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### Synthesis, characterizations and biological studies of symmetrically substituted 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanine complexes

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## ORIGINAL ARTICLE

### Synthesis, characterizations and biological studies of symmetrically substituted 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanine complexes

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The recent paper describes the synthesis and characterization of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines (M–OHPHmPc) of Co (II), Cu (II), Ni (II), and Zn (II). The dark bluish green colored tetramino substituted phthalocyanine derivatives are characterized by the various physico-chemical techniques such as elemental analysis, magnetic susceptibility, UV-Visible, IR, powder X-ray diffraction, and thermogravimetric analysis to check the structural integrity, purity, and thermal stability. The variations of magnetic moment as a function of field strength indicated the presence of intermolecular co-operative interactions. The above said compounds were screened for their antibacterial and antifungal activities.

**Keywords:** phthalocyanines; electronic spectra; IR spectra; magnetic susceptibility; antifungal activity; antibacterial activity

#### Introduction

Phthalocyanines are the second most important class of colorant and copper phthalocyanine is the single largest volume colorant sold. Phthalocyanines have been important industrial dyes and pigments since their early syntheses at the beginning of the last century (1,2). They have been employed as charge carriers in photocopiers and laser printers, as well as materials for optical storage in recent years (3–5). Many potential applications are expected for these molecular materials which have a high thermal and chemical stability, for instance, as potential industrial catalysts (6), solar cell functioning materials (7), gas sensors (8), non-linear optical limiting devices (9), as power leads and as molecular switches in nanotechnology (10), photodynamic therapy agents (11–13), anticancer treatments (14,15), antimycotic materials (16), antimicrobial agents (17), and as corrosion inhibitors (18).

Phthalocyanines form complexes with virtually all of the metals present in the periodic table. Various spectroscopic properties can be altered by changing the central metal ion as well as by introducing the different substituents at the peripheral positions of the phthalocyanine ring. Even though the information on synthesis and structural investigations of

metal (II) 2, 9, 16, 23-tetra-amino phthalocyanines (19) and the synthesis and properties of some novel salicylaldehyde–tetra-amino phthalocyanine Schiff base metal complexes were documented (20) in the literature, to our knowledge no evidence is available on the syntheses and structural studies on metal (II) 2, 9, 16, 23-tetra-imino 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-tetra-imino phthalocyanine complexes of cobalt (II), nickel (II), copper (II), and zinc (II). The procedure available from the literature (21) was suitably modified for the synthesis of the title complexes, reported here within by a microwave assisted method. The microwave assisted method has proven to be a more ecofriendly method compared to conventional means and has also enhanced the yield of the complexes significantly.

#### 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

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diffractometer was used to study the diffraction patterns of the complexes. The spectra were recorded using Cu K $\alpha$  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 tetra-thiocyanato cobaltate, Hg[Co(SCN)<sub>4</sub>] complex was used as calibrant (1). Thermogravimetric analysis (TGA) studies were carried out by using a Perkin Elmer TG/DTA thermal analyzer at a heating rate of 10°/min both in the air and nitrogen atmosphere.

### Result and discussions

The procedure adopted for the synthesis of M-OH PhImPcs yielded pure complexes. The title complexes are dark bluish green in color. These complexes gave a clear solution in dimethyl sulfoxide (DMSO), dimethyl formamide (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 1) were in good agreement with the calculated values and were consistent with the proposed structure.

