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Preparation and Some Properties of One Structural Isomer of Tetra-Substituted Phthalocyanine; 1,8,15,22-Tetrakis(pentan-3′-yloxy)phthalocyanine and Its Metal(II) Complexes[1)]

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The title phthalocyanine (**1**) was prepared from 3-(pentan-3′-yloxy)phthalonitrile, of which a bulky substituent on the 3-position caused an exclusive formation of **1** out of the possible structural isomers.

Complexes of magnesium(II), cobalt(II), nickel(II), copper(II), and zinc(II) were prepared by refluxing a DMF solution of **1** and corresponding metal(II) chlorides, and were characterized by the absorption and ^{1}H NMR spectra as well as elemental analyses.

Magnesium(II) and zinc(II) complexes showed a new band at the longer wavelength side of the Q band in chloroform, probably due to the formation of a face-to-face slipped dimer.

Compound **1** and its magnesium(II), nickel(II), or copper(II) complex showed three ring-oxidative and reductive processes, and the zinc(II) complex showed four in dichloromethane in their cyclic voltammograms. The cobalt(II) complex showed five processes, two of which arose from a central cobalt(II) ion. The oxidation of the cobalt(II) ion occurred at a more negative potential in DMF.

The crystal structure of the nickel(II) complex was determined by an X-ray analysis; substitution on the 1,8,15, and 22 positions of the ring by pentan-3-yloxy groups was confirmed. The molecules are stacked with a distance of 3.32 Å between the phthalocyanine rings.

Metallophthalocyanines in the solid state have evoked interests concerning their uses, such as dyestuffs, photoconducting agents in phatocopying machines, chemical sensors, and electrochromic display devices.[2)] However, their low solubility limits studies in solution. Many peripherally substituted phthalocyanine derivatives have then been prepared, and their increased solubility has facilitated their electrochemical and spectroscopic studies in solution.[3)]

Substituted phthalonitriles are generally used for preparing peripherally substituted phthalocyanine complexes; monosubstituted phthalonitrile gives a mixture of four structural isomers (Fig. 1). While the mixture has been usually employed for solution studies, the selective preparation of one structural isomer is required for their detailed studies in solution, and also for X-ray crystal-structure analyses.

The structural isomers were first identified based on the ^{1}H NMR spectra,[4)] and a few papers subsequently described the preparation of one structural isomer.[5—7)] It has also been reported that all four structural isomers of tetra-substituted phthalocyaninatonickel(II) were isolated by HPLC.[8—10)]

We report here on a facile preparation of one structural isomer out of the possible ones. Characterization including an X-ray structural analysis and some properties of 1,8,15,22-tetrakis(pentan-3′-yloxy)phthalocyanine (**1**) and its magnesium(II), cobalt(II), nickel(II), copper(II), and zinc(II) complexes are described.

Experimental

Preparation. The preparation of 3-(pentan-3′-yloxy)phthalonitrile and other alkoxy derivatives was preformed by a literature method.[11)] Compound **1** was prepared by heating a pentan-1-ol solution (5 mL) of 3-(pentan-3′-yloxy)phthalonitrile (1 g, 4.67 mmol) and lithium (10—20 mg, 1.4—2.9 mmol) for 4 h at ca. 120 °C. To the reaction mixture, methanol (100 mL) was poured and concd hydrochloric acid (1 mL) was subsequently added. The obtained precipitates 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 eluent. Yield 321 mg (32%). 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 ($\log \varepsilon$) = 318 (4.82), 358^{sh} (4.65), 624 (4.51), 664 (4.66), 696 (5.16), 729 nm (5.22). ^{1}H NMR ($CDCl_3$) δ = 1.38 (t, 24H), 2.32 (m, 16H), 4.92 (m, 4H), 7.64 (d, 4H), 8.12 (t, 4H), 9.05 (d, 4H).

The other phthalocyanine derivatives were prepared by a method

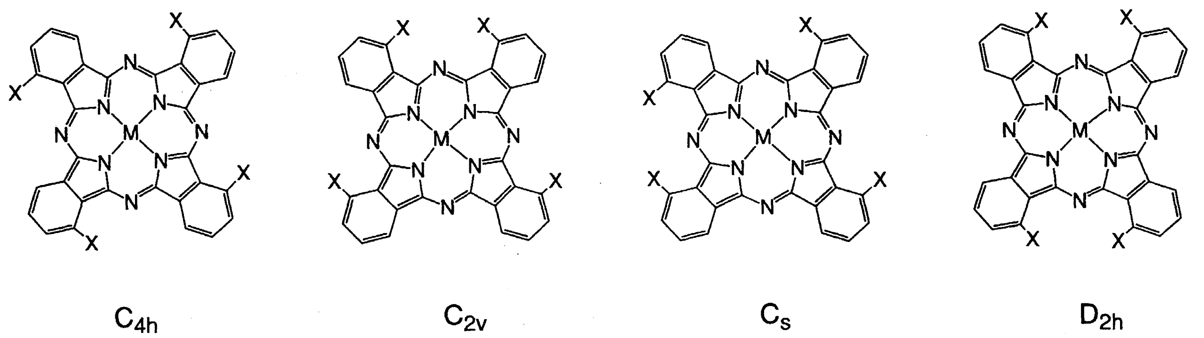


Fig. 1. Four structural isomers derived from the reaction of 3-substituted phthanonitrile.

similar to that described for **1**.

