



Synthesis, Structural Investigations and Antifungal Studies on Symmetrically Substituted Metal (II) Octa-1-(3-chlorophenyl) Methanimine Phthalocyanine

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Abstract

Metallophthalocyanine (M = Cu, Co, Ni, Zn) carrying eight (3-chlorophenyl) methanimine groups at peripheral positions were synthesized by an efficient simple and novel method. The precursor octaamino metal (II) phthalocyanines were synthesized by the reduction of the corresponding nitro metal phthalocyanines. The dark green octa-1-(3-chlorophenyl) methanimine phthalocyanine derivatives were characterized by elemental analysis, magnetic susceptibility, electronic, IR and powder X-ray diffraction studies to check the purity, structural integrity and crystalline properties of the complexes. Magnetic susceptibility studies on Co (II) and Cu (II) octa-1-(3-chlorophenyl) methanimine phthalocyanine complexes exhibit a variation of the magnetic moments as a function of field strength indicating the presence of inters molecular co-operative effect. The title complexes were screened for antifungal activity.

Keywords: Phthalocyanines, synthesis, octa-1-(3-chlorophenyl) methanimine, electronic, magnetic, XRD, thermal studies.

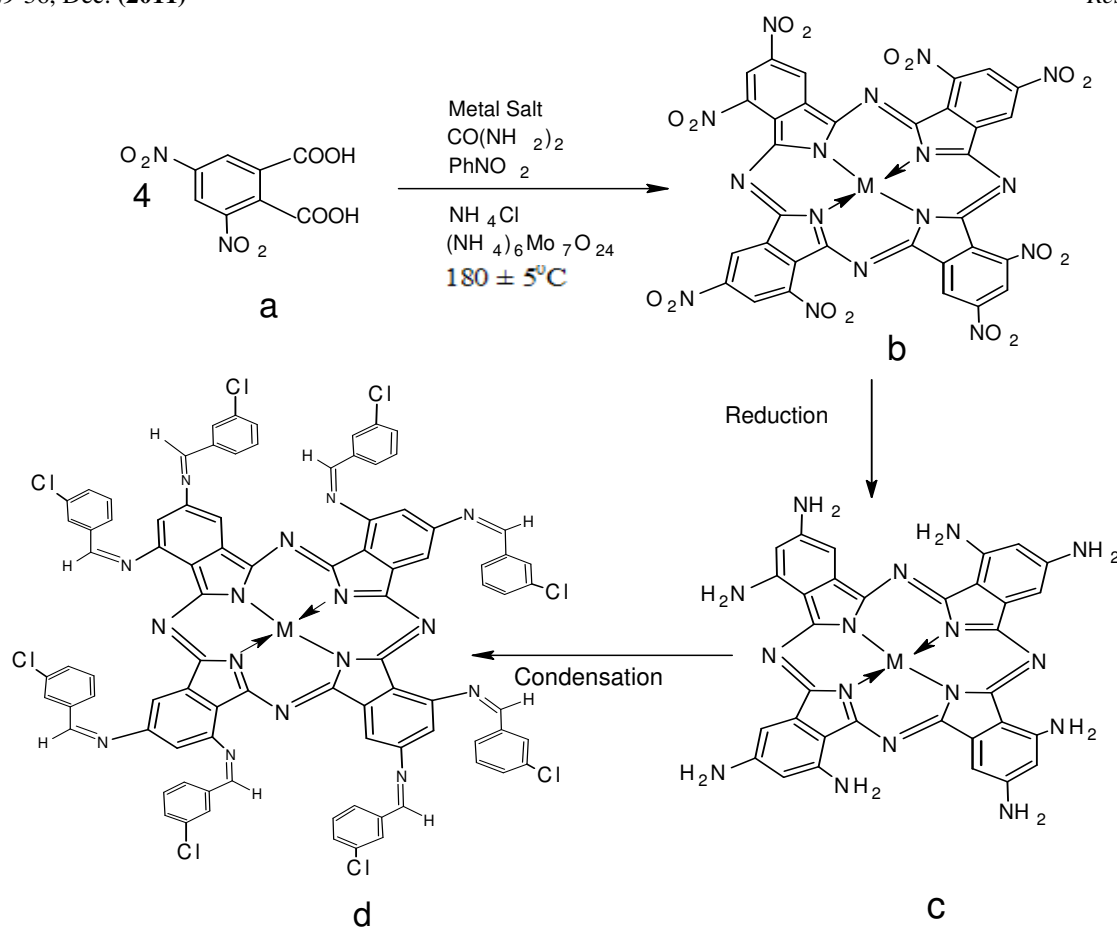
Introduction

Phthalocyanines are man's analogues of nature's pigments of life, the porphyrins, such as chlorophyll and hemoglobin. Since their discovery in 1928, phthalocyanines have become second only to the ubiquitous azo colorants in terms of commercial importance. Phthalocyanine ligand has a heteroaromatic π system and readily forms complexes with many groups and transition metals. The azo-nitrogen and peripheral fixed benzene rings imparts chemical and thermal stability to the ligand¹⁻².

The earlier interest in metal phthalocyanines was mainly because of their importance as dyes and pigments³. Phthalocyanines are well known commercial blue green pigments. The colour is due to intense absorption in the visible region of the spectrum, the Q-band⁴⁻⁵. Currently intensive research work is aiming at the production of useful phthalocyanines as sensitizers in PDT, catalysts in fuel cells⁶, sensors, display devices, information storage systems,

