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Synthesis of symmmetrically substituted octabromophthalocyanine pigments and their characterisation

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Abstract

A convenient and a simple route has been suggested for the synthesis of symmetrically substituted metal (II) 1,3,8,10,15,17,22,24-octabromophthalocyanine pigments (MPOBr), of cobalt (CoPOBr), nickel (NiPOBr), copper (CuPOBr) and zinc (ZnPOBr). MPOBr's are synthesised from the corresponding octaaminosubstituted metal phthalocyanines, MPOA's. Synthesised complexes are investigated by elemental analysis, electronic spectra, IR spectra, magnetic susceptibility measurements, powder XRD and thermogravimatric studies to evaluate the thermal stability, crystallinity, structural integrity and purity of the complexes. The effects of substituents on the electronic spectra and the orbital contribution to the magnetic moments over a range of field strengths are discussed. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Phthalocyanines are a class of compounds that has received a great deal of interest in recent years not only because of their structural similarity with the life sustaining biologically important molecules like chlorophyll and hemoglobin, but also because of the remarkable coloring property associated with them. These pigments are stabilized towards polymorphic transformation by incorporating suitable substituents at the periphery of the phthalocyanine ring. The halogen substituted metal phthalocyanines pigments are found to be exploited commercially in the manufacture of pigments, colour filters dyes etc. [1]. The phthalocyanine has an extensively conjugated aromatic chromophore (1), possesses a blue–green colour with a remarkably high molar absorption coefficient. In general, all phthalocyanines invariably consist of tetrabenzoporpharazine as a chromophore.

Metal phthalocyanines played a key role in the dyes and pigments industry because of their tinctorial power, brilliance and beauty of shades. They

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have an outstanding stability to light, heat, acids and alkalis. The above class of compounds were insoluble in water and most of the organic solvents and were extensively used in the manufacturing of printing inks, paints, coatings and plastics [2]. Phthalocyanines were used as toners in colour photocopiers and laser printers [3]. Phthalocyanine pigments were also used in colour filters for liquid crystal display. A literature survey revealed the methods for the synthesis of hexadecachloro, hexadecabromo, hexadecaiodo and mixed halogen substituted metal phthalocyanines and those pigments were mainly used for commercial purposes [4]. Most of the synthetic procedures are patented in literature and hence not readily available. Reports are available on the synthesis and structural investigations of symmetrically tetrasubstituted 2,9,16,23 and 1,8,15,22-bromosubstituted metal phthalocyanines [5,6]. However, no reports are available on the synthesis and structural investigations of symmetrically octa 1,3,8,10,15,17,22,24-bromosubstituted metal (II) phthalocyanines. Keeping the above facts in mind, we have undertaken the synthesis and structural studies on the title complexes.

In the present paper we have discussed the synthesis and structural investigations of symmetrically substituted metal-(II) 1,3,8,10,15,17,22, 24-octabromophthalocyanines. The documented procedure available in literature was suitably modified and used for the synthesis of the title complexes [5]. The effect of the substitutent of bromine at the positions 1,3,8,10,15,17,22,24 on the π electron system of the main phthalocyanine moiety and subsequent changes in the electronic spectra, thermal behavior, IR spectral data and crystallinity are discussed.

