"Synthesis, Spectral, Magnetic, Thermal and Antimicrobial Studies of Symmetrically Substituted 2, 9, 16, 23- tetraphenylpropene-1-imino phthalocyanine complexes"

M. H. Moinuddin Khan [1*], S. Raghavendra [4], S. G. Chethan [1], K. R. Venugopala Reddy[2], J. Keshavayya[3]

[1*] *Department of Chemistry, Jawaharlal Nehru National College of Engineering, Shimoga-577204, Karnataka, India*

[2] *Dept. of PG Studies & Research in Chemistry, Vijayanagar Sri Krishnadevaraya University, Bellary-583104, Karnataka, India.*

[3] *Department of PG Studies & Research in Chemistry, School of Chemical Sciences, Kuvempu University, Jnanasahyadri, Shankaraghatta – 577 451, Shimoga, Karnataka, India.*

[4] *Department of Biochemistry, University of Horticultural Sciences, Bagalkot-587102, Karnataka, India*

Correspondence author: Dr. M. H. Moinuddin Khan.

Abstract: **- Present paper describes the synthesis and characterization of metal (II) 2, 9, 16, 23-tetra-phenylpropene-1-imino phthalocyanines (M-PhproImPc) of Co (II), Cu (II), Ni (II) and Zn (II). The dark bluish green colored tetraimino substituted phthalocyanine derivatives were characterized by the various physico-chemical techniques like elemental analysis, magnetic susceptibility, UV-Visible, IR, powder X-ray diffraction and thermogravimetric analysis (TGA) to check the structural integrity, purity and thermal stability. The variations of magnetic moment as a function of field strength indicated the presence of inter molecular co-operative interactions. Above said compounds were screened for their antibacterial and antifungal activities.**

Keywords: **Interactions; Magnetic, Phenylpropene, Substituted, Susceptibility.**

I. INTRODUCTION

Phthalocyanines are planar macro cyclic aromatic ligands related to porphyrins and constituted by four isoindole units consisting of 18 π-electron cloud delocalized over an arrangement of alternative carbon and nitrogen atoms. A great number of unique properties arise from this electronic delocalization, which makes these compounds applicable in different fields of material science. Phthalocyanines are the second most important class of colorant and copper phthalocyanine is the single largest volume colorants sold. Various substituted metal phthalocyanines have been extensively used in solar cells, fuel cells, electrochorism and photochorisim, optical memory and data storage devices, liquid crystal displays, as dyes and pigments and in photodynamic therapy of cancer. The above class of compounds has also found extensive use in many modern high technologies, cyan dyes for inkjet printing, electro photography, as charge generation materials for laser printers and as colorants for cyano toners. Recently more intensive research work was initiated in this field to develop substituted metal phthalocyanine derivatives as catalysts [1-2], photoconductors [3], photosensitizers [4], photovoltaics [5] and semiconductors [6]. Metallophthalocyanines attract a great deal of interest in medicine for the treatment of cancer by photodynamic therapy (PDT) [7-9] and as electric carpets with deodorizer properties for indoor air [10].

Eventhough the information on synthesis and characterization of metal (II) 2, 9, 16, 23-tetraaminophthalocyanines were documented [11] in the literature, no evidences are available on synthesis and structural studies on metal (II) 2, 9, 16, 23-tetraimino phthalocyanines starting from the respective amino phthalocyanine complexes.

In the present paper we report the synthesis, structural investigations and magnetic susceptibility studies of

2, 9, 16, 23-tetraimino phthalocyanine complexes of cobalt (II), nickel (II), copper (II) and zinc (II). The procedure available from the literature [11-13] was suitably modified for the synthesis of title complexes. The title complexes have also been synthesized by microwave assisted method. Such microwave assisted synthesis of complexes was proved to be ecofriendly and **greener** method compared to conventional method. Reported compounds are non toxic and do not have any hazardous impact on the environment. Moreover use of microwave has enhanced the yield of complexes appreciably.

II. MATERIAL AND METHODS

A Varian Cary 5000 with 1 cm width silica cell was used for electronic absorption spectral studies. IR spectra were recorded using a Nicolet MX-FT IR spectrometer. A Philips analytical PW-1710 X-ray diffractrometer was used to study the diffraction patterns of the complexes. The spectra were recorded using Cu Kα at a voltage of 40 kV, a current of 20 mA, a time constant of 4, a channel width of 7 mm and a chart speed of 10 mm/min. C, H and N elemental analyses were done by STIC, Kochi, Kerala, India. Magnetic susceptibility studies of the complexes were carried out at room temperature using a Gouy magnetic balance consisting of NP-53 type electromagnets with a DC power supply unit and a semi microbalance. Pascal's constants were used to calculate the diamagnetic corrections. A mercury tetrathiocyanato cobaltate, $Hg[Co(SCN)_4]$ complex was used as calibrant [14]. TGA studies were carried out by using a Perkin Elmer TG/DTA thermal analyzer at a heating rate of 10^o/min both in the air and nitrogen atmosphere.