Nickel(II) Complex. Nickel(II) chloride hexahydrate (70 mg, 0.29 mmol) was added to a *N*,*N*-dimethylformamide (DMF) solution (1—2 mL) of **1** (100 mg, 0.12 mmol) and 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. A green solution was eluted out with chloroform, and dark-green precipitates were obtained upon the addition of hexane to the eluent. Yield 71 mg (67% based on **1**). Found: C, 67.87; H, 6.31; N, 12.03%. Calcd for $C_{52}H_{56}N_8NiO_4$: C, 68.20; H, 6.16; N, 12.24%. UV-vis ($CHCl_3$) λ ($\log \varepsilon$) = 298 (4.75), 404^{sh} (4.16), 628 (4.61), 664^{sh} (4.63), 699 nm (5.36). ^1H NMR ($CDCl_3$) $\delta = 1.36$ (t, 24H), 2.28 (m, 16H), 4.84 (m, 4H), 7.55 (d, 4H), 8.02 (t, 4H), 8.94 (d, 4H).

The other metal(II) complexes were also prepared by a similar method described as that for the nickel(II) complex using corresponding metal(II) chlorides.

Magnesium(II) Complex. Yield 44 mg (43%). Found: C, 70.72; H, 6.86; N, 12.37%. Calcd for $C_{52}H_{56}MgN_8O_4$: C, 70.86; H, 6.40; N, 12.71%. UV-vis ($CHCl_3$) λ ($\log \varepsilon$) = 319 (4.70), 634 (4.59), 674^{sh} (4.60), 705 (5.34), 758 nm (4.54). ^1H NMR (C_6D_6) $\delta = 0.76$ (t, 24H), 1.65 (m, 16H), 4.29 (m, 4H), 6.89 (d, 4H), 7.46 (t, 4H), 8.97 (d, 4H).

Cobalt(II) Complex. Yield 78 mg (73%). Found: C, 68.03; H, 6.27; N, 12.36%. Calcd for $C_{52}H_{56}CoN_8O_4$: C, 68.18; H, 6.12; N, 12.23%. UV-vis ($CHCl_3$) λ ($\log \varepsilon$) = 310 (4.65), 418^{sh} (4.00), 626 (4.45), 662^{sh} (4.51). 696 nm (5.11).

Copper(II) Complex. Yield 60 mg (56%). Found: C, 67.86; H, 6.03; N, 11.74%. Calcd for $C_{52}H_{56}CuN_8O_4$: C, 67.84; H, 6.13; N, 12.17%. UV-vis ($CHCl_3$) λ ($\log \varepsilon$) = 318 (4.76), 415^{sh} (4.16), 634 (4.70), 707 nm (5.43).

Zinc(II) Complex. Yield 97 mg (90%). Found: C, 67.70; H, 6.21; N, 12.12%. Calcd for $C_{52}H_{56}N_8O_4Zn$: C, 67.71; H, 6.12; N, 12.15%. UV-vis ($CHCl_3$) λ ($\log \varepsilon$) = 318 (4.78), 412^{sh} (4.41), 633 (4.68), 674^{sh} (4.72), 703 (5.39), 760 nm (4.63). ^1H NMR (C_6D_6) $\delta = 0.97$ (t, 24H), 1.83 (m, 16H), 4.42 (m, 4H), 7.09 (d, 4H), 7.67 (t, 4H), 9.13 (d, 4H).

Measurements. UV-vis and fluorescence spectra were recorded on Shimadzu UV-3100 and Hitachi 850 spectrometers, respectively. ^1H NMR spectra were measured with a JEOL GX270 spectrometer at 270 MHz. The chemical shifts were determined in ppm using TMS as an internal standard. Elemental analyses were carried out using a Yanako CHN Corder MT-5. Cyclic voltammetric measurements were performed in a dichloromethane or DMF solution containing tetrabutylammonium perchlorate (TBAP) on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator. A glassy carbon disk, a platinum coil, and a standard calomel electrode (SCE) were used as a working electrode, a counter electrode, and a reference electrode, respectively. HPLC chromatograms were recorded on a Shimadzu LC-10A high-performance liquid chromatograph. Column, Shimadzu Pack PREP-ODS (H), 250×4.6 mm, 5 mm (silica gel); eluent, methanol/chloroform (75 : 25); flow rate, 1 mL $\min^{-1}$; pressure, 60 bar (1 bar = 10^5 Pa).

