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Synthesis of phthalocyanines with tridentate branched bulky and alkylthio groups

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Abstract

The synthesis and characterisation of 4,5-octasubstituted metal free and metallo (Zn^{II} and Co^{II}) phthalocyanines carrying four alkylthio groups and four tridentate NNS substituents on periferal positions are reported. The distinct differences encountered in the newly synthesized compounds with four alkyl chains are their high solubility in common organic solvents, e.g. chloroform, dichlorometane, THF, acetone, DMF and DMSO and bathochromic shifts in the UV-Vis spectra in comparison with 4,5-substituted analogues with four chloro groups in addition to four branched bulky groups. ^{1}H NMR spectroscopy also shows a smaller up field shift in all protons for newly synthesised phthalocyanines with respect to the latter compounds.

Keywords: Phthalocyanines; Benzothiazoline; Hexhylthio; Zinc(II); Cobalt(II)

1. Introduction

In addition to their extensive use as dyes and pigments, phthalocyanines and metal phthalocyanines have been investigated for many years in detail because of their wide application fields including use in chemical sensors, liquid crystals, Langmuir-Blodgett films, nonlinear optics, optical data storage and as carrier generation materials in near-IR. Substituted derivatives can also be used for photodynamic cancer therapy and other processes driven by visible light [1, 2]. A decisive disadvantage of phthalocyanines and metal phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing bulky or long chain groups, e.g. alkyl, alkoxy into the peripheral positions of the phthalocyanine framework [3–10].

Although the symmetrically octasubstituted (where all the eight substituents are the same) and tetrasubstituted phthalocyanines have been frequently encountered, octasubstituted phthalocyanines obtained from disubstituted derivatives with two different substituents in the 4,5-positions are relatively less studied and only a few well characterized species are known [10,11]. This new class of substituted phthalocyanines usually exhibit higher solubilities and also give a mixture of positional isomers. A mixture of similar isomers may practically be more useful than a single, less soluble isomer [12].

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Recently, it has been shown that substitution of only one of the chlorine moieties in 4,5-dichlorophthalonitrile can be accomplished when the entering group is sufficiently bulky (e.g. 2-(2-pyridylmethylamino)phenyl-mercaptan) [11]. The aim of the present work is to test the reactivity of the remaining chlorine group with a flexible moiety and hexylthio-unit has been chosen for this purpose because of the ease with which it reacts with 4,5-dichlorophthalonitrile as reported earlier [7].

A consequence of incorporating a sulfanyl substituents on the periphery has been a shift of the Q-band absorption to longer wavelengths in the electronic spectra [13] and it is preferred in the case of number of applications such as IR absorbers and photosensitizers. While the presence of the chlorine group at the 4,5-positions causes a small blue shift, substitution with alkyl chains instead of chloro groups leads to an increase of this bathochromic shift [14]. In this work, the synthesis of substituted phthalonitrile with a branched bulky group in the 4-position and alklythioether group in the 5-position have been reported using the substituted reaction method. Metal free and metal phthalocyanines [M = Zn^{II} and Co^{II}] have been synthesized from these phthalonitrile derivative.

2. Experimental

Routine IR spectra were recorded on a ATI Unicom-Mattson 1000 spectrophotometer using KBr pellets, electronic spectra on ATI Unicom UV/Vis spectrophotometer UV2. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TÜBİTAK Marmara Research Centre. ^{1}H NMR and ^{13} C NMR spectra were recorded on a Bruker 200 MHz spectrometer, mass spectra on a VG Zabspec GS-MS spectrometer. All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified as describe by Perrin and Armarego [15]. The solvents were stored over molecular sieves (4 Å). The homogeneity of the products was tested in each step by TLC (SiO_2). 1,2-Dichloro-4,5-dicyanobenzene [16] and 1 - chloro - 3,4 - dicyano - 6 - [2 - (2 - pyridylmethylamino)phenyl-sulfanyl]benzene were prepared by reported procedures [11].

