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Synthesis, Spectral, Magnetic, Thermal and Antimicrobial Studies on Symmetrically Substituted 2, 9, 16, 23-tetra-phenyliminophthalocyanine Complexes

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1. Introduction

The Phthalocyanine (or tetraazatetrabenzporphyrin) ligand has a heteroaromatic π -system and readily forms complexes with many transition metals. The aza-nitrogen and peripheral fused benzene ring imparts chemical and thermal stability to the phthalocyanine macromolecule. The optical properties of metal phthalocyanine complexes have been studied extensively for several decades [1-3]. The low solubility of these complexes combined with the intense π - π^* bands associated with phthalocyanine ligand led to the industrial applications as pigments in paints and dyestuffs [4]. In recent decades, there has been renewed interest in the use of metal phthalocyanine complexes in number of high technological applications, including those based upon the close structural relationships of the phthalocyanine to porphyrin complexes. Mimicking the natural energy cycle of chlorophyll, the oxygen binding capacity and activation properties of the heme proteins has been a key role in phthalocyanine research [5-9]. New applications include as photosensitizers in PDT and in anti-scrapie treatments [10-11], as power leads and as molecular switches in nanotechnology [12] and as potential industrial catalysts [13].

Eventhough the information on synthesis and structural investigations of metal (II) 2, 9, 16, 23-tetraamino phthalocyanines were documented [14] 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 chapter we report the synthesis, characterization and antimicrobial studies of 2, 9, 16, 23-tetra-phenyliminophthalocyanine complexes of copper (II), cobalt (II), nickel (II)

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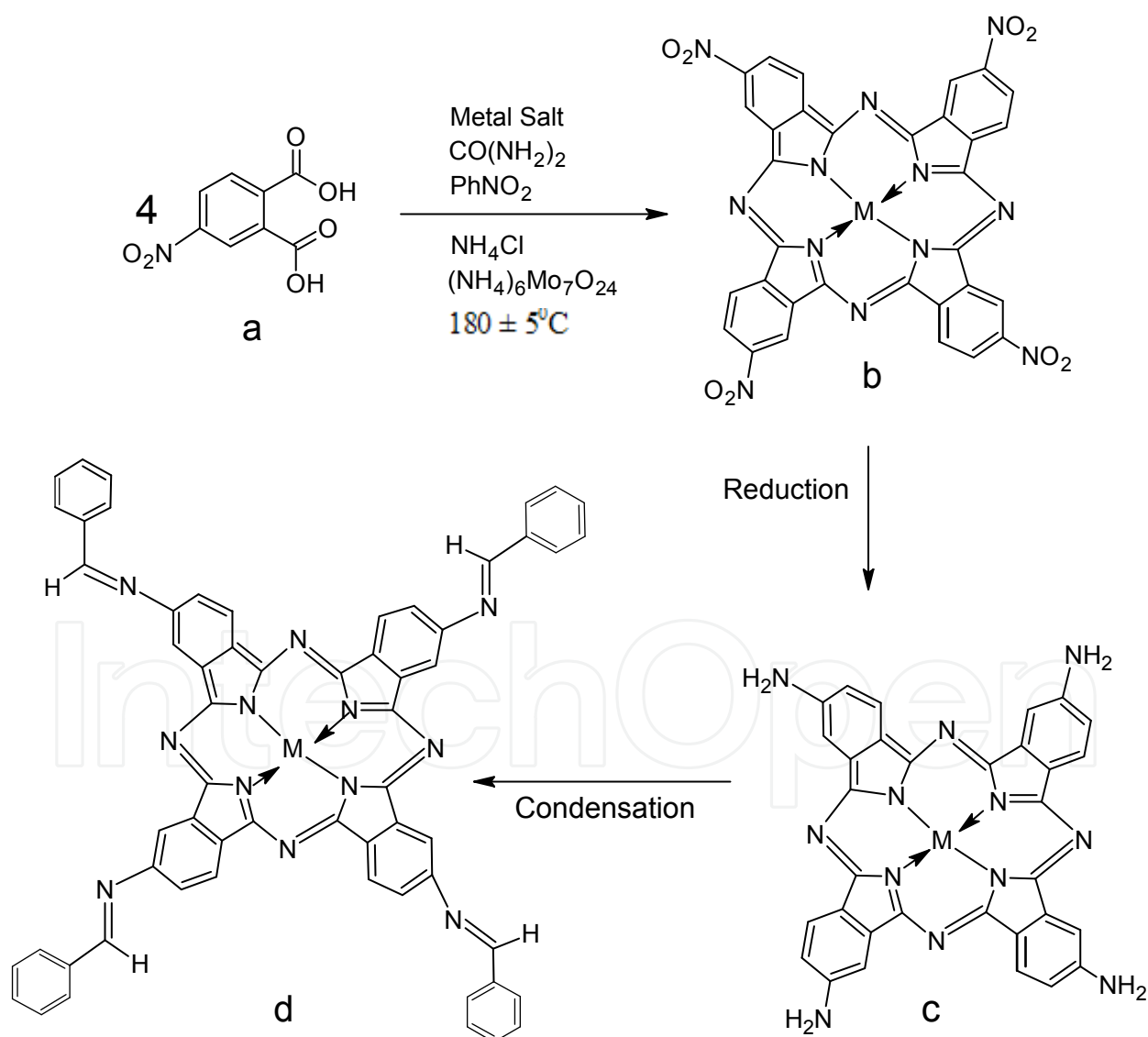
and zinc (II). The procedure available from the literature [14-16] was suitably modified and used for the synthesis of title complexes.

