

Synthesis and Characterization of a New Asymmetrical Phthalocyanine with Zn(II), Ni(II) and Co(II)

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In present studies, the synthesis and characterization of a new asymmetrically substituted metallophthalocyanine has been reported. Statistical condensation of two different dinitrile derivatives has been applied to synthesize asymmetrical metallophthalocyanine. In the first part of this study, 1,2-dichloro-4,5-dicyanobenzene and 1,2-bis(hexylthio)-4,5-dicyanobenzene was obtained as two dinitrile derivative. In the second part of the study, this products were reacted in the presence of a metal salt. The newly synthesized phthalocyanines were separated by column chromatography on silica gel and washed with common organic solvents. The structures of the synthesized compounds were characterized by the elemental analyzes, UV/Vis, FT-IR and ¹H NMR spectroscopies.

Key Words: Asymmetrical phthalocyanine, Zn(II), Ni(II), Co(II), Metallophthalocyanine.

INTRODUCTION

Coordination compounds containing macrocyclic ligands have been known and studied since the beginning of this century. However, number and variety of these compounds are limited.

The compound those were later called phthalocyanines were discovered by accident. After the investigations of Linstead and X-ray studies of Robertson the structure of phthalocyanines were published between 1933 and 1940. Phthalocyanine blues and greens are used as pigments because of their outstanding stability to light, heat, acids and alkalies and their insolubility in organic solvents and water. They are used extensively in printing inks, coating, paints and plastics. They yield outstanding, durable automobile colours and they can be used in the matching of colours in the plastics for car interiors. The phthalocyanines are also used in catalyst for control of sulfur effluents, lasers, lubricants, photodynamic reagents for cancer therapy and other medical applications, optical information storage systems, photography and xerography, high energy density batteries, high conductive molecular metals, chemical sensors, electrochromic display devices and liquid crystal colour display applications.

The special nature of the macrocyclic phthalocyanine and its metal complexes have been known for about 60 years. The unique physical and chemical properties of this class of coordination compound have been exploited from both the practical as well as the theoretical point of view. Thus, metallophthalocyanines have important uses as commercial dyes, optical and electrical materials and catalysts. They are most stable pigments and pigments should possess the following properties: opacity and good covering power, *etc.*¹⁻¹¹. In the present paper, the synthesis of a new asymmetrically substituted metallophthalocyanine with peripheral alkylthioether substituents has been described.

EXPERIMENTAL

1,2-Dichloro-4,5-dicyanobenzene (**1**), 1,2-*bis*(hexylthio)-4,5-dicyanobenzene (**2**) and 1,2-*bis*(hydroxyethylmercapto)-4,5-dicyanobenzene (**3**) were prepared by literature methods¹²⁻¹⁵. All other reagents and solvents were all of spectrophotometric grade and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego¹⁶.

IR spectra were recorded on a Mattson 1000 IR spectrophotometer using KBr pellets and electronic absorption spectra were recorded on a Unicam UV/Vis spectrophotometer and Proton NMR spectra were recorded on a Bruker 500 MHz spectrometer. Elemental analysis was carried out on an energy dispersive spectrometer and melting points were obtained with a Gallenkamp CAP MPD-350 apparatus in open capillaries.

Synthesis

2,3-Bis(hydroxyethylmercapto)-9,10,16,17,23,24-hexa(hexylthio)-phthalocyaninato Zn(II) (4a): A mixture of **3** (0.100 g, 0.357 mmol) and **2** (0.385 g, 1.071 mmol) was heated in DMF (20 mL) in the presence of Zn(CH₃COO)₂ (0.05 g) with stirring and refluxed for 12-16 h under argon. After cooling to room temperature the reaction mixture was treated with ethanol-water (1:1) to precipitate the product and then filtered. The crude product was washed with common organic solvents. The product was separated by column chromatography on silica gel with chloroform as the eluent. Yield: 0.062 g, m.p. >300 °C. This compound is soluble in CHCl₃, THF, DMF and DMSO. IR (KBr) ν_{\max} /cm⁻¹: 3436 (OH), 2854, 2925, 2954 (aliphatic CH), 1592 (C=C), 1370 (aliphatic CH₃), 741 (substituted benzene). ¹H NMR (CDCl₃): δ = 3.2 (br 2H, OH), δ = 2.9 (4H, SCH₂), δ = 7.15-7.4 (m, 8H, ArH), δ = 1.2-1.8 (m, 36H, SCH₂), δ = 0.8 (s, 18H, CH₃) ppm. Anal. (%) Calcd. for C₇₂H₉₆N₈O₂S₈Zn: C: 60.63, H: 6.74, N: 7.86, S: 17.96. Found: C: 58.99, H: 6.66, N: 7.83, S: 17.33.