III. EXPERIMENTAL

Pure 4-nitrophthalic acid was prepared by using phthalic anhydride by adopting the procedure reported elsewhere [11]. All other chemical reagents were used as received. Metal (II) 2, 9, 16, 23-tetraphenylpropene-1-imino phthalocyanines were prepared by conventional and microwave technique as per the scheme 1.

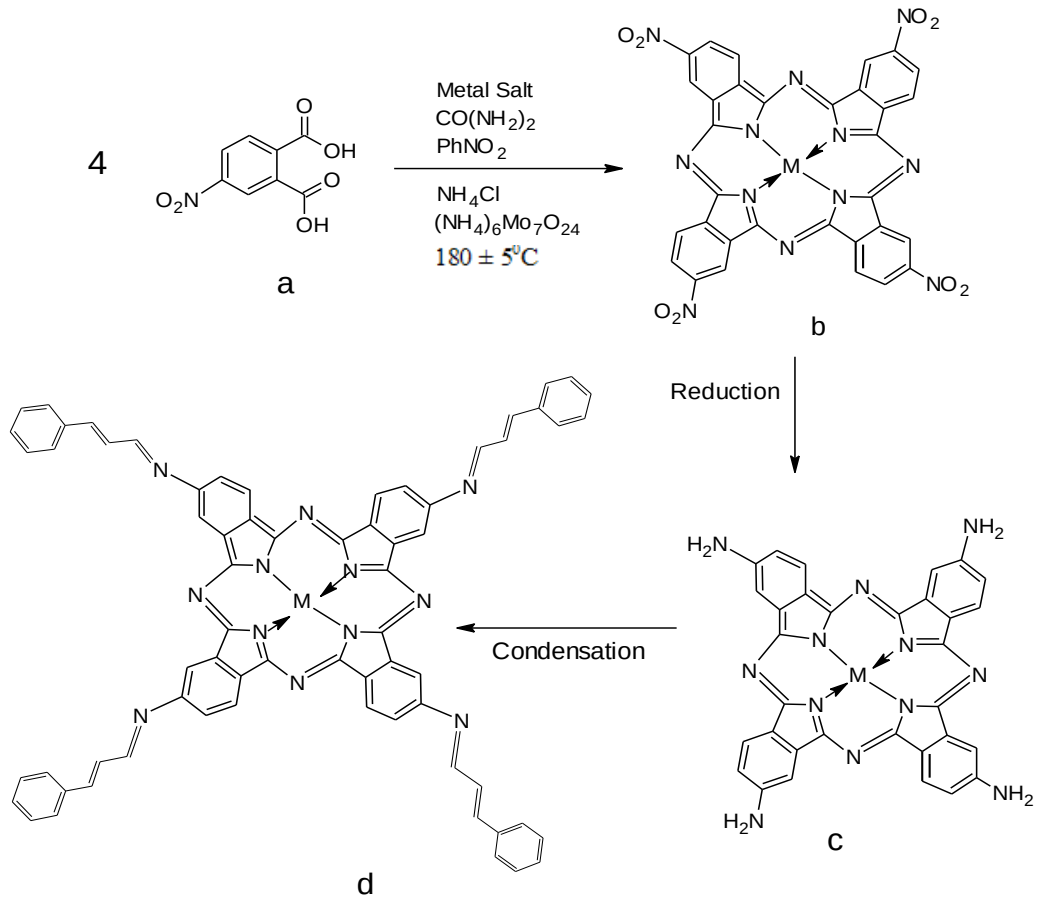
3.1. Preparation of cobalt (II) 2, 9, 16, 23-tetraphenylpropene-1-imino phthalocyanine (Co-PhproImPc) by conventional method:

The procedure adopted for the synthesis of cobalt (II) 2, 9, 16, 23-tetranitro phthalocyanines (M-PcTN) was reported elsewhere [11]. The nitro derivative of the complex was converted into amino derivative quantitatively by reduction using sodium sulfide nonahydrate in aqueous medium [19]. The finely powdered cobalt (II) 2, 9, 16, 23-tetraamino phthalocyanine (M-PcTA) (6.30 g 0.01 mole) was dissolved in DMSO and stirred with respective molar quantity of cinnamaldehyde (4.9 ml, 0.01 mole). Above mixture was refluxed for 5 hours in the presence of catalytic quantity of concentrated sulphuric acid. The contents were poured onto ice cold water. The settled bluish green colored precipitate of condensed imino phthalocyanine complex was washed alternatively with ethyl alcohol and acetone several times until it was free from cinnamaldehyde. The resulting solid product was dried in vacuum over anhydrous phosphorous pentoxide (P_2O_5). The yield of the complex was found to be about 48 %.

