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Synthesis, spectral characterization, *in vitro* biological, antioxidant studies of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines

B. Chidananda[a], K. R. Venugopala Reddy[b]*, M. N. K. Harish[c], K. M. Pradeep[a], C. D. Mruthyunjayachari[a], S. D. Ganesh[d] and T. R. Prashith Kekuda[e]

[a]*Department of Industrial Chemistry, Sahyadri Science College (Autonomous), Kuvempu University, Shivamogga, Karnataka, India*
[b]*Department of chemistry, Vijayanagar Srikrishna Devaraya University, Bellary, Karnataka, India*
[c]*PG Department of Chemistry, JSS college of Arts, Commerce & Science, Ooty Road, Mysore, Karnataka, India*
[d]*Department of Industrial Chemistry, Kuvempu University, Shankaraghatta, Shivamogga, Karnataka, India*
[e]*Department of microbiology, Sahyadri Science College (Autonomous), Kuvempu University, Shivamogga, Karnataka, India*

ABSTRACT

*This work reports on the synthesis of tetraamidophthalocyanine (**5-7**). The structure of tetraamidophthalocyanines was elucidated by FT-IR, ^{1}H NMR, UV-visible spectroscope and elemental analysis. General trends were described for the antimicrobial activity of synthesized metallophthalocyanines screened against a wide range of Gram-positive and Gram-negative bacteria showed modest zone of inhibition, MIC with standard drug was investigated in dimethylsulphoxide (DMSO) and antioxidant with standard ascorbic acid. The results of antimicrobial activity and antioxidant experiments reveal that compound (5-7) exhibit modest activity. All phthalocyanine complexes exhibited excellent solubility in organic solvents such as methanol, ethanol, dimethylformamide and dimethyl sulfoxide.*

Keywords: Metallophthalocyanines, oxadiazole, N, N'-Dicyclohexylcarbodiimide, minimum inhibitory concentrations, antimicrobial, antioxidant,

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INTRODUCTION

The chemistry of the supramolecular phthalocyanine complexes have been the subject of intensive studies. Wide variety of the nature and pattern of substituents on phthalocyanines have attracted a great deal of attention due to their unusual effect on the optical properties [1]. The special interest of their unique structure resembling biologically active molecules like hemoglobin and chlorophyll. In addition, these compounds are known for their chemical inertness, thermal stability, high coloring property, di-oxygen transports and various redox transformations with proteins [2]. Phthalocyanines are traditional industrial synthetic dyes [3] with widespread applications such as optical recording materials [4], catalysts for oxidative degradation of pollutants [5], molecular electronic devices [6] and photosensitizers for photodynamic therapy [7]. These versatile features have stimulated attempts on the synthesis of new phthalocyanine derivatives with objective of developing new materials containing improved or high functional characteristics [8-9]. Among them, copper phthalocyanine is one of the most important classes of colorants and has superior properties such as light fastness, tinting strength, covering power, and resistance to alkalis and acids [10]. Also, Metal phthalocyanine derivatives are known to exhibit high electron transfer properties. The electron transfer properties of phthalocyanines depends on the kind and the number of the substituents due to the interaction between the phthalocyanine ring and the metal center which is influenced by the conjugated 18л electrons of the phthalocyanine ring [11-13]. On the other hand, the rationale of our strategy is to design soluble phthalocyanines in form which proves to possess more pronounced biological and better pharmacological activity [14-25]. In this regard synthetic strategies to produce amide linked phthalocyanine derivatives with good solubility and low aggregation have been undertaken. Amide bonds play a major role in the elaboration and composition of biological systems, Amide bonds are not limited to biological systems and are indeed present in a huge array of molecules of material interest [26-29]. The synthetic strategy involves metallophthalocyanines moiety as a scaffold for our complexes thereby, these complexes would exhibit desirable therapeutic properties of biological evolution. In this work, reported the synthesis of peripheral amide substituted 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines, Their Q bands appeared at around 666-692 nm. These compounds are soluble finely in organic solvents, and synthesized target compounds characterized by FT-IR, ^{1}H NMR, UV-visible spectroscope and elemental analysis. Synthesized as the target compounds in order to examine their in vitro microbiological activity against various Gram-positive, Gram-negative bacteria and the different fungi in comparison with control drugs and the result reveals that all newly synthesized metallophthalocyanines possess modest activity. In addition to this free radical scavenging activity of metallophthalocyanines investigated.

