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Synthesis and characterization of new metallophthalocyanines bearing macrocyclic N_3O_2 groups on peripheral positions

Abstract: The synthesis and characterization of new zinc(II) **3**, nickel(II) **4** and cobalt(II) **5** phthalocyanines complexes carrying macrocyclic N_3O_2 groups on peripheral positions are described. The compounds were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, UV-Vis and MS spectral data.

Keywords: macrocyclic; metallophthalocyanine; mixed-donor macrocyclic; phthalocyanine; phthalonitrile; synthesis.

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Introduction

Phthalocyanines have been used as dyes and pigments for decades. They have also found practical applications as semiconductors, catalysts, chemical sensors, liquid crystals and materials for nonlinear optics (Moser and Thomas, 1983; Lkahl et al., 1986; Leznoff and Lever, 1996). A great number of remarkable applications of phthalocyanines arise from their unique 18π electron aromatic system, which instills high thermal and chemical stability and unique photoelectric properties (Du et al., 2003). A disadvantage of phthalocyanines is their limited solubility in common organic solvents. To increase solubility, phthalocyanines with long chains or macrocyclic moieties (Young and Onyebuagu, 1990; Bekaroğlu, 1996) have been synthesized. Although the term 'macrocyclic' was not included in the literature until the end of the third quarter of the 20th century, the natural macrocyclic structure bearing phthalocyanine rings as well as their metal complexes have been well known since the beginning of the 20th century. The chemistry of macrocyclic compounds and their complexes have shown rapid development after 1964. Synthetic macrocyclic compounds can be used as models for natural products (Gokel and Garcia, 1977).

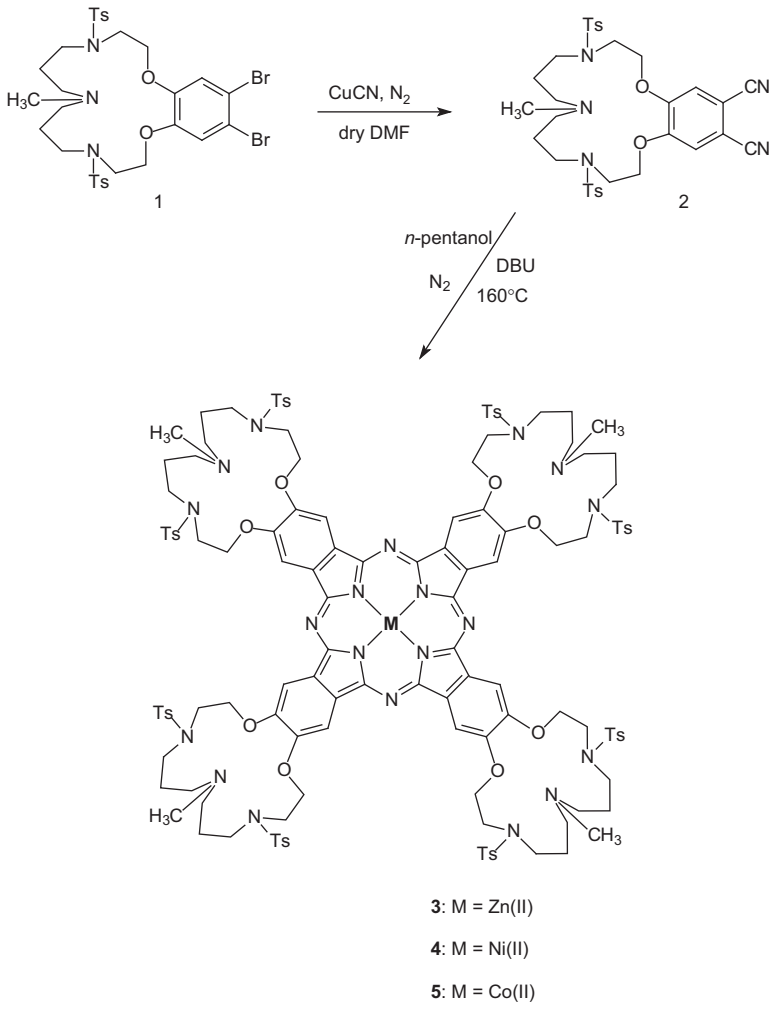
We have previously described the synthesis of new metal-free phthalocyanines and metallophthalocyanines bearing macrocyclic $N_2S_2O_2$ groups on peripheral positions (Kantekin et al., 2008). In this paper, we discuss metallophthalocyanines carrying symmetrically four macrocyclic N_3O_2 groups on peripheral positions.

