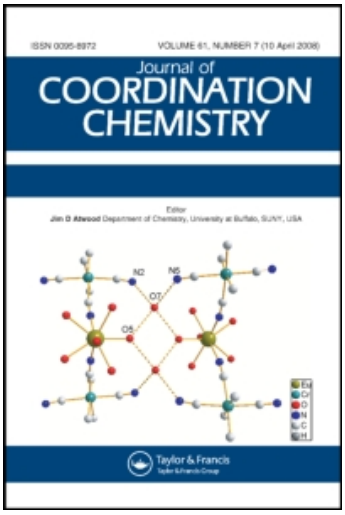

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Synthesis, structural investigations and biological studies on symmetrically substituted 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanine complexes

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The synthesis and characterization of novel metal(II) 4,4′,4″,4‴-tetra-methoxyphenylimino substituted phthalocyanines (MImPc) of copper(II), cobalt(II), nickel(II) and zinc(II) by condensing the 4,4′,4″,4‴-tetra amino phthalocyanines with anisaldehyde are described. The dark bluish green colored tetraimino substituted phthalocyanine derivatives are characterized by various physico-chemical techniques, elemental analysis, magnetic susceptibility, electronic, and IR spectra, powder X-ray diffraction and thermo gravimetric analysis (TGA) to check the structural integrity and purity. The variations of magnetic moment as a function of field strength indicated the presence of intermolecular co-operative interactions. The complexes are also evaluated for their antifungal and antibacterial activities.

Keywords: Crystallinity; Elemental; Magnetic susceptibility; Thermal; Tetramethoxyphenyl-imino phthalocyanines; Variations

1. Introduction

Phthalocyanines are planar, macrocyclic aromatic compounds isoelectronic with porphyrin, consisting of four isoindole units linked together by nitrogen atoms. The aza-nitrogen and peripheral fused benzene rings impart chemical and thermal stability to the phthalocyanine molecule. Various substituted metal phthalocyanines have been extensively used in solar cells, fuel cells, electrochorism and photochorism, optical memory and data storage devices, liquid crystal color displays, as dyes and pigments and in photodynamic therapy of cancer [1–4]. In recent decades, there has been renewed interest in the use of metal phthalocyanine complexes in high technology applications, including those based upon the close structural relationships of phthalocyanine to

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porphyrin complexes. Mimicking the natural energy cycle of chlorophyll, oxygen binding capacity and activation properties of heme proteins have played a key role in phthalocyanine research [4–6]. New applications include as photosensitizers in PDT and in anti-scrapie treatments [7, 8], as power leads and molecular switches in nanotechnology [9] and as potential industrial catalysts [10].

Even though synthesis and structural investigations of metal(II) 4,4′,4″,4‴ tetraaminophthalocyanines were documented [11] in the literature, to our knowledge syntheses and structural studies on metal(II) 4,4′,4″,4‴-tetraimino phthalocyanines starting from the respective amino phthalocyanine complexes have not been reported.

In the present article we report the synthesis, characterization and biological activities of 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanine complexes of copper(II), cobalt(II), nickel(II) and zinc(II). The procedure available from the literature [11–13] is suitably modified for synthesis of the title complexes.

