

Synthesis, Characterization and Antimicrobial Evaluation of a new Macrocyclic Ligand and Its Co (II), Ni (II), Cu (II) and Zn (II) Complexes

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Abstract: Coordination complexes derived from macrocyclic ligand metal complexes of Co (II), Ni (II), Cu (II) and Zn (II) have been synthesized. The Schiff base ligand was synthesized by condensation of 1-(5-bromo -2-hydroxyphenyl) -3- (furan -2-yl) propane -1,3-dione with o-phenylenediamine. The metal complexes ML (H₂O)_n are reported and characterized by conductivity, UV- visible, FTIR, H¹NMR, TGA-DTA and XRD analysis. All the complexes were found to be non-electrolytic in nature. The ligand acts as a hexadentate and coordinates through four nitrogen atoms of azomethine groups. The antibacterial and antifungal activities of the ligand and its metal complexes, has been screened in vitro against Gentamycin, Ampicillin, Chloramphenicol, Ciprofloxacin, Norfloxacin, Nystatin and Griseofulvin used as standard drug. All these complexes show higher biological activities than standard drugs.

Key Word: 1, 3 β- diketone o-phenylenediamine, spectral characteristic, metal nitrate, biological activity.

Introduction

Coordination chemistry of macrocyclic ligand containing a heteroatom is important complexing agents due to their antimicrobial characteristics. The stability of macrocyclic metal complexes depends upon a number of factors such as number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate ring formed on complex¹. The macrocyclic complexes are interested because there is flexibility in the preparation and study of different parameters such as ring size, the nature of donor atoms and effect of electrons on the macrocyclic ring². The metal complexes of Schiff bases derived from heterocyclic compounds have been the center of attraction for many researchers in recent years³. The various studies reveal azomethine linkage (C = N) in Schiff base⁴, macrocyclic ligands and their metal complexes have a wide range of biological activities⁵. Many reports have shown that some drugs have greater activity when overseen as metal complex as that as free organic compound⁶. Schiff base complexes derived from heterocyclic compounds have acquired more attention in the field of bioinorganic chemistry because of their biological activities such as antibacterial, antifungal, anticancer⁷, antioxidant⁸, anti-inflammatory, analgesic^{9,10}, antiviral activities¹¹, antitumor activity¹² and anticonvulsant¹³. The present investigation deals with synthesis and characterization of complexes of Co(II), Ni(II), Cu(II) and Zn(II) by Schiff base ligand derived from 1-(5-bromo -2- hydroxyphenyl) -3- (furan -2-yl) propane -1,3-dione and o-phenylenediamine using various techniques.

Experimental

All the AR grade quality chemicals obtained from Merck chemicals were used. 1-(5-bromo-2-hydroxyphenyl)-3-(furan-2-yl)propane-1,3-dione, o-phenylenediamine and metal nitrates of Co (II), Ni(II) Cu (II), and Zn(II). The solvents like ethanol, methanol, DMSO; DMF etc. were purified by ordinary methods.

Physical Measurements:

UV-VIS. spectra study was recorded in the region 200–900 nm for 1mM solutions in DMF at 25 °C using a Shimadzu 160 spectrophotometer. Molar conductance measurement was conducted using 10 mM solutions of the complexes in DMF on Elico – CM82 Conductivity Bridge at room temperature. Magnetic susceptibility measurement was carried out on a Gouy balance at room temperature. FT-IR spectra study was recorded in KBr medium on a Shimadzu spectrophotometer in wave number region 4000-400 cm^{-1} . ^1H NMR and ^{13}C NMR spectra were acquired in CDCl_3 solution using a Bruker 500 MHz spectrometer with tetramethyl silane (TMS) as an internal standard. The magnetic susceptibility measurements were determined on a Gouy balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant.