Results and discussion

A convenient method for synthesis of phthalocyanines containing macrocyclic moieties uses the dibromo or dicyano derivatives of the corresponding macrocyclic units. In this work, the dibromo compound **1** (Keleşoğlu et al., 2010) was allowed to react with CuCN under the conditions of the Rosenmund von Braun reaction (Koçak et al., 1994) to furnish the desired compound **2** in 66% yield after purification by chromatography (Scheme 1). The structure of **2** is fully supported by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

The synthesis of the Zn complex **3** was accomplished by reacting **2** with anhydrous $Zn(CH_3COO)_2$ in dry *n*-pentanol in the presence of a catalytic amount of DBU as a strong base at 160°C under nitrogen. The desired compound **3** was obtained in 18% yield after purification by chromatography. The IR spectrum of **3** clearly lacks the C≡N stretching vibration at 2228 cm^{-1} that is seen in the IR spectrum of **2**. The NMR spectrum of this compound is similar to the spectrum of the precursor dicyano compound **2**. The mass spectrum of **3** shows a peak at $m/z = 2729$ for $[M+1]^+$. The elemental analysis confirms the given composition of compound **3**.

The synthesis of NiPc **4** was accomplished by reacting **2** with anhydrous $NiCl_2$ under similar conditions. The product **4** was obtained in 17% yield after purification by chromatography. The synthesis of CoPc **5** was accomplished in a similar way by reacting **2** with anhydrous $CoCl_2$. After chromatography, the desired compound **5** was obtained in 15% yield. The given structures of **4** and **5** are fully consistent with their spectra and elemental analysis results.



Scheme 1 The synthesis of the new compounds.

The electronic spectra of phthalocyanines **3**–**5** (Figures 1–3) show the typical B and Q bands of symmetrically substituted phthalocyanine (Stillman et al., 2002). The UV-Vis absorption spectra of the metallophthalocyanines **4** and **5** show intense Q band absorptions at λ_{max} 685 nm (ε 5.28), 682 nm (ε 5.12), with weaker absorptions at λ_{max} 618 nm (ε 4.55) and 618 nm (ε 4.45), respectively. The UV-Vis absorption spectrum of the metallophthalocyanine **3** shows less intense and broader Q band at λ_{max} 680 nm (ε 5.12) nm, with weaker absorption at λ_{max} 616 nm (ε 4.59). These observations suggest that the Zn complex **3** is aggregated (Schutte et al., 1993; Arslan and Yilmaz, 2007). The B bands of compounds **3**, **4** and **5** are observed at λ_{max} 307 nm (ε 5.29), 324 nm (ε 5.24) and 256 nm (ε 5.23), respectively, as expected.

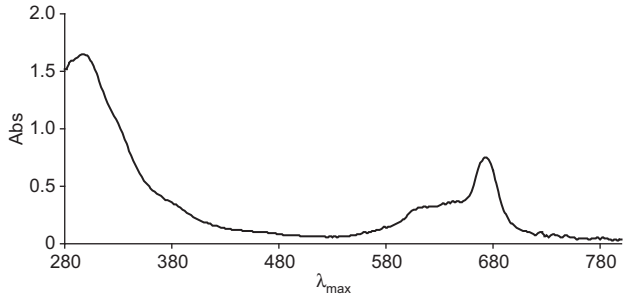


Figure 1 UV-Vis spectra of the Zn complex **3**.

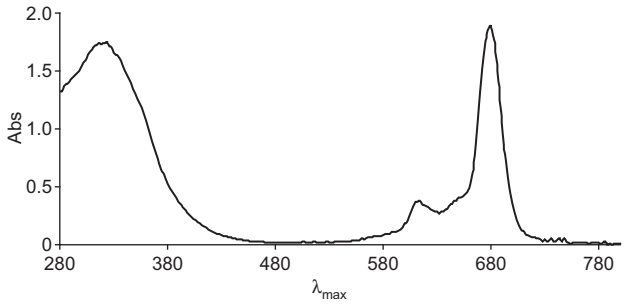


Figure 2 UV-Vis spectra of Ni complex **4**.

