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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF 4-HYDROXYCOUMARIN-SUBSTITUTED Be (II) AND Mg (II) PHTHALOCYANINE

U. A. Birnin-Yauri[1] S. Saydam[2],
M. G. Liman[1], M. Muhammad[3*] and A. S. Baki[4]
1. Department of Pure and Environmental Chemistry, Usmanu Danfodiyo University, Sokoto
2. Department of Chemistry, Firat University, Elazig
3. Department of Science and Technology Education, Bayero University, Kano
4.Department Microbiology, Usmanu Danfodiyo University, Sokoto
*Corresponding Author e-mail: mmuhammad.ste@buk.edu.ng

ABSTRACT

Novel peripherally Beryllium and Magnesium Phthalocyanine complexes of 4-(2-oxo-2H-chromen-4-yl) oxy phthalonitrile were synthesized by heating the mixture of the ligand and metal salts under argon atmosphere. Spectroscopic techniques such as Elemental Analysis, 1H-NMR, FTIR and UV-visible were used to characterized the newly synthesized compounds. The degradation temperature of the compounds was investigated by thermal analysis which revealed the high thermal stability of the compounds. The electronic spectra of the Beryllium Phthalocyanine and Magnesium Phthalocyanine complexes in DMSO show intense Q absorption bands observed at 675nm and 700 nm, which indicates π-π* transition from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The results of the antimicrobial studies revealed that metallo-phthalocyanines are good candidates for future biological applications

Keywords: Phthalocyanine, Metallo-phthalocyanines, 4-Hydroxycoumarine, Antimicrobial Activity

INTRODUCTION

Phthalocyanines (Pcs) are symmetrical 18 π-electron aromatic macrocycles that are closely linked to natural porphyrins. Phthalocyanines are typically synthetic compounds because they do not occur naturally (Bezzu *et al*., 2019). Phthalocyanines are chemically and thermally stable molecules that can accommodate over 70 different metal ions in their core cavity. Incorporating various substituents into the core of phthalocyanines at the non-peripheral (α) and peripheral (β) positions can provide a range of electronic characteristics (Calvete, 2016). Phthalocyanines are desirable chemical modifiers in electrochemical detectors because of their optical, electrochemical, and electrocatalytic properties (Rodriguez-Mendez *et al*., 2009), as well as their high thermal and chemical stability (strong acids and bases do not affect them). Phthalocyanines have extensively been utilized as colorants, but they have recently been employed in a variety of technological applications. Phthalocyanine has led to numerous interests in many fields, such as therapeutic medicine, photosensitizers for photodynamic therapy of cancer (PDT) (Mantareva *et al*., 2013), and antioxidants (Agırtas *et al*., 2018). Besides, many other applications have also been explored, including nonlinear optics (Artuc *et al*., 2018), optical limiting (Saydam *et al*., 2009), liquid-crystalline electronic charge carriers (Basova *et al.,* 2012), Langmuir–Blodgett films Masilela and Nyokong (2011), electron transfer mediators in electrochemical sensors (Xu *et al*., 2016), ink-jet printing (Agirtas, 2018), catalysis (Jia *et al*., 2018), layers of gas sensors (Ağırtaş *et al*., 2016), solar cells (Amitha *et al*., 2019), excitation-transport materials, and semi-conductors (Bayrak *et al.*, 2016), in addition to their traditional use as dyes and pigments (Cong *et al*., 2008). Weng *et*

al. (2018) investigated the copper phthalocyanine complexes for the electrocatalytic reduction of carbon dioxide to methane with a 66% faradic yield. In recent years, many metallophthalocyanine (MPc) complexes have been synthesized and studied. Metallophthalocyanines are among the most investigated functional molecular materials due to their unique properties such as strong electron transfer, high molar absorption coefficients, UV-vis light absorption, and good chemical and thermal stability (Atmaca *et al*., 2019).

Furthermore, metallopththalocyanines (MPcs) are being extensively researched due to their numerous technological applications, including photodynamic therapy, catalysts and photocatalysts, dyes and pigments, solar cells, antimicrobial agents and antioxidants, DNA-cleavage, and electrochemical sensors (Guzel *et al*., 2019).

