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Unusual Inner C-Alkylation of 2-N-Substituted N-Confused Porphyrin Cobalt Complexes in Toluene and *p*-Xylene

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Supporting Information

ABSTRACT: The inner C-benzyl- and C-*p*-xylyl-substituted cobalt(II) complexes of a 2-N-substituted N-confused porphyrin were synthesized from the reaction of 2-$NCH_2COOCH_2C_6H_5$NCTPPH (**1**) and $CoCl_2·6H_2O$ in toluene (or *p*-xylene), and the structures were revealed by single-crystal X-ray analysis.

An N-confused porphyrin (NCP) is a porphyrin with an inverted pyrrole ring.[1,2] There are three main reaction sites in the confused pyrrole ring, i.e., 2-N, 21-C, and 3-C.[1−4] At the external nitrogen of NCP (2-N), an electrophilic reaction can take place, resulting in the formation of alkylated products. Ziegler and co-workers reported the synthesis of 2-*N*-allyl-5,10,15,20-tetraphenyl-N-confused porphyrin 2-NC_3H_5NCTPPH.[5] In this study, the allyl group of 2-NC_3H_5NCTPPH is modified into a bulky [(benzyloxy)carbonyl]methyl group to derive the free base 2-aza-2-[(benzyloxy)carbonyl]methyl-5,10,15,20-tetraphenyl-N-confused porphyrin 2-$NCH_2COOCH_2C_6H_5$NCTPPH (**1**; Scheme 1).[6] Unlike the NH tautomerism that exists in $NCTPPH_2$, the free base **1** has only one stable form. The NCP **1** can provide N_3 or N_3C coordinated sites.

Previously, Ziegler and co-workers reported several cobalt complexes of 5,10,15,20-tetraphenyl-N-confused porphyrin (NCTPP), i.e., Co^{II}(NCTPP)py (**2**) and $Co^{II}(NCH_3NCTPP)$-py (**3**), with a pyridine axial ligand (Chart 1).[7,8] Hitherto, 2-NCH_2COOEtNCTPPH has been shown to coordinate with the metal in the core, forming a metal square-planar complex possessing a carbon−metal bond for Co^{II} in Co(2-NCH_2COOEtNCTPP)py (**4**) [or Co(NCTPP-AcOEt)py] with an axial pyridine (Chart 1).[5]

Scheme 1. Synthesis of 6 and 7

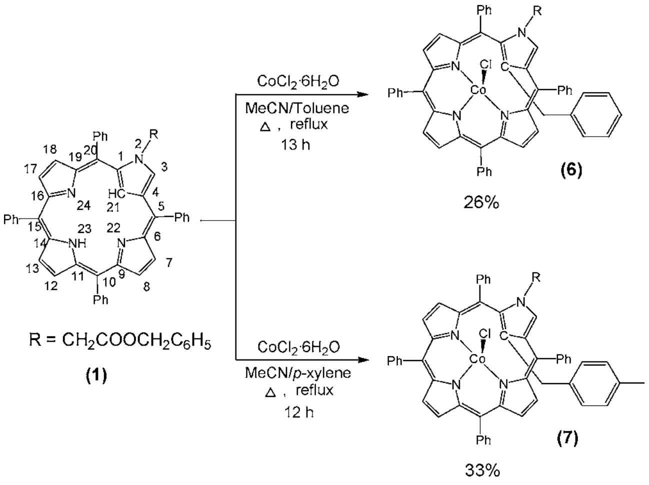
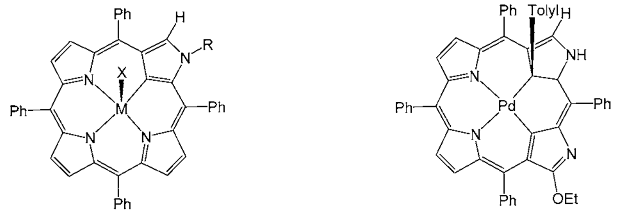


Chart 1. Structures of 2−5



(**2**) M = Co^{II}, X = py, R = H
(**3**) M = Co^{II}, X = py, R = CH_3
(**4**) M = Co^{II}, X = py, R = CH_2COOEt

Pd^{2+}-N_2CP-Tol (5)

