



SYNTHESIS, SPECTRAL AND MAGNETIC SUSCEPTIBILITY STUDIES OF 1,8,15,22-TETRAIODOPHTHALOCYANINE COMPLEXES OF COBALT, NICKEL, COPPER AND ZINC

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ABSTRACT

Some 1,8,15,22-tetraiodophthalocyanine complexes of cobalt (3-ICoPc), nickel (3-INiPc), copper (3-ICuPc) and zinc (3-IZnPc) were synthesized from the corresponding tetraamino substituted metal phthalocyanine complexes using modified Sandmayer's method. The corresponding 1,8,15,22-tetranitrophthalocyanine complexes of the metals were used as precursors for the synthesis of 1,8,15,22-tetraamino substituted metal phthalocyanines. 1,8,15,22-tetranitrophthalocyanine complexes were in turn synthesized from reaction between 3-nitrophthalic acid with corresponding metal salts. The characterization of bluish green colored complexes was done by elemental analyses, Uv-visible and IR spectroscopy, and magnetic susceptibility measurements in order to check their purity and structural integrity. Measurement of magnetic susceptibility with varying magnetic field strengths revealed that, the magnetic moments are higher than the spin only values and shows the presence of intermolecular cooperative effects.

Keywords: Characterization, Electronic spectroscopy, IR spectroscopy, Magnetic susceptibility, Synthesis, Tetraiodo metal (II) phthalocyanines.

1. INTRODUCTION

Phthalocyanines are planar, macrocyclic aromatic compounds with four isoindole units bridged through nitrogen atoms. The electronic structure of the phthalocyanine core resembles that of porphyrine molecule, with a central porphyrine ring cavity suitable to undergo ligand-to-metal charge transfer bonds with many dipositive and tripositive metals to form phthalocyanine complexes [1-2]. Most of the physicochemical properties of the phthalocyanine complexes depends on the functionalization of the phthalocyanine molecules on the peripheral carbon atoms and the consequent variation in electron charge cloud on the phthalocyanine plane. Applications of the peripherally substituted phthalocyanine complexes encompasses dyes and pigments [1-5], materials for solar cells [6-8], fuel cell electrodes [9, 10], electrochromic display devices [11-14], photochromic display devices [15, 16], data storage devices [17-19], liquid crystal color display devices [20, 21] and materials for photodynamic cancer therapy [22-24]. Peripherally substituted cobalt phthalocyanine

complexes in particular are used as catalyst for electrochemical biosensors and sensors for atmospheric pollutants [25-27].

Peripherally halogen substituted phthalocyanine complexes are extensively used as dyes and pigments [1-3]. Direct halogenation with harsh reaction conditions has been used to synthesize halogen substituted phthalocyanine complexes and the procedure results in random substitution of halogens at peripheral positions with uncertain number of halogen atoms [1-2]. The number and position of the halogen atoms on the periphery of the phthalocyanine moiety controls the colour shade and the physicochemical properties of the halogen substituted metal phthalocyanine derivatives. In our earlier studies, simple methods have been established for the synthesis of 1,8,15,22- and 2,9,16,23-tetraamino substituted metal phthalocyanines from the corresponding nitrosubstituted derivatives [28-30]. The 1,8,15,22- and 2,9,16,23-tetraamino metal phthalocyanines were further converted into respective hydroxy, cyano and chlorosubstituted metal

phthalocyanines [28-30]. Present paper describes the synthesis and structural studies of 1,8,15,22-tetraiodo, derivatives of cobalt (3-ICoPc), nickel (3-INiPc), copper (3-ICuPc) and zinc (3-IZnPc).

2. MATERIAL AND METHODS

2.1. Material

The chemicals used were procured from either Merck or SD Fine chemicals. Sodium sulphide nonahydrate was obtained from Sigma Aldrich. A Gouy magnetic balance consisting of NP- 53 type electromagnets with a dc power supply unit was used for magnetic susceptibility studies on complexes at room temperature. A semimicro digital analytical balance supplied by AMD electronics, Japan was used for measurement of mass changes. Magnetic flux density produced by the electromagnets was measured using a DG 900 model Gaussmeter from Ferrites India. Pascals constants were used to apply the diamagnetic corrections to the measured magnetic moments [31]. Mercury tetrathiocyanato cobaltate, $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibration standard. A Systronics uv-visible spectrophotometer 119 with 1 cm matched silica cells was used for electronic spectral studies. IR spectra were recorded on a 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 Euro Vector E 3000 Elemental Analyser. The metal contents were determined gravimetrically by incinerating weighed quantities of the complexes to form respective metal oxides.

