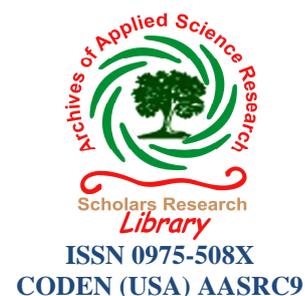




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## Synthesis and characterization of novel derivatives of oxadiazole substituted metal (II) phthalocyanines

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### ABSTRACT

The present paper describes about the synthesis and characterization of symmetrical [1, 3, 4] -oxadiazole bridged naphthoxy methylene substituted metal (II) phthalocyanines, which are prepared by condensing tetra carboxy metal (II) phthalocyanine with 2-naphthoxy acetohydrazide in the presence of suitable solvent and condensing agent. All the newly synthesized complexes are dark green in colour and are characterized by the various analytical techniques like Elemental analysis, Solid state UV-Visible, IR spectroscopic technique and X-ray diffraction studies. Thermo gravimetric studies were also carried to evaluate the thermal stability of the synthesized complexes. The  $Q$  band of the electronic spectra for the symmetrically functionalized phthalocyanine derivatives are red-shifted compared to those of corresponding parent phthalocyanine molecules due to the presence of substituents at the positions 2, 9, 16, 23 are more effectively involved in the extension of the  $\pi$ -electron cloud delocalization.

**Keywords:** Electronic spectra, Red shift, Thermal studies, Oxadiazole-phthalocyanine

### INTRODUCTION

Phthalocyanines are conjugated; aromatic and symmetrical macro cyclic molecules with an  $18\pi$  electron system containing four isoindole groups linked by four nitrogen atoms. They are structurally similar to naturally occurring porphyrins, but have extended conjugation engendered by benzene rings, hence have improved chemical and thermal stability. Phthalocyanines were discovered in the 1930s and were used as blue and blue-green pigments and dyes. Since their discovery early in the last century, phthalocyanines (Pcs) have been of great interest to chemists, physicists and industrial scientists and have become one of the most studied of all organic functional materials. In addition to their use as blue and green colorants, they are a versatile class of dyes, phthalocyanines have been widely studied for their applications in various disciplines and are of increasing interest for applications in nonlinear optics (including optical limitation), xerography as photoconductors, optical data storage as the laser absorption layer within recordable compact discs [1-4], molecular electronics, solar energy conversion, catalysis and as the active component of gas sensors [5-6]. Apart from the use in materials science, phthalocyanines are also highly promising for their applications as diagnostics and therapy in medicine, namely for magnetic resonance imaging (MRI) [7] and photodynamic therapy (PDT) [8-9]. In addition to these our research team synthesized and characterized efficiently 2, 9, 16, 23 - symmetrically oxadiazole substituted nickel (II) phthalocyanines by using various aliphatic (and aromatic) acid hydrazides under optimized experimental conditions and reported in the well reputed journal [10-11]. Although there have been a number of publications and reviews on the chemistry and applications of metal phthalocyanines, no work has been done on the phthalocyanine complexes which are substituted by naphthoxy methylene moiety and in particularly through oxadiazole ring. Keeping the above facts in mind we made an attempt to synthesize and characterize 1, 3, 4-oxadiazole bridged naphthoxy methylene substituted metal (II) phthalocyanines.

## MATERIALS AND METHODS

All chemicals used were of synthetic grade. Melting points were recorded on open capillary tube method and are uncorrected. The progress of reaction and purity of the precursor compounds was monitored by TLC on precoated silica F-254 plates (Merck, Mumbai, India) and spots were visualized by exposure to iodine vapours. Electronic spectra of the complexes are recorded in solid state by using UV-Vis spectrophotometer [OCAEN OPTICS, Model: 4000-USA]. IR spectra of the complexes were recorded in KBr pellets on Nicolet MX-1FT-IR spectrometer in the wavelength range of 4000-400 $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded at 300 MHz on Bruker spectrometer and their chemical shift values are expressed in  $\delta$  ppm with respect to TMS as an internal standard.

**Synthesis of Tetracarboxy Metal (II) Phthalocyanine**

Nickel (II) tetra formamido phthalocyanine was prepared by the reaction of 1, 2, 4-benzene tricarboxylic anhydride [Trimellitic anhydride] (50g; 1mole), nickel acetate (26g; 0.4mole), ammonium chloride (10g; 0.45moles), catalytic amount of ammonium molybdate and excess of urea (~100g) in 100 ml of nitrobenzene in three necked flask for 5 hours at 185°C. A blue-green solid nickel (II) tetra formamido phthalocyanine formed was transferred into 2M potassium hydroxide solution and the reaction was carried out at 90°C for 10 hours until no ammonia was evolved. The resulting solution was diluted with required amount of water and was brought to pH ~ 3 with concentrated hydrochloric acid and then filtered. The residue was redissolved with 0.5 M potassium hydroxide solution and filtered. The resulting solid was washed with water several times and then with methanol until a solid with metallic luster of tetra carboxylic Nickel (II) Phthalocyanine was obtained. Finally it was dried over anhydrous phosphorous pentoxide. Similar procedure was followed for the preparation of tetra carboxy Copper (II) and Cobalt (II) phthalocyanines.

