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Synthesis and Characterization of New Phthalocyanines Peripherally Fused to Four 21-Membered Dithiacrown Ether Macrocycles

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Summary. A novel metal-free phthalocyanine and its nickel(II) and copper(II) phthalocyaninato complexes were prepared. The new compounds were characterized by elemental analyses, ^{1}H- and ^{13}C-NMR, IR, UV-Vis, and mass spectral data. The NMR and/or UV-Vis spectra of these compounds showed extremely broad bands and/or peaks. This phenomenon seems to be related to the presence of the sulfur substituents, which is consistent with the data observed for similar compounds. The absorption spectra of these compounds were greatly affected by aggregation processes.

Keywords. Metal-free phthalocyanine; Dibromo-derivative; Pigments; Aggregation.

Introduction

Phthalocyanines comprise a remarkably versatile class of compounds because of their enormous technological significance for the manufacture of blue and green pigments. In recent years, various other properties have been investigated for new applications such as photodynamic cancer therapy, photosensitization is solution, electrocatalysts for dioxygen reduction in fuel cells, electrochromic processess as thin films, photoreductions or photooxidations in photoelectrochemical cells, material for electrophotography, optical information storage systems, catalysts for mercaptan oxidations, and use as sensors [1–4]. Solubility in conventional solvents is a common prerequisite for most of their technological applications [5]. Moreover, additional properties such as thermal stability, electrical conductivity, and wavelength of the Q band absorption have been obtained by generation of modified phthalocyanines and purpose-designed materials [6–8].

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The other important building blocks for constructing devices with appropriate properties are crown ethers. These structures are known to selectively bind alkali metal ions, and metal complexation can lead to a specific response such as a change in electrical conductivity [9, 10].

Substituted phthalocyanines with four crown ether rings have been reported independently by the groups of *Bekaroğlu*, *Kobayashi*, and *Nolte* [11]. These compounds have been reported to display solvent- and metal ion-induced aggregation behaviour [12]. Phthalocyanines with azacrown ether and thiacrown ether substituents being capable of binding transition metal ions have also been synthesized and characterized by the same groups [13]. Moreover, modifications have been made specifically on the connection of the crown ether rings to the phthalocyanine core [14]. With these derivatives, linear and two dimensional network polymers [15, 16] have been observed.

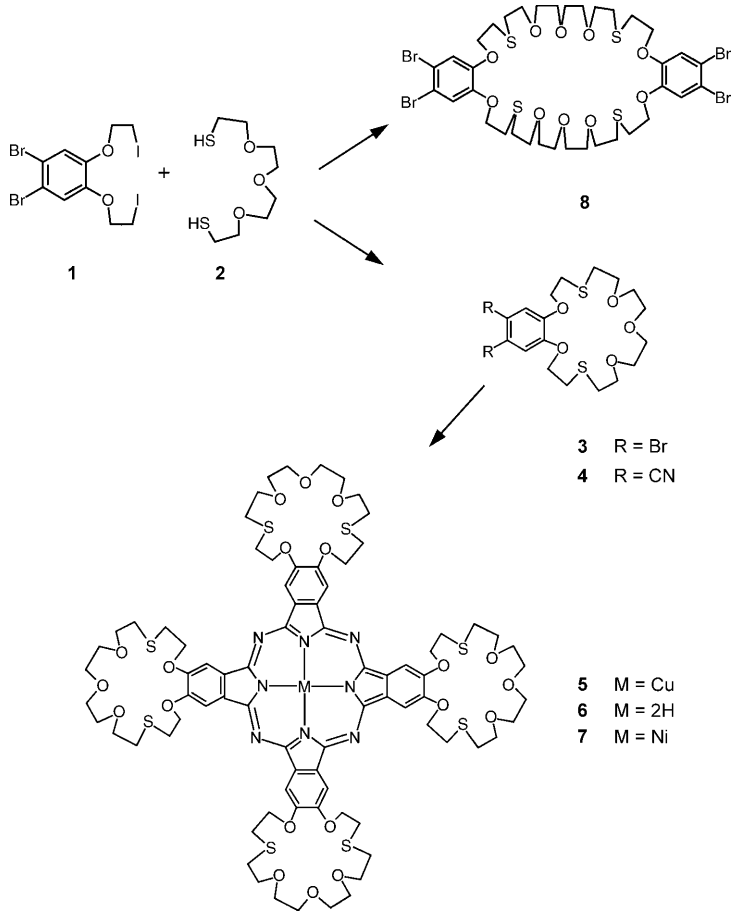
The primary aim of this work was the synthesis of new phthalocyanines with various functional groups and/or macrocycles. For this purpose, a dicyano derivative **4** was used to obtain both metal-free 21-membered symmetrical monobenzodithiacrown ether macrocycle **6** and its Ni(II) and Cu(II) complexes.

