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Synthesis, photophysical properties of novel fluorescent metal complexes from 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol, and their antimicrobial activity

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ABSTRACT

A series of novel metal complexes containing metal atoms such as Zn, Co, Cu, Cd, Ni, Mg and Sn have been synthesized from 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol. The synthesized ligand was well characterized by IR, ¹H-NMR and mass spectrometry. The electrochemical properties were studied by cyclic voltammetric analysis. The synthesized complexes are fluorescent and absorb in the range of 317 to 323 nm while emit in the range of 371 to 416 nm with good quantum yield. All metal complexes show significant in vitro antibacterial activity against E. coli and S. aureus strains and in vitro antifungal activity against C. albicans and A. niger strains by using serial dilution method. The antibacterial activities were expressed as the minimum inhibitory concentration (MIC) in µg/mL.

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1. Introduction

2-Substituted naphthoxazole and benzoxazoles are the major subunit of number of heterocycles which are biologically active compounds¹⁻³ and natural products⁴⁻⁵. Benzoxazole derivatives especially 2-aryl derivatives are known for their interesting biological activity long back. In the recent era, number of derivatives have been found to posses marked biological activities such as antifungal⁶, anti-inflammatory⁷, antitumor⁸ as well as antiproliferative agents⁹. Hydroxy benzoxazoles (HBOs) show excellent thermal and luminescent properties. Because of their good photo stabilities these are excellent materials for plastic scintillation applications and some of their metal complexes are of interest for the organic light emitting diode (OLED) technology 10-12. HBO

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also behaves as structural mimic DNA base pair for which tautomerism may be initiated at a defined time and position within duplex DNA¹³. Structurally similar natural product bis(benzoxazole) UK-1 has been reported to possess anticancer activity, and the metal-binding studies of UK-1 indicate that benzoxazole like compounds are capable of binding a variety of biologically important metal ions¹⁴. In biomedical and pharmaceutical field benzoxazole derivatives are used as building blocks as well as in other industrial applications such as fluorescent brightening agents, dyes and biomarkers or biosensors^{15–17}.

There are several reports in literature for the synthesis of benzoxazole-metal complexes for fluorescent probes¹⁸⁻²¹ and biological application²²⁻²⁵, but antimicrobial activity of these class of compounds have received little attention. In the literature, there are no reports available describing synthesis, photophysical properties and antimicrobial activities of metal complexes of 3-(1,3-benzoxazol-2 yl)naphthalen-2-ol. So in continuation of our research work on benzoxazole type metal complexes²⁶ here in this paper, we report the synthesis of novel fluorescent metal complexes of 3-(1,3-benzoxazol-2 yl)naphthalen-2-ol and their photophysical as well as antimicrobial activities.

2. Results and discussion

Metal

Synthetic route for 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol is shown in **Scheme 1**. 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol was obtained by reported procedure from 3-hydroxynaphthalene-2-carboxylic acid and 2- aminophenol in presence of PCl₃ by using chlorobenzene as a solvent at 130-135 °C within 4 h²⁷. The synthesized 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol (**3**), was reacted with different metal salts in the presence of catalytic amount of triethyl amine at room temperature in methanol to form **3**-(1,3-benzoxazol-2-yl)naphthalen-2-ol -metal complexes mentioned in **Table 1**. The purity of the compounds was checked by TLC using precoated silica gel as stationary phase, using appropriate solvent system as mobile phase and visualized under UV-light.

Reagent and Conditions: a) PCl₃, Chlorobenzene, Reflux (133-135 °C), 4 h, 79%, b) Methanol, metal salt, triethyl amine (0.5 mL), reflux, 1-1.5 h

Co

Ni

Scheme 1. Synthesis of ligand 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol and its metal complexes

Cu

Cd

Table 1. Synthesis of metal complexes by using 3-(1,3-Benzoxazol-2-yl)naphthalen-2-ol metal as a

ligand and metal salt as a complexing agent ^a

Entry	Compound No	a complexing agent " Metal Salt	Product	Time (h)	Yield ^b (%)
1	4	Zn(OAc) ₂ .2H ₂ O		2.5	66
2	5	Cd(OAc) ₂ .2H ₂ O		3	62
3	6	CuSO ₄ .5H ₂ O		2.5	69
4	7	Co(OAc) ₂ .4H ₂ O		3.5	66
5	8	Ni(OAc) ₂ .4H ₂ O		3	69
6	9	Mg(NO ₃) ₂ .6H ₂ O		3	69
7	10	SnCl ₂ .2H ₂ O		3.5	68

^a: Reaction conditions: 3-(1,3-Benzoxazol-2-yl)naphthalen-2-ol (1 eq), metal salt (1 eq), Solvent: methanol + 0.5 mL of triethyl amine

Temperature: Reflux temperature.

b: Isolated yield.

