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Synthesis, spectral, magnetic and antifungal studies on symmetrically substituted metal(II)octaiminophthalocyanine pigments

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Abstract

Symmetrically substituted metal(II) (M = Cu, Co, Ni, Zn)-1,3,8,10,15,17,22,24-octaiminophthalocyanines (M-ImPcO) were synthesized using an efficient, simple and novel method via the reduction of the corresponding nitro phthalocyanines. The dark green octaiminophthalocyanine derivatives were characterized by elemental analysis, magnetic susceptibility, electronic, IR and powder X-ray diffraction studies to check the purity, structural integrity and crystallinity of the complexes. Magnetic susceptibility studies of the Co(II) and Cu(II) octaiminophthalocyanine complexes revealed a variation in magnetic moments as a function of field strength indicating the presence of intermolecular co-operative effect. The complexes were screened for antifungal activity.

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1. Introduction

Phthalocyanines have been the subject of much research for over 50 years [1] and many patents have been recorded [2]. While the literature contains references to synthesis of a variety of metallosubstituted phthalocyanine derivatives [3–6], the main thrust of this work concerned the enhancement of the solubility of the phthalocyanines in various solvents. In general, these derivatives were synthesized by the tetramerization of a single type of substituted phthalyl compound resulting in the substitution of identical groups on each of the component benzenoid rings, giving tetra and octa substitution or higher, substitution.

Phthalocyanines are well-known commercial blue green pigments. The color is due to intense absorption in the visible region spectrum of the Q-band [7–9]. Phthalocyanines have also been used as catalysts for several manufacturing processes [10]. However, phthalocyanines also show interesting photophysical properties, redox properties and both photo and dark semiconductivities, which render them particularly interesting for more technologically advanced applications such as laser printing [11], optical data storage systems [12], and as photosensitizers in photodynamic therapy [13]. These compounds are also used in fabricating photovoltaic [14], and fuel cells [15], and also as the active compound in gas sensing systems [16].

Metal phthalocyanines are generally insoluble in most organic solvents and, as a consequence, their commercial exploitation is limited. Their solubility can be enhanced by substitution at the periphery of the molecule or by changing the central metal ion. In the present work, an attempt has been made to place a suitable substituent at the periphery of

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the molecule. The imine group was introduced by the reaction of amino derivatives of the phthalocyanines with aldehydes. Even though, the previous papers have concerned the synthesis and structural investigation of metal(II)-1,3,8,10,15,17,22,24-octaaminophthalocyanines, no documentary evidences are available on the synthesis and structural studies on metal(II)-1,3,8,10,15,17,22,24-octaiminophthalocyanine complexes.

This paper concerns the synthesis, characterization and magnetic susceptibility of 1,3,8,10,15,17,22,24-octaiminophthalocyanine complexes of copper(II), cobalt(II), nickel(II) and zinc(II). The synthetic route adopted for the synthesis of octaiminosubstituted metal(II) phthalocyanines is given in Scheme 1.