2.2. Methods

1,8,15,22-Tetraamino phthalocyanines of cobalt, nickel, copper and nickel were synthesized by adopting the procedures documented elsewhere [28, 29] with suitable modifications. The respective 1,8,15,22-tetraamino phthalocyanines were converted into 1,8,15,22-tetraiodophthalocyanines by employing modified Sandmeyer's reactions [30]. The methods followed for the synthesis of metal (II) 1,8,15,22-tetraiodo phthalocyanines are illustrated in the scheme 1.

2.2.1. Synthesis of cobalt (II) 1,8,15,22- tetraiodo-phthalocyanine, 3-ICoPc

Finely ground cobalt(II) 1,8,15,22-tetraamino-phthalocyanine (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 fell 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, $\text{CoPTN}_2^+\text{HSO}_4^-$. Aqueous solution of potassium iodide (4.8 g / 60 mL) was added slowly with continuous stirring to the chilled solution of cobalt(II) 1,8,15,22-tetradiazonium phthalocyanine hydrogen sulphate. The mixture was constantly stirred for 1 hour and then heated on a water bath until the evolution of gases ceases. The resulting dark green product was separated by decantation, purified by washing alternatively with 1.0 N NaOH and 1.0 N HCl and finally with water. Then the pure cobalt(II) 1,8,15,22-tetraiodophthalocyanine was separated by centrifugation and dried at 50°C for 1 hour (Yield, 93%).

1,8,15,22-tetraiodophthalocyanines of copper(II) [3-ICuPc] (yield 92 %), nickel(II) [3-INiPc], yield (90 %) and of zinc(II) [3-IZnPc] (yield 91 %), were prepared in the similar way by using the respective metal(II) tetraaminophthalocyanine derivatives.

3. RESULTS AND DISCUSSION

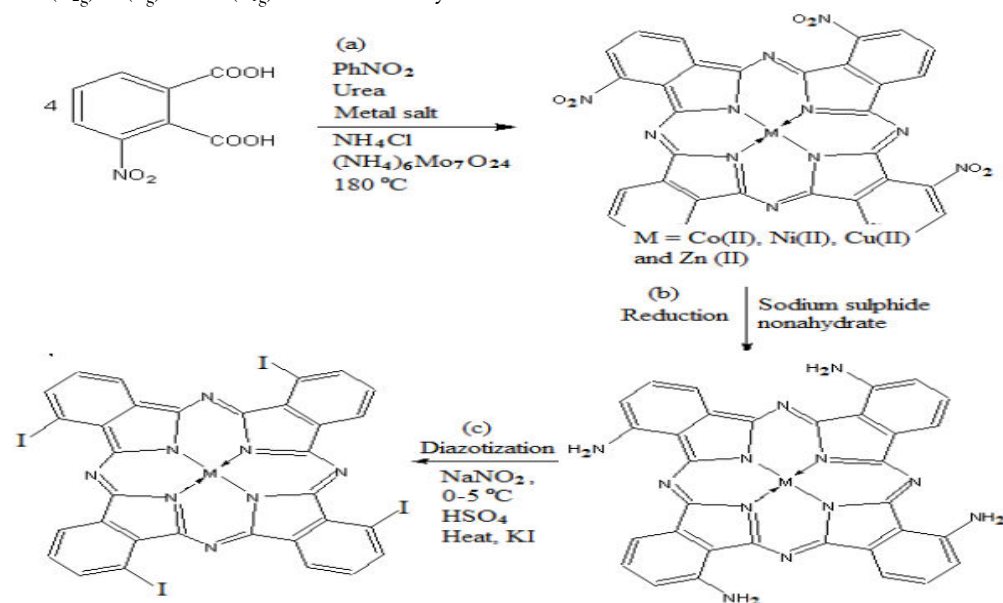
The title complexes have square planar geometry and belong to D_{4h} molecular symmetry group. Colour shades of the complexes ranges from bluish green to bluish black. The complexes are poorly soluble in water and most of the organic solvents like alcohol, carbon tetrachloride, chloroform, diethyl ether, hexane and acetone, however, they are soluble in DMF, DMSO, pyridine and concentrated sulphuric acid. Reactions employed for conversion of tetraamino derivatives in to tetraiodo complexes results in good yields (from 90% to 93%). Quantification of carbon, hydrogen, nitrogen and metals by elemental analysis are summarized in Table 1. The results obtained compares fairly well with calculated values and are consistent with the proposed structure in scheme 1.