2. Experimental

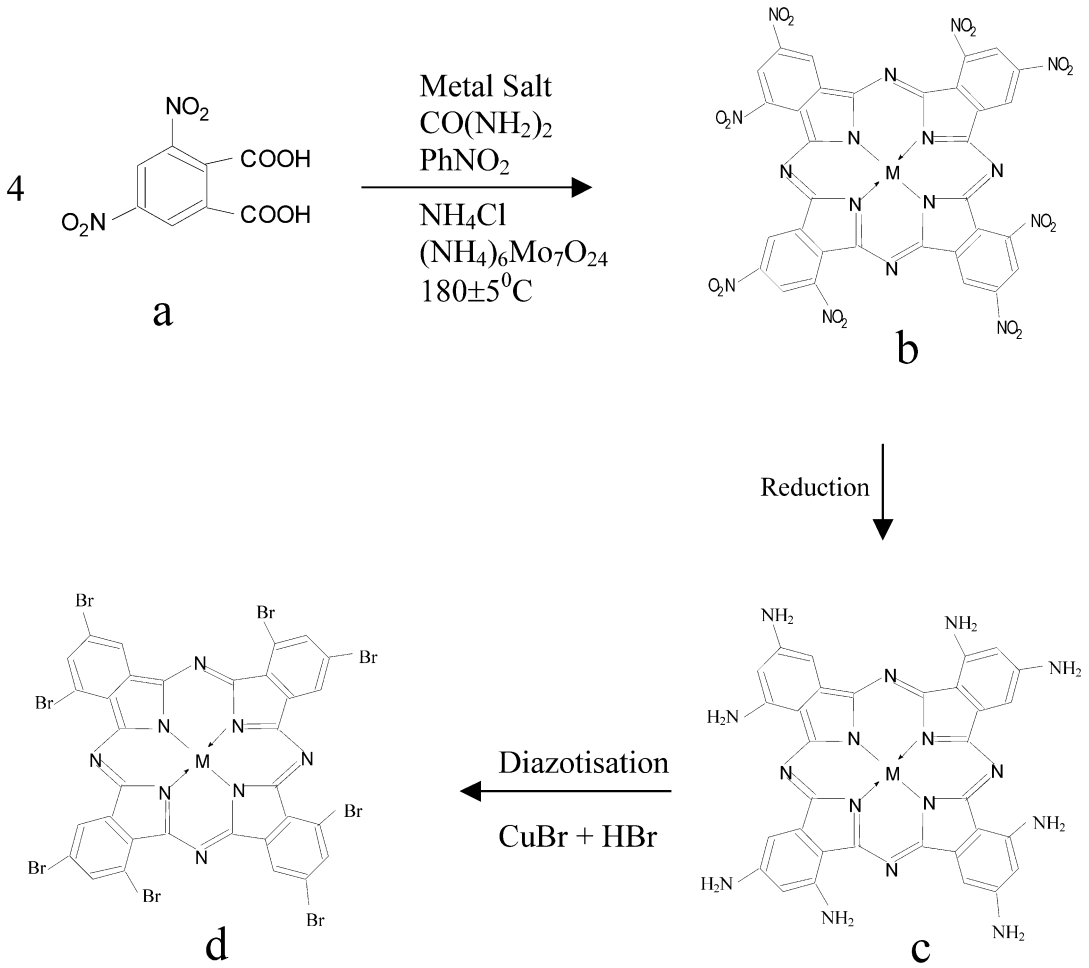
The procedures for the preparation of metal (II) 1,3,8,10,15,17,22,24-octaminophthalocyanines are reported elsewhere [7]. The obtained amino complexes are converted into corresponding bromo derivatives by adopting Sandmayer's reaction with suitable modification [8]. The general route for the synthesis of metal (II) 1,3,8,10,15,17,22,24-octabromphthalocyanines is shown in Scheme 1. All the chemicals used were of analytical grade.

2.1. Preparation of copper (II) 1,3,8,10,15,17,22, 24-octabromophthalocyanine pigment

Copper (II) 1,3,8,10,15,17,22,24-octaaminophthalocyanine (5 g) was diazotised in HCl medium to get octadiazonium salt of copper (II) phthalocyanine, $CuPON_2^+Cl^-$. The mixture was kept in a bath of crushed ice to maintain the temperature below 5 °C.

Copper sulphate pentahydrate (19.46 g) and sodium bromide dihydrate (11.3 g) were dissolved in 50 ml of water. Sodium bisulphite (5.12 g in 30 ml) was added very slowly with constant stirring and then allowed to attain room temperature. The precipitate was washed thrice by decantation with water containing a little sulphurous acid. The moist cuprous bromide was dissolved in 20 ml of 48% HBr. The chilled solution of copper (II) 1,3, 8,10,15,17,22,24-octabromophthalocyanine chloride was added slowly with constant stirring to chilled cuprous bromide solution. The mixture becomes thick due to the separation of the addition product between diazonium salt and cuprous bromide ($CuPON_2^+Cl^-$, CuBr). The adduct was then allowed to attain room temperature with occasional shaking. It was then warmed in a water bath to about 60 °C to complete the decomposition of the double salt and heating is continued till the evolution of nitrogen ceases.

A clear solution was removed by decantation and the residue was washed with water. The green product was centrifuged and washed with 1.0 M NaOH and 1.0 M HCl, alternatively four times and finally with distilled water. The solid copper (II) 1,3,8,10,15,17,22,24-octabromophthalocyanine was then dried at 50 °C for 1 h. The pigment form of the powder was obtained by the acid pasting process, in which 1 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 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 absolute alcohol repeatedly and dried in a vacuum desiccator for 2 days [9].



