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SYNTHESIS, SPECTRAL AND MAGNETIC SUSCEPTIBILITY STUDIES ON 1,8,15,22-TETRABROMO METAL (II) PHTHALOCYANINES

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ABSTRACT

Symmetrically substituted 1,8,15,22-tetrabromo phthalocyanines of cobalt (3-BrCoPc), nickel (3-BrNiPc), copper (3-BrCuPc) and zinc (3-BrZnPc) are synthesized from the corresponding tetraamino substituted metal phthalocyanines using modified Sandmayer's method. The tetraamino metal phthalocyanines were synthesized from tetranitro phthalocyanines and tetranitrophthalocyanines were in turn synthesized from 3-nitrophthalic acid with corresponding metal salts. The bluish green coloured complexes were characterized by elemental analyses, Uv-visible and IR spectroscopy, and magnetic susceptibility measurements in order to check their purity and structural integrity. The magnetic susceptibility studies revealed that, the experimentally determined magnetic moments are higher than the spin only magnetic moment values and shows the presence of intermolecular cooperative effects.

INTRODUCTION

Phthalocyanines are planar, macrocyclic aromatic compounds with four isoindole units. The core electronic structure is similar to that of porphyrine molecule, with central porphyazine ring structure suitable to undergo ligation with many metals to form phthalocyanine complexes. Substituted phthalocyanine complexes have been extensively explored to be applicable as dyes and pigments[1-5], materials for solar cells[6-8], fuel cell electrodes[9-10], electrochromic display devices[11-14] and photochromic display devices[15, 16], data storage devices[17-19], liquid crystal color display devices[20, 21] and in photodynamic cancer therapy[22-24]. Substituted cobalt phthalocyanine complexes are used as catalyst for electrochemical biosensors and sensors for atmospheric pollutants[25-27].

Halogen substitution upon phthalocyanine complexes involved direct halogenation with harsh conditions and the procedures resulted in random halogen substitution with various number of halogen atoms[1]. These halogen substituted phthalocyanines are extensively used as dyes and pigments[1-3]. The physicochemical properties and the colour shade of the halogen substituted phthalocyanine derivatives depends on the number and position of the halogen atoms present on the periphery of the phthalocyanine moity. Our methods of synthesis and characterization of some 1,8,15,22- and 2,9,16,23-substituted metal phthalocyanine derivatives, were documented in literature[28-32], where 1,8,15,22-tetranitro or 2,9,16,23-tetranitro metal phthalocyanines were reduced selectively to prepare corresponding aminosubstituted phthalocyanines which were further converted into corresponding hydroxy, cyano and chlorosubstituted metal phthalocyanines. Present work describes the synthesis and structural investigation of 1,8,15,22-tetrabromo, derivatives of cobalt (3-BrCoPc), nickel (3-BrNiPc), copper (3-BrCuPc) and zinc(3-BrZnPc) phthaocyanines.

EXPERIMENTAL SECTION

Materials

All the chemicals used were of analytical grade and from either Merck of SD Fine chemicals Sodium sulphide nonahydrate was from Sigma Aldrich. Magnetic susceptibility studies on complexes were carried out at room temperature by using Gouy magnetic balance consisting of NP- 53 type electromagnets with a dc power supply unit and semimicro electronic balance supplied by AMD electronics, Japan. A DG 900 model Gaussmeter from Ferrites India was used to measure the magnetic flux density produced by the

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electromagnets. Pascals constants were used to calculate the diamagnetic corrections[33]. Mercury tetrathiocyanato cobaltate, $Hg[Co(SCN)_4]$ was used as a calibration standard, and doubly distilled water was used throughout the experiment. A Systronics uv-visible spectrophotometer 119 with 1 cm matched silica cells was used for electronic spectral studies. IR spectra were recorded using Nicolet MX-1 FTIR spectrometer and IR spectra in the Far-IR region were recorded on Perkin – Elmer 577 IR spectrometer with a XY recorder. C, H and N analyses were performed on EuroVector E 3000 Elemental Analyser. The metal contents were determined gravimetrically by incinerating the complexes to form metal oxides.

