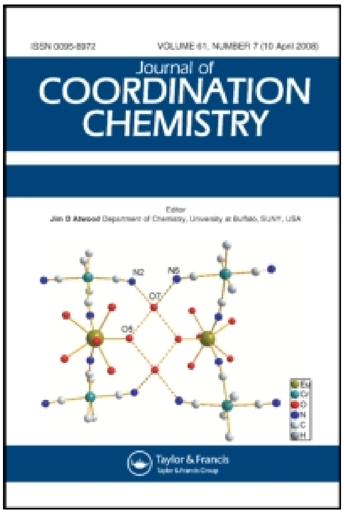

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Synthesis of new phthalocyanines substituted with four benzo[d]thiazol-2-ylthio groups

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Synthesis of new phthalocyanines substituted with four benzo[d]thiazol-2-ylthio groups

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The synthesis of a new phthalonitrile derivative (4-(benzo[d]thiazol-2-ylthio)phthalonitrile), its metal-free phthalocyanine, and metallo-phthalocyanines are described. Phthalocyanines are formed in high yield with template synthesis. These compounds showed considerable solubility in $CHCl_3$, DMF and DMSO, a primary condition for potential applications. The newly synthesized compounds have been characterized by elemental analyses, UV-Visible spectra, IR and ^{1}H-NMR.

Keywords: Phthalocyanines; Phthalonitrile derivatives; Template effect; Metal complexes; Synthesis

1. Introduction

Phthalocyanines are a class of macrocyclic compounds possessing conjugated π-electrons. Phthalocyanines have diverse application in the production of liquid crystals [1] as in laser-beam printer and photocopiers [2], in the production of data storage devices [3], dyes and green-blue pigments [4], nonlinear optics [5], photodynamic therapy [6], electrochromic and optical limiting devices [7], in photosensitizers [8], and in gas sensors [9]. Phthalocyanines have low solubility in most organic solvents and tend to aggregate [10–13]. This low solubility is a problem for applications, but can be addressed by introducing bulky substituents which will render them soluble by causing substantial disruption of the strong interactions of the parent phthalocyanine rings [13–15]. Metal phthalocyanines have attracted a great deal of interest due to their chemical inertness, very high thermal stability, electrical conductivity and catalytic activity [16–18]. The phthalocyanines are planar, divalent and tetradentate macrocyclic ligands forming complexes with a wide variety of metals and metalloids [19]. In this study, we explore a new synthetic route to functional macrocycles with (benzo[d]thiazol-2-ylthio)-substituents (scheme 1) which can be used in applications.