MATERIALS AND METHODS

All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Reactions were performed under nitrogen. N,N-Dimethylformamide (DMF) was predried with barium oxide and distilled under reduced pressure. The chloroform used in the UV/Vis studies was freshly Commercial TLC plates (silica gel 60 F254, SDS) were used to monitor the progress of the reaction, with spots observed under UV light at 254 and 365 nm. N,N'-Dicyclohexylcarbodiimide (DCC), calf thymus, O-phenylenediamine and benzoic acid were purchased from Sigma Aldrich , Bangalore, India and used without further purification. Ultrapure MilliQ water was used for all the experiments. Synthesis of 4-(5-phenyl-1,3,4-oxadiazol-2-yl)aniline was synthesized according to procedure [30]. The 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-metallophthalocyanines compounds (5-7) were prepared as described in literature [31-32].

Physical Measurements:

Elemental analyses (C, H and N) were recorded on a VarioMICROV 1.7.0. (Elementl Analysersysteme GmbH). The ^{1}H NMR spectra were measured at 400 MHz Varian-AS NMR spectrometer in dimethylsulfoxide-d$_6$ using tetramethylsilane as the internal standard. Elemental analysis was carried out using a Perkin Elmer 2400CHN instrument. UV-Vis spectra were measured on an ocean optics USB 4000.USA, using 1 cm path length cuvette at room temperature. Samples were prepared in dimethylsulphoxide at a concentration of 5.0 x 10^{-5} mol dm^{-3}. Infrared spectra were recorded using FT-IR 8400s Shimadzu spectrometer with KBR pellets in the range of 400-4500cm^{-1}.

Chemistry

Synthesis of 4-(5-phenyl-1,3,4-oxadiazol-2-yl)aniline

A mixture of benzoic hydrazide (1.0 g, 0.001 mmol), o-phenyldiamine (0.9 g, 0.0012 mmol) in polyphosphoric acid (12 g) was heated at 130ºC for 24h. The thick dark brown syrupy reaction mixture was poured into ice water (100 mL), the precipitate was filtered off and washed with methanol. The crude product was washed with methanol successively.

Yield: 87% found: Anal. (%) Calc. for [$C_{14}H_{11}N_3O$]: C, 70.87; H, 4.67; N, 17.71, O, 6.74 Found: C, 69.38; H, 4.82; N, 16.33; O, 6.43. IR (KBr, cm^{-1}): 3336.07 (-NH$_2$), 2155.26, 1650.59 (C=N), 1596.17 (C=C), 1502.87 (C-C). ^{1}H NMR (DMSO-d6, δ ppm): 6.51 to 6.67 (s, NH$_2$), 7.1-8.1 (m, Ar-H), 10.0-10.05 (s, NH). Mass (M)$^+$ cal m/z- 237.25, found m/z -238.0.

