Available online at www.sciencedirect.com

Dyes and Pigments 74 (2007) 692–698

www.elsevier.com/locate/dyepig

Synthesis and characterization of new metal-free and nickel(II) phthalocyanines containing tetraazatrioxa macrotricyclic moieties

Yaşar Gök, Halit Kantekin*, Meltem Betül Kılıçaslan, Hakan Alp

Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey

Received 24 April 2006; accepted 4 May 2006
Available online 21 June 2006

Abstract

Novel metal-free and nickel(II) phthalocyanines bearing four tetraazatrioxa macrotricycles on peripheral positions were synthesized. Metal-free phthalocyanine was prepared by the reaction of 9,10-(2′,3′-dicyano)-8,11,21-trioxa-1,5,14,18-tetraazatrioxa [12,9,2.2^{5,18}]heptacosane (**4**) with dry 2-(*N*,*N*-dimethylamino)ethanol under reflux. The nickel(II) phthalocyanine was synthesized by the anhydrous $NiCl_2$ and compound (**4**) in dry ethylene glycol under reflux. We also used compound (**4**) and metal-free phthalocyanine (**5**) in solvent extraction for some transition metal ions. The new symmetrical compounds were characterized by elemental analysis, ^1H, ^{13}C NMR, IR, UV–vis and mass spectral data.

Keywords: Macrotricycles; Phthalocyanine; Metallophthalocyanine; Cryptand

1. Introduction

Since their accidental synthesis in 1928, phthalocyanines (Pcs) have enjoyed considerable industrial importance for use in dyes, paints, colour for metal surfaces, fabrics and plastics. Meanwhile, chemical and physical studies of metal Pcs (MPcs) and their derivatives have been the subject of much research. The functions of metal Pcs and their derivatives are based on redox or electron transfer reactions; the electrochemical properties of MPcs have been intensively studied [1–4]. Various investigations have concerned the potential utility of MPcs as optical storage vehicles, electrocatalysts, solar cell functional materials, nonlinear optical limiting devices and photodynamic therapy agents [5–9].

A disadvantage of both metal-free and metallophthalocyanines is their limited solubility in common organic solvents. While it is possible to attach a wide variety of substituents at the periphery of the phthalocyanine, these can alter the electronic structure of the system. Substituents provide the prime means of solubilizing the ring system in either aqueous or non-aqueous media and offer a useful way of tuning the absorption wavelength of colourant in the visible region band [10–12].

As the complexes formed by cryptands with metal ions are more stable than similar complexes of crown ethers, cryptands can be more attractive ligands as selective extraction reagents. Investigations on the transport of metal ions with known macrobicyclic ligands such as [2.2.2]-cryptand and [2.2.1]-cryptand have been published [13,14]. Since the first spherical macrotricyclic polyethers and cylindrical macrotricyclic ligands were reported by Lehn [15] many macropolycyclic polyethers with unusual shapes have been prepared and their properties have been studied [16]. The compounds are easily prepared by linking two macrocycles together through two bridges, thus leading to the formation of three cavities: two latera (those of the macrocyclic subunits) and a central one [17]. To enhance the coordinating properties of these macrocycles, different modifications have been made such as the ring size, the nature of substituents, and the type of donor atoms [18].

---

* Corresponding author. Fax: +90 462 325 3196.
E-mail address: halit@ktu.edu.tr (H. Kantekin).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.05.001

We have previously described the synthesis of metal-free and metal phthalocyanines which contain four, 20-membered diazatetraoxa macrocycles each attached to a 15-crown-5 unit [19] and macrobicyclic moieties [20]. In this study, the synthesis and characterization and structural investigation of metal-free and Ni(II) phthalocyanines, which contain macrotricyclic moieties N_4O_3 are described, suggesting that the suitable combination of tetraazatrioxa macrotricycles and phthalocyanine may allow new functionalized materials to be prepared, which are of importance in analytical chemistry as novel alkali, alkaline-earth and transition metal extraction agents. In this paper we describe a general procedure for the preparation and characterization of new compounds which contain macrotricyclic N_4O_3 mixed donors. We also used compounds (**4**) and (**5**) in solvent extraction for some transition metal ions.

2. Experimental

The IR spectra were recorded on a Perkin Elmer 1600 FTIR Spectrophotometer, using KBr pellets or NaCl disc. ^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. The spectrophotometric measurements for compounds (**4**) and (**5**) were carried out with Unicam UV2 UV–vis spectrophotometer. In solvent extraction experiments Grant SS 30 type shaker with thermostat was used. Chloroform, picric acid, $Co(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Cd(NO_3)_2\cdot 4H_2O$, $Mn(NO_3)_2\cdot 4H_2O$, $Pb(NO_3)_2\cdot H_2O$ and $AgNO_3$ were the analytical grade reagents and were purchased from Merck. Demineralized water was used in extraction experiments. Melting points were measured on an electrothermal apparatus and were uncorrected. 1,2-Bis(2-iodoethoxy)-4,5-dibromobenzene (**1**) [21] and 17-oxa-1,4,8,11-tetraazabicyclo[6.6.5]nonadecane (**2**) [22] were synthesized according to reported procedures. Commercially available solvents were dried and purified by conventional procedure [23].