3.1. Magnetic susceptibility

Three independent determinations have been worked out to arrive at magnetic susceptibility (χ_m) and the magnetic moments (μ_{eff}) over a range of magnetic field strength from 1.27-4.68 kG, and the data are presented in Table 1. Among the synthesized complexes, 3-ICoPc and 3-ICuPc are paramagnetic, whereas 3-INiPc and 3-IZnPc are diamagnetic. The 3-ICoPc and 3-ICuPc are

found to show higher χ_m and μ_{eff} values at lower field strengths and these values decrease as the field strength increases. The magnetic moments for the 3-ICoPc and 3-ICuPc are higher than expected for a spin only magnetic moment. Higher magnetic moments observed at lower applied field strengths could be accounted for by orbital contribution consisting 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})² [32], and (ii) magnetic anisotropy of the strong phthalocyanine π -electron current [33]. Combined phenomenon of intermolecular cooperative effects and magnetic anisotropy [2, 34] in 3-ICoPc and 3-ICuPc, results in tapering of μ_{eff} values towards higher applied magnetic field strengths.



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-tetraiodophthalocyanine

Table 1: Magnetic susceptibility and elemental analysis data of metal (II) 1,8,15,22-tetraiodophthalocyanines

Complex	Empirical formulae, (formula weight)	Field strength (kG)	Magnetic susceptibility, $\lambda_m, \times 10^{-6}$, in cgs units.	Magnetic moments, μ_{eff} (BM)	Elemental analyses, found (calculated)
3-ICoPc	$\text{C}_{32}\text{H}_{12}\text{N}_8\text{I}_4\text{Co}$ (1074.53)	1.27	3196.60	2.79	
		1.71	2772.40	2.60	C, 34.9 (35.7)
		2.58	2513.72	2.47	H, 1.0 (1.1)
		3.44	2361.91	2.40	N, 9.8 (10.4)
		4.27	2189.97	2.31	Co, 6.0 (5.4)
3-ICuPc	$\text{C}_{32}\text{H}_{12}\text{N}_8\text{I}_4\text{Cu}$ (1079.15)	1.27	2820.17	2.62	
		1.71	2717.95	2.58	C, 34.9 (35.6)
		2.58	2343.75	2.39	H, 1.0 (1.1)
		3.44	2150.55	2.29	N, 9.2 (10.4)
		4.27	2075.53	2.25	Cu, 5.8 (5.8)
3-INiPc	$\text{C}_{32}\text{H}_{12}\text{N}_8\text{I}_4\text{Ni}$ (1074.30)	1.27	2820.17	2.62	
		1.71	2717.95	2.58	C, 35.0 (35.6)
		2.58	2343.75	2.39	H, 0.9 (1.1)
		3.44	2150.55	2.29	N, 9.8 (10.4)
		4.27	2075.53	2.25	Ni, 6.0 (5.4)
3-IZnPc	$\text{C}_{32}\text{H}_{12}\text{N}_8\text{I}_4\text{Zn}$ (1080.98)	1.27	2820.17	2.62	
		1.71	2717.95	2.58	C, 35.0 (35.5)
		2.58	2343.75	2.39	H, 0.8 (1.1)
		3.44	2150.55	2.29	N, 10.1 (10.4)
		4.27	2075.53	2.25	Zn, 6.0 (6.0)

X-ray crystallographic investigations of the unsubstituted phthalocyanine complexes of Co, Ni, Cu and Zn [1-2] reveals that they are isomorphous and their molecular stacks aligned as shown in fig. 1. The molecular stacking occurs along the short b-axis and the planes of the molecules are inclined to the a-c axis at an angle of $\theta = 45^\circ$. Thus the molecular stacks are aligned in columns in such a way that the N atoms of the phthalocyanine ligand are placed between the metal atoms of the two molecules with an interplanar distance of 3.4 Å [35].