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

Complex (Color) (Yield)	Empirical formulae (Molecular weight)	Field strength K Gauss	Magnetic susceptibility ( $\chi_m \times 10^{-6}$ cgs unit)	Magnetic moments $\mu_{\text{eff}}$ (B.M)	Elemental analysis found (Calculated)
Co-OHPhImPc (Dark green) (58%)	C <sub>60</sub> H <sub>36</sub> N <sub>12</sub> O <sub>4</sub> Co (1046.93)	2.20	+3754.20	3.02	C: 67.55; (68.80)
		2.66	+3439.03	2.91	H: 3.36; (3.40)
		3.10	+3127.39	2.75	N: 15.99; (16.00)
		3.58	+2983.82	2.68	Co: 5.60; (5.66)
		4.01	+2778.52	2.59	
Cu-OHPhImPc (Dark green) (59%)	C <sub>60</sub> H <sub>36</sub> N <sub>12</sub> O <sub>4</sub> Cu (1051.53)	2.20	+3574.75	2.94	C: 69.69; (68.59)
		2.66	+3390.05	2.88	H: 3.40; (3.41)
		3.10	+3135.61	2.76	N: 16.61; (16.12)
		3.58	+2975.12	2.69	Cu: 6.02; (6.34)
		4.01	+2582.05	2.51	
Ni-OHPhImPc (Dark green) (58%)	C <sub>60</sub> H <sub>36</sub> N <sub>12</sub> O <sub>4</sub> Ni (1046.69)	2.66	-580.15	-	C: 68.24; (68.80) H: 3.46; (3.40) N: 16.09; (16.10) Ni: 5.62; (5.85)
Zn-OHPhImPc (Dark green) (49%)	C <sub>60</sub> H <sub>36</sub> N <sub>12</sub> O <sub>4</sub> Zn (1053.39)	2.66	-675.23	-	C: 68.44; (68.44) H: 3.40; (3.40) N: 15.98; (15.98) Zn: 5.99; (6.10)

### Electronic spectra

The electronic spectra of M-OHPhImPcs were recorded in DMSO in the concentration range of 1.0–1.5  $\times 10^{-5}$  M and the summary of the results were presented in Table 2, and the graphs in Figure 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 (22). For all the complexes, absorption bands were observed in the wavelength range 732–770 nm, which were considerably higher than the corresponding parent metal phthalocyanines (21). This observed red shift was attributed to the increase in conjugation of  $\pi$ -electrons of the phthalocyanine molecule with that of peripherally substituted aromatic imino groups. The splitting of the Q-band was observed for all the complexes in the range 531–578 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 331–355 nm. A weak L-band was observed for all metal-imino phthalocyanines in the range 252–266 nm.

### IR Spectra

IR spectral data were recorded in KBr pellets and the only selected bands responsible for various vibrations of the functional groups were summarized in Table 2, and the graphs in Figure 2. A broad band observed in the range of 3408–3436  $\text{cm}^{-1}$  was attributed to O-H

Table 2. Spectral data of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines.

Complex	UV-Visible wavelength $\lambda$ nm (log $\epsilon$ )	IR spectral data ( $\text{cm}^{-1}$ )	Powder XRD data $2\theta$ angle ( $^\circ$ )	Relative intensity (%)
Co-OHPhImPc	256 (4.13)	607, 752,	25.96 (3.42)	100.00
	336 (3.98)	1123, 1316,	25.52 (3.48)	64.12
	572 (3.53)	1491, 1626,	43.71 (2.10)	24.25
	769 (4.19)	3408		
Cu-OHPhImPc	266 (3.62)	690, 747,	25.51 (3.48)	100.00
	335 (3.99)	1098, 1310,	28.95 (3.08)	59.59
	569 (3.00)	1497, 1629,	42.96 (2.10)	24.00
	770 (4.09)	3428		
Ni-OHPhImPc	260 (4.61)	648, 752,	26.54 (3.35)	100.00
	331 (4.60)	1098, 1316,	29.39 (4.27)	29.39
	531 (4.10)	1491, 1624,	40.31 (2.10)	25.45
	765 (4.53)	3436		
Zn-OHPhImPc	252 (4.02)	700, 742,	26.87 (3.56)	100.00
	365 (4.89)	1093, 1341,	28.58 (3.21)	62.29
	578 (4.45)	1486, 1634,	32.75 (2.54)	26.15
	772 (4.82)	3430		

stretching vibration. The high intensity and width of these bands indicate the coupling of O–H deformation with the coupled vibrations of C–H bending. The sharp

peaks of M–OHPhImPcs at  $1626\text{--}1634\text{ cm}^{-1}$  are attributed to C=N of aromatic imine group and peaks in the range  $1486\text{--}1497\text{ cm}^{-1}$  were due to C–N aromatic stretching. The peaks observed in the range of  $1310\text{--}1341\text{ cm}^{-1}$  were due to C–H symmetric bending. All the remaining bands observed in the range  $742\text{--}752$  and  $607\text{--}700\text{ cm}^{-1}$  may be assigned to various skeletal vibrations of the phthalocyanine ring (1).