X-Ray Crystal Structure Analysis. Crystals of the nickel(II) complex suitable for an X-ray analysis were grown by standing a sealed glass tube of its chloroform solution covered with adequate amounts of ethanol for a few weeks at room temperature. An automated Rigaku AFC-5R diffractometer with graphite-monochromated Cu $K\alpha$ radiation was used for data collection at room temperature. Three standard reflections, which were monitored every 150 data measurements, showed no deviation in the intensities. The intensity data were corrected for Lorentz-polarization and extinction effects, but not for absorption. The crystal data, intensity collection and structural refinement are summarized in Table 1.

The crystal structure was solved by a direct method and refined by a full-matrix least-squares analysis using SHELXS86[12] and SHELXL93[13] programs, respectively. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms located at the calculated positions (CH = 0.93 Å) were included, but not refined. Disordered terminal carbon atoms (C25A, C25B, and C26A, C26B) of the pentan-3-yloxy group were refined under the geometrical

Table 1. Crystal Data and Data Collection Details

Formula	$C_{52}H_{56}N_8O_4Ni$
Formula weight	915.77
Color	Dark green
Size /mm	0.65 × 0.30 × 0.25
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.364(3)
b/Å	13.833(4)
c/Å	18.063(2)
β/°	98.17(2)
V/Å^3	2315.9(8)
Z	2 (1/2 molecule /asym. unit)
D_{calcd}/g cm^{-3}	1.314
μ(Cu $K\alpha$)/mm^{-1}	1.042
λ (Cu $K\alpha$)/Å	1.5418
$2\theta_{max}$/°	125
Scan method	ω–2θ
No. of reflections measured	2885
No. of unique reflections with $I > 2\sigma(I)$	2391
$R^{a)}$	0.074
$wR^{b)}$	0.138

a) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. b) $w = 1/[\sigma^2 (F_o^2) + (0.0265P)^2 + 4.9347P]$ where $P = (F_o^2 + 2F_c^2)/3$.

restraint. All of the computations were performed on the SUN SPARC station IPC. The atomic coordinates and thermal parameters of the hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and $F_o - F_c$ tables have been deposited as Document No. 70026 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Structural Isomers. While the product resulting from a reaction using 3-(propan-2′-yloxy)phthalonitrile showed four peaks in an HPLC chromatogram, that obtained from 3-(pentan-3′-yloxy)phtalonitrile showed only one peak (Fig. 2). This means that the former contains four structural isomers of tetra-substituted phthalocyanine, but the latter is one structural isomer. It has been reported that the ^{1}H NMR spectra of tetrakis(2-ethylhexan-1-yloxy)phthalocyaninatonickel(II) showed three, six, twelve, and three signals of ring protons for C_{4h}-, C_{2v}-, C_s-, and D_{2h}- symmetry isomers, respectively (Fig. 1).[9] A structural determination based on the ^{1}H NMR spectra is applicable for the present case. That is, the structural isomers **I** and **IV** may show three ring-proton signals, and that of the isomer **II** or **III** shows six or twelve signals (Table 2). The product obtained from 3-(pentan-3′-yloxy)phthalonitrile showed three ring-proton signals at $\delta = 7.64$ (d, 4H), 8.12 (t, 4H), and 9.05 (d, 4H) and was assigned to be the isomer **I** or **IV**. The product was further identified with the isomer **I** (i.e., compound **1**) from the molecular structure of its nickel(II) complex, as described later.

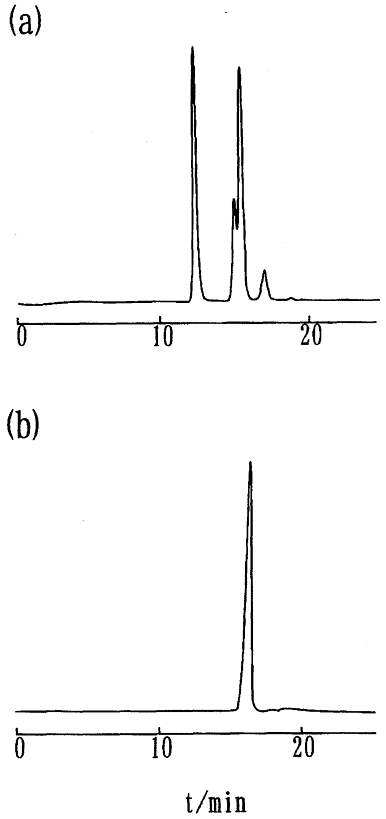
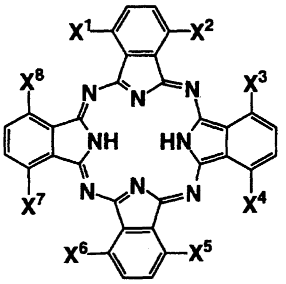


Fig. 2. HPLC chromatograms of tetrakis(propan-2-yloxy)phthalocyanine (a) and **1** (b).

