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New phthalocyanines bearing tetra(hydroxyethylthio) functionalities

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Abstract

Zn(II), Co(II), Ni(II) and metal-free phthalocyanines (**2**–**5**) bearing a hydroxyethylthio substituent on each benzo group were prepared from 4-(hydroxyethylthio)phthalonitrile (**1**) and the corresponding divalent metal salt. The reactivity of the hydroxyethyl groups was demonstrated by esterification of phthalocyanine derivatives (**2**–**5**) with acetic anhydride at reflux temperature and acetylated phthalocyanine compounds (**6**–**9**) were obtained. The new compounds have been characterized by elemental analyses, IR, UV–vis, mass and ^{1}H NMR spectroscopy.

Keywords: Phthalocyanine; Esterification; Cobalt; Nickel; Zinc

1. Introduction

Phthalocyanines (pcs) comprise a remarkably robust and versatile class of chemical compounds. They are still of enormous technological importance for the manufacture of green and blue pigments but other areas of current interest include application as in catalysis, as thermal stability batteries, chemical sensors as well as in electrochromism, liquid crystals, photodynamic therapy and as modified supports for gas–solid chromatography [1]. The growing use of phthalocyanines as advanced materials during the last decade has encouraged the synthesis of new materials which differ in terms of the central metal ion and peripheral substituents [2].

Although phthalocyanines have been extensively studied, their properties cannot be fully exploited as they have low solubility in common organic solvents and they tend to aggregate. These limitations can be addressed by introducing bulky substituents which renders them soluble by causing substantial disruption of the parent pcs rings and, at the same time, prevents aggregation to a great extent. The synthesis of these systems follows the classical cyclotetramerization of suitably substituted phthalonitriles and the majority of synthetic efforts have focused on the preparation of substituted phthalonitriles with different groups on the aromatic system [3]. Also, the presence of these substituents is known to offer a useful way of tuning the wavelength of the Q band [4,5]; for example, the substitution of the pcs ring with electrondonating groups at the α (non-peripheral) or β (peripheral) positions affords a bathochromic shift of the Q band [6–8]. Substitution at the more sterically crowded α position also reduces aggregation more than substitution at the β position [9–12].

Bis(hydroxyethylthio)phthalonitrile has become the starting point for number of pcs with cyclic and acyclic substituents [8,14–16].

The present paper reports for the first time the synthesis and characterization of 4-(hydroxyethylthio)-phthalonitrile from a single step reaction and its conversion into metal-free and metal phthalocyanines containing tetrakis(hydroxyethylthio) moieties at the periphery. The reactivity of the hydroxyethyl substituents has been demonstrated by preparation of more soluble acetyl esters from these pcs.

2. Experimental

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by

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the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^{1}H NMR spectra were recorded on 300 MHz on a Varian U-300 spectrometer using TMS as internal reference. Mass spectra were performed on Hewlett−Packard HP-1100 LC/MS in positive-ion mode. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. All solvents were dried and purified according to Ref. [17]. The homogeneity of the products was tested in each step by TLC (SiO_2). 4-Nitrophthalonitrile was prepared according to a reported procedure [18].

2.1. *4-(2-Hydroxyethylthio)phthalonitrile (**1**)*

4-Nitrophthalonitrile (1.73 g, 1.0 mmol) and 2-hydroxyethylmercaptane (1.6 ml, 1.8 g, 2.0 mmol) were added successively with stirring to dry DMSO (20 ml). Upon dissolution, anhydrous Na_2CO_3 (3.0 g, 2.8 mmol) was added portionwise over 2 h and the mixture was stirred vigorously at room temperature for a further 6 h. The reaction mass was then poured into cold water (200 ml) and the precipitate was filtered off, washed with water and crystallized from toluene to give a white crystalline product. It was washed first with cold hexane and then with cold diethyl ether. Yield: 1.55 g (76%); m.p. 92 °C. IR ν (cm^{-1}): 3324 (−OH), 3080 (Ar−H), 2930, 2880 (alkyl-CH), 2225 (−C≡N); ^{1}H NMR ($CDCl_3$ 250 MHz): 7.59 (d, 1H, Ar−H), 7.52 (d, 1H, Ar−H), 7.49 (d, 1H, Ar−H), 3.83 (t, 2H, OCH_2), 3.16 (t, 2H, SCH_2), 2.04 (s, 1H, OH); anal. calcd. for $C_{10}H_8N_2OS$; C, 58.80; H, 3.95; N, 13.72; found: C, 58.92; H, 3.86; N, 13.55%; MS: *m/z* 205 $[M+1]^+$, 206 $[M+2]^+$.