semiconductors⁷ and toners in colour photocopiers and laser printers and hexadeca fluorocopper phthalocyanines as the leading electron transport materials for organic semiconductors⁸⁻⁹. In the present paper an attempt has been made to have a suitable substituent at the periphery of the molecule. The imine group was introduced by the reaction of amino derivatives of the phthalocyanine with substituted aldehydes. Even though, the literature survey revealed about the reports on synthesis and structural investigation of metal (II) 1, 3, 8, 10, 15, 17, 22, 24-octaamino phthalocyanines, no documentary evidences were available on synthesis and structural studies on metal (II) 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-chlorophenyl) methanimine phthalocyanine complexes.

The procedure available in the literature is suitably modified and the synthetic route adopted for the synthesis of octa-1-(3-chlorophenyl) methanimine substituted metal (II) phthalocyanines is given in the scheme-1.



Material and Methods

The 3,5-dinitrothiophthalic acid was synthesized as reported elsewhere¹⁰ and all other chemicals used in the experiment were of analytical grade. The analytical data of the synthesized compounds were in good agreement with reported ones and are used in the synthesis of octa-1-(3-chlorophenyl) methanimine substituted metal phthalocyanines.

Preparation of Cobalt (II) 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-chlorophenyl)- methanimine phthalocyanine complex: The procedure adopted for the synthesis of cobalt (II), 1, 3, 8, 10, 15, 17, 22, 24- octanitrothiophthalocyanine complex is reported elsewhere¹¹. The nitro derivative of the aforesaid complex is converted into amino derivative quantitatively by reduction using sodium sulphide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) in aqueous medium¹². The finely grounded metal (II) 1, 3, 8, 10, 15, 17, 22, 24-octaaminophthalocyanine (6.30g, / 0.1mole) was dissolved in stoichiometric quantity of 15 M sulphuric acid, to this (12.9g, / 0.1mole) 3-chlorobenzaldehyde is dissolved in ethyl

alcohol and catalytic amount of concentrated sulphuric acid is added, and the contents were refluxed with stirring for about 5 hrs¹³. The settled green colored condensed octa-1-(3-chlorophenyl) methanimine phthalocyanine complex is washed with alcohol several times until it is free from aldehyde. Finally it is washed with distilled water and dried over anhydrous phosphorous pentoxide in vacuum desiccator.

The pigment form of the above complex is 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 is 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 is filtered off and washed with hot water. Finally it is washed with distilled water and dried in vacuum over phosphorous pentoxide.

