

## Research Article

## Studies on Substituted Cobalt (II) Phthalocyanines

Shoukat Ali R A, J Keshavayya\* and Keerthi Kumar C T

Department of Chemistry, School of Chemical Sciences, Jnana Sahyadri, Kuvempu University, Shankaraghatta - 577 451, Shimoga, Karnataka, India

**Abstract**

The present report describes about the synthesis and studies on 2, 9, 16, 23 - tetra substituted cobalt (II) phthalocyanines through oxadiazole. Which are prepared by the one pot condensation reaction between tetracarboxy cobalt (II) phthalocyanines with various carbo hydrazides in optimized experimental conditions. The title compounds are almost amorphous in nature and bottle green in color. The structural characterizations are made by various physico chemical methods like IR spectral, UV-Vis (electronic spectral), NMR spectral etc. Further X - ray diffraction studies and thermal studies were also performed to know the average crystalline size and thermal stability of the synthesized complexes. Sherrer's equation was used to calculate the average particle size of the compounds (found to be in the range 18 – 85 nm).

**Keywords:** Carbo hydrazides, Thermal studies Cobalt phthalocyanine, oxadiazole,

**\*Correspondence**

Author: J Keshavayya

Email: jkeshavayya@gmail.com

**Introduction**

Phthalocyanines are synthetic, macro cyclic molecules and were discovered over hundred and fifteen years ago. Investigations on phthalocyanines have undergone worldwide intensively because of their interesting special properties and high technological importance. Metal phthalocyanines are generally prepared in high yield by cyclo tetramerization of phthalic acid derivatives. A metal ion brings the reactants together by coordination and the reaction takes place in a series of stereo chemically controlled steps. Metallo phthalocyanines are colored materials which possess high thermal stability, light fastness, and inertness to acids and alkalis. They have been studied in detail for many years, especially with regard to their properties as pigments for printing inks and plastics [1]. Structural similarities of these compounds with naturally occurring biologically important molecules like chlorophyll and hemoglobin, forced the researchers to study the physicochemical properties of phthalocyanines [2]. Various substituted metal phthalocyanines have also been reported as conductors, semiconductors [3], photoconductors, photovoltaic materials, liquid crystals, catalysts, Photodynamic therapy of tumors (PDT), corrosion inhibitors, solar cell functioning materials, gas sensors, nonlinear optical limiting devices etc [4-5]. The researchers from our laboratory have reported many research articles on the synthesis and characterization of various metal phthalocyanine derivatives and reported in journal of good reputation [6-8]. In continuation of research work carried by our researcher we synthesized and characterized oxadiazole substituted cobalt (II) phthalocyanines.

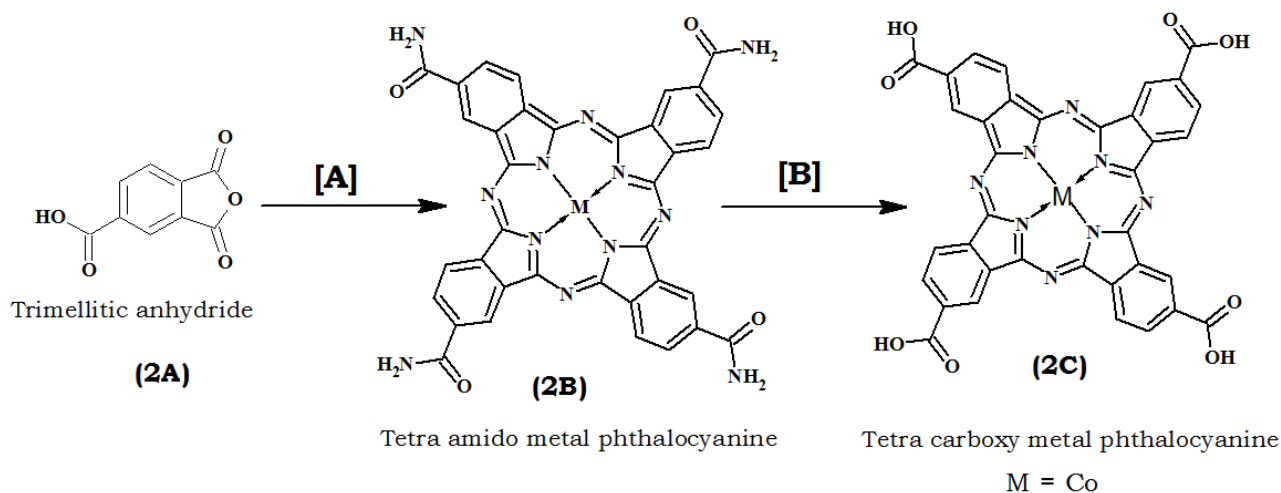
**Experimental****Materials and methods**

