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Nitric Oxide Dioxygenase Activity of a Nitrosyl Complex of Cobalt(II) Porphyrinate in the Presence of Hydrogen Peroxide via Putative Peroxynitrite Intermediate

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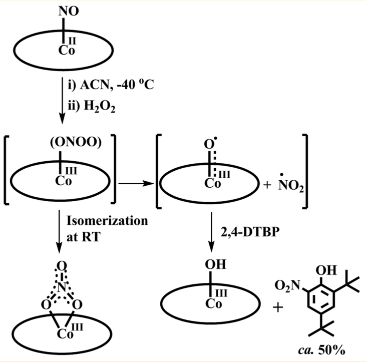
Supporting Information

ABSTRACT: The reaction of a cobalt porphyrin complex, [(F_8TPP)Co], **1** {F_8TPP = 5,10,15,20-*tetrakis*(2,6-difluorophenyl)porphyrinate dianion} in dichloromethane with nitric oxide (NO) led to the nitrosyl complex, [(F_8TPP)Co(NO)], **2**. Spectroscopic studies and structural characterization revealed it as a bent nitrosyl of $\{CoNO\}^8$ description. It was stable in the presence of dioxygen. However, it reacts with H_2O_2 in acetonitrile (or THF) solution at −40 °C (or −80 °C) to result in the corresponding Co(III)-nitrate complex, [(F_8TPP)Co(NO_3)], **3**. The reaction presumably proceeds via the formation of a Co-peroxynitrite intermediate. X-Band electron paramagnetic resonance and electrospray ionization−mass spectroscopic studies suggest the intermediate formation of the [(porphyrin)Co(III)−O$^\bullet$] radical, which in turn supports the generation of the corresponding Co(IV)-oxo species during the reaction. This is in accord with the homolytic cleavage of the O−O bond in heme-peroxynitrite proposed in the nitric oxide dioxygenases activity. In addition, the characteristic peroxynitrite-induced phenol ring reaction was also observed.



INTRODUCTION

Nitric oxide (NO) plays important roles in mammalian biology including neurotransmission and in immune response.[1,2] It is believed that only a submicromolar concentration of NO is required for its functions. However, when produced at high concentrations, it induces cytotoxicity via the formation of reactive nitrogen species (RNS) such as peroxynitrite ($ONOO^-$) or nitrogen dioxide (NO_2).[3,4] These RNS are proposed to form in the reaction of NO with superoxide radical ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and/or in the presence of transition metal ions.[3] The nitric oxide dioxygenases (NODs) control the level of NO by converting it into the biologically benign nitrate.[5,6] The oxy-heme species of the NODs upon reaction with NO results in nitrate (NO_3^-) through the intermediate formation of a peroxynitrite ion. A number of examples are reported where the involvement of a metal-peroxynitrite intermediate is proposed in the reaction of NO with metal−oxygen species. The superoxo complexes of heme and nonheme iron, cobalt, and copper are exemplified to result in the metal-peroxynitrite intermediates in the presence of NO.[7−9] Recently, a nonheme Cr^{IV}-peroxo complex was reported to react with NO to result in Cr^{III}-nitrate; whereas the Cr^{III}-superoxo analogue resulted in the corresponding Cr^{IV}-oxo and NO_2 presumably via a Cr^{III}-peroxynitrite intermediate.[10]

The examples related to the formation of a presumed metal-peroxynitrite in the reaction of a metal-nitrosyl and dioxygen (O_2) are known in the literature. The formation of the nitrite (NO_2^-) product in the reaction of cobalt-nitrosyl with O_2 was reported long back.[11] In recent time, the reaction of a nonheme dinitrosyliron complex with O_2 was found to afford the corresponding nitrate complex.[12] However, Cu(I)-nitrosyl complex was exemplified to result in nitrite product in the presence of O_2 through a presumed peroxynitrite intermediate.[13] In addition, $[Cu(NO)]^{10}$ complex in the presence of H_2O_2 was also found to result in the copper-nitrato complex through a presumed Cu^I-peroxynitrite intermediate formation.[14]

Hence, the reaction of the nitrosyl complexes of transition metal ions with O_2 and the reduced O_2 species is of great interest. In this direction, the examples involving the reaction of metal-nitrosyls with H_2O_2 are limited in the literature.