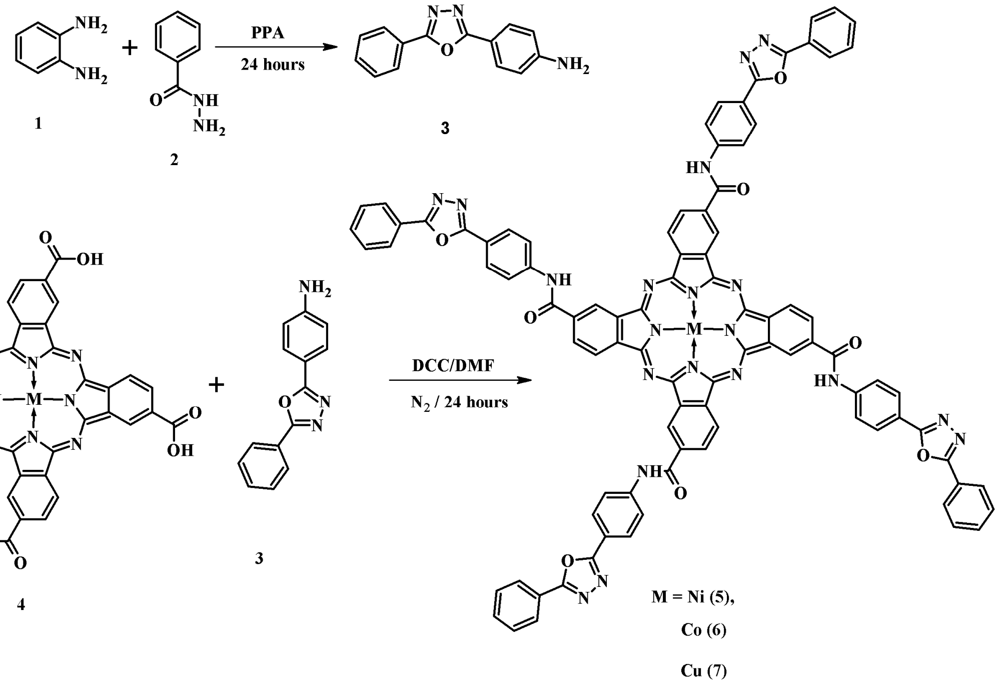
General procedure for the Synthesis of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-metallophthalocyanines compounds (5-7)

The template condensation reaction between a mixture of 4-(5-phenyl-1,3,4-oxadiazol-2-yl)aniline (1.9 g, 0.06 mmol), tetracarboxy metallophthalocyanines (1 g, 0.001 mol), K_2CO_3 (2.5 g, 0.0025 mmol) and DCC as catalyst in DMF (20 mL) and the mixture was stirred under nitrogen atmosphere for 24 h at room temperature. The progress of the reaction was observed by color change from blue to bluish green color and the precipitate was removed by filtration. The crude product so obtained was washed thoroughly with hot water and repeatedly with hexane. The product was dried in the oven for 1 h at 55°C obtained bluish green solid.

Synthesis of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-nickelphthalocyanines (**5**)
Yield: (78%) found: Anal. (%) Calc. for [$C_{92}H_{52}N_{20}O_8Ni$]: C, 68.03; H, 3.23; N, 17.25; O, 7.88; Ni, 3.61. Found: C, 67.78; H, 3.51; N, 17.03; Ni, 3.49; O, 8.02. IR (KBr, cm^{-1}): 3326.74 (-NH), 2925.53, 2852.51 (Ar-CH), 1622.61 (C=N), 1579.07 (C=C), 1504.44 (C-C), 1317.85, 1238.50, 111.70, 1083.07, 888.07, 845.17, 691.0, 643.04 are attributed to the various skeletal vibration of PC ring. ^1H NMR (DMSO-d6, δ ppm): 6.7 to 8.2 (m, Ar-H), 9.8 (s, NH).

Synthesis of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-cobalt phthalocyanine (**6**)
Yield: (80%) found: Anal. (%) Calc. for [$C_{92}H_{52}N_{20}O_8Co$]: C, 68.02; H, 3.23; N, 17.24; O, 7.88; Co, 3.63. Found: C, 67.83; H, 3.35; N, 16.87; O, 8.03; Co, 3.46. IR (KBr, cm^{-1}): 3320.52 (-NH), 2924.03, 2850.95 (Ar-CH), 1625.72 (C=N), 1574.41 (C=C), 1498.22 (C-C), 1317.88, 1227.67, 1227.67, 1087.73, 898.04, 845.17, 77.22, 636 are attributed to the various skeletal vibration of PC ring.

Synthesis of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-copper phthalocyanine (**7**)
Yield: (82%) found: Anal. (%) Calc. for [$C_{92}H_5N_{20}O_8Cu$]: C, 67.83; H, 3.22; N, 17.20; O, 7.86; Cu, 3.90. Found: C, 66.55; H, 3.56; N, 16.87; O, 8.08; Cu, 3.76. IR (KBr, cm^{-1}): 3322.07 (-NH), 2924.03, 2849.40 (Ar-CH), 1619.50 (C=N), 1582.18 (C=C), 1498.22 (C-C), 1310.84, 1246.33, 1171.70, 1087.73, 887.16, 840.51, 691.2, 643.04 are attributed to the various skeletal vibration of PC ring.