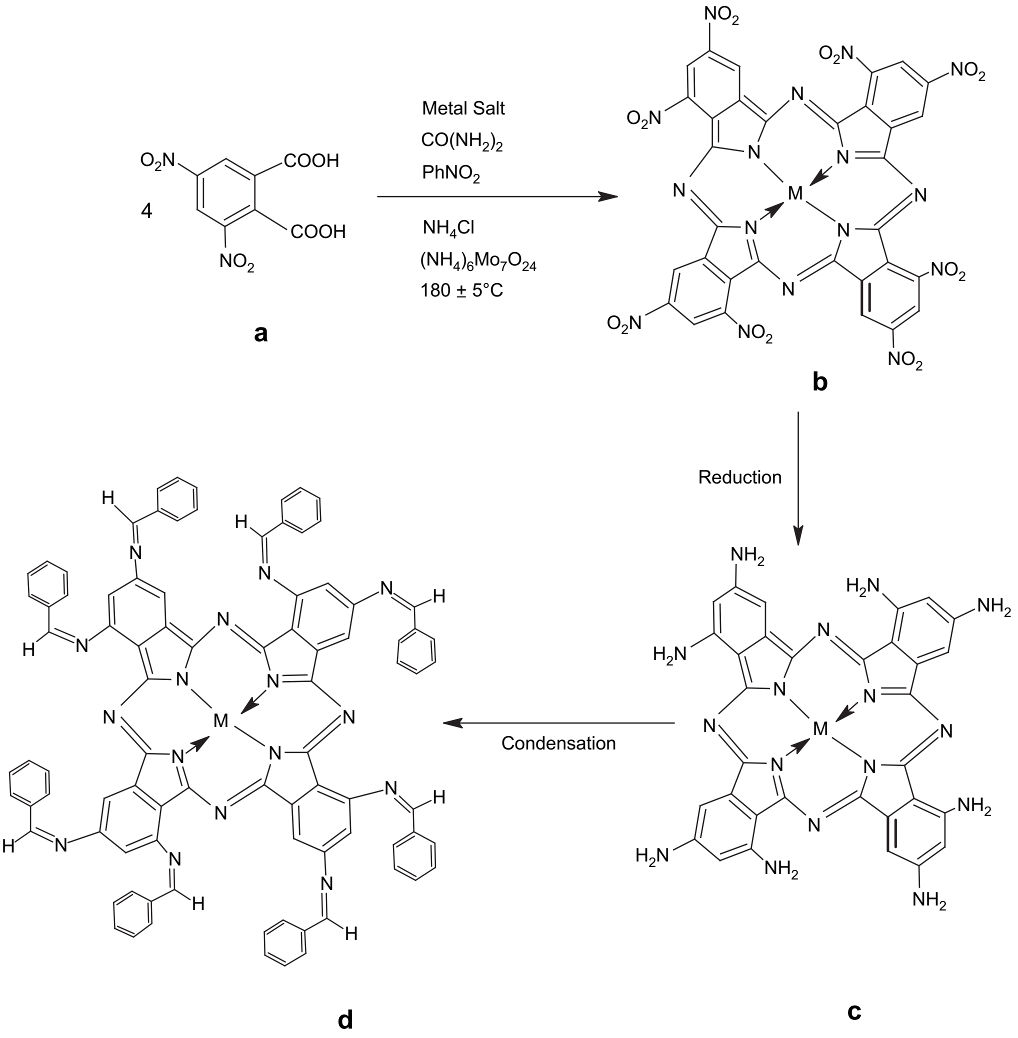
2. Experimental

3,5-Dinitrophthalic acid was prepared as reported [17]; all other chemicals were of analytical grade. The metal(II)-1,3,8,10,15,17,22,24-octanitrophthalocyanines were prepared by the reported procedure [18]. These complexes were converted into their respective amino derivatives using sodium sulphide nanohydrate [$Na_2S \cdot 9H_2O$] as reducing agent using the published procedure [19], quantitatively. The substituted amino complexes were converted to the imino derivatives by condensation [20].

2.1. Preparation of cobalt(II)-1,3,8,10,15,17,22,24-octaiminophthalocyanine complex

The procedure adopted for the synthesis of cobalt(II)-1,3,8,10,15,17,22,24-octanitrophthalocyanine complex is reported elsewhere [18]. The finely grounded metal(II)-1,3,8,10,15,17,22,24-octaaminophthalocyanine (6.30 g, 0.1 mol) was dissolved in stoichiometric quantity of 15 M sulphuric acid; to this benzaldehyde (4.8 ml, 0.01 mol) and catalytic amount of concentrated sulphuric acid was added. The ensuing mixture was refluxed with stirring for 5 h after which the green colored iminophthalocyanine complex was washed with alcohol several times until it was free from benzaldehyde. Finally it was washed with distilled water and dried over anhydrous phosphorous pentoxide in vacuum desiccator.