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

Results and Discussion

C, H and N analysis were performed at Cochin University, Sophisticated Test and Instrumentation Center, Kochi, Kerala, India. The metal content was determined by incinerating them to the oxides. Magnetic susceptibility studies were carried out at room temperature (301⁰K) using a Gouy 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 corrections¹⁴. A mercury tetra thiocyanato cobalt (II) (Hg [Co(SCN)₄]) complex is used as a calibrant and doubly distilled water used in the experiments. Shimadzu UV-Visible recording spectrophotometer, UV-160A with 1 cm width cells is used for electronic absorption spectral studies. IR spectra were recorded using Nicolet MX-FT IR spectrometer with KBr pellets in the range 4000-500cm⁻¹ Phillip Analytical PW1710 X-ray diffractometer is used to study the diffraction pattern. The spectra were recorded using Cu K α at the voltage of 40 KV, a current of 20 mA, a time constant of 4, a channel width of 7 mm and chart speed of 10mm/min. Perkin-Elmer Thermal analyzer is used for simultaneous record of TGA and DTA at the rate of 10 ⁰C/min both in air and nitrogen atmosphere.

The procedure used for the synthesis of M-CIPhImPcO's results in pure complexes and have dark green color for Cu (II), Co (II), Ni (II) and green with brown ting for Zn (II).

The metal phthalocyanine complexes, which are thermally stable and resistance towards concentrated sulfuric acid was attributed to the atomic radii of the metal in the close range of 1.35Å. These complexes give clear solution in DMSO, and DMF, but insoluble in water and most of the organic solvents, like alcohol, ether, carbon tetrachloride and benzene. The results of elemental analysis for carbon, hydrogen nitrogen and metal are in good agreement with the calculated and are summarized in table-1.

Electronic Spectra: The electronic spectra of 1, 3, 8, 10, 15, 17, 22, 24-octa1-(3-chlorophenyl) methanimine metal phthalocyanines are recorded in the range of 1.0 -1.5 $\times 10^{-4}$ in 18 M sulfuric acid and the results are tabulated in Table- I. For all the complexes, a peak in the range of 625-645 nm¹⁵ was observed and assigned to Q-band, attributed to a_{1u} \longrightarrow e_g transition. Peaks appeared in the range 232-240 nm¹⁶ are attributed to C-band. The M-CIPhImPcO's showed a peak in the range of 330-387 nm is assigned to B-band and is attributed to a_{2u} \longrightarrow e_g. The peaks in the longer wavelength region 727-748 nm. A weak L-band was observed in the range of 201-218 nm. For all the complexes showed a bathochromic shift with increasing intensity with respect to the corresponding parent phthalocyanines¹⁷. This is due to the presence of auxochrome -Cl groups on the periphery of benzene portion of the complex.

Table-1

Elemental analysis and magnetic susceptibility data of metal (II) -octa-1-(3-chlorophenyl) methanimine phthalocyanines

Complex (Yield) Colour	Empirical formulae (Formula weight)	Field strength KGauss	Magnetic susceptibility ($\chi_m \times 10^{-6}$ cgs units)	Magnetic moments μ_{eff} (B.M)	Elemental analysis (%) found (calcd)
CoClPhImPcO (85%) Dark green	$C_{88}H_{48}Cl_8N_{16}Co$ (1671.98)	2.20	+2592.42	2.53	C; 63.19; (63.15) H; 2.87; (2.86) N; 13.40; (13.38) Cl; 17.02; (17.02) Co; 3.52; (3.52)
		2.66	+2133.10	2.29	
		3.10	+1791.85	2.10	
		3.58	+1541.42	1.95	
		4.01	+1479.59	1.91	
CuClPhImPcO (85%) Dark green	$C_{88}H_{48}Cl_8N_{16}Cu$ (1676.59)	2.20	+2101.81	2.27	C; 63.02; (63.00) H; 2.86; (2.85) N; 13.36; (13.35) Cl; 16.97; (16.97) Cu; 3.79; (3.79)
		2.66	+1719.75	2.06	
		3.10	+1684.42	2.03	
		3.58	+1601.77	1.98	
		4.01	+1512.97	1.93	
NiClPhImPcO (80%) Dark green	$C_{88}H_{48}Cl_8N_{16}Ni$ (1671.74)	2.66	-680.15	---	C; 63.19; (63.18) H; 2.87; (2.86) N; 13.40; (13.39) Cl; 17.03; (17.02) Ni; 3.51; (3.51)
ZnClPhImPcO (75%) Green with brown ting	$C_{88}H_{48}Cl_8N_{16}Zn$ (1678.74)	2.66	-1189.23	---	C; 62.95; (63.92) H; 2.86; (2.85) N; 13.35; (13.33) Cl; 16.95; (16.95) Zn; 3.87; (3.87)