Scheme 1 synthesis of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines (5-7)

RESULTS AND DISCUSSION

Synthesis and characterization

The huge number of various kinds of substituted phthalocyanine compounds reported thus far, examples of soluble phthalocyanines with highly conjugated. In the present study, the soluble metallophthalocyanine (**5**-**7**) was prepared from 4-(5-phenyl-1,3,4-oxadiazol-2-yl)aniline (1.9 g, 0.006 mmol), tetracarboxy metallophthalocyanines (1 g, 0.001 mol), K_2CO_3 (2.5 g, 0.0025 mmol) and DCC as catalyst in DMF as shown in Scheme 1, complexes (**5–7**), which had been repeatedly purified with hot water and repeatedly with hexane. The products are soluble in N,N-dimethylformamide and dimethyl sulfoxide. These new compounds were also characterized with FT-IR, ^1H NMR, UV-visible spectroscope and elemental analysis. The ^{1}H NMR spectra of phthalocyanine compounds (**5**) in DMSO confirmed the proposed structure as shown in figure 1. The ^{1}H NMR spectra of **5** ring protons were observed in their respective regions. The phthalocyanine ring protons as unresolved multiplets (most likely due to the presence of isomers), integrating for a total of 48 protons, in the range 6.5–8.4 ppm and NH-protons at 9.8 ppm corresponding to the 4 protons of the complexes respectively. The observed spectra of the complexes were relatively well-resolved. IR spectra of all novel phthalocyanines were shown in figure 2 clearly indicates the formation of compound (5-7) by the appearance of new absorption bands at 3320.07-3326.74 cm^{-1} (Ar-NH), 2849.40-2925.28 (Ar-CH), 1619.52-1625.72 cm^{-1} for (C=N), 1574.41-1582.18 cm^{-1} for (C=C), 1450-1452 cm^{-1} for C-C, 1313.19, 1227.67, 1086,18, 887.16, 837.40, 741.00, 636.82 are attributed to the various skeletal vibration of PC ring and IR spectral data supports the proposed target structures. The elemental analyses results are consistent with the expected one.

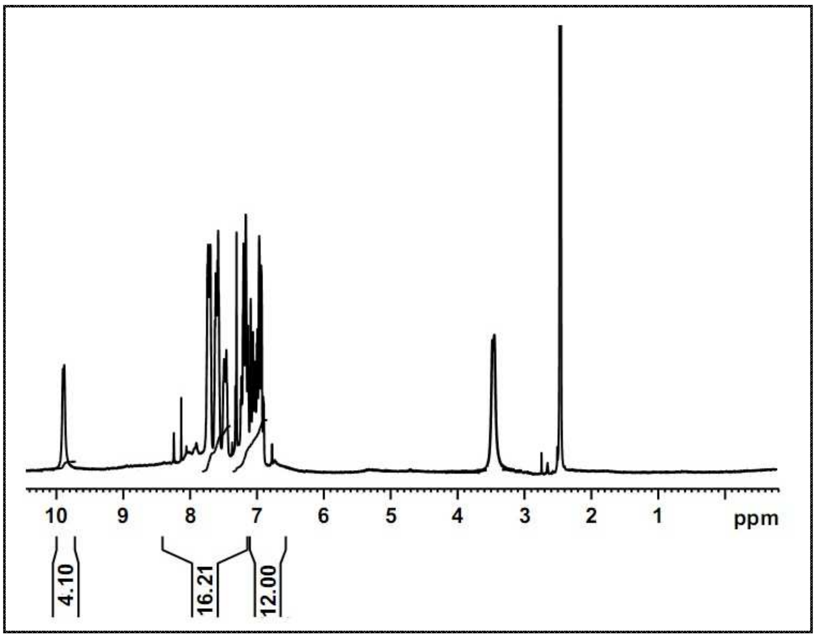


Figure 1. **^{1}H NMR spectra of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-nickel(II)phthalocyanines (5)**