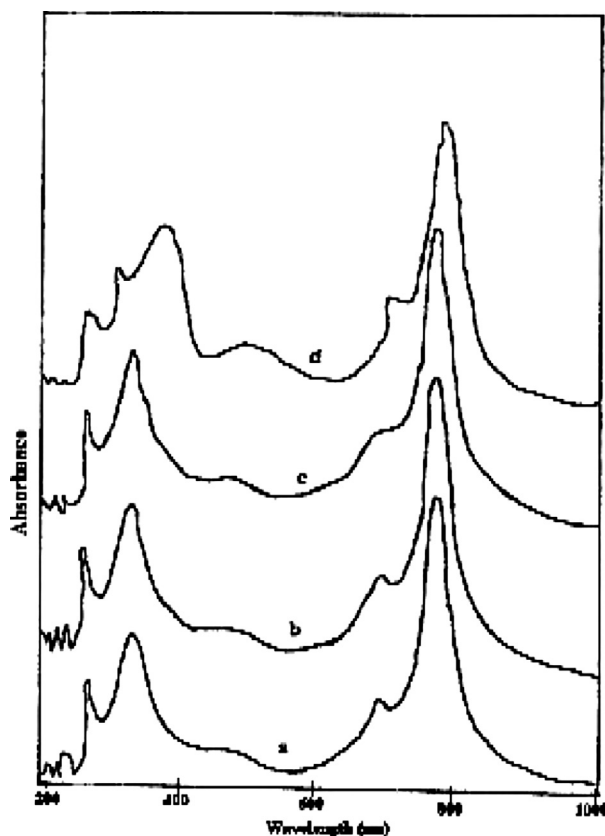


Figure 1. Electronic spectra of (a) Co-PhImPc; (b) Cu-PhImPc; (c) Ni-PhImPc; and (d) Zn-PhImPc.

#### Powder X-ray diffraction (XRD)

The Powder X-ray diffraction (XRD) patterns of M–OHPhImPcs were taken through a range of  $2\theta$  angles  $6\text{--}70^\circ$  showed identical peaks with relatively very poor crystallinity (Table 2, Figure 3). The observed patterns were very much similar to that of unsubstituted parent phthalocyanines except broadening of the peaks with diffused intensity. The broadening may be due to the presence of substituents 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.

#### Magnetic susceptibility

Magnetic susceptibility studies were carried out at ambient temperature and summary of the results are in Table 1, and the magnetic moment values reported in the table are the average of three independent determinations. The magnetic susceptibility studies revealed that Co–OHPhImPc and Cu–OHPhImPc are paramagnetic, whereas Ni–OHPhImPc and Zn–OHPhImPc are diamagnetic. The measured magnetic

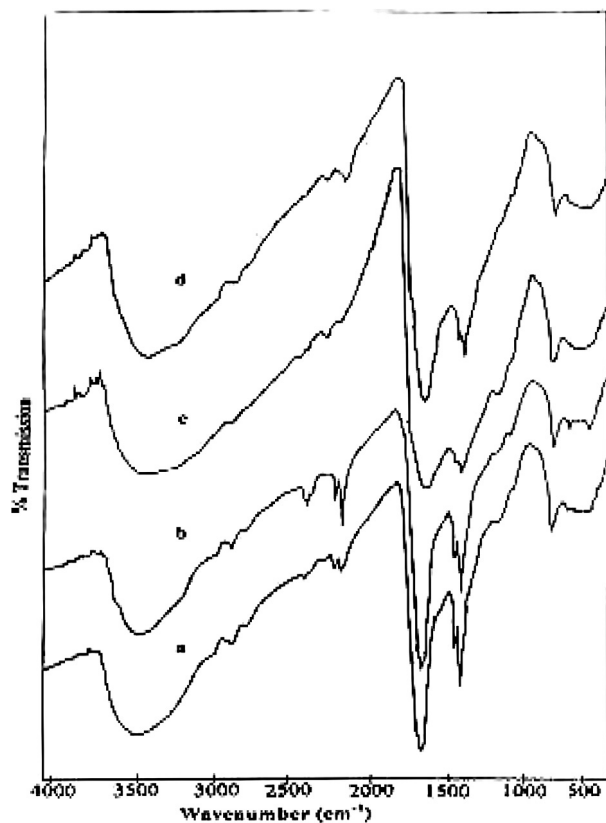


Figure 2. IR absorption spectra of (a) Co-PhImPc; (b) Cu-PhImPc; (c) Ni-PhImPc; and (d) Zn-PhImPc.

moments for Co-OHPHImPc and Cu-OHPHImPc 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 (22). This effect decreases with the increase in field strength and  $\mu_{\text{eff}}$  value approaches spin only value at higher field strength. The observed higher  $\mu_{\text{eff}}$  value at lower field strength is attributed to intermolecular magnetic interaction coupled with magnetic anisotropy of phthalocyanine  $\pi$ -current (23).