2.1. *1-Hexhylthio-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenyl-sulfanyl]benzene (2)*

1-Chloro-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenyl-sulfanyl]benzene **1** (2.26 g, 6.0 mmol) was dissolved in absolute tetrahydrofuran (100 cm^3) under nitrogen. A solution of hexanethiol (0.85 cm^3, 6.0 mmol) in absolute tetrahydrofuran (250 cm^3) was added dropwise. After stirring for 10 min finely ground anhydrous potassium carbonate (1.25 g, 9.0 mmol) was added. The reaction mixture was stirred under nitrogen at reflux temperature for 4 days. After cooling the mixture, the solvent was evaporated to dryness. Diethyl ether (100 cm^3) was added, the oily residue and the obtained precipitate was filtered off, washed with water several times, then washed with cold ethanol. The solid residue was crystallized from ethanol. Yield, 1.66 g (60%); m.p. 119–120 °C; ν~: 3391–3350 (NH), 3080, 3055, 2978-2927 (alkyl CH), 2233 (C≡N), 1583-1566 (pyridine C = N), 1523, 1472, 1446, 1344, 1319, 1293, 1242, 1140, 1114, 1038, 1012, 936, 885, 782, 757, 553, 525; ^{1}H NMR ($CDCl_3$): δ: 0.89 (t, 3H, CH_3), 1.28–1.35 (*m*, 4H, CCH_2C), 1.47–1.54 (*m*, 2H, CCH_2C), 1.78 (*qnt*, 2H, $SCCH_2$), 3.08 (*t*, 2H, SCH_2), 4.47 (*d*, 2H, CH_2), 5.72 (*bs*, 1H, NH), 6.69–7.69 (*m*, 9H, Ar-H), 8.49 (*d*, 1H, pyridine H-6); ^{13}C NMR (APT), ($CDCl_3$): δ: 13.99 (CH_3), 22.47, 28.23, 28.55, 31.24 (CH_2), 33.04 (CH_2S), 109.81 (aromatic C), 111.10 (aromatic CH), 112.09 (aromatic C), 115.64 (C≡N), 118.26, 128.98, 130.08, 133.23, 133.62 (aromatic CH), 136.89, 142.88 (aromatic C), 143.97 (aromatic C), 149.08 (aromatic C), 121.09 (pyridine CH), 122.34 (pyridine CH) 137.73 (pyridine CH), 149.32 (pyridine CH), 157.58 (pyridine C); MS (CI) m/z: 459 (M^+).

2.2. *Free phthalocyaninate (**3**)*

Compound **2** (0.2 g, 0.44 mmol) was heated in 2-(dimethylamino)ethanol (0.88 ml) with stirring and reflux for 4 h under nitrogen. After cooling to room temperature, ethanol (5 cm^3) was added in order to precipitate the product. The dark green product was filtered off and then washed with water and hot ethanol several times. It was isolated on silica gel column chromatography with chloroform/methanol (10:1 v/v) as an eluent. Yield, 0.042 g (21%); m.p. > 200 °C; ν∼: 3383–3366 (NH), 3310 (NH), 3080, 3029, 2978-2927 (alkyl CH), 1598–1583 (pyridine C=N), 1523, 1497, 1344, 1319, 1038, 782, 752. ^{1}H NMR ($CDCl_3$): δ:-4.11 (s, 2H, NH), 0.90 (t,12H, CH_3), 1.30–1.35 (*m*, 16H, CCH_2C), 1.45–1.55 (*m*, 8H, CCH_2C), 1.83 (*qnt*, 8H, $SCCH_2$), 3.09 (*t*, 8H, SCH_2), 4.49 (*s*, 8H, CH_2), 5.71 (*s*, 4H, NH), 6.66–7.72 (*m*, 36H, Ar-H), 8.49 (*d*, 4H, pyridine H-6).