Synthesis

1,8,15,22-Tetraamino metal phthalocyanines, MPTA's were carried out by adopting the procedures documented elsewhere[28,29] with suitable modifications. The obtained tetra amino phthalocyanines of copper, cobalt, nickel and zinc are converted in to the corresponding 1,8,15,22-tetrabromo phthalocyanines by employing modified Sandmeyer's reaction[30]. The general scheme followed for the synthesis of metal (II) 1,8,15,22- tetrabromo phthalocyannes is as shown in the scheme 1.

Synthesis of cobalt (II) 1,8,15,22–tetrabromophthalocyanine, 3-BrCoPc.

Finely ground cobalt (II) 1,8,15,22-tetraaminophthalocyanine (5g) was added to 50 ml of 1.0 N sulphuric acid solution in a 100 mL beaker. The mixture was kept in a bath of crushed ice until the temperature of the reaction mixture falls to 5 °C. To the cold solution of cobalt(II) 1,8,15,22-tetraamino phthalocyanine, the chilled aqueous solution of sodium nitrite (3.1 g / 7.5 ml) was added in small volumes with constant stirring to form cobalt(II) 1,8,15,22-tetradiazonium phthalocyanine hydrogen sulphate, $CoPTN_2^+HSO_4^-$

Cuprous bromide prepared as follows. To the mixture of copper sulphate pentahydrate (9.73 g) and sodium bromide dihydrate (5.65 g) in 250 mL of water, an aqueous solution of sodium bisulphate (2.56 g / 25 ml) was added slowly with constant stirring at 70 °C. The mixture was cooled to room temperature to settle the precipitate of cuprous bromide. The precipitate was washed several times by decantation with water containing sulpurous acid. It was dissolved in 10 ml of 48 % hydrobromic acid and heated to boiling.

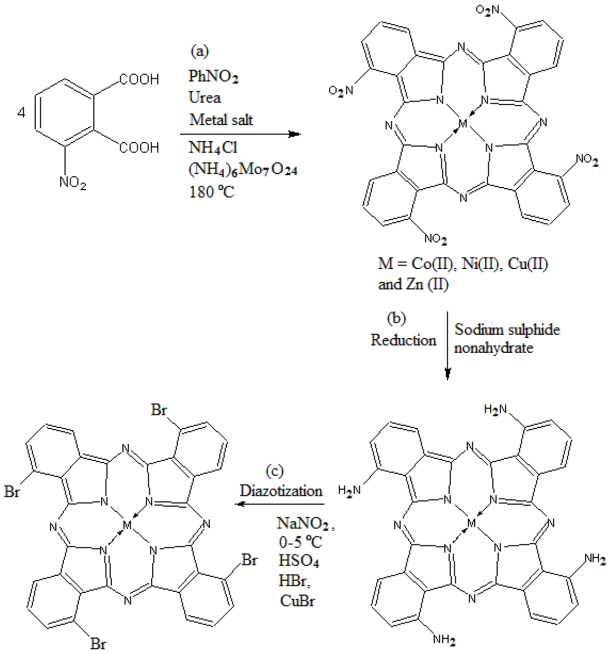
Chilled solution of cobalt(II) 1,8,15,22-tetradiazonium phthalocyanine hydrogen sulphate was added slowly with constant stirring to the boiling solution of cuprous bromide in hydrobromic acid over a period of 40 minutes. The green product settled upon cooling the mixture to room temperature was separated by decantation. The precipitate was washed thoroughly with water. The dark green cobalt(II) 1,8,15,22-tetrabromophthalocyanine was washed repeatedly with solution of 1.0 M hydrochloric acid and 1.0 M sodium hydroxide, dried, and finally washed with distilled water. The pure compound is then washed with absolute alcohol, filtered and dried at 50 °C for 1 h. Yield 90 %

1,8,15,22-tetrabromophthalocyanines of nickel (II) (3-BrNiPc), yield 93 % copper(II) (3-BrCuPc), yield 87 % and zinc(II) (3-BrZnPc) yield 88 % were synthesized by the same method as described above using the respective metal tetraamino phthalocyanine derivatives.