Scheme 1. Synthesis of metal—1,2,3,10,15,17,22,24-octabromophthalocyanine, MPOBr. (a) 3,5-Dinitrophthalic acid, (b) MPON, (c) MPOA and (d) MPOBr.

The pigment process was used for Cu(II), Co(II) and Ni(II) complexes, whereas Zn(II) undergoes demetallation.

Octabromophthalocyanine derivatives of Ni(II), Co(II) and Zn(II) were prepared by the method described above, by using the respective metal phthalocyanine octaamine derivatives.

The Regional Sophisticated Instrumentation Center, Punjab University, Chandighar, India made the C, H, and N elemental analysis. The magnetic susceptibility studies are made at room temperature (301 K) using Gouy magnetic balance consisting of NP-53 type electromagnets with a DC power supply unit and a semi microbalance. Pacal constants were used to calculate the diamagnetic corrections. A Hg [Co (SCN)$_4$] complex was used as calibrant [10] Shimadzo UV-visible recording spectrophotometer, UV-160A with 1 cm width cell was used for electronic absorption spectral studies. IR spectra were recorded using Nicolet MX-FT IR spectrometer. Philips analytical PW1710 X-ray diffractometer was used to study the diffraction pattern of the complexes. The spectra were recorded using Cu$K\alpha$ 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. TGA/SDTA 85e/SF 1100/MTI/057 thermal analyser was used for thermogravimatric studies at a rate of 10 °C min^{-1}.

3. Result and discussion

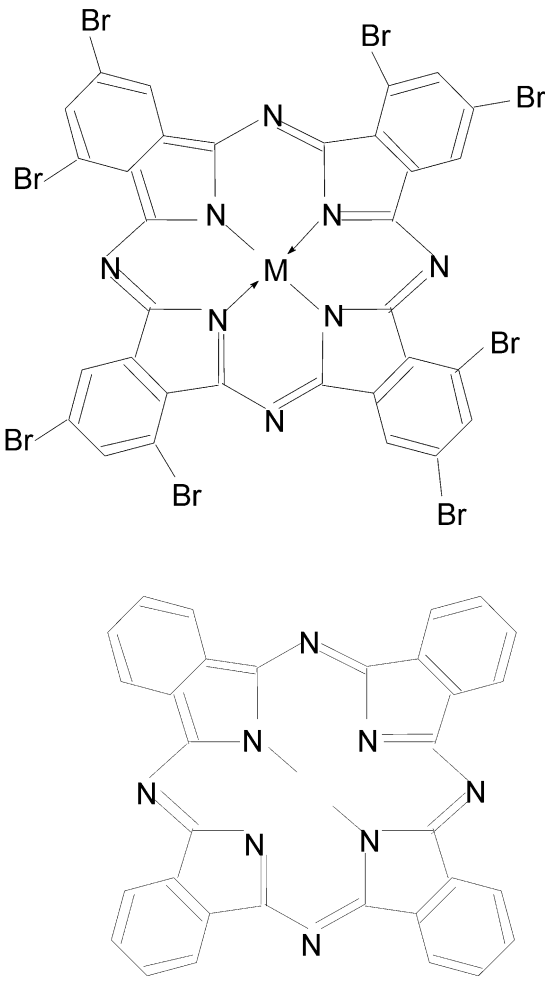
The metal with atomic radii very close to 1.35 Å forms metal phthalocyanine complexes which makes them thermally stable and a resistance towards concentrated sulfuric acid. The octabromophthalocyanine derivatives of copper, cobalt nickel and zinc have been prepared and are a deep green colour except that of zinc which is green with a brown tinge. They give a clear solution in concentrated sulfuric acid and are fairly soluble in DMSO, DMF and pyridine but insoluble in water and most of the organic solvents like alcohol, ether, carbon tetrachloride and benzene. Analytical results of the composition of carbon, hydrogen, nitrogen and metal are given in Table 1 and agree well with the calculated value and are consistent with the proposed structure, (Fig. 1).

4. IR spectra

IR data were recorded using KBr pellets and the results are summerised in Table 2 and the spectra are presented in Fig. 2. A broad absorption band at 3394–3410 cm^{-1} was observed for all the complexes and was assigned to the hydrogen bonding formed between the nitrogen atom of the phthalocyanine macromolecule and H atom of the moisture absorbed on the KBr pellets during pellatisation [11]. The sharp peaks at 1533–1616 cm^{-1} are assigned to C=C aromatic stretching. The peaks at 1341–1352 cm^{-1} are due to C–N aromatic stretching vibrations. Absorption around 752–757 cm^{-1} were assigned to C–Br stretching frequencies of the peripheral substitution on the ring. All other remaining peaks 876–88, 1072–, 1300–1345 cm^{-1} are attributed to various skeletal vibrations of the phthalocyanine ring [12].

