Preparation of One Structural Isomer of Tetra-substituted Phthalocyanine, 1,8,15,22-Tetra(3'-pentoxy)phthalocyanine, and a Crystal Structure of Its Nickel(II) Complex

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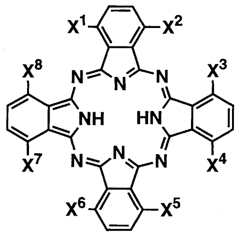
The selective preparation of 1,8,15,22-tetra(3'-pentoxy)-phthalocyanine from 3-(3'-pentoxy)-1,2-dicyanobenzene was carried out. Its nickel(II) complex was obtained from the phthalocyanine and nickel(II) chloride, and a crystal structure of the complex was determined by an X-ray analysis.

Metallophthalocyanines in the solid state have evoked interests in their uses as dyestuffs, photoconducting agents in photocopying machines, chemical sensors, and electrochromic display devices.[1] However, their low solubility limits their studies in solution. Many peripherally substituted phthalocyanine derivatives have been then prepared, and their increased solubility has facilitated their chemical and spectroscopic studies in solution.[2]

In tetra-substituted phthalocyanine derivatives, four structural isomers exist, and the mixture is usually employed (Figure 1).



isomer	X^1	X^2	X^3	X^4	X^5	X^6	X^7	X^8
I	H	OR	H	OR	H	OR	H	OR
II	H	OR	OR	H	OR	H	H	OR
III	H	OR	OR	H	H	OR	H	OR
IV	H	OR	OR	H	H	OR	OR	H

Figure 1. Four structural isomers.

The selective preparation of one structural isomer is required for the detail studies of its metal complexes in solution and also for their X-ray crystal structure analyses. The characterization of the structural isomers was at first confirmed by ^{1}H NMR,[3] and a few papers subsequently described the preparation of one structural isomer.[4-6] It has been also reported that all four structural isomers of tetra-substituted phthalocyaninatonickel(II) complexes were isolated by HPLC.[7,8] We report here a facile preparation of soluble one structural isomer of terta-substituted phthalocyanine, 1,8,15,22-tetra(3'-pentoxy)phthalocyanine (compound **1**), and also report a molecular structure of its nickel(II) complex as the first successful structure determination of the tetra-substituted one.

The preparation of 3-(3'-pentoxy)-1,2-dicyanobenzene and other alkoxy derivatives was performed by a literature method.[9] Compound **1** was prepared by heating a pentanol solution (5 mL) of 3-(3'-pentoxy)-1,2-dicyanobenzene (1 g, 4.67 mmol) and lithium (10 mg, 1.5 mmol) for 4 h at *ca.* 120 °C. To the reaction mixture, methanol (100 mL) was poured and conc. hydrochloric acid (1 mL) was subsequently added. Then, the precipitates obtained were washed by methanol and dissolved in adequate amounts of chloroform, being added on a silica gel column. The green solution was eluted out with chloroform, and the precipitates were obtained by the addition of hexane to the eluate (320 mg, 32%).[10] Other phthalocyanine derivatives were obtained in a similar manner.

Table 1. The relative yields of the isomer **I** for some alkoxy derivatives[11]

alkoxy group	yield(%)	alkoxy group	yield(%)
2-propoxy	62	2-methyl- 1-propoxy	82
1-propoxy	66	3-pentoxy	85
2-butoxy	76	3-methyl- 2-butoxy	86

While tetra(2-propoxy)phthalocyanine showed four peaks in a HPLC chromatogram, compound **1** showed only one peak (Figure 2). It has been reported that ^{1}H NMR spectra of the isomers **I** and **IV** show three ring-proton signals, and that of the isomer **II** or **III** showed six or twelve signals.[8] Compound **1** may be the isomer **I** or **IV** judging from its ring-proton signals: 7.64 (d, 4H, J = 8.1 Hz), 8.12 (t, 4H, J = 7.8 Hz), and 9.06 ppm (d, 4H, J = 7.3 Hz). Furthermore, compound **1** was identified to be the isomer **I** from the molecular structure of its nickel(II) complex as shown in Figure 3.

The bulky groups promoted the relative yield of the isomer **I** (Table 1), but too bulky group such as 2,4-dimethyl-3-pentoxy or 3,3-dimethyl-2-butoxy prevented the formation of the phthalocyanine structure.