2. Materials and methods

4-nitrophthalic acid was synthesized by using phthalic anhydride adopting the procedure reported elsewhere [14]. All other chemicals were of analytical grade and were used as such. Metal (II) 2, 9, 16, 23-tetra-phenyliminophthalocyanines (M-PhImPc) were prepared as per the scheme 1.

2.1 Preparation of cobalt (II) 2, 9, 16, 23-tetra-phenyliminophthalocyanine complex

The procedure adopted for the synthesis of cobalt (II) 2, 9, 16, 23-tetra-nitro phthalocyanine (M-PcTN) was reported elsewhere [15]. The nitro derivative of the aforesaid complex was



Scheme 1. Synthesis of Metal (II) 2, 9, 16, 23-tetra-phenyliminophthalocyanines, a) 4-nitrophthalic acid, b).M-PcTN, c) M-PcTA and d) M-PhImPc.

converted into amino derivative quantitatively by reduction using sodium sulfide nonahydrate in aqueous medium [14]. The finely powdered cobalt (II) 2, 9, 16, 23-tetra-amino phthalocyanine (M-PcTA) (6.30 g 0.01 mole) was dissolved in 4.2 mL of DMSO and stirred with benzaldehyde. Above mixture was refluxed for 5 hours in the presence of catalytic quantity of concentrated sulphuric acid and contents were poured into ice cold water. The settled bluish green coloured condensed phenylimino phthalocyanine complex was washed with alcohol several times till free from aldehyde.

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 on to 45-50 parts of crushed ice and stirred thoroughly. The pigment thus obtained was filtered off and washed with hot water. Finally it was washed with distilled water and dried in vacuum over phosphorous pentoxide.

Metal (II) 2, 9, 16, 23-tetra-phenyliminophthalocyanines of Cu (II), Ni (II) and Zn (II) were prepared by the above procedure using the respective metal amino phthalocyanines C, H and N elemental analyses were done at STIC, Kerala, India. Magnetic susceptibility studies were made at room temperature (29° C) using 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ complex was used as calibrant [17]. Varian Cary 5000 with 1 cm width silica cell was used for electronic absorption spectral studies. IR spectra were recorded using Nicolet MX-FT IR spectrometer. Philips analytical PW-1710 X-ray diffractometer was used to study the diffraction pattern 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 7mm and a chart speed of 10 mm/min. TGA studies were carried out by using a Perkin Elmer, Diamond TG/DTA thermal analyzer at a heating rate of 10°/min both in the air and nitrogen atmosphere.

3. Results and discussion

The procedure adopted for the synthesis of M-PhImPcs yield pure complexes. The title complexes are dark bluish green in color. These complexes give clear solution in concentrated sulfuric acid, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and pyridine and are sparingly soluble in alcohol. The results of elemental analysis for carbon, hydrogen and nitrogen and gravimetric methods for metals (Table II) are in good agreement with the calculated values and are consistent with the proposed structure.

3.1 Electronic spectra

The electronic spectra of M-PhImPcs were recorded in DMSO in the concentration range of $1.0-1.5 \times 10^{-4}$ M and the results were summarized in Table 1 and the graphs in Fig. 2. 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 [17]. For all the complexes absorption bands were observed in the wavelength range 732-770 nm, which are considerably higher than the corresponding parent metal phthalocyanines [17]. This observed red shift was attributed to the increase in conjugation of π -electrons of the phthalocyanine molecule with that of peripheral substituted aromatic imino groups. The splitting of the Q-band was observed in all the complexes in the wavelength range 531-572 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 in all

the complexes in the range of 331-355 nm. A weak L-band was observed for all metal-imino phthalocyanines at 252-266 nm.