Herein, we report the NOD activity of a cobalt-nitrosyl, [(F_8TPP)Co(NO)] (**2**), in the presence of hydrogen peroxide (H_2O_2) where the intermediate formation of peroxynitrite is implicated. Spectroscopic evidence suggests the formation of the [(F_8TPP)Co(III)-O$^\bullet$] radical and NO_2 in the reaction.

EXPERIMENTAL SECTION

Materials and Methods. All the reagents and solvents were purchased from commercial sources and used as received unless specified. All the reactions were carried out under Ar or N_2 atmosphere. Repeated vacuum/purge cycles or bubbling with Ar was used to remove the oxygen from the solvents and solutions. Acetonitrile was distilled over calcium hydride. UV−visible spectra were recorded on Agilent Cary 8454 UV−visible spectrophotometer using Chemstation software. FT-IR spectra were taken on a PerkinElmer spectrophotometer with samples prepared as KBr pellets

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or in solutions using NaCl cell having 1 cm path length. ^{1}H NMR spectra were recorded on a 600 MHz Varian FT spectrometer. Chemical shifts (ppm) were referenced with respect to Me_4Si as internal standard for organic compounds or to the residual solvent peaks. Elemental analyses were done on a PerkinElmer Series II Analyzer. Mass spectra were recorded on a Waters, Model Q-Tof Premier instrument with ESI mode of ionization. The X-band electron paramagnetic resonance (EPR) spectra were recorded on a JES-FA200 ESR spectrometer, at room temperature or at 77 K with microwave power, 0.998 mW; microwave frequency, 9.14 GHz; and modulation amplitude, 2.

Single crystals were grown from the respective dichloromethane and chloroform solutions using slow evaporation technique. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoK$_\alpha$ radiation (λ = 0.71073 Å) at 293(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software.[15] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[16] Structures were solved by direct methods using SHELXS-2016 and refined with full-matrix least-squares on F2 using SHELXL-2016/6.[17a] Structural illustrations have been drawn with ORTEP-3 for Windows.[17b]

Syntheses. *Synthesis of Ligand F_8TPPH_2, [5,10,15,20-tetrakis(2,6-Difluorophenyl)porphyrin)].* The ligand F_8TPPH_2 was prepared by general procedure of porphyrin synthesis with some modification. 2,6-Difluorobenzaldehyde (2.84 g, 20 mmol) and pyrrole (1.34 g, 20 mmol) were added to 37 mL of propionic acid. The solution was refluxed for 2 h and then brought to room temperature. The reaction mixture was neutralized using aqueous Na_2CO_3. The precipitated mass was filtered off, washed with water, and dried under vacuum. The crude mass was subjected to column chromatography to result in the pure ligand as a purple crystalline solid (0.61 g, ca.16% yield). Elemental analyses for $C_{44}H_{22}N_4F_8$, calcd (%): C, 69.66; H, 2.92; N, 7.38. Found (%): C, 69.80; H, 2.90; N, 7.46. FT-IR (in KBr): 3334, 2925, 2853, 2852, 1621, 1588, 1462, 1273, 1234, 1001, 962, 780, 573 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ_{ppm}, 8.88 (s, 8H), 7.82−7.77 (m, 4H), 7.40−7.37 (m, 8H). Mass (m/z): calcd 758.17, found 758.51 (molecular ion peak).

Syntheses of the Complexes. *Complex 1.* The ligand F_8TPPH_2 (0.15 g, 0.20 mmol) and $Co(OAc)_2 \cdot 4H_2O$ (0.50 g, 2.00 mmol) were taken in 200 mL of acetonitrile and refluxed for 12 h. The solid mass was filtered off and the filtrate was collected. After removal of the solvent, the crude product was subjected to column chromatography using neutral alumina column, and complex **1** was isolated as red solid (0.11 g, ca. 66% yield). Elemental analyses for $C_{44}H_{20}N_4F_8Co$, calcd (%): C, 64.80; H, 2.47; N, 6.87. Found (%): C, 64.90; H, 2.45; N, 6.99. FT-IR (in KBr): 1626, 1585, 1463, 1234, 1003, 783, 708, 586, and 508 cm^{-1}. UV−visible (CH_3CN): 406 nm (ε/M^{-1} cm^{-1}, 1.79 × 10^5), 525 nm (ε/M^{-1} cm^{-1}, 1.75 × 10^4). EPR in acetonitrile at 77 K: g_{av}, 2.37. ESI-Mass (m/z): calcd 815.08, found 815.09 (Molecular ion peak).