**Tetra carboxy nickel (II) phthalocyanine-[TCPcNi]**

Yield: 60 %; Anal. Calcd.For. $\text{C}_{36}\text{H}_{16}\text{N}_8\text{NiO}_8$ : C, 57.86; H, 2.16; N, 15.00; Ni, 7.85; O, 17.13. Found: C, 57.66; H, 2.26; N, 15.05; O, 17.27. IR (KBr,  $\text{cm}^{-1}$ ): 2995.78 $\text{cm}^{-1}$  (–OH group of –COOH), 1530 $\text{cm}^{-1}$  (Ar. C=N stretching), sharp signal at 1704 $\text{cm}^{-1}$  (C=O) and 3335, 1771 1614, 2330, 1591 $\text{cm}^{-1}$  reflects on the skeletal vibrations of the phthalocyanine molecule.

**Tetra carboxy copper (II) phthalocyanine-[TCPcCu]**

Yield: 62 %; Anal. Calcd.For. $\text{C}_{36}\text{H}_{16}\text{N}_8\text{CuO}_8$ : C, 57.49; H, 2.14; Cu, 8.45; N, 14.90; O, 17.02. Found: C, 57.55; H, 2.21; N, 15.09; O, 16.90. IR absorption bands: 3036 $\text{cm}^{-1}$  (–OH group of –COOH), 1513 $\text{cm}^{-1}$  (Ar. C=N stretching), sharp signal at 1712 $\text{cm}^{-1}$  (C=O) and 1921, 1763, 1614, 1588 $\text{cm}^{-1}$  reflects on the skeletal vibrations of the phthalocyanine molecule.

**Tetra carboxy cobalt (II) phthalocyanine –[TCPcCo]**

Yield: 62 %; Anal. Calcd.For. $\text{C}_{36}\text{H}_{16}\text{N}_8\text{CoO}_8$ : C, 57.84; H, 2.16; Co, 7.88; N, 14.99; O, 17.12. Found: C, 57.78; H, 2.26; Co, 7.78; N, 15.16; O, 17.02. IR absorption bands: 2986 $\text{cm}^{-1}$  (–OH group of –COOH), 1530 $\text{cm}^{-1}$  (Ar. C=N stretching), sharp signal at 1707 $\text{cm}^{-1}$  (C=O) and 1243, 1590, 1614, 2494, 1925 $\text{cm}^{-1}$  reflects on the skeletal vibrations of the phthalocyanine molecule.

**Preparation of 2-Naphthoxy ethyl acetate**

2-naphthol (0.1mol) was dissolved in ~250 ml of dry acetone and mixed with anhydrous potassium carbonate (~0.16mol). And it was treated with ethylchloroacetate (0.1mol) and the mixture was refluxed for 5-6 hours. The completion of reaction was monitored by thin layer chromatographic technique. After the completion of reaction, the reaction mixture was filtered and the filtrate was distilled under reduced pressure. The product obtained was recrystallized.

**Preparation of 2-naphthoxy acetohydrazide**

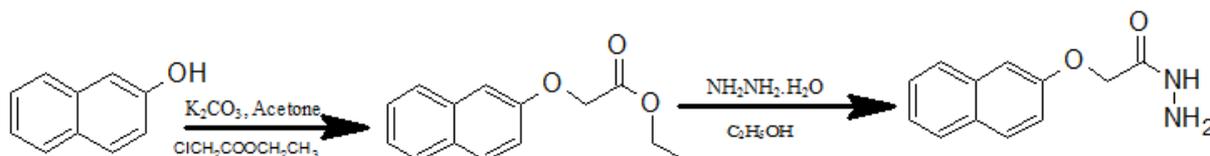
A mixture of 2-naphthoxy ethyl acetate (5.0 g, 0.01 mol) and hydrazine hydrate (1.6 g, 0.02 mol) in ethanol (20 ml) was heated under reflux for seven hours. The reaction mixture was cooled to room temperature and the solid separated was collected by filtration. It was washed with ethanol and recrystallized in methanol. The product was obtained as light colourless shiny solid. Similar procedure was adapted for the preparation of 1 - naphthoxy acetohydrazide and 6-Bromo naphthoxy acetohydrazide. General reaction route was shown in scheme – 1.