The pigment form of the above complex was obtained by the acid pasting process, in which 1 part of the powdered sample was dissolved in 6–10 parts of concentrated sulphuric acid. The mixture was allowed to stand for 1–2 h and then



Scheme 1. Synthesis of metal(II)-1,3,8,10,15,17,22,24-octaiminophthalocyanine: a. 3,5-dinitrophthalic acid, b. M-PcON, c. M-PcOA and d. M-imPcO.

poured on to 45–50 parts of crushed ice and stirred thoroughly. The pigment thus obtained was filtered off and washed with hot water before being finally washed with distilled water and dried under vacuum over phosphorous pentoxide.

Metal(II)-1,3,8,10,15,17,22,24-octaiminophthalocyanines of copper(II), nickel(II), and zinc(II) were prepared using the above procedure, employing the respective amino metal phthalocyanines.

2.2. Method

C, H and N analyses were performed at Cochin University, Sophisticated Test & Instrumentation Center, Kochi, Kerala, India. The magnetic susceptibility of the complexes were measured at room temperature (301 K) using a Gouy magnetic balance consisting of NP-53 type electromagnets with a DC power supply unit and a digital semi-micro balance; Pascal constants were used to calculate the diamagnetic corrections using a $Hg[Co(SCN)_4]$ complex as calibrant [21]. A. Shimadzu UV–Visible recording spectrometer, UV-160A with 1 cm path length cell was used for recording electronic absorption spectra. IR spectra were recorded using Nicolet MX-FTIR spectrometer. A Phillip Analytical PW1710 X-ray diffractometer was used to record diffraction patterns. Spectra were recorded using Cu Kα at 40 kV, 20 mA, using a time constant of 4, channel width of 7 mm and chart speed of 10 mm/min. Perkin–Elmer Thermal analyzer was used for simultaneous recording of TGA and DTA at the rate of 10 °C/min in air, as well as in a nitrogen atmosphere.

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

Aspergillus niger was used for its growth and sporulation color characteristics in the presence of the selected metal phthalocyanine complexes. *A. niger* was procured from the Department of Biotechnology, Sahyadri science college, Shimoga. A 100 ppm solution of different M-ImPcO complexes were prepared by dissolving required amount of complexes in 2 ml of DMSO and 98 ml of PDA medium and sealed with aluminum foil and sterilized in an autoclave at a temperature 120 °C and 15 psi pressure for 15 min. The hot sterilized medium was poured into sterile Petri plates in an aseptic chamber and cooled. *A. niger* was inoculated on the solidified medium as a point at the center of the plate. The inoculated plates were incubated at 23 ± 1 °C for one week, and the observations were made on 3rd, 5th and 7th day.

3. Results and discussion

The procedure used for the synthesis of M-ImPcO provides complexes and of dark green color in the case of Cu(II), Co(II), Ni(II) and green with brown tinge color in the case of Zn(II). The metal phthalocyanine complexes, which are thermally stable and resistant towards concentrated sulphuric acid have a metal atomic radii in the range of 1.35 Å. These complexes give clear solution in DMSO, DMF, and pyridine, but insoluble in water and common organic solvents, such as alcohol, ether, carbon tetrachloride and benzene. The elemental analyses were in good agreement with the calculated values and are given in Table 1. The above results are consistent with the suggested structure, as given in Fig. 1.

4. Electronic spectra

The electronic spectra of all M-ImPcO were recorded in the concentration range of $1.0–1.5 \times 10^{-4}$ M in 1; 1 M sulphuric acid (Table 2). The observed bluish green color of the complexes is attributed $a_{2u} \rightarrow e_g$ and $b_{2u} \rightarrow e_g$ transitions. For all the complexes, a peak was observed in the range of 725–732 nm and is assigned to Q-band of characteristic

Table 1
Elemental analysis and magnetic susceptibility data of metal(II)-1,3,8,10,15,17,22,24-octaiminophthalocyanines