Recently, Furuta et al. have reported the inner C-arylation of a doubly N-confused porphyrin palladium complex in toluene, Pd^{2+}-N_2CP-C-Tol (**5**; Chart 1).[9] It is noteworthy that such a C-arylation reaction has not been observed in NCP. The reported C-arylation complex **5** is a diamagnetic species. Chmielewski et al.[10] reported the first structurally characterized paramagnetic organonickel(II) complex (2-NCH_3-21-CH_3)Ni^{II}I and a dimeric complex 21,21′-*o*-xylene-linked bis[N-confused porphyrin nickel(II)].[4,11] Hung and co-workers[12] reported the preparation and oxygenation of cobalt N-confused porphyrin nitrosyl complexes $Co(CTPPC_2H_2Cl)(NO)$ and Co(CTPPO)(NO). Zilbermann et al.[13] reported the spectroscopic and electrochemical characterization of solutions and films of a new redox couple: N-confused porphyrin cobalt(II)/cobalt(III). These paramagnetic cobalt complexes were studied by electron spin resonance and UV−vis spectroscopy as well as by electrochemical methods. The shortfall in the study on a simultaneous metalation and C−H bond activation reaction of an externally alkylated NCP prompted us to undertake the synthesis and structural characterization on metalation of **1**, leading to the new paramagnetic cobalt(II) complexes. Interestingly, chloro(2-aza-

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2-[(benzyloxy)carbonyl]methyl-5,10,15,20-tetraphenyl-21-benzyl-21-carbaporphyrinato-*N,N′,N″*)cobalt(II) [**6**; Co(2-$NCH_2COOCH_2C_6H_5$-21-$CH_2C_6H_5$NCTPP)Cl] and chloro(2-aza-2-[(benzyloxy)carbonyl]methyl-5,10,15,20-tetraphenyl-21-*p*-xylyl-21-carbaporphyrinato-*N,N′,N″*)cobalt(II) [**7**; Co(2-$NCH_2COOCH_2C_6H_5$-21- $CH_2C_6H_4CH_3$NCTPP)Cl] were synthesized bearing the solvents toluene (in **6**) and *p*-xylene (in **7**), respectively, at the inner-core carbon. In this Communication, we report the first inner C-alkylation of the solvents toluene and *p*-xylene onto the cobalt(II) complexes of NCP in atmospheric air under no basic conditions. The X-ray structures and UV−vis−near-IR (NIR) spectra of the two novel cobalt complexes **6** and **7** are also reported.

When **1** was treated with 4 equiv of $CoCl_2 \cdot 6H_2O$ in refluxing MeCN/toluene (or MeCN/*p*-xylene) for 13 h (or 12 h), a yellow-greenish product of **6** (or **7**) was obtained in 26% (or 33%) yield (Scheme 1). Crystals of **6** (or **7**) were grown from cyclohexane/CH_2Cl_2 [1:1 (v/v)] (or cyclohexane/toluene [1:1 (v/v)]), and the X-ray frameworks for **6** and **7** are depicted in Figure 1.[14] The coordination sphere around the Co^{2+} ion in **6** and **7** is distorted tetrahedron. The distance between the inner carbon C(17) and the cobalt atom, 2.559(3) Å [or 2.529(3) Å], in **6** (or **7**) is longer than the sum of the cobalt and carbon covalent radii (2.03 Å).[15] The typical covalent bond distance of Co−C is 1.907(6) Å in **4** and 1.933(4) Å in **3**.[5,7] Hence, there is no side-on η' coordination between cobalt and C(17) in **6** and **7**. The C(17)-benzyl (or *p*-xylyl) substituent for **6** (or **7**) lies on the face opposite to the chloride. The cobalt is displaced 0.56 Å (or 0.57 Å) out by the N(1)−N(2)−N(3) plane (i.e., the 3N plane) toward the axial chloride for **6** (or **7**). The dihedral angles between the C(17) pyrrole plane and the 3N plane in complexes **6** and **7** are as follows: 57.5° (**6**) and 56.6° (**7**). This large dihedral angle of 56.6−57.5° in complexes **6** and **7** indicates that the pyrrole C(17) ring is highly tilted from the 3N plane. This distortion breaks the delocalization of the two lone-pair electrons from N(4) to the N(4)−C(19) bond and inhibits formation of the iminium ion with dipolar form in complexes **6** and **7**.[16] Hence, the covalent form should be a major canonical form for complexes **6** and **7**.[16] X-ray diffraction data indicate that the bond length of N(4)−C(19) for the dipolar form of metal N-confused complexes was 1.315 ± 0.011 Å, while that of the covalent form was 1.331 ± 0.008 Å.[16] The bond distance between N(4) and C(19) is 1.327(4) Å [or 1.336(4) Å] in **6** (or **7**). These data also support the existence of the N(4)−C(19)H(19A)(Ar) bond with a covalent form in complexes **6** and **7**.

