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RESEARCH ARTICLE

Synthesis, Characterization of Symmetrically Substituted Metal(II) Octa-1-(3-bromophenyl)methanimine Phthalocyanine

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Abstract: Metallophthalocyanine (M = Cu, Co, Ni and Zn) carrying eight (3-bromophenyl) 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- bromophenyl)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-bromophenyl) methanimine phthalocyanine complexes exhibit a variation of the magnetic moments as a function of field strength indicating the presence of inter molecular co-operative effect.

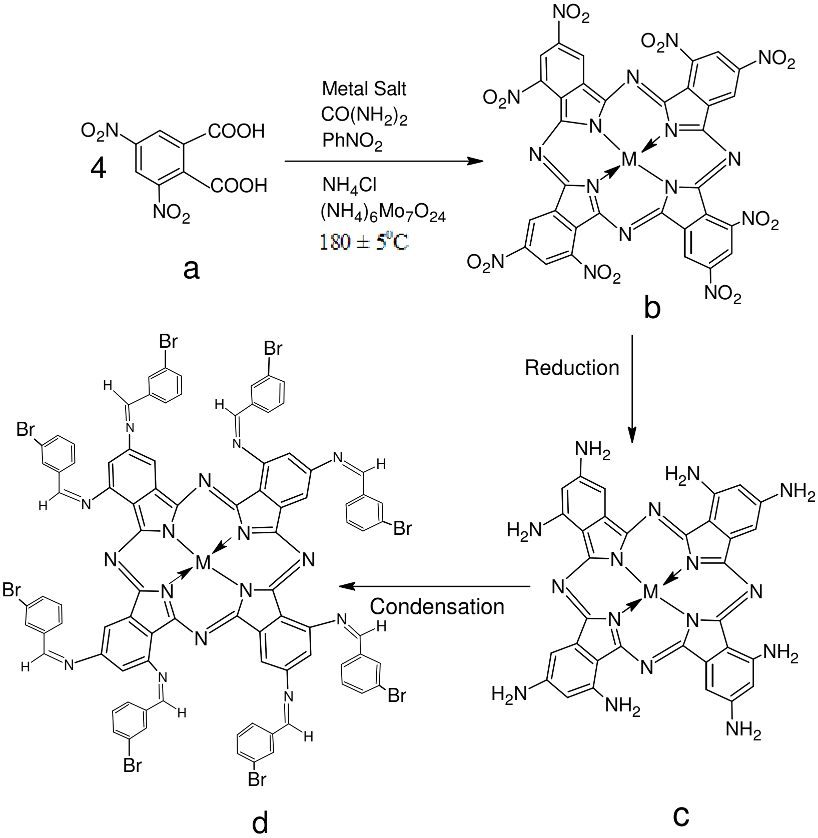
Keywords: Phthalocyanines, Synthesis, Octa-1-(3-bromophenyl)methanimine, Electronic, Magnetic, XRD, Thermal studies

Introduction

Phthalocyanines are man's analogues of nature's pigments of life, the porphyrins, such as chlorophyll and hemoglobin. Phthalocyanines have been the subject of much research for over 50 years[1] and many patents have been recorded[2]. The earlier interest in metal phthalocyanines was mainly because of their importance as dyes and pigments[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, semiconductors[7] and toners in colour photocopiers and laser printers and hexadeca flurocopper phthalocyanines as the leading electron transport materials for organic semiconductors[8-9].

In the present paper an attempt has been made to have a suitable subsitutent 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-bromophenyl) methanimine phthalocyanine complexes.

The procedure available in the literature is suitably modified and the synthetic route adopted for the synthesis of octa-1-(3-bromophenyl)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-bromophenyl) methanimine phthalocyanine.a. 3, 5-dinitrophthalic acid, b. M-PcON, c. M-PcOA and d. M-BrPhImPcO

Experimental

3,5-Dinitrophthalic acid was prepared as reported[10]; 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[11]. These complexes were converted into their respective amino derivatives using sodium sulphide nanohydrate [$Na_2S.9H_2O$] as reducing agent using the published procedure[12], quantitatively. The substituted amino complexes were converted to the imino derivatives by condensation[13].