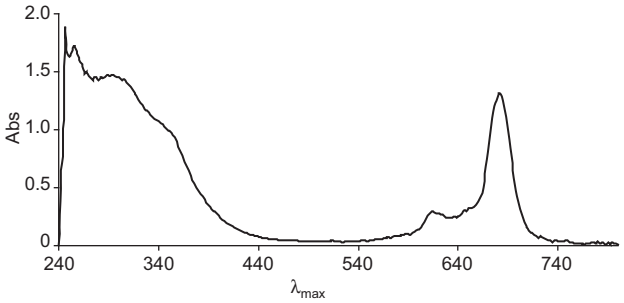


Figure 3 UV-Vis spectra of Co complex **5**.

Conclusion

New dicarbonitrile derivative **2** and metallophthalocyanines **3**–**5** carrying N_3O_2 groups on peripheral positions were synthesized and characterized. The compounds were characterized by IR, UV-Vis, ^{1}H NMR, ^{13}C NMR, mass spectra and elemental analysis.

Experimental

All reactions were carried out under dry nitrogen. The IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer using potassium bromide pellets. ^{1}H (200 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Mercury 200 spectrometer in $CDCl_3$. Electrospray mass spectra were measured on Varian 711 and VG Zapspec spectrometers. Elemental analysis was done on a LECO Elemental Analyzer (CHNS O932). UV-visible absorption spectra were measured by a Unicam 929 AA UV-visible spectrophotometer. Melting points were measured on an Electrothermal apparatus.

8-Methyl-4,12-ditosyl-3,4,5,6,7,8,9,10,11,12,13,14-dodecahydro-2*H*-benzo[*b*][1,4,7,11,15]dioxatriazacycloheptadecine-17,18-dicarbonitrile (2)

A mixture of 17,18-dibromo-8-methyl-4,12-ditosyl-3,4,5,6,7,8,9,10,11,12,13,14-dodecahydro-2*H*-benzo[*b*][1,4,7,11,15]dioxatriazacycloheptadecine **1** (1.67 g, 2.16 mmol) and CuCN (0.58 g, 6.48 mmol) in dry DMF (20 mL) was heated under reflux for 48 h. The mixture was cooled to room temperature and then poured into aqueous ammonia (25 mL, 25%). After stirring for 4 h, the mixture was extracted with chloroform (3 × 20 mL). The combined organic layers were washed with water, dried over anhydrous sodium sulfate, filtered and concentrated. Compound **2** was purified by column chromatography on silica gel using hexane/ethyl acetate (3:7) as eluent: yield 0.95 g (66%); mp 161–163°C; IR (ν_{max}/cm^{-1}): 3022(Ar-H), 2951–2798(Aliph. C-H), 2228(C≡N), 1596, 1509, 1459, 1337, 1270, 1217, 1154, 1089, 996, 755, 652; ^{1}H NMR: δ 7.66 (d, 4H, *J* = 8 Hz, Ar-Ts-H), 7.22 (d, 4H, *J* = 8 Hz, Ar-Ts-H), 6.87 (s, 2H, Ar-H), 4.04 (t, 4H, *J* = 8 Hz, O—CH_2), 3.64 (t, 4H, *J* = 5 Hz, N-CH_2), 3.45(t, 4H, *J* = 6 Hz, N-CH_2), 2.21 (t, 4H, *J* = 6 Hz, N-CH_2), 2.38 (s, 6H, CH_3), 2.08 (s, 3H, N-CH_3), 1.70–1.72 (m, 4H, CH_2); ^{13}C NMR: δ 152.4, 143.6, 136.9, 129.8, 126.9, 117.3, 116.9, 113.8, 69.4, 53.8, 48.4, 48.0, 41.5, 29.6, 21.5; MS: m/z 666 $[M+1]^+$. Anal. Calcd for $C_{33}N_5O_6S_2H_{39}$: C, 59.53; H, 5.90; N, 10.52; S, 9.63. Found: C, 59.62; H, 5.97; N, 10.64; S, 9.75.