Results and Discussion

Starting from 1,2-dibromo-4,5-bis-(2-iodoethoxy)-benzene (**1**) [17, 24], the general route for the synthesis of new phthalocyanines is outlined in Scheme 1. Under high dilution conditions, **1** was treated with 2-{2-[2-(2-mercaptoethoxy)-ethoxy]-ethoxy}-ethanethiol (**2**) [18] in dry ethanol using dry Na_2CO_3 as base to give the 21-membered symmetrical monobenzodithia crown ether macrocycle **3**. The ring closure reaction gave a relatively moderate yield of 44%. It was necessary to use equivalent amounts of the two reactants to promote a 1:1 condensation. However, 2:2 condensation products or other by-products could also be detected in low yields. Thus, the tetrabromo-derivative of dibenzotetrathia-42-crown-14 **8** could be separated chromatographically and it structure was established spectroscopically.

The dibromo-derivative **3** was directly converted into the copper(II) phthalocyanine derivative **5** by the reaction of with CuCN in dry tetramethylurea (*TMU*). The yield of the crude product was rather low as reported earlier for other derivatives [19]. The dicyano-derivative **4** was prepared under mild conditions as reported previously [13a]. Cyclotetramerization of the dicyano-derivative **4** to the metal-free phthalocyanine **6** was accomplished in dry *n*-pentanol in presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (*DBU*) [20a, 21]. The reaction of **4** in *n*-amyl alcohol with anhydrous nickel(II) acetate gave the monomeric nickel phthalocyanine **7** [20b]. All of the obtained compounds were characterized by elemental analysis, and IR, UV/VIS, mass, and NMR spectrocopic techniques.

Analytical and spectroscopic data of **3** confirmed the success of the cyclization reaction. In the ^{1}H-NMR spectrum of **3**, the chemical shifts belonging to aliphatic –SH protons ($\delta = 1.2$) in the precursor **2** disappeared after the macrocyclization and the two peaks connected to each other at $\delta = 2.816$–2.848 ppm of S–CH_2 and at $\delta = 2.878$–2.942 ppm belonging to CH_2–S were observed instead ^{13}C-NMR (APT) spectral data were also in agreement with the proposed structure. The three carbon resonances belonging to the phenyl group of the macrocycle appeared at $\delta = 115.9$,



Scheme 1

118.1, and 148.2 ppm respectively. The other carbon chemical shifts (methylene groups connected to oxygene and sulphur) were observed at $\delta = 32.0$, 33.8 and $\delta = 70.5$, 70.5, 72.0, and 72.1 ppm. In addition, comparison of the IR data of **2** and **3** gave support for the proposed structure. They indicated the formation of **3** by the disappearance of the aliphatic –SH band of **2** at 2256 cm^{-1} and of the CH_2–I band of **1** at 532 cm^{-1}, and the appearance of a new absorption at 1495–1462 cm^{-1} belonging to aliphatic CH_2–S. The spectrum of **3** also indicated the presence of alkyl protons by the intense stretching bands at 2900–2861 cm^{-1} (C–H). The mass spectrum of **3** confirmed the proposed structure with a molecular ion peak at $m/z = 546$ $[M]^+$. In the IR spectrum of dicyano compound **4** an intense absorption band thought to belong to C≡N was observed at 2226 cm^{-1}. The reminder of the spectrum is similar to that of the precursor dibromo-derivative. In the ^{1}H-NMR spectrum of **4**, the aromatic protons of the cyano-substituted benzene appeared as singlet at $\delta = 7.05$ and the other chemical shifts were observed at $\delta = 2.85$–2.88 ppm (SCH_2) and at $\delta = 3.04$–3.10 ppm (SCH_2), and $\delta = 4.14$–4.20 ppm ($ArOCH_2$). The ^{13}C-NMR (APT) spectrum of **4** showed slightly different signals for the aromatic carbons due to the C–Br to C–C≡N conversion as expected. The mass spectrum of **4** showed a molecular ion peak at $m/z = 439$ $[M + 1]^+$.