The structure of the ligand was confirmed by FT-IR, ¹H-NMR spectroscopy and mass spectrometry. The absence of broad IR peak at 3010 cm⁻¹ confirms that –COOH of 3-hydroxynaphthalene-2-carboxylic acid was converted to oxazole ring structure. Also the peaks at 1585, 1477 cm⁻¹ confirm the formation of –C=N of oxazole ring formation. The base peaks at 261.95 in mass spectrometry confirms the formation of ligand. The metal complex formation was confirmed by FT-IR, and atomic absorption spectroscopy. There was sharp modification between the FT-IR spectra of the metal

complexes **4-10** and the ligand 3-hydroxynaphthalene-2-carboxylic acid **3**; most of the bands change their pattern in the region due to coordination of the phenolic oxygen atom of OH group and nitrogen atom of oxazole ring to the metal ions. The thermal, photophysical property study as well as complexation of biologically important metals with 3-hydroxynaphthalene-2-carboxylic acid were further explored with the evaluation of their antimicrobial activity.

2.1. Photophysical properties

All synthesized complexes were found to be fluorescent (**Fig. 1**) and were studied for their photophysical properties. Their absorption and emission properties were recorded in methanol. All these compounds absorb from 217 to 323 nm (**Fig. 2**) and emit from 371 to 416 nm (**Fig. 3**) with good Stokes shift ranges from 51 to 96 nm. Out of these compounds, **4**, **5**, **9** and **10** show Stokes shift value of 51 and 71 nm while compounds **6-8** show Stokes shift value in between 90-96 nm. (**Table 2**).

Table 2. Absorption and emission at 1 x 10⁻⁶ M concentration of compounds **4-10** in methanol ^a

Comp. No	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Stokes Shift (nm)
Ligand			
4	317 (1.434)	380 (748.845)	63
5	317 (1.269)	378 (504.838)	61
6	320 (1.016)	410 (545.085)	90
7	317 (1.891)	413 (534.262)	96
8	320 (0.466)	416 (44.180)	96
9	323 (0.405)	394 (356.604)	71
10	320 (0.205)	371 (164.866)	51

c: Amax and Aem were measured in nm. Samples were prepared in DMF. Analyses were carried out at room temperature.

a) Day light photograph

4 5 6 7 8 9 10

b) UV light photograph



Fig. 1. Day light and UV light photographs of Compound 4-10

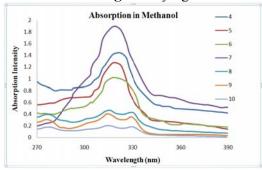


Fig. 2. Absorption in methanol

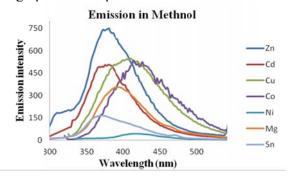


Fig. 3. Emission in methanol

An effective compound for the biological application should have good fluorescent intensity, high quantum yield and high photostability. Quantum yield of all compounds were recorded by using tinopal as a reference standard. Absorption and emission characteristics of standard as well as

unknown samples were measured at different concentration of unknown samples and standard at (2, 4, 6, 8 and 10 ppm level). Absorbance intensity values were plotted against emission intensity values. A linear plot was obtained. Gradients were calculated for each unknown compound and for standard. All the measurements were done by keeping the parameters such as solvent and slit width constant. Relative quantum yield of all synthesized compounds **4-10** were calculated by using the **Eq. (1)**²⁸.

Eq. 1. Relative fluorescence quantum yield

 $\Phi_X = \Phi_{ST} \left(\text{Grad}_X / \text{Grad}_{ST} \right) \left(\eta^2_X / \eta^2_{ST} \right)$

where:

 Φ_X : Quantum yield of unknown sample Grad_{ST}: Gradient of standard used

 Φ_{ST} : Quantum yield of standard used η^2_X : Refractive index of solvent for standard sample

Grad_X: Gradient of unknown sample η^2_{ST} : Refractive index of solvent for sample

The fluorescence quantum yields of all compounds were recorded in methanol at room temperature. Quantum yields of all compounds were found to be excellent and rang from 0.074 to 0.185 which are far excellent than that of any reported benzoxazoles and naphthoxazole derivatives (**Table 3**).