**2-Naphthoxy acetohydrazide**

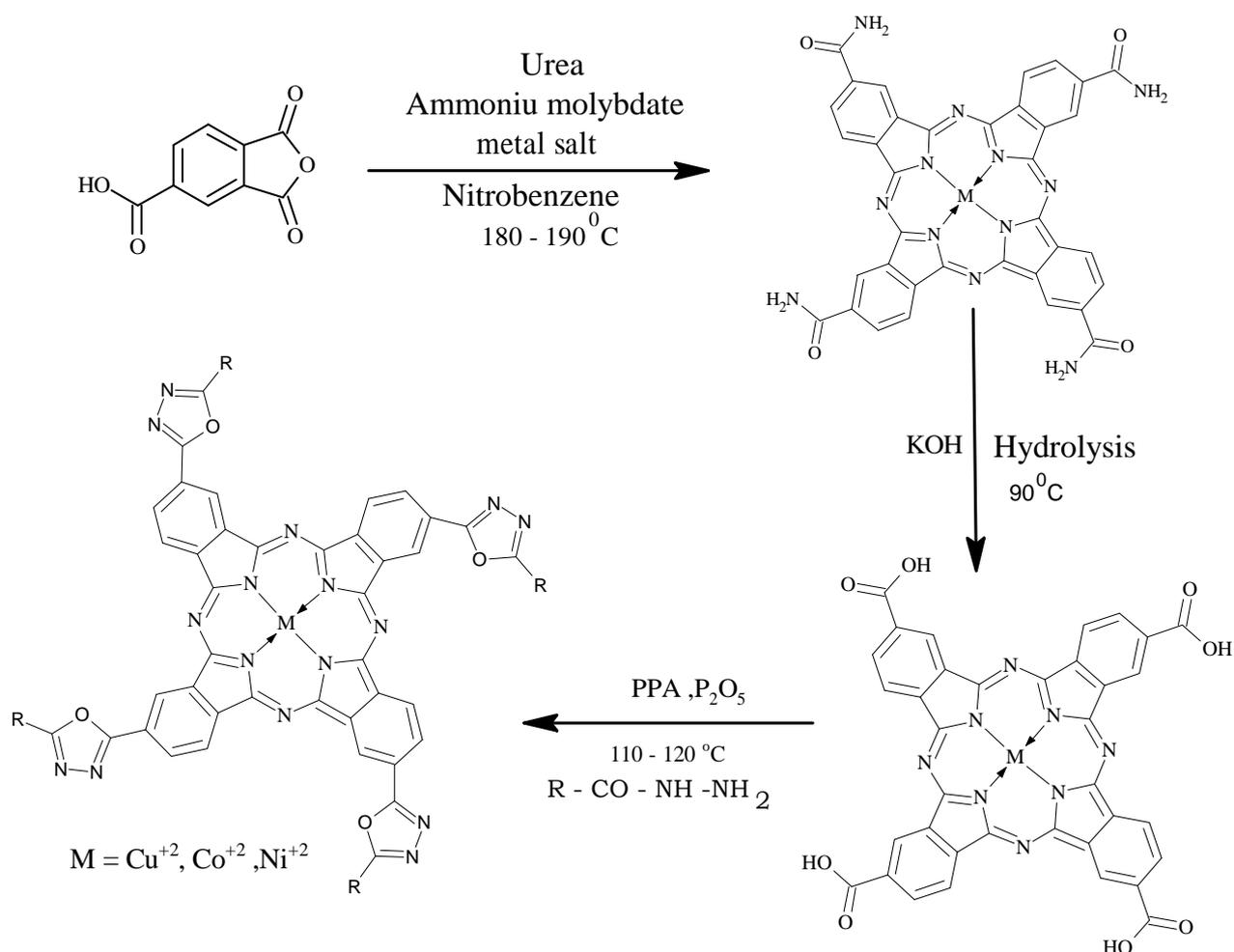
Yield: 69 %; Anal. Calcd.For. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 66.65; H, 5.59; N, 12.96; O, 14.80. Found: C, 64.55; H, 6.64; N, 12.46; O, 15.96. IR [(KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ ]: 3311 (NH<sub>2</sub>), 3206 (NH), 1667 (C=O), 1541 (C=C).  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ ppm): 6.9 – 7.6 (multiplet, 7H, due to aromatic protons), 4.83 (singlet 2H, CH<sub>2</sub>), 2.1 (doublet, NH<sub>2</sub>), 8 (triplet NH). The mass spectrum of this compound showed molecular ion peak at  $m/z$ : 217.

**General procedure for the preparation of naphthoxy methelene substituted metal (II) phthalocyanines through 1, 3, 4 - Oxadiazole Bridge**

Tetracarboxy copper(II)phthalocyanine (0.001 mol) and 2-naphthoxy acetoacetylhydrazide (0.006 mol) were stirred into preheated polyphosphoric acid (PPA) [ $\sim 100$  g] containing 10 g of  $P_2O_5$  at  $100^\circ C$  in a three-necked round bottom flask containing a mechanical stirrer, condenser, and a thermometer for 1 hour and then maintained at  $120^\circ C$  for eight hours. The reaction mixture was allowed to cool to room temperature and quenched in ice cold water and filtered. The product obtained was repeatedly treated with 0.1N sodium hydroxide solution followed by water and acetone to get the product. Similar procedure was employed for other metal phthalocyanines to obtain the desired products and synthetic route was shown in scheme - 2.