2.3. *Zinc (II) phthalocyaninate (**4**)*

A mixture of compound **2** (0.150 g, 0.33 mmol), anhydrous zinc acetate (0.015 g, 0.081 mmol) and anhydrous DMF (0.9 cm^3) was heated and stirred at 160 °C in a sealed glass tube for 10 h under nitrogen. After cooling to room temperature, ethanol (4 cm^3) was added in order to precipitate the product. The dark green product was filtered off and then washed several times successively with hot water, hot EtOH and diethyl ether. It was isolated by silica gel column chromatography with chloroform/methanol (10:1 v/v) as an eluent. Yield, 0.043 g (28%); m.p. > 200 °C; ν∼: 3386–3360 (NH), 3080, 3028, 2978-2876 (alkyl CH), 1597–1585 (pyridine C=N), 1574, 1523, 1472, 1395, 1114, 1089, 854, 782, 757; ^{1}H NMR ($CDCl_3$): δ: 0.84 (t,12H, CH_3), 1.25–1.44 (*m*, 24H, CCH_2C), 1.78 (*qnt*, 8H, $SCCH_2$), 3.01 (*t*, 8H, SCH_2), 4.45 (*s*, 8H, CH_2), 5.68 (*s*, 4H, NH), 6.81–8.49 (*m*, 40H, Ar-H).

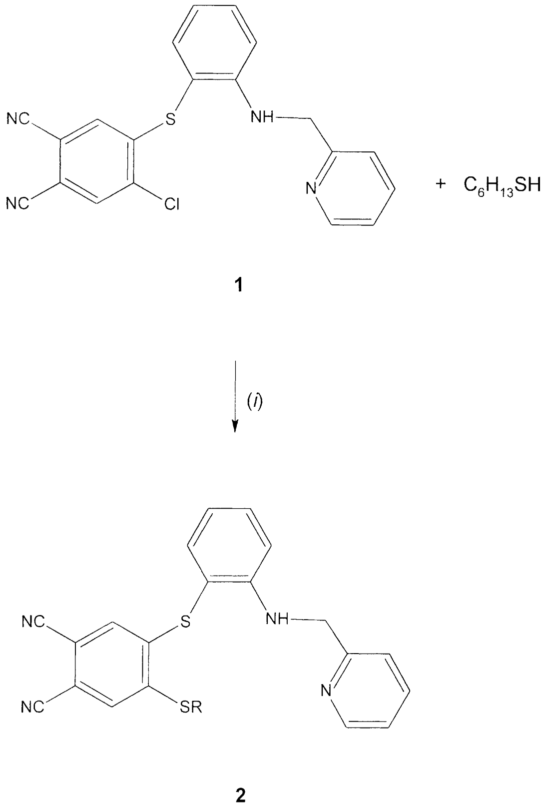
2.4. *Cobalt (II) Phthalocyaninate (**5**)*

A mixture of **2** (0.150 g, 0.33mmol), anhydrous $CoCl_2$ (0.011 g, 0.083 mmol) and anhydrous ethyleneglycol (0.7 cm^3) was heated and stirred at 160 °C for 5 h under nitrogen. After cooling to room temperature, ethanol (4 cm^3) was added in order to precipitate the product. The dark green product was filtered off and then washed several times successively with hot water, hot EtOH and diethyl ether. It was isolated by silica gel column chromatography with chloroform/methanol (10:1 v/v) as an eluent. Yield 0.025 g (16%); m.p. > 200 °C; ν∼: 3387-3361 (NH), 3080, 3029, 2979-2876 (alkyl CH), 1596-1584 (pyridine C=N), 1574, 1472, 1342, 1319, 1268, 1114, 961, 834, 757; MS (FAB) *m*/*z*: 1892.5 (M^+).

3. Results and discussion

The first step in the synthetic procedure outlined in Scheme 1 is the formation of the 1-hexhylthio-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenyl-sulfanyl]benzene (2).

Starting from 1-chloro-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenyl-sulfanyl]benzene (1) and n-hexanethiol, it has been accomplished by a base-catalyzed nucleophilic aromatic displacement [16, 17]. This reaction was carried out at reflux tem-