Synthesis of ligand:

A warm ethanolic solution of 30 ml of 1-(5-bromo-2-hydroxyphenyl)-3-(furan-2-yl)propane-1,3-dione (6.18 g 20 mmol) and a warm ethanolic solution 30 ml of o-phenylenediamine (2.16 g 20 mmol) were mixed slowly with constant stirring. This mixture was refluxed at 90 °C for 14-15 h in presence of hydrochloric acid. On cooling a solid yellow precipitate are obtained which was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10} and it was recrystallized from ethanol^{14,15} (yield- 60%). mp. 201 °C,

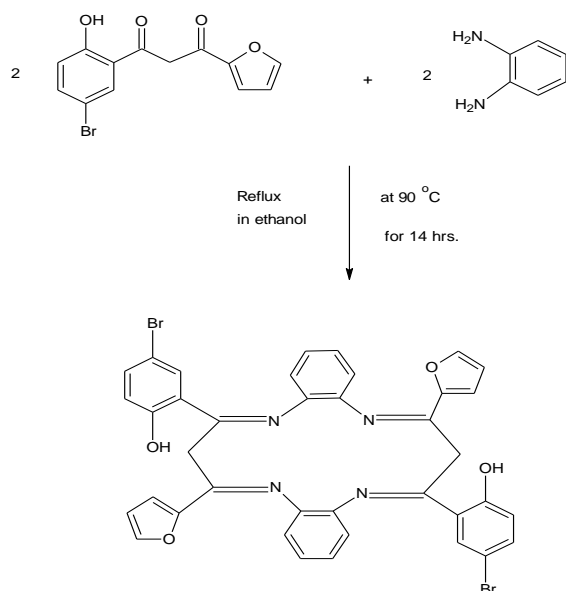


Figure 1: Synthesis of Schiff base ligand

Spectral Data of Ligand:

IR (KBr, cm^{-1}): 3267 $\nu(\text{OH})$, 1670 $\nu(\text{C}=\text{N})$, 536 $\nu(\text{C}-\text{Br})$. ^1H NMR (in CDCl_3) in figure 2 shows δ 1.25 -1.62 ppm (m, 6H) is due to the proton at the furan ring¹⁶, δ 2.62 ppm (s, 4H, - CH_2)^{2,17,26}, δ 6.62 ppm - 8.34 ppm corresponding to aromatic and phenyl ring protons (m, 14H Ar-H), δ 12.16 ppm (s, 2H, Ar-OH)¹⁸⁻²³. ^{13}C -NMR spectrum in figure 3 displayed a peak at δ (157.07) ppm which is due to the $\text{C}=\text{N}$ (azomethine group)^{21,22}. The multiplet peaks at δ (111.14-147.3) ppm are due to (Ar-H) aromatic region. The signals at δ (12.74) ppm are assigned to the CH_2 in the ligand^{21,23}. ESI MS (m/z) = 762 [M^+].

