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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL APPLICATIONS OF A MULTIDENTATE LIGAND AND ITS COPPER (II) COMPLEXES

Umapathy Chokkanathan* & Kannappan Geetha**
PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore, Tamilnadu

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Abstract:
A multidentate ligand was synthesized using 4-bromo-2,6-bis(hydroxymethyl)phenol and diethylenetriamine. It was characterized by UV-Visible, FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic techniques. The above ligand was coordinated with various copper precursors to form corresponding copper(II)complexes. The complexes were characterized by UV-Visible, FT-IR, Conductivity measurements and Cyclic Voltammetry. The biological applications of the ligand and their complexes were studied.

Key Words: Multidentate Ligand, Copper Precursors, Copper (II) Complexes & Biological Activity.

Introduction:

Coordination compounds based on transition metals and multidentate ligands has been the subject of extensive research due to their potential applications in chemistry, biochemistry, biomedical and environmental chemistry[1]**.** The family of complexes with Nitrogen donor atoms has remained a focus of scientific attention for many decades[2]. These complexes have enhanced thermo chemical and kinetic stability, that is, a lesser lability and larger association constants. Our ligand is having hexa-aza pendant arms, which can be coordinated to metal ions to form metal complexes. A ligand was synthesized using 4-bromo-2,6-bis (hydroxymethyl)phenol and diethylenetriamine which was reacted with copper(II) precursors to form copper(II) complexes.

Experimental:

Materials and Methods: All the chemicals and solvents were purchased from *SD-fine* chemicals. UV-Visible spectra were recorded using *Systronics* spectrophotometer operating in the range of 200-800 nm. FT-IR spectra were obtained in *Shimadzu* IR-Affinity-I spectrometer and sample pellets were prepared using KBr. ^{1}H NMR and ^{13}C NMR spectrum of ligand was recorded from *Bruker* 400 MHz spectrometer. Conductance of complexes was recorded using Elico conductometer. Cyclic Voltammetry was done in *HCH Instruments.* Antimicrobial analysis was followed using standard agar well diffusion method to study the antibacterial activity.

Synthesis of Starting Material:

4-bromo-2,6-bis(hydroxymethyl)phenol[3] was prepared by refluxing 4-bromo phenol with formaldehyde and sodium hydroxide in 1:2:2 ratio for 3 hours. The product formed was poured in water and neutralized with 5% phosphoric acid. A white solid was filtered and re-crystallized in ethanol. It was characterized by UV-Visible, FT-IR, ^{1}HNMR, ^{13}C NMR spectral studies.

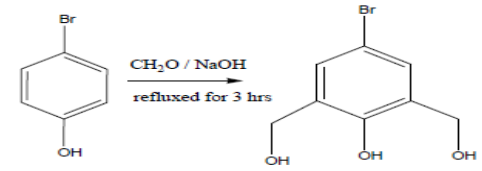

Fig:1Synthesis of starting material (SML):

Synthesis of Ligand: 4-bromo-2,6-bis(hydroxymethyl)phenol was treated with diethylenetriamine in ethanol in 1:2 ratio[4-5]. A yellow solid was obtained, filtered and re-crystallized in ethanol. It was characterized by UV-Visible, FT-IR, ^{1}HNMR, ^{13}C NMR and mass spectral studies.