2.2. *Tetra(2-hydroxyethylthio)phthalocyanine (**2**)*

A mixture of 0.5 mmol (0.102 g) 4-(2-hydroxyethylthio)phthalonitrile and 1.0 mmol lithium metal in 1.5 ml of pentanol was heated and stirred at 140 °C for 2 h under N_2 in a sealed tube. The resulting green suspension was cooled to ambient temperature. The reaction mass was then dissolved in DMF (1 ml) and poured into 250 ml ice-water mixture with the addition 4 ml conc. HCl. In this mixture, the Li_2pcs formed was converted into H_2pcs. The precipitate was filtered off and the crude product treated with boiling acetone, ethanol, hexane and then dried in vacuo. Yield: 0.066 g (64.7%); m.p. > 200 °C. IR ν (cm^{-1}): 3330 (−OH), 3275 (−NH), 2970−2860 (alkyl-CH); ^{1}H NMR (*d*-DMSO): 7.33 (m, 12H, Ar−H), 5.26 (br s, 4H, OH), 3.95 (m, 8H, OCH_2), 3.25 (m, 8H, SCH_2), −6.05 (br s, 2H, −NH); UV−vis λ_{max} (nm) (log ε) in DMF: 345 (3.98), 409 (3.64), 685 (4.14), 713 (4.12); anal. calcd. for $C_{40}H_{34}N_8O_4S_4$; C, 58.66; H, 4.18; N, 13.68; found: C, 58.82; H, 4.08; N, 13.58%.

2.3. *Tetra(2-hydroxyethylthio)phthalocyaninatometal derivatives (**3−5**)*

A mixture 0.5 mmol (0.102 g) 4-(2-hydroxyethylthio)phthalonitrile and 0.125 mmol anhydrous metal salt (zinc acetate 0.023 g, cobalt chloride 0.0163 g or nickel chloride 0.0163 g) in 0.5 ml of dry pyridine was heated and stirred at 142 °C for 48 h under N_2 in a sealed tube. After cooling to room temperature, the suspension was dissolved in 2 ml DMF and poured into 150 ml ice-water mixture with the addition of 4 ml HCl. After that, precipitated green-blue solid was filtered off. The precipitate was first refluxed in chloroform and then washed subsequently with ethanol and acetone and then dried in vacuo.

2.3.1. *Compound **3***

Yield: 0.052 g (49%); m.p. >200 °C. IR ν (cm^{-1}): 3320 (−OH), 3053 (Ar−H), 2916−2860 (alkyl-CH); ^{1}H NMR (*d*-DMSO): 8.82 (m, 8H, Ar−H), 8.02 (m, 4H, Ar−H), 5.30 (br s, 4H, OH), 4.03 (m, 8H, OCH_2), 3.64 (m, 8H, SCH_2); UV−vis λ_{max} (nm) (log ε) in DMF: 357 (4.48), 690 (4.86); anal. calcd. for $C_{40}H_{32}N_8O_4S_4Zn$; C, 54.45; H, 3.66; N, 12.70; found: C, 54.62; H, 3.58; N, 12.54%.