1, 2, 4-Benzene tricarboxylic anhydride [trimellitic anhydride] was purchased from Aldrich and other chemicals were obtained from Merck (India) and used as received for the synthesis. Mechanical and magnetic stirring methods are utilized for reaction processes. Tetracarboxy copper phthalocyanine was prepared according to the well reported procedure with slight modification. 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-1 FT-IR spectrometer in the wavelength range of 4000-400 $\text{cm}^{-1}$ . Thermal analysis was carried out in SHIMADZU TA-60WS Thermal Analyzer in air at a heating rate of 5° C min $^{-1}$ .

## Synthesis

### *Synthesis of 2, 9, 16, 23 - tetracarboxy Cobalt (II) phthalocyanine*

Cobalt (II) tetra formamido phthalocyanine was prepared by the reaction of finely powdered 1,2,4-benzene tricarboxylic anhydride (1mole), cobalt chloride (0.4mole), ammonium chloride (10g; 0.45 moles), catalytic amount of ammonium molybdate and excess of urea (~100g) in presence of 100 mL of nitrobenzene. The contents were heated in a three necked flask for seven hours at 185° C. A blue solid cobalt (II) tetra formamido phthalocyanine formed was transferred into 2M potassium hydroxide solution and the reaction was stirred out at 90° C for ten hours until no ammonia was evolved. The resulting solution was diluted with required amount of water and its pH was brought to 3 by adding hydrochloric acid and the contents were then filtered. The residue was dissolved 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 cobalt (II) phthalocyanine was obtained. It was dried over anhydrous phosphorus pentoxide. Synthetic route was outlined in the **scheme 1**.



**[A]** Urea, Ammonium molybdate, Ammonium chloride, Metal salt, Nitrobenzene, 180 - 190°C 9h.

**[B]** 1 M KOH, 90 °C, 10 - 12 h.

**Scheme 1** Synthesis of 2, 9, 16, 23 - tetracarboxy metal (II) phthalocyanines

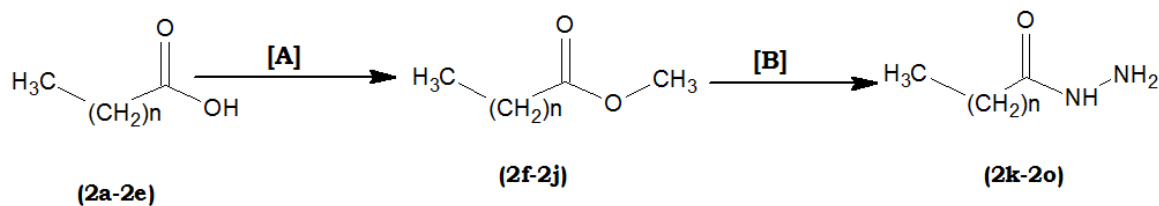
### *Synthesis of aliphatic acid hydrazides*

Various aliphatic acids of varying chain length [decanoic acid to stearic acid] (0.01 mol) was stirred in dry methanol (20-30 mL) for ten minutes; thionyl chloride (0.03 mol) was added drop wise with constant stirring. The mixture was brought to room temperature and refluxed for six hours. The excess methanol was removed by distillation and the shiny-oily product thus obtained was neutralized and extracted in diethyl ether. The ether layer was concentrated to get the methyl ester of the corresponding alkyl carboxylic acids. To a stirred solution of methyl ester alkyl carboxylic acid (0.01 mol) in methanol (25 mL), hydrazine hydrate 99% (0.04 mol) was added drop wise with constant stirring, the reaction mixture was refluxed for eight hours. The reaction mixture was cooled to room temperature and treated with brine solution. The solid product was collected via suction pump filtration, washed repeatedly with brine solution, and recrystallized from ethanol to get pure colorless needle like alkyl acid hydrazides. Synthetic route was shown in **Scheme 2**.