**Scheme-1:** Synthetic route and structure of the 2 - naphthoxy acetylhydrazide



**Scheme-2:** Synthetic route and structure of the naphthoxy methylene substituted metal (II) phthalocyanines through 1, 3, 4 - Oxadiazole bridge.

**2-Naphthoxy methelene substituted copper (II) phthalocyanines through 1, 3, 4 Oxadiazole Bridge [2-NCuPc] (2a):** Anal. Calcd. For.  $C_{84}H_{48}CuN_{16}O_8$ : C, 68.50; H, 3.28; Cu, 4.31; N, 15.22; O, 8.69. Found: C, 67.00; H, 4.58; N, 15.42. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3083 (Ar-CH), 2936(Ar-CH), 1614 (C=N), 1495 (C=C), 1287(C-O-C), and other signals at 1390, 1308, 822, 571 reflects on skeletal vibration of phthalocyanine.

**2-Naphthoxy methelene substituted cobalt (II) phthalocyanines through 1, 3, 4 - Oxadiazole Bridge[2-NCoPc] (2b):** Anal. Calcd. For.  $C_{84}H_{48}CoN_{16}O_8$ : C, 68.71; H, 3.30; Co, 4.01; N, 15.26; O, 8.72. Found: C, 68.30; H, 3.71; N, 15.72. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3076 (Ar-CH), 2846(Ar-CH), 1606 (C=N), 1525 (C=C), 1282 (C-O-C), and other signals at 1060, 816, 781 reflects on skeletal vibration of phthalocyanine.

**2-Naphthoxy methelene substituted Nickel (II) phthalocyanines through 1, 3, 4 -Oxadiazole Bridge[2-NNiPc] (2c):** Anal. Calcd. For:  $C_{84}H_{48}Ni_{16}NiO_8$ : C, 68.72; H, 3.30; N, 15.27; Ni, 4.00; O, 8.72. Found: C, 68.27; H, 3.72; N, 15.40. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3062 (Ar-CH), 3037(Ar-CH), 1613 (C=N), 1533 (C=C), 1266 (C-O-C), and other signals at 1406, 1166, 1201, 772 reflects on skeletal vibration of phthalocyanine.

**1-Naphthoxy methelene substituted copper (II) phthalocyanines through 1, 3, 4 Oxadiazole Bridge [1-NCuPc] (3a):** Anal. Calcd. For.  $C_{84}H_{48}CuN_{16}O_8$ : C, 68.50; H, 3.28; Cu, 4.31; N, 15.22; O, 8.69. Found: C, 68.30; H, 3.48; N, 15.29. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3062(Ar-CH), 2850(Ar-CH), 1614 (C=N), 1520(C=C), 1268(C-O-C), and various other signals at 1118, 1080, 776 reflects on skeletal vibration of phthalocyanine.

**1-Naphthoxy methelene substituted cobalt (II) phthalocyanines through 1, 3, 4 - Oxadiazole Bridge [1-NCoPc] (3b):** Anal. Calcd. For.  $C_{84}H_{48}CoN_{16}O_8$ : C, 68.71; H, 3.30; Co, 4.01; N, 15.26; O, 8.72. Found: C, 68.90; H, 3.19; N, 15.72. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3061 (Ar-CH), 2902(Ar-CH), 1606 (C=N), 1520 (C=C), 1280 (C-O-C), and other signals at 1363, 1161, 776 reflects on skeletal vibration of phthalocyanine.

**1-Naphthoxy methelene substituted Nickel (II) phthalocyanines through 1, 3, 4 -Oxadiazole Bridge [1-NNiPc] (3c):** Anal. Calcd. For.  $C_{84}H_{48}Ni_{16}NiO_8$ : C, 68.72; H, 3.30; N, 15.27; Ni, 4.00; O, 8.72. Found: C, 68.56; H, 3.70; N, 15.61. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3049 (Ar-CH), 3016(Ar-CH), 1613 (C=N), 1512(C=C), 1286(C-O-C), and other signals at 1078, 1059, 1201, 756 reflects on skeletal vibration of phthalocyanine.

**6-Bromo-Naphthoxy methelene substituted copper (II) phthalocyanines through 1, 3, 4 - Oxadiazole Bridge [6-BNCuPc] (4a):** Anal. Calcd. For.  $C_{84}H_{44}Br_4CuN_{16}O_8$ : C, 56.41; H, 2.48; Br, 17.87; Cu, 3.55; N, 12.53; O, 7.16. Found: C, 56.41; H, 2.48; N, 12.53. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3071(Ar-CH), 2936(Ar-CH), 1610(C=N), 1495(C=C), 1163(C-O-C), and other signals at 2666, 1288, 1003, 754 reflects on skeletal vibration of phthalocyanine.

