SHORT COMMUNICATION

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Preparation and Oxygenation of Cobalt N-Confused Porphyrin Nitrosyl Complexes

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The nitrosylation of Co(*H*CTPP) (**1**) in CH_2Cl_2 afforded [Co(CTPP*C_2H_2Cl*)(NO)] (**2**) with a chlorovinyl group substituent on the inner carbon atom of the N-confused porphyrin ring. The spectroscopic data suggest that **1** exhibits an $\{Co(NO)\}^8$ electronic structure. The nitrosylation of **1** in the presence of oxygen leads to [Co(CTPPO)(NO)] (**3**), which is a $\{Co(NO)\}^7$ cobalt nitrosyl complex. A bent axial Co–N–O conformation was observed in both nitric oxide complexes with an angle of 128.5(7)° for **2** and 146.9(11)° for **3**. An sp^3 hydride carbon atom was evidenced in the crystal structure of **2**, and an η^2 interaction between the cobalt center and the inner carbonyl group was observed.
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Introduction

The rapid progress on N-confused porphyrin[1] (NCP) chemistry has inspired new directions in porphyrin and metalloporphyrin studies. The presence of a unique peripheral nitrogen atom on NCP embeds an essential linkage site for assembling a multiporphyrin architecture.[2] The versatile tautomer forms of the conjugate system allow atypical ligand charges that can stabilize unusual metal oxidation states.[3] The interactions between the metal ion and the inner C–H bond and the formation of a reactive metal–carbon bond open up new chemistry that is unfeasible for regular porphyrins.[4]

The chemistry between heme and diatomic molecules plays crucial roles in many biological events.[5] Metalloporphyrins have been applied to explicit key steps in these events.[6] Nonetheless, the reactions of NCP complexes and diatomic molecules have only been briefly explored. It is known that iron NCP complexes activate oxygen, which results in the insertion of an oxygen atom into the iron–carbon bond.[7] Oxygenation appears to be a key step during the NCP core fragmentation in the copper NCP complex according to a recent report.[8] To the best of our knowledge, there is no report available on the reaction of nitric oxide with NCP complexes. To understand the role of the metal–carbon bond on the preparation and the electronic structure of cobalt NCP nitric oxide complex, we report herein the isolation of chlorovinyl-substituted [Co(CTPP*C_2H_2Cl*)(NO)] and oxygenated [Co(CTPP*O*)(NO)] from the reaction of Co(*H*CTPP) with nitric oxide in CH_2Cl_2.

Results and Discussion

Bettelheim et al. reported the preparation of [Co(*H*CTPP)] from $Co(ClO_4)_2$ and NCP, and a typical EPR spectrum of a high-spin Co^{II} ion was recorded.[9] A five-coordinate cobalt NCP complex with H_2O or PPh_3 as an axial ligand and a six-coordinate complex with pyridine as axial ligands were reported earlier by Ziegler et al.[10] The reaction of *meso*-tetraphenyl N-confused porphyrin with $CoCl_2$ under anaerobic conditions yielded four-coordinate [Co(*H*CTPP)] (**1**),[11] which was evidenced by single-crystal structure determination as shown in Figure S8 (Supporting Information). Although **1** contains an unsymmetrical porphyrin ring, only half of the molecule was located in the unit cell, which suggested conformational disorder in the inverted pyrrole ring. The assignment of 50% disorder between the inner carbon atom and the outer nitrogen atom gave reasonable thermal parameters after refinement. The chemical shifts of the β-pyrrolic protons in the ^1H NMR spectrum of **1** were between 36.13 and –5.55 ppm in $CDCl_3$ and confirmed by selectively deuterated $[D_{20}]$Co(*H*CTPP). Whereas detailed study is required to separate dipolar and contact shifts, the largest downfield-shifted resonance is more deshielded than a value of ≈16 ppm, which is the value observed in the low-spin Co(TPP) complex.[12,13] In comparison, the high-spin Co^{II} N-alkylated porphyrin complex $(NCH_3TPP)CoCl$ gave three downfield and one upfield

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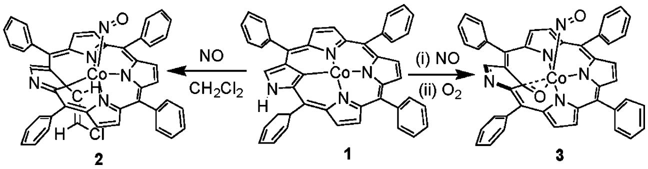
pyrrole resonances between 71 and –12 ppm.[14] The SQUID magnetic susceptibility measurement gave μ_{eff} = 4.36 μ_B and was consistent with the high-spin cobalt(II) center for **1**.