One of the best properties of phthalocyanines is solubility, where the soluble form provides the easiest way to conduct a variety of research on it. The solubility of phthalocyanines can be augmented by the incorporation of substituents such as phenoxy, alkyl, alkoxy and bulky or long chain groups at peripheral and non-peripheral positions to the phthalocyanine core (Senocak *et al*., 2019). In addition, tetra-substituted Phthalocyanine are generally more soluble than octa-substituted phthalocyanines (Jeong *et al*., 2017).

Chemical and thermal stabilities of phthalocyanines that have high link with electrochemical features are effective in all application fields. Both ways, varying the central metal atom and alternating the type, number, and positions of peripheral substituents, can be used to tune the electrochemical and spectroscopic features of phthalocyanine derivatives (Saka *et al*., 2020). Liu and Zhang (2022), reported a synthesis of alkaline earth metal complexes involving Group II alkaline-earth metals (BePC, MgPC, CaPC, SrPC, BaPC). The study focused on the photoluminescence and singlet oxygen photosensitizing properties of these complexes. Various characteristics were analyzed, including fluorescence emission and excitation spectra, quantum yields and lifetimes, UV–Vis electronic absorption, fluorescence emission, and singlet oxygen formation quantum yields. The alkaline earth metal phthalocyanine complexes exhibited high fluorescence quantum yields (0.50 to 0.70) and long fluorescence lifetimes (7.1 to 7.9 ns). Notably, SrPC and BaPC demonstrated a high quantum yield of singlet oxygen formation (0.40 to 0.50). These results revealed the potential of alkaline earth metal phthalocyanine complexes as effective fluorescence sensors and singlet oxygen photosensitizers for photodynamic therapy in tumor treatment (Liu and Zhang, 2022). The coordination of magnesium phthalocyanine derivatives resembles chlorophyll's 4+1 coordination, involving four isoindole N atoms and an apical O atom of water. Magnesium phthalocyanines possess unique chemical, catalytic, and spectroscopic characteristics that distinguish them from other divalent M(II) phthalocyanines. These derivatives are utilized as pigment materials in laser printers and optical disks and hold promise for solar energy conversion due to their electrochemical properties. Beryllium forms beryllium phthalocyanines, characterized by planar molecules and 4-coordinated beryllium ions, and is the smallest among Group IIA metals (Nombona *et al*., 2012). Both beryllium and magnesium phthalocyanines are unstable in ambient air. On the other hand, calcium, strontium, and barium exhibit remarkable electropositive traits, resulting in predominantly ionic metal-ligand interactions in Group II complexes. Strontium and barium, as heavy earth alkali metals, frequently form complexes with π-systems involving cyclopentadiene and cyclooctatetraene ligands (Fromm, 2020).

The purpose of this research work is to synthesize, characterize, and investigate the antibacterial properties of a 4-hydroxy coumarin substituted phthalonitrile ligand and its Be (II) and Mg (II) phthalocyanine complexes.

MATERIALS AND METHODS

Materials

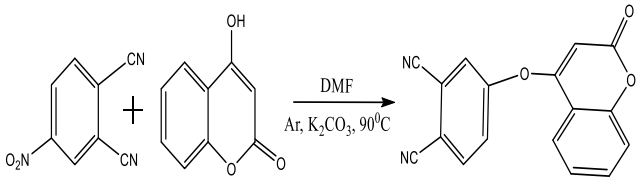
All the chemicals and solvents used were obtained from either Sigma Aldrich or Merck and were of analytical grade and used without further

purification. All the glass wares used for the reaction were soaked in 4% HNO_3 for 24 Hrs. washed with detergent and rinsed with distilled water and then dried in an oven at 110^0C. Transmission FT-IR spectra of the samples were recorded on an FT-IR spectrophotometer (Perkin Elmer), powder substances were ground with KBr and pressed to pellets. 1H-NMR spectra were determined using Bruker Ultra-shield 400 MHz with DMSO-d6 as solvents and tetramethylsilane as an internal standard. TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer (TGA-50 Instruments). UV–Vis spectra were recorded on a T80+UV/VIS spectrophotometer.