The values of μ_{eff} observed for complexes **6** (4.51 μ_B) and **7** (4.50 μ_B) at 300 K are very similar and lie in the range of known tetrahedral cobalt(II) complexes (4.2−5.1 μ_B) with $S = {}^3/_2$.[17,18] These values are higher than the expected spin-only value of 3.89 μ_B, suggesting the presence of spin−orbit coupling effects in **6** and **7**. The electronic spectra of high-spin cobalt(II) ($S = {}^3/_2$) with a $3d^7$ configuration and pseudotetrahedral C_{3v} symmetry for **6** (or **7**) are shown in Figure 2a (or Figure S6a in the Supporting Information).[19−23] Expanded NIR spectra of the ${}^4E(T_1,F) \leftarrow {}^4A_2(F)$ transitions of **6** (or **7**) at 300 K are shown in Figure 2b (or Figure S6b in the Supporting Information). The band at 711 nm (or 713 nm) in the UV−vis spectra of **6** (or **7**) in $CDCl_3$ might come from the relatively intense ligand absorption (Q band at 717 nm) of **1** in CH_2Cl_2 (Figure S7 in the Supporting Information).[24,25] The band at 786 nm (or 785 nm) in the spectra of **6** (or **7**) in $CDCl_3$ is assigned to the metal−ligand charge-transfer transition. The weak absorptions of **6** (or **7**) in $CDCl_3$ at 1089 (or 1093) and 1285 nm (or 1295 nm) in the NIR region are assigned to the ${}^4E(T_1,F) \leftarrow {}^4A_2(F)$ transition due to spin−orbit coupling.

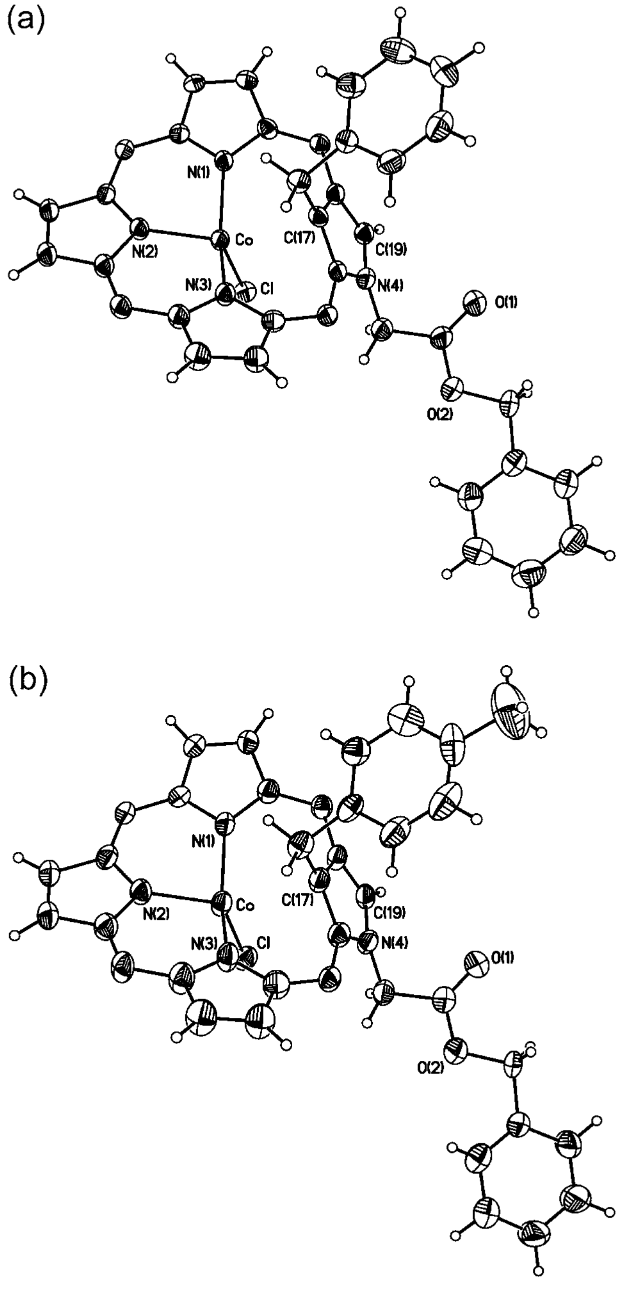

Figure 1. X-ray structures of (a) **6** and (b) **7**. Solvent and phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **6**: Co−Cl, 2.2806(9); Co−N(1), 2.106(2); Co−N(2), 2.005(3); Co−N(3), 2.085(3); N(4)−C(19), 1.327(4); Cl−Co−N(1), 104.72(7); Cl−Co−N(2), 119.61(9); Cl−Co−N(3), 103.56(8). Selected bond lengths (Å) and angles (deg) for **7**: Co−Cl, 2.2881(12); Co−N(1), 2.115(3); Co−N(2), 2.003(3); Co−N(3), 2.094(3); N(4)−C(19), 1.336(4); Cl−Co−N(1), 106.05(10); Cl−Co−N(2), 119.86(11); Cl−Co−N(3), 102.47(11).