**6-Bromo-Naphthoxy methelene substituted cobalt (II) phthalocyanines through 1, 3, 4 - Oxadiazole Bridge [6-BNCoPc] (4b):** Anal. Calcd. For.  $C_{84}H_{44}Br_4CoN_{16}O_8$ : C, 56.56; H, 2.49; Br, 17.92; Co, 3.30; N, 12.56; O, 7.18. Found: C, 56.59; H, 2.46; N, 12.32. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3077(Ar-CH), 2910(Ar-CH), 1610(C=N), 1525 (C=C), 1286 (C-O-C), and other signals at 1466, 1333, 1004, 879, 774 reflects on skeletal vibration of phthalocyanine.

**6-Bromo-Naphthoxy methelene substituted Nickel (II) phthalocyanines through 1, 3, 4 - Oxadiazole Bridge [6-BNNiPc] (4c):** Anal. Calcd. For.  $C_{84}H_{44}Br_4Ni_{16}NiO_8$ : C, 56.56; H, 2.49; Br, 17.92; N, 12.56; Ni, 3.29; O, 7.18. Found: C, 56.72; H, 2.34; N, 12.42. IR [(KBr):  $\nu_{max}/cm^{-1}$ ]: 3037 (Ar-CH), 2989(Ar-CH), 1619 (C=N), 1533 (C=C), 1291 (C-O-C), and other signals at 1121, 869, 781, 695 reflects on skeletal vibration of phthalocyanine.

## RESULTS AND DISCUSSION

### IR Spectra

IR spectra of the synthesized complexes are recorded in the region 400–4000  $cm^{-1}$  using the KBr. IR signals for different vibrations of the functional group cannot be identified separately since most of the stretching vibrations lie in the complicated region of the skeletal vibrations of the phthalocyanine molecule. The presence of functional groups in the periphery is confirmed by their characteristic bands. IR spectra for the synthesized compounds exhibited a series of absorptions at 729–781, 832–879, 926–958, 1038–1093, and 1145–1148  $cm^{-1}$ , which can be attributed to the skeletal vibration of phthalocyanine molecule. However the comparison of FT-IR spectra of tetracarboxy metal (II) phthalocyanines and the substituted metal (II) phthalocyanines shows some marked differences. The characteristic absorptions due to carbonyl group ( $-C=O$ ) of  $-COOH$  groups in tetracarboxy cobalt phthalocyanine at 1704  $cm^{-1}$ , tetracarboxy nickel phthalocyanine at 1702  $cm^{-1}$  and tetracarboxy copper phthalocyanine at 1693  $cm^{-1}$  has disappeared in the IR spectra of synthesized complexes indicating the effective involvement of carbonyl carbon in the starting material (tetra carboxy metal phthalocyanine) in the formation of the oxadiazole moiety.

Figure – 1: Electronic spectra of the synthesized complexes

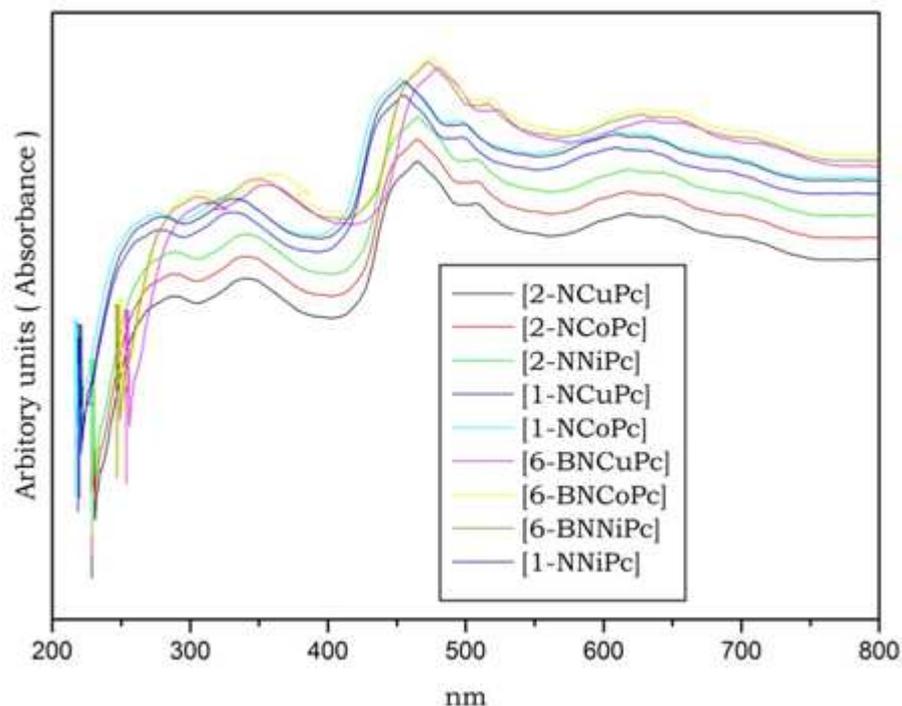


Table – 1: Electronic spectral data

SL.No	Complex code Number	Complex Code name	Metal	R	% Yield	Peaks $\lambda_{max}$ (in nm)
1	2a	[2-NCuPc]	Cu		77	466,507,617
2	2b	[2-NCoPc]	Co		68	464,508,618
3	2c	[2-NNiPc]	Ni		65	466,507,620
4	3a	[1-NCuPc]	Cu		70	454,499,611
5	3b	[1-NCoPc]	Co		67	452,495,614
6	3c	[1-NNiPc]	Ni		61	454,500,610
7	4a	[6-BNCuPc]	Cu		73	478,523,635
8	4b	[6-BNCoPc]	Co		68	476,518,629
9	4c	[6-BNNiPc]	Ni		70	473,515,626