3.2. Microwave assisted synthesis of cobalt (II) 2, 9, 16, 23-tetraphenylpropene-1-imino phthalocyanine (Co-PhproImPc):

The finely powdered cobalt (II) 2, 9, 16, 23-tetraamino phthalocyanine (M-PcTA) (6.30 g 0.01 mole) was dissolved in stoichiometric quantity of dimethyl sulphoxide (DMSO) taken in 500 ml beaker and stirred with respective molar quantity of cinnamaldehyde (4.9 ml, 0.01 mole) in the presence of catalytic quantity of concentrated sulphuric acid. It was then irradiated in microwaves for about 5 minutes. The contents were poured onto ice cold water. The settled bluish green colored precipitate of condensed iminophthalocyanine complex was washed alternatively with ethyl alcohol and acetone several times until it was free from cinnamaldehyde. The resulting solid product was dried in vacuum over anhydrous P_2O_5. The yield of the complex was found to be about 65 %.

The pigment form of the above complex was obtained by the acid pasting process, in which 1 part of powdered sample was dissolved in 6-10 parts of concentrated sulphuric acid. The mixture was allowed to stand for 1-2 hour and then poured onto 45-50 parts of crushed ice and stirred thoroughly. The pigments thus obtained were filtered off and washed with hot water. Finally it was washed with distilled water and dried in vacuum over P_2O_5.



Scheme 1: Synthesis of Metal (II) 2, 9, 16, 23-tetra-phenylpropene-1-imino phthalocyanines,
a) 4-nitrophthalic acid, b).M-PcTN, c) M-PcTA and d) M-PhproImPc.

Metal (II) 2, 9, 16, 23-tetraphenylpropene-1-imino phthalocyanines of Cu (II), Ni (II) and Zn (II) were prepared using the respective metal (II) amino phthalocyanines by employing the above procedure.

IV. RESULT AND DISCUSSIONS

The procedure adopted for the synthesis of M-PhproImPcs yielded pure complexes. The title complexes are dark bluish green in color. These complexes gave a clear solution in DMSO, DMF, pyridine and concentrated sulfuric acid and were sparingly soluble in alcohol. The results of elemental analyses for carbon, hydrogen, nitrogen and gravimetric methods for metals (Table 2) were in good agreement with the calculated values and were consistent with the proposed structure.

4.1. Electronic spectra:

The electronic spectra of M-PhproImPc's were recorded in dimethyl formamide (DMF) in the concentration range of 1.0-1.5 x 10^{-5} M and the summary of the results were presented in Table 1 and graphs in Fig. 1. The observed deep bluish green color of the complexes may be due to $a_{2u} \rightarrow e_g$ and $b_{2u} \rightarrow e_g$ transitions [8]. For all the complexes absorption bands were observed in the wavelength 746-769 nm, which are considerably higher than the corresponding parent metal phthalocyanine [8]. This observed red shift was attributed to the increase in conjugation of π-electron of the phthalocyanine molecule with that of peripheral substituted aromatic imino groups. The splitting of the Q-band was observed in all the complexes and appeared in the range of 446-475 nm. The origin of the Q-band was attributed to the $a_{1u} \rightarrow e_g$ transition of the phthalocyanine molecule. A sharp and intense B-band was observed for all the complexes in the range of 331-355 nm.

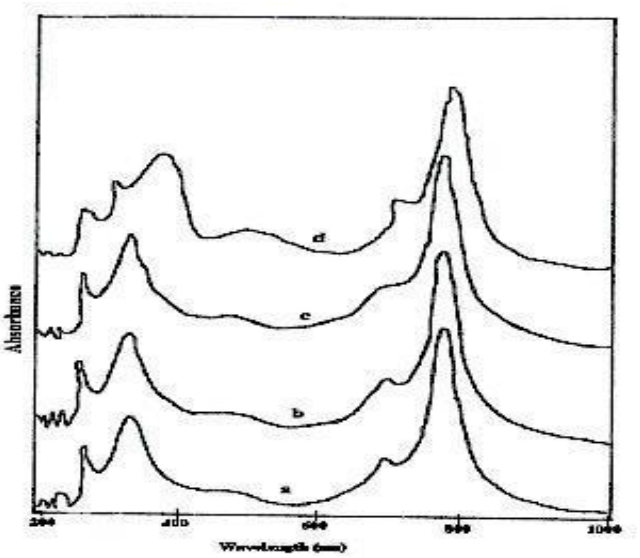


Figure 1. Electronic spectra of (a) Co–PhproImPc, (b) Cu–PhproImPc, (c) Ni–PhproImPc and (d) Zn–PhproImPc recorded in DMF.