2.1. 9,10-(2′,3′-Dibromobenzo)-8,11,21-trioxa-1,5,14,18-tetraazatricyclo[12.9.2.2^{5,18}]heptacosane (3)

To a solution of 17-oxa-1,4,8,11-tetraazabicyclo[6.6.5] nonadecane (**2**) (1.80 g, 6.66 mmol) in dry acetonitrile (50 ml) under an argon atmosphere in a vacuum line, 1,2-bis(iodoethoxy)-4,5-dibromobenzene (**1**) (3.84 g, 6.66 mmol) and dry acetonitrile (80 ml) were added. Finely ground anhydrous Na_2CO_3 (1.755 g, 16.65 mmol) and dry NaI (0.246 g, 1.65 mmol) were added to this solution, fitted with a condenser, evacuated and refilled three times with argon. The reaction mixture was refluxed for 6 days under an argon atmosphere. The reaction was monitored by TLC (chloroform:methanol) (97:3). The ensuing product was allowed to cool to room temperature and filtered and then the solvent was evaporated to dryness under reduced pressure. The residue was purified using silica gel chromotography with (v/v) (ethanol:petroleum ether) (4:1) as eluent to give compound (**3**) as a pale yellow viscous oil. This compound was soluble in chloroform, dichloromethane, and ethanol. Yield 1.71 g (43.51%); Calcd. for $C_{24}H_{38}N_4O_3Br_2$: C, 48.73; H, 6.42; N, 9.47%. Found: C, 48.55; H, 6.65; N, 9.25%. IR (NaCl disc) ν_{max} (cm^{-1}): 3085 (Ar–H), 2925–2858 (aliph. –CH), 1581 (C=C), 1249 (Ar–O–C), 1110 (C–O–C), 651 (C–Br); ^1H NMR ($CDCl_3$) δ: 7.30 (s, 2H, ArH), 4.32 (s, 4H, Ar–O–CH_2), 3.75 (t, 4H, OCH_2), 3.52 (m, 28H, N–CH_2) ppm. ^{13}C NMR ($CDCl_3$) δ: 147.71 (Ar–O–CH_2), 127.01(Ar–C–H), 125.32 (Ar–C–Br), 70.18–69.72 (OCH_2), 46.10 (NCH_2). (EI) MS $m/z = 591.2$ $[M]^+$.

2.2. 9,10-(2′,3′-Dicyano)-8,11,21-trioxa-1,5,14,18-tetraazatricyclo[12,9,2.2^{5,18}]heptacosane (4)

A mixture of compound (**3**) (1.64 g, 2.74 mmol), CuCN (1.135 g, 8.22 mmol), and dry pyridine (0.13 ml) in dry DMF (27.4 ml) was refluxed under an argon atmosphere in a vacuum line for 40 h. The mixture was cooled to room temperature and then poured into aqueous ammonia (20 ml). After stirring for 2 h at room temperature, the mixture was extracted with chloroform (3 × 30 ml). The combined organic layers were washed with water, dried over anhydrous $MgSO_4$ and the solution then evaporated to dryness under reduced pressure. The product was obtained as a pale brown oil. This compound was soluble in chloroform, dichloromethane, and ethanol. Yield 0.46 g (34.33%); Calcd. for $C_{26}H_{38}N_6O_3$: C, 64.73; H, 7.88; N, 17.42%. Found: C, 64.94; H, 7.66; N, 17.66%. IR (NaCl disc) ν_{max} (cm^{-1}): 3090 (Ar–H), 2924 (aliph. –CH), 2225 (C≡N), 1512–1455 (C=C), 1269 (Ar–O–C), 1127 (C–O–C). ^1H NMR ($CDCl_3$) δ: 7.85 (s, 2H, ArH), 4.40 (m, 4H, $ArOCH_2$), 3.86 (t, 4H, OCH_2), 3.66 (m, 28H, NCH_2). ^{13}C NMR ($CDCl_3$) δ: 148.10 (Ar–O–CH_2), 128.18 (Ar–CH), 119.64 (Ar–C), 114.91 (C≡N), 71.34–70.87 (O–CH_2), 46.40 (NCH_2). (EI) MS $m/z = 483.4$ $[M+1]^+$, 506.5 $[M+Na+1]^+$.