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 (24). 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  $45^\circ$ . Thus the complexes stacked in columns with N-atom above and below on every metal atom (Figure 4) and hence the nearest neighboring molecule along the  $b$ -axis contributes a nitrogen atom at the interplanar distance  $3.4 \text{ \AA}$  (25).

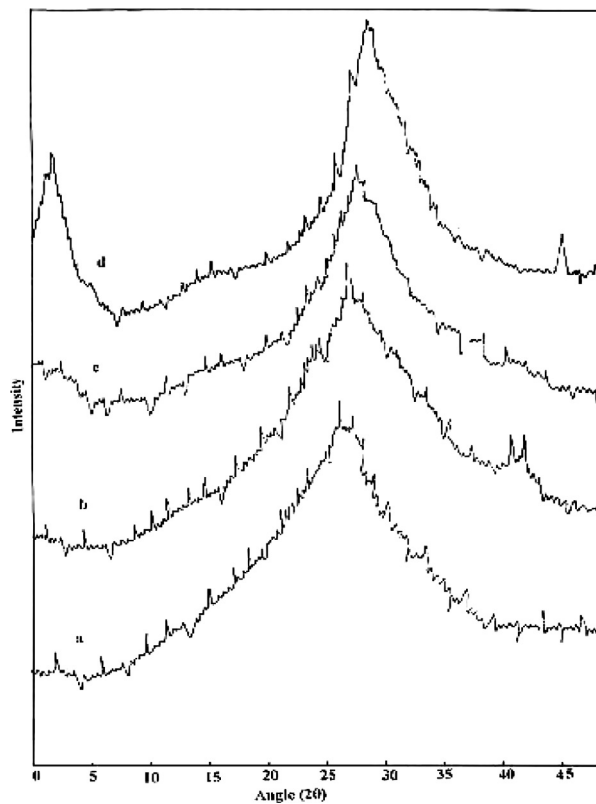


Figure 3. Powder X-ray diffraction patterns of (a) Co-PhImPc; (b) Cu-PhImPc; (c) Ni-PhImPc; and (d) Zn-PhImPc.

#### Thermogravimetric and kinetic studies

Thermogravimetric analytical data of imino substituted metal phthalocyanine complexes were summarized in Table 3. It was observed that the decomposition of the above complexes occurs generally in two steps.

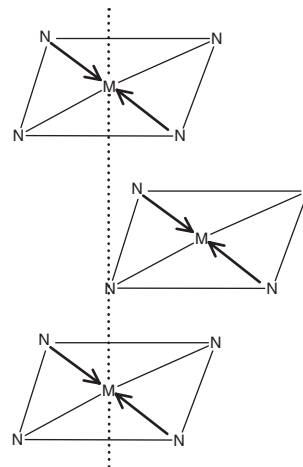


Figure 4. Probable molecular stacking of metal phthalocyanines,  $M = \text{Cu, Co, Ni, and Zn}$ ,  $N = \text{azamethine atom of phthalocyanine}$ .

Table 3. TGA data of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines.

Compound	Decomposition temperature (°C)	Mass loss		Probable mode of decomposition and fragments lost
		Found (%)	Calculated (%)	
Co-OHPhImPc	100–340	46.62	45.85	4 Imino groups Pc moiety
	340–510	45.85	46.99	
Cu-OHPhImPc	100–350	47.23	44.25	4 Imino groups Pc moiety
	350–470	46.25	45.65	
Ni-OHPhImPc	100–360	45.52	45.68	4 Imino groups Pc moiety
	360–480	44.95	46.99	
Zn-OHPhImPc	100–345	45.25	44.24	4 Imino groups Pc moiety
	345–580	45.79	45.56	