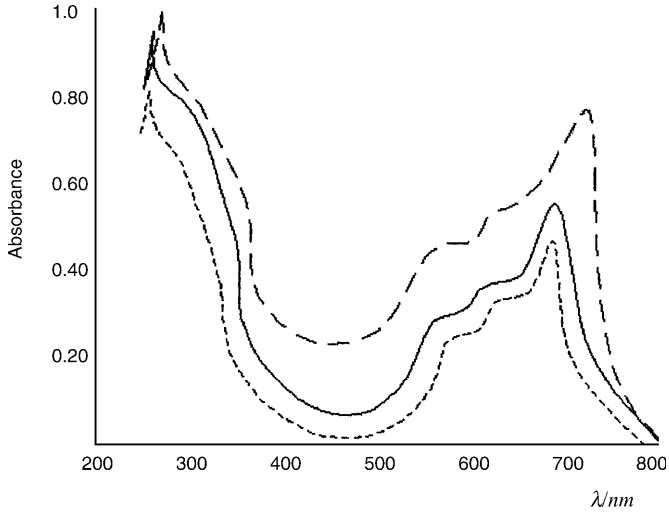


Fig. 1. UV-Vis spectra of (---) **5**, (— —) **6**, and (—) **7** in chloroform

Comparison of the IR, UV/Vis, MS spectral, and elemental analysis data of **5** supported the formation of the desired compound. The value of the observed molecular ion peak was consistent with the calculated value for copper(II) phthalocyanine ($m/z = 1834$ $[M + H_2O]^+$). The sharp C≡N vibration of **4** at 2226 cm^{-1} disappeared upon formation of metal-free phthalocyanine **6**, and the N–H band of the inner core of metal-free phthalocyanine was observed at 3430 cm^{-1} instead. The N–H protons of the metal-free phthalocyanine **6** could also be identified in the ^{1}H-NMR spectrum at $\delta = -4.81$ ppm, presenting the typical shielding of inner core protons as a weak broad band [22], which is a common feature of the ^{1}H-NMR spectra of phthalocyanines probably caused by aggregation [23a]. The mass spectrum (FAB) of **6** supported its structure with a molecular ion peak at $m/z = 1754$ $[M]^+$. In the same way, spectra of **7** were similar to those of **6** with absence of the weak broad N–H proton signals in NMR or of N–H stretching bands in the IR. The structure of **7** was verified by its mass spectrum with $m/z = 1751$ $[M–Ni\text{-}1]^+$.

The electronic absorption spectra of the compounds **5**, **6**, and **7** in chloroform are displayed in Fig. 1. All of the three compounds showed the intense Q band absorptions at 686, 690, and 722 nm together with two shoulders at about 626, 628, and 630 nm and 574, 578, and 579 nm. In the B band region, they showed peaks at 256, 259, and 267 nm with shoulders at about 287, 288, and 308 nm and weaker bands at 329, 350, and 363 nm. The shift of the Q band to the near-IR region is a result of *S*-substitution of the unsubstituted or *O*-substituted phthalocyanines [23b]. The absorption spectra of phthalocyanines are greatly affected by aggregation processes. In all cases, aggregation leads to significant shifts in the maximum of absorption in the visible region and to peak broadening.

Experimental

1,2-Dibromo-4,5-bis-(2-iodoethoxy)-benzene (**1**) [17, 24] and 2-{2-[2-(2-mercapto-ethoxy)-ethoxy]-ethoxy}-ethanethiol (**2**) [18] were prepared by reported procedures. ^{1}H- and ^{13}C-NMR (APT) spectra

were recorded on a Varian XL-200 NMR spectrophotometer. IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer in KBr pellets. FAB mass spectra were measured on a VG Zabspec GS-MS spectrometer. Elemental analyses were performed on a Hewlett-Packard 185 CHN analyzer; their values agreed with the calculated ones. UV/Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected.

2,3-Dibromo-6,7,9,10,12,13,15,16,18,19,21,22-dodecahydro-5,11,14,17,23-pentaoxa-8,20-dithia-benzocyclohenicosene (**3**, $C_{18}H_{26}Br_2O_5S_2$)
and $1^4,2^3,19^3,20^4$*-tetrabromo-3,9,12,15,21,23,29,32,35,41-dekaoxa-6,18,26,38-tetrathia-1,2,19,20-(1,2)-dibenzenacyclohentetraconta-phane* (**8**, $C_{36}H_{52}Br_4O_{10}S_4$)

To a boiling solution of 6.3 g dry Na_2CO_3 (59.68 mmol) in 600 cm^3 dry EtoH, a solution of 3.372 g **2** (14.92 mmol) and 8.59 g **1** (14.92 mmol) in 100 cm^3 dry EtoH was added over 8 h. The reaction mixture was refluxed for 51.5 h and EtoH was removed from the mixture. The oily residue was dissolved in 200 cm^3 $CHCl_3$ and the organic phase was washed with 50 cm^3 2N NaOH, 100 cm^3 brine and 2×150 cm^3 H_2O, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*. The residue was purified by column chromatography (silicagel, petroleum ether:ethyl acetate 1:1). Recrystallization from ethyl acetate yielded **3** as a white powder (3.6 g, 44%) and product **8** as a foamy solid (0.73 g, 9%).