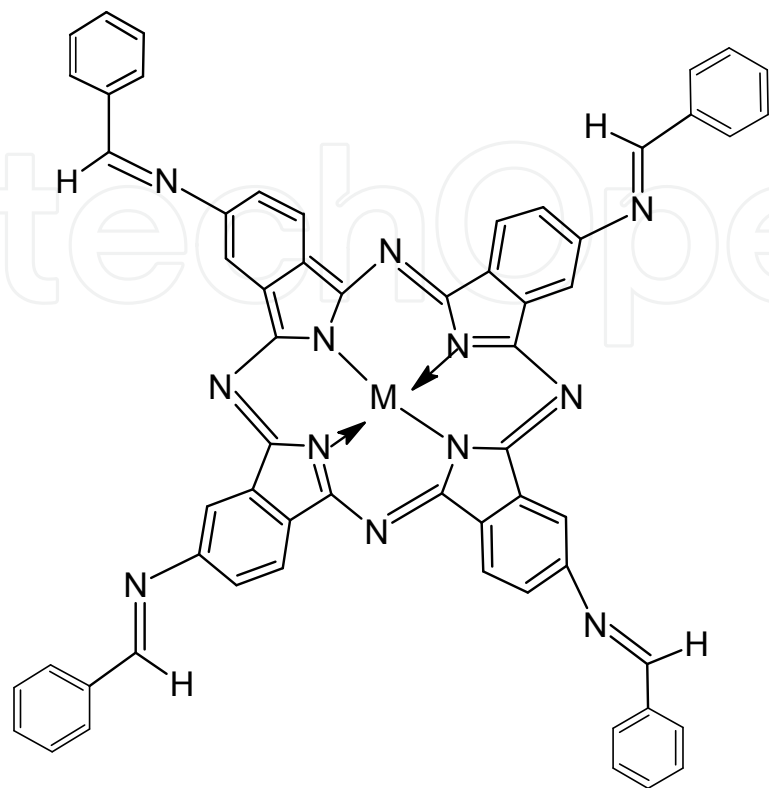


Fig. 1. Suggested structure of symmetrically tetra substituted phenyliminophthalocyanine, where M = Co, Cu, Ni and Zn.

Name of the Complex	UV-Visible wavelength λ nm (log ϵ)	IR Spectral Data (cm ⁻¹)	Powder XRD Data 2θ angle (d A ^o)	Relative Intensity %
Co-PhImPc	256 (4.13) 336 (3.98) 572 (3.53) 769 (4.19)	607,752,1103, 1316,1491,1626	25.96 (3.42) 25.52 (3.48) 43.71 (2.10)	100.00 64.12 24.25
Cu-PhImPc	266 (3.62) 335 (3.99) 569 (3.00) 770 (4.09)	690,747,1098, 1310,1497,1615	28.95 (3.08) 42.96 (2.10) 25.51 (3.48)	100.00 59.59 24.00
Ni-PhImPc	260 (4.61) 331 (4.60) 531 (4.10) 765 (4.53)	648,752,1098, 1316,1491,1624	26.54 (3.35) 29.39 (4.27) 40.31 (2.10)	100.00 29.39 25.45
Zn-PhImPc	252 (4.02) 355 (4.89) 578 (4.45) 732 (4.82)	700,742,1093, 1341,1486,1634	26.87 (3.56) 28.58 (3.21) 32.75 (2.54)	100.00 86.26 85.98