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

Complex	Emperical formulae (formula weight)	Colour	Field strength (kG)	Magnetic susceptibility (χ_mx10^{-6} cgs units)	Magnetic moments μ_{eff} (B.M)	Elemental analysis (%) found (calcd.)	Yield (%)
CuPOBr	$C_{32}H_8N_8Br_8Cu$ (1206.75)	Dark green	1.03 1.30 1.51 1.83 2.09 2.32	+4124.7 +3806.1 +3384.6 +2935.4 +2446.1 +1816.9	3.17 3.05 2.88 2.68 2.44 2.11	C, 32.01; (31.82) H, 0.69; (0.66) N, 9.45, (9.28) Br, 53.03, (52.97) Cu, 5.31; (5.27)	90%
CoPOBr	$C_{32}H_8N_8Br_8Co$ (1202.13)	Dark green	1.03 1.30 1.51 1.83 2.09 2.32	+1936.2 +1818.4 +1753.1 +1420.5 +1382.9 +1322.8	2.17 2.11 2.07 1.86 1.84 1.80	C, 32.08; (31.94) H, 0.72; (0.66) N, 9.82, (9.32) Br, 53.31; (53.17) Co, 5.01, (4.90)	94%
NiPOBr	$C_{32}H_8N_8Br_8Ni$ (1201.90)	Dark green	1.51	−1639.4	–	C, 32.01; (31.95) H, 0.78; (0.66) N, 9.49, (9.32) Br, 38.80; (38.64) Ni, 4.92; (4.88)	92%
ZnPOBr	$C_{32}H_8N_8Br_8Zn$ (1208.58)	Green with brown tinge	1.51	−1022.8	–	C, 31.82; (31.77) H, 0.72; (0.66) N, 9.41, (9.26 Br, 53.01; (52.90) Zn, 5.52; (5.41)	88%



Chromophore. **1**

Fig. 1. The proposed structure of metal 1,3,8,10,15,17,22,24-octabromophthalocyanines, MPOBr where M = Cu, Co, Ni and Zn.

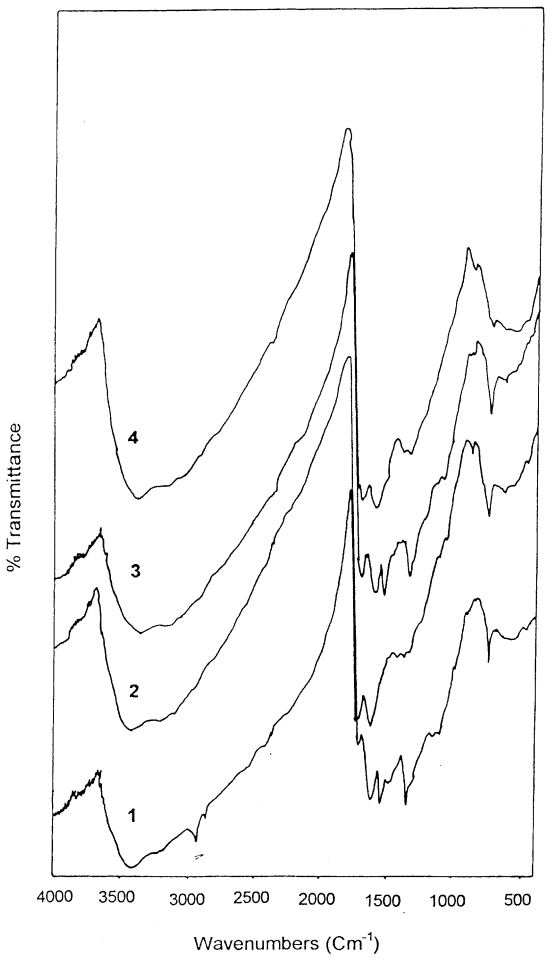


Fig. 2. IR absorption spectra of 1. CuPOBr, 2. CoPOBr, 3. NiPOBr and 4-. ZnPOBr.