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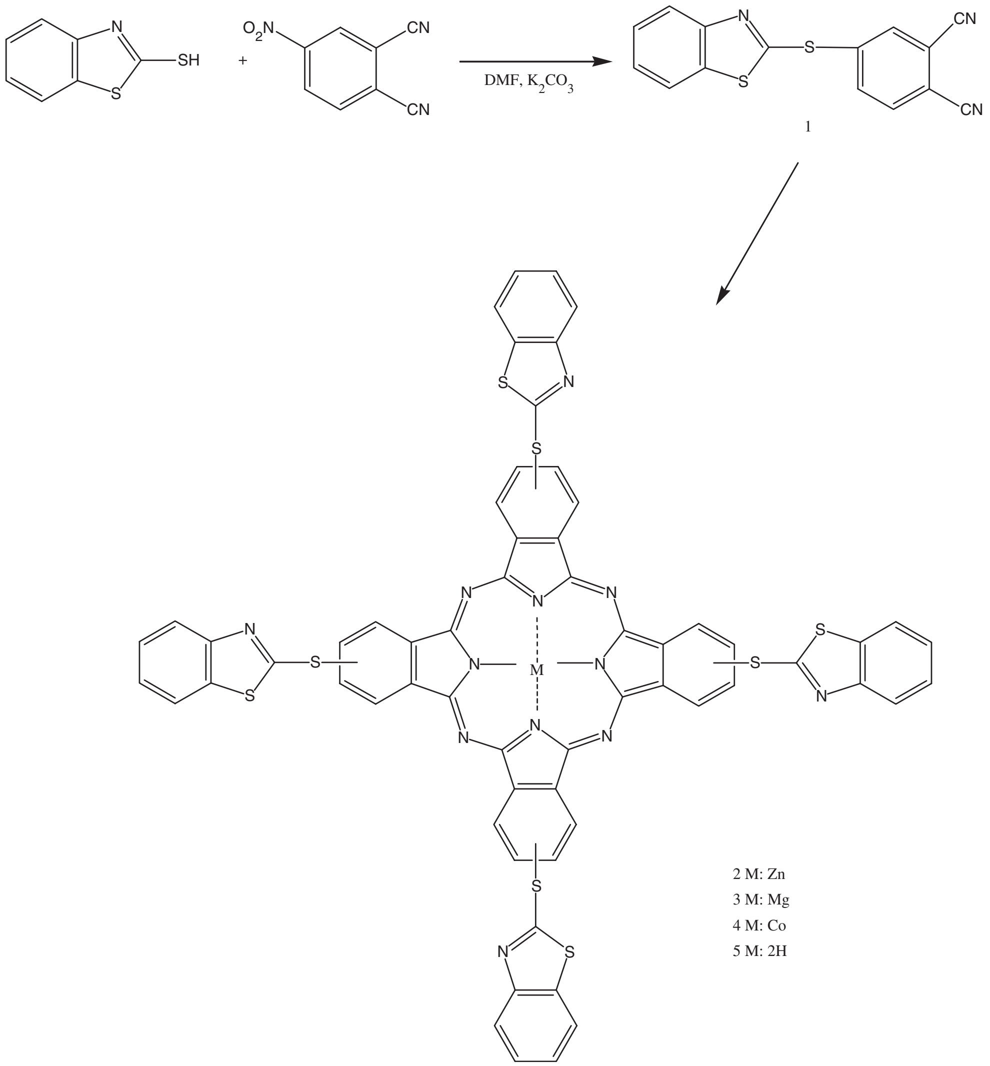

Scheme 1. Reagents and conditions: (1) DMF, K_2CO_3, N_2, room temperature; (2–4) MCl_2, 1-hexanol, DBU, N_2, 160°C; (5) Urea, 1-hexamol, N_2, 160°C.

2. Experimental

IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr pellets and electronic spectra on a SHIMADZU UV/Vis spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker 200 MHz spectrometer with tetramethylsilane as internal standard. Elemental analyses are in good agreement with calculated values. 4-nitrophthalonitrile was synthesized according to published procedures [20].

All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [21]; the solvents were stored over molecular sieves (4 Å).

2.1. *4-(benzo[d]thiazol-2-ylthio)phthalonitrile (1)*

The 4-nitrophthalonitrile (1.73 g, 0.01 mol) was dissolved in *N,N*-dimethylformamide (DMF) (30 cm^3) under nitrogen and benzo[d]thiaole-2-thiol (1.67 g, 0.01 mol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (5.52 g, 0.04 mol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Then the mixture was poured into ice-water, and the precipitate was filtered off, washed with water and dried. The residue was recrystallized from ethanol. The yield was 1.8 g (61.4%), m.p. 152–153°C. Calcd for $C_{15}H_7N_3S_2$: C, 61.41; H, 2.41; N, 14.32; S, 21.86%. Found: C, 61.35; H, 2.35; N, 14.15; S, 21.60%. IR spectrum (cm^{-1}): 3090, 3025, 2232, 1580, 1543, 1461, 1426, 1384, 1311, 966, 834, 753, 525. ^{1}H NMR (DMSO): $\delta = 7.45$ (1H, t, 7.3 Hz Ar–H), 7.53 (1H, t, 7.8 Hz Ar–H), 7.79 (1H, d, 8.3 Hz Ar–H), 7.85 (1H, d, 7.9 Hz Ar–H), 7.92 (1H, dd, 1.6 and 8.3 Hz, Ar–H), 8.02 (2H, m, Ar–H). ^{13}C NMR ($CDCl_3$): $\delta = 114.5$, 114.8, 115.0, 116.9, 121.3, 123.2, 126.1, 126.9, 133.8, 134.9, 135.0, 136.4, 140.2, 153.2, 159.4.

