Synthesis and Structural Investigation on Symmetrically Substituted Metal(II)- 3-prop-phenyl-2-en-1-Imine Phthalocyanine.

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ABSTRACT

Present paper discuss the synthesis and characterization of metal (II) octa-(2e)-3-prop-phenyl-2-en-1-imine phthalocyanines (M-PropPhImPcO) (M = Cu, Co, Ni, Zn) by an efficient, simple, and novel method. Octaamino metal (II) phthalocyanines were synthesized by the reduction of the corresponding nitro phthalocyanines. The dark green octa-1-(3-nitrophenyl) methaniminephthalocyanine 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-(2e)-3-prop-phenyl-2-en-1-iminephthalocyanine complexes exhibit a variation of the magnetic moments as a function of field strength indicating the presence of inter molecular co-operative effect.

Keywords: Phthalocyanines: Octa-(2e)-3-prop-phenyl-2-en-1-imine, Electronic, IR, XRD, Magnetic susceptibility, TGA.

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INTRODUCTION

Phthalocyanine class of compounds is considered to be interesting materials with unconventional and unique properties. Phthalocyanine ligand has a heteroaromatic π system and readily forms complexes with many groups and transitions metals. The azo-nitrogen and peripheral fixed benzene rings imparts chemical and thermal stability to the ligand [1]. The earlier interest in metal phthalocyanines was mainly because of their importance as dyes and pigments [2, 3]. Phthalocyanines are well known commercial blue green pigments. The colour is due to intense absorption in the visible region of the spectrum, the Q-band [4, 5].Currently intensive research work is aiming at the production of useful phthalocyanines as sensitizers in PDT, catalysts in fuel cells[6], sensors, display devices, information storage systems [6], semiconductors [7] and differential staining agents [7- 9], toners in colour photocopiers and laser printers and hexadecaflurocopper phthalocyanines as the leading electron transport materials for organic semiconductors[10]. The redox properties of phthalocyanines are related to most of their industrial applications [11].

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,

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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--(2E)-3-prop-phenyl-2-en-1-imine phthalocyanine complexes.

The procedure available in the literature is suitably modified and the synthetic route adopted for the synthesis of octa-1-(3-nitrophenyl) methanimine substituted metal (II) phthalocyanines is given in the scheme-1.
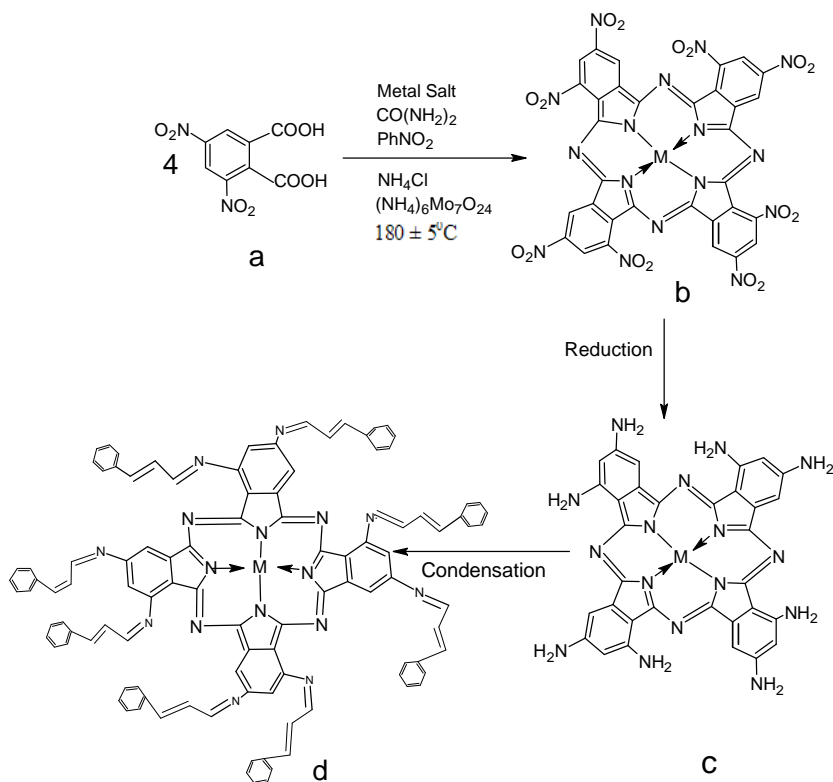
Scheme.1: Synthesis of metal (II) 1, 3, 8, 10, 15, 17, 22,24- octa-1-(3-nitrophenyl) methaniminephthalocyanine.a. 3, 5-dinitrophthalic acid, b. M-PcON, c. M-PcOA and d. M-PropPhImPcO