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

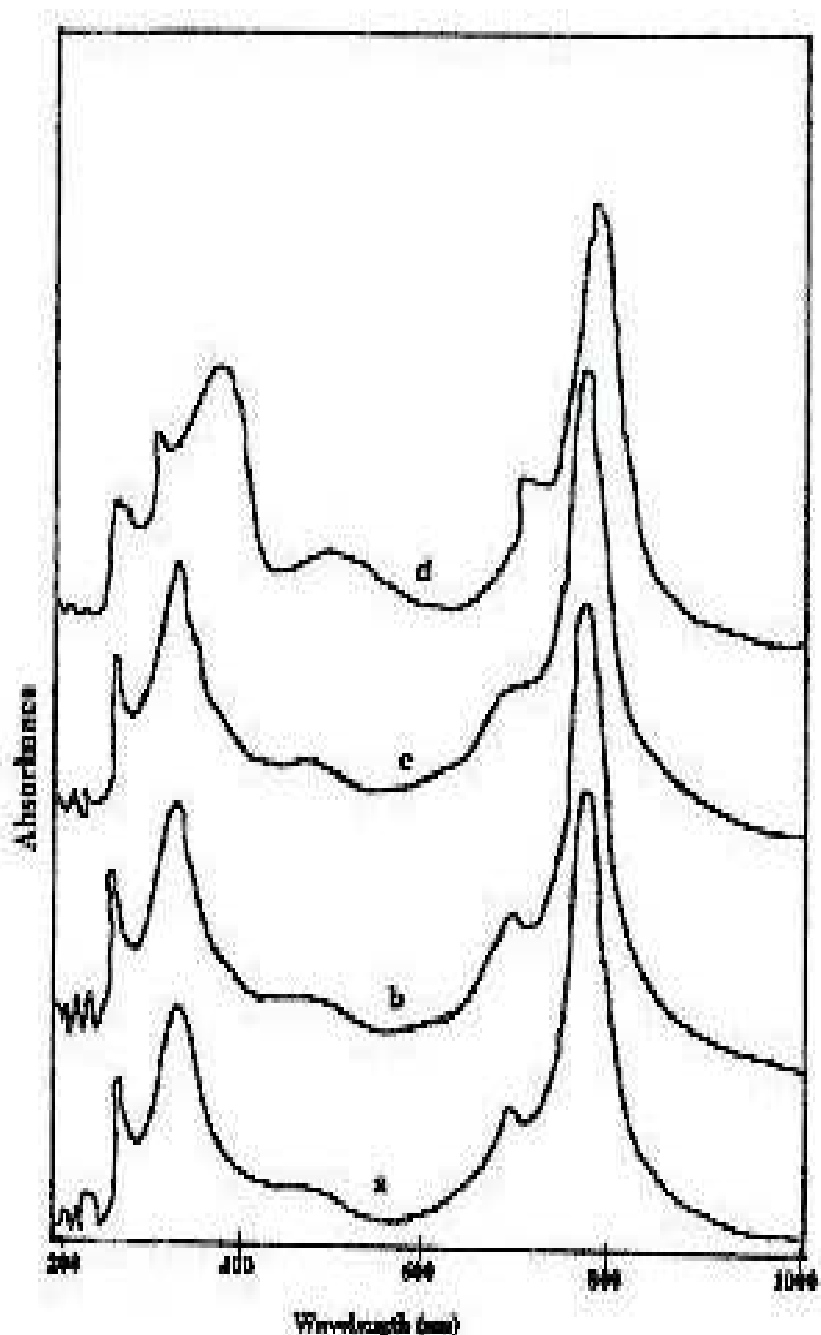


Fig. 2. Electronic spectra of (a) Co-PhImPc, (b) Cu-PhImPc, (c) Ni-PhImPc and (d) Zn-PhImPc.

3.2 IR spectra

IR spectral data were recorded in KBr pellets and the results were presented in Table 1 and the graphs in Fig. 3. The sharp peaks at the range of $1615\text{--}1634\text{ cm}^{-1}$ were attributed to $\text{C}=\text{N}$ of imine group and peaks at the range of $1468\text{--}1497\text{ cm}^{-1}$ were due to $\text{C}-\text{N}$ aromatic stretching. The peaks observed in the range of $1310\text{--}1341\text{ cm}^{-1}$ were due to $\text{C}-\text{H}$ 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.