4.2. IR Spectra:

IR spectral data were recorded in KBr pellets and the only selected bands responsible for various vibrations of the functional groups are summarized in Table 1, and the graphs in Fig. 2. The sharp peaks of M-PhproImPc's at 1631-1638 cm^{-1} are attributed to C=N of aromatic imino group and peaks in the range of 1486-1497 cm^{-1} are due to C—N aromatic stretching. The peaks observed in the range of 1310-1341 cm^{-1} are due to C—H symmetric bending. All the remaining bands observed in the range 742-752 and 607-700 cm^{-1} may be assigned to various skeletal vibrations of the phthalocyanine ring [8].

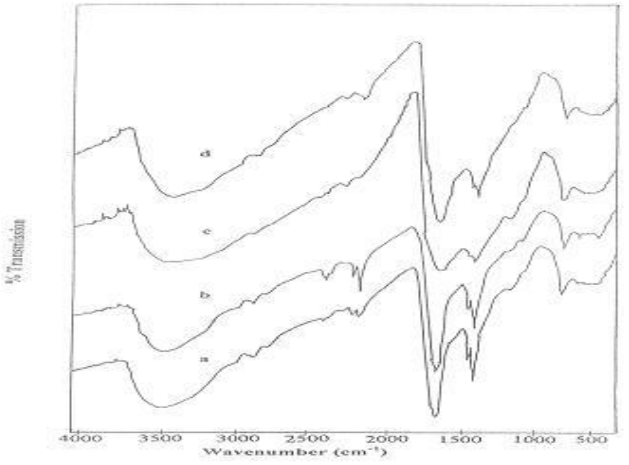


Figure 2. IR absorption spectra of (a) Co–PhproImPc, (b) Cu–PhproImPc, (c) Ni–PhproImPc and (d) Zn–PhproImPc.

4.3. Powder XRD:

The powder X-ray diffraction patterns of M-PhproImPc's were taken through a range of 2θ angles 6-70^0 showed identical peaks with relatively very poor crystallinity (Table 1, Fig. 3). The observed patterns are very much similar to that of unsubstituted parent phthalocyanines except for broadening of the peaks with diffused intensity. The broadening may be due to the presence of substitutents at the periphery of the molecule, which seems to provide hindrance for the effective stacking of the molecule and thus the poor crystallinity of the complexes.

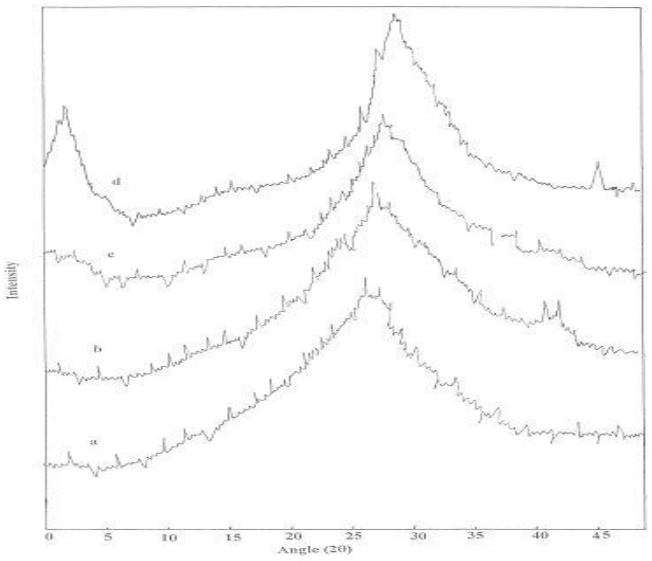


Figure 3. Powder X-ray diffraction patterns of (a) Co–PhproImPc, (b) Cu–PhproImPc, (c) Ni–PhproImPc and (d) Zn–PhproImPc.

4.4. Magnetic Susceptibility:

Magnetic susceptibility studies were carried out at ambient temperature and summary of the results are in Table 2, and the magnetic moment values reported in the table are the average of three independent determinations. The magnetic susceptibility studies revealed that Co-PhproImPc and Cu-PhproImPc are paramagnetic whereas Ni-PhproImPc and Zn-PhproImPc are diamagnetic. The measured magnetic moments for Co-PhproImPc and Cu-PhproImPc are higher than the spin only value corresponding to the one unpaired electron (1.73 BM), due to the mixing of ground state orbitals with higher energy degenerate states and intermolecular co-operative effect [14]. This effect decreases with the increase in field strength and μ_{eff} value approaches spin only value at higher field strength. The observed higher μ_{eff} value at lower field strength is attributed to intermolecular magnetic

interaction coupled with magnetic anisotropy of phthalocyanine π-current [15]. The crystallographic studies revealed that the metal phthalocyanines of Co, Cu, Ni and Zn have square planar structure with D_{4h} symmetry and are isomorphous. The molecular plane is approximately normal to a-b plane and molecules are stacked along the short b-axis. The molecular planes are inclined to the a-c axis at an angle of 45°. Thus the complexes stacked in columns with N-atom above and below on every metal atom (Fig. 4) and hence the nearest neighboring molecule along the b-axis contributes a nitrogen atom at the interplanar distance 3.4 Å [16].