The first step of degradation, which takes place in the temperature region of 100–360°C may be accounted for the loss of four imino groups. Major weight loss was observed for all the complexes in the last step in the temperature range of 360–580°C correspond to the oxidative degradation of phthalocyanine moiety. The residues remained after the thermal decomposition was found to be the corresponding metal oxides (26). The thermal decomposition of these imino substituted complexes in the nitrogen atmosphere appears to be very slow. For Co-OHPhImPc, 61% of the complex was found to be decomposed at 680°C. For Cu-OHPhImPc, Ni-OHPhImPc, and Zn-OHPhImPc about 58%, 52%, and 48% loss of mass was observed even at 680°C. The above trend confirms the relatively higher stability of these complexes in nitrogen atmosphere than in air. Even though all the four functional groups seem to be lost during first step, a dimer or a polymer was suspected to be formed via the nitrogen atoms of the peripheral end groups before the last step of decomposition starts (27). Differential thermal analysis (DTA) results revealed that all degradation

steps were exothermic in nature. Kinetic and thermodynamic parameters of the title complexes have been evaluated by Broido's method (28). Plots of  $\ln(\ln 1/y)$  versus  $1/T$  (where  $y$  is the fraction of the complex undecomposed) were developed for the decomposition segment where loss of functional group occurs. From the plots, the energy of activation ( $E_a$ ) and frequency factor ( $\ln A$ ) were evaluated. Enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and free energy ( $\Delta G$ ) of the title complexes have been evaluated by Broido's method (Table 4).

#### Biological 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.

#### Antifungal activity

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

Table 4. Kinetic and thermodynamic parameters of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines.

Compound	Activation energy $E_a$ KJ/mole	Frequency factor $\ln A$	$\Delta H$ KJ/mole	$\Delta S$ J/k	$\Delta G$ KJ/mole
Co-OHPhImPc	1.06 (0.72)	4.31 (03.55)	0.02 (0.51)	-148.61 (-184.9)	20.54 (29.22)
	4.14 (3.02)	5.11 (22.48)	3.03 (55.70)	-167.61 (457.9)	114.32 (-151.2)
Cu-OHPhImPc	0.79 (0.65)	3.74 (03.84)	0.32 (0.65)	-155.24 (-154.1)	18.19 (23.34)
	4.12 (3.22)	6.45 (25.64)	3.45 (48.56)	-172.12 (345.06)	116.76 (-109.6)
Ni-OHPhImPc	0.98 (0.86)	3.01 (01.98)	0.75 (1.54)	-138.85 (-149.8)	22.56 (38.85)
	5.06 (3.56)	5.54 (19.58)	2.85 (45.54)	-168.69 (168.87)	119.35 (-75.87)
Zn-OHPhImPc	1.05 (0.73)	3.52 (03.62)	0.35 (0.86)	-159.87 (-173.6)	19.85 (25.53)
	6.25 (4.51)	5.65 (24.52)	3.03 (56.65)	-162.19 (322.09)	115.55 (107.3)

Note: The values in the bracket corresponds to the nitrogen atmosphere.

*Aspergillus niger* and *Aspergillus flavus* were studied for their growth, color, and sporulation characteristics in the presence of the selected metal phthalocyanine complexes. The 200 ppm solutions of the each M–OHPHImPc 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°C and 15 psi. The hot sterilized media was poured into petriplates in an aseptic chamber and then cooled to room temperature (26°C). The *Aspergillus niger* and *Aspergillus flavus* were inoculated as a point at the center of the plate and were incubated at 23±1°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–OHPHImPc complexes inhibited the radial growth of the fungi compared to the corresponding tetra-amino phthalocyanines. After

two days of inoculation, the fungi exhibited minimal growth. It was observed that the inhibiting effect of both M–OHPHImPcs and tetra-amino phthalocyanines were more for *Aspergillus niger* compared to *Aspergillus flavus*. After five days, all the complexes showed distinct inhibiting effect. However, Zn–OHPHImPc induced maximum effect. The inhibition of growth effect was in the order of Zn–OHPHImPc > Cu–OHPHImPc > Ni–OHPHImPc > Co–OHPHImPc, compared to the corresponding tetra-amino phthalocyanines.

The interesting observation made during the investigation was the change in the color of the fungus. *Aspergillus niger* was known for its black color and *Aspergillus 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.

#### Antibacterial activity

Bacterial strains of *Xanthomonas* were procured from the department of Biotechnology, Sahyadri Science

Table 5. Antifungal data of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines.