Infrared spectra: IR spectral data of all the metal (II) octa-1-(3-chlorophenyl) methanimine phthalocyanine pigments were recorded in KBr pellets and the results are tabulated in table-2. A peak was observed for all M-CIPhImPcO's in the range 3400-3465 cm^{-1} may be accounted for the presence of hydrogen bonding between nitrogen group and hydrogen of moisture absorbed on KBr pellets¹⁸. A very weak signal observed in the range 2309-2325 cm^{-1} is due to C-H stretching vibration on the periphery of the phthalocyanine moiety. The sharp peak at 1616-1621 cm^{-1} is assigned to C=N of imine group and the peaks in the 1365-1388 cm^{-1} is due to C-N aromatic stretching frequency. The peaks at 1315 - 1327 cm^{-1} are due to C - H symmetric bending. The absorption bands appeared around 757 - 772 cm^{-1} were assigned to C - Cl stretching frequency of the peripheral substitution on the ring. All other remaining peaks appeared around 848 - 881 cm^{-1} , 1077, 1088, 1125 cm^{-1} are attributed to the various skeletal vibrations of phthalocyanine ring¹⁹.

Magnetic Susceptibility: The magnetic susceptibility measurements for 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-chlorophenyl) methanimine phthalocyanines of copper, cobalt are consistent with paramagnetic nature and nickel, zinc are diamagnetic nature. A summary of the magnetic properties over the range of applied magnetic field strength 2.20-4.45KGauss are reported in table-1. The values reported in the table are the average of the three independent determinations. Magnetic susceptibility measurements on Cu-CIPhImPcO and Co-CIPhImPcO are in agreement with paramagnetic nature of the complexes and that of Ni-CIPhImPcO and Zn-CIPhImPcO are diamagnetic. The observed magnetic moment values for Cu-CIPhImPcO and Co-CIPhImPcO are higher than expected for $S = \frac{1}{2}$ spin state but less than their corresponding unsubstituted counterparts. Also, the μ_{eff} values of the complexes are found to vary with the strength of the applied magnetic field and this is due to intermolecular cooperative effect²⁰.

The orbital contributions is found to be higher at lower magnetic field than that of higher one evidenced by higher μ_{eff} values at lower field strength and it may be accounted for the contribution of magnetic anisotropy of the strong phthalocyanines π electronic current as reported in the literature²¹.

The observed higher values of magnetic moment, at lower magnetic field strength may be due to the intermolecular magnetic interaction coupled with strong π -electron current of phthalocyanine molecule. Crystallographic studies²² on phthalocyanines revealed that, during the process of stacking, each phthalocyanine molecule is stacked to the neighbouring molecule along the b-axis contribute either a -N-atom at a distance of 3.38 \AA one above and one below about the central metal atom as shown in figure-2a or may be placed one above the other with the separation of two molecules by

a distance of 3.38 \AA as represented in figure-2b. This minimum interplanar distance seems to provide a suitable pathway for spin-spin coupling interaction between adjacent metal atoms either directly or super exchange through the N atoms of the molecule. The extent of super exchange interaction between the molecules depends primarily on angle of inclination of the plane of the molecules, type of the metal atom, nature of the substituent and metal-metal distance. It seems, the exchange interaction coupled with orbital contribution is the cause for the observed higher magnetic moments for Cu-CIPhImPcO and Co-CIPhImPcO at the lower magnetic field strength. But at higher magnetic fields, it seems molecules suffer tumbling, resulting in decrease in intermolecular distance which in turn favour an effective intermolecular interaction.

