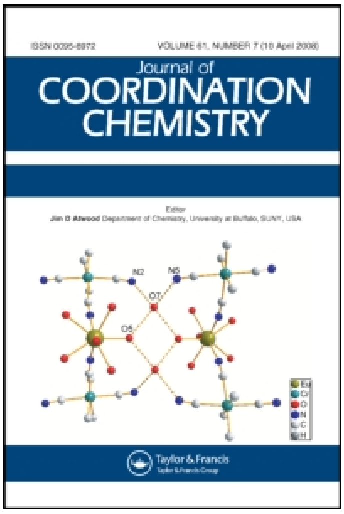

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The synthesis and characterization of new phthalocyanines containing hexaazadithia macrobicyclic moieties

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The new metal-free and metallo phthalocyanines (**4**) and (**5**) bearing four tetrasubstituted hexaazadithia macrobicycles on peripheral positions, have been synthesized. Phthalonitrile (**3**) has been synthesized from the reaction of (1,3,6,9,11,14 hexaazatricyclo [12.2.1.1^{6,9}]) (**1**) and 1,2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene (**2**). The new compounds were characterized by elemental analysis, and IR, ^{1}H, ^{13}C-NMR, UV-Visible and mass spectral data.

Keywords: Macrobicyclic; Phthalocyanine; Template effect; Metallophthalocyanine; Cryptand

1. Introduction

Phthalocyanines (Pcs), both metallo and non-metallo planar aromatic organic compounds, have been known for ca 70 years, not only as colorants but also an important class of organic functional materials due to their unique properties. They have the following fundamental characteristics: (1) being capable of diverse physical and chemical properties via changes in the identity of substituents attached to ring system; (2) having intense color and thus efficient energy absorption; (3) being capable of adding or subtracting many electrons without changing molecular structure and stability; and (4) permitting the facile design of special characteristics through symmetric and asymmetric substitution of the main phthalocyanine skeleton and through axial ligation to the central metal. These characteristics allow for applications in a wide range of fields [1]. Recently, they have been applied in such hi-tech applications as photosensitizers [2], chemical sensors [3], liquid crystals [4, 5], electro photographic photoconductors [6], photodynamic cancer therapy [7], and solar energy conversion [8].

The rich coordination chemistry of phthalocyanine complexes has encouraged researchers to ‘‘tailor’’ specific products with certain properties which are required for high technology applications. The two variables are the central metal ion and peripheral substituents: when the possibility of inserting a number of different metal ions into the

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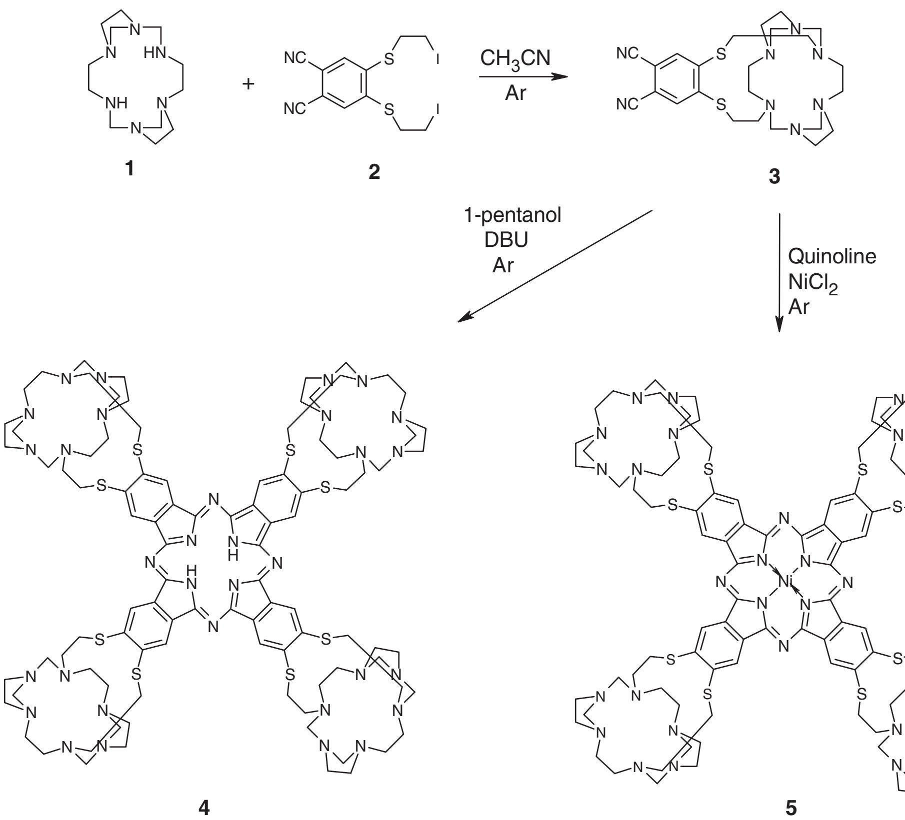
phthalocyanine core is combined with the unlimited number and type of substituents, the number of novel products is very large. The introduction of bulky substituents on peripheral positions of the macrocycle increases drastically their solubility in organic solvents. In addition to solubility, the spectral and electrochemical properties of phthalocyanines are also strongly influenced by the peripheral substituents on the macrocycles [9–12].