2.3.2. *Compound **4***

Yield: 0.066 g (60.5%); m.p. >200 °C. IR ν (cm^{-1}): 3300 (−OH), 3058 (Ar−H), 2954−2880 (alkyl-CH); UV−vis λ_{max} (nm) (log ε) in DMF: 338 (3.27), 677 (3.30); anal. calcd. for $C_{40}H_{32}CoN_8O_4S_4$; C, 54.85; H, 3.68; N, 12.79; found: C, 54.32; H, 3.38; N, 12.44%.

2.3.3. *Compound **5***

Yield: 0.046 g (42%); m.p. >200 °C. IR ν (cm^{-1}): 3326 (−OH), 3058 (Ar−H), 2921−2860 (alkyl-CH); ^{1}H NMR (*d*-DMSO): 7.01 (m, 12H, Ar−H), 5.37 (br s, 4H, OH), 3.77 (m, 8H, OCH_2), 3.05 (m, 8H, SCH_2); UV−vis λ_{max} (nm) (log ε) in DMF: 358 (4.05), 629 (4.26), 683 (4.3); anal. calcd. for $C_{40}H_{32}N_8NiO_4S_4$; C, 54.86; H, 3.68; N, 12.80; found: C, 54.42; H, 3.44; N, 12.46%.

2.4. *Tetra(acetoxyethylthio) phthalocyanine derivatives (**6−9**)*

A mixture of 0.050 g tetra(2-hydroxyethylthio)phthalocyanine derivative (0.061 mmol of **2**, 0.056 mmol of **3**, 0.057 mmol of **4** or 0.057 mmol of **5**) and acetic anhydride (10 ml) was stirred under reflux for 24 h after which, excess acetic anhydride was evaporated under vacuum. The residue was dissolved in chloroform (10 ml) and filtered off. After removal of the chloroform under reduced pressure, purification of the product was accomplished by column chromatography on silica gel using a suitable eluent.

2.4.1. *Compound **6***

Eluent: first methanol and then THF. Yield: 0.036 g (60%); m.p. >200 °C. IR (cm^{-1}): 3287 (−NH), 3053 (Ar−H), 2929−2850 (alkyl-CH), 1735 (C=O), 1220 (C−O−C=O); ^{1}H NMR ($CDCl_3$-d_6): δ: 8.06 (m, 8H, Ar−H), 7.48 (m, 4H, Ar−H), 4.61 (m, 8H, OCH_2), 3.53 (m, 8H, SCH_2), 2.19 (m, 12H, $-CH_3$), −6.3 (2H, br s, NH); UV−vis λ_{max} (nm) (log ε) in CH_2Cl_2: 343 (3.69), 676 (3.80), 709 (3.80); anal. calcd. for $C_{48}H_{42}N_8O_8S_4$; C, 58.40; H, 4.29; N, 11.35; found: C, 58.12; H, 4.03; N, 11.15%. MS: *m/z* 989.2 $[M+2]^+$.

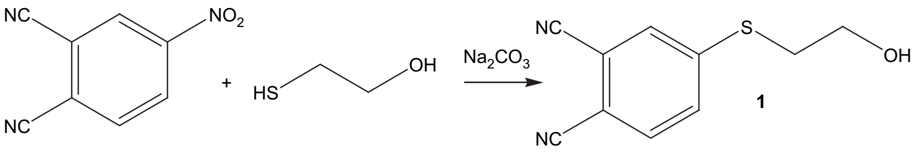

Fig. 1. Synthesis of 4-(2-hydroxyethylthio)phthalonitrile.

2.4.2. Compound **7**

Eluent: acetone/THF (1:2). Yield: 0.011 g (18.3%); m.p. >200 °C. IR ν (cm^{-1}): 3058 (Ar–H), 2970–2930 (alkyl-CH), 1737 (C=O), 1224 (C–O–C=O); ^{1}H NMR (CDCl$_3$-d_6): δ: 7.65 (m, 8H, Ar–H), 6.82 (m, 4H, Ar–H), 4.31 (m, 8H, OCH$_2$), 3.45 (m, 8H, SCH$_2$), 2.05 (m, 12H, –CH$_3$); UV–vis λ_{max} (nm) (log ε) in CH$_2$Cl$_2$: 350 (4.11), 689 (4.32); anal. calcd. for $C_{48}H_{40}N_8O_8S_4Zn$; C, 54.88; H, 3.84; N, 10.67; found: C, 54.42; H, 3.33; N, 10.35%. MS: *m/z* 1049.1 [M]$^+$.