Four-coordinate **1** contains a planar porphyrin core and a reactive metal–carbon bond; thus, it is a good template to study unique NCP coordination chemistry. As shown in Scheme 1, the bubbling of 1% NO (in N_2) into a CH_2Cl_2 solution of **1** for 20 min under anaerobic conditions led to compound **2** with a ν_{NO} at 1630 cm^{-1} in the IR spectrum. The ν_{NO} is lower than those observed for [Co(TPP)(NO)] [15] (1689 cm^{-1}) and [Co(OEP)(NO)][16] (1677 cm^{-1}), but it is in the range for a {Co(NO)}^{8} system in the Enemark–Feltham notation.[17] The broad Soret band at 428 nm with a shoulder at 372 nm (Figure 1) implies that there is a lack of π conjugation in **2**. Interestingly, the presence of a peak at *m*/*z* = 732.4 in the electrospray ionization (ESI) mass spectrometry spectrum for the [M + H]$^+$ mass peak of [Co(CTPPC_2H_2Cl)] suggests a chlorovinyl group as a substituent on the porphyrin core of **2**.



Scheme 1. Reaction routes toward N-confused porphyrin cobalt nitrosyl complexes.

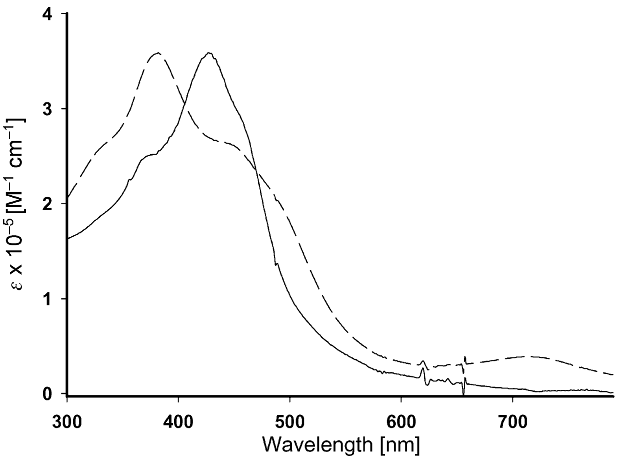


Figure 1. Optical absorption spectra of **2** (——) and **3** (– – –) in CH_2Cl_2.

An increase in the reaction time of NO and [Co(*H*CTPP)] from 20 to 80 min resulted in new product **3** with a Soret band at 383 nm. The blueshifted Soret band as well as the [M + H]$^+$ peak for [Co(CTPP*O*)] at *m*/*z* = 687.1 in the ESI mass spectrum indicated an oxygenated product with a CTPP*O* porphyrin core similar to that in an iron NCP system.[18] A ν_{NO} of 1752 cm^{-1} in the IR spectrum suggested that the isolated product exhibits an unusual {Co(NO)}^{7} electronic structure and that the axial NO did not oxidize to the nitrite group. It appears that the oxygen atom is incorporated from the scarce amount of oxygen introduced during extended NO bubbling, and this is supported by the fact that treatment of either {Co(NO)}^{8} nitrosylated complex **2** with oxygen or oxygenated [Co(CTPP*O*)] [19] with bubbling nitric oxide both resulted in oxygenated nitrosyl product **3**.

The identities of the products were unequivocally established by single-crystal X-ray diffraction.[20] As shown in Figure 2, the bent Co–N(5)–O(1) angle of 132.2(6)° as well as the Co–N(5) and N(5)–O(1) distances of 1.782(5) and 1.101(8) Å, respectively, for [Co(CTPPC_2H_2Cl)(NO)] (**2**) are consistent with the geometry of a {M(NO)}^{8} complex.[21] A twofold disorder between N(4) and C(17) on the periphery of the inverted pyrrole ring with a 50% occupancy for each site was observed, which suggested that NO approached the upper and lower face of the Co(*H*CTPP) ring with an equal ratio. Around the porphyrinic macrocycle, compound **2** displays a nonplanar porphyrin core with an inverted pyrrole ring tilted away from the mean porphyrin plane. The chlorovinyl group, which attaches to the inner carbon atom of the inverted pyrrole ring with a C(45)–C(46) double bond length of 1.290(6) Å and a C(46)–Cl(1) distance of 1.747(5) Å, is clearly evidenced. Interestingly, the inner C(19) atom appears to be a tetrahedron hybrid carbon center with distances of 1.481(6) and 1.468(6) Å to the neighboring pyrrolic carbon atoms. The Co–C(19) bond length of 2.046(5) Å and the Co–C(19)–C(45) angle of 91.4(3)° also imply the presence of an sp^3-like carbon center at C(19).