2. Experimental part

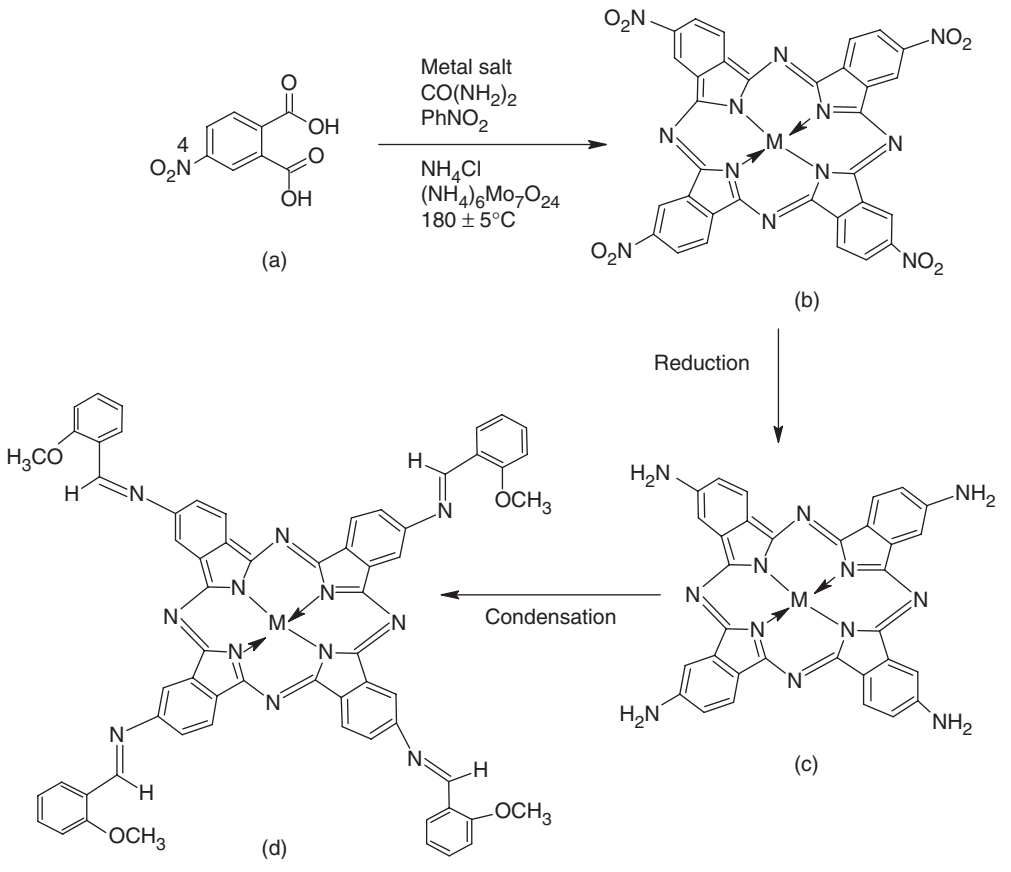
4-Nitrophthalic acid was synthesized by using phthalic anhydride adopting the procedure reported elsewhere [11]. All other chemicals were of analytical grade and used as received. Metal(II) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanines are prepared as per scheme 1.

2.1. *Preparation of cobalt(II) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanine*

The procedure adopted for the synthesis of cobalt(II) 4,4′,4″,4‴-tetra-nitro phthalocyanines (M-PcTN) is reported elsewhere [11]. The nitro derivative of the aforesaid complex is converted into the amino derivative quantitatively by reduction using sodium sulfide Nanahydrate (Na_2S9H_2O) in aqueous medium [12]. The finely powdered cobalt(II) 4,4′,4″,4‴-tetraamino phthalocyanine (M-PcTA) (6.30 g, 0.01 M) was dissolved in a stoichiometric quantity of DMSO, and mixed with anisaldehyde. After refluxing for 5 h in the presence of catalytic quantity of concentrated sulfuric acid, the contents were poured into ice cold water. The settled bluish green colored condensed imino phthalocyanine complex was washed with alcohol several times until it is free from aldehyde.

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 sulphuric acid. The mixture was allowed to stand for 1–2 h and then poured onto 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) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanines of Cu(II), Ni(II) and Zn(II) were prepared by the above procedure using the respective metal amino phthalocyanines.



Scheme 1. Synthesis of metal(II) 4,4′4″,4‴-tetra-methoxyphenylimino phthalocyanines; (a) 4–nitrophthalic acid; (b) M-PcTN; (c) M-PcTA and (d) M-ImPc.

3. Results and discussions

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. C, H and N elemental analyses were done by STIC, Kochi, Kerala, India. Magnetic susceptibility studies were made at room temperature (28°C) 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 $Hg[Co(SCN)_4]$ complex was used as calibrant [14]. A Philips analytical PW-1710 X-ray diffractometer was used to study the diffraction pattern 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^{-1}. Themo gravimetric analysis (TGA) studies were carried out by using a Perkin-Elmer, Diamond TG/DTA thermal analyzer at a heating rate of 10°min^{-1} both in the air and nitrogen atmosphere.