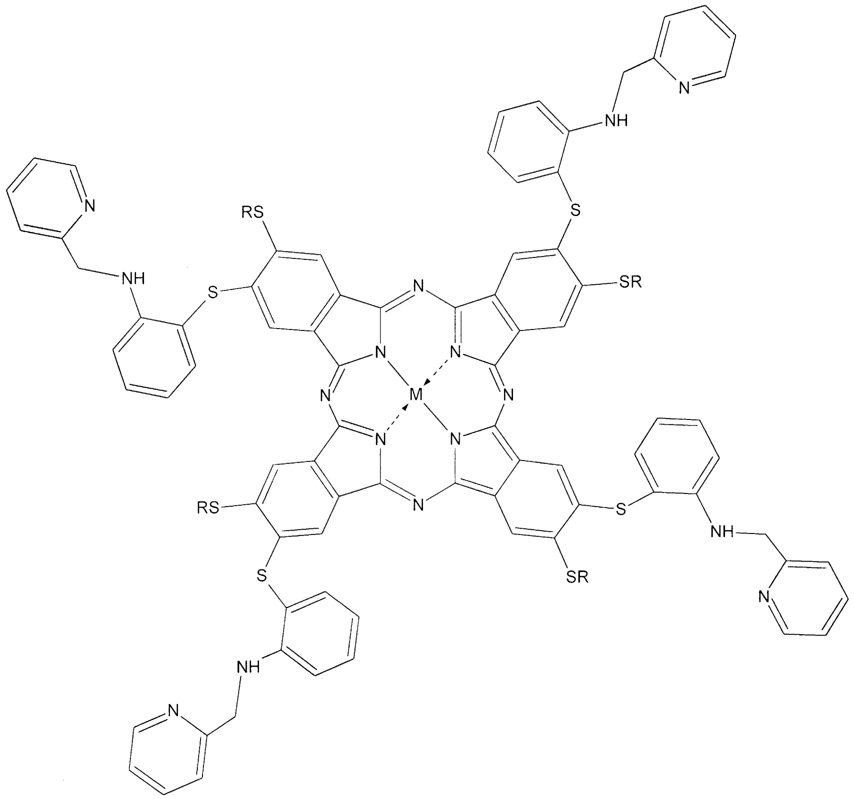
Scheme 1. K_2CO_3, THF.

perature in THF with K_2CO_3 as the base for 4 days. The yield of the reaction is 60%.

The usual synthetic routes were applied to obtain the metal-free phthalocyanine **3** and the phthalocyaninatometals **4**, **5**. Conversion of **2** into the metal free phthalocyanine **3** is accomplished directly by refluxing this reagent in a suitable solvent (i.e. 2-(dimethylamino)ethanol) to realise the cycloytetramerization [18].

The metal phthalocyaninates ($M = Zn^{II}$ or Co^{II}) are synthesized directly by cyclotetramerization of the corresponding dicyano compound **2** in the presence of the anhydrous metal salts ($Zn(OAc)_2$, $CoCl_2$) in a high boiling solvent such as DMF or ethyleneglycol.

The most obvious feature of the phthalocyanines **3–5**, when compared with that of the 1-chloro-3,4-dicyano-6(2-(2-pyridylmethyl-amino)phenyl-sulfanyl)-benzene substituted analog [11] is their extensive solubility in common organic solvents (e.g. chloroform, dichlormethan, tetrahydrofuran, DMF, ethylacetate...). The green products were isolated by column chromatography. Characterization of the products involved a combination of methods including elemental analysis (Table 1), ^1H and ^{13}C NMR, UV/Vis (Table 2), IR and mass spectroscopy. It might be generally expected that when a mixture of positional isomers are investigated by ^1H and ^{13} C-NMR spectra, peaks for each proton or carbon



R= C_6H_{13}

3 M = 2H

4 M = Zn

5 M = Co

Table 1
Elemental analyses result

Compound	Formula	Analysis calcd. (found)		
		C	H	N
3	$C_{104}H_{106}N_{16}S_8$	68.05 (67.82)	5.78 (5.45)	12.21 (12.06)
4	$C_{104}H_{104}N_{16}S_8Zn$	65.79 (65.27)	5.48 (5.23)	11.81 (11.67)
5	$C_{104}H_{104}N_{16}S_8Co$	65.99 (65.51)	5.50 (5.29)	11.85 (11.64)

Table 2
Electronic spectra of phthalocyanines in chloroform

Compound	λ_{max}/nm($10^{-4}\epsilon$/dm^{3}mol^{-1}cm^{-1})
3	730 (15.76), 700 (13.75), 667 (4.49), 359 (10.60)
4	713 (14.73), 645 (4.20), 371 (9.26)
5	702 (8.30), 635 (2.61), 321 (5.09)

atom should be either further splitted or broadened. However, although the phthalocyanines **3–5** are mixtures of isomers, we could observed neither broadening nor further splitting in the ^{1}H NMR spectra. The reason for this might be the relatively identical chemical environment in each case.