Zinc(II) complex 3

A mixture of compound **2** (300 mg, 0.45 mmol), anhydrous $Zn(CH_3COO)_2$ (20.5 mg, 0.112 mmol), DBU (five drops) and dry *n*-pentanol (5 mL) was heated and stirred in a Schlenk tube at 160°C for 24 h under nitrogen atmosphere. After cooling, the mixture was treated with ethanol (25 mL) and the solid precipitate was filtered and washed with ethanol. The green solid product was chromatographed on silica gel with chloroform/methanol (8:1) as eluent: yield 55 mg (18% yield); IR (ν_{max}/cm^{-1}): 3065(Ar-H), 2925–2851(Aliph. C-H), 1738, 1668, 1597, 1438, 1372, 1337, 1242, 1158, 1089, 1021, 815, 706; ^{1}H NMR: δ 7.72–7.69 (m, 16H, Ar-Ts-H), 7.58–7.55 (m, 16H, Ar-Ts-H), 7.19–7.21 (m, 8H, Ar-H), 4.90–4.79 (m, 16H, O-CH_2), 4.08 (d, 16H, *J* = 7 Hz, N-CH_2), 3.65–3.44(m, 16H, N-CH_2), 2.25–2.40 (m, 16H, N-CH_2), 2.02 (s, 24H, CH_3), 1.78–1.42(m, 16H, CH_2), 1.25 (s, 12H, N-CH_3); ^{13}C NMR: δ 170.5, 170.4, 130.9, 129.7, 129.7, 128.8, 127.2, 127.1, 71.8, 55.2, 47.2, 39.8, 39.2, 21.1, 29.8; MS: m/z 2729 $[M+1]^+$; UV-Vis (λ_{max}, nm; ε, M^{-1} cm^{-1}): 680 (5.12), 616 (4.59), 351 (5.19), 307 (5.29). Anal. Calcd for $C_{132}H_{156}N_{20}O_{24}S_8Zn$: C, 58.10; H, 5.76; N, 10.27; S, 9.40. Found: C, 58.28; H, 5.60; N, 10.45; S, 9.66.

Nickel(II) complex 4

This green complex was obtained from anhydrous $NiCl_2$ (14.6 mg, 0.112 mmol) by using the procedure described above and purified by silica gel chromatography eluting with chloroform/methanol (9:1): yield 52 mg (17%); IR (ν_{max}/cm^{-1}): 3060(Ar-H), 2924–2852(Aliph. C-H), 1596, 1445, 1336, 1267, 1157, 1089, 815, 703; ^{1}H NMR: δ 7.70–7.65 (m, 16H, Ar-Ts-H), 7.40–7.27 (m, 16H, Ar-Ts-H), 7.20 (s, 8H, Ar-H), 4.27–4.21 (m, 16H, O-CH_2), 3.60–3.48(m, 32H, N-CH_2), 2.91 (d, 16H, *J* = 7 Hz, N-CH_2), 2.37 (s, 24H, CH_3), 2.03 (s, 12H, N-CH_3), 1.75–1.73(m, 16H, CH_2); ^{13}C NMR: δ 165.1, 162.6, 156.5, 155.3, 130.5, 127.4, 121.8, 120.4, 118.6, 63.7, 51.1, 49.8, 36.9, 35.1, 22.5, 29.7; MS: m/z 2760 $[M+K]^+$; UV-Vis (λ_{max}, nm; ε, M^{-1} cm^{-1}): 685 (5.28), 618 (4.55), 324 (5.24). Anal. Calcd for $C_{132}H_{156}N_{20}O_{24}S_8Ni$: C, 58.24; H, 5.78; N, 10.29; S, 9.42. Found: C, 58.47; H, 5.95; N, 10.45; S, 9.65.

Cobalt(II) complex 5

This green complex was obtained from anhydrous $CoCl_2$ (14.6 mg, 0.112 mmol) by using the procedure described above and purified by silica gel chromatography eluting with chloroform/methanol (8:1): yield 48 mg (15%); IR (ν_{max}/cm^{-1}): 3060(Ar-H), 2956–2927(Aliph. C-H), 1732, 1597, 1439, 1371, 1337, 1271, 1157, 1089, 816, 705; MS: m/z 2722 $[M+1]^+$; UV-Vis (λ_{max}, nm; ε, M^{-1} cm^{1}): 682 (5.12), 618 (4.45), 302 (5.16), 256 (5.23). Anal. Calcd for $C_{132}H_{156}N_{20}O_{24}S_8Co$: C, 58.24; H, 5.78; N, 10.29; S, 9.42. Found: C, 58.11; H, 5.96; N, 10.13; S, 9.67.

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