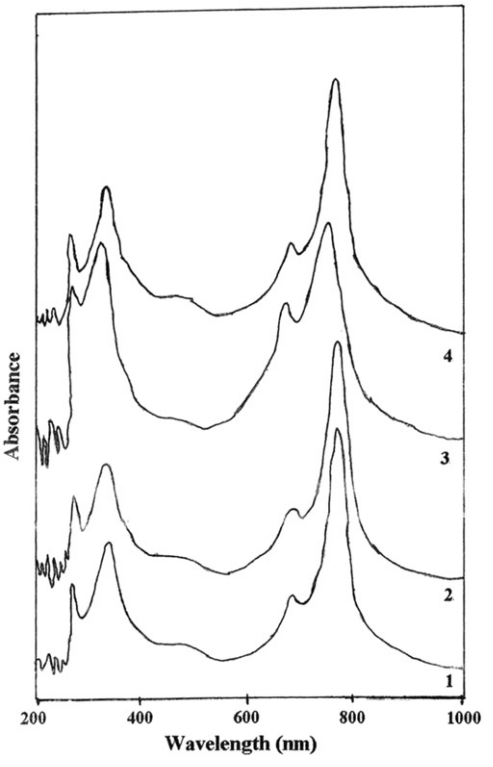
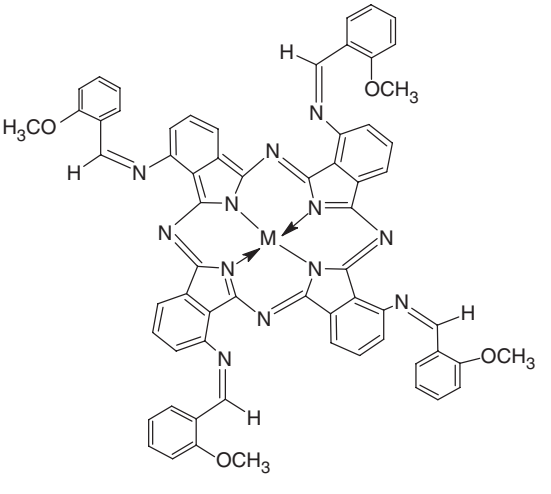


Figure 1. Electronic spectra. (1) Co–ImPc, (2) Cu–ImPc, (3) Ni–ImPc and (4) Zn–ImPc.

The synthesis of M-ImPcs yields pure dark bluish green complexes. These complexes give clear solutions in DMSO and concentrated sulfuric acid and are sparingly soluble in alcohol, DMF and pyridine. The elemental analyses for carbon, hydrogen and nitrogen and gravimetric methods for metals (table 2) are in good agreement with the calculated values and consistent with the proposed structure given below.



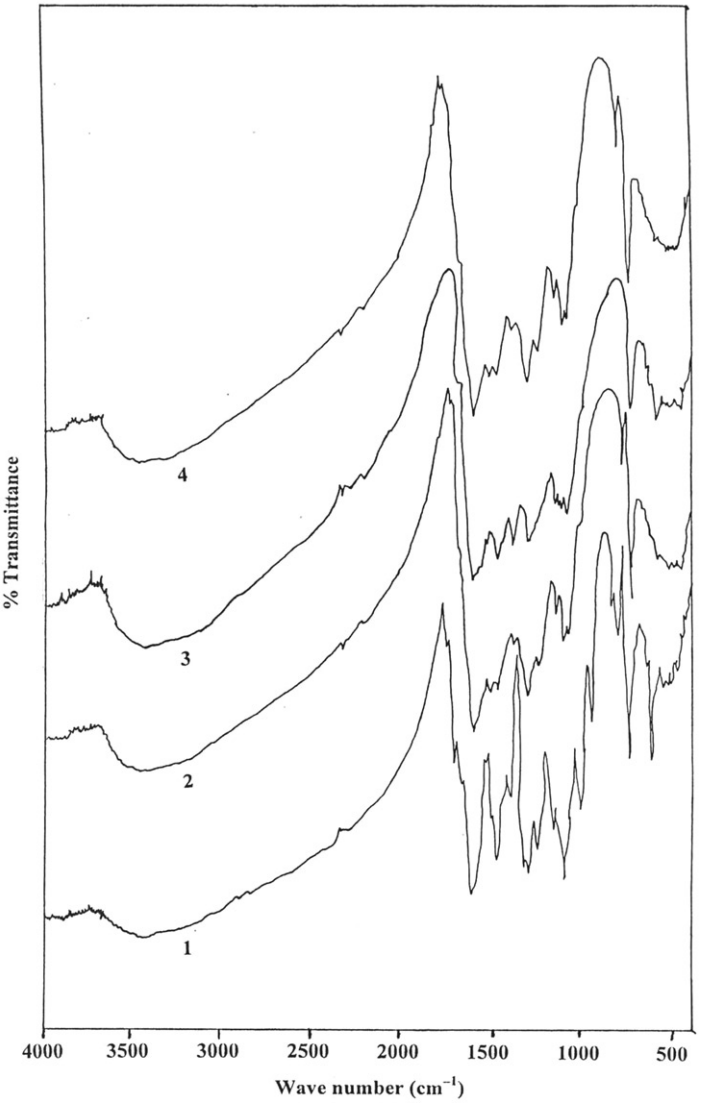


Figure 2. IK absorption spectra. (1) Co–ImPc, (2) Cu–IrnPc, (3) Ni–ImPc and (4) Zn–ImPc.