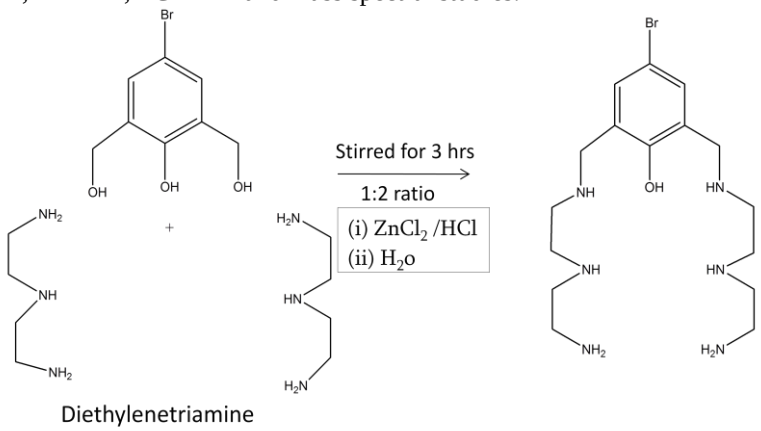

Figure 2: Synthesis of ligand

Synthesis of copper Precursors: 4-nitro benzoic acid was dissolved in water by heating above room temperature. To this sodium hydroxide was added and stirred in a magnetic stirrer. A solution of copper sulphate ($CuSO_4.5H_2O$) in water was slowly added to the above mixture in 1:2 ratio [6-8]. A light blue solid obtained, filtered and washed with water.

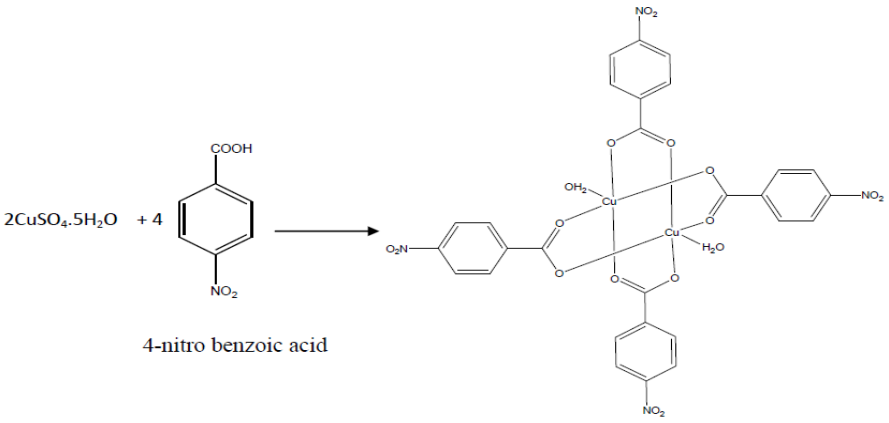

Fig:3 Synthesis of copper precursor

Synthesis of Copper Complexes: The above ligand was dissolved in ethanol and to this sodium hydroxide was added. Stirred for few minutes. A solution of copper precursors in ethanol was slowly added to this in 1:1:1 ratio and continued stirring for 5 hours [9-11]. A dark green solid was obtained and filtered.

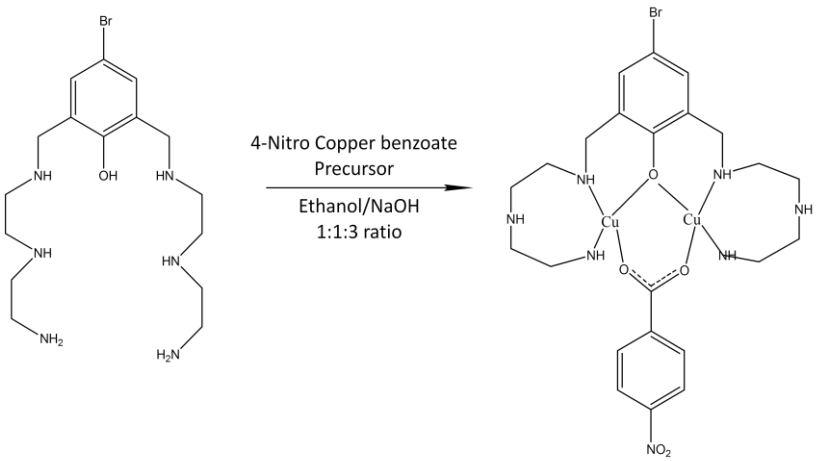

Figure 4: Synthesis of copper complex (C3P1)

Similarly copper hydroxy (C3P2) and 4-chloro copper benzoate (C3P3) complexes were synthesized.