Complex 2. Complex **1** (0.81 g, 1 mmol) was dissolved in dry and degassed CH_2Cl_2. NO gas was bubbled for ca. 10 min to this solution. The color of the solution changes to deep orange red. After removal of the excess NO, the product was isolated by continuous argon flash with ca. 85% yield (0.72 g). Elemental analyses for $C_{44}H_{20}N_5OF_8Co$, calcd (%): C, 62.50; H, 2.38; N, 8.28. Found (%): C, 62.58; H, 2.35; N, 8.39. FT-IR (in KBr): 1692, 1461, 1000, 783, 710, 588, 509 cm^{-1}. UV−visible (CH_3CN): 404 nm (ε/M^{-1} cm^{-1}, 1.40 × 10^5), 531 nm (ε/M^{-1} cm^{-1}, 1.53 × 10^4). ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm}, 8.95 (s, 8H), 7.80−7.75 (m, 4H), 7.39−7.36 (m, 8H). ESI-Mass (m/z): calcd 815.08, found 815.27 {molecular ion peak for [$Co(F_8TPP)$]}.

Complex 3. Complex **2** (0.42 g, 0.5 mmol) was taken in 20 mL of dry and degassed CH_3CN and cooled at −40 °C. Precooled hydrogen peroxide (37% v/v, 2.2 mmol) in acetonitrile was added to this cold solution and stirred for 2 h. The solution was brought to room temperature and dried in a rotavapor (0.26 g, ca. 60% yield). Elemental analyses for $C_{44}H_{20}N_5O_3F_8Co$, calcd (%): C, 60.22; H, 2.30; N, 7.98. Found (%): C, 60.30; H, 2.31; N, 8.06. FT-IR (in KBr): 1622, 1466, 1385, 1238, 1024, 880, 805, and 791 cm^{-1}. UV−visible (CH_3CN): 430 nm (ε/M^{-1} cm^{-1}, 2.18 × 10^5), 542 nm (ε/M^{-1} cm^{-1}, 1.77 × 10^4). ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm}, 9.10 (s, 8H), 7.83−7.76 (m, 4H), 7.43−7.35 (m, 8H). ESI-Mass (m/z): calcd 877.07, found 877.05 {molecular ion peak for [$Co(F_8TPP)(NO_3)$]}.

Complex 4 and 2,4-Di-tert-butyl-6-nitrophenol. To a dry and degassed acetonitrile solution of complex **2** (0.84 g, 1 mmol), precooled solution of 2,4-ditertiarybutylphenol (1.03 g, 5 mmol) was added followed by precooled H_2O_2 (37% v/v, 2.2 mmol) in acetonitrile at −40 °C and stirred for 1/2 h at the same temperature. The reaction mixture was then brought to room temperature and dried in a rotavapor. Purification of the crude mass through column chromatography resulted in pure 2,4-ditertiarybutyl-6-nitrophenol. Yield: 0.125 g (ca. 50%). Complex **4** yield: 0.558 g (ca. 67%).

2,4-Di-tert-butyl-6-nitrophenol. Elemental analyses for $C_{14}H_{21}NO_3$, calcd (%): C, 66.91; H, 8.42; N, 5.57. Found (%): C, 67.07; H, 8.40; N, 5.68. ^{1}H NMR (600 MHz, $CDCl_3$): δ_{ppm}, 1.32 (s, 9H), 1.45 (s, 9H), 5.22 (s, 1H), 7.11 (s, 1H), 7.40 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ_{ppm}, 29.6, 31.6, 34.4, 35.2, 122.3, 124.8, 125.2, 136.1, 142.9, 149.7. ESI-Mass (m/z): calcd 251.10, found 250.53 (M − 1).