2.4.3. Compound **8**

Eluent: first methanol and then THF. Yield: 0.018 g (30%); m.p. >200 °C. IR ν (cm^{-1}): 3058 (Ar–H), 2934 (alkyl-CH), 1736 (C=O), 1222 (C–O–C=O); UV–vis λ_{max} (nm) (log ε) in CH$_2$Cl$_2$: 369 (3.90), 681 (3.72); anal. calcd. for $C_{48}H_{40}CoN_8O_8S_4$; C, 55.22; H, 3.86; N, 10.73; found: C, 54.82; H, 3.33; N, 10.38%.

2.4.4. Compound **9**

Eluent: first methanol and then THF. Yield: 0.022 g (37%); m.p. >200 °C. IR ν (cm^{-1}): 3058 (Ar–H), 2924–2865 (alkyl-CH), 1735 (C=O), 1220 (C–O–C=O); ^{1}H NMR (CDCl$_3$-d_6): δ: 8.10 (m, 8H, Ar–H), 7.20 (m, 4H, Ar–H), 4.42 (m, 8H, OCH$_2$), 3.24 (m, 8H, SCH$_2$), 2.19 (m, 12H, –CH$_3$); UV–vis λ_{max} (nm) (log ε) in CH$_2$Cl$_2$: 367 (3.77), 626 (4.09), 680 (4.08); anal. calcd. for $C_{48}H_{40}N_8NiO_8S_4$; C, 55.23; H, 3.86; N, 10.73; found: C, 54.92; H, 3.23; N, 10.45%. MS: *m/z* 1043.9 [M+1]$^+$.

3. Results and discussion

As used in the preparation of a variety of ether or thioether-substituted phthalonitriles, the principle reaction to obtain 4-(2-hydroxyethylthio)phthalonitrile (**1**) was the base-catalysed aromatic nitro-displacement of 4-nitrophthalonitrile with 2-hydroxyethylmercaptane [19–21]. The base of choice in this reaction was Na$_2$CO$_3$ and dry DMSO was preferred as the solvent (Fig. 1).

Conversion of **1** into phthalocyanine derivatives was accomplished through the usual cyclotetramerization reactions in the presence of a reductant and/or metal salt, i.e., lithium was used to obtain the metal-free derivative **2**, while the metal salt [Zn(OAc)$_2$, NiCl$_2$ or CoCl$_2$] and a suitable solvent, dry pyridine were required for the metal phthalocyanines **3**, **4** and **5**, respectively. These phthalocyanines are soluble to a certain extent in donor solvents such as DMSO, DMF and pyridine.

Esterification of the hydroxyethyl groups of the phthalocyanine derivatives (**2–5**) was carried out in order to show the reactivity of these side groups. Esterification of all four –OH groups on each pcs core was accomplished by treatment with excess acetic anhydride at reflux temperature and acetoxyethylthio-substituted phthalocyanine compounds **6–9** were obtained. While **2–5** were almost insoluble in acetic anhyride at the beginning of the reaction, they were dissolved gradually and the colour of the reaction solution turned into dark blue (Fig. 2).

Characterization of the new products involved combination of elemental analysis and spectroscopic data (UV–vis, FT-IR, ^{1}H NMR and mass spectroscopy). Spectral investigations for all the new products were consistent with the assigned structures.

The IR spectrum of **1** clearly indicates the presence of CN groups by the intense stretching bands at 2225 cm^{-1}. In the ^{1}H NMR analysis of **1** in deuterated in chloroform, the aromatic protons appear as a doublet at 7.59, 7.52, 7.49 ppm for each of the aromatic protons, alky protons appear as a triplet at 3.83 ppm for O–CH$_2$ protons, triplet at 3.16 ppm for CH$_2$–S protons and broad peak at 2.04 ppm for OH protons. In the mass spectra of these compounds, the presence of the characteristic molecular ion peaks at $m/z = 205$ $[M+1]^+$ and 206 $[M+2]^+$ confirmed the proposed structure.