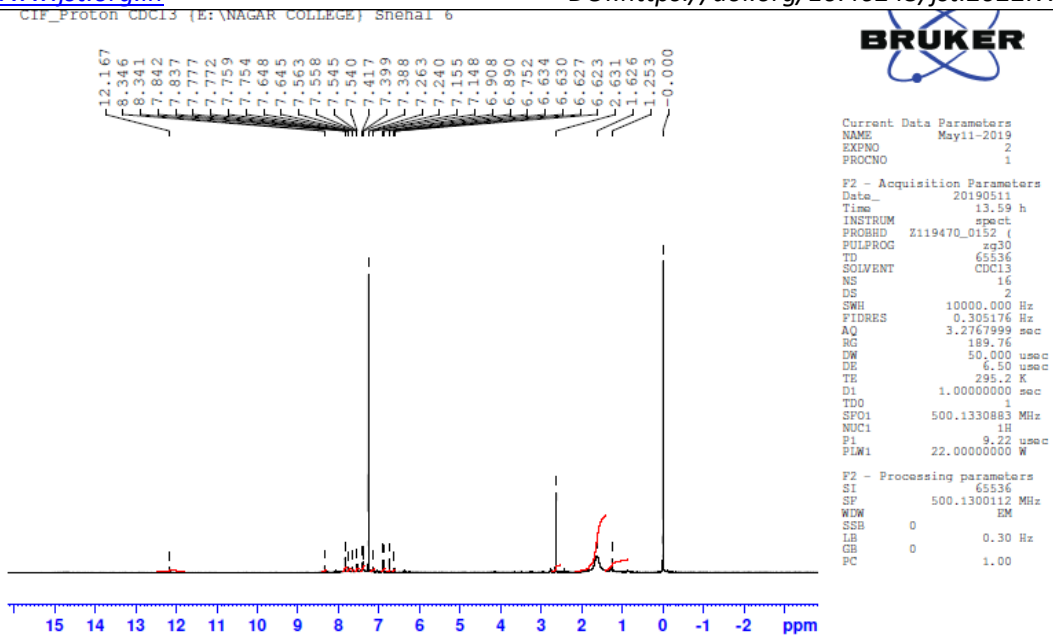


Figure 2: ¹H-NMR spectrum of ligand

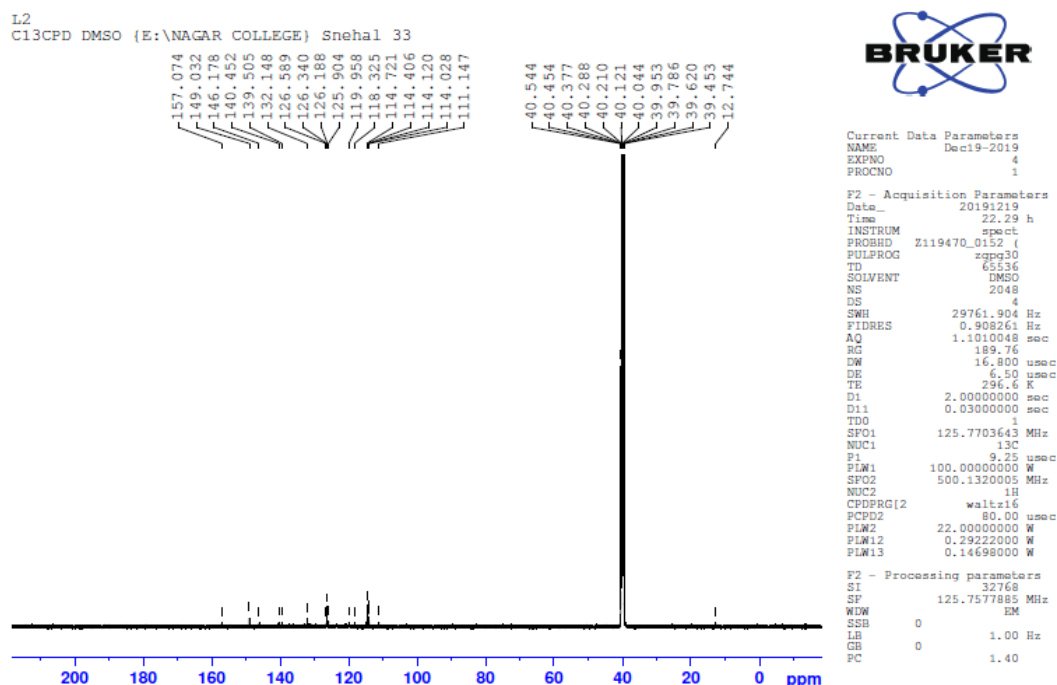


Figure 3: ¹³C-NMR spectrum of ligand

Synthesis of Complexes:

The various complexes were prepared by warm ethanolic (20 ml) solution of the ligand (0.762 g 10 mmol) and a warm ethanolic (20 ml) solution of corresponding (10 mmol) metal nitrate of Co (NO₃)₂ 2H₂O, Ni(NO₃)₂ 2H₂O,

Cu(NO₃)₂·2H₂O and Zn(NO₃)₂ were mixed together with constant stirring. The pH of the mixture was adjusted in the range of 7-8 by adding 10% alcoholic ammonia solution. The reaction mixture was refluxed for 7-8 h at 90 °C on cooling a solid yellow precipitate are obtained which was filtered, washed with cold ethanol and dried under vacuum over P₄O₁₀ and it was recrystallized from ethanol^{14,15}(yield- 58-60%).