Table 2. The Four Structural Isomers of Alkoxy-Substituted Phthalocyanione[a)]



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

a) OR denotes alkoxy group.

Although bulky groups promoted the relative yield of isomer **I** (Table 3), the overwhelming bulkiness of a group, such as 2,4-dimethylpentan-3-yloxy or 3,3-dimethylbutan-2-yloxy, prevented the formation of phthalocyanine. Upon lowering the reaction temperature, the relative yields increased (Fig. 3). However, the formation did not proceed below the lowest temperature in the plotted data for each complex.

Absorption Spectra of the Metal(II) Complexes. Cer-

Table 3. The Relative Yields of the Isomer I for Some Alkoxy Derivatives[14)]

Alkoxy group	Yield/%	Alkoxy group	Yield/%
Propan-2-yloxy	62	2-Methylpropan-1-yloxy	82
Propan-1-yloxy	66	Pentan-3-yloxy	85
Butan-2-yloxy	76	3-Methylbutan-2-yloxy	86

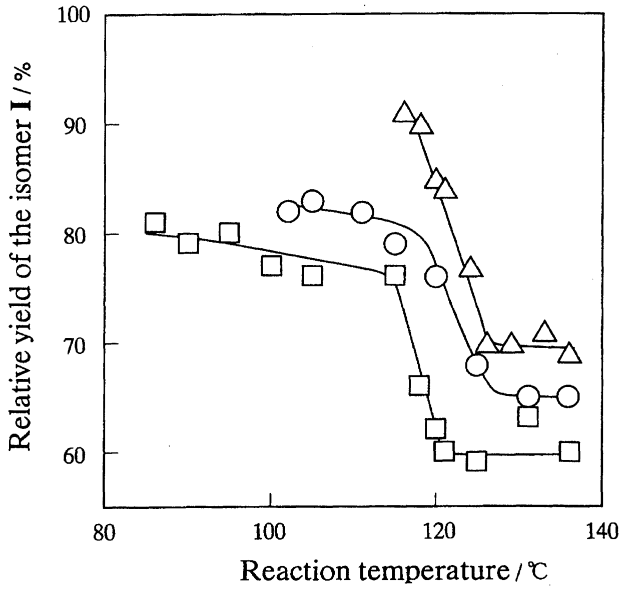


Fig. 3. The effects of reaction temperature on the yield of the isomer I: □, propan-2-yloxy; ○, butan-2-yloxy; △, pentan-3-yloxy.[14)]

tain metal(II) complexes of **1** {Mg(II), Co(II), Ni(II), Cu(II), and Zn(II)} were prepared by refluxing a DMF solution of **1** and corresponding metal(II) chlorides for 4 h. Although the Co(II), Ni(II), and Cu(II) complexes have a typical spectral pattern in the visible region for the metallophthalocyanines (λ_{max} for the Q band = 670 – 700 nm), the Mg(II) and Zn(II) complexes showed a weak band at ca. 760 nm in addition to a Q band in chloroform (Fig. 4). A weak band also appeared in dichloromethane or benzene, but did not appear in a polar solvent, such as methanol, acetone or DMF.

It has been known that dimerization in phthalocyanines generally blue-shifts the Q band in an absorption spectrum.[15] However, it was recently reported that sulfonato-substituted phthalocyanine complexes of zinc(II) and aluminum(III) showed an absorption band at the longer wavelength side of the Q band of their monomer species in aqueous acetonitrile or alcohol.[16,17] The band was tentatively assigned to result from the formation of a face-to-face slipped dimer by a mutual interaction of two phthalocyanines through contact of the aluminum(III) ion and the outer-bridging nitrogen atom.[16] It was further reported that a zinc(II) complex of imidazolyl-porphyrin formed a face-to-face slipped dimer showing a red shift of both the Q and Soret bands.[18] The shift of the Q and Soret bands has been explained by exciton interactions.[19] Hence, it is likely that the face-to-face slipped dimer formation may occur in the case of Mg(II) and Zn(II) complexes.

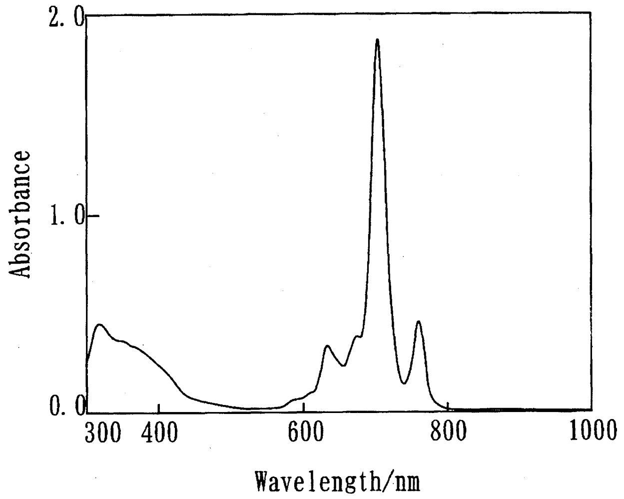


Fig. 4. Absorption spectrum of the Zn(II) complex in chloroform: [complex] = 1×10^{-5} mol dm^{-3}.