We have previously described the synthesis of free and metal phthalocyanines which contain four 20-membered diazatetraoxa macrocycles, each attached to a 15-crown-5 unit [13] and macrobicyclic moieties which contain tetrathiadiaza donor atoms [14]. In this study, we described the synthesis and characterization of a new class of metal-free phthalocyanines, the hexaazadithiamacrobicyclic and phthalocyanines which may allow novel functionalized materials to be prepared of importance for analytical chemistry as new kinds of transition metal extraction agents.

2. Result and discussion

The preparations of the target metal-free **4** and nickel(II) phthalocyanine **5** are shown in scheme 1. Compound **3** was synthesized by reaction of (1,3,6,9,11,14-hexaazatricyclo-[12.2.1.1.6.9])octane (**1**) [15] with 1,2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene (**2**) [14] in acetonitrile containing finely ground anhydrous Na_2CO_3 as a template agent at reflux temperature in a Schlenk system under argon. The hexaazadithia macrobicyclic compound **3** was obtained in 67.65% (scheme 1). The formation of the macrobicycle **3** is evident by the characteristic changes in the IR vibrations. The occurrence of single bands at 3078 and 2231 cm^{-1} is attributable to the presence of Ar–H and C≡N vibrations, respectively, and is diagnostic of macrobicyclization. The disappearance of bands characteristic of N–H groups in precursor compound **1** also confirms the formation of **3**. In the ^{1}H-NMR spectra of this compound, the chemical shifts of NH protons in **1** disappear after the macrobicyclization reaction. The other resonances in the ^{1}H-NMR and ^{13}C-NMR spectra, concerning SCH_2, NCH_2 and aromatic protons and carbons, are very similar to those of the precursor compounds **1** and **2**. The mass spectra of this compound show the base peak at $m/z = 499$ corresponding to the proposed formulation $[M+1]^+$.

Condensation of four molecules of the dinitrile derivative of macrobicyclic **(3)** into the metal-free phthalocyanine (**4**) was carried out in a Schlenk tube in a high-boiling solvent (1-pentanol) in the presence of a few drops of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a strong base at reflux for 24 h under argon. The target compound **4** was obtained in 57.14% yield as a dark green solid. When comparing the IR spectrum of **3**, with **4**, the proposed structure is confirmed by disappearance of the C≡N vibration at 2231 cm^{-1} and the appearance of medium new absorptions at 3434 and 1644 cm^{-1} attributable to N–H and C=N groups, respectively [17, 18]. The inner core N–H protons of the metal-free phthalocyanine were also identified in the ^{1}H-NMR spectrum. At high concentration strong shielding of the cavity protons in the phthalocyanine core of this compound was indicated by a broad resonance at $\delta = -4.38$ ppm [14, 19] which could be attributed to the NH resonance and identified easily by deuterium exchange. In the ^{1}H-NMR spectrum of **4**, signals related to aromatic and aliphatic protons of the macrobicycles and phthalocyanine skeleton