RESULTS AND DISCUSSION

The colour shades of the complexes synthesized ranges from bluish green to bluish black with a metallic luster. These complexes with square planar geometry belong to D_{4h} molecular symmetry group. Their solubility in water and most of the organic solvents like alcohol, carbon tetrachloride, chloroform, diethyl ether, hexane and acetone is very poor but are soluble in DMF, DMSO, pyridine and concentrated sulphuric acid. Conversion of tetraamino derivatives in to corresponding tetrabromo complexes results in good yields, from 87% to 93%. Results of elemental analyses for quantification of carbon, hydrogen, nitrogen and metals are summarized in table - 1. The results are in good

Scheme 1. Synthesis of (a) metal(II) 1,8,15,22-tetranitrophthalocyanine(b) metal(II) 1,8,15,22-tetraaminophthalocyanine, (c) metal(II) 1,8,15,22-tetrabromophthalocyanine.



agreement with the calculated values and are consistent with the proposed structure in scheme 1.

Magnetic susceptibility

The magnetic susceptibility (χ_m) and the magnetic moments (μ_{eff}) measured and averaged out of three independent determinations, over a range of magnetic field strength from 1.27 – 4.68 kG are presented in table 1.

Table 1 Elemental analysis and magnetic susceptibility data of metal (II) 1,8,15,22 tetrabromo phthalocyanines

Complex	Emperical formulae, (formula weight)	Field strength (kG)	Magnetic susceptibility, λ_m, × 10^{-6}, in cgs units.	Magnetic moments, μ_{eff} (BM)	Elemental analyses, found (calculated)
3-BrCoPc	$C_{32}H_{12}N_8Br_4Co$ (886.53)	1.27 1.71 2.58 3.44 4.27 4.68	3656.50 3633.94 3484.06 2356.14 2144.13 2118.07	2.98 2.98 2.91 2.39 2.28 2.27	C, 42.9 (43.3) H, 1.3 (1.3) N, 12.5 (12.6) Co, 6.7 (6.7)
3-BrCuPc	$C_{32}H_{12}N_8Br_4Cu$ (891.15)	1.27 1.71 2.58 3.44 4.27 4.68	4678.44 4022.40 3102.50 2692.79 2415.14 2303.09	3.38 3.13 2.75 2.56 2.42 2.37	C, 42.1 (43.1) H, 1.3 (1.3) N, 12.4 (12.6) Cu, 6.8 (7.1)
3-BrNiPc	$C_{32}H_{12}N_8Br_4Ni$ (886.30)	3.44	-241.72	----	C, 43.0 (43.3) H, 1.2 (1.4) N, 12.5 (12.6) Ni, 6.5 (6.6)
3-BrZnPc	$C_{32}H_{12}N_8Br_4Zn$ (892.98)	3.44	-198.03	----	C, 42.1 (43.0) H, 1.1 (1.3) N, 12.0 (12.5) Zn, 7.5 (7.2)

The magnetic moments revealed that 3-BrCoPc and 3-BrCuPc are paramagnetic, and 3-BrNiPc and 3-BrZnPc are diamagnetic. The χ_m and μ_{eff} values for 3-BrCoPc and 3-BrCuPc are found to be considerably higher at lower field strengths and decreases as the field strength increases. The measured magnetic moments for the paramagnetic complexes are higher than expected for a spin only magnetic moment. Both the paramagnetic complexes did not show spin only magnetic moment (1.73 BM) even at 4.68 kG of magnetic field. The higher magnetic moments observed at lower applied field strength is due to orbital contribution. The orbital contribution to the magnetic moments is consisted of (i) intermixing of ground state orbitals $(b_{2g})^2$, $(e_g)^4$ and $(a_{1g})^1$ with orbitally degenerate high energy states $(b_{2g})^2$, $(e_g)^3$ and $(a_{1g})^{234}$, and (ii) magnetic anisotropy of the strong phthalocyanine π – electron current[35]. The decrease of the magnetic moment values towards higher applied magnetic field for 3-BrCoPc and 3-Br-CuPc is due the combined phenomenon of intermolecular cooperative effects and magnetic anisotropy[2,36].