Methods

Synthesis of ligand (4-(2-oxo-2H chromen-4-yl)oxy) phthalonitrile)

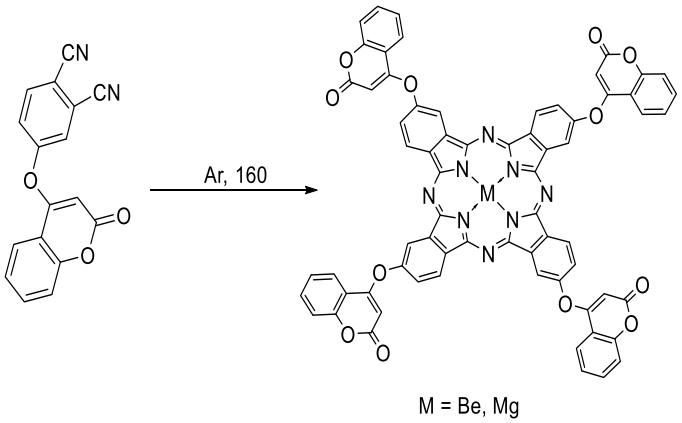
In a three-neck round bottom flask with a stirrer, 1.73g of 4-Nitrophthalonitrile was dissolved in a 50cm^3 N,N-dimethylformamide followed by 1.62g of 4-Hydroxycoumarin under an argon atmosphere at room temperature and stirred for 15 minutes, then heated. At 90 °C, 2.5g of anhydrous K_2CO_3 was added in portions within 2 hours while maintaining the temperature at 90 °C. The reaction was kept for 72 hours at 90 °C with constant stirring in an argon atmosphere. The reaction mixture was precipitated in 350 cm^3 of distilled water by drop wise addition. Brine was added to speed up the precipitation, and drops of HCl (1 Molar) were also added to neutralize the solution and obtain a good precipitate (Yalazan *et al*., 2020).



Scheme 1: Synthesis of substituted ligand II (4-(2-oxo-2H chromen-4-yl) oxy) phthalonitrile

Synthesis of Be (II) and Mg (II) phthalocyanine complexes of 4-(2-oxo-2H chromen-4-yl) oxy phthalonitrile.

Metal complexes of 4-hydroxycoumarin substituted phthalonitrile were synthesized by adding 0.4g of the ligand in two different reaction tubes, followed by the addition of 0.1g of the metal salts ($BeCl_2$ and $MgCl_2$) in each reaction tube containing the ligand. 3cm^3 of triethanolamine was then added to each of the reaction tubes. The reaction tubes were placed on a heating mantle and heated at 160 °C. The reaction tubes were connected to a hose through which Ar gas was supplied. The reaction was completed within 7 hours, and reaction mixtures were precipitated in ethanol and water and dried on filter paper to constant weight (Yabas *et al*., 2011).



Scheme 2: Synthesis of Be (II) and Mg (II) phthalocyanine complexes of 4-(2-oxo-2H chromen-4-yl) oxy phthalonitrile

Melting point and Decomposition Temperature

To determine the ligand melting points and complex decomposition temperatures, the samples were placed into a capillary tube that had been sealed at one end. The thermometer and sealed capillary tube were placed into the proper holes in the melting point apparatus. Three (3) measurements of the melting or decomposition temperature were made for each sample, and the mean value was used to determine the temperature at which the sample melted or decomposed.

Solubility Test

In a test tube containing 10 ml of each organic solvent, (50 mg) of the ligand and phthalocyanine complexes were added. They were stirred for a few seconds using a glass rod and allowed to stand for 15 minutes, and then the solubility of the compounds was observed and recorded in each

case (Sani *et al*., 2017).

FT-IR Spectra

Transmission FT-IR spectra of the samples were recorded on an FT-IR spectrophotometer (Perkin Elmer). The compounds (powder) were ground with KBr and pressed to pellets then placed in to the FT-IR spectrophotometer and the peaks were observed (Saydam *et al*., 2009).

UV-visible

To conduct UV-visible analysis, the compounds were dissolved in dimethyl sulfoxide (DMSO) and placed in cuvettes. The cuvette was then inserted into the ultraviolet spectrophotometer to measure the absorptions of each compound. (Febrian *et al*., 2019).

Nuclear Magnetic Resonance (NMR) spectroscopy

^{1}H-NMR spectra were determined using Bruker Ultra-shield 400 MHz with DMSO-d6 as solvents and tetramethyl silane as an internal standard (Dauda *et al*., 2020).