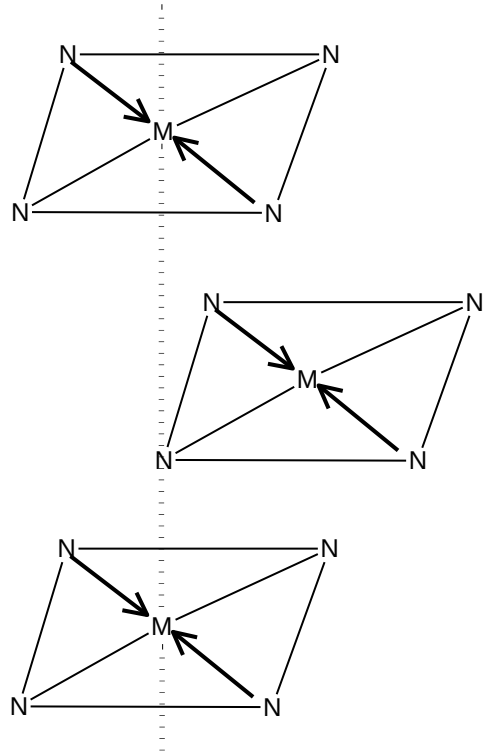


Figure 4: Probable molecular stacking of metal phthalocyanines.

M = Cu, Co, Ni and Zn, N = azamethine atom of phthalocyanine.

4.5. Thermogravimetric and Kinetic Studies:

Thermogravimetric analytical data of imino substituted metal phthalocyanine complexes are summarized in the Table 3. It was observed that the decomposition of the above complexes in air occurs generally in two steps. The first step of degradation which takes place in the temperature region of 128-360°C may be accounted for the loss of four imino groups. The major weight loss was observed in the last step for all the complexes in the temperature region of 360-580°C corresponds to the oxidative degradation of phthalocyanine moiety. Destruction of phthalocyanine macrocycle occurs generally in the second step. The residues remained after the thermal decomposition was found to be the corresponding metal oxides [17]. The thermal decomposition of these imino substituted complexes in the nitrogen atmosphere appears to be very slow. For Co-PhproImPc, 65% of the complex was found to be decomposed at 700° C. For Cu-PhproImPc, Ni-PhproImPc and Zn-PhproImPc about 62%, 58% and 52% loss of the mass was observed even at 700°C. The above trend confirms the relatively higher stability of these complexes in nitrogen atmosphere than that in air. Even though, all the four functional groups seem to be lost during first step, a dimer or a polymer is suspected to be formed via the nitrogen atoms of the peripheral end groups before the second step of decomposition starts [18]. DTA results revealed that all degradation steps are exothermic in nature. Kinetic and thermodynamic parameters of the title complexes have been evaluated by Broido's method [19]. Plots of ln (ln1/y) versus 1/T (where y is the fraction of the complex undecomposed) were developed for the decomposition segment where loss of functional groups occur. From the plots, energy of activation (Ea), frequency factor (ln A), enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) of the title complexes have been computed by using standard equations (Table 4).

4.6. Antimicrobial Activities:

The ligand and all the complexes synthesized in the present investigation and the respective metal salts were evaluated for their antifungal and antibacterial activity.

4.6.1. Antifungal Activity:

Aspergilus niger and *Aspergilus flavus* were procured from the department of Biotechnology, Sahyadri Science College, Shimoga.

The *Aspergilus niger* and *Aspergilus flavus* were studied for its growth, color and sporulation characteristics in the presence of the selected metal phthalocyanine complexes. The 200 ppm solutions of the each M-PhproImPc complexes were prepared by dissolving the required quantity of complexes in DMF. The corresponding tetra amino phthalocyanine complexes were also dissolved in DMF to prepare 200 ppm solution and antifungal studies were carried out under similar conditions for comparison. Above solutions were further diluted with DMF to get 50 ppm, 100 ppm and 150 ppm solutions. Control was maintained by adding 2 mL of DMF to the media separately. Potato Dextrose Agar (PDA) media with the above preparations were sealed with aluminum

foil and sterilized in an autoclave at a temperature of 120 ^{o}C and 15 psi. The hot sterilized media was poured into petriplates in an aseptic chamber and then cooled to room temperature (26 ^{o}C). The *Aspergilus niger* and *Aspergilus flavus* were inoculated as a point at the center of the plate and were incubated at 23±1 ^{o}C for one week and the observations were made daily and the summary of the observations were presented in Table 5. It was found that all the M-PhproImPc complexes inhibited the radial growth of the fungi compared to the corresponding tetraamino phthalocyanines. After 2 days of inoculation, the fungi exhibited minimal growth. It was observed that the inhibiting effect of both M-PhproImPcs and tetraamino phthalocyanines were more for *Aspergilus niger* compared to *Aspergilus flavus*. After 5 days, all the complexes showed distinct inhibiting effect. However, Zn-PhproImPc induced maximum effect. The inhibition of growth effect was in the order of Zn-PhproImPc > Cu-PhproImPc > Ni-PhproImPc > Co-PhproImPc, compared to the corresponding tetraamino phthalocyanines.