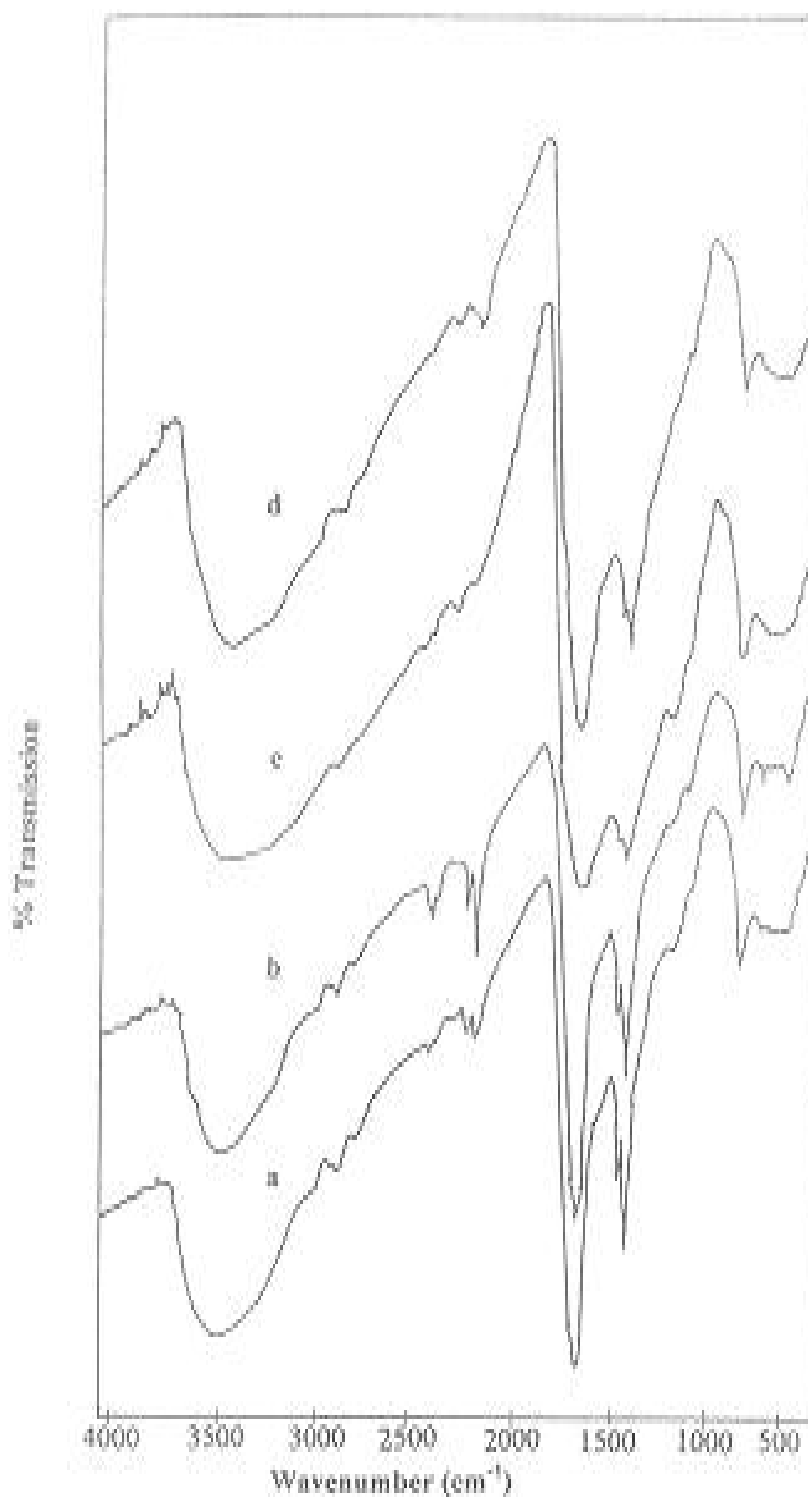


Fig. 3. IR absorption spectra of (a) Co-PhImPc, (b) Cu-PhImPc, (c) Ni-PhImPc and (d) Zn-PhImPc.

3.3 Powder XRD

Powder X-ray diffraction patterns of M-PhImPcs were taken in the range of 2θ angles 6-70° showed identical peaks with relatively poor crystallinity (Table 1, Fig. 4). The observed

patterns were very much similar to that of unsubstituted parent phthalocyanines except for the 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.

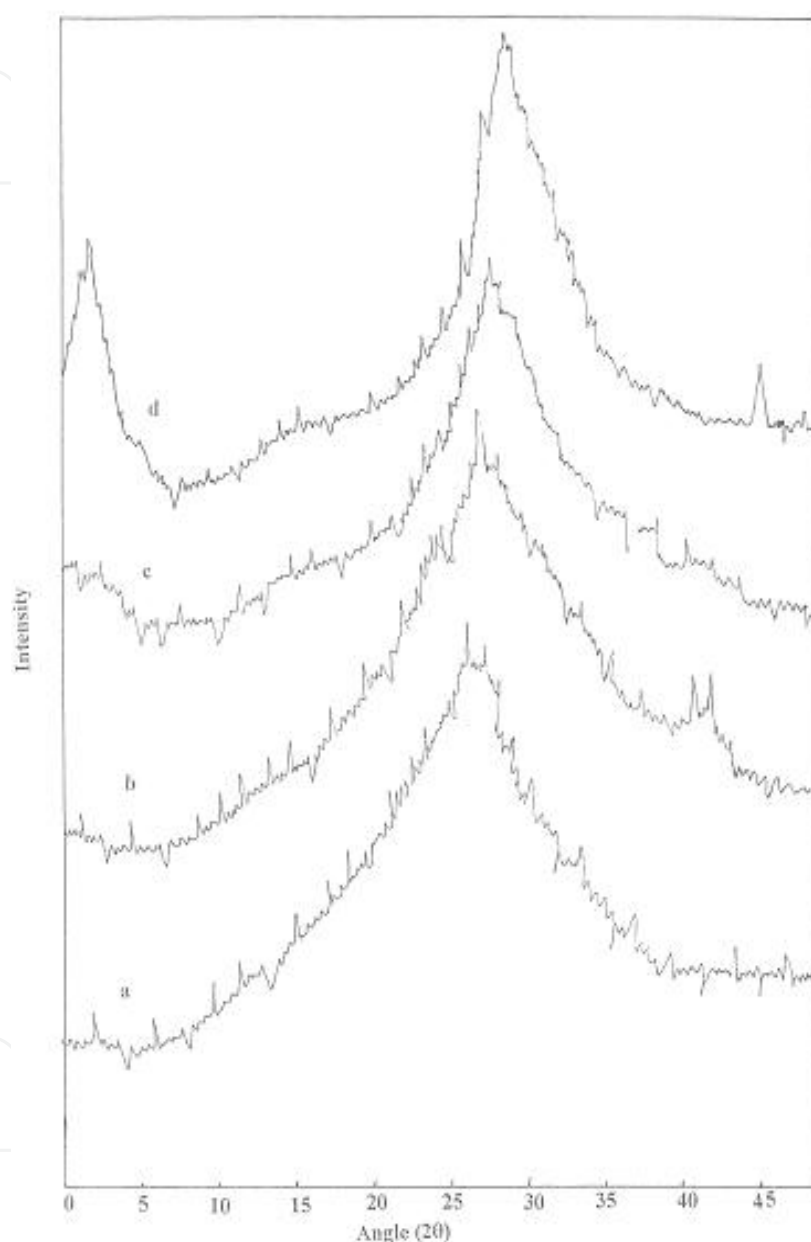


Fig. 4. Powder X-ray diffraction patterns of (a) Co-PhImPc, (b) Cu-PhImPc, (c) Ni-PhImPc and (d) Zn-PhImPc.