Cyclic Voltammetry. The separation between the Ox 1 and Ox 2 half-wave potentials of all complexes, except for the Zn(II) complex, is about 0.4—0.5 V in dichloromethane (Table 4), as generally shown for most of the metallophthalocyanines.[20] It has been reported that the first ring oxidation is separated from the first ring reduction by approximately 1.5 V, corresponding to the magnitude of the energy difference between the HOMO and LUMO of the phthalocyanine ring.[21,22] The separation of the Red 1 and Ox 1 half-wave potentials is about 1.4—1.7 V, except for 0.94 V of the Co(II) complex (Table 4).

It is known that the first oxidation of phthalocyaninatocobalt(II) occurs on the ring in non-donor solvents, such as dichloromethane, and on the central metal ion in donor solvents, such as DMF.[20] Based on the many data reported previously,[20,23] Ox 2 and Red 1 in dichloromethane

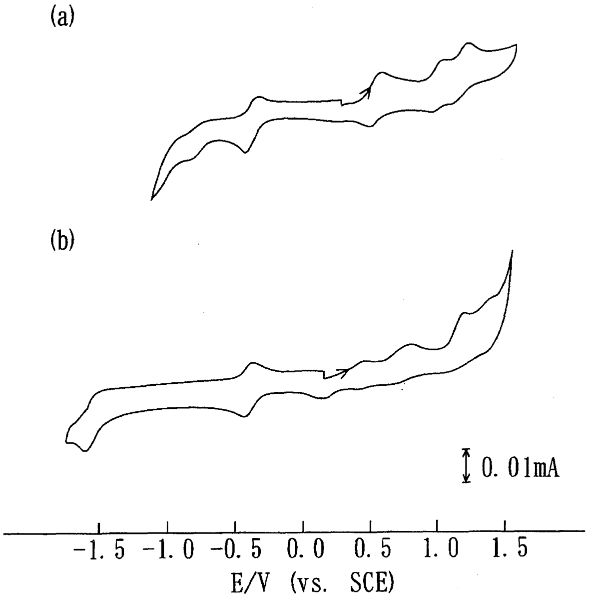


Fig. 5. Cyclic voltammograms of the Co(II) complex at scan rate of 20 mV s^{-1}; [complex] = 1×10^{-3} mol dm^{-3}. [TBAP] = 0.1 mol dm^{-3}. (a) in dichloromethane, (b) in DMF.

Table 4. Half-Wave Potentials for **1** and Its Metal(II) Complexes in Dichloromethane (V vs. SCE)

	Red 2	Red 1	Ox 1	Ox 2	Ox 3
1		−0.86(150)	0.79(irr)	1.18(irr)	
Mg(II) complex		−0.96(170)	0.76(irr)	1.19(160)	
Co(II) complex	−0.85(irr)	−0.40(150)	0.54(140)	1.01(120)	1.26(irr)
Co(II) complex[a]	−1.59(irr)	−0.44(80)	0.36(70)	0.66(120)	1.19(irr)
Ni(II) complex		−0.99(170)	0.82(irr)	1.33(irr)	
Cu(II) complex		−0.97(160)	0.80(irr)	1.19(160)	
Zn(II) complex	−1.28(irr)	−0.92(irr)	0.46(130)	1.05(140)	

a) in DMF. [Compound] = 1×10^{-3} mol dm^{-3}, [TBAP] = 0.1 mol dm^{-3}, $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$. Scan rate = 100 mV s^{-1}. The values in parentheses denote ΔE_{p} (mV). The half-wave potentials were estimated from $E_{\text{p}}/2$ in the case of the irreversible steps.

and Ox 1 and Red 1 in DMF are tentatively assigned to the oxidation and reduction of the cobalt(II) ion, respectively. The shift of the cobalt(II) oxidation to the negative side in DMF is explained by the fact that the low-spin cobalt(III) ion is stabilized by the coordination of DMF, resulting in the promotion of the oxidation of the cobalt(II) ion (Fig. 5).[20]

Broad redox waves for the oxidation of phthalocyanine rings are commonly observed due to their aggregation.[24] However, the metal complexes of **1** showed well-defined processes, due to the prevention of the dimer formation by the steric hindrance of the alkoxy substituents.