### *Synthesis of alkyl [1,3,4]-oxadiazole substituted metal (II) phthalocyanines*

Tetracarboxy cobalt (II) phthalocyanine (0.001 mol) and aliphatic acid hydrazides (0.006 mol) were stirred into preheated polyphosphoric acid (PPA) (100 g) containing 10 g of phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) at 100° C in a three-

necked round bottom flask containing a mechanical stirrer, condenser, and a thermometer for one hour and then maintained at 150° C for 10 hour. The reaction mixture was allowed to cool to 100° C, quenched with ice cold water and filtered. The product obtained was repeatedly treated with 0.1N sodium hydroxide solution followed by water, hot acetic acid, 10% sodium bicarbonate solution, water, and acetone to get the alkyl [1,3,4] - oxadiazole substituted cobalt (II) phthalocyanines. Synthetic route and structures of alkyl [1,3,4] - oxadiazole substituted metal (II) phthalocyanines was shown in **scheme 3**.

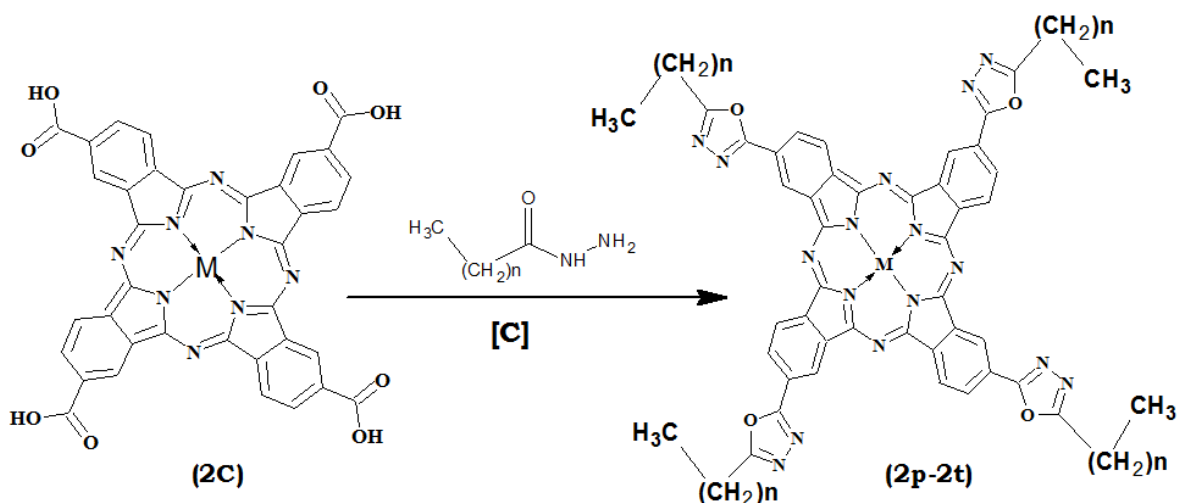


where  $n = 8, 10, 12, 14, 16$

**[A]:** Methanol(dry), Thionyl chloride,  $\Delta$  6 h

**[B]:** Hydrazine hydrate,  $\Delta$  8 h.

**Scheme 2** Synthetic route and structures of the aliphatic hydrazides



Where **[C]:** Poly phosphoric acid, Phosphorous pentoxide, 130 °C,  $\Delta$  10 h

**2p**, M = Co,  $n = 08$     **2q**, M = Co,  $n = 10$     **2r**, M = Co,  $n = 12$

**2s**, M = Co,  $n = 14$     **2t**, M = Co,  $n = 16$

**Scheme 3** Synthesis of 2,9,16,23 - tetra alkyl [1,3,4]-oxadiazole substituted metal phthalocyanines

## Results and Discussions

### IR Spectral Studies

IR spectra of the synthesized complexes are recorded in the region 400–4000  $\text{cm}^{-1}$  using the KBr. Various IR signals responsible 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. However, the presence of functional groups in the periphery is confirmed by their characteristic absorption bands. IR spectra of the