Scheme 1. Preparation of metal-free (4) and nickel(II) phthalocyanine (5) compounds.

provided characterization of the proposed structure. This spectrum closely resembles that of precursor **3** as expected. A distinct difference encountered in the ^{1}H-NMR of **3** and **4** when compared with previously obtained polymacrocycle substituted derivates, are the sharp signals, which indicate a lower tendency to aggregate even at concentration used for proton NMR measurements [20]. The proton-decoupled ^{13}C-NMR spectrum of **4** gave absorbances characteristic of the structure, closely resembling that of the dicyano derivative **3**; the differences are the signals of carbon atoms of the cyano groups at $\delta = 114.86$ ppm and the phthalocyanine ring (C=N) group at $\delta = 150.21$ ppm. The mass spectrum of metal-free phthalocyanine was obtained by the LS-MS MS technique and the molecular ion peak at $m/z = 1994$ $[M+1]^+$ was observed.

The nickel(II) phthalocyanine (**5**) was obtained from reaction of **4** with anhydrous nickel(II) chloride in high boiling solvents. The high boiling solvent of choice was quinoline for Ni(II) [21]. The stretching vibration at 3434 cm^{-1} belonging to N–H group disappears after formation of **5**. The ^{1}H-NMR spectrum of **5** in chloroform shows a singlet at $\delta = 7.60$ ppm for aromatic protons. Aliphatic protons which belong to Ar–S–CH_2, and NCH_2 appear at $\delta = 3.58$ and 3.42 ppm respectively, in accord with metal-free phthalocyanine (**4**). The proton decoupled ^{13}C-NMR spectrum of **5** showed a singlet at $\delta = 151.24$ ppm for the carbons which belong to C=N groups of the

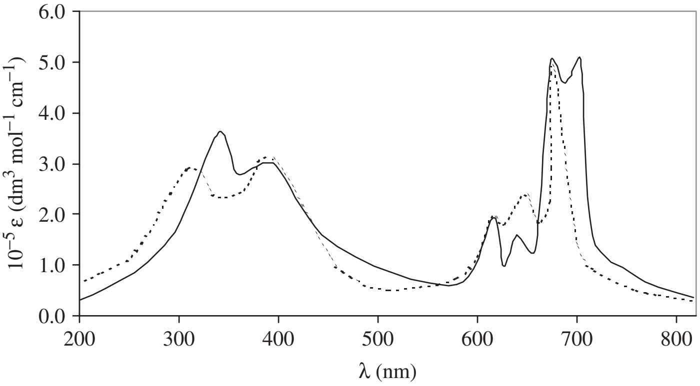


Figure 1. UV-Vis spectra of compounds **4** and **5**.

phthalocyanine ring. The NMR characteristics of **5** were quite similar to **4**. The Ni(II) phthalocyanine gave a reproducible mass spectrum with the $M+1$ and $M+Na+1$ peaks at $m/z=2052$ and 2075, respectively instead of the molecular ion in **5**.