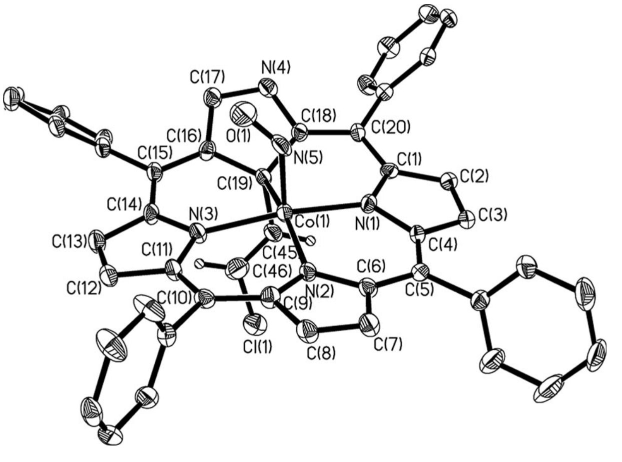


Figure 2. Molecular structure of **2** (thermal ellipsoids at the 25% probability level). Only one conformation of the disordered outer nitrogen N(4) is shown. Bond lengths [Å] and angles [°]: Co–N(5) 1.782(5), N(5)–O(1) 1.101(8), Co–C(19) 2.046(5), C(19)–C(45) 1.527(6), C(45)–C(46) 1.290(6), C(46)–Cl(1) 1.747(5); Co–N(5)–O(1) 132.2(6), C(19)–C(45)–C(46) 128.0(5), C(45)–C(46)–Cl(1) 122.0(5).

A porphyrin core that exhibits severe saddle-shape distortion was obtained in the oxygenated cobalt nitrosyl NCP complex [Co(CTPP*O*)(NO)] (**3**). Similar to the case of **2**, the peripheral N(4) and C(1) atoms in the inverted pyrrole ring have mutual disorders with 50% carbon and 50% nitrogen on each site. As shown in Figure 3, the axial NO is tilted significantly towards the inverted pyrrole ring with the vector of nitric oxide projected on the Co–C(20) bond.

The angle between the normal of the porphyrin plane, defined by 17 atoms on the tripyrrin unit, and Co(1)–N(5) is 13.16°. The short distance of 1.284(7) Å for C(20)–O(1) as well as near-single bond lengths of 1.506(9) and 1.482(9) Å for C(20)–C(2) and C(20)–C(19), respectively, suggest that the keto tautomeric form dominants in the CTPPO moiety. Interestingly, the short distances of 2.052(5) Å for Co(1)–O(1) and 2.162(7) Å for Co(1)–C(20) clearly signify an η^2 interaction between the metal center and the inner carbonyl group. In the axial position, a bent NO with Co(1)–N(5)–O(2) of 146.9(11)° was located. The angle is larger than other $\{Co(NO)\}^7$ cobalt nitrosyl porphyrin complexes available in the literature.[21]

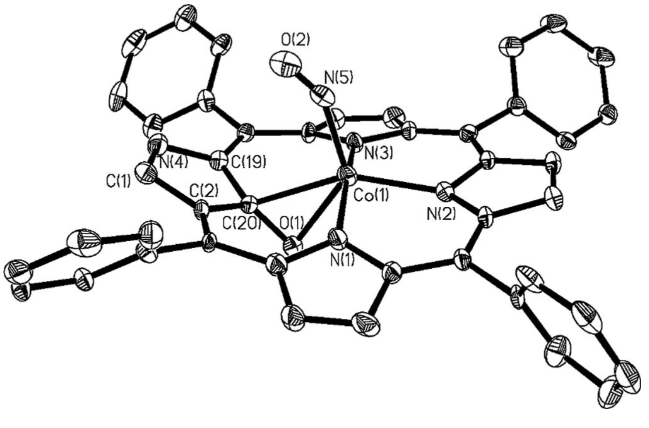


Figure 3. Molecular structure of **3** (thermal ellipsoids at the 25% probability level). Only one conformation of the disordered outer N(4) atom is shown. Bond lengths [Å] and angles [°]: Co(1)–N(5) 1.790(7), N(5)–O(2) 0.980(7), Co(1)–C(20) 2.162(7), Co(1)–O(1) 2.052(5), C(19)–C(20) 1.482(9), C(20)–C(2) 1.506(9), C(20)–O(1) 1.284(7); Co(1)–N(5)–O(2) 146.9(10).