Table 3. Quantum yield of compounds **4-10** in methanol ^d

Compound No	4	5	6	7	8	9	10
Quantum Yield	0.185	0.173	0.092	0.154	0.106	0.074	0.086

d: λmax and λem were measured in nm, at room temperature. Samples were prepared in methanol

2.2. Thermal Analysis

To investigate the thermal stability of synthesized complexes 4-10 thermal stability study has been carried out using thermo gravimetric analysis (TGA) technique. The thermal gravimetric analysis has been carried out over the temperature range of 50-600 °C under nitrogen atmosphere. TGA results in **Table 4** indicate that the stability of metal complexes are varies from 291 to 312 °C. Amongst all these complexes nickel complex (Compound 8) shows very good thermal stability, it is 97.17 % stable up to 312 °C, above 400 °C it starts to decompose. Other complexes start to decompose in between 290-305 °C. TGA analysis curves of all compounds (**4-10**) as shown in **Fig. 4** state that even up to 600 °C, the complexes are stable up to 36.45%-75.83%, none of the complexes does not decompose completely. The comparison of T_d (decomposition temperature) showed that the thermal stability of the compounds **4-10** decrease in the order 8 > 10 > 9 > 7 > 4 > 6 > 5 as shown in **Table 4**.

Table 4. Thermal Gravimetric Analysis (TGA) of compound 8-12

Compound	4	5	6	7	8	9	10
TGA (°C)	298 (91.67 %)	291 (86.23 %)	299 (88.45 %)	302 (89.86 %)	312 (97.17%)	303 (92.12 %)	304 (95.23 %)

TGA was measured in °C.

2.3. Electrochemical measurement

The electrochemical experiments were performed in a conventional three electrode cell with working, counter and reference electrodes at room temperature using a PGSTAT 30 GPES Interface (Metrohm) instrument. The glassy carbon acts as the working electrode as well as counter electrode, platinum as the reference. The electrolyte was 0.1 M [NMP][HSO₄] in dry acetonitrile. The concentration of the dyes in the electrolyte was 0.5 mM. Scans are initiated at 0 V versus platinum in positive direction at

the rates of 50 mV/s. The solutions were purged with nitrogen and stirred for over 15 min prior to the measurements.

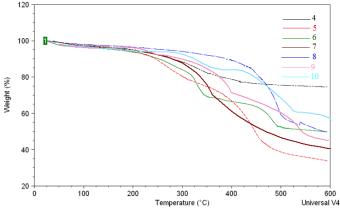


Fig. 4. TGA curves of compound 4-10

The synthesized compounds are less soluble in dry acetonitrile but the anion HSO_4^- of ionic liquid increases the solubility of metal complex in the electrolyte to a maximum concentration of 0.5 mM to 1.0 mM. The voltammograms of compounds **4-10** were recorded (**Fig. 5**) and E_{Oxi} and E_{Red} for each compound were determined from each data set and tabulated in **Table 5**. Electrochemical analysis of all compounds (**Table 5**) shows that the onset oxidation and reduction potentials are in the range of 0.261 to 0.622 V and -0.444 to -0.928 V, respectively.

Table 5. Onset and oxidation and reduction potential for compound 4-10 by using [NMP] [HSO4] as supporting electrolyte^e.

Compound No	Oxidation Potential (V)	Reduction Potential (V)
4	0.552	-0.578
5	0.528	-0.657
6	0.261	-0.928
7	0.413	-0.675
8	0.510	-0.748
9	0.601	-0.637
10	0.622	-0.444

Experimental conditions: Electrolyte: [NMP] [HSO₄] (0.1 M), Compound **4-10:** (0.5 mM in 0.1 M electrolyte), Solvent: Acetonitrile, Scan rate: 50 mV/s, Electrodes: Glassy Carbon (working and counter electrode), platinum (reference electrode), room tempreature