### Electronic Spectra

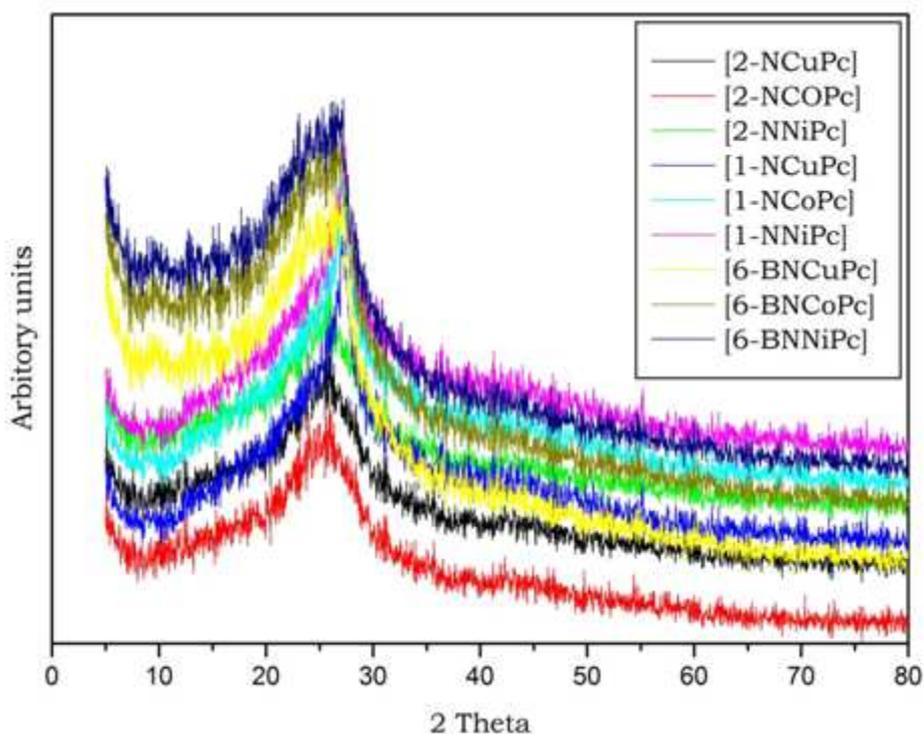
Electronic absorption Spectroscopy is used as an excellent tool for phthalocyanine investigation and characterization. Electronic spectra of the synthesized compounds are recorded in solid state and exhibited characteristic ( $Q_1$ ) band in the region  $\sim$  590-620 nm and a second ( $Q_2$ ) band in the region at  $\sim$  760 to 790 nm. The naphthoxy acet oxadiazole substituents induced redshift and splitting of the Q-band may be attributed due to  $a_2u$ -to-

$e_g$  and  $b_{2u}$ -to- $e_g$  transitions, indicating effective electronic communication between the two different ring systems with in the products (phthalocyanine core and oxadiazole). The shifts in the Q bands may be accounted for the decrease in various  $\pi$  to  $\pi^*$  transitional energies due to extensive conjugation of the  $18\pi$ -electron system towards the atoms of substituent groups. The spectra are shown in fig-1, and results obtained are summarized in table-1.

Table – 2: Data of X-ray diffraction studies

Sl.No	Complex Compound (Code name)	2 -Theta	Lattice spacings D [Å]	Relative Intensity [%]
1	[2-NCuPc]	25.68	3.6253	100.0
		14.31	7.8114	62.5
		31.25	2.3622	56.2
2	[2-NCoPc]	25.70	3.4653	100.0
		12.01	7.0814	56.1
		31.05	2.8622	64.2
3	[2-NNiPc]	25.23	3.1253	100.0
		12.41	7.1104	57.2
		33.05	2.1022	63.8
4	[1-NCuPc]	27.52	3.2401	100.0
		36.31	2.4730	41.92
		46.72	1.9430	17.40
5	[1-NCoPc]	27.99	3.4123	100.0
		33.41	2.3214	42.32
		43.12	1.2365	19.20
6	[1-NNiPc]	27.23	3.4212	100.0
		32.35	2.1215	41.92
		49.25	1.3653	17.40
7	[6-BNCuPc]	26.20	3.4000	100.0
		32.44	2.7259	38.2
		46.72	1.5943	16.7
8	[6-BNCoPc]	26.20	3.4000	100.0
		32.44	2.7591	38.2
		46.72	1.9453	14.9
9	[6-BNNiPc]	27.12	3.1500	100.0
		32.44	2.9215	38.2
		46.72	1.9748	13.6