Preparation of cobalt(II) 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-bromophenyl)methanimine phthalocyanine complex

The procedure adopted for the synthesis of cobalt(II), 1, 3, 8, 10, 15, 17, 22, 24- octanitrophthalocyanine complex is reported elsewhere[11]. The nitro derivative of the aforesaid complex is converted into amino derivative quantitatively by reduction using sodium sulphide nonahydrate (Na_2S $9H_2O$) in aqueous medium[12]. The finely grounded metal(II) 1, 3, 8, 10, 15, 17, 22, 24-octaaminophthalocyanine (6.30 g, / 0.1 mole) was dissolved in stiochiometric quantity of 15 M sulphuric acid, to this (19.8 g, / 0.01 mole) 3-bromobenzaldehyde was dissolved in ethyl alcohol and catalytic amount of concentrated sulphuric acid was added, and the contents were refluxed with stirring for about 5 h[13].

The settled green colored condensed octa-1-(3-bromophenyl)methanimine phthalocyanine complex was washed with alcohol several times until it is 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-1-(3-bromophenyl)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 & 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[14.] 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 4000-500 cm^{-1} Phillip Analytical PW1710 x-ray diffractrometer is used to study the diffraction pattern. The spectra were recorded using Cu Kα 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 10 mm/min. Perkin-Elmer Thermal analyzer was used for simultaneous record of TGA and DTA at the rate of 10 ^{0}C/min both in air, and nitrogen atmosphere.

The procedure used for the synthesis of *M*-BrPhImPcO's results in pure complexes and have dark green color for Cu(II), Co(II) and 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. The above results are consistent with the suggested structure in Figure 1.

Table 1. Elemental analysis and magnetic susceptibility data of metal(II)-octa-1-(3-bromophenyl)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)
CoBrPhImPcO		2.20	+2577.09	2.92	C; 52.96; (52.99)
(85%)	$C_{88}H_{48}Br$	2.66	+2204.79	2.72	H; 2.35; (2.35)
Dark green	$_{8}N_{16}Co$	3.10	+2115.05	2.51	N; 11.01; (11.01)
	(1914.9)	3.58	+1546.46	1.98	Br; 31.50; (31.50)
		4.01	+1471.49	1.94	Co; 3.11; (3.11)
CuBrPhImPcO		2.20	+2387.91	2.46	C; 51.97; (51.99)
(85%)		2.66	+2093.09	2.27	H; 2.34; (2.36)
Dark green	$C_{88}H_{48}Br$	3.10	+1673.44	2.01	N;11.01; (11.03)
	$_{8}N_{16}Cu$	3.58	+1605.75	1.97	Br;31.49; (31.50)
	(1919.5)	4.01	+1514.01	1.94	Cu; 3.11; (3.12)
NiBrPhImPcO					C; 52.10; (52.12)
(80%)	$C_{88}H_{48}Br\ _{8}N_{16}$	2.66	-720.56	---	H; 2.35; (2.37)
Dark Green	Ni				N; 11.03; (11.05)
	(1914.7)				Br; 31.57; (31.57)
					Ni; 2.87; (2.89)
ZnBrPhImPcO					C; 51.13; (51.15)
(74%)	$C_{88}H_{48}Br$	2.66	-1145.65	---	H; 2.35; (2.36)
Green with	$_{8}N_{16}Zn$				N; 11.00; (11.02)
brown ting	(1921.4)				Br; 32.26; (32.26)
					Zn; 3.21; (3.21)