Results and Discussion:

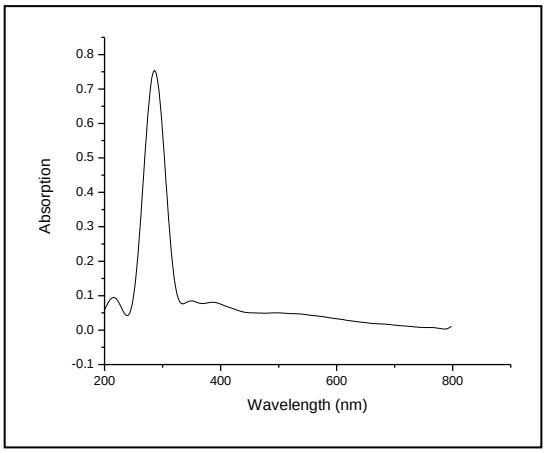

Figure 5: UV-Visible spectrum of Ligand

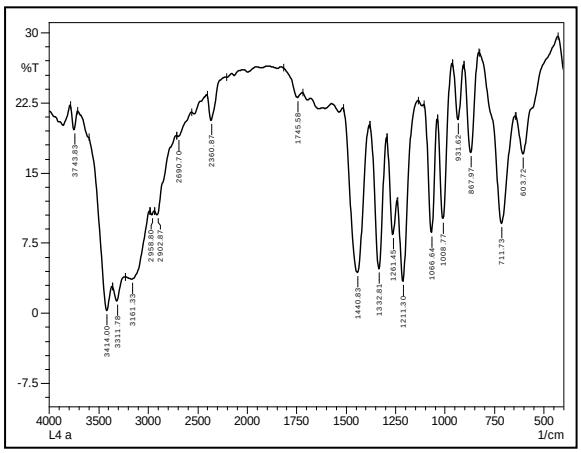

Figure 6: FT-IR spectrum of Ligand

The above ligand was characterized by UV-Visible, FT-IR, ^{1}H-NMR, ^{13}C-NMR spectral studies. The UV-Visible spectrum of the ligand shows π - π * transition at 286 nm, n- π * transition at 338 nm and charge transfer at 387 nm. The FT-IR Spectrum shows OH stretching at 3414 cm^{-1}, NH stretching at 3311 cm^{-1}, CH stretching at 2958 cm^{-1}, CO stretching at 1211 cm^{-1}. The ^{1}H NMR Spectrum shows aromatic Protons at 7.289, methylene proton at 4.516. ^{13}C NMR Spectrum shows hydroxyl carbon at 150.3, bromo carbon at 116.5, aromatic carbon around125-130. The mass spectrum shows peaks at m/e values 403, 344, 284 etc., shows the presence of molecular ion peak and fragmented ion peaks [12-13].