MATERIALS AND METHODS

C, H and N analysis were performed at Cochin University, Sophisticated Test & 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 (301 ^{0}K) 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 corrections [16]. A mercury tetra thiocyanato cobalt (II) (Hg [Co(SCN)$_4$]) complex was used as a calibrant and doubly distilled water used in the experiments. Shimadzu UV-Visible recording spectrophotometer, UV-160A with 1 cm width cells was 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 diffractrometer was used to study the diffraction pattern. The spectra were recorded using Cu Kα at the voltage of 40 KV, a current of 20mA, A time constant of 4, a channel width of 7mm and chart speed of 10mm/min. Perkin-Elmer Thermal analyzer was used for simultaneous record of TGA and DTA at the rate of 10 ^{0}C/min in air, and nitrogen atmosphere.

The 3,5-dintrophthalic acid was synthesized as reported elsewhere [12] 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-(2E)-3-prop-phenyl-2-en-1-imine substituted metal phthalocyanines.

Preparation of Cobalt (II) 1, 3, 8, 10, 15, 17, 22, 24-octa--(2E)-3-prop-phenyl-2-en-1-imine phthalocyanine complex.

The procedure adopted for the synthesis of cobalt (II), 1, 3, 8, 10, 15, 17, 22, 24- octanitrophthalocyanine complex was reported elsewhere [13]. The nitro derivative of the aforesaid complex was converted into amino derivative quantitatively by reduction using sodium sulphidenonahydrate (Na_2S $9H_2O$) in aqueous medium [14]. The finely grounded metal (II) 1, 3, 8, 10, 15, 17, 22, 24-octaaminophthalocyanine (6.30g, / 0.1mole) was dissolved in stiochiometric quantity of 15 M sulphuric acid, to this (12.9g, / 0.1mole) 3-nitrobenzaldehyde is dissolved in ethyl alcohol and catalytic amount of concentrated sulphuric acid was added, and the contents were refluxed with stirring for about 5 hrs [15]. The settled green colored condensed octa-(2E)-3-prop-phenyl-2-en-1-imine -(2E)-3-prop-phenyl-2-en-1-imine phthalocyanine complex was washed with alcohol several times until it was free from aldehyde. Finally it was washed with distilled water and dried over anhydrous phosphorous pentaoxide in vacuum descicator.

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 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 pentaoxide.

Metal (II) 1, 3, 8, 10, 15, 17, 22, 24- octa-(2E)-3-prop-phenyl-2-en-1-imine phthalocyanines of copper (II), nickel (II), and zinc (II) were prepared by the above procedure using respective amino metal phthalocyanines.

RESULTS AND DISCUSSION

The procedure used for the synthesis of M-PropPhImPcO'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 and nitrogen and metal are in good agreement with the calculated and are summarized in Table. I. The above results are consistent with the suggested structure in Fig-1.
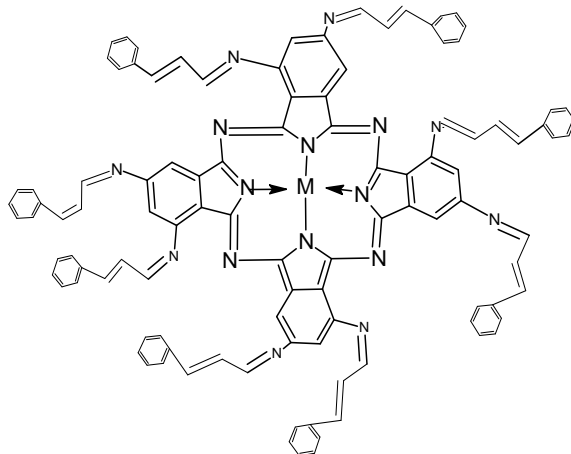