The Ox 1 half-wave potentials of the Mg(II), Ni(II), Cu(II), and Zn(II) complexes show that the ring was oxidized in the order Mg(II) > Ni(II) < Cu(II) < Zn(II). It was reported that the less the polarizing power (Ze/r) of the ion, the easier it was to oxidize the ring.[20,23] Since the radii of the metal(II) ions show the tendency of Mg(II) > Ni(II) < Cu(II) < Zn(II),[25] the potential order of Ox 1 for the complexes might be explained by the polarizing power of the central ion.[20]

Table 5. Fractional Coordinates and Equivalent Isotropic Displacement Parameters of Non-Hydrogen Atoms

Atom	x	y	z	$U_{eq}/Å^2$ [a)]
Ni	0.0000	0.0000	0.0000	0.0465(4)
O1	−0.2484(4)	0.2834(3)	−0.2263(2)	0.0838(13)
O2	0.5616(4)	0.2089(3)	0.0361(2)	0.0786(12)
N1	0.0087(4)	0.1153(3)	−0.0545(2)	0.0489(10)
N2	0.1961(4)	0.0149(2)	0.0409(2)	0.0437(9)
N3	0.2570(4)	0.1662(3)	−0.0151(2)	0.0532(10)
N4	0.2352(4)	−0.1263(3)	0.1195(2)	0.0530(10)
C1	−0.1007(6)	0.1565(3)	−0.1044(2)	0.0496(12)
C2	−0.0487(5)	0.2416(3)	−0.1385(2)	0.0551(13)
C3	−0.1132(6)	0.3048(4)	−0.1950(3)	0.069(2)
C4	−0.0288(6)	0.3814(4)	−0.2121(3)	0.080(2)
C5	0.1114(7)	0.3952(4)	−0.1773(3)	0.085(2)
C6	0.1765(6)	0.3321(4)	−0.1238(3)	0.075(2)
C7	0.0928(5)	0.2559(3)	−0.1051(2)	0.0568(13)
C8	0.1262(5)	0.1757(3)	−0.0531(2)	0.0525(12)
C9	0.2889(5)	0.0899(3)	0.0276(2)	0.0465(11)
C10	0.4322(5)	0.0727(3)	0.0667(2)	0.0511(12)
C11	0.5624(6)	0.1228(3)	0.0718(3)	0.0581(13)
C12	0.6835(6)	0.0794(4)	0.1120(3)	0.0620(14)
C13	0.6740(6)	−0.0086(4)	0.1469(3)	0.0594(13)
C14	0.5473(5)	−0.0591(4)	0.1439(2)	0.0577(13)
C15	0.4263(5)	−0.0153(3)	0.1032(2)	0.0488(12)
C16	0.2785(5)	−0.0479(3)	0.0881(2)	0.0454(11)
C17	−0.3128(6)	0.3329(4)	−0.2934(3)	0.074(2)
C18	−0.4105(7)	0.2609(5)	−0.3376(3)	0.096(2)
C19	−0.3322(10)	0.1727(6)	−0.3620(5)	0.145(3)
C20	−0.3949(7)	0.4225(5)	−0.2718(4)	0.096(2)
C21	−0.5017(9)	0.4010(6)	−0.2206(4)	0.135(3)
C22	0.6817(7)	0.2755(4)	0.0498(3)	0.083(2)
C23	0.6651(7)	0.3408(4)	−0.0167(3)	0.089(2)
C24	0.7884(8)	0.4133(5)	−0.0158(4)	0.124(3)
C25A	0.6495(35)	0.3450(19)	0.1151(10)	0.126(12)
C25B	0.7073(20)	0.3073(16)	0.1310(9)	0.081(7)
C26A	0.6383(44)	0.3094(20)	0.1941(13)	0.126(12)
C26B	0.5633(20)	0.3540(17)	0.1438(17)	0.177(13)

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Molecular Structure of the Nickel(II) Complex. The final atomic coordinates and equivalent isotropic thermal factors of the Ni(II) complex are given in Table 5. Selected bond length and angles of the complex are listed in Table 6.

An ORTEP drawing of the complex is shown in Fig. 6 together with the numbering scheme. Since there is an inversion center at the nickel ion, one half of phthalocyanine constructs its full molecule. The four alkoxy groups are directed spirally around the S_2 axis of the molecule. The nickel ion is just fitted to the center hole of a ring consisting of four nitrogen atoms of pyrrole rings. The Ni–N bond distances are 1.883(3) and 1.891(3) Å. These values are comparable to those of the M–N bond lengths for unsubstituted phthalocyanine complexes of the first transition metals (ca. 1.83—1.979(2) Å).[26]

The deviations of all atoms from the plane composing of the four pyrrole nitrogens are illustrated in Fig. 7. The average displacement of sixteen atoms surrounding the nickel ion from the N_4 plane is only ca. 0.002 Å, which is indicative of the good planariry of the surrounding rings. However, the

