Monatshefte für Chemie 134, 1027–1031 (2003)
DOI 10.1007/s00706-003-0004-6

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Metal-Containing Phthalocyanines Substituted with One Branched Bulky Moiety and Six Alkylthio Groups

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Received November 27, 2002; accepted (revised) December 2, 2002

Summary. Unsymmetrically substituted metal-phthalocyanines composed of three hexylthio groups and one 1-chloro-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenylthio]benzene moiety was prepared by cyclization of the reactants in the presence of the anhydrous metal salts $Zn(CH_3COO)_2$, $NiCl_2$, and $CoCl_2$. The new unsymmetric phthalocyanines are very soluble in common organic solvents. The compounds were characterised by their elemental analyses, IR, ^{1}H NMR, MS and UV/Vis spectra.

Keyword. Metal-phthalocyanines, unsymmetric.

Introduction

Phthalocyanines exhibit a number of unique properties that make them of great interest in different scientific and technological areas. Some technological applications of these macrocycles have been intensively investigated, such as electrophotograpy, photovoltaic and solar cells, semiconductor devices, rectifying devices, molecular electronics, *Langmuir-Blodgett* films, electrochromic display devices, low-dimensional conductors and synthetic metals, gas sensors, liquid crystals, nonlinear optics, optical disks, photosensitizers in photodynamic cancer therapy, and electrocatalytic agents [1].

Phthalocyanines are highly stable and versatile aromatic macrocyclic compounds, capable of including more than 70 metallic and non-metallic ions in the ring cavity. Moreover, the properties of phthalocyanines can be tuned in a wide range, by introducing various substituents into the periphery of the macrocycle, alkyl chains and alkoxy groups [2–7].

The synthesis and isolation of unsymmetrically substituted phthalocyanines are still of great interest. There are three principal synthetic strategies for preparing 3:1 phthalocyanines: the polymer support route, the subphthalocyanine route, and the statistical condensation route [8–11]. The most common method is the statistical condensation of two differently substituted dinitriles or diiminoisoindolines followed by chromatographic separation of the resulting mixture.

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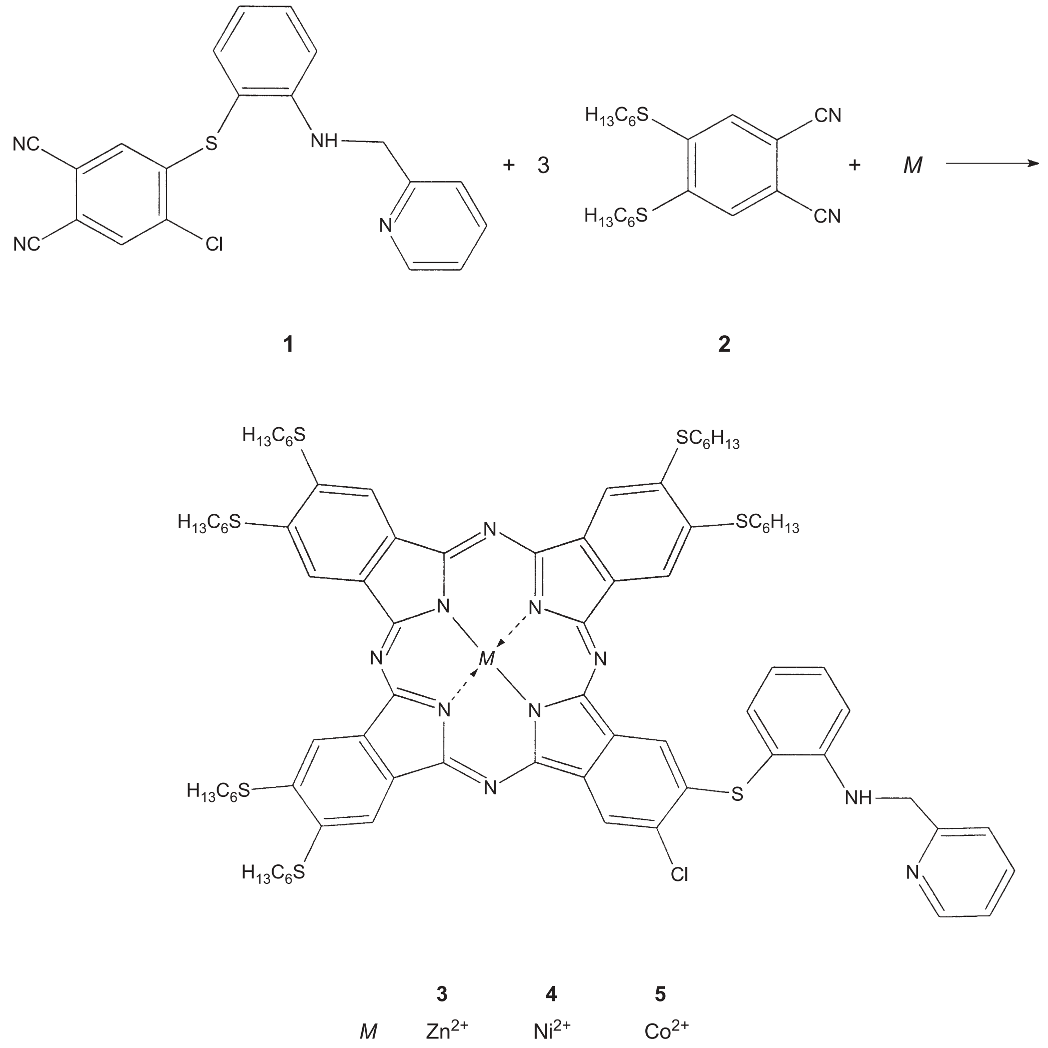