In this paper, the synthesis and structural elucidations of two different cobalt complexes, **6** and **7**, are reported with an inner C-alkylation reaction that has been observed for the first time for cobalt(II) in NCP. These paramagnetic cobalt(II) complexes are high-spin state ($S = {}^3/_2$) with the ${}^4A_2(F)$ ground term for a $3d^7$ configuration and pseudotetahedral C_{3v} symmetry. Importantly, this inner C-alkylation works well without any basic catalyst for

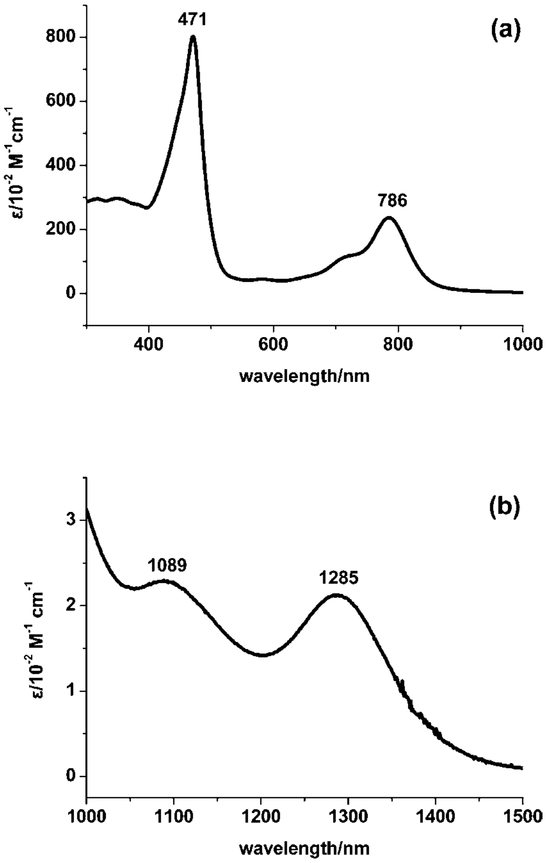

Figure 2. UV−vis−NIR spectra of **6** in $CDCl_3$ at 300 K: (a) 300−1000 nm; (b) 1000−1500 nm.

cobalt(II) but not for zinc(II), nickel(II), platinum(II), palladium(II), and manganese(III) in metal N-confused porphyrin complexes. Electron paramagnetic resonance and magnetic susceptibility studies on high-spin pseudotetrahedral cobalt(II) complexes **6** and **7** are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, preparation and X-ray structures of **1**, **6**, and **7**, ^1H and ^{13}C NMR and UV−vis spectra of **1**, UV−vis−NIR spectra of **7**, and magnetic susceptibility measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Crystal data for **6** and **7**: data were collected at 150(2) K on a Oxford Diffraction Gemini S diffractometer system. For **6**: $C_{60}H_{43}ClCoN_4O_2$, M = 946.36, blue parallelepiped, 0.34 × 0.17 × 0.16 mm^3, monoclinic, space group $P2_1/n$, Z = 4 in a cell of dimensions a = 16.9416(9) Å, b = 14.6567(8) Å, c = 18.1670(8) Å, α = 90°, β = 97.735(2)°, γ = 90°, V = 4470.0(4) $Å^3$, D_c = 1.406 Mg m^{-3}, μ(Mo Kα) = 0.496 mm^{-1}, F(000) = 1964; final R indices on 9208 independent reflections $[I > 2\sigma(I)]$ of R1 = 0.0540 and wR2 = 0.1384. The C(47) atom within **6** is disordered with an occupancy factor of 0.78 for C(47) and 0.22 for C(47′). For **7**: $C_{61}H_{45}ClCoN_4O_2$, M = 960.39, blue parallelepiped, 0.40 × 0.20 × 0.17 mm^3, monoclinic, space group $P2_1/n$, Z = 4 in a cell of dimensions a = 17.0400(5) Å, b = 15.1258(10) Å, c = 18.4773(7) Å, α = 90°, β = 99.081(3)°, γ = 90°, V = 4702.7(4) $Å^3$, D_c = 1.356 Mg m^{-3}, μ(Mo Kα) = 0.473 mm^{-1}, F(000) = 1996; final R indices on 10757 independent reflections $[I > 2\sigma(I)]$ of R1 = 0.0717 and wR2 = 0.1404. The C(47), C(48), C(51), C(52), and C(53) atoms within **7** are disordered with an occupancy factor of 0.82 for C(47), C(48), C(51), C(52), and C(53) and 0.18 for C(47′), C(48′), C(51′), C(52′), and C(53′). CCDC 939034−939035.

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