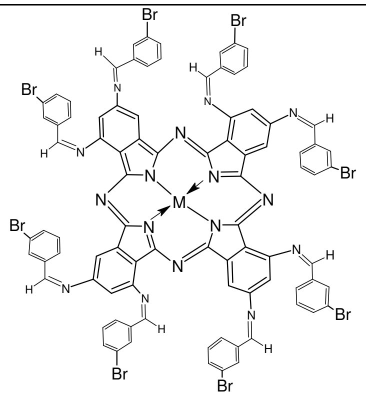


Figure 1. Suggested structure of symmetrically substituted octa-1-(3-bromophenyl)methanimine phthalocyanines, where M= Co, Cu, Ni and Zn

Electronic spectra

The electronic spectra of 1, 3, 8, 10, 15, 17, 22, 24-octa1-(3-bromophenyl)methanimine metal phthalocyanines were recorded in the range of 1.0 -1.5x10^{-4} in 1:1 sulfuric acid and the results are tabulated in Table 1. For all the complexes, a peak in the range of 609-638 nm[15] was observed and assigned to Q-band, attributed to $a_{1u} \rightarrow e_g$ transition. Peaks appeared in the range 236-239 nm[16] are attributed to C-band. The M-BrPhImPcO's showed a peak in the range of 344-370 nm is assigned to B-band and is attributed to $a_{2u} \rightarrow e_g$. The peaks in the longer wavelength region 730-746 nm. A weak *L*-band was observed in the range of 205-217. For all the complexes showed a bathochromic shift with increasing intensity with respect to the corresponding parent phthalocyanines[17]. This is due to the presence of auxochrome –Br groups on the periphery of benzene portion of the complex**.**

IR spectra

The infrared spectra were recorded using KBr pellets and the results are presented in Table 2 and their spectra are given in Figure 2. A broad absorption band at 3386–3386 cm^{-1} was observed for all the complexes and was assigned to the hydrogen bonding formed between the nitrogen atom of the phthalocyanine molecule and hydrogen atom of the moisture absorbed on KBr pellets during pelletization[18]. A very weak signal observed in the range 2315-2330 cm^{-1} is due to C-H stretching vibration on the periphery of the phthalocyanine moiety. The sharp peak at 1612-1620 cm^{-1} is assigned to C=N of imine group and the peaks in the 1388-1409 cm^{-1} is due to C-N aromatic stretching frequency. The absorption bands appeared around 560 - 652 cm^{-1} were assigned to C − Br stretching frequency of the peripheral substitution on the ring. All other remaining peaks appeared around 1052-1095 cm^{-1}, 1341-1352 cm^{-1} are attributed to the various skeletal vibrations of phthalocyanine ring[19].

Table 2. Electronic, IR and powder XRD data of metal(II)-octa-1-(3-bromophenyl)-methanimine phthalocyanines

Complex	UV-visible absorption λ nm (log∈)	IR-Spectral cm^{-1}	Powder. XRD data 2θ angle (d Å)	Relative Intensity, %
Co-BrPhImPcO	217 (5.58) 239 (5.59) 370 (5.51) 617 (5.03) 744 (5.18)	643, 1052, 1347, 1407, 1616,1714, 2355, 3395.	28.67 (2.28) 44.53 (2.76) 41.25 (3.06) 37.68 (3.85)	100.00 76.04 52.19 33.74
Cu-BrPhImPcO	216 (5.59) 236 (5.60) 344 (5.41) 638 (4.82) 746 (4.97)	652, 1088, 1347, 1533, 1620, 1714, 2357, 3390.	26.13 (2.36) 23.58 (2.48) 44.38 (2.76) 36.89 (3.12)	100.00 71.58 53.44 31.27
Ni-BrPhImPcO	214 (5.58) 238 (5.59) 365 (5.46) 609 (4.89) 730 (4.95)	643. 1093, 1341, 1548, 1612, 1719, 2349, 3405.	27.75 (2.20) 22.29 (2.86) 42.18 (3.01) 38.64 (3.21)	100.00 76.45 50.35 31.64
Zn-BrPhImPcO	205 (5.58) 239 (5.59) 368 (5.57) 619 (5.41) 759 (5.32)	560, 1095, 1352, 1409, 1616, 1714, 2350, 3410.	30.45 (2.29) 24.95 (2.84) 41.38 (3.34) 39.98 (3.54)	100.00 74.65 49.39 34.90