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

3.1. Electronic spectra

The electronic spectra of M-ImPcs were recorded in DMSO in the concentration range of $1.0–1.5 \times 10^{-4}$ M and the summary of the results are presented in table 1

(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 [2]. For all the complexes absorption bands are observed in the wavelength range 773–783nm, which are considerably higher than the corresponding parent metal phthalocyanine [2]. This observed red shift is attributed to

Table 1. Spectral data of metal(II) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanines.

Complex	UV-visible wavelength λ nm (log ε)	IR spectral data (cm^{-1})	Powder XRD data 2θ angle (d A°)	Relative intensity (%)
Co–ImPc	205 (3.44)	607,752,1093,	26.59 (3.34)	100.00
	241 (3.58)	1259,1316,1403,	28.67 (3.11)	93.97
	480 (3.21)	1491,1616.	32.71 (2.73)	91.57
	691 (4.35)			
	783(3.81)			
Cu–ImPc	206 (3.34)	690,747,1021,	26.85 (3.26)	100.00
	256(4.12)	1253,1310,1405,	28.70 (3.16)	97.81
	479 (3.99)	1497,1631.	32.84 (2.15)	96.05
	690 (4.22)			
	775 (3.41)			
Ni–ImPc	224 (3.44)	648,752,1021,	26.83 (3.79)	100.00
	257 (4.17)	1253,1316,1403,	28.92 (3.18)	98.86
	479 (3.39)	1491,1631.	32.74 (2.27)	98.48
	690 (4.56)			
	773 (3.55)			
Zn–ImPc	215 (3.66)	700,742,1088,	26.87 (3.56)	100.00
	262 (4.49)	1259,1341,1409,	28.58 (3.21)	86.26
	468 (3.69)	1486,1636.	32.75 (2.54)	85.98
	690 (4.22)			
	773 (4.65)			

Table 2. Elemental analysis and magnetic susceptibility data of metal(II) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanines.

Complex (color) (yield)	Empirical formulae (Molecular weight)	Field strength KGuass	Magnetic susceptibility ($\chi_m \times 10^{-6}$ cgs unit)	Magnetic moments μ_{eff} (BM)	Elemental analysis found (Calcd)
Co–ImPc	$C_{64}H_{44}N_{12}O_4Co$	2.20	+3276.96	2.81	C: 69.63; (69.5)
(Dark green)	(1102.93)	2.66	+3149.45	2.76	H: 3.99; (3.92)
(95%)		3.10	+3033.10	2.70	N: 15.23; (15.1)
		3.58	+2890.65	2.64	O: 5.80; (5.78)
		4.01	+2688.01	2.54	Co: 5.34; (5.38)
Cu–ImPc	$C_{64}H_{44}N_{12}O_4Cu$	2.20	+3152.90	2.76	C: 69.37; (69.4)
(Dark green)	(1107.54)	2.66	+3051.12	2.71	H: 3.97; (3.95)
(95%)		3.10	+2824.80	2.61	N: 15.17; (15.1)
		3.58	+2772.60	2.59	O: 5.78; (5.80)
		4.01	+2555.11	2.48	Co: 5.73; (5.80)
Ni–ImPc	$C_{64}H_{44}N_{12}O_4Ni$				C: 69.65; (69.6)
(Dark green)	(1102.69)	2.66	−637.50	–	H: 3.99; (3.95)
(95%)					N: 15.23; (15.1)
					O: 5.80; (5.82)
					Ni: 5.32; (5.36)
Zn–ImPc	$C_{64}H_{44}N_{12}O_4Zn$	2.66	−847.35		C: 69.25; (69.2)
(Dark green)	(1109.39)			–	H: 3.96; (3.95)
(85%)					N: 15.14; (15.1)
					O: 5.77; (5.73)
					Zn: 5.89; (5.84)

the increase in conjugation of the phthalocyanine B-electrons with that of peripheral substituted aromatic imino group. Also for Cu–ImPc and Co–ImPc absorption bands were observed at 690 nm and for Ni–ImPc and Zn–ImPc shoulders were observed. The origin of the Q-band is attributed to the $a_{1u} \rightarrow e_g$ transition of the phthalocyanine molecule. A sharp and intense B-band is observed in all the complexes in the range of 331–355 nm. A weak L-band is observed for all metal-imino phthalocyanines at 241–262 nm. A band observed for all the complexes in the range of 205–224 nm may be the C-band of the phthalocyanine molecule.