Figure – 2: X-ray diffraction pattern of the synthesized complexes



### X-Ray Diffraction Studies

The powder X-ray diffraction pattern of synthesized metal (II) phthalocyanines are obtained using Cu- K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). X-ray diffraction studies for the complexes are done in the range  $2\theta$  angles  $2-70^\circ$ . The X-ray diffraction pattern of the complexes showed few peaks in the spectrum indicating the crystalline nature of the sample. The non-crystalline portion simply scatters the X-ray beam to give a continuous base line. The  $2\theta$  angles are obtained from the patterns of the samples, intra planar spacing ( $d$ ) are calculated using the well-known Bragg's equation. Crystallinity of the samples were calculated by using Scherer's formula  $D(hkl) = K\lambda / \beta \cos\theta$ , where  $D$  is the average crystal size,  $\lambda$  is the wavelength of the X- ray irradiation,  $\beta$  is related to the full width half maxima (FWHM) of diffraction peak corrected for the instrumental line broadening using silicon as a standard, and  $\theta$  is angle of diffraction. It was found that the synthesized substituted metal (II) phthalocyanines through the oxadiazole bridge and its derivatives are relatively poor crystalline than the corresponding tetra carboxy metal (II) phthalocyanine. The overlaid patterns are shown in the figure -2. The data are summarized in the table -2.

### Thermal Analysis

Thermal analysis of the synthesizing complexes was carried out in SHIMADZU TA- 60WS thermal analyzer in air at a heating rate of  $5^\circ\text{C min}^{-1}$ , TG analytical curve obtained for title complexes showed that the decomposition of tetra carboxy metal (II) phthalocyanine occurs in two steps. The first step of degradation {occurs in a temperature range  $356-408^\circ\text{C}$  for [TCPcCu],  $360-423^\circ\text{C}$  for [TCPcCo],  $353-403^\circ\text{C}$  for [TCPcNi]} was attributed due to the loss of peripheral carboxylic group and the second step of decomposition {occurs in the temperature range of  $425-476^\circ\text{C}$  for [TCPcCu],  $437-483^\circ\text{C}$  for [TCPcCo],  $416-468^\circ\text{C}$  for [TCPcNi]} was assigned due to gradual destruction of the parent phthalocyanine moiety. Whereas the title complexes undergone decomposition in three steps. First step decomposition in the range { $298-413^\circ\text{C}$  for copper phthalocyanine derivatives,  $298.5-424^\circ\text{C}$  for cobalt phthalocyanine derivatives,  $301.5-409^\circ\text{C}$  nickel phthalocyanine derivatives} was due to the loss of naphthoxy methylene moiety\6-bromo naphthoxy methylene moiety. Second step was because of the loss of oxadiazole group { $442-465^\circ\text{C}$  for copper phthalocyanine derivatives,  $439-476^\circ\text{C}$  for cobalt phthalocyanine derivatives,  $441-460^\circ\text{C}$  nickel phthalocyanine derivatives} and the third step { $502-532^\circ\text{C}$  for copper phthalocyanine derivatives,  $506-534^\circ\text{C}$  for cobalt phthalocyanine derivatives,  $501.5-532^\circ\text{C}$  nickel phthalocyanine derivatives} was assigned for the gradual destruction of the parent phthalocyanine moiety. DTA results revealed that all degradation steps are exothermic in nature. Kinetic and thermodynamic parameters of the complexes have been evaluated by Broido's method [12-13]. Plots of  $\ln(-\ln Y)$  versus  $1/T$  (where  $Y$  is the fraction of the complex undecomposed) were developed and from that the energy of activation ( $E_a$ ) and frequency factor ( $\ln A$ ) were evaluated. Enthalpy ( $\Delta H$ ), Entropy ( $\Delta S$ ) and free energy ( $\Delta G$ ) have been computed using standard equations. The overlaid thermal decomposition pattern is shown in figure-3. The data are summarized in the table-3.