Fig.1: Suggested structure of symmetrically substituted octa-(2E)-3-prop-phenyl-2-en-1-imine phthalocyanines, where M= Co, Cu, Ni, and Zn

Electronic Spectra

The electronic spectra of title complexes were recorded in the concentration range of 1.0-1.5 x 10^{-4} M in DMSO and the results are summarized in Table 2. Observed   absorption peaks are interpreted in terms of Q, B, L and C characteristic of phthalocyanine molecule. For all the complexes a peak was observed in the range of 720-739 nm, which was attributed to Q-band, $a_{1u} \rightarrow e_g$ transition and 329-338 nm assigned to B-band due to $a_{2u} \rightarrow e_g$ transition [17]. The Q-band in all M-PropPhImPcO's was found to be shifted to higher wavelength range. Peaks are observed

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in the range 575-591 nm for   Cu-PropPhImPcO, Co-PropPhImPcO, Ni-PropPhImPcO, and Zn-PropPhImPcO which is accounted for aggregation of complexes in the solvent. For all M-PropPhImPcO's a band was observed in the range of 209-217nm [18] may account for C-band of the phthalocyanine molecule.

Infrared Spectra

IR spectral data of all the metal (II) octa-(2E)-3-prop-phenyl-2-en-1-iminephthalocyanine pigments were recorded in KBr pellets and the results are tabulated in Table 2 and their spectra are given in Fig 2. A broad absorption band at 3421-3443cm^{-1} was observed for all complexes and was assigned to the hydrogen bonding formed between nitrogen atom of the phthalocyanine molecules and hydrogen atom of moisture absorbed on KBr pellets during pelletization[17]. The very weak signal observed in the range 2360-2366cm^{-1} is due to C-H stretching vibration on the periphery of the phthalocyanine moiety. The sharp peak at 1625-1635cm^{-1} is assigned to C=N of imine group and the peaks in the 1368-1388cm^{-1} is due to C-N aromatic stretching frequency [19]. The bands at 1041-1120, and 743-775cm^{-1} are assigned to the various phthalocyanines skeletal vibration [20].

Magnetic Susceptibility.

The magnetic susceptibility χ_m and magnetic moments μ_{eff} values of square planner M-PropPhImPcO's have been investigated in the solid state over a range of 2.20-4.45KGauss and results are summarized in Table 1. The values reported are the average of three independent determinations. The magnetic susceptibility studies revealed that CuPropPhImPcO and CoPropPhImPcO are paramagnetic and NiPropPhImPcO and ZnPropPhImPcO are diamagnetic complexes. The observed magnetic moments for CuPropPhImPcO and CoPropPhImPcO are higher than the expected spin only value corresponding to one unpaired electron (1.73BM) the mixing of ground state orbital with higher energy degenerate states and intermolecular co-operative effects [21]. The observed higher magnetic moment then spin only value is due to the orbital contribution to μ_{eff} which may arise as a result of mixing of ground state orbitals $(b_{2g})^2$, $(e_g)^4$, and $(a_{1g})^1$ with higher orbitally degenerate states ($b_{2g})^2$, $(e_g)^3$ and $(a_{1g})^2$. The orbital contributes is found to be higher at magnetic field then that of higher one evidenced by higher μ_{eff} values at lower field strength and it is attributed to intermolecular magnetic interaction coupled with magnetic anisotropy of phthalocynaninesπ electronic current as reported in the literature [19].

The crystallographic studies recorded that the metal phthalocyanines of Cu, Co, Ni and Zn has square planar structure with D_{4h} symmetry and are isomorphous [20,23]. The molecular plan 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[o] . Thus the complexes stacked in column with N-atoms above and below on every metal atom (Fig.3) and hence the nearest neighbouring molecule along the b-axis contributes N-atom at the interplanar distance 3.8 A[o] [17].

The overlapping of two neighboring molecules depends on the crystal modification. The XRD data reveals that the M-PropPhImPcO's as in β-form. The metal (ii) of one of the phthalocyanine overlap with N-atom of azamethine atom of the other metal phthalocyanine molecule.