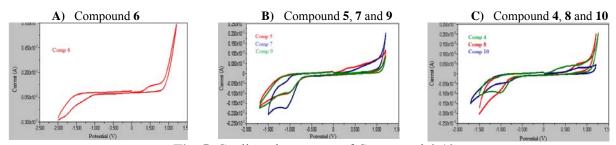


Fig. 5. Cyclic voltammetry of Compound 4-10

2.4. Atomic Absorption Spectroscopy

The percentage of metal element for each complex was determined by using atomic absorption spectrometer model GBC 932 (Make: GBC Scientific Equipment, Australia). Exactly weighed dye samples were dissolved in 20 mL of dimethyl sulphoxide and diluted to 100 mL with distilled water

and analyzed by GBC 932 plus atomic absorption spectrometer (AAS). Air was used as a carrier gas and acetylene was used as fuel. Certified 1000 mg/L standard solution of iron (Merck, Mumbai) was used to perform calibration using hallow cathode lamp for iron at 248.3 nm wavelength. All samples were prepared in such a manner that they will result in 2 mg/L solution containing 1: 2 complexes. Samples were analyzed for different metals using atomic absorption spectrometer analysis. The comparison of experimental results of AAS analysis with one calculated on the theoretical basis are as shown in **Table 6**. The results of AAS analysis are in good agreement with the predicted results within the limitations of the experimental error, which confirms the proposed 1: 2 metal complex stoichiometry between the metals and ligand.

Table 6. Atomic absorption spectrometer analysis of Compound **4-10**

Compound	Molecular Formula	Molecular	Theoretical	Experimental Conc.
No	Moleculal Follilula	Weight	Conc. (ppm)	(ppm)
4	$C_{34}H_{20}N_2O_4Zn$	585.92	2.00	1.89
5	$C_{34}H_{20}N_2O_4Cd$	632.94	2.00	1.93
6	$C_{34}H_{20}N_2O_4Cu$	584.08	2.00	1.95
7	$C_{34}H_{20}N_2O_4Co$	579.47	2.00	1.90
8	$C_{34}H_{20}N_2O_4Ni$	579.22	2.00	1.87
9	$C_{34}H_{20}N_2O_4Mg$	544.83	2.00	1.92
10	$C_{34}H_{20}N_2O_4Sn$	641.25	2.00	1.93

2.5. Biological activity

All compounds were evaluated for *in vitro* antibacterial activities against *E. coli* and *S. aureus* strains and *in vitro* antifungal activity against *C. albicans* and *A. niger* strains by using serial dilution method.

2.5.1. General

Incubation at 37 $^{\circ}$ C; pipettes of various sizes (Gilson); sterile tips, 100, 200, 500, and 1000 μ L; sterile normal saline; sterile isosensitest agar (Southern Group Laboratory, SGL); antibiotic solutions (Sigma–Aldrich); sterile solution of 10% (v/v) DMSO in water (Sigma–Aldrich).

2.5.2. Medium

Isosensitest medium was used throughout the assay, as it is pH buffered. Although NCCLS recommends the use of Mueller Hinton medium for susceptibility testing²⁹, the isosensitest medium has comparable results for most of the tested bacterial strains³⁰.

2.5.3. Preparation of the plates

Plates were prepared under aseptic conditions. A sterile 96 well plate was labelled. A volume of 100 μ L of test material in 10% (v/v) DMSO (usually a stock concentration of 4 mg/ml) was pipetted into the first row of the plate. To all other wells 50 μ L of nutrient broth was added. Serial dilutions were performed using a multichannel pipette. Tips were discarded after use such that each well had 50 μ L of the test material in serially descending concentrations. To each well, 10 μ L of resazurin indicator solution was added. Using a pipette 30 μ L of 3.3 × strength isosensitised broth was added to each well to ensure that the final volume was single strength of the nutrient broth. Finally, 10 μ L of bacterial suspension (5 × 10⁶ cfu/ mL) was added to each well to achieve a concentration of 5 × 10⁵ cfu/ mL. Each plate was wrapped loosely with cling film to ensure that bacteria do not become dehydrated. Each plate had a set of controls: a column with a broad-spectrum antibiotic as positive control, a column with all solutions with the exception of the test compound, and a column with all solutions with the exception of the bacterial solution, adding 10 μ L of nutrient broth instead. The

plates were prepared in triplicate, and placed in an incubator set at 37 °C for 18–24 h. The color change was then assessed visually. Any color changes from purple to pink or colorless were recorded as positive. The lowest concentration at which color change occurred was taken as the MIC value. The average of three values was calculated and that was the MIC for the test material and bacterial or fungal strain³¹.