5. Magnetic susceptibility

The magnetic susceptibility and magnetic moments of square planar MPOBrs have been studied in the solid state over the range of 1.03–2.32 kG (Table 2) The values revealed that CuPOBr and CoPOBr are paramagnetic and that NiPOBr and ZnPOBr are diamagnetic. The observed magnetic moments for CuPOBr and CoPOBr are higher than the one unpaired electron (1.73 BM). These higher values may be due to the orbital contributions due to the mixing of ground state orbitals $(b_{2g})^2$, $(e_g)^4$ and $(a_{1g})^1$, and higher orbitally degenerate states $(b_{2g})^2$, $(e_g)^3$ and $(a_{1g})^2$. This orbital contribution decreases as field strength increases. The magnetic moments of MPOBrs corresponds to spin only values at higher filed strength. The observed higher values of μ_{eff} at lower field strength for CuPOBr and CoPOBr may be due to intermolecular magnetic interaction coupled with the magnetic anisotropy of the strong phthalocyanine π- electron current [12,13].

It may be noticed from the trend of varitation of χ_m and μ_{eff}, that the spin–spin coupling between

the adjecent metal atom is direct in the case of CoPOBr and it may be superexchange through N-atom of the phthalocyanine molecule in CuPOBr [13,14].

Hall mobility factor, due to the interaction of metal orbitals and the π-orbitals of the neighbouring phthalocyanine ring [15,16] expect higher values of μ_{eff} in measured field strength for both CuPOBr and CoPOBr over their unsubstituted phthalocyanines. However the measured values of μ_{eff} did not match with that of unsubstituted phthalocyanine of the same metal [17]. This may be due to the dominance of hindered stacking due to functional groups over the expected degree of Hall mobility.

6. Electronic spectra

The electronic spectra of MPOBr's in 18 M sulfuric acid in the concentration range of 5.1–5.2×10^{-4} M are recorded and the summary of the results are presented in Table 2. For all the complexes peak was observed in the range of 611–647 nm, which was a characteristic for phthalocyanines and is assigned to a Q-band, attributed to $a_{1u}\rightarrow e_g$ transition. The observed peak at 224–231 nm is attributed to A C-band. All the complexes of MPOBr's shows a peak in the range of 471–482 nm assigned for a B-band attributed to $a_{2u}\rightarrow e_g$. The peaks in the range of 240–258 nm of weak intensity was observed for all the complexes assigned to the L-band.

7. Powder XRD

Powder diffraction patterns of Copper (II), Cobalt (II), Nickel (II) and Zinc (II) octabromophthalocyanines are taken in the range of 2θ, angle 6–70 (Table 2) showed identical features with relatively poor crystallinity. The observed patterns though resembles qualitatively that of the corresponding unsubstituted metal phthalocyanines, in MPOBr's peaks are found to be broadened with diffused intensity, which is obvious

Table 2
Spectral data of metal (II)-1,3,8,10,15,17,22,24-octabromophthalocyanines

Complex	UV-visible absorption λ nm (logϵ)	IR Spectral data cm^{-1}	Powder XRD data 2θ angle (d Å)	Relative intensity (%)
CuPOBr	231 (3.81)	752, 1088, 1140,	23.61, (3.77)	53.64
	240 (2.79)	1347, 1533, 1714,	26.97, (3.30)	100.00
	471 (2.40)	3390, 3410.	29.21, (3.05)	41.98
	647 (2.13)		36.49, (2.46)	52.61
			51.45, (1.77)	54.68
CoPOBr	224 (3.80)	643, 752, 886,	30.94, (2.88)	70.84
	258 (2.77)	1052, 1347, 1616,	32.85, (2.72)	61.36
	479 (2.39)	1714, 3395.	34.73, (2.58)	100.00
	615 (2.39)		35.70, (2.51)	62.67
			43.72, (2.07)	55.01
NiPOBr	225 (3.72)	643, 757, 1093,	13.69, (6.46)	48.10
	249 (2.76)	1341, 1548, 1719.	25.12, (2.54)	70.34
	475 (2.29)	3405.	26.25, (3.39)	100.00
	620 (2.19)		27.61, (3.22)	90.56
			32.17, (2.78)	61.19
ZnPOBr	227 (3.78)	560, 757, 891,	20.66, (4.29)	67.29
	242 (2.76)	1352, 1409, 1616,	25.41, (3.50)	77.94
	482 (2.39)	1714, 3410.	26.22, (3.39)	100.00
	611 (2.03)		27.34, (3.25)	69.88
			27.67, (3.22)	83.55

from the graph shown in Fig. 3. This revealed that the title compounds are less crystalline than their corresponding unsubstituted metal phthalocyanines. This may be due to the presence of bulky substitutent bromine, and seems to play a dominant role in deciding the stacking of metal phthalocyanine derivatives. X-ray powder diffraction patterns are used only to explain the degree of crystallinity, which is qualitative. The effect of the bromine substitution (increasing size) may be clearly identified from the first *d* values of all the complexes.