Co(II) Complex

Yield 58% Elemental Analysis: C₃₈H₃₈Br₂N₄O₁₀ Co Calculated C=46.47%, H=3.46%, N=5.70 %, Co=5.90% ; Found C=47.96%, H=3.65%, N=9.06 %, Co=6.14% , IR (KBr, cm⁻¹): 3287 ν(OH), 1656 ν(C=N), 536 ν(C-Br), 418 ν(M-N), molar conductance (λν) = 12.42 mhos cm².

Ni(II) Complex

Yield 60% Elemental Analysis: C₃₈H₃₈Br₂N₄O₁₀ Ni Calculated C=45.98%, H=3.06%, N=5.64 %, Ni=5.80% ; Found C=47.10%, H=2.87%, N=7.98 %, Ni=6.20% IR (KBr, cm⁻¹): 3580 ν(OH), 1655 ν(C=N), 536 ν(C-Br), 418 ν(M-N), molar conductance (λν) 11.25 mhos cm².

Cu(II) Complex

Yield 59% Elemental Analysis: C₃₈H₃₂Br₂N₄O₇ Cu Calculated C=46.25%, H=3.04%, N=5.88%, Cu= 6.39 % ; Found C=45.20%, H=2.84%, N=9.14 % Cu= 7.26 % IR (KBr, cm⁻¹): 3276 ν(OH), 1655 ν(C=N), 536 ν(C-Br), 428 ν(M-N), molar conductance (λν) 12.50 mhos cm².

Zn(II) Complex

Yield 58% Elemental Analysis: C₃₈H₂₆Br₂N₄O₄ Zn Calculated C=47.90%, H=2.73%, N=8.82 %, Zn=6.83% ; Found C=48.20%, H=3.14%, N=9.20 % , Zn=7.82% IR (KBr, cm⁻¹): 3367 ν(OH), 1657 ν(C=N), 536 ν(C-Br), 418 ν(M-N), molar conductance (λν) 12.32 mhos cm².

I. Result and Discussion

The UV-visible spectra (1mM) of the ligand and its metal complexes are measured by using spectrophotometer at room temperature is shown in Table 1. Co(II), Ni(II) and Cu(II) complexes showed magnetic moment 3.80 2.64 and 1.92 B.M. corresponding to 3, 2 and 1 unpaired electrons, while Zn(II) complex was diamagnetic as expected for square planer geometry paired electrons system^{24,25}.

Table 1: Magnetic measurements and electronic spectra of metal complexes

Compound	Solution spectra		Assignments	μ _{eff} in B.M.
	(λ) (nm)	ν in cm ⁻¹		
L	(258) 38759.68 (261) 38314.17 (321) 31152.60	0.345 0.153 0.640	π → π* π → π* n → π*	----
CoL 2H ₂ O	261 (38314) 280 (35714) 321 (31152)	0.345 0.153 0.640	π → π* π → π* n → π*	3.80
NiL 2H ₂ O	261 (38314) 280 (35714) 321 (31152)	0.207 0.090 0.325	π → π* π → π* n → π*	2.64
CuL 2H ₂ O	262 (38167) 280 (35714) 321 (31152)	0.298 0.292 0534	π → π* π → π* n → π*	1.92
ZnL 2H ₂ O	261 (38314) 280 (35714) 322 (31055)	0.359 0.140 0.664	π → π* π → π* n → π*	Diamagnetic

OD = optical density (absorption)

FTIR spectra

The IR spectrum of the macrocyclic ligand (L) and its complexes shows a ν(C=N) peak at 1670 cm⁻¹²⁶ and the absence of ν(C=O) peak at 1700 cm⁻¹ and ν(NH₂) peak at 3250 cm⁻¹ is indicative of Schiff base condensation²⁷. The IR spectrum of ligand appearance of a new strong absorption band at 1670 cm⁻¹ attributable to the characteristic stretching frequencies of the imino linkage ν(C=N) which provides strong evidence for the presence of cyclic