Cyclotetramerization of the dinitrile derivative was confirmed by the disappearance of the sharp C≡N vibration at 2225 cm^{-1}. The IR spectra of phthalocyanines **3–5** are very

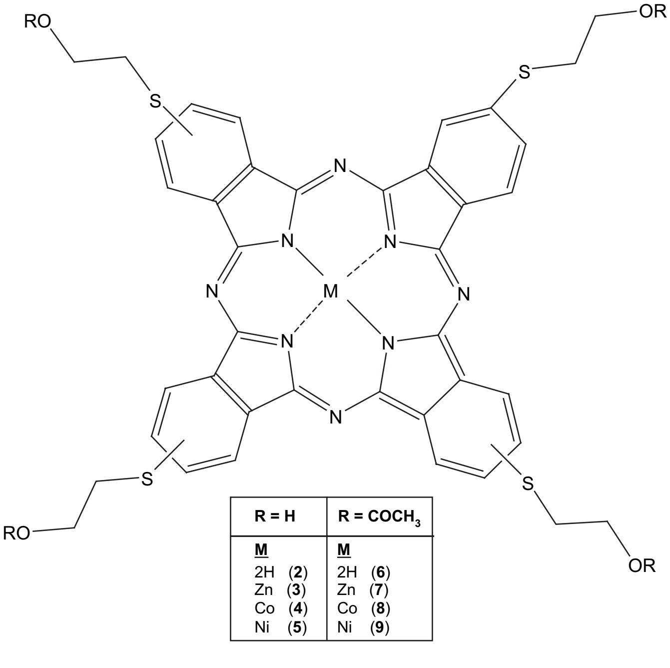

Fig. 2. Metallo and metal-free tetra(2-hydroxyethylthio)- and tetra(acetoxyethylthio)phthalocyanines (**2–9**).

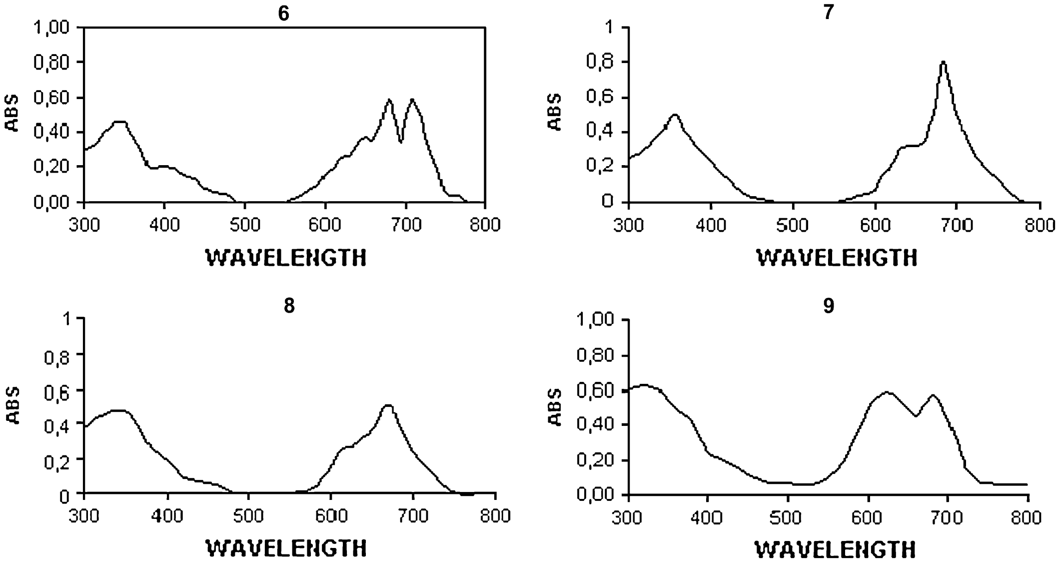

Fig. 3. UV–vis spectra of **6–9** in dichloromethane.