2.3. Metal-free phthalocyanine (5)

A solution of compound (**4**) (0.30 g, 0.63 mmol) in dry 2-(*N*,*N*-dimethylamino)ethanol (2.5 ml) was refluxed and stirred under an argon atmosphere in a vacuum line for 24 h. After cooling to room temperature, the solvent of the reaction mixture was evaporated to dryness under reduced pressure. Ethanol (5 ml) was added, with stirring, to the green mixture, which was then filtered and washed with water, cold ethanol and diethyl ether. The filtrate was evaporated to dryness under reduced pressure. The green oil product was dissolved in chloroform (5 ml), and purified using silica gel chromatography with ethanol:chloroform (1:4) as the eluent to give compound (**5**) as a dark green solid. This compound is soluble in chloroform, dichloromethane, ethanol, and DMF. Yield 0.09 g (30%); mp 243–245 °C. Calcd. for $C_{104}H_{154}N_{24}O_{12}$: C, 64.66; H, 7.97; N, 17.40%. Found: C, 64.39; H, 7.82; N, 17.54%. IR (KBr pellets) ν_{max} (cm^{-1}): 3271 (N–H), 3092 (ArH), 2922–2852 (aliph. C–H), 1620 (C=N), 1595–1499 (C=C), 1215 ($ArOCH_2$), 1123 (OCH_2). ^1H NMR ($CDCl_3$) δ: 7.60 (s, 8H, ArH), 4.28 (m, 16H, $ArOCH_2$), 3.64 (m, 16H, OCH_2), 3.41 (m, 112H, NCH_2) −4.11 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ: 152.39 (C=N), 147.31 ($ArOCH_2$), 127.03 (ArCH), 111.00 (ArC), 70.20–69.31 (OCH_2), 45.84 (NCH_2). UV–vis ($CHCl_3$) λ_{max} (nm) [(10^{-5} ε (mol^{-1} cm^{-1}))]: 680 (3.98), 668 (3.95), 620 (3.77), 410 (4.08), 308 (3.11). (FAB) MS $m/z = 1931.3$ $[M+1]^+$, 1954.3 $[M+Na+1]^+$.

2.4. Nickel(II) phthalocyanine (6)

A mixture of compound (**4**) (0.30 g, 0.624 mmol), anhydrous $NiCl_2$ (0.051 g, 0.384 mmol) and dry ethylene glycol (3 ml) was heated and stirred at 200 °C for 12 h in a sealed glass tube under argon atmosphere. After cooled to room temperature, the reaction was treated with methanol (10 ml). The reaction mixture was stirred 2 h at room temperature and solvent was evaporated to dryness under reduced pressure. The greenish oil was dissolved in chloroform (10 ml) and two layers were obtained. The chloroform layer was purified by column chromatography with silica gel (chloroform as the eluent). This product is soluble in chloroform, dichloromethane, DMF, THF, and pyridine. Yield 0.15 g (48.39%); mp > 300 °C. Calcd. for $C_{104}H_{152}N_{24}O_{12}Ni$: C, 62.83; H, 7.65; N, 16.91; Ni, 2.97%. Found: C, 62.93; H, 7.52; N 16.82; Ni, 2.65%. IR (KBr pellets) ν_{max} (cm^{-1}): 3087 (Ar–H), 2924–2854 (aliph. C–H), 1632 (C=N), 1575–1462 (C=C), 1307 (Ar–OCH_2), 1138 (OCH_2). ^1H NMR ($CDCl_3$) δ: 7.55 (m, 8H, ArH), 4.31 (m, 16H, $ArOCH_2$), 3.73 (m, 16H, OCH_2), 3.51 (m, 112H, NCH_2). ^{13}C NMR ($CDCl_3$) δ: 153.15 (C=N), 147.96 ($ArOCH_2$), 128.12 (ArCH), 112.19 (ArC), 70.20-69.13 (OCH_2), 45.32 (NCH_2). UV–vis ($CHCl_3$): λ_{max} (nm) [(10^{-5} ε (mol^{-1} cm^{-1}))]: 670 (3.21), 613 (3.14), 336 (4.02), 303 (3.33). MS $m/z = 1987.4$ $[M+1]^+$, 2010.2 $[M+Na+1]^+$.

2.5. Solvent extraction

Extraction was performed according to the published procedure [24]. Transition metal picrates were prepared by the stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 1.25×10^{-5} M aqueous picric acid solution and shaking at 25 °C for 1 h.

An organic solution (10 ml) of ligand (1.25×10^{-4} M) and an aqueous solution (10 ml) containing metal picrate (1.25×10^{-5} M) were placed in stoppered flask, and shaken for 2 h at 25 ± 0.1 °C. The resulting mixtures were then allowed to stand for at least 2 h at that temperature in order to achieve complete phase separation. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of the ligand. The extractability was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated using Eq. (1).

$$E(\%) = [(A_0 - A)/A_0] \times 100 \qquad (1)$$

where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction.