Powder XRD

The X-ray diffraction spectra of M-PropPhImPcO's are taken through a range of   2θ angles 6-70[o] 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-PropPhImPcO 3.59, 27.97 Å; Cu-PropPhImPcO 2.80, 45.64 Å; Ni-PropPhImPcO 3.75, 27.91 Å and Zn-PropPhImPcO 3.58, 27.92 Å, clearly indicating the crystanilline nature of the complex. The observed patterns are very much similar to those of the unsubstituted parent phthalocyanines except the broadening of the peaks in the case of M-PropPhImPcO's which 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.
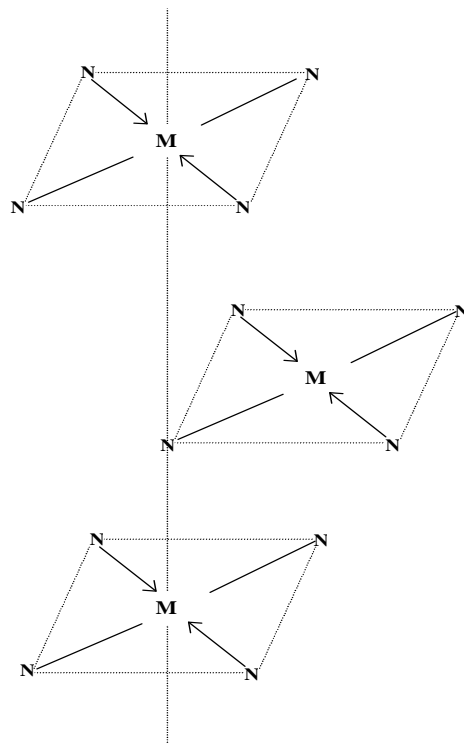
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Fig.3. Probable molecular stacking of metal phthalocyanine crystal, (M = Cu, Co, Ni, Zn.)N= azamethanic atom of phthalocyanine

Thermogravimatric and Kinetic Studies

Thermogravimatric analytical data of octa-(2E)-3-prop-phenyl-2-en-1-iminephthalocyanine complexes both in air and nitrogen atmosphere are summarized in the Table 3 and 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 four 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 four substituted imine groups and phthalocyanine moiety. Analysis of the final charred residue corresponds to the corresponding metal oxides [23]. The thermal decomposition of imino substituted metal phthalocyanine complexes in the nitrogen atmosphere appears to be very slow. For Co-PropPhImPcO, 69% of the complex was found to be decomposed at 700 °C. For Cu-PropPhImPcO, Ni-PropPhImPcO about 56%, 53% and 42% loss of the mass was observed for Zn-PropPhImPcO. Above trend conforms the relatively stability of these complexes in the order Co-PropPhImPcO>Cu-PropPhImPcO> Ni-PropPhImPcO> Zn-PropPhImPcO. 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 method [24].