Antibacterial Activity

The antibacterial properties of the substituted phthalonitrile ligand and its phthalocyanine complexes were tested against three bacterial isolates: *Escherichia coli, Salmonella typhi,* and *Staphylococcus aureus*, using disc diffusion method. Three concentrations (15, 30, and 60 ug/ml) of the ligand and its phthalocyanine complexes in dimethylsulfoxide were prepared by serial dilution, placed on the prepared disc, and incubated at 37^{0}C for 24 hours. The zone of inhibition (mm) was determined and recorded for each compound (Muhammad and Kurawa, 2019).

Antifungal Activity

The *in vitro* antifungal activity of the substituted phthalonitrile ligand and its phthalocyanine complexes were screened against three fungi namely; *Candida albican, Aspergillus niger* and *Aspergillus flavus* using disc diffusion method. Concentrations (15, 30 and 60)ug/ml of the compounds were prepared via serial dilution method and placed on the media at room temperature for 48hrs. Activities were determined by measuring the diameter of zone of inhibition (in mm) (Muhammad and Kurawa, 2019).

RESULTS AND DISCUSSION

The novel phthalonitrile derivative and its corresponding phthalocyanine complexes were synthesized following the procedure in Scheme I and 2. The synthesis of the phthalonitrile derivative, serving as the ligand, involved a nucleophilic substitution reaction between 4-nitrophthalonitrile and 4-hydroxycoumarin (Jlali and Jamoussi, 2016). The phthalocyanine complexes of Be (II) and Mg (II) were obtained through the cyclotetramerization of the ligand a 1600C (Febrian *et al.,* 2019). The resulting phthalocyanine compounds were purified in sulfuric acid. Characteristically, the phthalocyanine complexes displayed were greenish while the ligand appeared off-white as illustrated in Table 1.0. Various spectroscopic techniques, including elemental analysis, FTIR, ^{1}HNMR, and UV-vis spectra, were utilized to characterize the newly synthesized compounds. These analyses confirmed the proposed structure of the phthalocyanine compounds. Specifically, the structure of the ligand was confirmed by ^{1}HNMR, demonstrating the presence of aromatic ring protons within its expected spectral region. The aromatic protons were observed in the range of 7.0ppm to 8.0ppm (Dauda *et al*., 2020).

Table 1.0: Physical Properties of the ligand and its Be (II) and Mg (II) phthalocyanine complexes

Compound	Molecular Formula	Molecular Weight	Colour	Melting point/ Decomposition Temperature (^{0}C)	% Yield	λ_{max} (nm)
Ligand	$C_{17}H_8N_2O_3$	162	Off White	276	80%	----
BePc	$C_{68}H_{32}BeN_8O_{12}$	1162	Green	118	21.31	675
MgPc	$C_{68}H_{32}MgN_8O_{12}$	1177	Green	227	30.00	700

FT-IR Spectra

Ligand = 4-(2-oxo-2H-chromen-4-yl) oxy) phthalonitrile, **Pc** = Phthalocyanine

The FTIR spectrum of 4-(2-oxo-2H-chromen-4-yl)oxy phthalonitrile exhibits characteristic frequencies at 2920 cm^{-1} (Ar-CH) and 2233 cm^{-1} (C≡N) (Dauda *et al*., 2021). A stretching vibration at 1607 cm^{-1} (C=C), 1250 cm^{-1} (C-O-C), and 1666 cm^{-1} (C=O) confirmed the formation of the 4-(2-oxo-2H-chromen-4-yl)oxy) phthalonitrile as indicated in table **2.0**. The absence of a nitrile peak at 2233 cm^{-1} in the spectrum of 4-(2-oxo-2H-chromen-4-yl) oxy phthalonitrile and the emergence of new peaks at 747 and 750 cm^{-1} (M-N) in the spectra of BePc and MgPc are good indications of the formation of phthalocyanine complexes (Rajavel *et al*., 2008). The spectra of BePc and MgPc. The FTIR spectra of the complexes exhibited bands at 2921 and 2921 cm^{-1} and are attributed to the stretching vibration of Ar-CH in the aromatic ring; 1216 and 1257 cm^{-1} are assigned to (C-O-C), whereas 1722 and 1707 cm^{-1} are attributed to C=O stretching vibration. and those at 1607 and 1598 cm^{-1} assigned to (C=C) stretching vibration. (Kose *et al*., 2020).