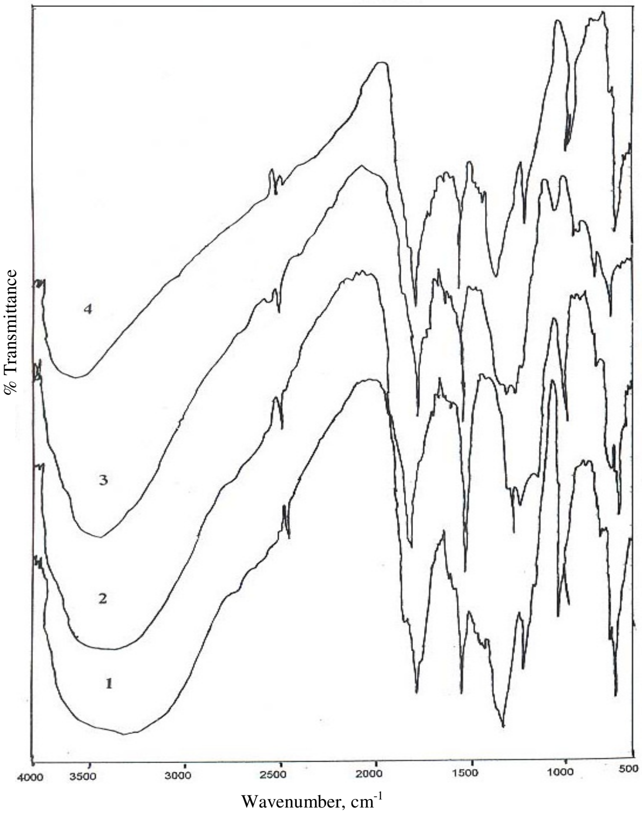


Figure 2. IR absorption spectra of (1) Cu-BrPhImPcO (2) Co-BrPhImPcO (3) Ni-BrPhImPcO (4) Zn-BrPhImPcO

Magnetic susceptibility

The magnetic susceptibility measurements for 1, 3, 8, 10, 15, 17, 22, 24-octa-1-(3-bromophenyl)methanimine phthalocyanines of copper, cobalt, are consistent with paramagnetic nature and nickel, zinc an diamagnetic nature. A summary of the magnetic properties over the range of applied magnetic field strength 2.20-4.45 KGauss are reported in Table 1. The values reported in the table are the average of the three independent determinations. Magnetic susceptibility measurements on Cu-BrPhImPcO and Co-BrPhImPcO are in agreement with paramagnetic nature of the complexes and that of Ni-BrPhImPcO and Zn-BrPhImPcO are diamagnetic. The observed magnetic moment values for Cu-BrPhImPcO and Co-BrPhImPcO are higher than expected for S = ½ 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 effect[20].

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 literature[21].

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 studies[22] 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 Å one above and one below about the central metal atom as shown in Figure 3(a) or may be placed one above the other with the separation of two molecules by a distance of 3.38 Å as represented in Figure 3(b). 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 substitutent and metal-metal distance. It seems, the exchange interaction coupled with orbital contribution is the cause for the observed higher magnetic moments for Cu-BrPhImPcO and Co-BrPhImPcO 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.

The crystallographic studies revealed that the metal phthalocyanines of Cu, Co, Ni and Zn has square planar structure with D_{4h} symmetry and are isomerphous[19]. 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^o. 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[16] *N*-atom at the interplanar distance 3.4 Å.

Powder XRD

The x-ray diffraction spectra of M-BrPhImPcO's are taken through a range of 2θ angles $6\text{-}70^o$ 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-BrPhImPcO 3.85, 37.68 Å; Cu-BrPhImPcO 3.12, 36.89 Å; Ni-BrPhImPcO 3.21, 38.64 Å and Zn-BrPhImPcO 3.54, 38.98 Å clearly indicating the crystanilline 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.