Scheme

In the present paper, we report the synthesis and characterization of unsymmetrically substituted metallo phthalocyanines, obtained by mixed condensation of 1-chloro-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenylthio]benzene (**1**) and 1,2-di(hexylthio)-4,5-dicyanobenzene (**2**).

Results and Discussion

The most simple approach to the preparation of unsymmetrically substituted phthalocyanines is the mixed condensation of two different substituted phythalonitriles. In principle, by using two different precursors there are six possible products. The desired unsymmetrical phthalocyanines can be synthesised by controlling the relative amount of the two phthalonitriles. Using two different phthalyl derivatives in a 3:1 ratio provides a mixture of products A_4 (33%), A_3B (44%), and other phthalocyanine products (23%) [12]. The precursors' different polarities may permit separation of the unsymmetrical phthalocyanines.

The synthesis of unsymmetrical phthalocyanines started with the cocyclization of **1** with **2** which was synthesized by treating 1,2-dichloro-4,5-dicyanobenzene with hexanethiol in *DMF*. K_2CO_3 was used as base for this nucleophilic aromatic displacement [13, 14]. The second precursor, **1**, was prepared from 1,2-dicloro-4,5-dicyanobenzene with 2-(2-pyridylmethylamino)benzenethiol in the presence of K_2CO_3 in *THF* [15, 16].

In this work, the statistical method was chosen to synthesize the unsymmetrical metallophthalocyanines **3**–**5**. The phthalocyanines were synthesized by cocyclotetramerization of three equivalents of **2** and one equivalent of **1** in the presence of the anhydrous metal salts $Zn(CH_3COO)_2$, $NiCl_2$, and $CoCl_2$ in anhydrous *n*-hexanol using 1,8-diazabicyclo[5.4.0]undec-7-ene (*DBU*) as a strong base. After work-up the product mixtures were purified by chromatography over silica. The first fraction proved to be the corresponding octa(hexylthio)phthalocyanine, identified by TLC comparison with an authentic sample [17]. The second fraction which still contained traces of the octa(hexylthio)phthalocyanine together with the slower-moving compound gave after an additional chromatography the products **3**–**5** with yields in the order of 10%. The pure compounds were characterized by elemental analyses, IR, ^{1}H NMR, MS, and UV/Vis spectra. The hexakis(hexylthio) substituted phthalocyanines **3**–**5** are highly soluble in organic solvents like the symmetrically octakis(alkylthio) substituted phthalocyanines [14, 17].