Table 2.0: Important IR spectral bands of the ligand and Be (II) and Mg (II) phthalocyanine complexes

Compounds	**v(Ar-CH) cm^{-1}**	**v(-C≡N) cm^{-1}**	**v(C=C) cm^{-1}**	**v(C-O-C) cm^{-1}**	**v(C=O) cm^{-1}**	**v(M-N) cm^{-1}**
Ligand	2920	2233	1607	1250	1666	-
[BePc]	2921	-	1607	1216	1722	747
[MgPc]	2921	-	1598	1257	1707	750

Ligand = 4-(2-oxo-2H-chromen-4-yl) oxy) phthalonitrile, **Pc** = Phthalocyanine

Phthalocyanines generally has low solubility in most common organic solvents, but bulky or long chain groups can be incorporated as either peripheral or non-peripheral substituents to the core phthalocyanine to improve their solubility (Lau *et al*., 2011). The solubility test of 4-(2-oxo-2H-chromen-4-yl)oxy) phthalonitrile against some common organic solvents revealed that the ligand is readily soluble in dimethyl sulfoxide, N,N-dimethylformamide and Tetrahydrofuran while slightly soluble in ethanol and methanol and insoluble in n-hexane, water, acetone, toluene and ethyl acetate. The test also revealed that phthalocyanine complexes of Be (II) and Mg (II) were readily soluble in dimethyl sulfoxide, N,N-dimethylformamide and Tetrahydrofuran but slightly soluble in water and insoluble in ethanol, methanol, n-hexane, toluene and ethyl acetate as indicated in table 3.0.

Table 3.0: Solubility of the Ligand and its Be (II) and Mg (II) Phthalocyanine Complexes in Some Common Organic Solvents

Compound	EtOH	Hexane	Water	Toluene	Ethyl-acetate	Acetone	Acetonitrile	THF	DMF	DMSO
Ligand	IS	SS	IS	IS	IS	IS	IS	S	S	S
BePc	IS	IS	IS	SS	IS	IS	IS	S	S	S
MgPc	IS	SS	IS	SS	SS	IS	IS	S	S	S

Ligand = 4-(2-oxo-2H-chromen-4-yl)oxy) phthalonitrile, Pc = Phthalocyanine, S = Soluble, SS = Slightly soluble, IS = Insoluble

Thermal Analysis

Figure 1.0 and 2.0 above show the thermal analysis of Be (II) and Mg (II) phthalocyanine of 4-(2-oxo-2H chromen-4-yl)oxy) phthalonitrile which was carried out to investigate the degradation temperature of the compounds by heating at a temperature of 600^0C. The thermographic analysis result of the complexes shows that the synthesized complexes begin to exhibit weight loss at a temperature of (BePc at 118^0C and MgPc at 227^0C, which indicates high thermal stability of the compounds as shown in figures 1 and 2.

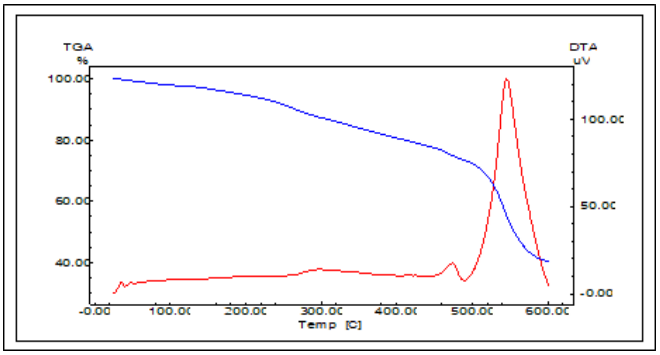


Fig. 1.0: Thermal analysis of BePc

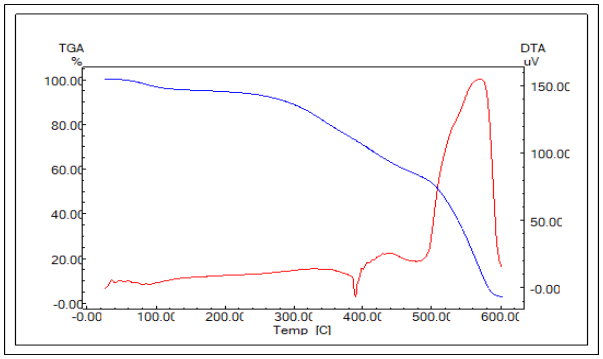


Fig. 2.0: Thermal analysis of MgPc

UV-Visible

The ground state electronic spectra (UV-Vis Spectroscopy) is the best spectroscopic technique for the determination of formation of phthalocyanine compounds through two strong absorption bands called Q and B (Soret) bands. The results in Fig.3.0 and Fig. 4.0 revealed the electronic spectra of the Phthalocyanines compounds (BePc, and MgPc) which show an intense Q band that were observed in the visible region at 675nm and 700nm attributed to π-π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Phthalocyanine ring (Saka *et al*., 2016).