Complex 4. Elemental analyses for $C_{44}H_{21}N_4OF_8Co$, calcd (%): C, 63.47; H, 2.54; N, 6.73. Found (%): C, 63.56; H, 2.55; N, 6.88. FT-IR (in KBr): 3449, 2925, 2855, 1624, 1574, 1464, 1428, 1372, 1348, 1276, 1234, 1074, 999, and 761 cm^{-1}. UV−visible (CH_2Cl_2/CH_3CN): 426 nm (ε/M^{-1} cm^{-1}, 1.91 × 10^5), 548 nm (ε/M^{-1} cm^{-1}, 1.96 × 10^4).

■ RESULTS AND DISCUSSION

The ligand, F_8TPPH_2, and its cobalt(II) complex (**1**) were prepared by following the literature methods.[18] The single crystal structure of the ligand was reported earlier.[18] Complex **1** was characterized spectroscopically as well as by its X-ray single crystal structure determination (Experimental Section and Figures S5−S8). The nitrosyl complex of cobalt(II) porphyrin (**2**) was prepared by bubbling NO gas into the degassed dichloromethane solution of the cobalt(II) precursor. Complex **2** was characterized by UV−visible, Fourier-transform infrared (FT-IR) spectroscopy, mass spectrometry, and X-ray structure determination (Experimental Section and Figures S9−S10). The crystallographic data and the metric parameters are listed in Tables S1−S3. The ORTEP views of complexes **1** and **2** are shown in Figures 1 and 2, respectively. In complex **1**, the central metal ion Co(II) is coordinated by four N atoms from the porphyrinate dianion in a square planar geometry. The Co−N$_p$ distances are in the limit of reported distances in analogous complexes.[19] In complex **2**, the Co(II) center is coordinated by four N atoms from the porphyrinate moiety. The NO group is coordinated to the metal ion from the axial position resulting in a square pyramidal geometry around the Co(II) center. The Co−N$_{NO}$ and N−O distances are 1.894(10) and 1.158(13) Å, respectively, which are within the range in other reported analogues.[20] The observed Co−N−O angle is 127.40(14)°. The metric parameters of the nitrosyl complex are in accord with the bent nitrosyls having $\{CoNO\}^8$ configuration.[20] It would be worth mentioning here that the Spiro's group reported the same compound in situ generated for ^{1}H NMR and FT-IR studies; however, it was not isolated in solid state and structurally characterized.[21] The Co−N$_{NO}$ and N−O bond lengths were calculated to 1.810 and 1.186 Å, respectively.[21] The calculated Co−N−O bond angle is 121°.[21] These are also in good agreement with the structurally characterized parameters.

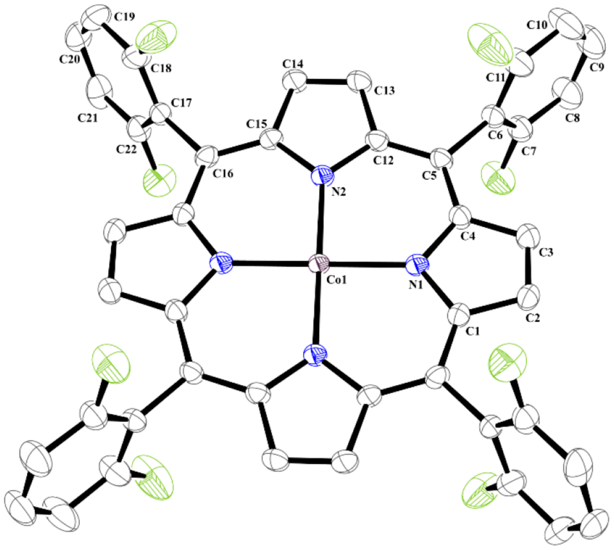


Figure 1. ORTEP diagram of complex **1** (35% thermal ellipsoid plot; H atoms and solvent molecules are not shown for clarity).

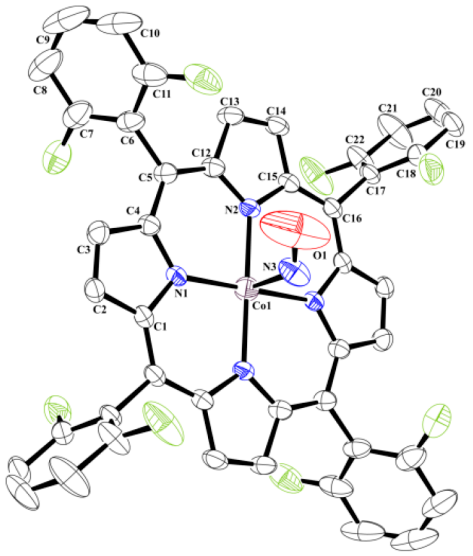


Figure 2. ORTEP diagram of complex **2** (35% thermal ellipsoid plot; H atoms are not shown for clarity).