product. On complete formation the $\nu(\text{C}=\text{N})$ shifted towards lower side by $15\text{-}13\text{cm}^{-1}$ hence the ligand is tetradentate, nitrogen donor coordinates through nitrogen of $\nu(\text{C}=\text{N})$ group. The band in the $418\text{-}426\text{cm}^{-1}$ regions may be assigned to $\nu(\text{M}-\text{N})$ vibration^{28,29}. The $\nu(\text{OH})$ vibration of phenolic proton appears as a broad band in the region $3200\text{-}3600\text{cm}^{-1}$ probably due to the overlapping of the symmetric and antisymmetric OH stretching vibration of lattice water³⁰. The appearances of strong band in the range $1354\text{-}1394\text{cm}^{-1}$ indicate the presence of ionic nitrate³¹.

Antibacterial activity:

All the synthesized metal complexes were tested against pathogenic clinically isolated standard bacterial strains *E. coli* (MTCC 442), *P. aeruginosa* (MTCC 441), *S. aureus* (MTCC 96), and *S. Pyogenus* (MTCC 443) using broth dilution method shown in Table-2. Antibacterial activity of ligand and their metal complexes are shown in figure 4. This bar diagram shows comparative antibacterial activity against bacterial strain and standard drugs. All metal complexes show higher antibacterial activity as compare to the ligand⁵. Gentamycine, Ampicillin, Chloramphenicol, Ciprofloxacin and Norfloxacin were used as a reference drug for bacteria. The complexe of Co(II) and Cu(II) shows higher activity against *S. Pyogenus*. Zn(II) complex shows higher activity against *S. aureus* than Ampicillin. Co(II), Ni(II) and Cu(II) complexes shows moderate antibacterial activity against the *E. coli*, *P. aeruginosa*, *S. aureus* and *S. Pyogenus*.

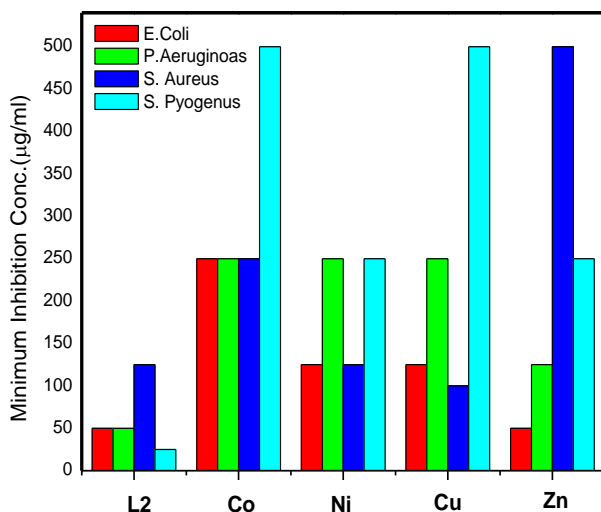


Figure 4: Minimum Inhibition Concentration ($\mu\text{g/ml}$) of Ligand and Their Metal Complexes

Antifungal activity

All the synthesized metal complexes were tested against pathogenic clinically isolated standard bacterial strains *C. Albicans*(MTCC 227), *A. Niger*, (MTCC 282), *A. Clavatus* and (MTCC 1323), using broth dilution method shown in Table-2. Antifungal activity of ligand and their metal complexes are shown in figure 5. This bar diagram shows comparative antifungal activity against fungal strain and standard drugs. All metal complexes show higher antifungal activity as compare to the ligand⁵. The Co(II), Ni(II) and Zn(II) metal complexes better effective against *A. Niger* and *C. Albicans*. Cu(II) also shows higher activity against *C. Albicans* than *Greseofulvin*. Cu(II) and Zn(II), metal complexes show moderate antifungal activity against *A. Niger*, *C. Albicans*. It is also observed that some moieties, such as an azomethine linkage or a heteroaromatic nucleus, introduced into such compounds shows more biological activities that may be responsible for the increase in the hydrophobic character and liposolubility of the molecules in crossing the cell membrane of the microorganism, thereby increasing the biological utilization ratio and activity of these complexes^{28,29}.