3.4 Magnetic susceptibility

Magnetic susceptibility studies were carried out at ambient temperature and summary of the results were in Table 2 and the magnetic moment values reported in the table were the average of three independent determinations. The measured magnetic moment of

complexes was higher than the spin only values due to orbital contributions, and these values were higher than those for the corresponding parent phthalocyanines. The magnetic susceptibility studies revealed that Co-PhImPc and Cu-PhImPc are paramagnetic, whereas Ni-PhImPc and Zn-PhImPc are diamagnetic. The measured magnetic moments for Co-PhImPc and Cu-PhImPc 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 [18]. 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 [19].

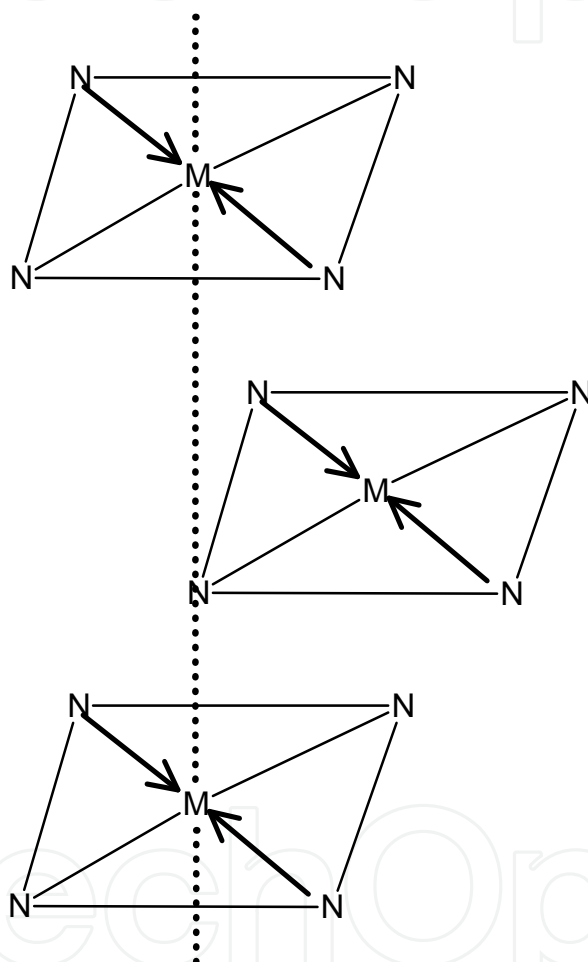


Fig. 5. Probable molecular stacking of metal phthalocyanines. M = Cu, Co, Ni and Zn, N = azamethine atom of phthalocyanine.

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 [20]. 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 [21].

Complex (Colour) (Yield)	Empirical Formulae (Molecular weight)	Field strength K Guass	Magnetic susceptibility ($\chi_m \times 10^{-6}$ cgs unit)	Magneti c moments μ_{eff} (B.M)	Elemental analysis Found (Calc.)
Co-PhImPc (Dark green) (45%)	C ₆₀ H ₃₆ N ₁₂ Co (982.93)	1.02	+3754.20	3.02	C: 72.68; (73.25) H: 3.48; (3.66) N:16.96; (17.09) Co: 5.82; (5.99)
		1.30	+3439.03	2.91	
		1.50	+3127.39	2.75	
		1.82	+2983.82	2.68	
		2.09	+2778.52	2.59	
Cu-PhImPc (Dark green) (43%)	C ₆₀ H ₃₆ N ₁₂ Cu (987.53)	1.02	+3574.75	2.94	C: 72.59; (72.91) H: 3.65; (3.64) N: 16.98; (17.01) Cu: 6.38; (6.43)
		1.30	+3390.05	2.88	
		1.50	+3135.61	2.76	
		1.82	+2975.12	2.69	
		2.09	+2582.05	2.51	
Ni-PhImPc (Dark green) (40%)	C ₆₀ H ₃₆ N ₁₂ Ni (982.69)	1.50	-580.15	---	C: 72.98; (73.24) H: 3.67; (3.66) N: 16.69; (16.09) Ni: 5.90; (5.97)
Zn-PhImPc (Dark green) (32%)	C ₆₀ H ₃₆ N ₁₂ Zn (989.39)	1.50	-675.23	---	C: 72.22; (72.77) H: 3.63; (3.63) N: 16.76; (16.98) Zn: 6.66; (6.60)