Comparison of the IR spectra of **1** and **2** gave some hints as the nature of the products. The IR spectrum of the 2 clearly indicates the presence of the alkyl groups by the intense stretching bands at 2978-2927 cm^{-1} (C–H). The rest of the spectrum of **2** is closely similar to that of 1 including the characteristic vibrations of CN, NH and pyridine groups. The band at 3350 cm^{-1} for **2** can be attributed to the NH stretching frequency. In addition, the characteristic vibrations of the C≡N and pyridine C=N appear at 2233 and 1583-1566 cm^{-1} respectively.

In the ^{1}H NMR analysis of **2** in deuterated $CHCl_3$, the pyridine protons appear as a doublet of doublet δ 8.49 ppm, the NH protons as a singlet δ 5.72 ppm, the aliphatic CH_3 protons as a triplet at δ 0.89 ppm and the SCH_2, $SCCH_2$ protons at δ 3.08 and 1.78 ppm, respectively.

The ^{13}C NMR spectral data are in accord with the expected structure. In the attached proton test (APT) ^{13}C NMR spectra of the phthalonitrile derivative **2** quaternary pyridine carbon atom is at lowest field δ 157.58 ppm, and the rest of the protonated aromatic and unsaturated carbon atoms appear in the range at δ 109.81–149.32 ppm. Two different groups are attached to the phthalonitrile unit, nitrile carbons come out as a single peak at 115.64 ppm. This might be contradictory to the two separate peaks reported for compound **1** at 115.17–115.48 ppm. However, it can be rationalised by the presence of two thioether substituents in compound **2** so the appearance of a single peak is reasonable. Also the alkyl carbon atoms are observed as six signals at δ 13.99–33.04 ppm.

A diagnostic feature of the phthalocyanine formation from the dicyano compound **2** is the disappearance of the sharp C≡N peak of the reactant. In the IR spectra of metal free phthalocyanine **3**, the cavity NH stretching vibrations are observed at 3310 cm^{-1}.

The ^{1}H NMR spectrum of the **3** indicates aromatic protons δ 6.66–7.72 ppm, NH proton δ 5,71 ppm, as well as the protons of the internal NH groups δ−4.11ppm. The shift to higher field for the NH protons is a result of the 18 π-electron system of the phthalocyanine ring. The high up field shift of the cavity NH protons was also verified by deuterium exchange with D_2O.

^{1}H NMR investigations of zincphthalocyanine **4** provided the characteristic chemical shifts for the structure expected. ^{1}H NMR spectrum of the **4** exhibited the aromatic protons around δ 8.49–6.81 ppm as multiplets, NH protons as a singlet at δ 5.68 ppm and the aliphatic CH_3 protons as a triplet at δ 0.84 ppm.

Naturally, octasubstituted phthalocyanines obtained from disubstituted phthalonitriles containing two different substituents in the 4,5 positions are a mixture of four structural isomers, but the isolation and characterization of these isomers are hardly possible. In this work these isomers could not be separated by column chromatography and HPLC methods using different solvents.

The UV-VIS spectra of the phthalocyanines were highly solvent- and concentration- dependent. At high concentrations or with solvents of high protic character, aggregates are formed. In general, phthalocyanines show typical electronic spectra with two strong absorption regions, 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 UV spectrum of **3–5** exhibited intense Q absorption band above 700 nm. When compared with octakis(alkyl, alkoxy) substituted ones, the shift of this intense band is especially important and will receive further attention for various near-IR applications. The electronic absorption spectrum of metal free phthalocyanine **3** exhibits a partly split Q band absorption at ca. 730 and 700 nm, which is due to the $\pi \rightarrow \pi^*$ transition of this completely conjugated 18 π electron system. Metalo derivatives **4**,**5** show only a single band in this region.

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