In the FT-IR spectrum, the strong stretching frequency at 1692 cm^{-1} in KBr is assignable to the coordinated NO moiety (Figure 3). Spiro and co-workers reported the ν_{NO} stretching to appear at 1699 cm^{-1} in CH_2Cl_2.[21] In earlier reported examples like [(TPP)Co(NO)] and [(OEP)Co(NO)], the NO stretching was observed at 1689 cm^{-1} (in KBr) and 1675 cm^{-1} (in CH_2Cl_2), respectively.[22] In the cases of cobalt porphyrin nitrosyls having general formula [{T(*p*/*m*-X)PP}-Co(NO)] [*p*/*m*-X = *p*-OCH_3, *p*-CH_3, *m*-CH_3, *p*-H, *m*-OCH_3, *p*-OCF_3, *p*-CF_3, *p*-CN, etc.] in CH_2Cl_2, the NO stretching frequency appeared in the range of 1681−1695 cm^{-1}.[22] It appeared at 1701 cm^{-1} in KBr disc for complex [(Cl_4TPP)-Co(NO)].[23] In the ESI mass spectrum, complex **2** displayed a peak at *m*/*z* 815.27 assignable to the [Co(F_8TPP)] (calcd *m*/*z* = 815.08). This is attributed to the facile loss of the axial NO group, which has been observed earlier in other nitrosyl complexes of Co(II)-porphyrinates.[23,24]

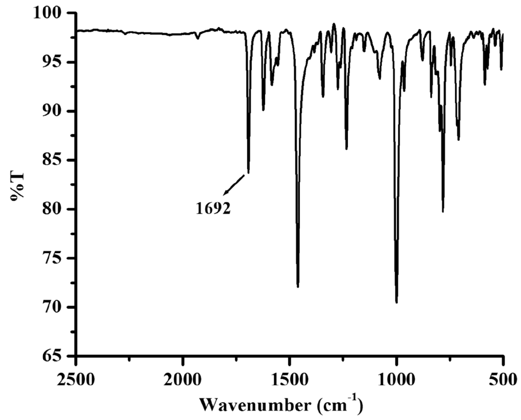
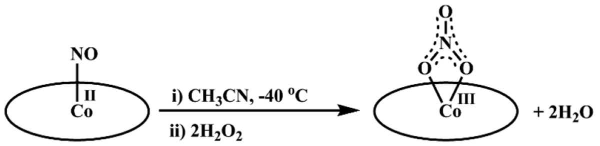


Figure 3. FT-IR spectrum of complex **2** in KBr.

Complex **2** in CH_2Cl_2 or CH_3CN solution did not react with dioxygen; however, it reacts with H_2O_2. Upon addition of 2.2 equiv of H_2O_2, complex **2** in CH_3CN solution at −40 °C resulted in the formation of corresponding nitrate complex, **3** (Scheme 1).

Scheme 1. Reaction of Complex 2 with H_2O_2



The complex **2** in acetonitrile solution at −40 °C shows absorption at 531 and 404 nm, respectively. Addition of 2.2 equiv of precooled H_2O_2 resulted in the gradual decay of these absorption maxima along with a simultaneous formation of new absorption bands at 542 and 430 nm, respectively (Figure 4). These are assignable to the complex **3**. The reaction was also carried out in THF solution at −80 °C (Figure S11), and no intermediate formation was observed. Isolation as solid and spectroscopic characterization revealed complex **3** as the nitrate complex of the corresponding Co(III) porphyrinate, [(F_8TPP)Co(NO_3)] (Experimental Section). Even after