3.2. *IR spectra*

IR spectral data were recorded in KBr pellets and the results are presented in table 2 (Figure 2). A sharp peak at 1616–1636 cm^{-1} is attributed to C=N of imine group and peaks in the range 1486–1497 cm^{-1} are due to C–N aromatic stretching. The peaks in the range of 1403–1409 cm^{-1} were attributed to CH_3 bending. The 1253–1259 cm^{-1} peaks are attributed to C–O–C asymmetric stretching vibrations and 1021–1093 cm^{-1} to C–O–C symmetric stretching vibrations. 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.

3.3. *Powder XRD*

The powder X-ray diffraction patterns of M-ImPc's taken through a range of 2θ angles 6–70° showed identical peaks with very poor crystallinity (table 1). The observed patterns are very similar to those 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 appears to hinder the effective stacking of the molecules, and thus give rise to the poor crystallinity of the complexes.

3.4. *Magnetic susceptibility*

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

Table 3. Thermodynamic degradation pattern of metal(II) 4, 4′, 4″, 4‴-tetra-methoxyphenylimino phthalocyanines.

Compound	Decomposition temp. (°C)	Mass loss		Probable mode of decomposition and fragments lost
		% Found	% Calcud	
Co–ImPc	135–350°C	48.6	48.38	4 Imino group
	350–490°C	45.6	44.96	Pc moiety
Cu–ImPc	128–350°C	46.4	48.04	4 Imino group
	350–470°C	44.2	44.78	Pc moiety
Ni–ImPc	135–360°C	47.5	48.10	4 Imino group
	360–480°C	43.6	44.76	Pc moiety
Zn–ImPc	135–340° C	46.2	47.93	4 Imino group
	340–580°C	44.1	44.71	Pc moiety

Pc, Phthalocyanine.

3.5. *Thermogravimetric and kinetic studies*

Thermogravimetric analytical data of imino substituted metal phthalocyanine complexes are summarized in table 3. Decomposition of the complexes occurs in two steps. The first step of degradation which takes place in the temperature region of 128–360°C is 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 range of 360–580°C corresponds to the oxidative degradation of phthalocyanine moiety. The residues remaining after the thermal decomposition were found to be the corresponding metal oxides [15]. The thermal decomposition of these imino substituted complexes in the nitrogen atmosphere appears to be very slow. For Co–ImPc, 65% of the complex was found to be decomposed at 700°C. For Cu–ImPc, Ni–ImPc and Zn–ImPc only about 62, 58 and 52% loss of the mass was observed even at 700°C, confirming the relatively higher stability of these complexes in nitrogen than in air. Even though all four functional groups seem to be lost during first and second steps, a dimer or polymer is suspected to be formed via the nitrogen atoms of the peripheral end groups before the second step of decomposition starts [16]. 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 [17] (Figure 3). 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 the functional groups occurs. From the plots, the energy of activation (E_a) and frequency factor ($\ln A$) were evaluated. Enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) have been computed using standard equations (table 4).