compounds exhibited a series of absorptions at 729–794, 839–847, 926–928, 1088–1093, and 1145–1148  $\text{cm}^{-1}$ , which can be attributed to the skeleton. The presence of peaks at 1610–1626 and 1506–1557  $\text{cm}^{-1}$  are assigned to aromatic  $\text{C}=\text{N}$ - and  $\text{C}=\text{C}$ - in plane skeletal vibrations of the phthalocyanine core respectively. Peaks at 3167–3190  $\text{cm}^{-1}$  are associated with aromatic  $\text{C}-\text{H}$  stretching vibrations and in the region 1089–1093  $\text{cm}^{-1}$  is due to aromatic  $\text{C}-\text{H}$  bending vibrations. However, the comparison of FT-IR spectra of tetracarboxy cobalt (II) phthalocyanine and products reveals some marked differences, the characteristic absorptions due to  $\text{C}=\text{O}$  of  $\text{COOH}$  groups 2C (shown in figure 1) at 1707  $\text{cm}^{-1}$  has disappeared in the IR spectra of one of product 2p (shown in figure 2) indicating the involvement of carbonyl carbon in the formation of the oxadiazole moiety.

### **Electronic Spectral Studies**

Electronic absorption spectroscopy is an excellent tool for phthalocyanine investigation and characterization. Electronic spectra of the synthesized complexes are recorded in solid state and they exhibit characteristic Q-band in the region  $\sim 410 - 480 \text{ nm}$  and a second band (B band) of moderate intensity in the region at  $\sim 560$  to  $670 \text{ nm}$ . The electron-acceptor oxadiazole pendants at the periphery of phthalocyanine induced red shift and splitting of the Q-band due to  $a_{2u}$ -to- $e_g$  and  $b_{2u}$ -to- $e_g$  transitions, indicating effective electronic communication between the two different ring systems of the phthalocyanine core and oxadiazole moiety. UV-Vis spectra of cobalt (II) phthalocyanines were shown in figure 3 and data are summarized in table 1.

### **X-ray diffraction studies**

The powder X-ray diffraction patterns of oxadiazole substituted cobalt (II) phthalocyanine are obtained using  $\text{Cu} - \text{K}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ), which are shown in figure 4 and the data are shown in table 2. Powder X-ray diffraction methods based on the study of the pattern of diffracted rays produced when monochromatic beam strikes the specimen. The degree of crystallinity of the sample can be determined using X-ray powder patterns. The non-crystalline portion simply scatters the X-rays to give a continuous base line or background. Crystallinity of the samples were calculated by using Scherer's formula  $D = K\lambda/\beta\cos\theta$ , where  $D$  is the average crystalline size,  $\lambda$  is the wavelength of the X-ray irradiation,  $K$  is constant usually taken as 0.89,  $\beta$  is the full width half maxima (FWHM) of diffraction peak corrected for the instrumental line broadening using silicon as a standard and  $\theta$  angle of diffraction. It is evident that the X-ray diffraction patterns of the alkyl [1,3,4]-oxadiazole substituted metal (II) phthalocyanines are amorphous in nature. The diffraction pattern of the aliphatic oxadiazole substituted metal phthalocyanines exhibits almost identical broad peaks with relatively slight variable diffused intensity, but it is observed that the peak intensity gradually increased with increase in the methylene group in the alkyl chain which is very much comparable with the reported literature.

### **Thermo gravimetric studies**

Thermal analysis of the synthesized complexes was carried out in SHIMADZU TA-60WS thermal analyzer in air at a heating rate of  $5^\circ\text{C min}^{-1}$ . It was noticed that there is no clear cut step wise decomposition of the phthalocyanine compounds but a gradual degradation was observed. The Kinetic and thermodynamic parameters of the complexes were deduced using Broido's graphical procedure for the straight line decomposition of the thermo gravimetric analytical curves. The graphical Plots of  $\ln(-\ln 1/y)$  versus  $1/T$  (where  $Y$  is the fraction of the complex undecomposed) were developed and from the slopes of those plots, energy of activation ( $E_a$ ) and frequency factor ( $\ln A$ ) were evaluated. The activation energy depends on the chemical structure and crystalline nature of the complex. If the crystallinity of the material is higher, the activation energy will also be higher. Thermodynamic properties like change in enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and free energy ( $\Delta G$ ) have been computed using standard equations.