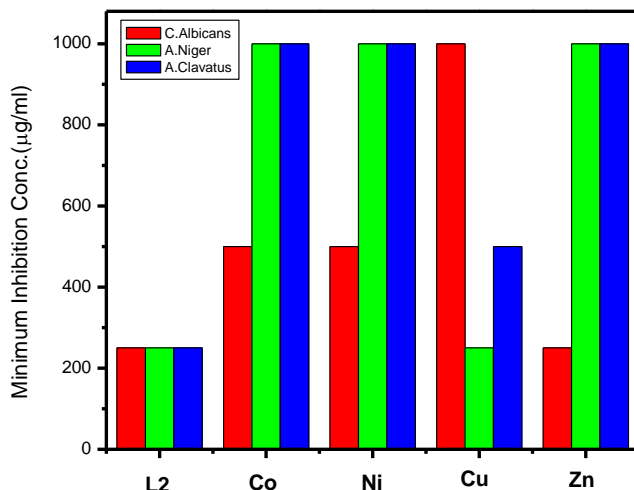


Figure 5: Minimum Inhibition Concentration (µg/ml) of Ligand and Their Metal Complexes.

Table 2: Antibacterial and antifungal activity of compounds

Sr. No	Code No	Antibacterial activity MIC (µg/ml)				Antifungal activity MIC (µg/ml)		
		<i>E. Coli</i> MTCC 42	<i>P. Aeruginos</i> MTCC 441	<i>S. Aureus</i> MTCC 96	<i>S. Pyogenus</i> MTCC 443	<i>C. Albicans</i> MTCC 227	<i>A. Niger</i> MTCC 282	<i>A. Clavatus</i> MTCC 1323
1	L ₂	50	50	50	25	250	250	250
2	CoL 2H ₂ O	250	250	250	500	500	1000	1000
3	NiL 2H ₂ O	125	250	250	250	500	1000	1000
4	CuL 2H ₂ O	125	250	250	500	1000	250	500
5	ZnL 2H ₂ O	50	125	125	250	250	1000	1000
6	Gentamycin	0.05	1	1	0.5	--	--	--
7	Ampicillin	100	100	100	100	--	--	--
8	Chloramphenicol	50	50	50	50	--	--	--
9	Ciprofloxacin	25	25	25	50	--	--	--
10	Norfloxacin	10	10	10	10	--	--	--
11	Nystatin	--	--	--	--	100	100	100
12	Greseofulvin	--	--	--	--	500	100	100

MIC = Minimum Inhibition Concentration

II. Conclusion

In this paper, we describe the synthesis and characterization of hexadentate macrocyclic ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes. Based on conductance, electronic visible and biological activity all these complexes exhibit coordination number six. The FTIR spectral data suggest that ligand behaves as a tetradentate ligand with N₄ donor atoms towards central metal ion. Some of these metal complexes show higher microbial activity than the Schiff base ligand and standard drugs because naturally transition metals are biologically active.

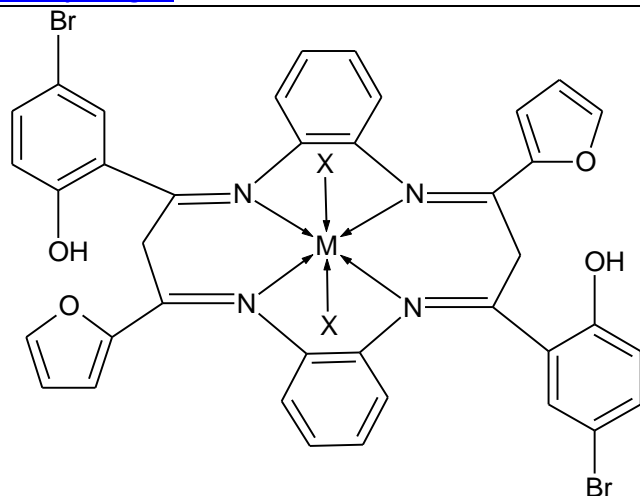


Figure 6: Proposed structure of complex Where $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) $X = 2\text{H}_2\text{O}$

III. Acknowledgement

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