8. Thermogravimetric studies

Thermogravimetric studies of MPOBr's in static air reveals that these complexes degrade in single

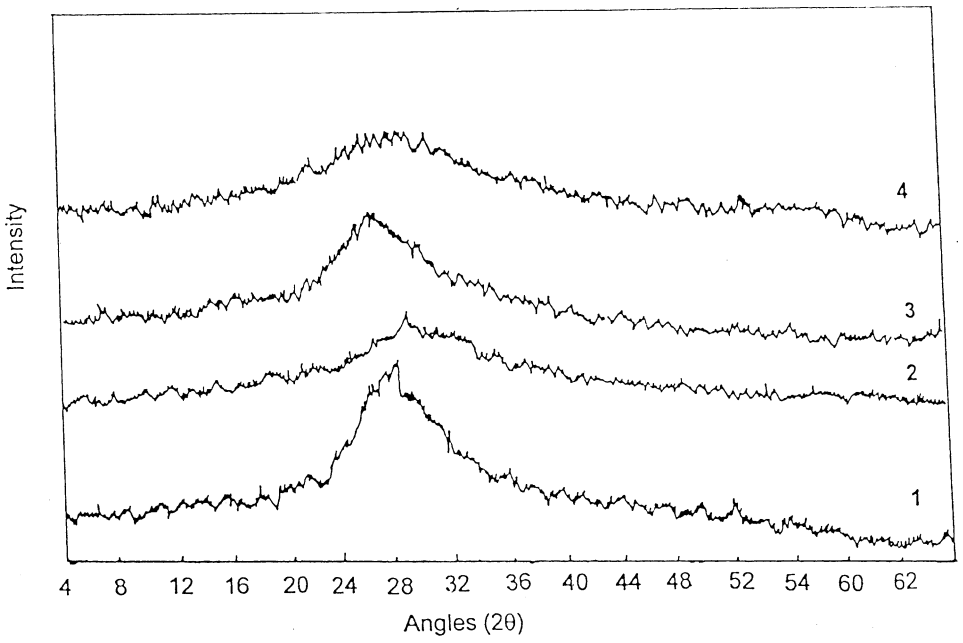


Fig. 3. Powder X-ray diffraction pattern of 1. CuPOBr, 2. CoPOBr, 3. NiPOBr and 4. ZnPOBr.

Table 3
TGA data of 1,3,8,10,15,17,22,24-octabromopthalocyanines

Complex	Temperature of decomposition (°C)	Mass loss		Probable mode of fragmentation.
		(%) Found	(%) Calcd.	
CuPOBr	220–240	19.86	19.99	−3Br groups
	450–650	80.12	79.99	−5Br + Pc moiety[a]
CoPOBr	220–240	26.58	26.50	−4Br groups
	450–650	73.41	73.49	−4Br + Pc moiety
NiPOBr	220–240	26.58	26.49	−4Br groups
	440–650	73.40	72.50	−4Br + Pc moiety
ZnPOBr	210–240	26.44	26.00	−4Br groups
	450–650	73.55	73.49	−4Br + Pc moiety

[a] Pc = Phthalocyanine.

step. CuPOBr, CoPOBr, NiPOBr and ZnPOBr have shown the weight loss in the range of 220–440 °C, which corresponds to the loss of Br functional groups present in the periphery of the molecule. The major weight loss was observed for all the complexes in the range of 440–650 °C corresponding to the degradation of phthalocyanine moiety. The final undecomposed products were found to be corresponding metal oxides and are characterised by X-ray diffraction studies. The observed thermal stability is ZnPOBr > CoPOBr > CuPOBr > NiPOBr. The probable modes of fragmentation of the complexes were tabulated in the Table 3.

9. Conclusion

Magnetic susceptibility studies on the MPOBr's have shown that, CoPOBr and CuPOBr are paramagnetic and ZnPOBr and NiPOBr are diamagnetic. The measured magnetic moment values are found to be higher than the corresponding spin only value indicated the orbital contributions and the observed variation of magnetic moment values with field strength is due to intermolecular magnetic interaction. Thermiogravimetric studies revealed the thermal stability of the MPOBr's in air in the order ZnPOBr > CoPOBr > CuPOBr > NiPOBr.

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