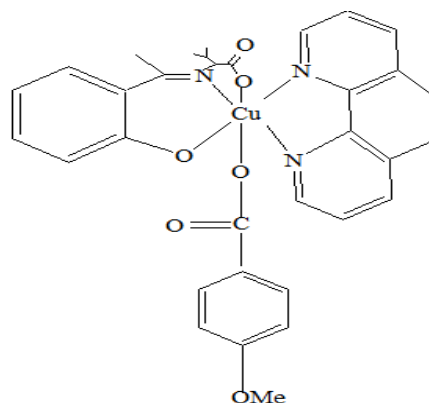
S.No	Micro Organisms	C1	C2	Amphotericin-B
1.	<i>Aspergillus niger</i>	32mm	30mm	28mm
2.	<i>Aspergillus flavus</i>	15mm	13mm	24mm
3.	<i>Mucor indicus</i>	27mm	23mm	20mm

4. Conclusion:

- ✓ Two mononuclear Ternary Schiff Base Copper (II) complexes containing 1,10-Phenanthroline as Co-ligand have been prepared.
- ✓ The copper (II) complex of composition [CuL(Phen)], where L is Ternary Schiff base derived from L-Valine and O-hydroxy acetophenone have been prepared.
- ✓ The synthesized Copper (II) complexes were characterized by using various analytical techniques such as UV-Visible, FT-IR, and Molar conductance.
- ✓ The synthesized Copper (II) complexes were screened for their antibacterial activity against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and antifungal activity against *Aspergillus flavus*, *Aspergillus niger* and *Mucor indicus*.



Cu(II)COMPLEX - I



Cu(II)COMPLEX - II

5. References:

1. K. Geetha, M. Nethaji, N.Y. Vasanthacharya, A.R. Chakravarty, J. Co-ord. Chem. (1999), 44, 77.
2. P.A. Vigato, S. Tamburini. Coordination Chemistry Reviews, (2004), 24, 81717–2128.
3. N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk. Chemical Reviews, (2007), 107, 46-79.

4. P.G Cozzi. Chemical Society Reviews, (2004), 33, 410-421.
5. M. Kojima, H. Taguchi, M. Tsuchimoto, K. Nakajima. Coordination Chemistry Reviews (2003), 237,183-196
6. Neeraj Kumar Gupta, Chandrabhan Verma, MA Quraishi, AK Mukherjee, J. Mol. Liq, (2016), 215, 47-54.
7. SN Shukla, P Gaur P, JP Gupta, S Mathews, N Rai, Int. J. Basic App. Chem. Sci., (2015), 5(1), 18-28.
8. CP Raptopoulou, AN Papadopoulos, DA Malamatar, E Loannidi, G Molsidis, A Terzis, Inorg. Chim. Acta, (1998), 272, 283-290.
9. J Saranya, S Santha Lakshmi, J. Chem. Pharm. Res., (2015), 7(4), 180-186.
10. K Robert Boggess, A David Zatko, J. Chem. Edn., (1975), 52(10), 649 - 665.
11. K Saranya, S Santha Lakshmi, P Mahadevi, G Logesh, J. Chem. Pharm., (2015), 7(7), 851-858.
12. SB Kalia, K Lumba, G Kaushal G, M Sharma, Int. J. Chem., (2007), 46 A, 1233-1239.
13. A Majumder, GM Rosair, A Mallick, N Chattopadhyay, S Mitra, Polyhedron, (2006), 25, 1753-1762.
14. G Gowri, S Santha Lakshmi, Int. J. Front. Sci. Tech., (2015), 3(1) 26-35.
15. PM Reddy, AVSS Prasad, K Shanker, V Ravinder, Spectrochim. Acta. A., (2007), 68, 1000-1006.