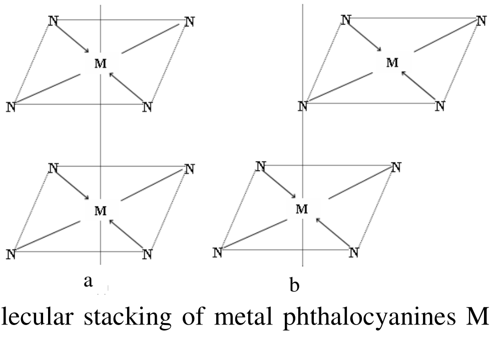


Figure 3. Probable molecular stacking of metal phthalocyanines M = Cu, Co, Ni and Zn, N = central nitrogen atoms of the phthalocyanine structure

Thermogravimetric and kinetic studies

Thermogravimatric analytical data of octa-1-(3-bromophenyl)methanimine phthalocyanine complexes both in air and nitrogen atmosphere are summarized in the Table 3 & 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 ^{o}C, may be accounted for the loss of eight substituted imine groups.

Table 3. Kinetics and Thermodynamic parameters of metal(II)-octa-1-(3-bromophenyl)-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
	5.87	6.18	2.74	-165.06	62.40
Cu-BrPhImPcO I	(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)	(-149.78)	(79.54)
	0.89	6.39	-1.38	-176.08	74.95
Co-BrPhImPcO I	(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)
	1.45	5.21	-1.22	-159.67	72.84
Ni-BrPhImPcO I	(0.70)	(2.24)	(-.0.76)	(-157.58)	(70.58)
II	5.87	4.45	-0.83	-149.79	81.76
	(1.54)	(3.81)	(-0.82)	(-143.63)	(84.21)
	1.95	3.48	-0.95	-175.97	75.24
Zn-BrPhImPcO I	(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)

Table 4. TGA data of metal(II) -octa-1-(3-bromophenyl)methanimine phthalocyanines

Compound	Temperature of decomposition, ^{o}C	Mass Loss		Probable fragment loss	Nature of DTA peak
		%, Found	%, Calcd		
Cu-BrPhImPcO	250-350	37.34	36.40	8 Br-groups	Exothermic
	350-540	62.67	62.01	+ Pc moiety	
Co-BrPhImPcO	250-350	37.58	36.40	8 Br-groups	Exothermic
	350-540	62.51	62.08	+ Pc moiety	
Ni-Br PhImPcO	250-350	36.89.	37.02	8 Br-groups	Exothermic
	350-540	62.21	65.01	+ Pc moiety	
Zn-Br PhImPcO	250-350	36.78	37.49	8 Br-groups	Exothermic
	350-540	62.37	62.45	+ Pc moiety	

The major weight loss was observed for all the complexes in the second step in the temperature ranges of 350-600 ^{o}C corresponds to the oxidative degradation of remaining phthalocyanine moiety. Analysis of the final charred residue corresponds to the corresponding metal oxides[23]. The thermal decomposition of bromo substituted metal phthalocyanine complexes in the nitrogen atmosphere appears to be very slow. For Co-BrPhImPcO, 62% of the complex was found to be decomposed at 700 ^{o}C. For Cu-BrPhImPcO, Ni-BrPhImPcO about 55%, 52% and 41% loss of the mass was observed for Zn-BrPhImPcO. Above trend confirms the relative stability of these complexes in the order Co-BrPhImPcO >Cu-BrPhImPcO > Ni-BrPhImPcO > Zn-BrPhImPcO. 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] for the two stages of decomposition.

The activation energies, (E_0) for the loss of periphery 3-bromo substitutent compound lies in the range of 0.89 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 -176.08 kJ. It is clear from the values of entropies for the decomposition that the removal of functional groups are associated with more negative entropies.

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-bromophenyl)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-bromophenyl)methanimine phthalocyanine 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-BrPhImPcO > Co- BrPhImPcO > Ni-BrPhImPcO > Zn-BrPhImPcO.

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