2,3-Bis(hydroxyethylmercapto)-9,10,16,17,23,24-hexa(hexylthio)-phthalocyaninato Ni(II) (4b): A mixture of **3** (0.100 g, 0.357 mmol) and **2**

(0.385 g, 1.071 mmol) was heated in DMF (20 mL) in the presence of $\text{Ni}(\text{CH}_3\text{COO})_2$ (0.05 g) with stirring and refluxed for 20 h under argon. After cooling to room temperature the reaction mixture was treated with ethanol-water(1:1) to precipitate the product and then filtered. The crude product was treated was washed with common organic solvents. The product was separated by column chromatography on silica gel with chloroform as the eluent. Yield: 0.055 g, m.p. $>300^\circ\text{C}$. This compound is soluble in CHCl_3 , THF, DMF and DMSO. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3435 (OH), 2854, 2924, 2954 (aliphatic CH), 1592 (C=C), 1380 (aliphatic CH_3), 741 (substituted benzene). ^1H NMR (CDCl_3): $\delta = 3.2$ (br 2H, OH), $\delta = 2.9$ (4H, SCH_2), $\delta = 7.15$ -7.4 (m, 8H, ArH), $\delta = 1.2$ -1.8 (m, 36H, SCCH_2), $\delta = 0.8$ (s, 18H, CH_3) ppm. Anal. (%) Calcd. for $\text{C}_{72}\text{H}_{96}\text{N}_8\text{O}_2\text{S}_8\text{Ni}$: C: 60.89, H: 6.76, N: 7.89, S: 18.04. Found: C: 61.34, H: 6.99, N: 7.85, S: 17.84.

2,3-Bis(hydroxyethylmercapto)-9,10,16,17,23,24-hexa(hexylthio)-phthalocyaninato Co(II) (4c): A mixture of **3** (0.100 g, 0.357 mmol), **2** (0.385 g, 1.071 mmol) and Co(II) acetate (0.063 g, 0.357 mmol) was heated in anhydrous ethylene glycol (5 mL) with stirring and refluxed for 24 h under argon. After cooling to room temperature the reaction mixture was treated with ethanol to precipitate the product and then filtered. The crude product was treated was washed with common organic solvents. The product was separated by column chromatography on silica gel with chloroform as the eluent. The product was separated by column chromatography on silica gel with chloroform as eluent. Yield: 0.048 g, m.p. $>300^\circ\text{C}$. This compound is soluble in CHCl_3 , THF. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3445 (OH), 2854, 2923, 2954 (aliphatic CH), 1600 (C=C), 1380 (aliphatic CH_3), 751 (substituted benzene). ^1H NMR spectra could not be taken. Anal. (%) Calcd. for $\text{C}_{72}\text{H}_{96}\text{N}_8\text{O}_2\text{S}_8\text{Co}$: C: 60.89, H: 6.76, N: 7.89, S: 18.04. Found: C: 60.54, H: 6.89, N: 7.83, S: 18.54.

RESULTS AND DISCUSSION

1,2-Dichloro-4,5-dicyanobenzene (**1**) was used recently to prepare 4,5-disubstituted phthalonitrile derivatives through base catalyzed nucleophilic aromatic displacement. The same route was applied to prepare 1,2-bis(hexylthio)-4,5-dicyanobenzene (**2**) and 1,2-bis(hydroxymercaptoethanol)-4,5-dicyanobenzene (**3**) from the corresponding 2-mercaptoethanol, hexanthiol and 1,2-dichloro-4,5-dicyanobenzene. For this purpose, 1,2-dichloro-4,5-dicyanobenzene was reacted with 2-mercaptoethanol, hexanthiol in dimethylformamide and Na_2CO_3 , K_2CO_3 , respectively.

Cyclotetramerization of the phthalonitrile derivative to the metallo phthalocyanine (**4**) was accomplished in DMF or ethylene glycol in the presence of a metal salt at reflux temperature (Fig. 1).