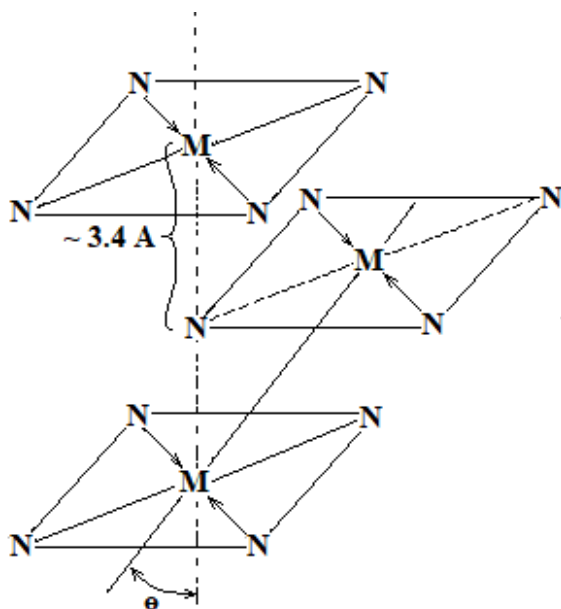


Fig. 1: Molecular stacking of metal phthalocyanines complexes. M = Cu, Co, Ni and Zn, N = azamethine atom of phthalocyanine plane

3.2. Electronic spectra

Fig. 2 shows the UV-visible absorption spectra of the title complexes recorded in DMSO, with a concentration of 1×10^{-4} M. This data is compared with that for unsubstituted phthalocyanine complexes with same metal atoms. The UV-visible absorption maxima of the B-band, due to $a_{2u} \rightarrow e_g$ transitions of the phthalocyanine ligand [2] appears at 323 nm, 320 nm, 321 nm and 336 nm respectively for unsubstituted phthalocyanine of cobalt (CoPc), nickel (NiPc), copper (CuPc) and zinc (ZnPc). The same B-band absorption for the 1,8,15,22-tetraiodosubstituted phthalocyanine complexes appearing at 331 nm (3-ICoPc), 342 nm (3-INiPc), 341 nm (3-ICuPc) and 357 nm (3-IZnPc) respectively, are found to be slightly shifted to higher wavelengths. The Q-band absorption, characteristic of

$a_{1u} \rightarrow e_g$ transitions in unsubstituted phthalocyanine ligand show their maxima at 659 nm (CoPc), 668 nm (NiPc), 665 nm (CuPc) and 666 nm (ZnPc). In the case of 1,8,15,22-tetraiodosubstituted phthalocyanine complexes Q bands also shifted by few nanometers towards higher wavelengths and appears at 672 nm (3-ICoPc), 676 nm (3-INiPc), 672 nm (3-ICuPc) and 670 nm (3-IZnPc). A small red shift of both the B band and Q bands is attributable to delocalization of the 18-electron π -cloud until peripherally substituted more electronegative iodine atoms on the phthalocyanine ligand and the consequent relative lowering of the energy of the e_g orbital. The shoulders at the lower wavelength base of the Q band are characteristic of metal phthalocyanine complexes, and are consistent with literature reports [2].

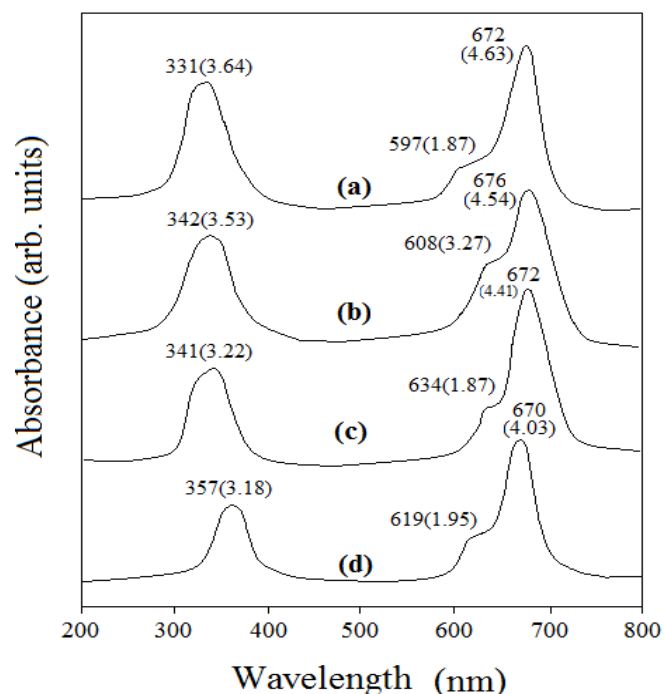


Fig. 2: Uv-visible absorption spectra of (a) Cobalt (II) 1,8,15,22-tetraiodophthalocyanine (b) Nickel (II) 1,8,15,22-tetraiodophthalocyanine, (c) Copper(II) 1,8,15,22-tetraiodophthalocyanine and (d) Zinc(II) 1,8,15,22-tetraiodophthalocyanine