Although chlorovinyl-substituted NCP complex **2** is EPR silent, the ^{1}H NMR spectrum shows broad resonances, which makes precise peak assignment difficult. Nevertheless, to further confirm the origin of the product, CD_2Cl_2 was used as a solvent for the preparation of deuterated chlorovinyl substituent **2**. Two pairs of signals are present for the [D$_2$]chlorovinyl group in the ^{2}H NMR spectrum (δ = 1.21, 3.41 and 0.81, 3.01 ppm). It is not likely that the chlorovinyl group originated from dichloroethylene present in the solvent as an impurity, as no dichloroethylene resonance was observed when the starting mixture was examined by ^{1}H NMR spectroscopy.

In contrast to the abundance of $\{Co(NO)\}^8$ cobalt nitrosyl electronic structures, $\{Co(NO)\}^7$ porphyrin complexes are scarce.[22] It was reported that the one-electron oxidation of a $\{Co(NO)\}^8$ [Co(Por)(NO)] resulted in a porphyrin radical cation rather than metal oxidation.[23,24] The small ν_{NO} shifts in the IR spectrum upon oxidation and isotropic ESR signals with a *g* value around 2.009 and hyperfine splitting around 18 G supported the presence of a porphyrin cation radical.[25] On the contrary, the oxidation of **2** to **3** gave a ν_{NO} difference of 124 cm^{-1}, which suggests a change in the electronic structure of the Co–NO moiety. The EPR spectrum of **3** shows a ten-line pattern with a central *g* value around 2.056 and a peak-to-peak separation as large as 100 G, which is in agreement with a Co–NO-based unpaired electron in **3**. It is likely that a diminished porphyrin π system in cobalt NCP increases the oxidation potential and makes the metal oxidation favorable over porphyrin-ring oxidation.

Conclusions

The isolation of novel [Co(CTPP*O*)(NO)] (**3**) demonstrates that a NCP ligand can stabilize the $\{Co(NO)\}^7$ electronic structure without the formation of a porphyrinic cationic radical. Importantly, the appearance of a chlorovinyl substituent on the cobalt NCP complex in [Co(CTPPC_2H_2Cl)(NO)] (**2**) implies that the reactive metal–carbon bond can promote the decomposition of dichloromethane and also demonstrates the unique reactivity of NCP metal complexes. A related reaction for the formation of an ethylene-bridged dimer on nickel(II) N-confused porphyrin from dihalomethanes has been reported to go through substitution on the inner carbon atom, homolytic halogen abstraction, and free-radical coupling.[26] Presumably, the chlorovinylation reaction on the inner carbon atom of the cobalt(II) N-confused porphyrin complex can occur through a similar pathway. Further studies are in progress to understand the reaction mechanism that leads to the formation of the chlorovinyl substituent and the detailed electronic structure of the reaction products. We are also attempting to establish a catalytic cycle for this reaction.

Experimental Section

[Co(*H*CTPP)] (1): To a solution of *meso*-tetraphenyl N-confused porphyrin (250 mg, 0.406 mmol) dissolved in CH_3CN/THF (2:1, 75 mL) was added $CoCl_2·6H_2O$ (290 mg, 1.22 mmol) and 2,6-lutidine (10 drops). The reaction mixture was heated to 65 °C with stirring. The progress of the reaction was monitored by UV/Vis spectra, which showed the completion of the reaction after 2 h. The solution was then concentrated to ~20 mL until **1** precipitated from the solution. The solid was filtered, washed with CH_3CN (10 mL), and dried to afford **1** (0.240 g, 89% yield). The product was recrystallized by dissolving the solid in THF, followed by the addition of *n*-hexane to afford analytically pure **1**. Crystals suitable for X-ray single-crystal analysis were obtained by dissolving **1** in CH_2Cl_2, followed by diffusion with hexane. UV/Vis (CH_2Cl_2): λ (log ε, $\text{M}^{-1}\,\text{cm}^{-1}$) = 365 (4.55), 430 (4.78), 541 (3.89), 610 (3.78), 665 (3.87) nm. MS (FAB): 671 [M]$^+$. HRMS (FAB): calcd. for $CoC_{44}H_{28}N_4$ [M]$^+$ 671.1645828; found 671.1645950. $CoC_{44}H_{28}N_4·2THF$ (815.86): calcd. C 76.56, H 5.44, N 6.87; found C 77.46, H 5.36, N 6.42.