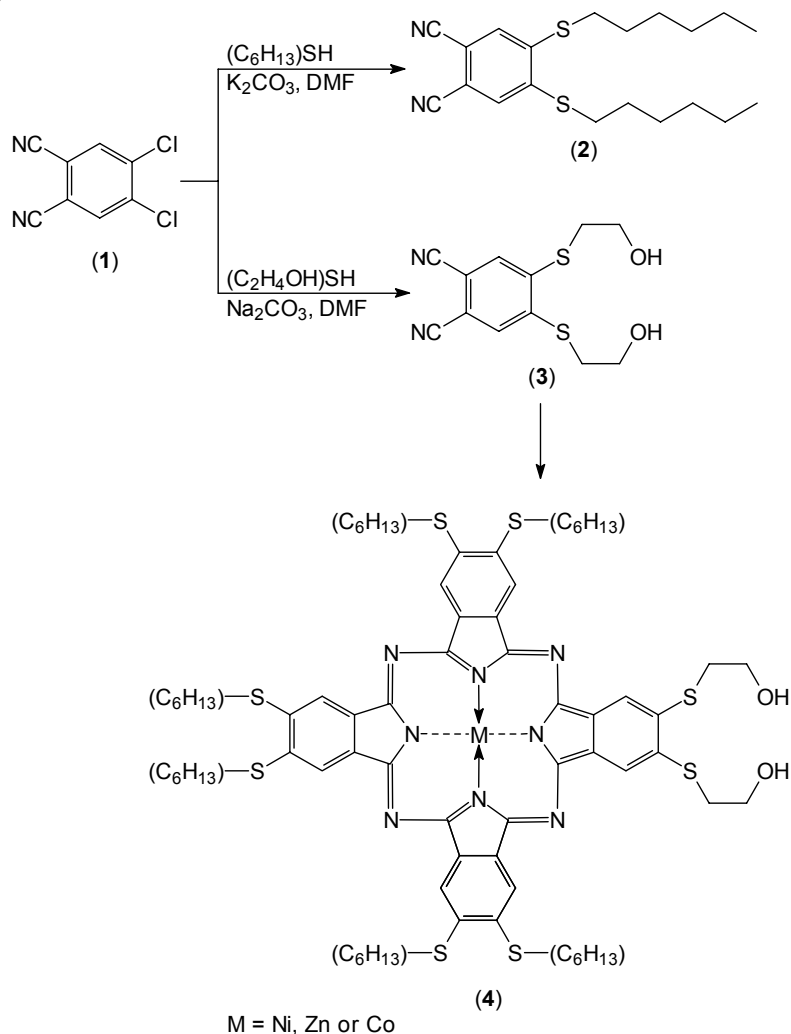


Fig. 1. Synthesis of Zn(II), Ni(II) and Co(II) phthalocyanine

Column chromatography with silica gel was employed to obtain the pure products from the reaction mixture. The intense green product is soluble in a number of solvents such as CHCl_3 , THF, DMF, DMSO. But, CoPc is not soluble in DMF and DMSO.

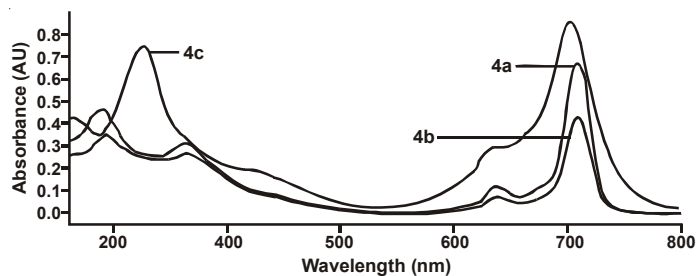
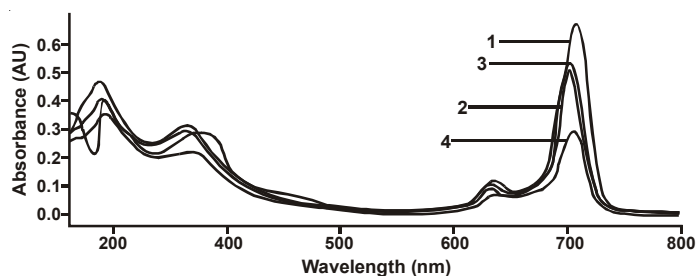
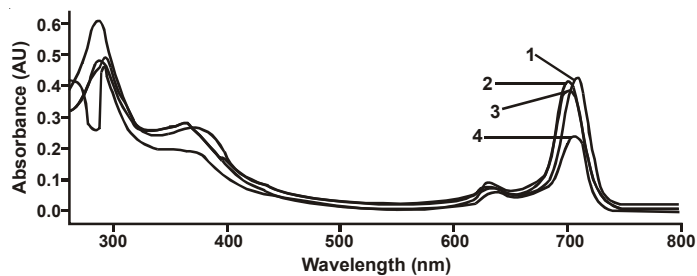
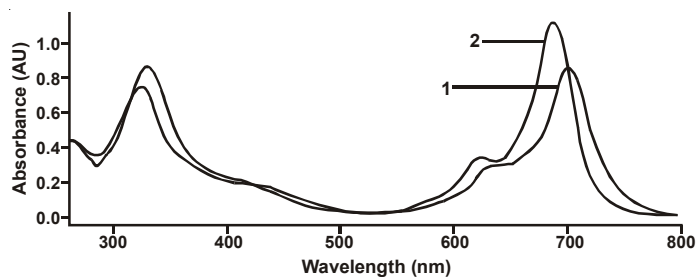
In the IR spectra of **4**, there is no band at 2233 cm^{-1} corresponding to the $-\text{C}\equiv\text{N}$ groups, disappear with the conversion into the phthalocyanine, after reacting from **2** and **3** and there is a broad absorption band at 3435 , 3436 , 3445 cm^{-1} corresponding to the Ar-OH. There was a band at 3250 cm^{-1} corresponding to the Ar-OH in infrared spectrum of **3**, also. The IR spectra of **4** clearly indicates the presence of OH groups by the intense stretching bands.