The best indications for phthalocyanine systems are given by their UV-Vis spectra in solution (figure 1). The electronic spectra of phthalocyanines (**4**) and (**5**) show the same typical B and Q bands of symmetrical macrobicyclic substituted *Pc*. The energy level location corresponding to those bands is illustrated in figure 1. In the UV-Vis spectrum of metal-free phthalocyanine in chloroform, the characteristic split Q band was observed with absorptions at 704 and 674 nm. These intense Q bands around 700 nm indicate monomers with D_{2h} symmetry [22]. The lower absorption than the typical split Q band at 616 nm is due to dimeric association and up to 615 nm for higher aggregates [23]. Such split Q band absorptions are due to the $\pi \Rightarrow \pi^*$ transition from the HOMO to the LUMO of the phthalocyanine ring related to a fully conjugated 18π electron system. The presence of strong absorption bands in **5** at λ_{max} 400 and 300 nm shows superimposed bands of the phthalocyanine due to the existence of Soret bands of *Pc* which have been ascribed to deeper $\pi \Rightarrow \pi^*$ LUMO transitions [24]. However, in **5** the average Q-bands are slightly shifted to the blue with respect to the parent metal-free compound [25]. The position of the Q band of metallophthalocyanine (**5**) changed due to the central Ni(II) centered at around 674 nm without splitting. The single Q band in a metallo derivative and split in its metal-free counterpart is characteristic [26]. Observed peaks as mentioned above indicate that the symmetry of the molecule has been changed, and is typical of metal complexes of substituted and unsubstituted *Pc* with D_{4h} symmetry [27].

3. Experimental

The IR spectra were recorded on a Perkin-Elmer 1600 FTIR Spectrophotometer, using KBr pellets or NaCl discs. ^1H and ^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro

LC/ULTIMA LC-MS MS spectrometer. Elemental analysis and metal contents of these compounds were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. Electronic spectra were recorded on a Unicam UV-Vis spectrophotometer. Melting points were measured on an Electrothermal apparatus and were uncorrected. (1,3,6,9,11,14 Hexaazatricyclo [12.2.1.1^{6,9}]) octadecane (**1**) [15] and 1,2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene (**2**) [14] were synthesized according to reported procedures. Commercially available solvents were dried and purified by conventional procedure [28].

3.1. *5,6-(2′-3′-Dicyanobenzo)-4,7-dioxa-1,10,12,15,19,22-hexaazatetracyclo[8·7·7^{12,15}·1^{19,22}]hexacosane (3)*

A two necked round-bottom flask containing anhydrous DMF (20 mL) and dry acetonitrile (50 mL) was fitted with a condenser and evacuated, refilled two times with argon. Under argon the flask was charged with (1,3,6,9,11,14 hexaazatricyclo [12.2.1.1^{6,9}]) octadecane (**1**) [15] (2 g, 7.916 mmol) 1,2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene (**2**) [14] (0.69 g, 1.38 mmol), anhydrous Na_2CO_3 (0.435 g, 4.14 mmol) and dry NaI (0.69 g, 1.38 mmol). The reaction mixture was heated and stirred at 85°C for 158 h. The reaction mixture was monitored by thin layer chromatography [diethyl ether : acetone (50 : 1)]. After evaporation of the reaction mixture to dryness, the oily residue was dissolved with diethyl ether (50 mL) at room temperature then insoluble parts of the mixture were removed by filtration and the filtrate was evaporated under vacuum to dryness to give an oily substance, which was dissolved in methanol (3 mL) and purified by silica gel column chromatography. The elution was carried out successively with *n*-hexane at the beginning then diethyl ether–acetone (50 : 1). The eluates were combined and concentrated to dryness. The oily pale yellow residue was reprecipitated by adding diethyl ether and dried *in vacuo*. Yield 0.46 g (67.65%).^{1}H-NMR ($CDCl_3$): δ 7.68 (s, 8H, Ar–H), 3.69 (t, 16H, SCH_2), 3.26 (t, 16H, NCH_2), 3.15 (s, 32H, NCH_2), 3.05 (t, 32H, NCH_2 CH_2–N), 2.90 (t, 32H, CH_2–CH_2). ^{13}C-NMR ($CDCI_3$): δ 135.85 (ArCH), 128.42 (ArCH), 119.28 (ArCH), 114.86 (C≡N), 46.52 (NCH_2), 35.18 (SCH_2). IR (KBr, cm^{-1}): 3078 (Ar–H), 2925–2854 (C–H), 2231 (C≡N), 1582–1445 (Ar-skelt. vib.). Anal. Calcd for $C_{24}H_{34}N_8S_2$ (%): C, 57.80; H, 6.87; N, 22.47. Found: C, 57.83; H, 6.82; N, 22.49. Electron impact (EI) mass spectrum: $m/z = 499\ [M+1]^+$.