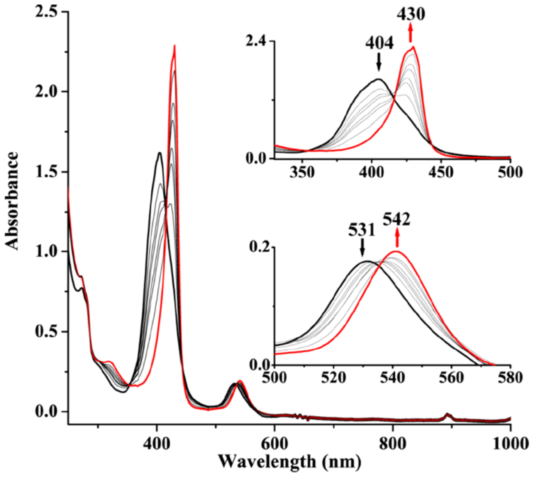


Figure 4. UV−visible spectral monitoring of complex **2** (11.50 μM) (black) and after addition of 2.2 equiv of H_2O_2 to result in complex **3** (red) at −40 °C in acetonitrile.

several attempts we could not grow the X-ray quality crystals of complex **3**. In the FT-IR spectroscopy, the nitrate stretching frequency was observed at 1385 cm^{-1} (Figure S12). The assignment has been done based on the observed stretching frequencies for the nitrate groups in the earlier reported metal porphyrin complexes.[25] In ^{1}H NMR spectrum, complex **3** displays well-resolved signals in $CDCl_3$ suggesting the presence of a low spin cobalt(III) ion in the complex (Figure S14). The signal at 9.10 ppm corresponding to altogether eight protons is assignable to the protons from pyrrole moiety. The signals appearing at 7.83 and 7.43 ppm, respectively, are assigned to the protons from the phenyl group (Experimental Section and Supporting Information).

Complex **3** shows the molecular ion peak at *m*/*z* 877.05 (calcd. 877.07) corresponding to [$(F_8TPP)Co(NO_3)$] in the ESI-mass spectrum (Figure 5). The isotopic distribution pattern was found to be in accord with the simulated spectrum (Figure 5).

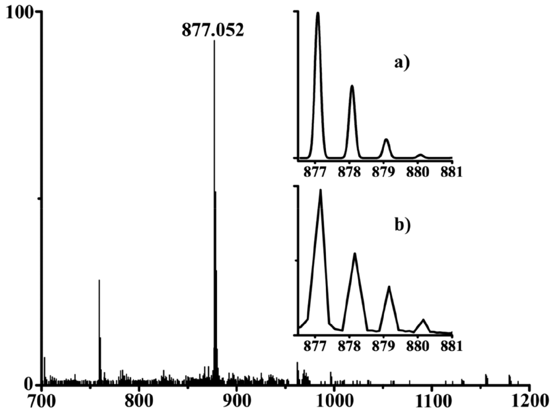


Figure 5. ESI-mass spectrum of complex **3** in acetonitrile [Inset: (a) simulated and (b) experimental isotopic distribution pattern].