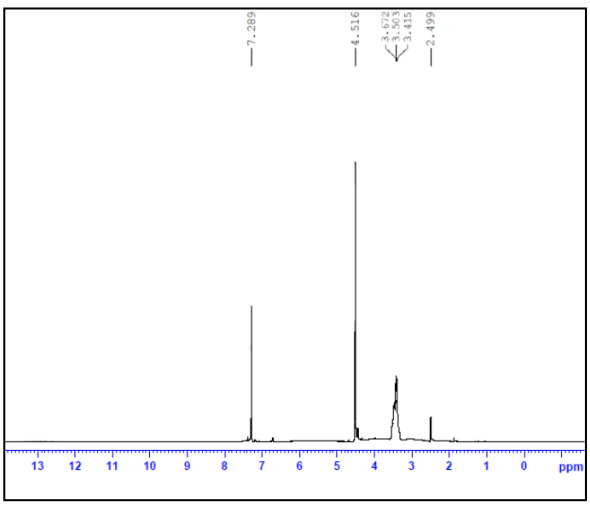

Figure 7: ^{1}H-NMR spectrum of ligand

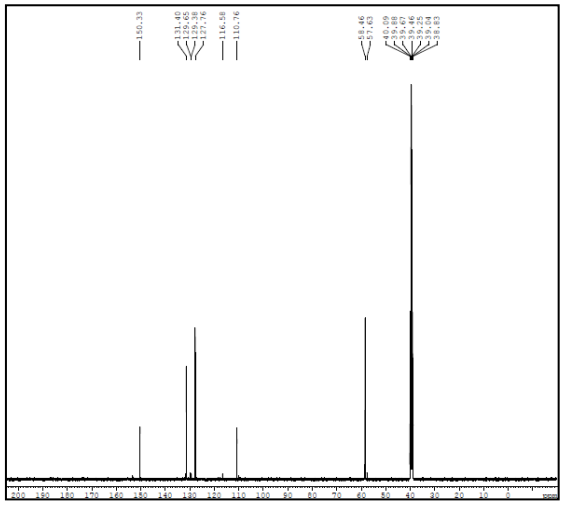

Figure 8: ^{13}C-NMR spectrum of ligand

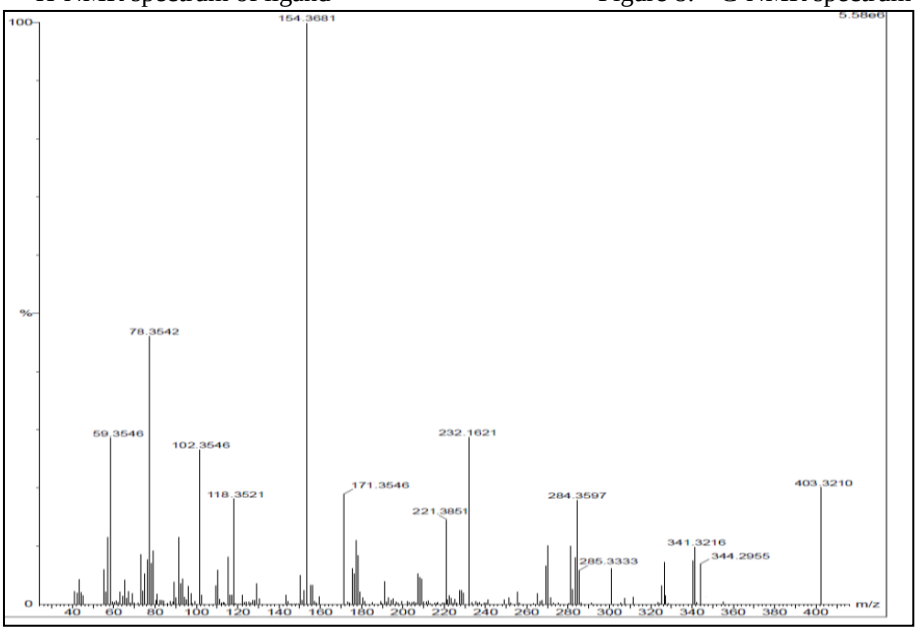

Figure 9: Mass spectrum of ligand

The copper complexes were characterized by UV-Visible, FT-IR spectral studies, Conductivity measurements and Cyclic Voltammetry.

UV-Visible Spectra: The UV-Visible spectra of the complexes were recorded in DMSO solution in the wavelength range 200-800 nm. The band around 286 nm is due to π-π* transition of the benzene ring present in the ligand and it was shifted to higher wavelength (red shift) upon complexation and the band was observed at 318 nm for complexes. The band around 570 nm is due to d-d transition[14].

S.No	Sample Code	λ max value (nm)			
		π - π * transition	n - π * transition	Charge Transfer	d-d transition
1	L3	286.6	338.2	387.5	-
2	C3P1	318.8	358.4	392.0	569.6