Complex (color) (yield)	Empirical formulae (formula weight)	Field strength (kG)	Magnetic susceptibility ($\chi_m \times 10^{-6}$ cgs unit)	Magnetic moments, μ_{eff} (BM)	Elemental analysis found (calcd)
Co-ImPcO (dark green) (90%)	$C_{88}H_{56}N_{16}Co$ (1394.93)	2.20	+3601.02	2.963	C: 75.45 (75.40);
		2.66	+3450.91	2.897	H: 4.00 (4.00);
		3.10	+3165.91	2.770	N: 16.00 (15.95);
		3.58	+2901.16	2.657	Co: 4.54 (4.50)
		4.01	+2681.40	2.554	
Cu-ImPcO (dark green) (90%)	$C_{88}H_{56}N_{16}Cu$ (1399.54)	2.20	+3674.41	2.962	C: 75.70 (75.65);
		2.66	+3248.54	2.791	H: 4.01 (4.00);
		3.10	+2980.79	2.672	N: 16.05 (15.95);
		3.58	+2732.47	2.540	Cu: 4.22 (4.20)
		4.01	+2632.20	2.456	
Ni-ImPcO (dark green) (85%)	$C_{88}H_{56}N_{16}Ni$ (1394.69)	2.66	−907.40	–	C: 75.75 (75.70);
					H: 4.01 (4.00);
					N: 16.06 (16.01);
					Ni: 4.20 (4.18)
Zn-ImPcO (green with brown tinge) (80%)	$C_{88}H_{56}N_{16}Zn$ (1401.39)	2.66	−1575.72	–	C: 75.35 (75.30);
					H: 3.99 (3.95);
					N: 15.98 (15.95);
					Zn: 4.66 (4.63)

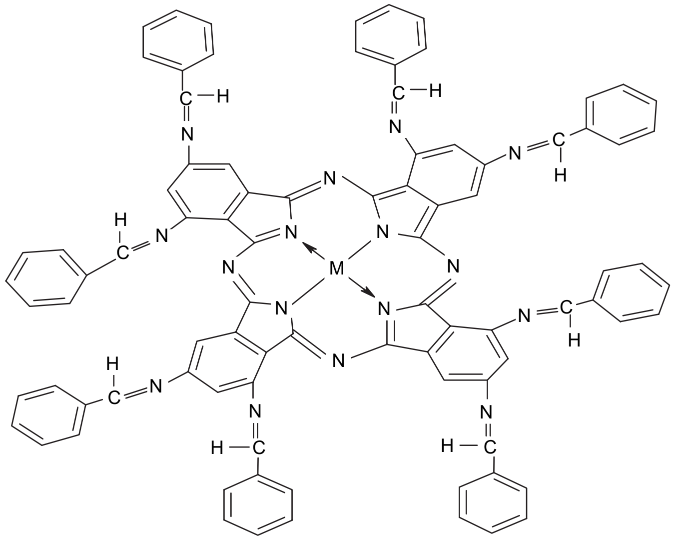


Fig. 1. Suggested structure of symmetrically substituted octaiminophthalocyanines where M = Co, Cu, Ni, and Zn.

phthalocyanine moiety. Compared to the corresponding parent metal phthalocyanines the Q-band in each of the M-ImPcO underwent a bathochromic shift which may be assigned to the extension of the π-delocalized electron cloud over the aromatic component of the substituents that are present at the periphery of the phthalocyanine molecule. However, splitting of the Q-band was observed in all the complexes and appeared in the 636–674 nm [22]. The origin of the Q-band was attributed to the $a_{1u} \rightarrow e_g$ transition of the phthalocyanine molecule [22]. A sharp intense B-band and a weak L-band was observed for all the complexes in the range of 305–327 nm and 208–218 nm [19] respectively.