The activation energies (Eo) for the loss of periphery iminosubstitutent compound lies in the range of 0.68 to 5.87 KJ/mole. It may be expected that as soon as the periphery substitutents are expelled, the rupture of the main phthalocyanines ring takes place. Exothermic behavior of the degradation clearly indicated by their negative entropies. The changes in entropies ΔS are negative for little complexes and varies from –159.67 to-175.97 KJ. It is clear from the values of entropies for the decomposition that the removal of functional groups are associated with more negative entropies
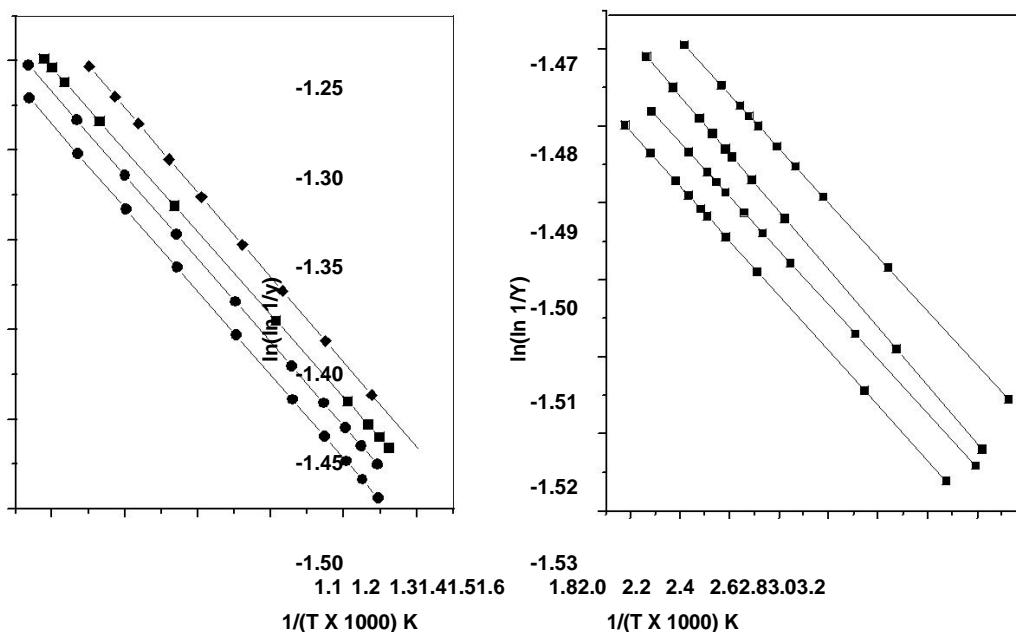
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Fig.4. Plots of ln(ln 1/y) versus 1/T for thermal degradation of (● ● ● ●) Cu-PropPhImPcO, (● ● ● ●) Co-PropPhImPcO, (♦ ♦ ♦ ♦) Ni-PropPhImPcO and (■ ■ ■ ■) Zn-PropPhImPcO in air

CONCLUSION

A simple and convenient method has been optimized for the synthesis of pigments 1, 3, 8, 10, 15, 17, 22, 24-octa-(2E)-3-prop-phenyl-2-en-1-iminephthalocyanines of Cu(II), Co(II), Ni(II) and Zn(II). Magnetic susceptibility studies revealed the paramagnetic behavior of Cu(II) and Co(II) octa-(2E)-3-prop-phenyl-2-en-1-iminephthalocyanine derivatives and the variation of magnetic moments with magnetic field indicated the presence of intermolecular co-operative effect. Thermogravimatric analysis of the complexes in an inert atmosphere revealed the stability in the order Cu-PropPhImPcO>Co-PropPhImPcO> Ni-PropPhImPcO> Zn-PropPhImPcO.