3.3. IR spectra

The structural integrity of the 1,8,15,22-tetraiodosubstituted phthalocyanines of cobalt(II), nickel(II), copper(II) and zinc(II) have been checked by recording and analyzing the IR spectra, for identification of various characteristic skeletal vibrations of the phthalocyanine

ligand, metal-ligand vibrations, and peripheral iodine substitution. The characteristic vibrations are in good

agreement with those reported in literature [36]. The IR spectral data were summarized in Table 2.

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

Sl. No.	Complex	IR spectral signals in cm^{-1} .
1	3-ICoPc	373 w, 751s, 806m, 948w, 1103sb, 1240w, 1315w, 1375vs, 1532s, 1625m, 1720w, 2360w, 3086w 3450w
2	3-INiPc	370w, 749s, 802m, 935w, 1105s, 1238w, 1297w, 1536vs, 1620m, 1724w, 2170w, 2929vw, 3085w, 3448w
3	3-ICuPc	372w, 748s, 810m, 981w, 1050w, 1118s, 1241w, 1338s, 1405m, 1536vs, 1615w, 2365w, 3086w, 3449b
4	3-IZnPc	370w, 750s, 805m, 948w, 1052w, 1127s, 1259s, 1342b, 1411w, 1556vs, 1616w, 2365w, 3084w, 3440b

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

The coupled vibrations of C=N aza stretch, C=C pyrrole stretch and C=C stretch of the phthalocyanine ligand were observed as very sharp signals at 1532-1556 cm^{-1} , for all the complexes. Medium intensity signals at 1615-1625 cm^{-1} are indicative of the coupled stretching vibrations of C=C benzene and C=C pyrrole. The double bonded carbon-hydrogen stretching vibrations of aromatic molecules are expected to appear at 3030 cm^{-1} [37]. It is understood from the literature [36] that a weak signal above 3000 cm^{-1} is characteristic of C-H stretching on the unsubstituted metal phthalocyanine complexes [36]. For the title complexes however the C-H stretching vibrations are seen as weak signals in the range of 3084 - 3086 cm^{-1} . The characteristic metal - ligand vibrations for the phthalocyanines complexes are identified to be appearing between 888 cm^{-1} and 919 cm^{-1} [35]. In the present case, weak to medium intensity signals appeared between 938 cm^{-1} and 981 cm^{-1} are assigned to metal-ligand stretching vibrations. Shifting of these vibrations to higher frequency compared to those in unsubstituted phthalocyanine complexes may be attributed to a relatively higher energy requirement for the vibration as a result of higher total mass of the ligand upon iodine substitution on the peripheral positions. Medium intensity signals shown between 802 cm^{-1} and 810 cm^{-1} accounts for the C-H out-of-plane bending vibrations on the periphery of the molecules. Sharp IR absorption bands observed in a very narrow range of 748-751 cm^{-1} are due to the in-plane pyrrole stretching vibrations [36]. Recording IR spectra of the complexes in the far IR region showed weak signals at 370- 373 cm^{-1} indicating C-I stretching vibrations. All the remaining spectral signals observed and summarized in table - II are attributed to the various skeletal vibrations of phthalocyanine ligand [35, 38].

4. CONCLUSIONS

The method of synthesis and the laboratory conditions used were very simple, and results in good yield. Structural information in the core of the complexes is been revealed by magnetic susceptibility studies. Magnetic susceptibility measurements at varied magnetic field strengths revealed that the phenomena of intermolecular cooperative effects and magnetic anisotropy operates together at higher magnetic fields. Iodine substitution on peripheral position of the phthalocyanine ligand red shift the intense Q band absorption.

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Conflict of interest:

Authors declare that they have no conflict of interest.

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