The dependence of the distribution ratio D of the cation between the aqueous phase and the organic phase upon the ligand concentration was examined. The range of the ligand was from 2.5×10^{-6} to 1.25×10^{-4} M.

The general extraction equilibrium is assumed to be given by Eq. (2).

$$M^{n+}_{aq} + n\mathrm{Pic}^-_{aq} + m\mathrm{L}_{org} \rightleftarrows \left[\mathrm{M(Pic)}_n(\mathrm{L})_m\right]_{org} \qquad (2)$$

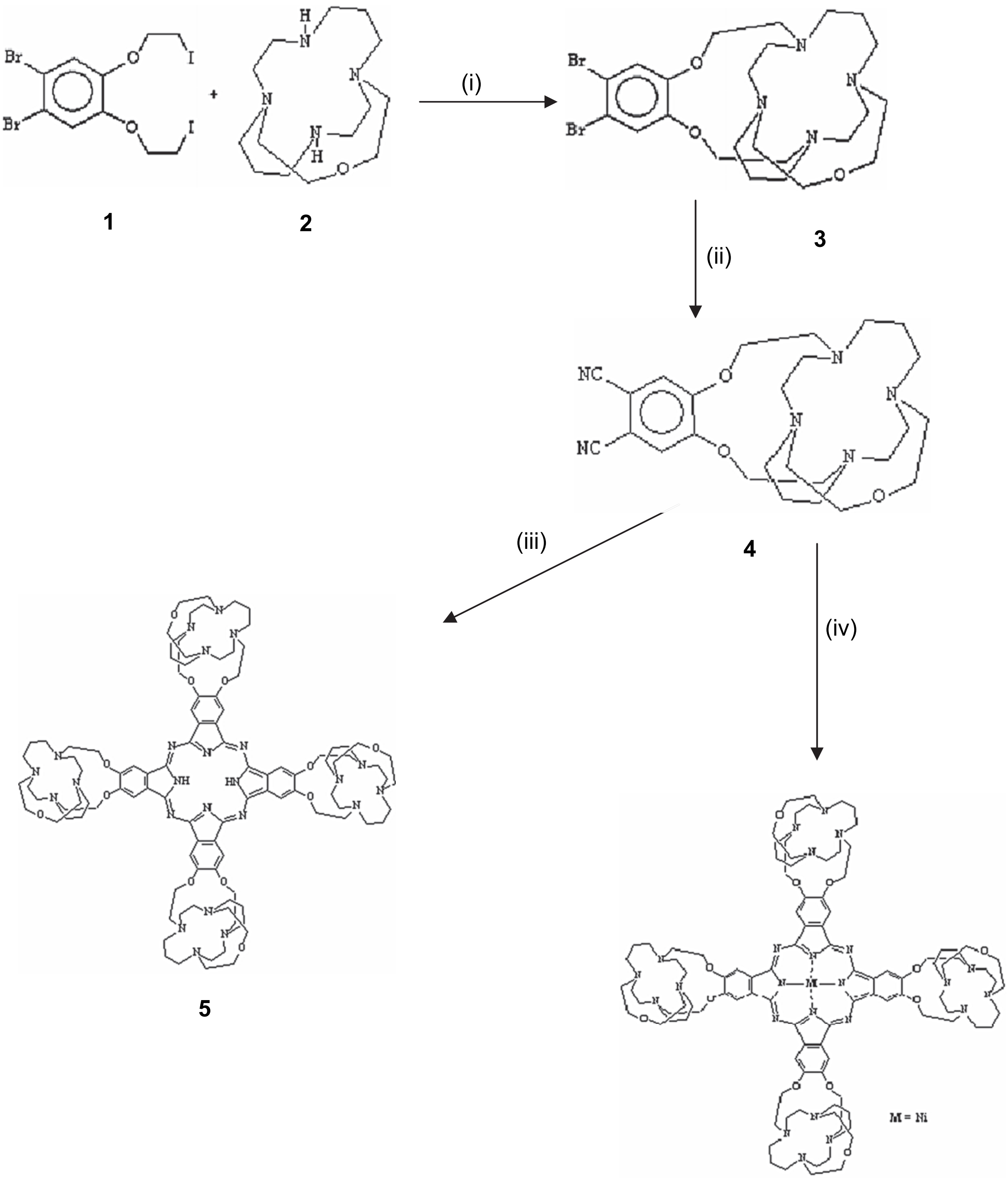
where the subscript "aq" denotes aqueous solution and the subscript "org" denotes organic solution. The following logarithmic expression is valid for the above extraction system [24].