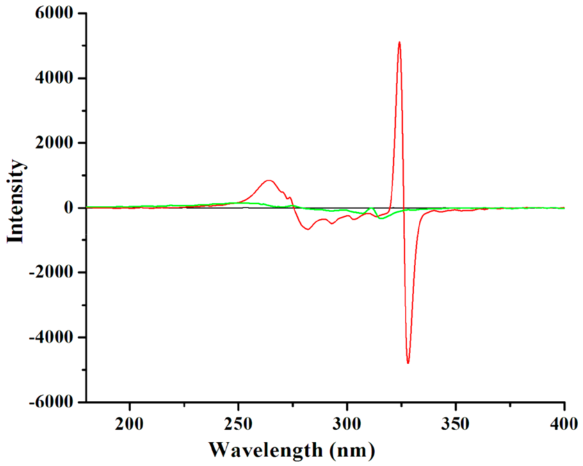


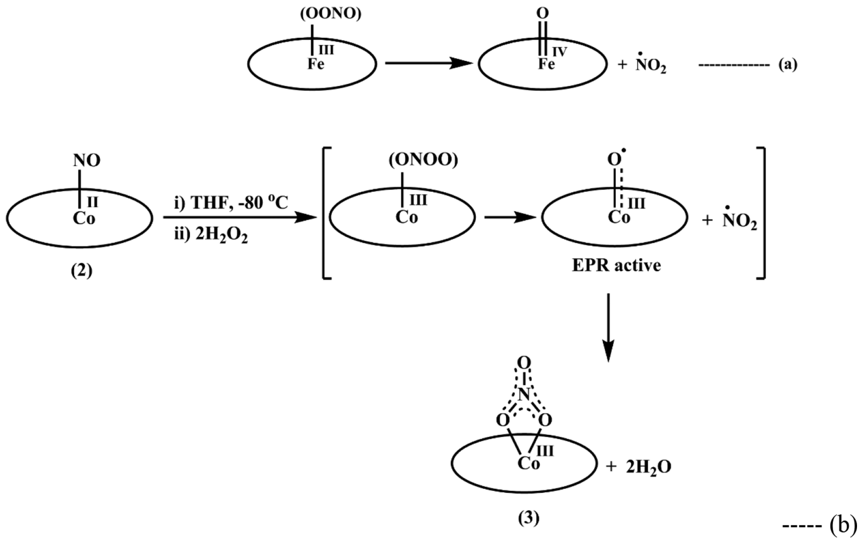
Figure 6. X-band EPR spectra of complex **2** (24.5 mM) (black), the intermediate (red) formed in the reaction of complex **2** and H_2O_2, and complex **3** (green) in THF at 77 K.

It is proposed that the reaction of complex **2** with H_2O_2 leading to the formation of the complex **3** proceeds through the formation of a Co-peroxynitrite intermediate; however, no intermediate was observed in UV−visible spectroscopy even when the reaction was carried out in THF at −80 °C. It is to be noted here that thermo-kinetic and theoretical studies suggested that peroxynitrite intermediates should be too short-lived to detect.[26] Interestingly, when the reaction was carried out in THF solution at −80 °C and followed by freezing at 77 K, the frozen (at 77 K) reaction mixture displayed a signal at $g = 2.002$ in the X-band EPR spectrum (Figure 6). The sharp and isotropic nature of the signal suggested the presence of a radical in the mixture. The spectrum was contaminated with a small fraction of Co(II) species. Even after several attempts we could not remove this. Similar signal was reported earlier for the Co(III) porphyrin radical cations generated by electro-oxidation of the Co(II)-porphyrinates.[27] It is to be noted that the Co(III) porphyrin radical cations show characteristic bleaching of their Soret bands due to loss of π-conjugation.[27] However, in the present case no indication of such feature was observed even at −80 °C temperature. The intensity of the signal decreases gradually with warming it up and finally disappeared suggesting the formation of final product, complex **3**. It is proposed that in case of NODs the reaction of the Fe(III)-oxy complex with NO resulted in the formation of the peroxynitrite intermediate. In a subsequent step, the O−O bond cleaved homolytically to produce an oxo-ferryl ($Fe^{IV}=O$) species and NO_2 (Scheme 2).[7−9] In the present case, the appearance of the isotropic signal at $g = 2.002$ is actually suggestive to the formation of a Co(IV)-oxo species and NO_2 (Scheme 2). It has been reported by Winkler and Gray that for oxo-metal complexes having d^5 configuration, the [$M^{III}-O^{\bullet}$] is more likely than [$M^{IV}=O$] configuration.[28] In the present case, the Co(IV)-oxo species owing to its d^5 configuration would convert into $(F_8TPP)Co^{III}-O^{\bullet}$. This accounts for the appearance of sharp EPR signal at $g = 2.002$ and non-observance of the quenching of Soret band in UV−visible spectroscopy. NO_2 at 77 K dimerizes to form diamagnetic N_2O_4. The $(F_8TPP)Co^{III}-O^{\bullet}$ in the presence of NO_2 undergoes fast decomposition to the final product, complex **3**. In the ESI-mass spectrum of this reaction mixture, a molecular ion peak (*m*/*z*) was observed at 831.09 (calculated: 831.08), which is assignable to the $(F_8TPP)Co^{III}-O^{\bullet}$ (Figure 7).

Comparison of the spectral characteristics with an authentic sample generated in a separate reaction of Co(II) porphyrin complex and *m*-CPBA also support the proposition (Figures S17−S19). Highly unstable nature of the species precluded its further characterization.