Cyclotetramerization of the dinitriles was confirmed by the disappearance of the sharp C≡N vibration of the reagents **1** and **2**. The IR spectrum of **3** clearly indicated the presence of alkyl groups by the intense stretching bands at 2980–2865 cm^{-1}. The absorption bands at 3390 and 1588–1569 cm^{-1} in the IR spectrum of **3** can be assigned to NH and C=N groups. The IR spectra of the phthalocyanines **4** and **5** are very similar to that of **3**.

NMR investigations of unsymmetrical metalophthalocyanines **3** and **4** have provided the characteristic chemical shifts for the structures expected. In the ^{1}H NMR spectrum of **3**, the aromatic protons appear as a multiplet at 8.64–7.01 ppm and the NH and CH_2 protons of the pyridylmethylamino moiety at 6.71 and 5.08 ppm. Chemical shifts due to the alkyl protons of **3** are observed between 2.97 and 0.91 ppm as expected. The FAB mass spectrum of the phthalocyaninatocobalt(II) **5** confirmed the proposed structure. The M^+ ion is observed at $m/z = 1515.4$.

Phthalocyanines show remarkable optical properties. UV/Vis spectra of these compounds are dominated by two intense bands, the Q band at around 680 nm and the B band in the near UV region at around 330 nm, both correlated to $\pi \rightarrow \pi^*$ transitions. Octakis(alkylthio) substituted phthalocyanines show intense Q absorption bands above 700 nm [17], UV/Vis spectra of phthalocyanines **3**–**5** in *THF* exhibited the intense Q band absorptions of the $\pi \rightarrow \pi^*$ transitions at 702, 696, and 690 nm. B bands of this phthalocyanines appeared in the UV region at about 350 nm. An increase in concentration resulted in aggregation of phthalocyanine molecules, which is accompanied by a blue shift of the Q band with some decrease in intensity. It has also been concluded that aggregation is enhanced by solvent polarity and the presence of aliphatic side chains [18–20].

Conclusion

In conclusion, we have described the synthesis and spectra of a new group of unsymmetric pythalocyanines carrying both hexylthio and substituted phenylthio moieties simultaneously in order to make use of their solubilizing effect in organic solvents and their red shift of the Q bands. In addition, the peripheral chloro group on the phthalocyanine core offers a number of possibilities for further reactions, such as preparing a dimeric unsymmetrical phthalocyanine.

Experimental

IR spectra were recorded on a Mattison 1000 FTIR spectrophotometer using KBr pellets, electronic spectra on a Unicam UV2 spectrophotometer. Elementel analyses were performed by the Instrumental Analysis Laboratory of the TÜBİTAK Marmara Research Centre; these results agreed favourably with the calculated values (C, H, N). ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer using *TMS* as internal reference. Mass spectra were obtained with a VG Zabspec GS_MS spectrometer. Compounds **1** [15, 16] and **2** [14, 17] were synthesised according to published methods.

2,3,9,16,17-Hexakis(hexylthio)-23-chloro-24-[2-(2-pyridylmethylamino)phenylthio]-29H,31H-phthalocyaninatozinc(II) (**3**, $C_{80}H_{97}N_{10}S_7ClZn$)