### **Analytical Data**

#### **2, 9, 16, 23 - tetracarboxy Cobalt (II) phthalocyanine[2C]**

% Yield: 62; Molecular Formula -  $\text{C}_{36}\text{H}_{16}\text{N}_8\text{CoO}_8$ : % Elemental analysis; calculated: C(57.84), H(2.16), Co(7.88), N(14.99) and O(17.12). Found: C(57.78) H(2.26), N(15.16). IR [(KBr), ( $1/\lambda$ ) in  $\text{cm}^{-1}$ ]: 3397 $\text{cm}^{-1}$  ( $-\text{OH}$ ), 3012  $\text{cm}^{-1}$

(Ar. CH),  $1530\text{cm}^{-1}$  (Ar. C=N),  $1707\text{cm}^{-1}$  (C=O) and other signals at 1243, 1042, 1614,  $1078\text{cm}^{-1}$  reflects on the skeletal vibrations of the phthalocyanine molecule. Uv-Vis (solid state)  $\lambda_{\text{max}}$  in nm: 483, 585.

#### ***Decanoic acid hydrazide[2k]***

Yield- 70% ; IR [(KBr), (1/  $\lambda$ ) in  $\text{cm}^{-1}$ ]: 3282 (–NH str.), 3179 (–NH<sub>2</sub> str.), 2911 (–C–H str.), 1629 (–C=O str.); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 8.87 (br, s, –NH, 1H), 4.1 (s, –NH<sub>2</sub>, 2H), 1.99–1.94 (br, m, –CH, 2H), 1.44 (br, –CH, 2H), 1.2 (br, –CH, 12H), 0.83–0.81 (br, m, –CH<sub>3</sub>, 3H).

#### ***Lauric acid hydrazide [2l]***

Yield- 72% ; IR [(KBr), (1/  $\lambda$ ) in  $\text{cm}^{-1}$ ]: 3316 (–NH str.), 3180 (–NH<sub>2</sub> str.), 2919 (–C–H str.), 1629 (–C=O str.); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 8.89 (br, s, –NH, 1H), 4.2 (s, –NH<sub>2</sub>, 2H), 1.99–1.94 (br, m, –CH, 2H), 1.45(br, –CH, 2H), 1.22–1.13 (br, m, –CH, 16H), 0.84–0.81 (br, m, –CH<sub>3</sub>, 3H).

#### ***Myristic acid hydrazide[2m]***

Yield- 70% ; IR [(KBr), (1/  $\lambda$ ) in  $\text{cm}^{-1}$ ]: 3314(–NH str.), 3179 (–NH<sub>2</sub> str.), 2921(–C–H str.), 1630 (–C=O str.); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 8.87 (br, s, –NH, 1 H), 4.1 (s, –NH<sub>2</sub>, 2H), 1.99–1.94 (br, m, –CH, 2H), 1.45 (br, –CH, 2H), 1.28–1.14 (br, –CH, 20 H), 0.83–0.81 (br, m, –CH<sub>3</sub>, 3H).

#### ***Palmitic acid hydrazide[2n]***

Yield-56% ; IR [(KBr), (1/  $\lambda$ ) in  $\text{cm}^{-1}$ ]: 3318 (–NH str.), 3180 (–NH<sub>2</sub> str.), 2919 (–C–H str.), 1630 (–C=O str.); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 8.89 (br, s, –NH, 1H), 4.2 (s, –NH<sub>2</sub>, 2H), 1.99–1.94 (br, m, –CH, 2H), 1.44 (br, –CH, 2H), 1.23–1.14 (br, –CH, 24H), 0.83–0.81 (br, m, –CH<sub>3</sub>, 3H).

#### ***Stearic acid hydrazide[2o]***

Yield- 59% ; IR [(KBr), (1/  $\lambda$ ) in  $\text{cm}^{-1}$ ]: 3318 (–NH str.), 3185 (–NH<sub>2</sub> str.), 2919 (–C–H str.), 1629 (–C=O str.); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 8.87 (br, s, –NH, 1H), 4.1 (s, –NH<sub>2</sub>, 2H), 1.99–1.94 (br, m, –CH,2H), 1.44 (br, –CH, 2H), 1.2 (br, –CH, 28H), 0.83–0.81 (br, m, –CH<sub>3</sub>, 3H).