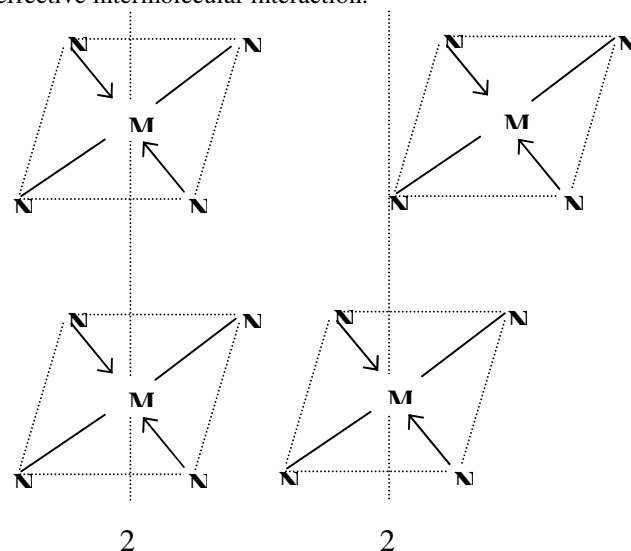


Figure-2
Probable molecular stacking of metal phthalocyanines M = Cu, Co, Ni and Zn, N = central nitrogen atoms of the phthalocyanine structure

The crystallographic studies revealed that the metal phthalocyanines of Cu, Co, Ni and Zn has square planar structure with D_{4h} symmetry and are isomorphous¹⁹. 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 column with N-atoms above and below on every metal atom figure-3 and hence the nearest neighbouring molecule along the b-axis contributes N-atom at the interplanar distance 3.4 \AA ¹⁶.

Powder XRD: The X-ray diffraction spectra of M-CIPhImPcO's are taken through a range of 2θ angles 6-70° showed are not identical peaks table-2. Two peaks were observed with one sharp at lower angle with maximum intensity and the other at higher angle with higher intensity.

The inter planar spacings on these angle gave the following values. Co-NPhImPcO 3.58, 27.98 Å; Cu-NPhImPcO 3.47, 29.98 Å; Ni-NPhImPcO 3.42, 24.21 Å and Zn-NPhImPcO 4.36, 3.22.54Å clearly indicating the cristanilline nature of the complex. The observed patterns are very much similar to unsubstituted parent phthalocyanines except the broadening

of the peaks in the case of title complexes with diffused intensity. The broadening may be due to the presence of substituents and which seems to play an important role in the stacking of the metal phthalocyanine derivatives. X-ray diffraction patterns are used only to explain crystallinity qualitatively.

Table-2
Electronic, IR and powder XRD data of metal (II) 1, 3, 8, 10, 15, 17, 22, 24 –octa-1-(3-chlorophenyl) methanimine phthalocyanines