The interesting observation made during the investigation was the change in the color of the fungus. *Aspergilus niger* was known for its black color and *Aspergilus flavus* for its green color. However, in the presence of metal complexes the matured colonies of both the fungi were pale brown and the new colonies were pale green. It was confirmed by the parallel experiment with and without the addition of 2 ml of DMF in the media that the change in color of the fungi was not due to the presence of DMF in the medium. The change of color of the fungi may be due to the effect of complexes on the pigmentation properties of the growing fungi.

4.6.2. Antibacterial studies:

Bacterial strains of *Xanthomonas* were procured from the department of Biotechnology, Sahyadri Science College, Shimoga. The above said imino phthalocyanine complexes were tested against pathogenic bacteria *Xanthomonas citri* and *Xanthomonas compstris*.

The agar diffusion cup plate method was followed for antibacterial assay as described in Indian pharmacopia [20]. Inoculum was prepared from 24 hr old culture in nutrient broth. The 200 ppm solutions of the each M-PhproImPc complexes were prepared by dissolving the required quantity of complexes in DMF. The corresponding tetraamino phthalocyanine complexes were also dissolved in DMF to prepare 200 ppm solution and antibacterial studies were carried out under similar conditions for comparison. Above solutions were further diluted with DMF to prepare of 50 ppm, 100 ppm and 150 ppm solutions. With the help of stainless steel well cutter (6 mm) cups were cut out and into each of these cups 100 µl of each of the solutions of different concentration and control (DMF) were placed separately under aseptic conditions with the help of a sterile micropipette. The plates were then maintained at room temperature (26 ^{o}C) for 1 hr to allow the diffusion of the solutions into medium and then incubated at 37 ^{o}C for *Xanthomonas citri* and *Xanthomonas compstris*. Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 hr [21-24]. It was observed that, the maximum inhibition effect was observed in Zn-PhproImPc with tested organism and the least inhibition effect was observed in Co-PhproImPc, compared to the corresponding tetraamino phthalocyanines. The data of zone of inhibition were given in Table 6.

V. CONCLUSIONS

The complexes have been synthesized by both conventional and microwave method. Microwave assisted synthesis of complexes were proved to be ecofriendly and **greener** method compare to conventional method. Reported compounds are non toxic and do not have any hazardous impact on the environment. Moreover use of microwave has enhanced the yield of complexes appreciably. The red shift of the complexes compared to the parent phthalocyanine was due to increase in conjugation of π-electron with the π-electron cloud of peripheral substituted imino groups. The magnetic susceptibility studies clearly revealed the structural information of the complexes. The peripheral substituted hydroxyphenylimino groups enhance the solubility of phthalocyanine complexes.

ACKNOWLEDGEMENTS

One of the authors, Dr. M. H. Moinuddin Khan would like to extend sincere thanks to Prof. A. M. A. Khader, Mangalore University and Prof. M. A. Pasha, Bangalore University, for their timely help in recording spectra. Authors also extend their thanks to the Principal, Sahyadri Science College, Shimoga for providing an opportunity to carryout antibacterial studies.

Table 1: Spectral data of metal (II) 2, 9, 16, 23-tetra-phenylpropene-1-imino phthalocyanines.

Complex	UV-Visible wavelength λ nm (log ε) in DMF	IR Spectral Data (cm^{-1})	Powder XRD Data 2θ angle (d Á)	Powder XRD Relative Intensity %
Co-PhproImPc	336 (3.98) 478 (3.53) 768 (4.19)	607, 752, 1123, 1316, 1491, 1635, 3418.	26.12 (3.28) 25.74 (3.58) 38.33 (2.35)	100.00 64.12 24.25
Cu-PhproImPc	335 (3.99) 431 (3.00) 766 (4.09)	690, 747, 1098, 1310, 1497, 1631, 3428.	26.25 (3.48) 28.54 (3.18) 40.50 (2.10)	100.00 59.59 24.00
Ni-PhproImPc	328 (4.60) 454 (4.10) 765 (4.53)	648, 750, 1098, 1338, 1491, 1638, 3436.	25.90 (3.35) 29.75 (3.25) 40.31 (2.10)	100.00 55.26 25.45
Zn-PhproImPc	338 (4.89) 475 (4.45) 744 (4.82)	700, 742, 1093, 1341, 1486, 1637, 3430.	26.66 (3.56) 28.85 (3.21) 45.75 (2.54)	100.00 62.45 30.25

Pc- Phthalocyanine

Table 2: Elemental analysis and magnetic susceptibility data of metal (II) 2, 9, 16, 23-tetraphenylpropene-1-imino phthalocyanines.