similar, with the exception of the metal-free **2** showing an NH stretching band at 3275 cm^{-1} due to the inner core imino group. These protons are also very well characterized by the ^1H NMR which show a peak at δ −6.05 ppm as a result of the 18 π-electron system of the phthalocyanine ring [19–22]. ^1H NMR investigations of metallo-phthalocyanines have provided the characteristic chemical shifts for the structures expected. The ^1H NMR spectra of metal-free (**2**), zinc(II) (**3**) and nickel(II) (**5**) phthalocyanines are almost identical, the only difference being the disappearance of the broad NH protons of **2**. The OH protons are observed at δ 5.26 ppm for metal-free (**2**), δ 5.30 ppm for zinc(II) (**3**) phthalocyanines and δ 5.37 ppm for nickel(II) (**5**) phthalocyanines and the signal disappeared by deuterium exchange.

In the IR spectra of the acetoxyethylthio-substituted phthalocyanines (**6–9**) the intense stretching bands of C=O at 1735 cm^{-1} and O–C=O at 1220 cm^{-1} clearly appear. A comparison of the ^1H NMR spectra of tetrahydroxy derivatives **2**, **3**, **5** with those of acetylated ones **6**, **7**, **9** are disappearance of −OH and appearance of CH_3–C=O chemical shifts (at 2.19 ppm for compounds **6** and **9**, and 2.05 ppm for compound **7**) in the latter group.

In the mass spectra of compounds **6**, **7** and **9**, the presence of the characteristic molecular ion peaks at $m/z = 989.2$ (**6**) $[M+2]^+$ and 1049.1 $[M]^+$ (**7**) and 1043.9 $[M+1]^+$, 1045 $[M+2]^+$ (**9**) confirmed the proposed structure. In addition to molecular ion peaks, fragment ions corresponding to the loss of O=C–CH_3 ($[M-43]^+$), 2 O=C–CH_3 ($[M-86]^+$), 3 O=C–CH_3 ($[M-129]^+$) for compound **6**, O=C–CH_3 ($[M-43]^+$), 2 O=C–CH_3 ($[M-86]^+$), 3 O=C–CH_3 ($[M-129]^+$) for compound **7** and CH_3 ($[M-17]^+$), O=C–CH_3 ($[M-43]^+$), 2 O=C–CH_3 ($[M-86]^+$) for compound **9** were easily identified.

Phthalocyanines **2–9** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–400 nm (B band) arising from the deeper π-levels → LUMO transition and the other in the visible part of the spectrum around 600–700 nm (Q band) attributed to the π–π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the pcs^{-2} ring (Fig. 3). Tetra substitution with sulfur bridged groups causes a shift of the intense Q band to longer wavelengths when compared with the unsubstituted derivatives [13,22]. The characteristic Q band transition of metallo-phthalocyanines with D_{4h} symmetry is observed as a single band of high intensity in visible region. The D_{2h} symmetry of metal-free phthalocyanine is verified by two absorptions in the visible region (685 and 713 nm). Compared with