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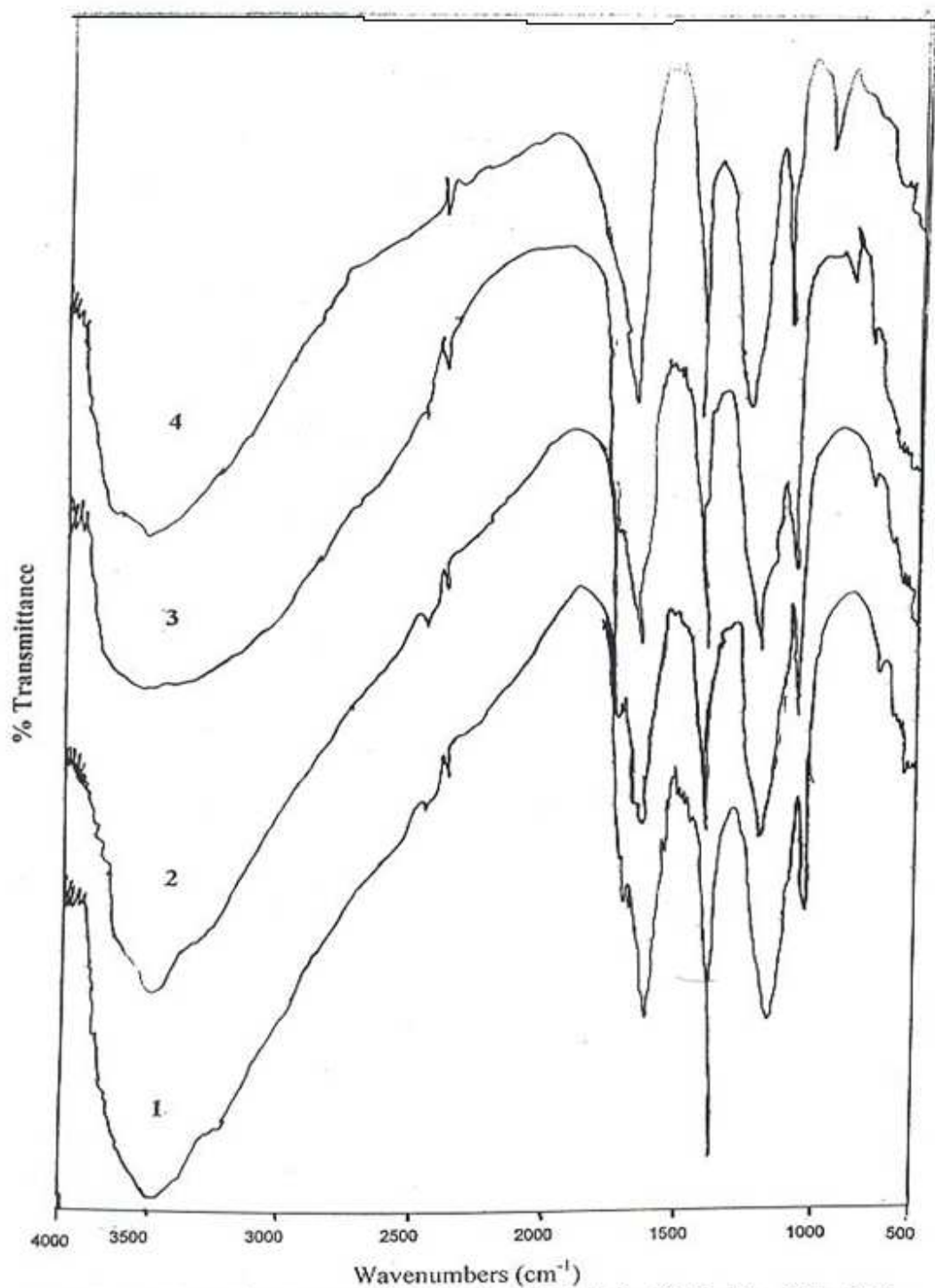[24] A. Broido, *J. Polym Sci*., Part A-**2** (7) **1969,** 1761.

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

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Table.1: Elemental analysis and magnetic susceptibility data of metal (II)-octa-(2E)-3-prop-phenyl-2-en-1-imine phthalocyanines.

Complex (Yield) Colour	Empirical formulae. (Formula weight)	Field strength KGauss	Magnetic susceptibility (χm ×10^{-6}cgs units)	Magnetic moments μeff (B.M)	Elemental analysis (%) found (calcd)
CoPropPhImPcO (85%) Dark green	C$_{104}$H$_{72}$N$_{16}$Co (1616.73)	2.20 2.66 3.10 3.58 4.01	+2621.14 +2444.06 +2104.42 +1928.01 +1803.05	2.63 2.45 2.27 2.18 2.11	C, 77.83; (77.85) H, 4.46; (4.49) N, 13.95; (13.97) Co, 3.66; (3.67)
CuPropPhImPcO (84%) Dark green	C$_{104}$H$_{72}$N$_{16}$Cu (1621.34)	2.20 2.66 3.10 3.58 4.01	+2611.09 +2475.18 +2122.43 +1947.56 +1835.52	2.59 2.47 2.29 2.19 2.12	C, 77.63; (77.63) H, 4.44; (4.47) N, 13.90; (13.93) Co, 3.94; (3.95)
NiPropPhImPcO (80%) Dark Green	C$_{104}$H$_{72}$N$_{16}$Ni (1616.49)	2.66	-776.81	---	C, 77.85; (77.86) H, 4.46; (4.49) N, 13.95; (13.97) Co, 3.64; (3.66)
ZnPropPhImPcO (75%) Green with brown ting	C$_{104}$H$_{72}$N$_{16}$Zn (1623.19)	2.66	-1249.00	---	C, 77.54; (77.64) H, 4.43; (4.47) N, 13.92; (13.93) Co, 4.04; (4.06)

Table.2: Electronic, IR and powder XRD data of metal (II) -octa-(2E)-3-prop-phenyl-2-en-1-iminephthalocyanines.