3	C3P2	318.8	365.6	401.6	574.4
4	C3P3	318.8	351.2	398.0	574.4

Table - 1

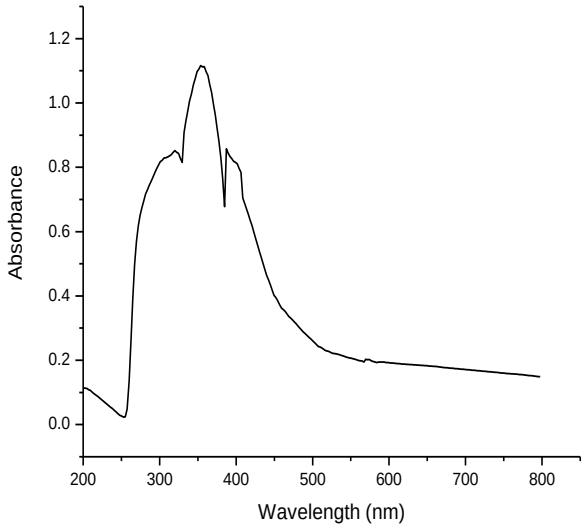

Figure 10: UV-Visible spectrum of complex C3P1

FT-IR Spectra: The FT-IR Spectrum shows OH stretching around 3410 cm^{-1}, NH stretching around 3310 cm^{-1}, CH stretching around 2925 cm^{-1}, OCO stretching around 1260 cm^{-1}, M-N stretching around 550 cm^{-1}, M-O stretching around 450 cm^{-1}.

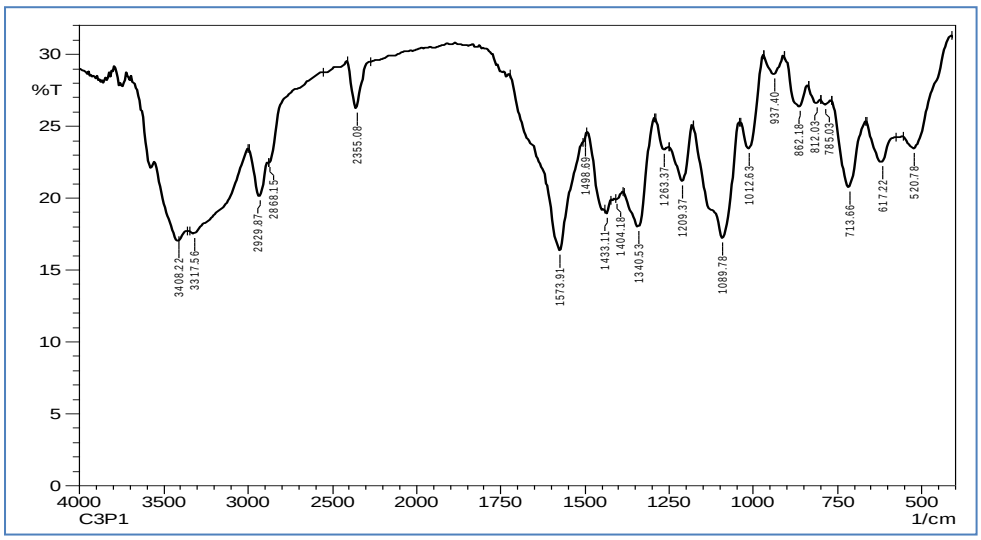

Figure 11: FT-IR spectrum of complex C3P1

S.No	Sample Code	Type Stretching Vibration in cm^{-1}						
		OH	NH	CH	O-C-O	C-O	M-N	M-O
1	C3P1	3408	3317	2929	1573	1263	520	445
2	C3P2	3410	3311	2924	1600	1257	565	472
3	C3P3	3412	3311	2924	1595	1261	557	470

Table 2

Conductance Measurements: The molar conductance of complexes was found to be less than 60 shows that, all the complexes are found to be neutral or non-electrolytic in nature.

S.No	Sample Code	Molar Conductance (Mho cm^2 mol^{-1})
1	C3P1	46

2	C3P2	17
3	C3P3	27

Table 3

Cyclic Voltammetry: The Cyclic Voltammetric data reveals that all the complexes exhibit a one electron transfer and the complexes are quasi reversible. The electron movement is sluggish.

S.No	Sample Code	IPa e-5	IPc e-5	IPa/IPc
1	C3P1	3.156 1.253	3.078 1.189	1.025 1.054
2	C3P2	2.574 1.053	2.845 1.128	0.904 0.934
3	C3P3	3.221 0.892	3.832 0.983	0.841 0.909