2.5.4. Antimicrobial Activity

The new ligand and their metal complexes were evaluated for their in vitro antibacterial activity against $E.\ coli$ and $S.\ aureus$ strains and in vitro antifungal activity against $C.\ albicans$ and $A.\ niger$ strains by using serial dilution method. The minimum inhibitory concentration (MIC) measurement determined for compounds showed significant growth inhibition zones using serial dilution method. The graphical presentation as shown in **Fig. 6** indicates that most of the tested compounds display variable inhibitory effects on growth of tested bacterial strain and antifungal strain. The minimum inhibitory concentration MIC (μ g/mL) values are recorded in **Table 7.**

Antimicrobial data was compared with standard drug Streptomycin and Fluconazole. The MIC values from **Table 7** reveal that ligand does not show any type of activity against bacterial or fungal strains. But as soon as the metal ion gets bound with the ligand its activity increases and becomes better than the previous one. As compared to the antibacterial activity, all synthesized compounds (**4-10**) showed good antifungal activity against antifungal strains *C. albicans* and *A. niger*. Compound **4, 6** and **7** exhibit good to moderate activity against *E. coli* and *S. aureus*. Compound **6** shows good activity against antibacterial strain *E. coli* compound **7** showed good activity against antibacterial strain *S. aureus*. Comp **8** and **10** are not as much active against antibacterial strains.

Results mentioned in **Table 7** showed that all compounds shows good to moderate activity against antifungal strain *C. albicans* and *A.* niger Compound **4**, **6**, **8** and **10** showed good inhibition of growth in case of *C. albicans* and comp **4**, **5**, **7**, **9** show good inhibition of growth in case of *A. niger*. Electron donating and electron withdrawing groups present on phenyl ring does not affect the growth inhibitory activity against tested bacterial and fungal strains. In general, most of the tested compounds revealed better activity against the antibacterial strain (*E. coli, S. aureus*) and antifungal strain (*C. albicans, A. niger*). Novel compounds are very reactive against fungal strain as compared to bacterial strains over tested microorganisms.

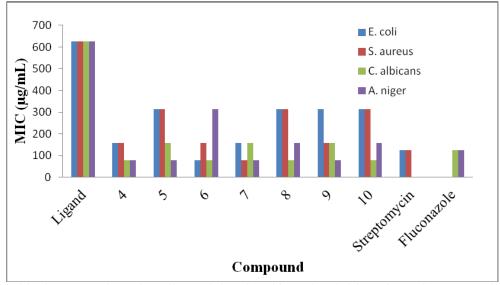


Fig. 6: Graphical presentation of Antibacterial and antifungal activities of novel compounds 4-10

Table 7. Antibacterial and antifungal activities of novel compounds indicated by MIC ($\mu g/mL$) using the modified resazurin assay ^f

Comp. No		cterial Strain IIC (µg/mL)	Fungal Strain MIC (μg/mL)		
comp. Te	E. Coli S. aureus		C. albicans	A. niger	
Ligand	625	625	625	625	
4	156.2	156.2	78	78	
5	312.5	312.5	156.2	78	
6	78	156.2	78	312.5	
7	156.2	78	156.2	78	
8	312.5	312.5	78	156.2	
9	312.5	156.2	156.2	78	
10	312.5	312.5	78	156.2	
Streptomycin	125	125	0	0	
Fluconazole	0	0	125	125	

f: Antimicrobial activities were expressed in MIC (Minimal inhibitory concentration) values.

Bacterial strain: *E. coli; S. aureus*. Fungal Strain: *C. albicans; A. niger*. Solvent: DMSO. Standards: Bacterial strain: Streptomycin-125 μg/mL, Fungal strains: Fluconazole-125 μg/mL.

3. Experimental

3.1. Materials and equipments

All commercial reagents were used as received without purification and all solvents were reagent grade. The reaction was monitored by TLC using on 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder Industrial Product Mumbai, and are uncorrected. The IR spectra were recorded on a PerkinElmer 257 spectrometer using KBr discs. ¹H NMR spectra were recorded on a VXR-400 MHz instrument using TMS as an internal standard. Elemental analysis was carried out by using FLASH EA 1112 Series instrument of Thermo Finnigan make.