Complex	UV-visible absorption λ nm (log∈)	IR-Spectral Data (cm-1)	Powder. XRD data 2θ angle (d Å)	Relative intensity (%)
Co-PropPhImPcO	213 (4.92) 261 (4.89) 334 (5.44) 591 (5.09) 739 (5.22)	743, 1041, 1176, 1388, 1631, 1709, 2366, 3452.	27.97, (3.59) 28.83, (3.09) 24.43, (3.43) 31.20, (2.82)	100.00 79.32 49.15 31.56
Cu-PropPhImPcO	209 (4.93). 265 (4.89) 338 (5.47) 588 (5.05) 737 (5.17)	775,1092, 1388, 1631, 1714, 2365, 3441.	45.64, (2.80) 31.71, (2.81) 43.71, (2.75) 25.95, (3.43)	100.00 81.23 50.48 33.25
Ni-PropPhImPcO	210 (4.89) 264 (4.65) 329 (5.01) 586(4.54) 726 (4.64)	757, 1114, 1368, 1403, 1625, 2221, 2360, 3421.	27.91, (3.75) 28.80, (3.09) 23.23, (3.42) 42.78, (2.81)	100.00 79.79 44.14 28.59
Zn-PropPhImPcO	217 (5.59) 249 (5.60) 331 (5.49) 575 (5.42) 720 (5.07)	772, 1120, 1388, 1635,2325, 2362, 3443.	27.92, (3.58) 28.88, (3.08) 42.92, (2.80) 20.51, (4.32)	100.00 80.88 50.14 35.94

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Table-3.TGA data of Cu(II), Co(II), Ni(II) and Zn(II)-octa-(2E)-3-prop-phenyl-2-en-1-imine phthalocyanines.

Complex	Temperature of Decomposition °C	Mass Loss (%) Found	(%)Calcd	Probable mode of Fragmentation
Cu-PropPhImPcO	250-350	29.84	30.04	8-Imino groups
	350-600	65.46	65.83	Pc moiety
Co-PropPhImPcO	250-350	29.82	30.15	8-Imino groups
	350-600	65.96	65.01	Pc moiety
Ni-PropPhImPcO	250-350	29.79	30.19	8-Imino groups
	350-600	65.87	65.19	Pc moiety
Zn-PropPhImPcO	250-350	29.64	30.10	8-Imino groups
	350-600	65.52	65.11	Pc moiety

Table: 4. Kinetic and thermodynamic parameters of 1, 3, 8, 10, 15, 17, 22, 24- octa- (2E)-1-(3-propene phenyl)-2-en-1-imine phthalocyanines of Cu, Co, Ni and Zn in air and inert atmosphere.

Compounds		Activation energy E^0 KJ/mole	Frequency factor. lnA min^{-1}	ΔH KJ/mole	ΔS J/K	ΔG KJ/mole
CuPropPhImPcO	I	5.87	6.18	2.74	-165.06	62.40
		(0.73)	(2.01)	(-1.29)	(-160.01)	(61.54)
	II	3.74	5.38	-0.75	-152.27	81.65
		(1.51)	(5.48)	(-2.41)	(-149.75)	(79.54)
CuPropPhImPcO	I	0.89	6.39	-1.38	-176.08	74.95
		(0.69)	(3.38)	(-1.10)	(-174.10)	(74.78)
	II	4.65	7.41	2.87	-143.94	79.54
		(1.24)	(4.68)	(-1.31)	(-141.99)	(77.21)
NiPropPhImPcO	I	1.45	5.21	-1.22	-159.67	72.84
		(0.70)	(2.24)	(-0.76)	(-157.58)	(70.58)
	II	5.87	4.45	-0.83	-149.79	81.76
		(1.54)	(4.81)	(-0.82)	(-143.63)	(80.21)
NiPropPhImPcO	I	1.95	3.48	-0.95	-175.97	75.24
		(0.68)	(2.39)	(-1.49)	(-173.37)	(74.98)
	II	8.54	7.98	2.84	-142.72	82.49
		(5.54)	(6.44)	(-1.51)	(-140.44)	(80.93)

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