5. IR spectra

IR spectral data of the metal(II)-octaiminophthalocyanine pigments were recorded using KBr pellets (Table 2 and Fig. 2). The sharp peak observed in the range 3436–3493 cm^{-1} is assigned to the hydrogen bonding formed between the nitrogen atom of the phthalocyanine macromolecule and H-atom of moisture observed on the KBr pellets during pellatisation [23]. The very weak signal observed in the range 2344–2360 cm^{-1} is due to C–H stretching at the periphery of the phthalocyanine moiety. The sharp peak at 1616–1641 cm^{-1} is assigned to C=N of imine group and the peaks in the range 1388–1403 cm^{-1} are due to C–N aromatic stretching [24]. All the remaining bands observed in the range 1201–1284, 1041–1180, and 596–875 cm^{-1} can be assigned to various characteristic skeletal vibrations of the phthalocyanines [25].

6. Magnetic susceptibility

The magnetic susceptibility measurements of M-ImPcO were investigated in solid state (Table 1). The reported values

Table 2
Electronic, IR and powder XRD data of metal(II)-1,3,8,10,15,17,22,24-octaiminophthalocyanines

Complex	UV–vis absorption λ, nm (log ε)	IR spectral data (cm^{-1})	Powder XRD data 2θ angle (d Å)	Relative intensity (%)
Co-ImPcO	213 (4.88), 305 (5.45), 636 (4.68), 725 (4.68)	628, 1093, 1284, 1388, 1471, 1616, 2355, 3472	25.93 (3.43), 28.83 (3.09), 24.43 (3.43), 31.20 (2.82)	100.00, 79.32, 49.15, 31.56
Cu-ImPcO	215 (4.88), 325 (5.45), 640 (4.68), 732 (4.68)	611, 1041, 1129, 1180, 1393, 1641, 2360, 3477	45.48 (1.99), 31.71 (2.81), 43.71 (2.10), 25.95 (3.43)	100.00, 81.23, 50.48, 33.25
Ni-ImPcO	218 (2.77), 316 (3.52), 674 (5.42), 720 (4.67)	617, 1186, 1326, 1388, 1626, 2350, 3214, 3436	25.93 (3.45), 28.80 (3.09), 23.23 (3.42), 42.78 (2.11)	100.0, 79.79, 44.14, 28.59
Zn-ImPcO	208 (2.79), 306 (3.40), 671 (3.30), 725 (3.07)	596, 875, 1061, 1201, 1403, 1636, 2344, 3493	25.95 (3.42), 28.88 (3.08), 42.92 (2.10), 20.51 (4.32)	100.00, 80.88, 50.14, 35.94

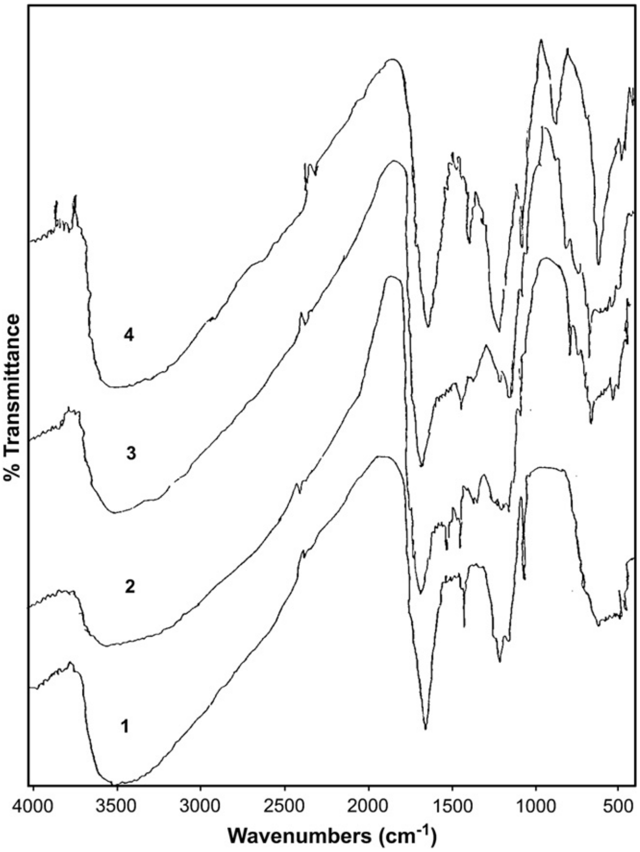


Fig. 2. IR absorption spectra of (1) Cu-ImPcO, (2) Co-ImPcO, (3) Ni-ImPcO, and (4) Zn-ImPcO.