Complex (Color) (Yield)	Empirical formulae (Molecular weight)	Field strength K Gauss	Magnetic susceptibility (χ_m X 10^{-6} cgs unit)	Magnetic moments μ_{eff} (B.M)	Elemental analysis Found (Calc.)
Co-PhproImPc (Bluish green) (68 %)	$C_{68}H_{44}N_{12}Co$ (1086.93)	2.20 2.66 3.10 3.58 4.01	+3599.20 +3439.03 +3127.39 +2983.82 +2778.52	2.97 2.88 2.75 2.68 2.59	C: 74.86; (75.13) H: 3.88; (4.02) N: 15.21; (15.44) Co: 5.23; (5.33)
Cu-PhproImPc (Bluish green) (64 %)	$C_{68}H_{44}N_{12}Cu$ (1091.53)	2.20 2.66 3.10 3.58 4.01	+3522.75 +3390.05 +3135.61 +2975.12 +2582.05	2.93 2.81 2.76 2.69 2.51	C: 74.54; (74.79) H: 3.90; (4.03) N: 15.44; (15.39) Cu: 5.45; (5.76)
Ni-PhproImPc (Bluish green) (67 %)	$C_{68}H_{44}N_{12}Ni$ (1086.69)	2.66	–655.22	---	C: 74.98; (75.13) H: 3.86; (4.05) N: 15.32; (15.47) Ni: 5.28; (5.36)
Zn-PhproImPc (Bluish green) (59 %)	$C_{68}H_{44}N_{12}Zn$ (1093.39)	2.66	–725.65	---	C: 74.36; (74.65) H: 3.95; (4.02) N: 15.34; (15.37) Zn: 5.79; (5.91)

Table 3: TGA data of metal (II) 2, 9, 16, 23-tetraphenypropene-1-iminophthalocyanines.

Compound	Decomposition Temp °C	Mass loss		Probable mode of decomposition and fragments lost
		%Found	%Calculated	
Co-PhproImPc	100-340 °C 350-510 °C	46.66 45.58	45.84 46.99	4 Imino groups Pc moiety
Cu-PhproImPc	100-350 °C 350-470 °C	47.13 44.25	45.23 45.65	4 Imino groups Pc moiety
Ni-PhproImPc	100-360 °C 360-480 °C	45.62 45.61	45.03 46.99	4 Imino groups Pc moiety
Zn-PhproImPc	100-340 °C 340-580 °C	45.44 44.22	45.16 45.56	4 Imino groups Pc moiety

Table 4: Kinetic and thermodynamic parameters of metal (II) 2, 9, 16, 23-tetraphenylpropene-1-imino phthalocyanines.

Compound	Activation energy Ea KJ/mole	Frequency factor Ln A,	ΔH KJ/mole	ΔS J/k	ΔG KJ/mole
Co-PhproImPc	1.24 (0.59) 5.62 (3.35)	3.95 (03.55) 5.11 (22.48)	0.04 (0.51) 3.21 (55.70)	-135.61 (-189.9) -169.68 (457.9)	20.54 (29.22) 121.37 (-151.2)
Cu-PhproImPc	0.99 (0.68) 4.89 (3.11)	3.62 (03.84) 6.45 (25.64)	0.32 (0.65) 3.45 (48.56)	-155.24 (-154.1) -172.12 (345.06)	18.19 (23.34) 113.56 (-109.6)
Ni-PhproImPc	0.98 (0.86) 5.77 (3.24)	3.45 (01.98) 5.41 (19.58)	0.75 (1.54) 2.85 (45.54)	-140.85 (-149.8) -166.69 (168.87)	22.56 (38.85) 119.35 (-75.87)
Zn-PhproImPc	1.00 (0.73) 6.33 (3.25)	3.58 (03.62) 5.68 (24.52)	0.35 (0.86) 3.03 (56.65)	-159.87 (-173.6) -164.19 (322.09)	19.85 (25.53) 116.34 (-109.3)

The values in the bracket corresponds to the nitrogen atmosphere

Table 5: Antifungal data of metal (II) 2, 9, 16, 23-tetra- phenylpropene-1-imino phthalocyanines