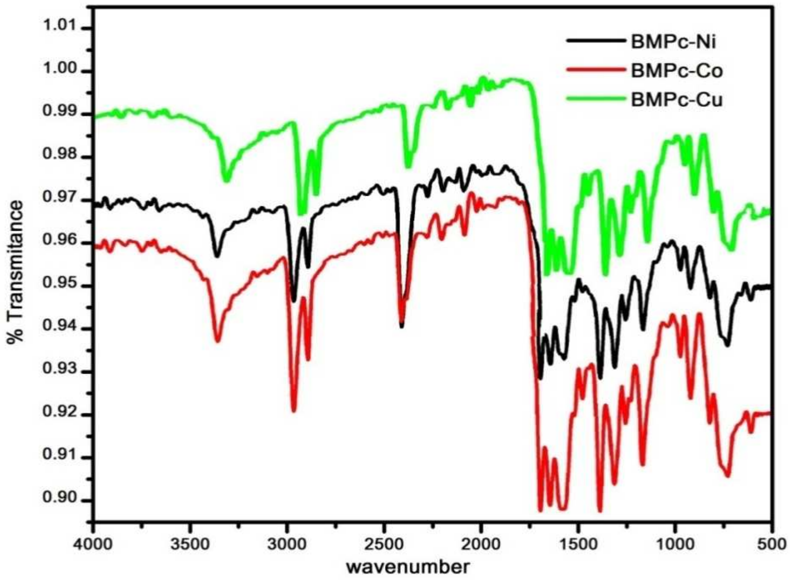


Figure 2. IR spectra of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-metallophthalocyanines (5-7)

UV-visible Absorption Spectra

All phthalocyanines were soluble in organic solvents such as DMF and DMSO. For metallophthalocyanines (5-7) in DMSO, the Q bands caused by π to π* transitions were observed at 666, 692 and 672 nm respectively (Figs. 3). The shoulders of these metallophthalocyanines were observed at: 603 for 5, 632 for 6 and 600 for 7, 647. For Q band regions of metallophthalocyanines, the longer wavelength absorptions are due to the monomeric species and shorter wavelength absorptions (shoulders) are due to the aggregated species [33]. So, in DMSO at 1x10^{-5} mol dm^{-3} concentrations, monomeric behaviour of metallophthalocyanines was proved by the dominance of the longer wavelength absorptions. The B bands arising from deeper π levels to LUMO were observed at: 317 nm for 5, 304 nm for 6 and 302 nm for 7 respectively (Figs. 3). The strong absorptions between 433, 431 and 460 nm in the spectra of 5, 6 and 7 arose from ligand metal charge transfer (LMCT) transitions [22].

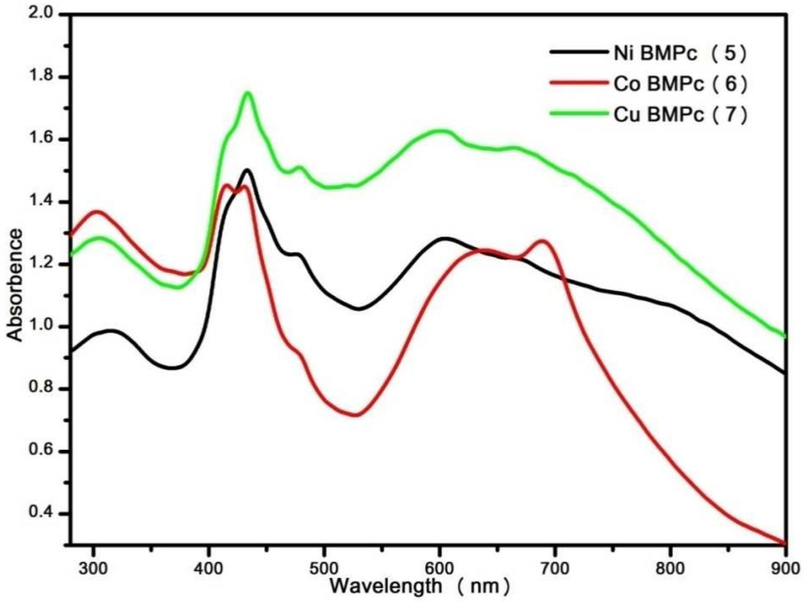


Figure 3. Electronic absorption spectra of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines (5-7)