are measured over the applied magnetic field strength of 2.20–4.45 kG and are the average of the three independent determinations. It was found that both Cu-ImPcO and Co-ImPcO are paramagnetic, while Ni-ImPcO and Zn-ImPcO are diamagnetic. The measured magnetic moments for Cu-ImPcO and Co-ImPcO are higher than the spin-only value corresponding to the one unpaired electron (1.73 BM), due to the mixing of ground state $(b_{2g})^2$ $(e_g)^4$ $(a_{1g})^1$ orbitals with higher energy $(b_{2g})^2$ $(e_g)^3$ $(a_{1g})^2$ degenerate states and intermolecular cooperative effect [26]. This effect decreased with the increases field strength. The higher μ_{eff} value at lower field strength is attributed to intermolecular magnetic interaction coupled with magnetic anisotropy of the phthalocyanine π-electron cloud [27].

7. Powder XRD

The X-ray diffraction spectra were taken through a range of 2θ angles 6°–70° and showed identical peaks (Table 2). Two peaks were observed: one sharp at a lower angle with maximum intensity and the other at a higher angle with high intensity. The inter-planar spacing gave the following values: Co-ImPcO 3.43, 25.93 Å; Cu-ImPcO 1.99, 45.48 Å; Ni-ImPcO 3.45, 25.93 Å and Zn-ImPcO 3.42, 25.95 Å, clearly indicating the crystalline nature of the complex. The observed patterns are very much similar to those of the unsubstituted phthalocyanines except for broadening of the peaks in the case of M-Im-PcO which may be due to the presence of substituents which seems to play an important role in the stacking of the metal phthalocyanine derivatives. X-ray diffraction patterns are used only to explain the crystallinity qualitatively.

8. Thermogravimetric and kinetic studies

Thermogravimetric analytical data of iminosubstituted metal phthalocyanine complexes are carried out both in air and nitrogen atmosphere (Tables 3 and 4). It is found that the decomposition of the above complexes occurred in two steps. The first step degradation in air took place in the temperature range of 250–350 °C and may be accounted for by the loss of four imino groups. The major weight loss was observed for all the complexes in the second degradation step in the temperature range of 350–600 °C, which corresponds to the oxidative degradation of phthalocyanine. The residue remaining after thermal decomposition corresponds to the metal oxide [28]. The thermal decomposition of iminosubstituted metal phthalocyanine complexes in a nitrogen atmosphere appears to be very slow. For Co-ImPcO, 65% of the complex was found to be decomposed at 700 °C while for Cu-ImPcO, Ni-ImPcO and Zn-ImPcO, about 58%, 55% and 48% mass losses were observed. The above trend confirms the relatively higher stability of these complexes in air as Co-ImPcO > Cu-ImPcO > Ni-ImPcO > Zn-ImPcO. DTA results revealed that all degradation steps are exothermic in nature. Kinetic and

Table 3
Kinetics and thermodynamic parameters of 1,3,8,10,15,17,22,24-octaiminophthalocyanines of Cu, Co, Ni and Zn, in air and nitrogen atmosphere