Compound	Concentration (in ppm)	<i>Aspergillus Niger</i> Radial growth (in cm)		<i>Aspergillus Flavous</i> Radial growth (in cm)	
		2 days	5 days	2 days	5 days
Control (DMF)		1.40	3.75	1.55	3.60
Co–OHPHImPc	50	1.35 (1.45)	3.60 (3.85)	1.40 (1.35)	3.30 (3.40)
	100	1.10 (1.35)	3.25 (3.75)	1.25 (1.30)	3.10 (3.30)
	150	0.95 (1.20)	3.05 (3.55)	1.05 (1.20)	2.85 (3.25)
	200	0.70 (1.05)	2.85 (3.40)	0.90 (1.10)	2.25 (3.15)
Cu–OHPHImPc	50	1.30 (1.40)	3.60 (3.75)	1.25 (1.35)	3.30 (3.50)
	100	1.15 (1.35)	2.25 (3.70)	1.15 (1.30)	2.90 (3.40)
	150	1.00 (1.20)	2.05 (3.45)	1.00 (1.15)	2.55 (3.25)
	200	0.80 (1.05)	1.90 (3.25)	0.80 (1.05)	1.95 (3.10)
Ni–OHPHImPc	50	1.30 (1.50)	3.55 (3.80)	1.30 (1.30)	3.40 (3.45)
	100	1.20 (1.45)	3.10 (3.65)	1.20 (1.25)	3.15 (3.20)
	150	0.90 (1.35)	2.70 (3.55)	1.05 (1.15)	2.65 (3.05)
	200	0.65 (1.05)	2.20 (3.15)	0.85 (1.05)	2.00 (2.85)
Zn–OHPHImPc	50	1.40 (1.45)	3.70 (3.60)	1.20 (1.25)	3.45 (3.45)
	100	1.10 (1.40)	3.15 (3.45)	0.95 (1.40)	2.95 (3.05)
	150	0.85 (1.25)	2.25 (3.20)	0.70 (1.15)	2.25 (2.85)
	200	0.50 (1.00)	1.40 (2.85)	0.55 (1.05)	1.55 (2.55)

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 pharmacopoeia (29). Inoculum was prepared from 24 hr old culture in nutrient broth. The 200 ppm solutions of the each M–OHPHImPc 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 antibacterial studies were carried out under similar conditions for comparison. Above solutions were further diluted with DMF to prepare 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°C) for 1 hr to allow the diffusion of the solutions into medium and then incubated at 37°C for *Xanthomonas citri* and *Xanthomonas compstris*. Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 hr (30,31). It was observed that, the maximum inhibition effect was observed in Zn–OHPHImPc with tested organism and the least inhibition effect was observed in Co–OHPHImPc, compared to the corresponding tetra-amino phthalocyanines. The data of zone of inhibition were given in Table 6.

## Experimental

Pure 4-nitrophthalic acid was prepared by using phthalic anhydride by adopting the procedure reported elsewhere (19). All other chemical reagents were used as received. Metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines were prepared by conventional and microwave technique as per Scheme 1.