Table 6. Bond Length (Å) and Angles (°) of the Ni(II) Complex

Ni–N1	1.883(3)	C3–C4	1.383(7)
Ni–N2	1.891(3)	C4–C5	1.386(7)
N1–C1	1.386(5)	C5–C6	1.379(7)
N1–C8	1.379(6)	C6–C7	1.383(7)
N2–C16	1.374(5)	C7–C8	1.458(6)
N2–C9	1.396(5)	C9–C10	1.444(6)
N3–C9	1.315(5)	C10–C15	1.389(6)
N3–C8	1.324(6)	C10–C11	1.394(6)
N4–C1	1.317(6)	C11–C12	1.392(7)
N4–C16	1.314(5)	C12–C13	1.380(7)
C1–C2	1.446(6)	C13–C14	1.372(7)
C2–C3	1.413(6)	C14–C15	1.398(6)
C2–C7	1.389(6)	C15–C16	1.445(6)
Ni–Ni–N2	90.0(2)	C2–C7–C6	122.8(4)
N1–Ni–N1′	80.0	C2–C7–C8	105.9(4)
C3–O1–C17	120.3(4)	C6–C7–C8	131.3(5)
C11–O2–C22	121.8(4)	N1–C8–N3	128.8(4)
Ni–N1–C1	127.2(3)	N1–C8–C7	110.6(4)
Ni–N1–C8	126.7(3)	N3–C8–C7	120.6(4)
C1–N1–C8	106.1(4)	N2–C9–N3	127.0(4)
Ni–N2–C9	127.4(3)	N2–C9–C10	110.5(4)
Ni–N2–C16	127.0(3)	N3–C9–C10	122.5(4)
C9–N2–C16	105.6(3)	C9–C10–C11	133.9(4)
C8–N3–C9	120.1(4)	C9–C10–C15	106.3(4)
C1–N4–C16	121.0(4)	C11–C10–C15	119.8(4)
N1–C1–N4	127.0(4)	O2–C11–C10	117.4(4)
N1–C1–C2	110.3(4)	O2–C11–C12	125.2(5)
N4–C1–C2	122.7(4)	C10–C11–C12	117.4(5)
C1–C2–C3	132.6(5)	C11–C12–C13	121.1(5)
C1–C2–C7	106.9(4)	C12–C13–C14	122.9(5)
C3–C2–C7	120.6(4)	C13–C14–C15	115.5(5)
O1–C3–C2	116.6(4)	C10–C15–C14	123.1(4)
O1–C3–C4	127.5(5)	C10–C15–C16	106.6(4)
C2–C3–C4	115.9(5)	C14–C15–C16	130.3(4)
C3–C4–C5	122.6(5)	N2–C16–N4	127.5(4)
C4–C5–C6	121.8(5)	N2–C16–C15	111.0(4)
C5–C6–C7	116.4(5)	N4–C16–C15	121.5(4)

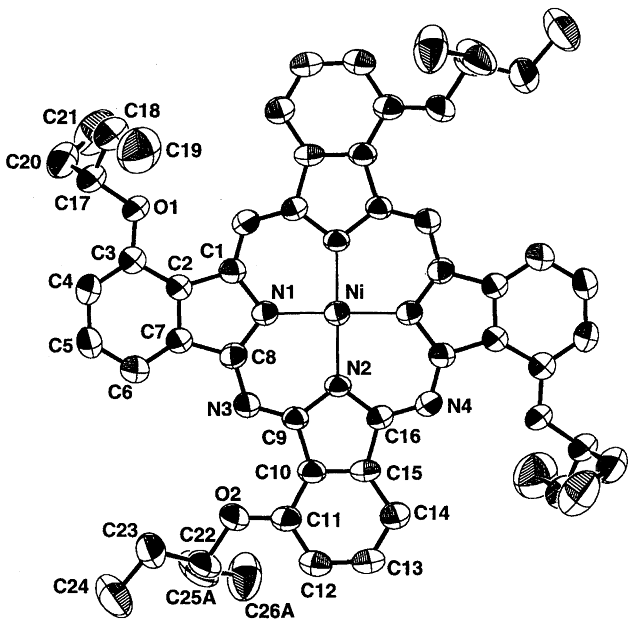


Fig. 6. ORTEP drawing of the Ni(II) complex with the atom-numbering scheme. A pair of the disordered terminal carbons of the pentan-3-yloxy group, C25B and C26B is omitted for clarity.