Compound	Concentration (in ppm)	*Aspergilus Niger* Radial growth in cm 2 days	5 days	*Aspergilus Flavus* Radial growth in cm 2 days	5 days
Control		1.50	3.90	1.35	3.50
Co-PhproImPc	50	1.25	3.45	1.25	3.30
	100	1.00	3.20	1.10	3.10
	150	0.80	3.05	0.90	2.95
	200	0.65	2.70	0.75	2.65
Cu-PhproImPc	50	1.30	3.60	1.25	3.30
	100	1.10	2.30	0.90	2.40
	150	0.95	2.05	0.80	2.15
	200	0.70	1.80	0.70	2.00
Ni-PhproImPc	50	1.35	3.55	1.25	3.30
	100	1.05	3.15	1.00	3.05
	150	0.80	2.70	0.80	2.85
	200	0.50	2.20	0.60	2.35
Zn-PhproImPc	50	1.40	3.65	1.20	3.45
	100	0.85	1.80	0.95	1.95
	150	0.60	1.40	0.70	1.55
	200	0.45	1.15	0.55	1.25

Table 6: Zone of inhibition of metal (II) 2, 9, 16, 23-tetra- phenylpropene-1-imino phthalocyanines.

Compound	Conc. (in ppm)	*Xanthomonas compstris* Zone of inhibition (mm)	*Xanthomonas citri* Zone of inhibition (mm)
Control		02	03
Co-PhproImPc	50	04(03)	05(03)
	100	07(05)	08(05)
	150	12(06)	13(08)
	200	18(08)	19(10)
Cu-PhproImPc	50	05(04)	06(03)
	100	08(07)	09(05)
	150	13(09)	14(07)
	200	19(10)	19(11)
Ni-PhproImPc	50	05(04)	04(03)
	100	07(06)	07(05)
	150	14(08)	13(07)
	200	18(11)	19(10)
Zn-PhproImPc	50	06(04)	05(04)
	100	09(05)	09(07)
	150	14(07)	15(09)
	200	20(10)	21(11)

The values in the bracket correspond to the parent metal (II) amino phthalocyanines.

REFERENCES

[1]. Wohrle D, *Adv. Polym. Sci.* Review Article, 1983, 50..
[2]. Jasinski R, Nature 1964, 201, 1212-1213.
[3]. Kobel W, Hanack M, *Inorg. Chem.*, 1986, 25, 103.
[4]. Lkahl J, Faulkner LR, Dwarakanath K, Tachikawa H, 1986, *J. Am. Chem. Soc.*, 108.
[5]. Achar BN, Fohlen GM, Parker JA, *J. Polym. Sci., Polym. Chem*., 1983, 21.
[6]. Hanack M, Lange A, *Coord. Chem. Rev., 1988*, 83, 115.
[7]. Margaron P, Langlosis R, Van-lier JE, Gaspard S, *J. Photochem. Photobiol*., 1992, 14, 3.
[8]. Leznzoff CC, Lever ABP, Phthalocyanine Properties and Applications: Vol. 1, VCH Publishers, USA, (1989).
[9]. Rosa A, Baerends EJ, *Inorg. Chem.*, 1994, 33.
[10]. Takako O, Mustuba I, Japan Patent 5, 133534; P187652e 1993.
[11]. Somashekarappa MP, Keshavayya J, *Synth. React. Inorg. Met-org. Chem*, 1999, 29, 5.
[12]. Venugopala Reddy KR, Keshavayya J, *Synth. React. Inorg Metal-Org Chem.*, 2002, 32, 7.
[13]. Achar BN, Fohlen GM. Parker JA, Keshavayya J, *Polyhedron,1989*, 6, 6.
[14]. Selwood P, Magnetochemistry, New York, Interscience. 1956.
[15]. Somashakarappa MP, Keshavayya J, *Spectrochemica Act.*, Part-A, 2003, 59.
[16]. Achar BN, Bhandari JM, *Trans. Metal. Chem.*, 1993, 18.
[17]. Arthur I. Vogel, Quantitative Inorganic analysis, 3rd Ed., Longmans Publishers, London, 1964.
[18]. Somashekarappa MP, Venugopala Reddy KR, Harish MNK, Keshavayya J, *J. T. R. chem.*, 2004, 11, 1.
[19]. Broido A, *J. Polym. Sci.*, Part A-2, 1969, 7, 1761.
[20]. "Indian pharmacopeia,; 3rd Edition, New Delhi, Appendix IV p. 90. 1985".
[21]. Ahmed L, Mohammed Z, Mohammed F, J. *Ethnopharmacol.*, 1998, 62, 183-193.
[22]. Padhy SN, Mahato SB, Dutta NL, *Phytochem.*, 1973, 12, 217-221.
[23]. Moinuddin Khan MH, Fasiulla, Keshavayya J, Venugopala Reddy KR, ***Russian Journal of Inorganic chemistry.,*** 2008, 53(1), p. 66-77.
[24]. Moinuddin Khan MH, Venugopala Reddy KR, Keshavayya J, ***Inorganic chemistry: An Indian Journal***., 2008, 3(1), p. 36-43.