#### ***Tetra {2-nonyl [1,3,4]-oxadiazole} - cobalt (II) phthalocyanine (2p)***

% yield – 62; Molecular Formula - C<sub>76</sub>H<sub>88</sub>CoN<sub>16</sub>O<sub>4</sub>; Elemental Composition(%), calculated: C(67.69), H(6.58), Co(4.37), N(16.62) and O(4.75%) ; Found: C(67.73), H(6.76), and N(16.40). IR [(KBr), (1/  $\lambda$ ) in  $\text{cm}^{-1}$ ]: 1610 (C=N), 2820, 3038 (Ar-CH), 1411 (C=C), and other signals at (1243, 1089, 945, 813 etc) corresponds to phthalocyanine skeletal vibrations.

#### ***Tetra {2-undecyl [1,3,4]-oxadiazole} - cobalt (II) phthalocyanine (2q)***

% yield – 68; Molecular Formula - C<sub>84</sub>H<sub>104</sub>CoN<sub>16</sub>O<sub>4</sub>; Elemental Composition(%) calculated: C(69.07), H(7.18), Co(4.03), N(15.34) and O(4.38); Found: C(68.88), H(6.49) and N(15.32). IR [(KBr), (1/ $\lambda$ ) in  $\text{cm}^{-1}$ ]: 1613 (C=N), 3009 (Ar-CH), 1510 (C=C), and other signals at (1413, 1244, 1091, 976) corresponds to the phthalocyanine skeletal vibrations.

#### ***Tetra {2-tridecyl [1,3,4]-oxadiazole} - cobalt (II) phthalocyanine (2r)***

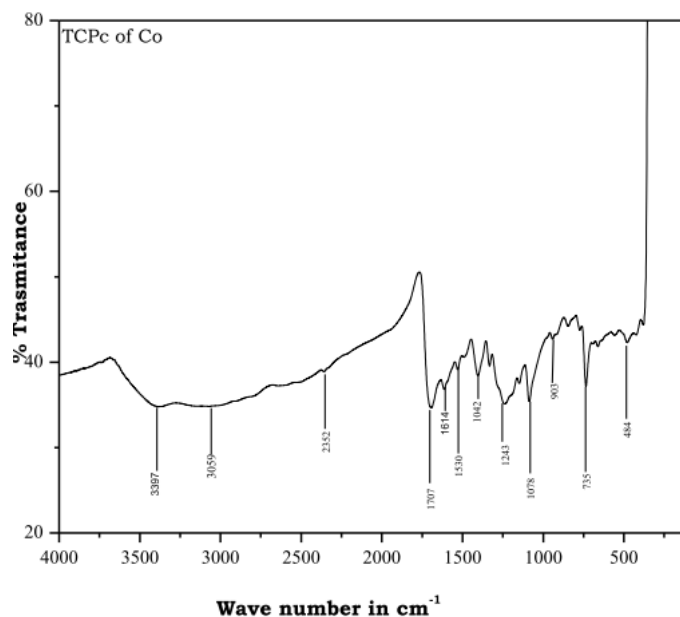
% yield – 70; Molecular Formula - C<sub>92</sub>H<sub>120</sub>CoN<sub>16</sub>O<sub>4</sub>; Elemental Composition(%) calculated: C(70.25), H(7.69), Co(3.75), N(14.25) and O(4.07); Found: C(68.36), H(7.89) and N(15.30). IR [(KBr), (1/ $\lambda$ ) in  $\text{cm}^{-1}$ ]: 1628 (C=N), 1559 (C=C), 3010 (Ar-CH), and other signals at (1382, 1239, 1091, 960) corresponds to the phthalocyanine skeletal vibrations.