Compounds		Activation energy E_0 (kJ/mol)	Frequency factor $\ln A$ (min^{-1})	ΔH (kJ/mol)	ΔS (J/K)	ΔG (kJ/mol)
Cu-ImPcO	I	0.593 (0.538)	3.0431 (3.011)	−1.485 (−1.540)	−43.006 (−1.811)	12.23 (43.95)
	II	3.4476 (1.184)	5.4201 (3.872)	−0.709 (−2.972)	−173.05 (−180.32)	85.81 (87.19)
Co-ImPcO	I	0.467 (0.8895)	2.818 (3.628)	−1610.75 (−1.188)	−182.69 (−180.64)	43.96 (43.97)
	II	3.058 (1.184)	5.422 (3.872)	−1098.44 (−2972.90)	−101.09 (−181.50)	49.61 (87.19)
Ni-ImPcO	I	0.3754 (0.3266)	2.522 (2.406)	−1709.37 (−1751.85)	−182.69 (−186.25)	43.97 (44.81)
	II	4.5614 (0.6117)	5.966 (3.048)	−404.00 (−3545.24)	−104.09 (−181.50)	52.45 (87.20)
Zn-ImPcO	I	0.538 (0.524)	2.918 (2.915)	−1540.47 (−1506.45)	−182.10 (−181.28)	43.98 (43.87)
	II	6.981 (0.786)	7.007 (5.435)	−2824.04 (−1954.23)	−108.97 (−182.41)	51.66 (61.56)

I and II corresponds to the I and II stages of degradation and the values in parenthesis are for nitrogen atmosphere.

Table 4
TGA data of Cu(II), Co(II), Ni(II) and Zn(II)-1,3,8,10,15,17,22,24-octaimino-phthalocyanines

Complex	Temperature of decomposition (°C)	Mass loss		Probable mode of fragmentation
		(%) Found	(%) Calcd	
Cu-ImPcO	250–350	29.72	30.00	4 Imino groups
	350–600	65.73	65.49	4 Imino groups + Pc moiety
Co-ImPcO	250–350	29.81	65.49	4 Imino groups
	350–600	65.96	65.00	4 Imino groups + Pc moiety
Ni-ImPcO	250–350	29.81	29.98	4 Imino groups
	350–600	65.97	65.01	4 Imino groups + Pc moiety
Zn-ImPcO	250–350	29.67	29.99	4 Imino groups
	350–600	65.65	65.00	4 Imino groups + Pc moiety

thermodynamic parameters were evaluated using Boride's method [29].

9. Antifungal activity

It was found that each of the complexes inhibited radial growth of *A. niger*. After the 3rd day of inoculation, the fungus exhibited minimum growth. The inhibition was greatest for Ni complex compared to other complexes; the rate of inhibition was of the order: Ni-ImPcO > Zn-ImPcO > Co-ImPcO > Cu-ImPcO (Table 5).

An interesting observation made during the investigation was the change in the color of fungus sporulation. *A. niger* was known for its black color; however, in the presence of metal complexes, the fungus displayed a pale brown sporulation. It was confirmed by a parallel experiment both with and without addition of 2 ml DMSO in the medium that the change in color of the fungus was not due to the presence of DMSO in the medium. The color change of the fungus may be due to the effect of metal complexes on spore pigmentation [30].

10. Conclusion

Cu-ImPcCo and Co-ImPcCo are paramagnetic and exhibited variation in magnetic moment as a function of magnetic field due to intermolecular co-operative effects. X-ray diffraction studies revealed the crystalline nature of the complexes. The thermal stability of the M-ImPcO in air was of the order of Cu-ImPcO > Co-ImPcO > Ni-ImPcO > Zn-ImPcO. The antifungal activity of the M-ImPcO was of the order: Ni-ImPcO > Zn-ImPcO > Co-ImPcO > Cu-ImPcO.

Table 5
Antifungal data Cu(II), Co(II), Ni(II), Zn(II)-1,3,8,10,15,17,22,24-octaimino-phthalocyanines

Samples	Concentration in ppm	Radial growth of *Aspergillus niger* (in cm) in respective incubation period		
		3rd Day	5th Day	7th Day
Control (DMSO)	–	1.2	2.0	3.2
Ni-ImPcO	100	0.7	1.2	2.1
Co-ImPcO	100	0.9	1.4	2.5
Cu-ImPcO	100	1.0	1.8	2.6
Zn-ImPcO	100	0.9	1.3	2.4

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