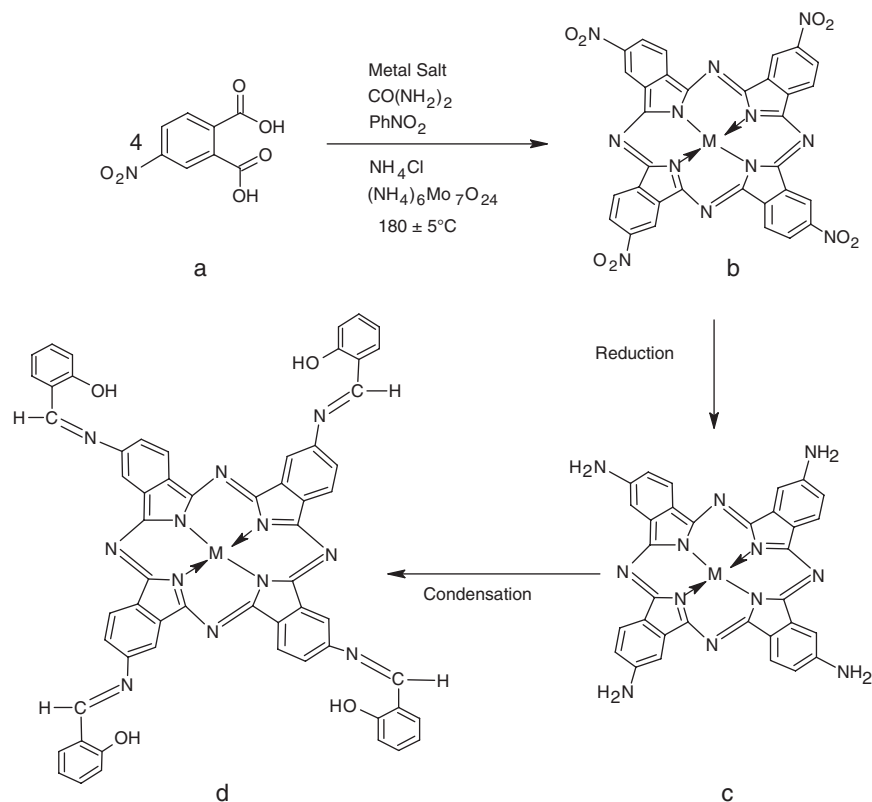
### Preparation of cobalt (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanine (Co–OHPHImPc) by conventional method

The procedure adopted for the synthesis of cobalt (II) 2, 9, 16, 23-tetra-nitro phthalocyanines (M–PcTN) was reported elsewhere (21). 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-tetra-amino phthalocyanine (M–PcTA) (6.30 g, 0.01 mole) was dissolved in DMSO and stirred with respective molar quantity of salicylaldehyde (4.9 ml, 0.01 mole). Above mixture was refluxed for 5 hours in the presence of catalytic quantity of concentrated sulfuric 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 salicylaldehyde. The resulting solid product was dried in vacuum over anhydrous

Table 6. Zone of inhibition of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines.

Compound	Concentration (in ppm)	<i>Xanthomonas species</i> Zone of inhibition (in mm)	<i>Xanthomonas citri</i> Zone of inhibition (in mm)
Control (DMF)		04	03
Co–OHPHImPc	50	06 (03)	07 (03)
	100	08 (05)	09 (05)
	150	12 (06)	12 (08)
	200	18 (08)	19 (10)
Cu–OHPHImPc	50	07 (04)	06 (03)
	100	10 (07)	09 (05)
	150	14 (09)	13 (07)
	200	20 (10)	18 (11)
Ni–OHPHImPc	50	06 (04)	08 (03)
	100	09 (06)	10 (05)
	150	13 (08)	14 (07)
	200	18 (11)	19 (10)
Zn–OHPHImPc	50	06 (04)	08 (04)
	100	08 (05)	10 (07)
	150	13 (07)	14 (09)
	200	21 (10)	19 (11)





Scheme 1. Synthesis of metal (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanines (a) 4-Nitrophthalic acid; (b) M-PcTN; (c) M-PcTA; and (d) M-OHPhImPc.

phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>). The yield of the complex was found to be 42%.

#### Microwave assisted synthesis of cobalt (II) 2, 9, 16, 23-tetra-hydroxyphenylimino phthalocyanine (Co-OHPhImPc)

The finely powdered cobalt (II) 2, 9, 16, 23-tetra-amino phthalocyanine (M-PcTA) (6.30 g, 0.01 mole) was dissolved in stoichiometric quantity of DMSO taken in 500 ml beaker and stirred with respective molar quantity of salicylaldehyde (4.9 ml, 0.01 mole) in the presence of catalytic quantity of concentrated sulphuric acid. It was then irradiated by 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 salicylaldehyde. The resulting solid product was dried in vacuum over anhydrous P<sub>2</sub>O<sub>5</sub>. The yield of the complex was found to be 58%.

The pigment form of the above complex was obtained by the acid pasting process, in which one part of powdered sample was dissolved in 6–10 parts

of concentrated sulfuric acid. The mixture was allowed to stand for 1–2 hours 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<sub>2</sub>O<sub>5</sub>.

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

#### Conclusions

The complexes have been synthesized by both conventional and microwave methods. The microwave method had advantages of the synthetic route adopted, and was very simple and expected to give good yield. The red shift of the complexes compared to the parent phthalocyanine was due to increase in conjugation of  $\pi$ -electron with the  $\pi$ -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.

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