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

3.5 Thermogravimetric and kinetic studies

Thermogravimetric analytical data of M-PhImPc pigments were summarized in the Table 3. It was observed that the decomposition of the title complexes occur generally in two steps. The first step of degradation in air, which takes place in the temperature region of 100-360°C may be accounted for the loss of four substituted imino groups. The 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 decompositions were found to be the corresponding metal oxides [22]. The thermal decomposition of these imino substituted complexes in the nitrogen atmosphere appears to be very slow. For Co-PhImPc, 54% of the complex was found to be decomposed at 700°C. For Cu-PhImPc, Ni-PhImPc and Zn-PhImPc about 48%, 58% and 55% loss of the mass was observed even at 700°C. Above trend confirms the relatively higher stability of these complexes in nitrogen atmosphere than in air. Eventhough, all the four functional groups seem to be lost in first step, a dimer or a polymer was suspected to be formed via the nitrogen atoms of the peripheral end groups before the second step of decomposition starts [23]. 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 [24]. 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 groups occur. From the plots, energy of activation (E_a), frequency factor ($\ln A$), enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) of the title complexes have been computed by using standard equations (Table 3).

Name of the Compound	Activation energy E_a KJ mole ⁻¹	Frequency factor $\ln A$	ΔH KJ mole ⁻¹	ΔS J k ⁻¹	ΔG KJ mole ⁻¹
Co-PhImPc	1.059 (0.733)	4.314 (3.557)	0.021	-159.87 (-	20.80
	3.038 (59.86)	5.118 (22.48)	(0.513)	173.6)	(25.53)
			3.030	-162.19	115.37
			(55.708)	(322.09)	(105.3)
Cu-PhImPc	0.943 (0.333)	4.096 (2.446)	0.136	-156.11 (-	20.43
	3.829 (71.77)	5.462 (26.59)	(0.914)	184.9)	(26.82)
			2.156	-157.61	111.32
			(67.86)	(457.92)	(147.2)
Ni-PhImPc	0.857 (0.542)	3.913 (3.544)	0.223	-153.38 (-	20.163
	3.168 (65.40)	5.137 (22.58)	(0.516)	174.4)	(24.94)
			2.983	-161.82	116.76
			(56.20)	(326.56)	(107.3)
Zn-PhImPc	0.426 (0.435)	2.841 (2.734)	0.575	-141.35 (-	17.53
	4.352 (48.687)	5.545 (18.04)	(1.060)	182.5)	(31.79)
			2.631	-157.14	129.36
			(43.865)	(174.37)	(57.27)

The values in the bracket corresponds to the nitrogen atmosphere

Table 3. TGA and Kinetic parameters of metal (II) 2, 9, 16, 23-tetra phenyliminophthalocyanine.

3.6 Antimicrobial studies

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

3.7 Antibacterial activity

Bacterial strains: Bacterial strains of *Xanthomonas* were procured from department of Biotechnology, Sahyadri Science College, Kuvempu University, Shimoga.

Method: 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 [25]. Inoculum was prepared from 24 hr old culture in nutrient broth. The M-PhImPc complexes of 500 ppm were prepared by dissolving the required quantity of complexes in DMSO. It was further diluted with DMSO for the preparations of 200 ppm, 100 ppm and 50 ppm solution of M-PhImPc. With the help of stainless steel well cutter (6mm) cups were cut out and into each of these cups 100 µl of each of the complexes of different concentrations were placed separately under aseptic conditions with the help of a sterile

micropipette. Ciprofloxacin was used as standard drug. The plates were then maintained at room temperature (26°) for 1 hr to allow the diffusion of the solutions into medium and 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 and compared with standard drug [26-27]. As per the observations made, the maximum inhibition effect was observed in Zn-PhImPc with tested organism and the least inhibition effect was observed in Co-PhImPc. The datas for zone of inhibition was presented in Table 4.

Name of the Compound	Conc. (in ppm)	<i>Xanthomonas compstris</i> Zone of inhibition (in mm)	<i>Xanthomonas citri</i> Zone of inhibition (in mm)
Ciprofloxacin (Standard drug)	50	04	05
	100	06	07
	200	09	10
	500	14	15
Co-PhImPc	50	06(03)	07(03)
	100	09(05)	11(05)
	200	13(06)	15(08)
	500	16(08)	17(10)
Cu-PhImPc	50	06(04)	08(02)
	100	11(07)	13(05)
	200	16(09)	16(07)
	500	19(10)	19(11)
Ni-PhImPc	50	07(04)	06(03)
	100	11(06)	09(05)
	200	14(08)	13(07)
	500	18(11)	18(10)
Zn-PhImPc	50	06(04)	08(04)
	100	11(05)	13(07)
	200	16(08)	16(09)
	500	19(11)	19(11)

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

Table 4. Zone of inhibition of metal (II) 2, 9, 16, 23-tetra-phenylimino phthalocyanines.