***Tetra {2-pentadecyl [1,3,4]-oxadiazole} - cobalt(II) Phthalocyanine (2s)***

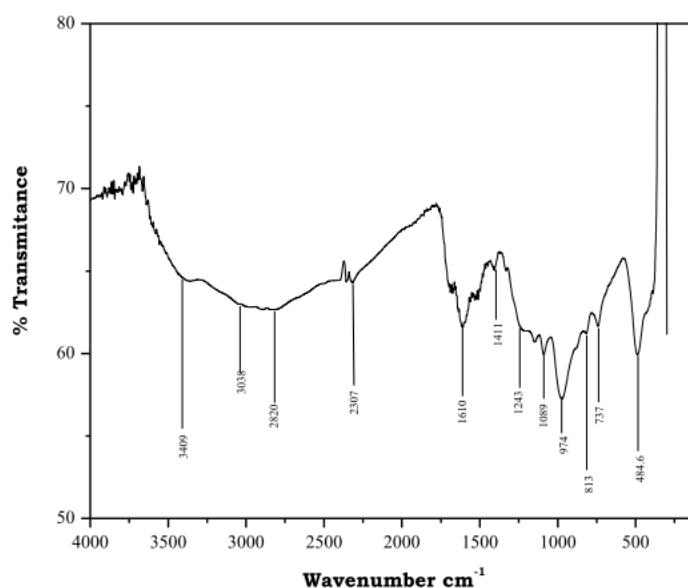
% yield – 72; Molecular Formula -  $C_{100}H_{136}CoN_{16}O_4$ ; Elemental Composition(%) calculated: C(71.27), H(8.13), Co(3.50), N(13.30) and O(3.80); Found: C(69.43), H(7.42) and N(14.37). IR [(KBr),  $(1/\lambda)$  in  $cm^{-1}$ ]: 1613 (C=N), 3013 (Ar-CH), 1510 (C=C), and other signals at (1414, 1245, 1092, 977) corresponds to the phthalocyanine skeletal vibrations.

***Tetra {2-heptadecyl [1,3,4]-oxadiazole} - cobalt (II) phthalocyanine (2t)***

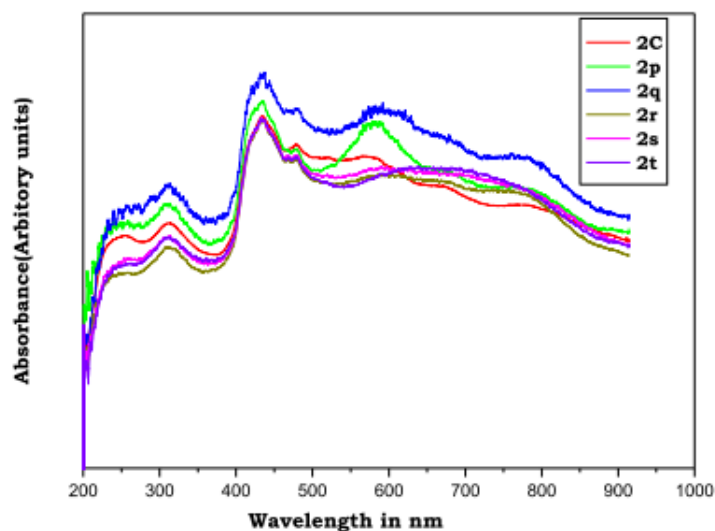
% yield – 70; Molecular Formula -  $C_{108}H_{152}CoN_{16}O_4$ ; Elemental Composition(%) calculated: C(72.17), H(8.52), Co(3.28), N(12.47) and O(3.56); Found: C(70.67), H(7.21) and N(14.24). IR [(KBr),  $(1/\lambda)$  in  $cm^{-1}$ ]: 1612 (C=N), 3016 (Ar-CH), 1508 (C=C), and other signals at (1407, 1720, 1245, 1093, 796) corresponds to phthalocyanine skeletal vibrations.



**Figure 1** IR Spectrum of 2, 9, 16, 23 – tetra carboxy cobalt (II) phthalocyanine



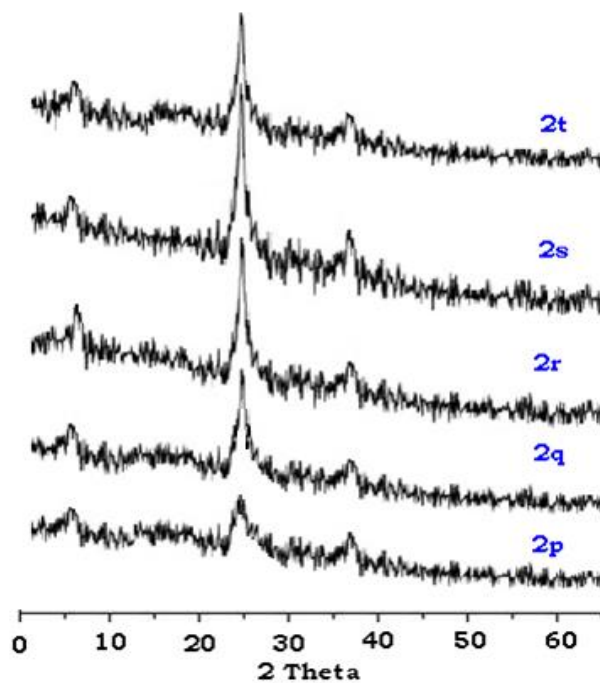
**Figure 2** IR Spectrum of 2, 9, 16, 23 – tetra oxadiazole substituted cobalt (II) phthalocyanine.