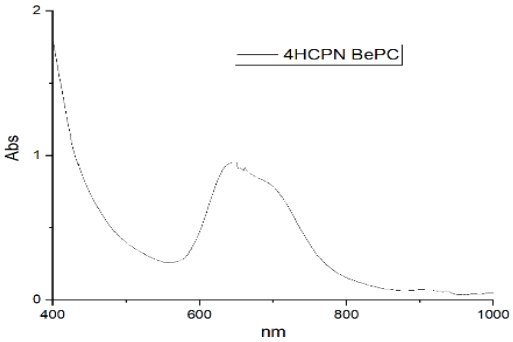


Fig. 3.0: UV Spectrum of BePc

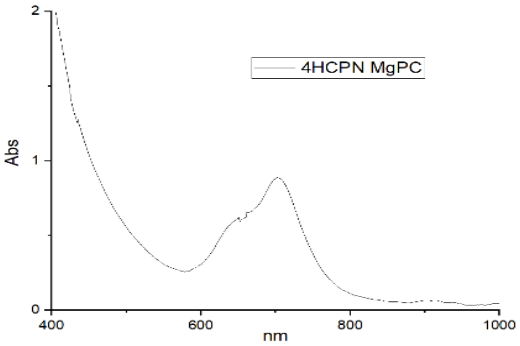


Fig. 4.0: UV Spectrum of MgPc

Antibacterial Activity

Three bacterial isolates were used to test the antibacterial properties of the synthesized phthalocyanine complexes of Be (II) and Mg (II). The results as indicated in fig 5.0 below revealed that all the compounds have an appreciable activity. The activity increased with an increase in concentration. It was also observed that MgPc had a higher activity than the ligand as a result of introducing the metal to the central cavity of the core phthalocyanine (Sen *et al*., 2022). Generally, the activity of the bacterial isolates recorded was lower compared to the standard. (Ciprofloxacin-Escherichia. coli (27mm), Staphylococcus aureus (33mm) and Salmonella typhi (30mm)). The ligand and its BePc and MgPc complexes exhibited appreciable activity against all the isolates, which makes them good materials for biological applications.

Antifungal Activity

The antifungal assay of the phthalonitrile substituted ligand and its phthalocyanine complexes carried out against fungal species (*Candida albican, Aspergillus niger and Aspergillus flavus*). The results of the antifungal test of Be (II) and Mg (II) phthalocyanine complexes (4-(2-oxo-2H chromen-7-yl) oxy) phthalonitrile against three fungal isolates *Candida albican, Aspergillus flavus* ana *Aspergillus niger* revealed high activities in all the isolates except Be (II), which has no activity at low concentration (15mm) against *Aspergillus niger* isolate (Ozturk *et al*., 2020). The results also show the activity of the isolate against the ligand was low, which increases after the complexation of the metals. The results also indicated low activity against the control (Ketoconazole: *Candida albican* (25mm), *Aspergillus niger* (34mm) and *Aspergillus flavus*(26mm)).