Complex	UV-visible absorption λ nm (log ϵ)	IR-Spectral cm^{-1}	Powder. XRD data 2θ angle (d Å)	Relative intensity (%)
Co-ClPhImPcO	201 (5.59) 333 (5.47) 235 (5.60) 625 (4.87) 748 (5.02)	757, 876, 1088, 1315, 1388, 1620, 2309, 3400	27.98 (3.58) 28.83 (3.05) 25.44 (3.47) 32.25 (2.85)	100.00 78.42 48.17 30.53
Cu-ClPhImPcO	215 (5.59) 232 (5.10) 387 (5.59) 628 (5.09) 742 (5.18)	757, 881, 1088, 1320, 1377, 1616, 2314, 3410	45.64 (2.78) 31.78 (2.88) 43.65 (2.76) 29.98 (3.47)	100.00 80.24 50.38 32.27
Ni-ClPhImPcO	218 (5.59) 240 (5.47) 331 (5.48) 637(4.92) 727 (4.98)	772, 865, 1077, 1325, 1368, 1616, 2314, 3415	27.75 (3.70) 28.82 (3.02) 24.21 (3.42) 41.78 (2.84)	100.00 79.71 43.18 28.54
Zn-ClPhImPcO	218 (5.59) 233 (5.60) 330 (5.43) 640 (4.88) 729 (4.95)	761, 848, 1125, 1327, 1365, 1621, 2325, 3465	27.94 (3.54) 28.87 (3.07) 42.99 (2.84) 22.54 (4.36)	100.00 80.87 50.17 34.94

Table-3
TGA data of metal (II) 1, 3, 8, 10, 15, 17, 22, -octa-1-(3-chlorophenyl) methanimine Phthalocyanines

Complex	Temperature of Decomposition °C	Mass Loss		Probable mode of Fragmentation
		(%) Found	(%) Calcd	
CuClPhImPcO	250-350	30.74	31.02	8-Cl-Imino groups Pc moiety
	350-600	65.46	65.81	
CoClPhImPcO	250-350	30.75	31.41	8-Cl-Imino groups Pc moiety
	350-600	65.94	65.04	
NiClPhImPcO	250-350	30.72	31.74	8-Cl-Imino groups Pc moiety
	350-600	65.94	65.02	
ZnClPhImPcO	250-350	30.64	31.85	8-Cl-Imino groups Pc moiety
	350-600	65.61	65.04	

Table-4
Kinetics and Thermodynamic parameters of metal (II) 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-chlorophenyl) methanimine phthalocyanines in air and nitrogen atmosphere

Compounds	Activation energy Eo KJ/mole	Frequency Factor lnA min ⁻¹	ΔH KJ/mole	ΔS J/K	ΔG KJ/mole
Cu-ClPhImPcO I	4.87	6.18	2.47	-173.74	40.47
	(0.52)	(2.35)	(-1.94)	(-175.54)	(42.36)
II	3.58	5.58	-0.76	-167.54	83.35
	(1.40)	(6.21)	(-2.32)	(-173.54)	(85.24)
Co-ClPhImPcO I	0.78	2.54	-1.86	-169.25	40.87
	(0.46)	(2.68)	(-1.65)	-175.30	(42.01)
II	3.89	5.65	3.21	-163.01	83.36
	(1.35)	(4.12)	(-2.67)	(-174.21)	(84.44)
Ni-ClPhImPcO I	1.82	4.88	-0.29	171.82	42.71
	(1.45)	(4.48)	(-0.57)	(-171.82)	(42.43)
II	3.86	5.94	-0.49	-169.28	83.64
	(1.59)	(4.98)	(-2.59)	(-173.28)	(84.01)
Zn-ClPhImPcO I	1.34	4.25	4.25	-172.79	42.75
	(0.45)	(2.58)	(-1.71)	(-176.58)	(42.34)
II	7.67	7.41	3.25	-153.78	78.62
	(1.43)	(4.15)	(-2.79)	(-2.79)	(78.58)

(I and II corresponds to the I and II stage of degradation and the values in the parenthesis are for nitrogen atmosphere)

Table-5
Anti-fungal data metal(II), 1, 3, 8, 10, 15, 17, 22, 24- octa-1-(3-chlorophenyl) Methanimine phthalocyanines

Samples	Concentration in Ppm	Radial growth of <i>Aspergillus niger</i> (in cm) in respective incubation period		
		3 rd day	5 th day	7 th day
Control (DMSO)	-	1.5	2.3	3.6
Ni-ClPhImPcO	100	0.9	1.4	2.3
Co-ClPhImPcO	100	1.1	1.5	2.7
Cu-ClPhImPcO	100	1.3	1.9	2.8
Zn-ClPhImPcO	100	1.0	1.5	2.4