3.2. Experimental Procedure for the synthesis of 3-(1,3-benzoxazol-2-vl)naphthalen-2-ol (3)

A mixture of 2-aminophenol 2 (1.09 g, 0.01 mol) and 3-hydroxynaphthalene-2-carboxylic acid 1 (1.88 g, 0.01 mol) was refluxed (133-135 $^{\circ}$ C) in chlorobenzene (10 mL) in presence of PCl₃ (2 g, 1.3 mL, 0.01 mol) for 4 hours. After completion of reaction, the solid product was precipitated out and was filtered to get crude product 3 which was further recrystalized from ethanol.

- 3.3. General experimental Procedure for the synthesis of metal complexes of 3-(1,3-benzoxazol-2-yl)naphthalen-2-ol (4-10)
- 3-(1,3-Benzoxazol-2-yl)naphthalen-2-ol (0.010 mol) was refluxed in methanol (10 mL) along with 4-5 drops of triethyl amine. At this temperature the corresponding metal salt (0.010 mol) was added and then the whole reaction mass was refluxed for the corresponding time as mentioned in **Table 1.**
- 3.4. Spectral data of compounds (3-10)

3-(1,3-benzoxazol-2-yl)naphthalen-2-ol (3)

Mp: 171-173 °C.

% Yield: 79 %, recrystalized from ethyl alcohol.

FT-IR (**KBr**): 3452, 3357 (-OH), 3028 (Aromatic -CH Stretching), 1615, 1585, 1477, (C=C, C=N ring stretching), 1222, 1132 (C-O stretching), 750 (Aromatic -CH out of plane bending) cm⁻¹.

¹*H* NMR: (DMSO-*d6*) δ= 6.98 (d, J= 7.9 Hz, 2H, Ar-H), 7.30-7.43 (dd, J= 7.8, 8.2, 1.8 Hz, 5H, Ar-H), 7.58 (d, J= 8.2, 1.9 Hz, 1H, Ar-H), 7.93 (d, J= 8.5, 1.6 Hz, 1H, Ar-H), 8.83 (s, 1H, Ar-H), 10.12 (s, 1H, -OH) ppm

LC MS (*m/z*): 261.9 (M+1, 98 %),

Anal. Calcd. for C₁₇H₁₁NO₂: C, 78.20; H, 4.27; N, 5.36. Found: C, 78.29; H, 4.16; N, 5.41.

Zn Complex (4):

Mp: > 300 °C % Yield: 66 %

FT-IR (**KBr**): 3029 (Aromatic -CH Stretching), 1614, 1578, 1482, (C=C, C=N ring stretching), 1225, 1142 (C-O stretching), 765 (Aromatic -CH out of plane bending) cm⁻¹.

Cd Complex (5):

Mp: > 288-290 °C % Yield: 62 %

FT-IR (**KBr**): 3032 (Aromatic -CH Stretching), 1611, 1580, 1471, (C=C, C=N ring stretching), 1210, 1135 (C-O stretching), 751 (Aromatic -CH out of plane bending) cm⁻¹.

Cu Complex (6):

% Yield: 69 %

Mp: > 300 °C FT-IR (KBr): 3023 (Aromatic -CH Stretching), 1620, 1585, 1465, (C=C, C=N ring stretching), 1216, 1131 (C-O stretching), 754 (Aromatic -CH out of plane bending) cm⁻¹.

Co Complex (7):

% Yield: 66 %

Mp: > **300** °C **FT-IR** (**KBr**): 3028 (Aromatic -CH Stretching), 1611, 1565, 1437, (C=C, C=N ring stretching), 1212, 1145 (C-O stretching), 748 (Aromatic -CH out of plane bending) cm⁻¹.

Ni Complex (8):

% Yield: 69 %

Mp: > **300** °C **FT-IR** (**KBr**): 3012 (Aromatic -CH Stretching), 1618, 1588, 1473, (C=C, C=N ring stretching), 1231, 1152 (C-O stretching), 750 (Aromatic -CH out of plane bending) cm⁻¹.

Mg Complex (9):

% Yield: 69 %

Mp: > **300** °C **FT-IR** (**KBr**): 3048 (Aromatic -CH Stretching), 1610, 1575, 1475, (C=C, C=N ring stretching), 1211, 1149 (C-O stretching), 758 (Aromatic -CH out of plane bending) cm⁻¹.

Sn Complex (10):

% Yield: 68 %

Mp: > **300** °C **FT-IR** (**KBr**): 3034 (Aromatic -CH Stretching), 1618, 1569, 1479, (C=C, C=N ring stretching), 1219, 1121 (C-O stretching), 767 (Aromatic -CH out of plane bending) cm⁻¹.

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