$$\log\{D/[\mathrm{Pic}^-]^n\} = \log K_{ex} + m \log[\mathrm{L}] \qquad (3)$$

3. Result and discussion

The preparation of the target metal-free (**5**) and Ni(II) phthalocyanine (**6**) is shown in Scheme 1. Compound (**3**) was synthesized by the reaction of 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**1**) [21] with 17-oxa-1,4,8,11-tetraazabicyclo[6.6.5]nonadecane (**2**) [22] in acetonitrile containing finely ground anhydrous Na_2CO_3 as a template agent at reflux temperature in a Schlenk system under argon atmosphere. Compound (**3**) was obtained in 43.51% yield (Scheme 1). The formation of the macrotricycle (**3**) was evident by the characteristic changes in the IR vibrations. The occurrence of a single band at 3085 and 1249 cm^{-1} is attributable to the presence of Ar–H and Ar–O–C resonances, respectively, and is diagnostic of macrotricyclization. The absence of bands characteristic of N–H groups also confirms the formation of compound (**3**). In the ^1H NMR spectra of this compound, the chemical shifts of NH protons in precursor compound (**1**) disappear after the macrotricyclization reaction. The other resonances in the ^1H NMR and ^{13}C NMR spectra, concerning OCH_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 $m/z = 591.2$, corresponding to the proposed formulation $[M+1]^+$.

Compound (**4**) was synthesized by treating compound (**3**) with three equivalents of the CuCN according to Rosenmund von Braun reaction [25] in a moderately high-boiling solvent such as dimethyl formamide to avoid the formation of Cu(II) phthalocyanine derivative DMF at reflux temperature under argon atmosphere. The Ar–Br groups of compound (**3**) were converted to a leaving group via a standard step to afford compound (**4**) in an overall 34.33% yield. Comparison of the IR spectra of compounds (**3**) and (**4**) clearly shows the conversion



Scheme 1. (i) Ar, CH_3CN, Na_2CO_3, NaI, 92 °C; (ii) CuCN, Ar, DMF, 145 °C; (iii) Ar, 2-(*N*,*N*-dimethylamino)ethanol, 138 °C, and (iv) Ar, anhydrous $NiCl_2$, ethylene glycol, 200 °C.

of the aromatic bromo substituents into the cyano form by the disappearance of the C–Br vibrations at 651 cm^{-1} in compound (**3**) and so the sharp stretching vibrations at 2225 cm^{-1} were easily verified with C≡N absorptions. The ^{1}H NMR spectrum of compound (**4**) closely resembles that of the precursor compound (**3**) as expected. The ^{1}H NMR of compound (**4**) in chloroform shows a singlet at $\delta = 7.85$ ppm, indicating the presence of Ar–H protons. Owing to formation of compound (**4**) chemical shifts which belong to Ar–H protons appear down field at approximately 0.55 ppm [26]. In the proton-decoupled ^{13}C NMR spectrum of compound (**4**), C≡N groups are present as singlet at $\delta = 114.91$ ppm which indicate that they are substituted with the C–Br groups in compound (**3**). The other chemical shifts belonging to aromatic, crown or azacrown carbons come out very close to those of precursor compound (**3**). In the mass spectrum of compound (**4**), medium $[M + 1]^+$ peaks are observed for this compound at $m/z = 483.4$ and at $m/z = 506.5$ together with strong $[M + Na + 1]^+$ peaks and this can be attributed to the substitution reaction which occurred between C–Br and C≡N in compound (**4**).

Condensation of four molecules of macrotricyclic compound (**4**) into the metal-free phthalocyanine compound (**5**) was carried out in standard Schlenk tube in 2-(dimethylamino) ethanol at reflux temperature for 24 h under argon atmosphere. The target compound (**5**) was obtained in a 30% yield as a dark green solid after purification on chromatographic separation on silica gel [ethanol:chloroform (3:7)]. The comparison of the IR spectrum of compound (**5**), with that of compound (**4**) confirmed the proposed structure by disappearance of the C≡N vibration at 2225 cm^{-1} and the appearance of a medium new absorptions at 3271 and 1620 cm^{-1} attributable to N–H and C–N groups, respectively [20,27]. The inner core N–H protons of the metal-free phthalocyanine were also identified in the ^1H NMR spectrum. Strong shielding of the cavity protons in the phthalocyanine core of this compound was manifested by a broad resonance at $\delta = -4.11$ ppm [28] at high concentration which could be attributed to the NH resonance and identified easily with deuterium exchange. In the ^1H NMR spectrum of compound (**5**), the signals related to aromatic and aliphatic protons of the macrotricycles and phthalocyanine skeleton gave the significant characteristic of the proposed structure. This spectrum closely resembles that of the precursor compound (**4**) as expected. A distinct difference, encountered in the ^1H NMR of compounds (**4**) and (**5**) when compared with previously obtained polymacrocycle-substituted derivatives, is the sharp signals, which indicate a lower tendency to aggregate even at concentration used for proton NMR measurements [29]. The proton-decoupled ^{13}C NMR spectrum of compound (**5**) gave significant absorbance characteristic of the given structure. This spectrum closely resembles that of the dicyano derivative compound (**4**), the differences being the signals of carbon atoms of the cyano groups at $\delta = 114.91$ ppm and the phthalocyanine ring (C=N) at $\delta = 152.39$ ppm. The mass spectrum of metal-free phthalocyanine was obtained by the LS–MS/MS technique and the molecular ion peak at $m/z = 1931.3$ $[M + 1]^+$ was observed.