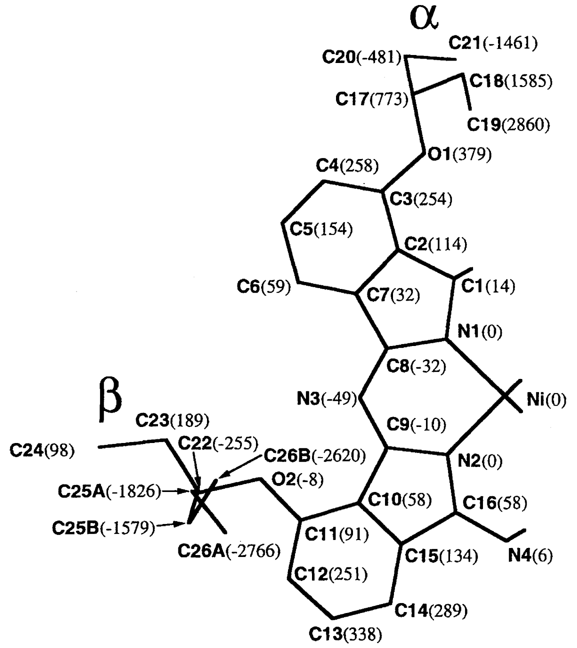


Fig. 7. Stick-bond models of the Ni(II) complex with the atom-numbering scheme. The numbers enclosed in parentheses give the deviations in 0.001 Å units of the atoms with respect to the N_4 plane.

deviations of carbon atoms on the benzene ring are relatively large. The terminal carbons of the pentan-3-yloxy group, designated by α, have large plus and minus values, which means that the group is spread up and down relative to the phthalocyanine ring. However, the pentan-3-yloxy group, designated by β, is spread to one side (C25A, C25B, C26A, and C26B have large minus values, where C23 and C24 have the values close to zero). The spatial configuration enables the stacking of neighboring molecules in the crystal. This stacking feature is clearly seen in Fig. 8. The distance between the phthalocyanine mean planes is 3.32 Å,[27] which is almost the same as those of the unsubstituted phthalocyanine complexes (ca. 3.4 Å).[28] The value 3.32 Å is much shorter than 8.5 Å, which was reported for octa-substituted phthalocyanines.[29,30] The stacking columns are extended along the *a*-axis (Fig. 9). The angle between the axis and the normal to the plane through the NiN_4 coordination planes is 69.2°.

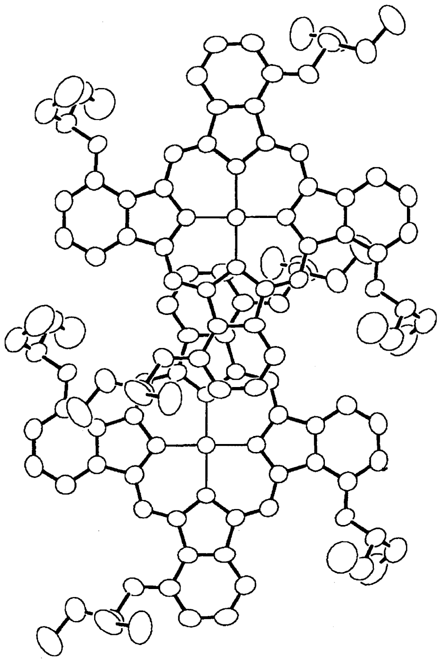


Fig. 8. ORTEP drawing of two molecules of the Ni(II) complex viewed perpendicular to the N_4 coordination planes.

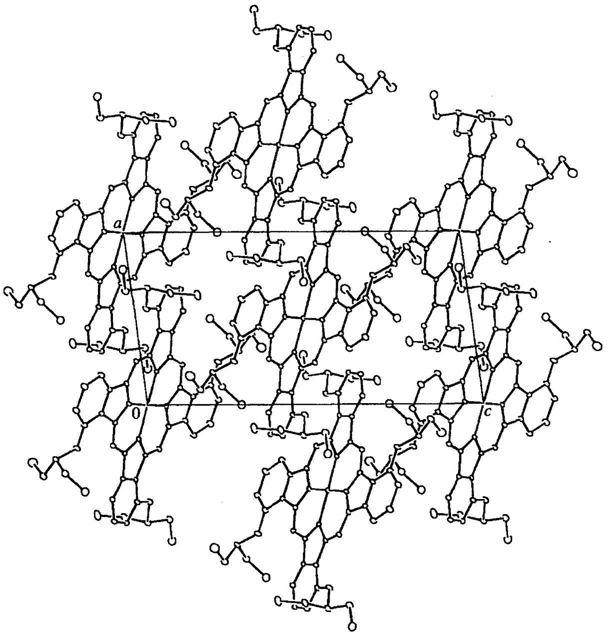


Fig. 9. Crystal packing view of the Ni(II) complex down to *c* axis.

The intra-columnar Ni–Ni distance is 9.364 Å, much longer than those of the unsubstituted phthalocyanine complexes (ca. 4.8 Å).[28] However, the short intra-columnar distance between the phthalocyanine rings arouses our interest in the conductive properties of partially oxidized metal complexes of **1**, as has been shown for the unsubstituted phthalocyanine complexes, which increased their conductivities in a great deal on the oxidation (e.g., $\sigma_{\mathrm{RT}} = 1\times10^{-11}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ for Ni(pc) and $\sigma_{\mathrm{RT}} = 0.7\ \Omega^{-1}\,\mathrm{cm}^{-1}$ for Ni(pc)I; pc = phthalocyaninato ligand).[31] Such a study is in progress in our laboratory.

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