**Figure 3** UV-Vis spectra of cobalt (II) phthalocyanines.

**Table 1** UV-Vis spectral data of cobalt (II) phthalocyanines

S. No	Compound code	Peaks $\lambda_{\max}$ (in nm)
01	2C	483, 585
02	2p	454, 589, 698, 783
03	2q	438, 592, 679, 784
04	2r	438, 606, 682, 778
05	2s	439, 596, 698, 779
06	2t	436, 609, 689



**Figure 4** X-ray diffraction patterns of cobalt (II) phthalocyanines.

**Table 2** X-ray diffraction data of cobalt (II) phthalocyanines

S.No	Compound Code	2-Theta	Lattice spacing (d) [Å]	Relative Intensity [%]
01	2p	5.587	15.8046	13.16
		25.99	03.3352	92.36
02	2q	5.995	14.2463	43.64
		25.96	03.5492	99.46
03	2r	5.812	11.6164	23.62
		26.11	03.5592	100.0
04	2s	5.126	13.2439	29.42
		25.92	03.3761	100.0
05	2t	5.021	14.6182	21.46
		26.19	03.3342	82.25

## Conclusions

We followed a convenient, economical and useful method for the synthesis of tetra oxadiazole substituted cobalt (II) phthalocyanine compounds in good yield. Thermo gravimetric studies revealed that the complexes are thermally more stable than the starting material. From powder X-ray diffraction studies we came to know that synthesized complexes are amorphous in nature and average crystallinity is in the nanometer range. As the substitution of oxadiazole moiety to phthalocyanine core enhances the conjugation, (red shift in the electronic spectra) the title compounds may be more useful materials in the preparation of charge storage/carrier devices. Study about these compounds under the heading Liquid Crystal is under progress.

## References

- [1] Phthalocyanines Properties and Applications, Leznoff CC and Lever ABP. VCH Publishers, New - York, vol 1-3, 1989-1993.
- [2] The Porphyrin Handbook, K.M. Kadish, K.M. Smith and R. Guilard, Vol. 19, Academic Press, San Diego, 2003.
- [3] Decorating nickel phthalocyanine periphery by aryl-1,3,4-Oxadiazolependants, M. N. K. Harisha, J. Keshavayya, K.R. Venugopala Reddy, H. R. Mallikarjuna, R.A. Shoukat Ali, T.Rajesh, : Jouranl of Coordination Chemistry, Vol. 63, 2010, 4050.
- [4] Forest I. Bohrer, Corneliu N. Colesniuc, J. Am. Chem. Soc. Vol. 131, 2009, 477.
- [5] ChuanXiang Sheng, Robert A. Norwood, Applied Optics, Vol. 48, 2009, 2731.
- [6] Synthesis and characterization of 2, 9, 16, 23 - tetra anilido nickel (II) phthalocyanines, Shoukat Ali R.A., Keshavayya J., Harish M.N.K., RajeshaT and Prashantha A.G, International Journal of ChemTech Research, Vol 3(3), 2011, 1146-1151.
- [7] Synthesis and Characterization of novel oxadiazole substituted metal Phthalocyanines, Shoukat Ali R.A., Keshavayya J., Prasanna. S., Rajesha and Keerthi Kumar C. T., Archives of Applied Science Research, vol5 (2), 2013, 189-196.
- [8] Synthesis and Characterization of Tetraformamido [2-amino-5-(phenyl) thiazole] substituted metal Phthalocyanines, Tantry Rajesh N., Jathi Keshavayya, Prasanna S.M., Angadi Shoukat Ali R. and Chinnagiri Keerthi Kumar T., Res. J. Chem. Sci., Vol. 4(1), 2014, 1-6.

## Publication History

Received	31 <sup>st</sup> Mar 2016
Accepted	04 <sup>th</sup> May 2016
Online	30 <sup>th</sup> June 2016

© 2016, by the Authors. The articles published from this journal are distributed to the public under “Creative Commons Attribution License” (<http://creativecommons.org/licenses/by/3.0/>). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.