In ^1H NMR spectra in CDCl_3 of **4a** and **4b**, the OH protons are observed as broad signals at 3.2 ppm and the signal disappeared by deuterium exchange. This results is in agreement with the proposed structure.

The UV/Vis spectral data given in Table-1 are also in accord with the expected structure. The phthalocyanines show typical electronic spectra with two strong absorption region, one of them in the UV region at about 300-350 nm (B band) and the other in the visible portion at 600-700 nm (Q band). The characteristic Q band transition of metallophthalocyanines with D_{4h} symmetry is observed as a single band of high intensity in the visible region. Compound solutions were prepared in 8.6×10^{-6} M of CHCl_3 , THF, DMF and DMSO. UV/Vis spectra of compound solutions were recorded against its solvents and then they were compared to each other. In order to test the effect of the metal ion on the changes in the B band and Q band, the spectra of all phthalocyanines **4** in CHCl_3 and then in order to test the effect of any solvent polarity on the changes in the this bands. The spectra of all phthalocyanines **4** in various solvents have been carefully investigated (Figs. 2-5). When the electronic spectra of the phthalocyanines **4a**, **4b** and **4c** in CHCl_3 investigated some peculiarities were observed. Similar spectra have been obtained in the cases of both **4a** and **4b**, with only small changes in shifts. But, the CoPc showed a completely novel behaviour at same concentration. In this concentration, results in the aggregation of phthalocyanine molecules, which is accompanied by a blue shift of the Q band with some increase in intensity as well as in the molar absorption coefficient ($\epsilon = \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$). In addition, it gave only a single band in the B band region at 325 nm. Any increase in solvent polarity results was observed by a blue shift of the Q band and with some increase in intensity. Comparison of the spectra showed that the assay results obtained by spectra were in good agreement (Figs. 2 and 5). As shown in Figs. 3 and 4, increasing the polarity of the solvent showed a blue shift of

TABLE-1
UV/VIS SPECTROSCOPY DATA FOR PHTHALOCYANINES

Compd.	Solvent	λ/nm ($10^{-5} \epsilon/\text{L mol}_1 \text{cm}^{-1}$)		
4a	1	708 (0.778)	637 (0.142)	362 (0.365)
	2	701 (0.582)	631 (0.112)	362 (0.345)
	3	703 (0.620)	632 (0.124)	374 (0.331)
	4	707 (0.337)	637 (0.744)	362 (0.256)
4b	1	709 (0.498)	637 (0.849)	362 (0.310)
	2	701 (0.484)	631 (0.860)	362 (0.330)
	3	703 (0.456)	632 (0.103)	370 (0.313)
	4	707 (0.279)	636 (0.663)	362 (0.230)
4c	1	702 (1.001)	638 (0.345)	326 (0.866)
	2	690 (1.300)	624 (0.401)	331 (1.003)

Fig. 2. Electronic spectra of complex **4a**, **4b** and **4c** in CHCl_3 Fig. 3. Electronic spectra of complex **4a** in 1: CHCl_3 , 2: THF, 3: DMF and 4: DMSOFig. 4. Electronic spectra of complex **4b** in 1: CHCl_3 , 2: THF, 3: DMF and 4: DMSOFig. 5. Electronic spectra of complex **4c** in 1: CHCl_3 and 2: THF

the Q band with some decrease in intensity at almost same wavelength. Similar results were observed when the assay results obtained by both spectra were compared. The assay results obtained for each solvent are summarized in Table-1 as 1: CHCl₃, 2: THF, 3: DMF and 4: DMSO. It has also been concluded that aggregation is enhanced by solvent polarity and the presence of aliphatic side chains with thioether groups. This results might be interpreted in terms of the formation of some intermolecular interactions between the central metal ion of one molecule with the thioether groups of another¹⁴. In conclusion, the donor capabilities of the thio groups should be taken into account together with the high solubility and the effects of binding transition metal ions. Elemental analyses, IR, UV/Vis, ¹H NMR spectra confirm the proposed structure of the compound.

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