[Co(CTPPC_2H_2Cl)(NO)] (2): The [Co(*H*CTPP)] (50 mg, 0.074 mmol) was dissolved in CH_2Cl_2 (30 mL) under anaerobic conditions and NO (1% in nitrogen) was bubbled through the solution for 20 min. The solution was stirred for another 20 min after NO bubbling ceased. The solution was dried under vacuum, and the resulting solid was brought into a drybox and recrystallized from CH_2Cl_2/hexane. The precipitate was filtered and dried under vacuum to afford **2** (31 mg, 56% yield). UV/Vis (CH_2Cl_2): λ (log ε, $\text{M}^{-1}\,\text{cm}^{-1}$) = 372 (sh), 428 (4.90) nm. IR (KBr): $\tilde{\nu}$ = 1630 [ν(NO)] cm^{-1}. MS (ESI): *m*/*z* (%) = 671.4 [M – NO – C_2H_2Cl + H]$^+$ (40), 687.6 {[Co(CTPP*O*)] + H}$^+$ (100), 701.0 [M – C_2H_2Cl + H]$^+$ (15), 732.4 [M – NO + H]$^+$ (15). $C_{46}H_{29}ClCoN_5O{\cdot}CH_2Cl_2$ (847.07): calcd. C 66.64, H 3.69, N 8.27; found C 66.89, H 4.55, N 8.03.

[Co(CTPP*O*)(NO)] (3): Following the procedure for the preparation of **2**, a continuous stream of NO gas was bubbled into the THF solution of **1** for 80 min and stirring was continued after NO introduction was terminated. The solvent was removed under vacuum when the Soret band of the reaction solution shifted to 383 nm. The workup procedures were the same as those used in the preparation of **2** to afford **3** (36 mg, 77% yield). Alternatively, [Co(CTPP*O*)] can be prepared by dissolving **1** in THF, bubbling with oxygen for 1 min, and then stirring for 11 h. The reaction of [Co(CTPP*O*)] solution with NO gas (1% NO in N_2) for 20 min obtained desired compound **3** after workup. UV/Vis (CH_2Cl_2): λ (log ε, $\text{M}^{-1}\,\text{cm}^{-1}$) = 383 (5.54), 454 (sh), 719 (4.59) nm. IR (KBr): $\tilde{\nu}$ = 1752 [ν(NO)] cm^{-1}. MS (ESI): *m*/*z* = 687.1 [M – NO + H]$^+$. $CoC_{44}H_{27}N_5O_2{\cdot}C_4H_8O{\cdot}H_2O$ (806.77): calcd. C 71.46, H 4.62, N 8.68, O 7.93; found C 70.43, H 4.65, N 8.64, O 7.53.

[Co(CTPPC_2D_2Cl)(NO)]: CD_2Cl_2 (99.9%D, Aldrich) was dried with calcium hydride and degassed by bulb-to-bulb transformation. The dried solvent was stored in a drybox. Compound **1** (50 mg, 0.074 mmol) was dissolved in CD_2Cl_2 (10 mL) in the drybox. The reaction flask was removed from the box and 1% NO gas was introduced for 20 min. The solvent was removed under vacuum, and the resulting solid was put into the drybox. The solid was dissolved in a minimum amount of CH_2Cl_2 and *n*-hexane was added to obtain 43 mg of [Co(CTPPC_2D_2Cl)(NO)]. The spectroscopic data were the same as in **2**.

Supporting Information (see footnote on the first page of this article): X-ray analysis of the structures of **1**, **2**, and **3**; NMR spectra of the products; absorption spectra and IR spectra of the cobalt nitrosyl complexes; ESI mass spectra of the cobalt nitrosyl complexes; complete atomic labels of the crystal structures; EPR spectrum of [Co(CTPP*O*)(NO)]; and ^2H NMR spectrum of [Co(CTPPC_2D_2Cl)(NO)].

Acknowledgments

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[11] We use the symbol CTPP to denote the N-confused porphyrin core. The groups attached to the peripheral nitrogen atom will be indicated by a prefix in italics and the group attached to inner coordination sphere carbon atom will appear as a suffix in italics.
[12] Abbreviations used: P, general porphyrin; OEP, octaethylporphyrin dianion; TPP: *meso*-tetraphenylporphyrin dianion.
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[19] Compound **4** was not isolated, but its identity was confirmed from the UV/Vis spectrum with absorption maxima at 380 and 460 (sh) nm and MS (ESI) with *m*/*z* = 687.29 [M + H]$^+$.
[20] CCDC-662314 (for **1**), -293465 (for **2**), and -293466 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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