2.2. *Tetrakis[(benzo[d]thiazol-2-ylthio)phthalocyaninato]zinc(II) (2)*

4-(benzo[d]thiazol-2-ylthio) phthalonitrile (0.146 g, 0.0005 mol) and $ZnCl_2$ (0.017 g) were dissolved in 1-hexanol (1.8 cm^3) under nitrogen and in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.05 mL), heated with stirring at 160°C for 24 h under N_2. The mixture was then cooled to room temperature and product precipitated by adding the reaction mixture dropwise into ethanol. The crude product was purified by column chromatography (silica, $CHCI_3$: EtOH/4 : 1). This phthalocyanine is soluble in $CHCI_3$, DMF and DMSO. The yield was 0.055 g (35.5%). Calcd for $C_{60}H_{28}N_{12}S_8Zn$: C, 58.17; H, 2.38; N, 13.57; S, 20.71%. Found: C, 58.11; H, 2.40; N, 13.60; S, 20.69%. IR spectrum (cm^{-1}): 2916, 2848, 1708, 1637, 1538, 1441, 1303, 1087, 993, 742. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 688, 621 and 360. ^{1}H NMR (DMSO): $\delta = 7.2$–9.2 (28 H, m, Ar–H).

2.3. *Tetrakis[(benzo[d]thiazol-2-ylthio)phthalocyaninato]magnesium(II) (3)*

4-(benzo[d]thiazol-2-ylthio)phthalonitrile (0.146 g, 0.0005 mol) and $MgCl_2$ (0.026 g) were dissolved in 1-hexanol (1.8 cm^3) under nitrogen in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 mL), then heated with stirring at 160°C for 24 h under N_2. The mixture was then cooled to room temperature and product precipitated by adding the reaction mixture dropwise into ethanol. The crude product was purified by column chromatography (silica, $CHCI_3$: EtOH/5 : 1). This phthalocyanine is soluble in $CHCI_3$, DMF and DMSO. The yield was 0.057 g (38%). Calcd for $C_{60}H_{28}N_{12}S_8Mg$: C, 60.17; H, 2.36; N, 14.03; S, 21.42%. Found: C, 60.13; H, 2.38; N, 14.07; S, 21.37%. IR spectrum (cm^{-1}): 3474, 1706, 1643, 1598, 1479, 1453, 1420, 1382, 1304, 1087, 981, 750. UV–Vis ($CHCl_3$) λ_{max} nm (log ε): 692, 624 and 365. ^{1}H NMR (DMSO): $\delta = 7.2$–9.3 (28 H, m, Ar–H).

2.4. *Tetrakis[(benzo[d]thiazol-2-ylthio)phthalocyaninato]cobalt(II) (4)*

4-(benzo[d]thiazol-2-ylthio) phthalonitrile (0.146 g, 0.0005 mol) and $CoCl_2$ (0.017 g) were dissolved in 1-hexanol (1.8 cm^3) under nitrogen in the presence of

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 mL), then heated with stirring at 160°C for 21 h under N_2. The mixture was then cooled to room temperature and product precipitated by adding the reaction mixture dropwise into ethanol. The crude product was washed several times with EtOH to dissolve unreacted metal salt. The crude product was dissolved in DMF, the solution was filtered, and the product precipitated by adding EtOH. The crude product was washed several times with hot EtOH and methanol and dried *in vacuum* over $CaCl_2$. This phthalocyanine is soluble in $CHCl_3$, DMF and DMSO. The yield was 0.045 g (29%). Calcd for $C_{60}H_{28}N_{12}S_8Co$: C, 58.47; H, 2.29; N, 13.64; S, 20.81%. Found: C, 58.44; H, 2.32; N, 13.61; S, 20.85%. IR spectrum (cm^{-1}): 2914, 2843, 1591, 1515, 1406, 1304, 1247, 1089, 980, 746. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 669.