In vitro antibacterial and antifungal assay

All the synthesized metallophthalocyanines complexes were screened in vitro for their biological activity, *Gram positive Staphylococcus aureus, Gram negative, Klebsiella pneumonia, Pseudomonas aures, Escherichia coli,* two fungal strains were *aspergillus niger and candida albicans* with metallophthalocyanines (**5-7**) complexes was performed by the Agar well diffusion method [34]. The bacterial strains were collected from different infectious status of patients who had not administered any antibacterial drugs for at least two weeks with the suggestions of an authorized physician, in Kiran diagnostic health centre of Chitradurga, Karnataka state, India. Fungal strains were procured from the culture maintained at National College of Pharmacy Shimoga. The compounds were tested at 40 µg/mL concentration against both bacterial and fungal strains. DMSO was used as a vehicle. Streptomycin (40 µg in100µl) and Fluconazole (40 µg in100µl) were used as standard drugs for comparison of antibacterial and antifungal activities respectively. The zone of inhibition was compared with standard drug after 24 h of incubation at 37 °C for antibacterial activity and 72 h at 25 °C for antifungal activity. The results revealed that the tested compounds were considered to be modest since the values obtained were close to each other. The compounds **6** and **7** exhibited higher antimicrobial activity than compound **5** as compared with standard drugs. Microbial results are systematized in tables 1. The antibacterial and antifungal studies suggest that all synthesized metallophthalocyanine (5-7) were showed modest antibacterial and antifungal. In the case of bacteriological studies, the results were compared with the standard drug (Streptomycin). Antifungal activities were compared with the standard drug (Flucanazole). All metallophthalocyanine (5-7) were showed modest against fungal species. Among the compounds **6** and **7** exhibited higher antimicrobial activity than compound **5** as compared with standard drugs

Table 1: Anti-microbial activity of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines (5-7)

Zone of inhibition test (in cm)						
bacterial strains				fungal Strains		
Compound	***S.aureus***	***P.aeruginosa***	***K.pneumoniae***	***E.coli***	***A.niger***	***C.albicans***
5	2.3	2.5	2.6	2.4	1.8	1.9
6	2.7	2.6	2.7	2.6	2.1	1.9
7	2.8	2.9	2.8	2.8	1.9	1.9
DMSO	0.0	0.0	0.0	0.0	0.0	0.0
Standard	4.1	3.4	3.7	3.6	2.2	2.3

Standard - Streptomycin (antibacterial)
Standard - Flucanazole (antifungal)

Minimum Inhibitory Concentrations (MIC)

The Minimum Inhibitory Concentrations (MIC) of 22,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-metallophthalocyanines (**5**-**7**) was determined by a micro dilution method [34]. The respective clinical strain was spread separately on the medium. The wells were created using a stainless steel sterilized cork borer under aseptic conditions. The synthesized 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines (**5**-**7**) at different concentrations viz. 10, 20, 30, 40 and 50 µg was dissolved respectively in 25, 50, 75, 100 and 125 µL of DMSO. And later loaded into corresponding wells. The standard drug Streptomycin (40 µg in100µl) and Fluconazole (40 µg in100µl) were used as standard drugs for comparison of antibacterial and antifungal activities respectively. The zone of inhibition was compared with standard drug after 24 h of incubation at 37 °C for antibacterial activity and 72 h at 25 °C for antifungal activity. The results are recorded in mm in Table 2.