3.2. *Metal-free phthalocyanine (4)*

Compound **3** (0.42 g, 0.901 mmol), DBU (0.13 mL) and 1-pentanol (2 mL) were placed in a well-stoppered Schlenk tube under argon. The mixture was gently heated to 165°C and allowed to stand at this temperature for 24 h. During this period, the colour of the solution changed from yellow to green. At the end of this period, the reaction mixture was cooled to room temperature, filtered and the dark green precipitate refluxed two times with ethanol to remove unreacted organic materials. Finally, pure dark green product **4** was obtained by washing with ethanol and diethyl ether. Yield 0.24 g (57.14%); m.p. 192–194°C. ^{1}H-NMR ($CDCl_3$): δ 7.65 (s, 8H, Ar-H), 4.20 (t, 16H, OCH_2), 3.85 (t, 16H, NCH_2), 3.41 (s, 32H, NCH_2), 3.17 (t, 32H, NCH_2CH_2–N), 2.95 (t, 32H, CH_2–CH_2), −4.38 (s, 2H, NH). ^{13}C–NMR ($CDCI_3$): δ 150.21 (C=N), 130.35 (ArH), 128.09 (ArCH), 112.01 (ArC), 47.82 (NCH_2), 34.53 (SCH_2). IR (KBr, cm^{-1}): 3434 (N–H), 3093 (Ar–H), 2925–2855 (Aliph–H), 1644 (C=N), 1585–1446 (Aliph skel), 1262–1205 (Ar–S–CH_2). Anal. Calcd for $C_{96}H_{138}N_{32}S_8$ (%): C, 57.74; H, 6.97; N, 22.45. Found: C, 57.77; H, 6.82; N, 22.47. UV-Vis ($CHCl_3$): λ (nm) [($10^{-5}\,\varepsilon\,dm^3\,mol^{-1}cm^{-1}$)]: 704 (5.05), 674 (5.02), 640 (1.60), 616 (1.93), 398 (2.97), 340 (3.60). (FAB) mass spectrum: $m/z = 1994$ $[M+1]^+$.

3.3. *Ni(II) phthalocyanine (5)*

A well-stoppered Schlenk tube was charged with metal-free phthalocyanine (**4**) (0.2 g, 0.1025 mmol), anhydrous $NiCI_2$ (0.07 g, 0.543 mmol) and dry quinoline under argon and heated at 210°C for 24 h. After cooling to room temperature, the dark green product was filtered off, washed with hot ethanol and diethyl ether and dried *in vacuo*. Yield 0.08 g (38.89%); m.p. > 300°C. ^{1}H-NMR ($CDCl_3$): δ 7.60 (s, 8H, Ar–H), 3.58 (t, 48H, SCH_2), 3.42 (t, 32, NCH_2), 3.16 (t, 32H, NCH_2CH_2–N), 2.95 (t, 32H, CH_2–CH_2). ^{13}C-NMR ($CDCI_3$): δ 151.24 (C=N), 132.35 (ArCH), 127.03 (ArCH), 111.00 (ArCH), 46.82 (NCH_2), 33.38 (SCH_2). IR (KBr, cm^{-1}): 3085 (Ar–H), 2926–2858 (Aliph-H), 1625 (C=N), 1585–1446 (Aliph. Skelt.), 1260–1198 (Ar–S–CH_2). Anal. Calcd for $C_{96}H_{138}N_{32}NiS_8$ (%): C, 56.10; H, 6.77; N, 21.81; Ni, 2.86. Found: C, 56.16; H, 6.63; N, 21.84; Ni, 2.88. UV-Vis ($CHCl_3$): λ (nm) [($10^{-5}\,\varepsilon\,dm^3\,mol^{-1}cm^{-1}$)]: 674 (4.93), 648 (2.40), 613 (1.93), 395 (3.09), 309 (2.91). (FAB) mass spectrum: $m/z = 2051$ $[M+1]^+$.

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