The crystallographic studies of the metal phthalocyanines of Co, Ni, Cu and Zn[1,2] reveals that they are isomorphous and the molecular stacking of the unsubstituted metal phthalocyanines has been understood to be as shown in figure 1. The molecules are stacked along the short b-axis. The planes of the molecules are inclined to the a–c axis at an angle of θ = 45º. Therefore the complexes are stacked in columns having N atoms of the phthalocyanine ligand placed between the metal atoms of the two molecules with an interplanar distance of 3.4 Å[37].

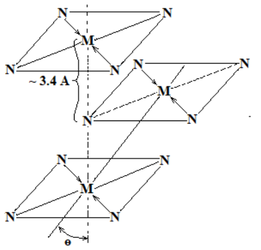


Fig 1 Probable molecular stacking of metal phthalocyanines. M = Cu, Co, Ni and Zn, N = azamethine atom of phthalocyanine plane.

Electronic spectra

The UV-visible absorption spectra of the title complexes were recorded with a concentration of 1 × 10^{-4} M in dimethyl sulfoxide (DMSO) and the data are presented in figure 2. The absorption maxima of the B-band for unsubstituted phthalocyanine of cobalt (CoPc), nickel (NiPc), copper (CuPc) and zinc (ZnPc) appears respectively at 323 nm, 320 nm, 321 nm and 336 nm. These bands are due to $a_{2u} \rightarrow e_g$ transitions of the phthalocyanine ligand[2]. However for the 1,8, 15, 22-bromosubstituted complexes the B-bands observed to be slightly shifted to higher wavelength and appear at 327 nm (3-BrCoPc), 324 nm (3-BrNiPc), 325 nm (3-BrCuPc) and 342 nm (3-BrZnPc) respectively. The characteristic Q-band absorption due to transition between a_{1u} and e_g orbitals of the phthalocyanine ring for unsubstituted phthalocyanines show their maxima at 659 nm (CoPc), 668 (NiPc), 665 nm (CuPc) and 666 nm (ZnPc) All the 1,8,15,22-bromosubstituted complexes show intense Q bands but shifted by few nanometers towards higher wavelengths as they peaks at 663 nm (3-BrCoPc), 664 nm (3-BrNiPc), 671 nm (3-BrCuPc) and 676 nm (3-BrZnPc). The shoulders at the lower absorption edge of the Q band are consistent with those reported in literature[2]. A small red shift of both the B band and Q bands may be accounted for by an extension of the 18-electron π-cloud delocalization due to more electronegative bromine atoms on the periphery of the phthalocyanine ring and the consequent relative lowering of the energy of the e_g orbital.

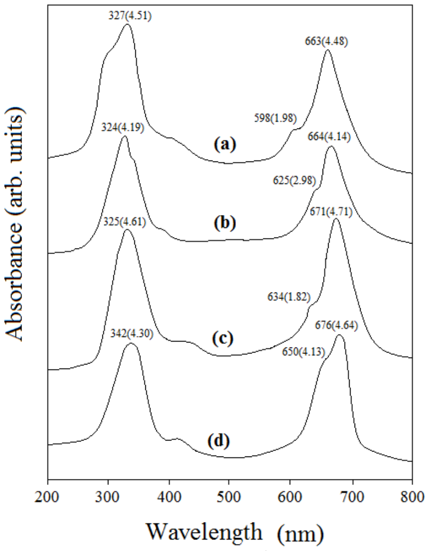


Fig 2 Uv-visible absorption spectra of (a) Cobalt(II) 1,8,15,22-tetrabromophtalocyanine (3-BrCoPc) (b) Nickel(II) 1,8,15,22-tetrabromophtalocyanine (3-BrNiPc), (c) Copper(II) 1,8,15,22-tetrabromophtalocyanine (3-BrCuPc) and (d) Zinc(II) 1,8,15,22-tetrabromophtalocyanine (3-BrZnPc).