4. Biological activities

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

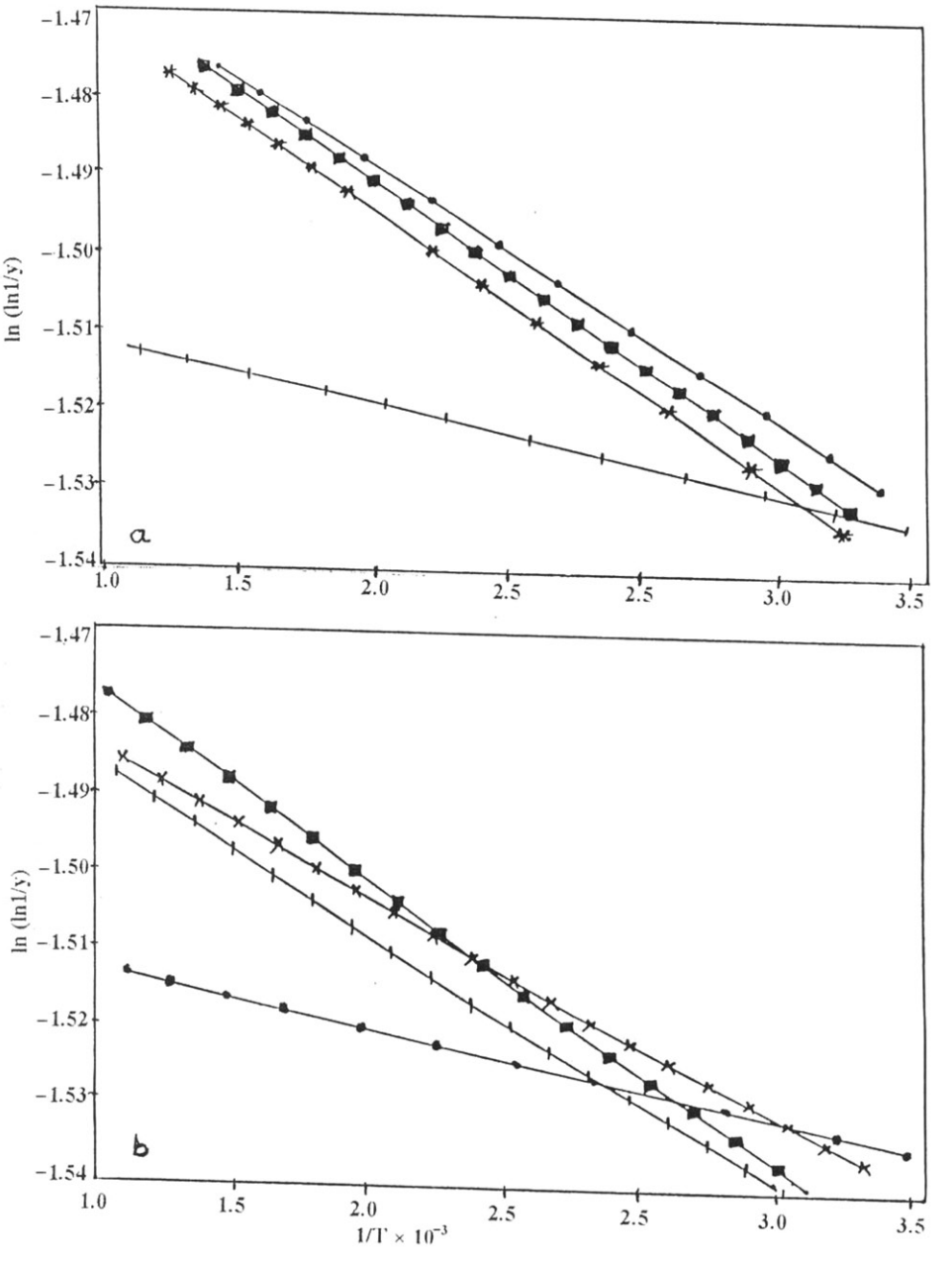


Figure 3. Plots of In (Inl/y) *vs.* $1/T \times 10^3$ for the thermal degradation or Co–ImPc (–◆–), Cu–ImPc (–●–), Ni–ImPc (–×–) and Zn–ImPc (–////–) in air (a) and in nitrogen atmosphere (b).

4.1. *Antifungal activity*

The *Aspergilus niger* and *Aspergilus flavons* were studied for growth, color and sporulation characteristics in the presence of the metal phthalocyanine complexes. M-ImPc and complexes of 1000 ppm were prepared by dissolving the required

quantity of complex in DMSO. The corresponding tetra amino phthalocyanine complexes were also dissolved in DMSO to prepare 1000 ppm solution and antifungal studies were carried out under similar conditions for comparison. They were further diluted with DMSO for the preparations of 500, 100 and 50 ppm solution. Control was maintained by adding 2 mL of DMSO 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 cooled to room temperature (26°). The *A. niger* and *A. flavons* were inoculated as a point at the center of the plate and incubated at 23 ± 1°C for one week; observations were made daily. The summary of the observations of the experiments were presented in table 5. All the complexes inhibit the radial growth of the fungi. After 2 days of inoculation, the fungi

Table 4. Thermodynamic parameters of metal(II) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanines.