The nickel(II) complex was prepared as follows; nickel(II) chloride hexahydrate (70 mg, 0.29 mmol) was added to the DMF solution (1 - 2 mL) of compound **1** (100 mg, 0.13 mmol), being refluxed for 4 h. After the addition of adequate amounts of chloroform to the reaction mixture, the solution was poured on a silica gel column. The green solution was eluted out with chloroform, and the dark green precipitates were obtained by the

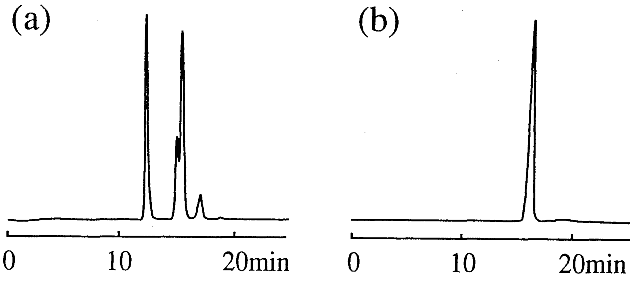


Figure 2. HPLC chromatograms of tetra(2-propoxy)phthalocyanine (a) and compound **1** (b). Column: Shimadzu Pack PREP-ODS (H) 250 x 4.6 mm; 5 μm (silica gel); eluent: methanol / chloroform (75 : 25); flow rate: 1 mL min^{-1}; pressure: 60 bar.

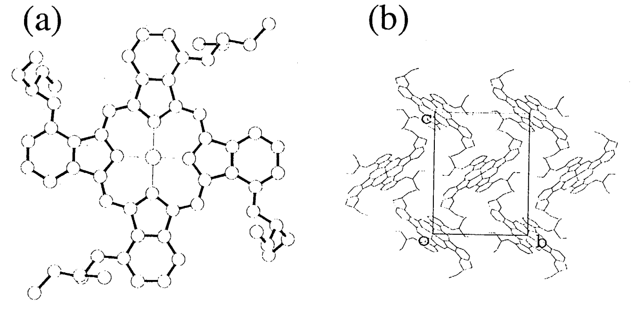


Figure 3. Representations of the molecular structure of the nickel(II) complex (a) and the packing of the molecules in the lattice (b).

addition of hexane to the eluate (80 mg, 67%).[12] The single crystal of the nickel(II) complex was obtained from the mixture solvent of chloroform and ethanol.

The molecular structure of the complex shows that the four alkoxy substituents occupy equivalent positions (Figure 3).[13] There is an S_2 axis through the nickel center, perpendicular to the phthalocyanine plane. The phthalocyanine ring including nickel atom is roughly planar.

The molecules are arranged in 'herring bone' assemblies with a much larger inter-ring distance of 9.364 Å than those of 3.4 Å in α and β forms of unsubstituted phthalocyaninatocopper(II)[14] and 8.5 Å in octa-substituted phthalocyanine.[15] The loose molecular packing is known by van der Waals drawing, and there is a disorder in the terminal substituted group.

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10 Anal. Found: C, 72.73; H, 6.80; N, 12.87%. Calcd for $C_{52}H_{58}N_8O_4$: C, 72.70; H, 6.81; N, 13.04%. UV-VIS ($CHCl_3$) λ_{max}/nm (log ε) 318 (4.82), 358^{sh} (4.65), 624 (4.51), 664 (4.66), 696(5.16), 729 (5.22). ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 24H, J = 7.3 Hz), 2.32 - 2.45 (m, 16H), 4.89 - 4.94 (m, 4H), 7.64 (d, 4H, J = 8.1 Hz), 8.12 (t, 4H, J = 7.8 Hz), 9.06 (d, 4H, J = 7.3 Hz).

11 With the purification by reprecipitation and column chromatography, the relative yield of the isomer **I** considerably increased (10 - 15%). For HPLC analyses, the reaction mixtures without the purification were used. The relative yield was calculated from the relative peak height of the isomer **I** for those of all isomers.

12 Anal. Found: C, 67.87; H, 6.31; N, 12.03%. Calcd for $C_{52}H_{56}N_8O_4Ni$: C, 68.20; H, 6.16; N, 12.24%. UV-VIS ($CHCl_3$) λ_{max}/nm (log ε) 298 (4.75), 404^{sh} (4.16), 628 (4.61), 664^{sh} (4.63), 699 (5.36). ^{1}H NMR (C_6D_6) δ 0.90 (t, 24H, J = 7.6 Hz), 1.18 - 1.93 (m, 16H), 4.28 - 4.32(m, 4H), 6.93 (d, 4H, J = 8.1 Hz), 7.53 (t, 4H, J = 7.8 Hz), 8.97 (d, 4H, J = 7.6 Hz).

13 Crystal data: $C_{52}H_{56}N_8O_4Ni$, M_r = 915.77, monoclinic, $P2_1/n$, a = 9.364(3), b = 13.833(4), c = 18.063(2) Å, β = 98.17(2) °,U = 2315.9(8) Å^3, Z = 2, D_c = 1.3137 g cm^{-3}, Cu-$K\alpha$,λ = 1.5418 Å, μ = 1.042 mm^{-1}, $F(000)$ = 968, 2391 observed with $I>2\sigma(I)$, 2885 collected at 19 °C, $\omega-2\theta$ scan. No absorption correction. Structure solved by direct methods on F^2 using SHELXS-86 and SHELXL-93. Hydrogen atoms placed in calculated positions. Disordered terminal two carbon atoms refined under geometric restraint. Final R = 0.074 and R_w = 0.138.

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