Table 4

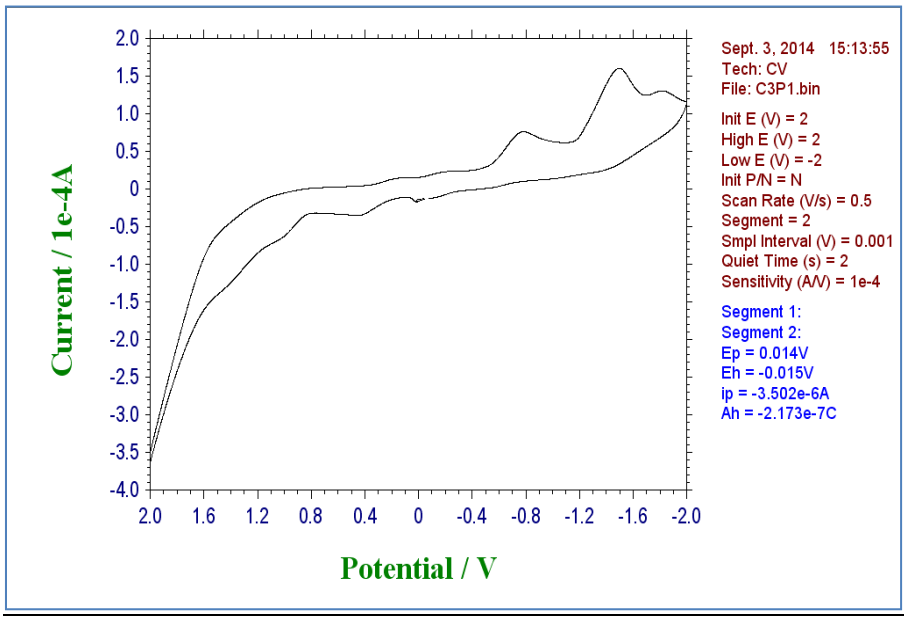

Figure 12: Cyclic Voltammetry of complex C3P1

Anti-Bacterial Activity:

S.No	Bacteria	Control (Solvent)	L	C1	C2	C3	Ciprofloxacin
1.	*Streptococcus faecalis*	-	5mm	8mm	10mm	6 mm	27 mm
2.	*E.coli*	-	4mm	11mm	9 mm	8 mm	24 mm

Table 5

All the copper complexes show moderate activity against the bacteria's like *Staphylococcus faecalis and E. coli.*

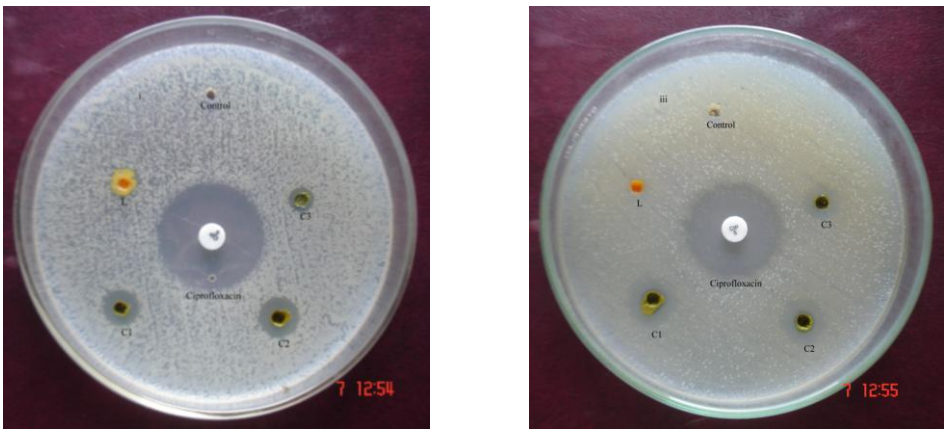

Figure 13: Antibacterial Activity

Conclusion:

A multi-dentate ligand was synthesized using 4-bromo-2,6-bis - (hydroxymethyl) phenol and diethylenetriamine. It was characterized by UV-Visible, FT-IR, ^{1}H-NMR, ^{13}C-NMR spectral studies. The above ligand was coordinated with various copper precursors to form corresponding copper complexes. The complexes were characterized by UV-Visible, FT-IR, Conductivity measurements and Cyclic Voltammetry. The molar conductance values show that all the complexes are found to be Neutral and Non-electrolytic in nature. Anti-bacterial applications of the ligand and their complexes were studied and found to be active against *Staphylococcu faecalis and E.coli*.

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