The cyclotetramerization of macrotricyclic dicyano compound (**4**) in the presence of anhydrous metal salt gave the metallophthalocyanine compound (**6**). The high-boiling solvent of choice for this reaction was ethylene glycol for Ni(II) phthalocyanine [30]. Compound (**6**) was purified by column chromatography on silica gel by using chloroform as an eluent in a 48.39% yield. In the IR spectrum of this compound, the stretching vibrations at 2225 cm^{-1} belonging to C≡N group disappear after formation of compound (**6**). A diagnostic feature of the formation of cyclotetramerization reaction from compound (**4**) appears C=N stretching vibration at 1632 cm^{-1}. The significant difference is the absence of N–H vibration of the inner phthalocyanine core which is assigned to the expected result. The ^1H NMR spectrum of compound (**6**) in chloroform shows a singlet at $\delta = 7.55$ ppm which indicates aromatic protons. Aliphatic protons which belong to Ar–O–CH_2, OCH_2 and NCH_2 appearing at $\delta = 4.31$, 3.73 and 3.51 ppm, respectively, are in accordance with precursor compound (**4**) and metal-free phthalocyanine (**5**). In the proton-decoupled ^{13}C NMR spectrum of compound (**6**) showed a singlet NMR absorbance peak for that identical carbons for C=N group at $\delta = 153.15$ ppm, the phthalocyanine ring was made up. The NMR characteristics of compound (**6**) were quite similar to that of the precursor dicyano compound (**4**) and metal-free phthalocyanine compound (**5**) except the disappearance of chemical shift of C≡N. The Ni(II) phthalocyanine gave reproducible mass spectrum and here we observed the M + 1 and M + Na + 1 peaks, instead of the molecular ion in compound (**6**), at $m/z = 1987.4$ and 2010.2, respectively.

The best indications for phthalocyanine systems are given by their UV–vis spectra in solution (Fig. 2). The electronic spectra of compounds (**5**) and (**6**) show the same typical B and Q bands of symmetrical macrotricyclic substituted Pc. The energy level location corresponding to those bands is illustrated in Fig. 1. In the UV–vis spectrum of metal-free phthalocyanine in chloroform, the characteristic split Q band was observed with absorptions at 680 and 668 nm. These intense Q bands indicate monomeric species as species with D_{2h} symmetry show two intense absorptions around 700 nm [31]. The lower absorption than the typical split Q band at 620 nm, is due to the dimeric association and up to 615 nm for higher aggregates [32]. 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 fully conjugated 18π electron system. The presence of strong absorption bands in compound (**5**) in the UV region at λ_{max} 400 and 300 nm shows superimposed bands of the phthalocyanine due to the existence of Soret band of Pc which have been ascribed to the deeper $\pi \Rightarrow \pi^*$ levels of LUMO transition [33]. However, in the state of Ni(II) derivative of phthalocyanine, the average Q bands are slightly shifted to the blue with respect to the parent metal-free compound (**5**) [34]. The position of Q band of metallophthalocyanine compound (**6**) changed due to the central Ni(II) where Q band absorption was observed without splitting and was centered at around 670 nm. The single Q band in metallo derivative and its splitted form in its metal-free derivatives are characteristic [35]. Observed peaks as mentioned above indicate that the symmetry of the molecule

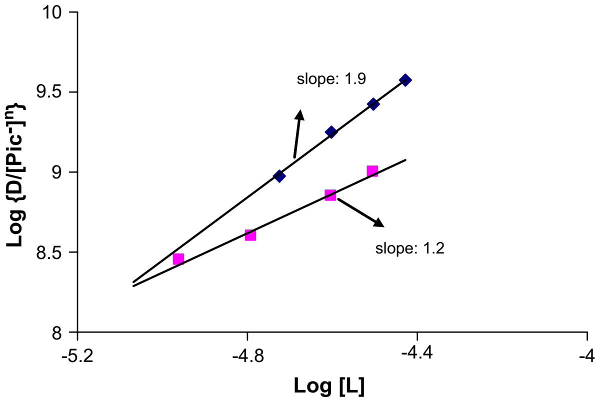


Fig. 1. Log $\{D/[Pic^-]^n\}$ versus log [L] for the extraction of Cd-picrate. ■: compound (**4**); ◆: compound (**5**).