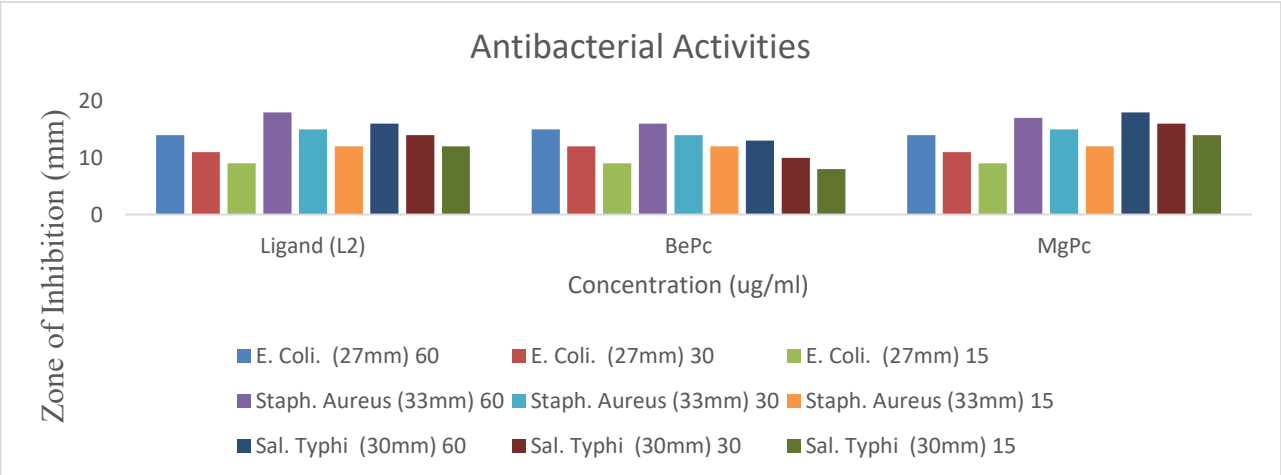
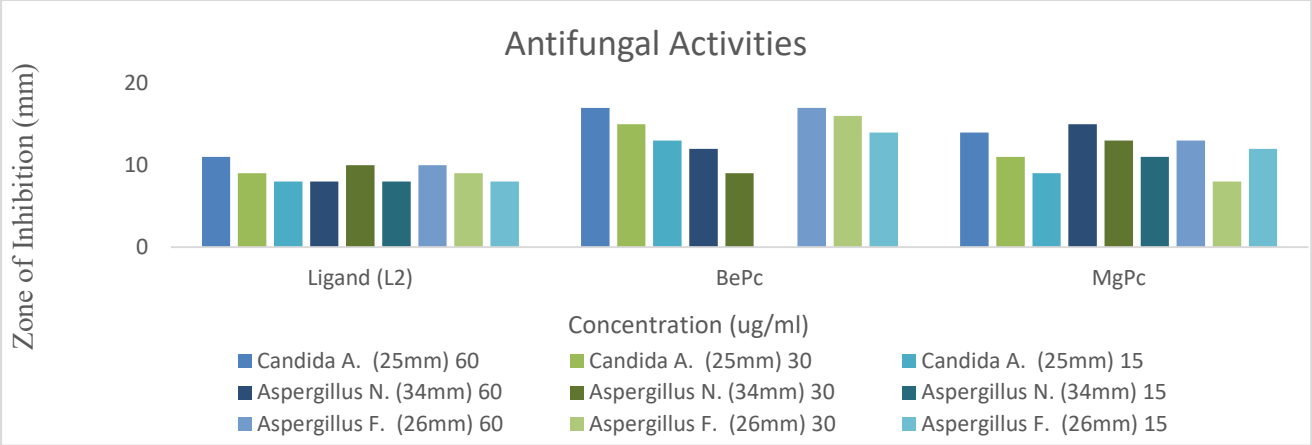


Fig. 5.0: Antibacterial activities of 4-(2-oxo-2H Chromen-4-yl)oxy phthalonitrile and its Be(II) and

Mg(II) Phthalocyanine complexes



. **Fig. 6.0: Antifungal activities of 4-(2-oxo- 2H Chromen- 4-yl)oxy) phthalonitrile and its Be(II) and Mg(II) Phthalocyanine complexes**

CONCLUSION

In conclusion, the synthesis and characterization of Be (II) and Mg (II) phthalocyanine complexes derived from 4-(2-oxo-2H chromen-7-yl) oxy phthalonitrile were successfully achieved. Spectroscopic techniques including elemental analysis, ^{1}HNMR, FTIR, TGA/DTA and UV-visible spectroscopy supported the proposed structures of these compounds. The solubility of the compounds was observed in DMSO, DMF and THF while insolubility was noted in most common organic solvents. High thermal stability of the compounds was evidenced by weight loss at elevated temperatures. Importantly, the electronic spectra revealed an intense Q-band in the visible region between 675nm and 700nm, indicative of the π-π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Phthalocyanine ring. Moreover, the synthesized compounds demonstrated appreciable activity against various bacterial and fungal isolates suggesting their potential for biological applications.

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