Compound	Activation energy Ea $(KJ\,mol)^{-1}$	Frequency factor ln A	ΔH $(KJ\,mol)^{-1}$	ΔS $(J\,K)^{-1}$	ΔG $(KJ\,mol)^{-1}$
Co–ImPc	1.062 (0.721)	4.314 (3.557)	0.021 (−0.513)	−159.87 (−173.6)	20.80 (25.53)
	3.038 (59.86)	5.118 (22.48)	−3.030 (55.708)	−162.19 (322.09)	115.37 (−105.3)
Cu–ImPc	0.943 (0.333)	4.096 (2.446)	0.136 (−0.914)	−156.11 (−184.9)	20.43 (26.82)
	3.829 (71.77)	5.464 (26.59)	−2.156 (67.862)	−157.61 (457.9)	111.32 (−147.2)
Ni–ImPc	0.857 (0.542)	3.913 (3.544)	0.223 (−0.516)	−153.38 (−174.4)	20.16 (24.94)
	3.168 (65.4)	5.137 (22.58)	2.983 (56.20)	−161.82 (326.56)	116.76 (−107.3)
Zn–ImPc	1.236 (0.435)	2.843 (2.734)	0.576 (−1.060)	−141.35 (−182.5)	17.53 (31.79)
	4.352 (48.687)	5.542 (18.04)	−2.631 (43.865)	−157.14 (174.37)	129.36 (−57.27)

The values in the bracket corresponds to the nitrogen atmosphere.

Table 5. Anti-fungal data of metal(II) 4,4′,4″,4‴-tetra-methoxyphenylimino phthalocyanines.

		A. niger		*A. flavons*	
		Radial growth in cm		Radial growth in cm	
Compound	Concentration (in ppm)	2 days	5 days	2 days	5 days
Control		1.50	3.90	1.35	3.50
Co–ImPc	50	1.25 (1.45)	3.45 (3.85)	1.25 (1.35)	3.30 (3.40)
	100	1.00 (1.35)	3.20 (3.75)	1.10 (1.30)	3.10 (3.30)
	500	0.80 (1.20)	3.05 (3.55)	0.90 (1.20)	2.95 (3.25)
	1000	0.65 (1.05)	2.70 (3.40)	0.75 (1.10)	2.65 (3.15)
Cu–ImPc	50	1.30 (1.50)	3.60 (3.80)	1.25 (1.30)	3.30 (3.45)
	100	1.10 (1.45)	2.30 (3.65)	0.90 (1.25)	2.40 (3.20)
	500	0.95 (1.35)	2.05 (3.55)	0.80 (1.15)	2.15 (3.05)
	1000	0.70 (1.25)	1.80 (3.15)	0.70 (1.05)	2.00 (2.85)
Ni–ImPc	50	1.35 (1.40)	3.55 (3.75)	1.25 (1.35)	3.30 (3.50)
	100	1.05 (1.35)	3.15 (3.70)	1.00 (1.30)	3.05 (3.40)
	500	0.80 (1.20)	2.70 (3.45)	0.80 (1.15)	2.85 (3.25)
	1000	0.50 (1.05)	2.20 (3.25)	0.60 (1.05)	2.35 (3.10)
Zn–ImPc	50	1.40 (1.45)	3.65 (3.60)	1.20 (1.25)	3.45 (3.45)
	100	0.85 (1.40)	1.80 (3.45)	0.95 (1.40)	1.95 (3.05)
	500	0.60 (1.25)	1.40 (3.20)	0.70 (1.25)	1.55 (2.85)
	1000	0.45 (1.00)	1.15 (2.85)	0.55 (1.05)	1.25 (2.55)

exhibited minimal growth. It was observed that the inhibiting effects of both M-ImPcs and tetra amino phthalocyanine were more for *A. niger* compared to *A. flavons*. After 5 days, all the complexes showed distinct inhibiting effect. However, Zn–ImPc induced maximum effect. The inhibition of growth is in the order Zn–ImPc > Co–ImPc > Cu–ImPc > Ni–ImPc, compared to the corresponding tetra amino phthalocyanines.

The change in the color of the fungi during the investigation was interesting. *A. niger* is known for its black color and *A. flavons* for its green color. However, in the presence of metal complexes, the mature colonies of the fungus were pale brown and the new colonies were pale green. It was confirmed by parallel experiments with and without the addition of 2 mL DMSO in the media that the change in color of the fungi was not due to the presence of DMSO 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.

4.2. *Antibacterial activity*

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

Method: The imino phthalocyanine complexes were tested against pathogenic bacteria *Xanthomonas citri* and *Xanthomonas* sp.