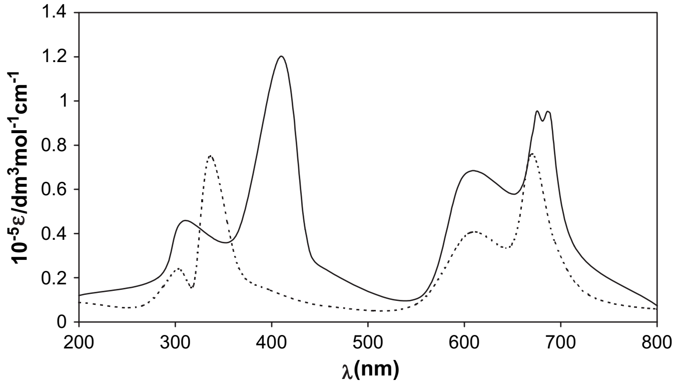


Fig. 2. UV–vis spectra of compound (**5**) (solid line) and compound (**6**) (broken line) in chloroform.

has been changed. This result is typical of metal complexes of substituted and unsubstituted Pc with D_{4h} symmetry [36].

Table 1 shows the extractability of Ag^+, Co^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Mn^{2+}, picrates from the aqueous phase into chloroform phase by compound (**4**) and metal-free compound (**5**). It can be seen that the ligands transfer only Cd-picrate to the organic phase. The values of extractability of all the other metal picrates are below 1% for compound (**5**). Compound (**4**) extracts the metal picrates below 5.4% except for Cd-picrate. However, the extraction ratio of Cd for compound (**4**) is higher than that of compound (**5**). When compound (**4**) was used as ligand, the extraction ratio reached 38.5%, but the other metal ions were not extracted effectively. It is interesting to note that the percentage of the extraction with compound (**5**) containing four macrotricyclic moieties is less than that of model compound (**4**).

In order to determine the composition of extracted Cd complex, the effect of changing ligand concentration over the distribution ratio at constant picrate concentration was investigated for both of the ligands. The results are shown in Fig. 1. The plot of $\log\{D/[\mathrm{Pic}^-]^n\}$ as a function of $\log[\mathrm{L}]$ should give a straight line with a slope of m and $\log K_{ex}$ can be calculated from the intercept by using Eq. (3).

The results of the experiments at different concentrations of the ligand but constant picrate concentration revealed the 2:1 composition for compound (**5**) while the 1:1 composition for compound (**4**).

Table 1
The extractability of aqueous metal picrates for compounds (**4**) and (**5**) into chloroform[a]

Metal ion	Extractability[a] (%)	
	Compound (**4**)	Compound (**5**)
Ag^+	5.4 ± 0.4	<1
Co^{2+}	4.2 ± 0.6	<1
Cd^{2+}	38.5 ± 0.1	34.9 ± 0.8
Zn^{2+}	2.2 ± 0.1	<1
Cu^{2+}	2.6 ± 0.4	<1
Ni^{2+}	<1	<1
Mn^{2+}	5.3 ± 0.2	<1
Pb^{2+}	<1	<1

[a] Temperature: 25.0 ± 0.1 °C; aqueous phase (10 ml); $[\mathrm{Pic}^-] = 1.25 \times 10^{-5}$ M, organic phase (10 ml); and $[\mathrm{L}] = 1.25 \times 10^{-4}$ M. The values and standard deviations are calculated from three independent extraction experiments.

Acknowledgements

This study was supported by the Research Fund of Karadeniz Technical University (Trabzon–Turkey), Project Number: 2002.111.2.8.