IR spectra

The IR spectra recorded for the 1,8,15,22-tetrabromosubstituted phthalocyanines of cobalt, nickel, copper and zinc were analyzed for identification of various characteristic skeletal vibrations of the phthaocyanine ligand and the results were consistent with those reported in literature[38]. Presence of bromine substitution on the periphery of the phthalocyanine was confirmed by characteristic carbon - bromine vibrations observed in the Far – IR regions of the IR spectra. The IR spectral data were summarized in Table 2.

Table 2. IR Spectral data of metal (II) 1,8,15,22-tetrabromophthalocyanines.

Sl. No.	Complex	IR spectral signals in cm^{-1}.
1	3-BrCoPc	381 w, 750s, 814w, 946w, 1110s, 1260w, 1338w, 1480s, 1510s, 1715s, 2362s, 3086vw
2	3-BrNiPc	382w, 751s, 808s, 949m, 1052w, 1106s, 1260m, 1379b, 1538vs, 1726m, 2361s, 3086vw
3	3-BrCuPc	382w, 749s, 806m, 938w, 1100w, 1159s, 1249w, 1340b, 1535vs, 1617w, 1720w, 2369s, 3084vw
4	3-BrZnPc	381w, 750s, 815m, 946w, 1110s, 1260w, 1338b, 1480s, 1510s, 1715s, 2362s, 3084vw

s = sharp, vs = very sharp, b = broad, m = medium, vw = very weak, w = weak.

Very sharp signals observed at 1510 – 1538 cm^{-1}, for all the complexes are indicative of the coupled vibrations of C═N aza stretch, C═C pyrrole stretch and C═C stretch. More commonly seen sharp signals at 1715 – 1726 cm^{-1} and a weak signal observed at 1617 cm^{-1}, in the case of 3-BrCuPc, are due to coupled stretching vibrations of C═C benzene and C═C pyrrole. The C—H stretching vibrations of aromatic molecules are expected to appear at 3030 cm^{-1} [39]. It is also reported that a weak signal is always separated and appears above 3000 cm^{-1} for the unsubstituted metal phthalocyanine complexes[38]. In the present study, very weak signals observed in the range of 3084 – 3086 cm^{-1} for all the bromo substituted complexes are attributed to C—H stretching vibration on the periphery of the phthalocyanine ligand. Weak to medium intensity signals appeared around 938 – 949 cm^{-1} for all the four complexs are assigned to metal – ligand stretching vibrations, and the data are in good agreement with the reported IR spectral results and respective assignments, for the unsubstituted metal phthalocyanines[40]. These metal-ligand stretching vibrations appeared at higher frequencies than for unsubstituted metal phthalocyanines for which they appear between 888 cm^{-1} and 919 cm^{-1} [40]. Signals with medium to high intensity between 806 cm^{-1} and 815 cm^{-1} are due to C—H out-of-plane bending vibrations. Sharp IR absorption band were observed for all the title complexes in a very narrow range of 749 – 751 cm^{-1}.These sharp bands are due to the in-plane pyrrole stretching vibrations[38].

The IR spectra recorded in the far IR region for the complexes showed weak signals at 381- 382 cm^{-1}. These signals indicate the C—Br stretching vibrations. All the other signals appeared in the spectra are attributed to the various skeletal vibrations of phthalocyanine ligand[38,40].

CONCLUSIONS

The synthetic method used was very simple and expected to give the good yield in all the cases. Magnetic susceptibility studies revealed the structural information of the complexes. Combined phenomenon of intermolecular cooperative effects and magnetic anisotropy has been found operating at higher magnetic fields. Peripheral substitution of metal phthalocyanine moiety with electronegative bromine results in red shift of the intense Q band absorption and indicates the title material to be promising visible and near IR absorbers.

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