Figure – 3: TGA plots of synthesized complexes

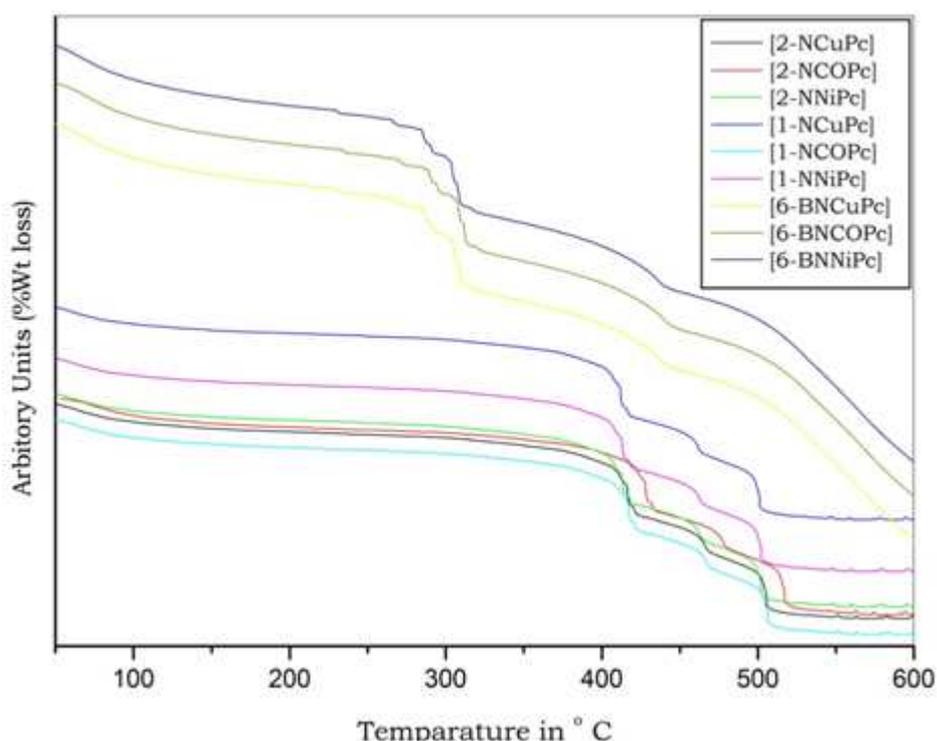


Table – 3: Kinetic and thermodynamic parameters

Complex compound	Decomposition Temperature Range (°C) – Mid temperature.	Ea (kJ/mol)	In A (s-1)	Δ H (kJ/mol)	Δ S (kJ/mol)	Δ G (kJ/mol)
[2-NCuPc]	(404-423)-413.5	34.4520	6.5002	28.7217	-136.90	100.31
	(461-469)-465.0	38.7429	7.3098	32.2989	-153.96	112.80
	(500-513)-506.5	42.2006	7.9621	35.1814	-167.70	122.87
[2-NCoPc]	(416-432)-424.0	35.3269	6.6652	29.4510	-140.38	102.86
	(469-483)-476.0	39.6555	7.4827	33.0629	-157.60	115.47
	(512-525)-518.5	43.1962	8.1429	36.0150	-171.67	125.78
[2-NNiPc]	(397-421)-409.0	34.0737	6.4294	28.4091	-135.41	99.22
	(450-470)-460.0	38.3226	7.2312	31.9516	-152.30	111.59
	(493-510)-501.5	41.7383	7.8835	34.8341	-166.04	121.66
[1-NCuPc]	(403-416)-409.5	33.8083	6.3800	28.1858	-134.35	98.44
	(456-467)-461.5	38.0601	7.1901	31.7650	-151.41	111.08
	(495-510)-502.5	41.4864	7.8289	34.5870	-164.87	120.95
[1-NCoPc]	(407-423)-415.0	34.2624	6.4657	28.5644	-136.16	99.89
	(462-470)-466.0	38.4729	7.2602	32.0747	-152.89	112.16
	(500-512)-506.0	41.7753	7.8834	34.8279	-166.01	121.79
[1-NNiPc]	(403-419)-411.0	33.9321	6.4033	28.2891	-134.84	98.92
	(458-469)-463.5	38.2665	7.2213	31.9027	-152.07	111.56
	(497-515)-506.0	41.7753	7.8834	34.8279	-166.01	121.79
[6-BNCuPc]	(284-312)-298.0	25.1780	4.7501	20.9941	-100.06	73.33
	(433-452)-442.5	37.3868	7.0534	31.1741	-148.59	108.89
	(482-582)-532.0	44.9486	8.4800	37.4794	-178.64	130.92
[6-BNCoPc]	(285-312)-298.5	25.2202	4.7580	21.0293	-100.23	73.46
	(427-451)-439.0	37.0911	6.9976	30.9275	-147.41	108.03
	(486-583)-534.5	45.1937	8.5199	37.6203	-179.48	131.54
[6-BNNiPc]	(288-315)-301.5	25.4737	4.8059	21.2406	-101.24	74.19
	(431-451)-441.0	37.2600	7.0295	31.0684	-148.08	108.53
	(480-585)-532.5	44.9909	8.4880	37.5146	-178.81	131.04

## CONCLUSION

We reported new derivatives of metal (II) phthalocyanines bearing naphthoxy methylene oxadiazole moiety at the periphery. Synthetic method was economical; the products obtained are in good yield and dark green to dull green in colour. As the substitution of naphthoxy methylene oxadiazole moiety to phthalocyanine core enhances the conjugation (showed red shift), the reported derivatives are expected to show higher conductivity (conductivity study is in progress) so that compounds may be more useful material in charge carrier storage devices, hence the title compounds may acquire a great deal of interest in material science.

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