The agar diffusion cup plate method was followed for antibacterial assay as described in Indian pharmacopoeia [18]. Inoculum was prepared from 24 h old culture in nutrient broth. The M-ImPc complexes of 1000 ppm were prepared by dissolving the required quantity of complex in DMSO. The corresponding tetra amino phthalocyanine complexes were also dissolved in DMSO to prepare 1000 ppm solution and antibacterial studies were carried out under similar conditions for comparison. They were further diluted with DMSO for the preparations of 500, 200 and 100 ppm solution. With the help of stainless steel well cutter (6 mm) cups were cut out and into each of these cups 10 µl of each complex of different concentrations and blank (DMSO) were placed separately under aseptic conditions with the help of a sterile micropipette. The plates were then maintained at room temperature (26°) for 1 h to allow the diffusion of the solutions into medium and incubated at 37°C for *X. citri* and *X.* sp. Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 h [19–20]. Maximum inhibition was observed in Zn–ImPc and the least inhibition effect was observed in Co–ImPc, compared to the corresponding tetra amino phthalocyanines. The data of Zone of inhibition are presented in table 6.

5. Conclusions

The synthetic route adopted was very simple and gave good yields. 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 group.

Table 6. Zone of inhibition of metal(II) 4, 4′, 4″, 4‴-tetra-methoxy-phenylimino phthalocyanines.

Compound	Concentration (in ppm)	*X.* species Zone of inhibition (in mm)	*X. citri* Zone of inhibition (in mm)
Control		05	06
Co–ImPc	50	07 (03)	08 (06)
	100	09 (05	11 (08)
	200	12 (06)	15 (11)
	500	16 (09)	19 (14)
Cu–ImPc	50	07 (04)	06 (06)
	100	11 (07)	09 (08)
	200	14 (09)	13 (10)
	500	18 (13)	18 (13)
Ni–ImPc	50	06 (03)	08 (07)
	100	11 (06)	13 (09)
	200	16 (09)	16 (13)
	500	19 (14)	19 (16)
Zn–ImPc	50	06 (04)	06 (06)
	100	09 (06)	10 (08)
	200	15 (09)	14 (11)
	500	20 (13)	21 (15)

The magnetic susceptibility studies clearly revealed the structural information of the complexes.

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References

[1] F.H. Moser, A.L. Thomas. *Phthalocyanines Compounds*, Rheinhold Publishing Corporation, New York (1963).
[2] C.C. Leznoff, A.B.P. Lever. *Phthalocyanines, Properties and Applications*, Vol. 1, V.C.H. Publications Inc., New York (1989).
[3] M. Phillipe, L. Regean, J. E. Van-liar Gasperd, *J. Photochem. Photobiol.*, **14**(3), 187 (1992).
[4] P. Gregory. *J. Porphy. Phthalocyan.*, **4**, 432 (2000).
[5] J.F. Bartoli, P. Brigoud, P. Battioni, D. Mansuy. *J. Chem. Soc., Chem. Commun.*, 440 (1994).
[6] M.W. Grinstaff, M.G. Hill, I. Labinger, H.B. Gray. *Science*, **264**, 1311 (1994).
[7] S.A. Priola, A. Raines, W.S. Caughey. *Science*, **287**, 1503 (2000).
[8] M.C. Harsans, N.P. Guisinger, J.W. Lyding. *Nanotechnology*, **11**, 70 (2000).
[9] D. Scblewein, E. Karmann, T. Ockermann, H. Yanagi. *Electrochim. Acta*, **45**, 4697 (2000).
[10] R. Jasinski. *Nature*, **201**, 1212 (1964).

[11] M.P. Somashekarappa. *J. Keshavayya. Synth. React. Inorg. Met.-org. Chem.*, **29**(5), 767 (1999).
[12] M.P. Somashekarappa, J. Keshavayya. *J. Soudi. Chem. Soc.*, **3**(2), 113 (1999).
[13] B.N. Achar, G.M. Fohlen, J. A. Parker, Keshavayya. *Polyhedron*, **6**(6), 1463 (1989).
[14] P. Selwood. *Magnetochemistry*, Interscience, New York (1956).
[15] A. I. Vogel. *Quant. Inorgan. Analys.*, 3rd Edn, Longmans Publishers, London (1964).
[16] M.P. Somashekarappa, K.R. Venugopala Reddy, M.N.K. Harish, J. Keshavayya. *J. T. R. Chem.*, **11**(1), 1 (2004).
[17] A. Broido. *J. Polym. Sci., Part A-2*, **7**, 1761 (1969).
[18] Indian pharmacopoeia. 3rd Edn, p. 90, New Delhi, Appendix IV, (1985).
[19] L. Ahmed, Z. Mohammed, F. Mohammed. *J. Ethnopharmacol*, **62**, 183 (1998).
[20] S.N. Padhy, S.B. Mahato, N.L. Dutta. *Phytochem.*, **12**, 217 (1973).