3.8 Antifungal activity

The *Aspergillus Niger* and *Aspergillus Flavous* were studied for its growth, color and sporulation characteristics in the presence of the selected metal phthalocyanine complexes. The M-PhImPc complexes of 500 ppm were prepared by dissolving the required quantity of complexes in DMSO. It was further diluted with DMSO for the preparations of 200 ppm, 100 ppm and 50 ppm solution of M-PhImPc. Ketaconazole was used as a standard drug. Potato Dextrose Agar (PDA) media with the above preparations were sealed with aluminum foils 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 to room temperature (26°). The *Aspergillus Niger* and *Aspergillus Flavous* were inoculated as a point at the center of the plate and are incubated at 23±1° C for one week and the observations were made everyday [28].

The summary of the observations were presented in Table 5. It was found that all the complexes inhibit the radial growth of the fungi. After 2 days of inoculation, the fungi exhibited minimal growth. It was observed that the inhibiting effects of M-PhImPcs were more for *Aspergillus Niger* compared to *Aspergillus Flavous*. After 5 days, all the complexes show distinct inhibiting effect. However, Zn-PhImPc induced maximum effect. The inhibition of growth effect is in the order of Zn-PhImPc > Co-PhImPc > Cu-PhImPc > Ni-PhImPc.

Name of the Compound	Conc. (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
Ketaconazole (Standard drug)	50	1.50	4.15	1.45	3.80
	100	1.35	3.90	1.35	3.65
	200	1.25	3.60	1.20	3.45
	500	1.00	3.35	1.05	3.10
Co-PhImPc	50	1.20 (1.45)	3.60 (3.85)	1.25 (1.35)	3.35 (3.40)
	100	1.00 (1.35)	3.30 (3.75)	1.15 (1.30)	3.15 (3.30)
	200	0.95 (1.20)	3.15 (3.55)	1.00 (1.20)	3.00 (3.25)
	500	0.75 (1.05)	3.00 (3.40)	0.90 (1.10)	2.85 (3.15)
Cu-PhImPc	50	1.35 (1.40)	3.50 (3.75)	1.20 (1.35)	3.30 (3.50)
	100	1.00 (1.35)	3.10 (3.70)	1.00 (1.30)	3.15 (3.40)
	200	0.80 (1.20)	2.70 (3.45)	0.90 (1.15)	3.05 (3.25)
	500	0.50 (1.05)	2.20 (3.25)	0.80 (1.05)	1.95 (3.10)
Ni-PhImPc	50	1.30 (1.50)	3.60 (3.80)	1.25 (1.30)	3.30 (3.45)
	100	1.20 (1.45)	3.10 (3.65)	0.90 (1.25)	2.95 (3.20)
	200	1.00 (1.35)	2.85 (3.55)	0.80 (1.15)	2.65 (3.05)
	500	0.85 (1.05)	2.35 (3.15)	0.70 (1.05)	2.00 (2.85)
Zn-PhImPc	50	1.45 (1.45)	3.75 (3.60)	1.20 (1.25)	3.45 (3.45)
	100	1.10 (1.40)	1.80 (3.45)	0.95 (1.40)	1.93 (3.05)
	200	0.85 (1.25)	1.50 (3.20)	0.70 (1.15)	1.65 (2.85)
	500	0.50 (1.00)	1.30 (2.85)	0.55 (1.05)	1.45 (2.55)

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

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

The interesting observation made during the investigation was the change in the colour of the fungus. *Aspergillus Niger* was known for its black colour and *Aspergillus Flavous* for its green colour. However, in the presence of metal complexes the matured colonies of the fungus were pale brown and the new colonies were pale green [29]. It was confirmed by the parallel experiment with and with out the addition of 2 ml DMSO in the media that the change in colour of the fungi was not due to the presence of DMSO in the medium. The change of colour of the fungi may be due to the effect of complexes as the pigmentation properties of the growing fungi.

4. Conclusions

The synthetic route adopted was very simple and give good yield. The measured magnetic moment of complexes was higher than the spin only values due to orbital contributions, and

these values were higher than those for the corresponding parent phthalocyanines. The variations of magnetic moment as a function of field strength indicated the presence of inter molecular co-operative interactions. The magnetic susceptibility studies clearly revealed the structural information of the complexes. The red shift of the complexes compared to the parent phthalocyanine is due to increase in conjugation of π -electron with the π -electron cloud of peripheral substituted imino groups. Metal phthalocyanines are biologically active and the complexes show enhanced antimicrobial activity against one or more strains compared to conventional standard drugs. Imino substituents tend to make the complexes act as more powerful and potent bactericidal agent.

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