References

[1] Lever ABP, Leznoff CC. Phthalocyanine: properties and applications, vols. 1–4. New York: VCH; 1989–1996;
McKeown NB. Phthalocyanines materials: synthesis, structure and function. New York: Cambridge University Press; 1998;
Kadish KM, Smith KM, Guilard R. The porphyrin handbook, vols. 1–20. San Diego, CA: Academic Press; 2000–2003.
[2] Gouloumis A, Torres T. Org Lett 1999;1:1807–11.
[3] Ka-Wo P, Yan Y, Xi-You L. Organometallics 1999;18:3528–32.
[4] Fluda T, Kobayashi N. Chem Eur J 2004;10:117–33.
[5] Gregory P. High-technology applications of organic colorants. New York: Plenum Press; 1991;
Gregory P. J Porphyrins Phthalocyanines 2000;4:432.
[6] Brown RJC, Kucernak AR. Electrochim Acta 2001;46:2573–82.
[7] Wöhrle D, Meissner D. Adv Mater 1991;3:129;
Eichhorn H. J Porphyrins Phthalocyanines 2000;4:88.
[8] Shirk JS, Pong RGS, Flom SR, Heckmann H, Hanack M. J Phys Chem 2000;104:1438–49.
[9] Zimcik P, Miletin M, Ponec J, Kostka M, Fiedler Z. J Photochem Photobiol A Chem 2003;155:127–31.
[10] Cook MJ. J Mater Chem 1996;6:677–89.
[11] Vagin S, Hanack M. Eur J Org Chem; 2003:2661–9.
[12] Bekaroğlu Ö. Appl Organomet Chem 1996;10:605–22.
[13] Arous O, Gherrou A, Kerdjoudj H. Desalination 2004;161:295–303.
[14] Henriksen G, Hoff P, Larsen RH. Appl Radiat Isot 2002;56:667–71.
[15] Lehn JM. Pure Appl Chem 1977;49:857.
[16] Graf E, Lehn JM. Helv Chim Acta 1981;64:1040–57.
[17] Potvin PG, Lehn J-M. Synthesis of macrocycles: the design of selective complexing agents. In: Izatt RM, Christiansen JJ, editors. Progress in macrocyclic chemistry. New York: J. Wiley and Sons; 1987. p. 3.
[18] An H, Bradshaw JS, Izatt RM. Chem Rev 1992;92:543–72.
[19] Kantekin H, Değirmencioğlu I, Gök Y. Acta Chem Scand 1999;53: 247–52.
[20] Gök Y, Kantekin H, Değirmencioğlu I. Supramol Chem 2003;15: 335–43.
[21] Yildiz SZ, Gök Y. New J Chem 1998;22:1365–9.
[22] Brandes S, Lacour S, Deneat F, Pullumbi P, Guilard R. J Chem Soc Perkin Trans 1; 1998:639–41.
[23] Perrin DD, Armerago WLF. Purification of laboratory chemicals. 2nd ed. Oxford: Pergamon; 1980.
[24] Kantekin H, Ocak Ü, Gök Y, Acar İ. J Inclusion Phenom Macrocycl Chem 2004;48:95–101.
[25] Dontz DA, Buschmann H, Schollmeyer E. Polyhedron 1998;17:1891–5.
[26] Musluoğlu E, Ahsen V, Gül A, Bekaroğlu Ö. Chem Ber 1991;124:2531.
[27] Steinbach F, Joswing HJ. J Chem Soc Faraday Trans 1 1979;75:2579.
[28] Bilgin A, Ertem B, Gök Y. Tetrahedron Lett 2003;44:3829–33;
Gürol I, Ahsen V. J Porphyrins Phthalocyanines 2000;4:621–6.
[29] Yıldız SZ, Kantekin H, Gök Y. J Porphyrins Phthalocyanines 2001;5:367–75.
[30] Tion M, Wada T, Sasabe H. Dyes Pigments 2002;52:1–8.
[31] Gürek AG, Bekaroğlu Ö. J Chem Soc Dalton Trans; 1994:1419–23;
van Nastrum CF, Picken SJ, Schouten A-J, Nolte RJM. J Am Chem Soc 1995;117:9957–65;
Wang C, Bryce MR, Batsanow AS, Stanley CF, Beeby A, Howard JAK. J Chem Soc Perkin Trans 2; 1997:1671–8.

[32] Hu Y, Shen Y. J Heterocycl Chem 2002;39:1071–5;
Brewis M, Hassan BM, Li H, Makhseed S, Mckeown NB, Thompson NJ. J Porphyrins Phthalocyanines 2000;4:460–4;
Fujiki M, Tabie H, Kurihara T. J Phys Chem 1988;92:1281;
Dodsworth ES, Lever ABP, Seymour P, Leznoff CC. J Phys Chem 1985;89:5698.

[33] Lange SJ, Sibert JW, Barrett AGM, Hofmann BM. Tetrahedron 2000;56:7371–7;
Gürsoy S, Bayır ZA, Hamuryudan E, Bekaroğlu Ö. Monatsch Chem 2000;131:287–92.

[34] Rojo G, De la Torre G, Garcia-Ruiz J, Ledoux I, Torres T, Zyss J, et al. Chem Phys 1999;27:245.

[35] Pullen AE, Faulmann C, Cassoux P. Eur J Inorg Chem; 2000:269.

[36] Takahashi K, Kawashima M, Tomita Y, Itoh M. Inorg Chim Acta 1995;232:69–73;
Bilgin A, Ertem B, Gök Y. Supramol Chem 2005;17(4):277–81.