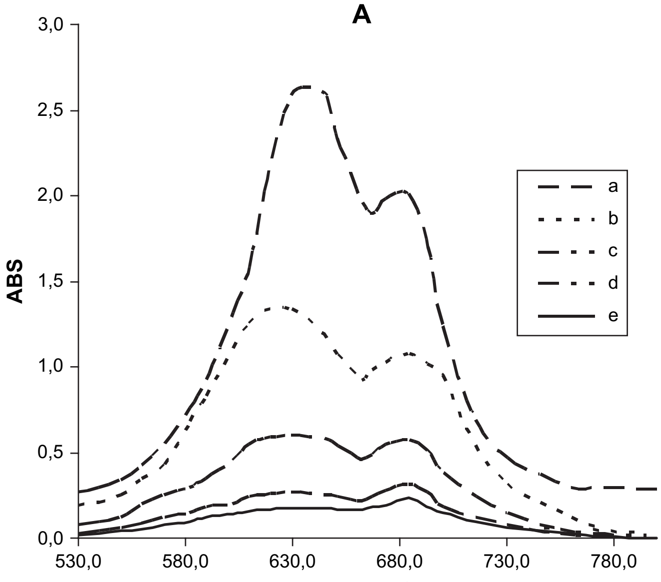

Fig. 4. Changes in the UV–vis spectra of **5** with different concentrations ((a – 1,72; b – 0,86; c – 0,43; d – 0,215; e – 0,108)×10^{-4} M) in DMF.

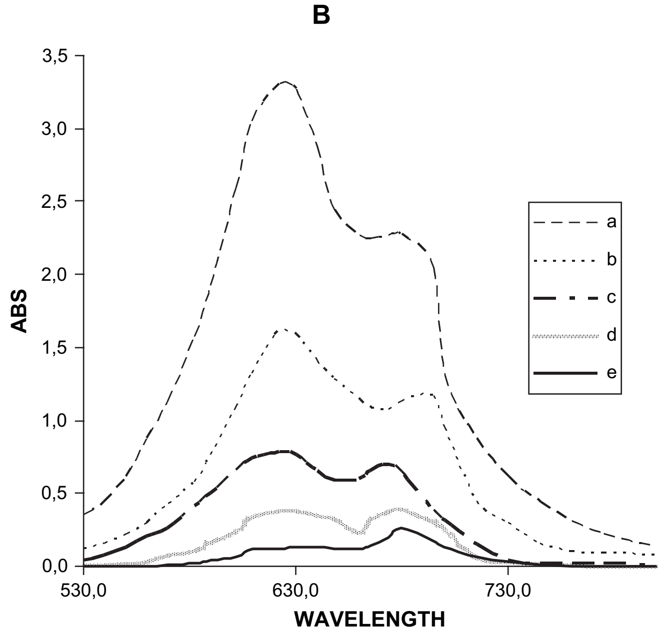

Fig. 5. Changes in the UV–vis spectra of **9** with different concentration ((a – 5,95; b – 2,97; c – 1,49; d – 0,745; e – 0,38)×10^{-4} M) in CH_2Cl_2.

H_2pcs, the λ_{max} of the metallo-pcs moved to shorter wavelengths and decreased in the order Znpcs, Nipcs, Copcs, due to the nature of the central metal ion. Zn and Co derivatives of the newly synthesized metallo-phthalocyanines (**7**, **8**) exhibit intense Q bands around 660–680 nm without any shoulder on the higher energy side, which would correspond to aggregated species [13,19–22].

When the electronic spectra of the nickel(II) phthalocyaninates **5** and **9** were carefully examined, a clear difference from the other metallo-pcs could be easily observed. The Q band was split into two peaks at 629 and 683 nm in DMF in the case of compound **5** and at 626 and 680 nm in dichloromethane in the case of compound **9** (Figs. 4 and 5). At higher concentrations ($\geq 10^{-4}$ M), the intensity of the higher energy peak corresponding to aggregated species has increased while that of the monomeric ones at lower energy decreased. At lower concentrations, the intensity of the peak corresponding to monomeric species increased. These can be assigned to the perfect planarity of the d^8 metal pcs in the case of **5** and **9** [8].

In conclusion, phthalocyanines simultaneously containing S-donor groups capable of binding transition metal ions and four hydroxyethyl substituents with reactive end groups are described. Four hydroxyethyl-substituted phthalocyanines show more solubility in organic solvents such as DMSO, DMF, and pyridine than eight hydroxyethyl-substituted phthalocyanines. The reason for the enhancement of solubility in the tetra substitution is probably based on it being a mixture of positional isomers rather than a single product. Esterification of hydroxyethyl groups brings forward more soluble products in less polar solvents such as chloroform, THF, and dichloromethane.

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