Because of very short lifetime of the proposed Co-peroxynitrite, no direct spectroscopic evidence has been observed, and indirect chemical evidence for the postulated species has been sought. It is to be noted that commonly a phenol nitration reaction is used to provide evidence in support of the presence of metal-peroxynitrite. It has been observed that when the reaction of complex **2** with H_2O_2 was done in the presence of 2,4-ditertiarybutylphenol (DTBP), it resulted in an effective phenol ring nitration (ca. 50%). Isolation and characterization of the products from the mixture revealed the formation of the corresponding Co^{III}-hydroxo product, [$(F_8TPP)Co(OH)$] **4** (ca. 67%) and 2,4-ditertiarybutyl-6-nitrophenol (ca. 50%) (Scheme 3; Experimental Section and Figures S15−S16 and S20−S22). No product corresponding to the oxidative coupled phenol is observed in isolable scale. However, when reaction is followed by the addition of 2,4-ditertiarybutylphenol (DTBP), exclusive formation of complex **3** was observed along with unreacted DTBP.

Scheme 2



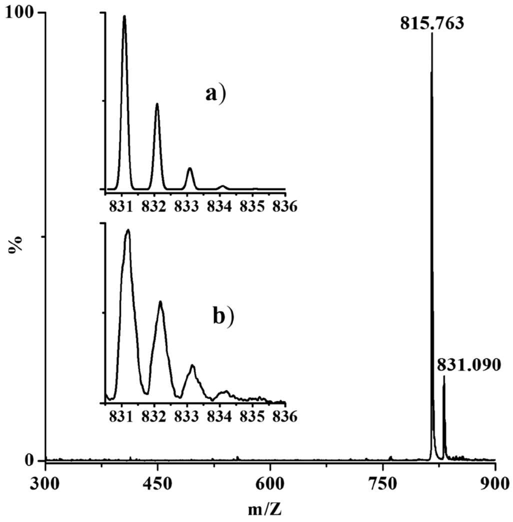
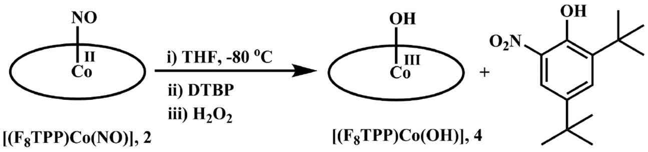


Figure 7. ESI-mass spectrum of the reaction mixture obtained from the reaction of complex **2** and H_2O_2 (in CH_3CN) in THF at −80 °C. [Inset: (a) simulated and (b) experimental isotopic distribution pattern].

Scheme 3. Phenol Ring Nitration Reaction by Complex 2 in the Presence of H_2O_2



It is to be noted that the reaction of the nitrosyl of copper(II) complexes of methyl 2-(2-hydroxybenzylamino)-3-(1*H*-imidazol-5-yl)propanoate[29] and *bis*(2-ethyl-4-methyl-imidazol-5yl)methane[14] ligands with H_2O_2 in CH_3CN at −40 °C also led to the corresponding nitrate products through a presumed peroxynitrite intermediate. An appreciable amount of phenol ring nitration was observed in those cases. Recently, $[(Cl_4TPP)Co(NO)]$ complex in the presence of H_2O_2 in acetonitrile at −40 °C was exemplified to result in the corresponding nitrite complex, $[(Cl_4TPP)Co(NO_2)]$, and the formation of a peroxynitrite intermediate was implicated.[25] However, in that case no indication of the formation of Co(IV)-oxo ↔ $(porphyrin)Co^{III}{-}O^{\bullet}$ was evidenced.

■ CONCLUSION

Thus, the nitrosyl complex of cobalt porphyrin, $[(F_8TPP)Co(NO)]$, in acetonitrile (or THF) solution at −40 °C (or −80 °C) was found to react with H_2O_2 to result in the corresponding Co-nitrate complex, $[(F_8TPP)Co(NO_3)]$. The reaction proceeds via the formation of a presumed Co-peroxynitrite intermediate. X-Band EPR and ESI-Mass spectroscopic studies suggest the intermediate formation of the $(F_8TPP)Co^{III}{-}O^{\bullet}$, which in turn supports the generation of the corresponding Co(IV)-oxo species during the reaction. This is in accord with the homolytic cleavage of the O−O bond in heme-peroxynitrite proposed in the NOD activity. In addition, the nitration of phenol ring induced by the above reaction also suggests the formation of a peroxynitrite intermediate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02722.

Spectral analyses, crystallographic data, and metric parameters of the complexes (PDF)

Accession Codes

CCDC 1869139−1869141 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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