Table 2. (MIC) of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido- metallophthalocyanines (5-7)

	MIC (µg/µL)					
Compound	bacterial strains				fungal Strains	
10-50 (µg)	***S.aureus***	***P.aeruginosa***	***K.pneumoniae***	***E.coli***	***A.niger***	***C.albicans***
5	30	20	30	20	20	30
6	40	40	30	40	40	30
7	40	30	40	30	40	40
Control DMSO	0	0	0	0	0	0

Antioxidant activity

The DPPH radical scavenging activity of the compounds and the ascorbic acid (standard) was measured according to the method [34]. The DPPH radical is a stable free radical having λ_{max} at 517 nm. Different concentration (5, 10, 25, 50, 100 and 200 µg/ml) of compounds and standard were prepared in methanol. In clean and labeled test tubes 2ml of DPPH solution (0.002% in methanol) was measured at 517 nm using UV-visible spectrophotometer. The absorbance of the DPPH control was also noted. The scavenging activity was calculated using the formula: scavenging activity (%) = A-B/A x 100, where A is the absorbance of DPPH and B is the absorbance of DPPH in standard combination. The Figure 4 reveals that antioxidant activity at different activity concentration of compounds (5-7) in methanol and ascorbic acid in terms of free radical scavenging ability which was evaluated using DPPH free radical assay. The compounds exhibited marked antioxidant activity by scavenging DPPH* found to be dose dependent. The compound **5** and **7** was shown to be more potent than compound **6** as compared with standard ascorbic acid and results were tabulated in table 3.

Table 3. DPPH radical scavenging activity of 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-metallophthalocyanines (5-7)

compounds	**Radical scavenging activity (%)**					
(µg/ml)	**5**	**10**	**25**	**50**	**100**	**200**
5	55.54	68.69	65.25	77.25	76.14	84.36
6	53.26	62.45	70.69	78.89	80.63	86.66
7	57.52	65.25	71.06	79.61	80.19	87.69
Ascorbic acid	64.96	75.08	85.46	91.36	95.09	98.06

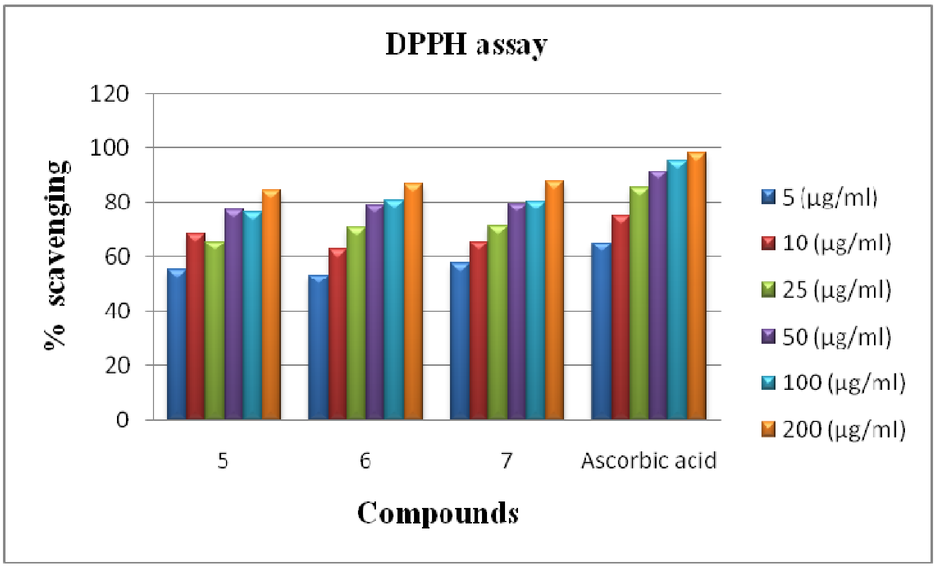


Figure 8. Plots of the radical scavenging effects (%) of the 2,9,16,23-tetra-N-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]benzamido-metallophthalocyanines (5-7) at various concentrations

CONCLUSION

In the present work, new 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido- metallophthalocyanines (**5-7**) were synthesized and the target compounds were characterized by elemental analysis, FT-IR,^{1}H NMR and UV-visible absorption spectra. These complexes has good solubility in N,N-dimethylformamide and dimethyl sulfoxide. The main goal of the work is to address the possible use of novel phthalocyanines for biological evaluation and antioxidant applications. This present study showed that lack of bacterial growth was observed and confirming successful bacterial growth inhibition. The minimum inhibition concentration results showed w 50% of the bacterial inhibition at w1.25 mM MPc concentration in DMSO. Moreover, complexes have modest antioxidant activity when compared with standard.

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