Compound **3**: Mp 118–122°C; elemental anal. calcd. (%): C 39.57, H 4.80; found: C 39.47, H 4.87; IR (KBr): 2900–2861 (–CH_2), 1495–1462 (CH_2–S–C), 1249–1201 (Ar–O–C), 1117 (C–O), 655 (Ar–Br) cm^{-1}; ^{1}H-NMR($CDCl_3$): $\delta = 6.98$ (s, 2H-ar), 4.07 (t, $J = 6.3$ Hz, 2ArOCH_2), 3.67 (t, $J = 6.4$ Hz, 2OCH_2), 3.56 (s, 4OCH_2), 2.91 (t, $J = 6.4$ Hz, 2SCH_2), 2.82 (t, $J = 6.4$ Hz, 2SCH_2) ppm; ^{13}C-NMR(APT)($CDCl_3$): $\delta = 148.2$, 118.1, 115.9, 72.1, 72.0, 70.5, 70.5, 33.8, 32.0 ppm; FAB-MS: $m/z = 546\,[M]^+$.

Compound **8**: Mp 104–109°C; elemental anal. calcd. (%): C 39.57, H 4.80; found: C 39.40, H 4.90; IR (KBr): 3020 (Ar–H), 2902–2860 (–CH_2), 1498–1462 (CH_2–S–C) 1251–1200 (Ar–O–C), 1119–1117 (C–O), 649 (Ar–Br) cm^{-1}; ^{1}H-NMR($CDCl_3$): $\delta = 6.99$ (s, 4H-ar), 4.20 (m, 4ArOCH_2), 3.60 (m, 4OCH_2), 3.48 (s, 8OCH_2), 2.84 (m, 4SCH_2), 2.61 (m, 4SCH_2) ppm; ^{13}C-NMR(APT)($CDCl_3$): $\delta = 147.3$, 118.0, 116.0, 71.9, 72.0, 69.2, 68.3, 32.1, 31.0 ppm; FAB-MS: $m/z = 1094\,[M+1]^+$.

2,3-Dicyano-6,7,9,10,12,13,15,16,18,19,21,22-dodecahydro-5,11,14,17,23-pentaoxa-8,20-di-thia-benzocyclohenicosene (**4**, $C_{20}H_{26}N_2O_5S_2$)

A *Schlenk* tube was charged with 0.5 g **3** (0.915 mmol), 0.2471 g CuCN (2.746 mmol), and 3.5 cm^3 dry pyridine under Ar and then sealed. The reaction was held at 175–180°C for 8 h. After the brown mixture was cooled, it was diluted with 10 cm^{-3} dry ethanol, filtered to remove the inorganic impurities, and the filtrate was concentrated. The crude oily product was recrystallized from dry EtoH to give **4** as a light-brown powder. Yield 0.112 g (28%); mp 148–152°C; elemental anal. calcd. (%): C 54.77, H 5.98, N 6.39; found: C 54.69, H 5.46, N 6.46; IR (KBr): 2901–2863 (–CH_2), 2226 (C≡N) cm^{-1}; ^{1}H-NMR($CDCl_3$): $\delta = 7.05$ (s, 2H-ar), 4.17 (t, $J = 6.4$ Hz, 2ArOCH_2), 3.76 (t, $J = 6.6$ Hz, 2OCH_2), 3.69 (s, 4OCH_2), 3.07 (t, $J = 6.6$ Hz, 2SCH_2), 2.87 (t, $J = 6.6$ Hz, 2SCH_2) ppm; ^{13}C-NMR(APT)($CDCl_3$): $\delta = 149.0$, 117.5, 115.1 (C≡N), 106.1, 74.0, 72.3, 71.1, 70.4, 33.8, 31.4 ppm; FAB-MS: m/z: 439 $[M+1]^+$.