Thermogravimetric and Kinetic studies:
Thermogravimetric analytical data of octa-1-(3-chlorophenyl) methanimine phthalocyanine complexes both in air and nitrogen atmosphere are summarized in the table -3 and table -4. It is observed that the decomposition of the above complexes occurs generally in two steps, revealed that

the initial weight loss of 2-3% corresponding to moisture. The first step degradation in air, which takes place in the temperature range of 250-350°C, may be accounted for the loss of eight substituted imine groups. The major weight loss is observed for all the complexes in the second step in the temperature ranges of 350-600°C corresponds to the

oxidative degradation of remaining phthalocyanine moiety. Analysis of the final charred residue corresponds to the corresponding metal oxides²³. The thermal decomposition of imino substituted metal phthalocyanine complexes in the nitrogen atmosphere appears to be very slow. For Co-CIPhImPcO, 69% of the complex was found to be decomposed at 700°C. For Cu-CIPhImPcO, Ni-CIPhImPcO about 54%, 51% and 40% loss of the mass was observed for Zn-CIPhImPcO. Above trend confirms the relative stability of these complexes in the order Co-CIPhImPcO > Cu-CIPhImPcO > Ni-CIPhImPcO > Zn-CIPhImPcO. DTA results revealed that all degradation steps are exothermic in nature. Kinetic and thermodynamic parameters of the title complexes have been evaluated by Boride's method²⁴

The activation energies (E₀) for the loss of periphery 3-chloro imino substituent compound lies in the range of 0.78 to 4.87 KJ/mole. It may be expected that as soon as the periphery substituents are expelled, the rupture of the main phthalocyanines ring takes place. Exothermic behavior of the degradation clearly indicated by their negative entropies. The change in entropies ΔS is negative for little complexes and varies from -169.25 to -173.74 KJ. It is clear from the values of entropies for the decomposition that the removal of functional groups is associated with more negative entropies

Antifungal Activity: The ligand and all complexes synthesized in the present investigation and the respective metal salts were evaluated for antifungal activity. The *Aspergillus niger* was studied for its growth and sporulation colour characteristics in the presence of the selected metal phthalocyanine complexes. The *Aspergillus niger* was procured from. The Department of Biotechnology, Sahyadri Science college, Shimoga. 100 ppm solution of different M-CIPhImPcO's complexes were prepared by dissolving required amount of complexes in 2ml of DMSO and 98ml 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 petriplates in an aseptic chamber and cooled. The *Aspergillus niger* is inoculated on solidified medium as a point at the center of the plate. Inoculated plates were incubated at 23 ±1°C for one week and the observation was made at 3rd, 5th and 7th day.

An interesting observation made during the investigation is the change in the color of fungus sporulation. *Aspergillus niger* is known for its black color. However in the presence of metal complexes the fungus is pale brown sporulation. It is confirmed by the parallel experiment with and without addition of 2ml DMSO in the medium that the change in colour 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 [15].

Conclusion

A simple and convenient method has been optimized for the synthesis of pigments 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-chlorophenyl) methanimine phthalocyanines of Cu (II), Co(II), Ni(II) and Zn(II). Magnetic susceptibility studies revealed the paramagnetic behavior of Cu(II) and Co(II) octa-1-(3-chlorophenyl) methanimine phthalocyanine derivatives and the variation of magnetic moments with magnetic field indicated the presence of intermolecular cooperative effect. Thermogravimetric analysis of the complexes in an inert atmosphere revealed the stability in the order Cu-CIPhImPcO > Co-CIPhImPcO > Ni-CIPhImPcO > Zn-CIPhImPcO. The antifungal activity of the M-CIPhImPcO's is in the order of Ni-CIPhImPcO > Zn-CIPhImPcO > Co-CIPhImPcO > Cu-CIPhImPcO.

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