A mixture of 0.298 g of **1** (0.79 mmol), 0.858 g of **2** (2.38 mmol), 0.145 g of anhydrous $Zn(CH_3COO)_2$ (0.79 mmol) and 0.063 ml of *DBU* was heated in 3.6 cm^3 of anhydrous *n*-hexanol with stirring and reflux at 155°C for 14 h under N_2. After cooling to room temperature, 4 cm^3 of ethanol were added in order to precipitate the product. This was filtered off and then washed several times with hot ethanol. It was subjected to a silica gel column using $CHCl_3$ as eluent to yield the symmetrical octahexylthiozincphthalocyanine. The eluent was then changed to *THF* and a second fraction was collected. This fraction was further purified by column chromatography (silica gel, CCl_4:*THF* = 10:1) to yield 0.135 g (12%) of **3**. IR: $\bar{\nu}_{max} = 3390$ (NH), 3075, 2980–2865 (alkyl CH), 1605, 1588–1569 (pyridine C=N), 1530, 1475, 1420, 1390, 1295, 1145, 970, 785, 756, 706, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.97$ (t, $J = 6.85$ Hz, $18CH_3$), 1.56 (m, $36CCH_2C$), 1.76 (dd, $J = 7.06$, 7.50 Hz, $12SCCH_2$), 3.01 (t, $J = 6.95$ Hz, $12SCH_2$), 5.13 (d, $J = 7.14$ Hz, $2CH_2$), 6.73 (s, NH), 8.64–7.01 (m, 16aryl-H); UV/Vis (*THF*): λ_{max} (lg ε) = 702 (4.72), 632 (3.94), 365 (4.25) nm.

2,3,9,16,17-Hexakis(hexylthio)-23-chloro-24-[2-(2-pyridylmethylamino)phenylthio]-29H,31H-phthalocyaninatonickel(II) (**4**, $C_{80}H_{97}N_{10}S_7ClNi$)

A mixture of 0.350 g of **1** (0.929 mmol), 1.003 g of **2** (2.787 mmol), and 0.119 g of anhydrous $NiCl_2$ (0.929 mmol) was heated in 4 cm^3 of anhydrous *n*-hexanol in the presence of 0.07 cm^3 of *DBU* at 150°C under N_2 with stirring for 24 h. After cooling to room temperature, the dark green mixture was diluted with ethanol until the crude product precipitated. It was filtered off and washed several times with hot ethanol. Finally, pure **4** was obtained by chromatography with silica gel using $CHCl_3$ as first eluent and then CCl_4:*THF* = 10:1 in a yield of 0.118 g (9%). IR: $\bar{\nu}_{max} = 3390$ (NH), 3071, 2978–2863 (alkyl CH), 1600, 1587–1564 (pyridine C=N), 1527, 1462, 1430, 1395, 1290, 1149, 972, 781, 756, 704, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 6.81$ Hz, $18CH_3$), 1.55 (m, $36CCH_2C$), 1.76 (dd, $J = 7.02$, 7.55 Hz, $12SCCH_2$), 2.97 (t, $J = 6.98$ Hz, $12SCH_2$), 5.08 (d, $J = 7.12$ Hz, $2CH_2$), 6.71 (s, NH), 8.59–6.98 (m, 16aryl-H); UV/Vis (*THF*): λ_{max} (lg ε) = 696 (4.29), 630 (3.97), 335 (4.25) nm.

2,3,9,16,17-Hexakis(hexylthio)-23-chloro-24-[2-(2-pyridylmethylamino)phenylthio]-29H,31H-phthalocyaninatocobalt(II) (**5**, $C_{80}H_{97}N_{10}S_7ClCo$)

A mixture of 0.300 g of **1** (0.80 mmol), 0.860 g of **2** (2.39 mmol), 0.104 g of anhydrous $CoCl_2$ (0.80 mmol), 0.063 cm^3 of *DBU* and 3.6 cm^3 of anhydrous *n*-hexanol was heated and stirred at 155°C for 18 h under N_2. The resulting green suspension was cooled and the crude product was precipitated by addition of 5 cm^3 of ethanol. The dark green product was filtered off and then washed several times with hot ethanol to remove unreacted materials. **5** was isolated on a silica gel column first with $CHCl_3$ and then with CCl_4:*THF* = 10:1 as eluents in a yield of 0.113 g (10%). IR: $\bar{\nu}_{max} = 3390$ (NH), 3076, 2980–2863 (alkyl CH), 1610, 1585–1572 (pyridine C=N), 1530, 1462, 1420, 1392, 1290, 1147, 970, 782, 756, 706, 664 cm^{-1}; UV/Vis (*THF*): λ_{max} (lg ε) = 690 (4.14), 635 (3.78), 329 (4.27) nm. MS (FAB): m/z (%) = 1515.4.

Acknowledgements

We thank the Research Fund of the Technical University of Istanbul.

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