2.5. *Tetrakis[(benzo[d]thiazol-2-ylthio) phthalocyanine (5)*

4-(benzo[d]thiazol-2-ylthio) phthalonitrile (0.146 g, 0.0005 mol) and urea were dissolved in 1-hexanol (1.8 cm^3) under nitrogen, then heated with stirring at 160°C for 65 h under N_2. The mixture was then cooled to room temperature and washed several times with EtOH, acetone and chloroform. The crude product was dissolved in DMF, the solution filtered, and the product precipitated by adding EtOH. The product was washed several times with hot EtOH and methanol and dried *in vacuum* over $CaCl_2$. This phthalocyanine is soluble in DMF and DMSO. The yield was 0.036 g (24.5%). Calcd for $C_{60}H_{30}N_{12}S_8$: C, 61.31; H, 2.57; N, 14.30; S, 21.82%. Found: C, 61.26; H, 2.51; N, 14.33; S, 21.75%. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 682, 644 and 280. ^1H NMR (DMSO): $\delta = 8.1–7.42$ (30H, m, Ar–H).

3. Results and discussion

The synthetic route followed in this work is shown in scheme 1. 4-(benzo[d]thiazol-2-ylthio) phthalonitrile was prepared by nucleophilic displacement of nitro in 4-nitrophthalonitrile with benzo[d]thiaole-2-thiol. Cyclotetramerization of phthalonitrile derivatives in presence of the metal salts gave the desired metallophthalocyanines **2**–**4**. The free-metal phthalocyanine was obtained by cyclotetramerization of phthalonitrile derivatives in presence of urea.

The spectroscopic characterization of the newly synthesized compounds was performed by elemental analysis, ^1H NMR, IR and UV–Vis spectroscopy. The analyses were in accord with the proposed structures. In the IR spectrum of **1** (supplementary data), the intense absorption band at 2232 cm^{-1}, corresponding to $C{\equiv}N$ vibrations, disappears after conversion into phthalocyanines (**2**–**4**) [22]. The ^1H NMR spectrum of **1** indicates aromatic protons at δ 8.02, 7.92, 7.85, 7.79, 7.53, 7.45. The ^1H NMR spectra of **2**–**3** are similar with broad bands from aromatic protons at 9.2–7.2 and 9.3–7.2 ppm, respectively. The ^1H NMR spectrum of **5** appears as multiplets at 8.1–7.4 ppm.

The UV-Vis spectra of **2** (in $CHCl_3$, figure 1) and **3** (in $CHCl_3$, supplementary data) show the typical pattern of phthalocyaninato metal complexes, dominated by π–π* transitions within the heteroaromatic 18-π-electron system [6]. The electronic

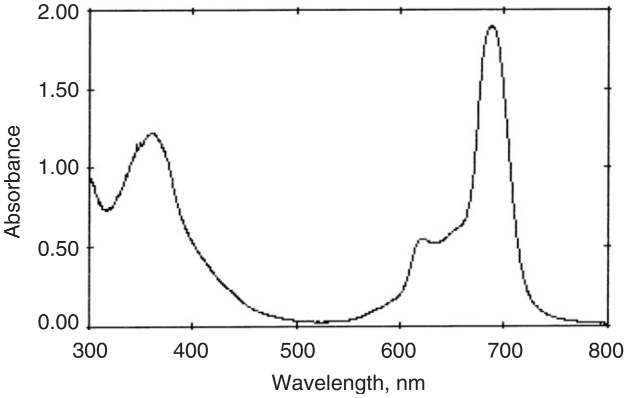

Figure 1. Electronic spectra of **2** in chloroform.

absorption spectra of **2**–**5** exhibited characteristic Q and B-bands. The peak at 621–692 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 Pc^{2-} ring, and the peak at 280–365 nm (B-band) arising from the deeper π-levels correspond to LUMO transition.

Tetra benzo[d]thiazol-2-ylthio-substituted Pcs showed enhanced solubility in a number of organic solvents, e.g. chloroform, DMF and DMSO, etc. as a primary condition for potential applications. Another important feature of these compounds is that they may be obtained in high yield through the template effect.

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