{Tetrakis([1,4,7,10,13,16,19]pentaoxadithiacyclohenicosano)[17,18-b: 17′,18′-g: 17″, 18″-l:17‴,18‴-q] phthalocyaninato}copper(II) (**5**, $C_{80}H_{104}CuN_8O_{20}S_8$)

A mixture of 0.2 g **3** (0.3663 mmol), 0.092 g CuCN (1.017 mmol), and 0.37 cm^3 dry *TMU* was heated and stirred at 190–195°C in a sealed glass tube for 3 h under N_2. After cooling to room temperature,

the dark green mixture was diluted with 5 cm^3 EtoH, mixed with 30 cm^3 aqueous NH_4OH (%25), and air was passed through the solution for 24 h. The solution became dark blue and a greenish-blue precipitate formed. This precipitate was isolated by filtration, washed with H_2O until the filtrate was neutral, and dried *in vacuo*. Yield 0.071 g (10.6%); mp 255–260°C (decomp.); elemental anal. calcd. (%): C 52.86, H 5.77, N 6.16, Cu 3.50; found: C 52.66, H 5.65, N 6.33, Cu 3.69; IR (KBr) 3064 (Ar–H), 2930–2870 (–CH_2), 1581, 1496, 1462, 1382, 1353, 1295, 1249, 1201, 1117, 1115, 1016, 906, 838, 801, 650 cm^{-1}; UV-Vis ($CHCl_3$, λ_{max}, nm)($10^{-4}\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 686 (4000), 626 (3250), 574 (2375), 329 (3812), 287 (6625), 256 (8125); FAB-MS: $m/z = 1834\,[M + H_2O]^+$.

Tetrakis([1,4,7,10,13,16,19]pentaoxadithiacyclohenicosano)[17,18-b: 17′,18′-g: 17″, 18″-l:17‴,18‴-q] phthalocyanine (**6**, $C_{80}H_{106}N_8O_{20}S_8$)

Compound **4** (0.147 g; 0.336 mmol) was refluxed for 18 h under stirring and Ar in 11 cm^3 dry *n*-pentanol in the presence of 0.06 cm^3 *DBU* (0.369 mmol). After the hot mixture was filtered, the dark green precipitate was washed with 50 cm^3 hot EtoH. The precipitate was then treated at 60–70°C with dry 5 cm^3 *DMF*, filtered, washed with hot EtoH and Et_2O, and dried *in vacuo*. Yield 0.15 g (26%); mp 278–284 (decomp.); elemental anal. calcd. (%): C 54.71, H 6.08, N 6.38; found: C 54.89, H 5.94, N 6.20; IR (KBr): 3430 (–NH) cm^{-1}; ^{1}H-NMR($CDCl_3$): $\delta = 6.9$–7.3 (m, 8H-ar), 4.31–4.21 (m, 8ArOCH_2), 3.79–3.73 (m, 8OCH_2), 3.71 (s, 16OCH_2), 3.04–2.86 (m, 16SCH_2), −4.81 (a weak broad, 2NH) ppm; UV-Vis ($CHCl_3$, λ_{max}, nm) ($10^{-4}\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 722 (7875), 630 (5500), 579 (4438), 363 (5312), 308 (8000), 267 (10000); FAB-MS: $m/z = 1754\,[M]^+$.

{Tetrakis([1,4,7,10,13,16,19]pentaoxadithiacyclohenicosano)[17,18-b: 17′,18′-g: 17″, 18″-l:17‴,18‴-q] phthalocyaninato}nickel(II) (**7**, $C_{80}H_{104}N_8NiO_{20}S_8$)

A mixture of 0.2 g **4** (0.4567 mmol) and 5 mg dry Ni $(OAc)_2$ (0.1685 mmol) in 11 cm^3 dry *n*-pentanol was heated to 90°C, and then a few drops *DBU* were added. The mixture was refluxed for 20 h. The solvent was then removed under reduced pressure to give a dark green solid. The crude product obtained was dissolved in a minimum amount of ethyl acetate and was precipitated by adding 10 cm^3 EtoH. A dark green solid was obtained after filtration and drying *in vacuo*. Yield 0.17 g (21%); mp > 300°C; elemental anal. calcd. (%): C 53.0, H 5.78, N 6.18, Ni 3.24; found: C 52.84, H 5.92, N 6.39, Ni 3.06; IR (KBr): 3020 (Ar–H), 2927–2871 (–CH_2), 1271–1221 (Ar–O–C) cm^{-1}; UV-Vis ($CHCl_3$, λ_{max}, nm) ($10^{-4}\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 690 (5625), 628 (3625), 578 (2900), 350 (4875), 288 (7750), 259 (9625); FAB-MS: $m/z = 1751\,[M–Ni-1]^+$.

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