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Reaction of a Co(III)-Peroxo Complex and NO: Formation of a Putative Peroxynitrite Intermediate

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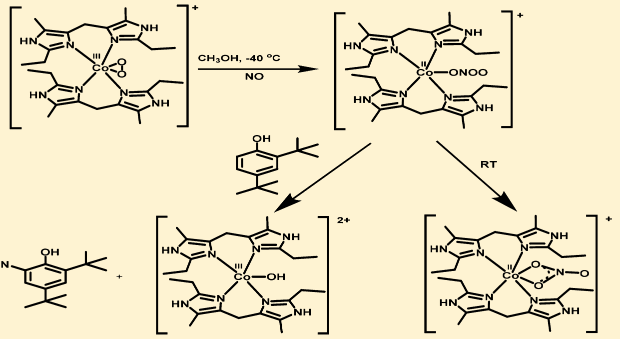
Supporting Information

ABSTRACT: A Co(II) complex, $[Co(L)_2]Cl_2$, **1** of the ligand **L** (**L** = bis(2-ethyl-4-methylimidazol-5-yl)methane) upon reaction with H_2O_2 in methanol solution at −40 °C resulted in the formation of the corresponding Co(III)-peroxo complex $[Co(L)_2(O_2)]^+$ (**2**). The addition of NO gas to the freshly generated solution of the complex **2** led to the formation of the Co(II)-nitrato complex **3** through the putative formation of a Co(II)-peroxynitrite intermediate, **2a**. The intermediate **2a** was found to mediate the nitration of the externally added phenol resembling the nitration of tyrosine in biological systems.



INTRODUCTION

Nitric oxide (NO) is an important small molecule that is involved in various physiological processes such as neurotransmission, vasodilation, immune response, etc.[1−4] Under normal conditions, NO is produced by the nitric oxide synthases (NOS) at low concentration.[5] However, an excess production of NO can have detrimental effects via the formation of secondary reactive nitrogen species (RNS) such as nitrogen dioxide (NO_2) and peroxynitrite ($ONOO^-$).[6] Both of these RNS are known to play important roles in biomolecule oxidation leading to the oxidative and nitrosative stress.[7] The nitric oxide deoxygenases (NODs) are known to control the in vivo level of NO by converting it into the biologically benign nitrate (NO_3^-) and thereby removing the excess of it.[8] The conversion of NO to NO_3^- by NODs is believed to proceed through the formation of a peroxynitrite intermediate.[8,9] Peroxynitrite is proposed to form in vivo in a diffusion-controlled reaction of NO and O_2^- anion or H_2O_2 and nitrite (NO_2^-) in the presence of the peroxidase enzymes.[10,11] An aqueous peroxynitrite is known to isomerize to the nitrate (NO_3^-) very easily.[8] In the literature, peroxynitrites are exemplified to form either in the reaction of oxy-heme (formally, $Fe^{III}-O_2^{\cdot-}$) proteins with NO or metal-nitrosyls with O_2 or O_2^-.[9,12] Recently, the peroxynitrite intermediates have been shown to form in the reaction of NO with Cr−superoxo or peroxo species. A Cr(IV)-peroxo complex ($[Cr^{IV}(12\text{-TMC})(O_2)(Cl)]^+$) {12-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane} is reported to react with NO to result in a Cr(III)-nitrato complex, ($[Cr^{III}(12\text{-TMC})(NO_3)(Cl)]^+$), whereas the reaction of Cr(III)-superoxo complex $[Cr^{III}(14\text{-TMC})(O_2)(Cl)]^+$ and NO resulted in the corresponding Cr(IV)-oxo complex ($[Cr^{IV}\text{-}(14\text{-TMC})(O)(Cl)]^+$) and NO_2 presumably via the formation of a Cr(III)-peroxynitrite intermediate, $[Cr^{III}(14\text{-TMC})(OON{=}O)(Cl)]^+$.[13−15] On the one hand, Nam et al. reported the reactivity of an Fe(III)-peroxo complex, $[Fe^{III}(14\text{-TMC})(O_2)]^+$, with NO^+ as an approach for generating the peroxynitrite intermediate, which led to the formation of an Fe(III)-nitrato complex, $[Fe^{III}(14\text{-TMC})(NO_3)(F)]^+$.[16] On the other hand, Basalo et al. reported the reaction of a Co-nitrosyl with O_2 to result in the Co-nitrite, where the intermediate formation of a peroxynitrite is presumed.[17] Similarly, a nonheme dinitrosyliron complex has been shown to result in the corresponding nitrite in its reaction with O_2.[18] Recently, Karlin and co-workers reported the reaction of a mixed-valent nitrosyl complex of Cu(I)Cu(II), namely, $[Cu^{I,II}_2(UN\text{-}O^-)(NO)]^{2+}$ with O_2, to result in the superoxide and nitrosyl adduct, $[Cu^{II}_2(UN\text{-}O^-)(NO)(O_2^-)]^{2+}$, which was subsequently converted to the corresponding peroxynitrite complex.[19]

In our laboratory, we have been working on the reactivity of the metal nitrosyls with O_2^- anion and H_2O_2 with an aim to generate a peroxynitrite species. For example, $\{CuNO\}^{10}$ complex of the bis(2-ethyl-4-methylimidazol-5-yl)methane ligand was found to react with H_2O_2 to afford the corresponding Cu(I)-nitrite, and the formation of a Cu(I)-peroxynitrite intermediate is presumed.[20] The same nitrosyl complex, upon reaction with O_2^- anion, was observed to result in Cu(II)-nitrite.[20] In an another example, the $\{CuNO\}^{10}$ complex in the presence of H_2O_2 was shown to form Cu(II)-nitrite via a presumed peroxynitrite intermediate.[21] Cobalt nitrosyls, both with porphyrin and nonporphyrin ligands, were reported to react with O_2 and O_2^- to afford cobalt-nitrate/nitrite complexes.[17,22] The involvement of a peroxynitrite

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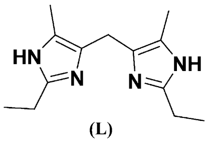
intermediate in these reactions was implicated. However, the examples involving the reactions of the cobalt-peroxo complexes of nonporphyrinate ligands with NO are limited.

The present work describes the reactivity of a Co(II) complex, $[Co(L)_2]Cl_2$, **1** of the ligand **L** (**L** = bis(2-ethyl-4-methylimidazol-5-yl)methane; Figure 1) with H_2O_2 in methanol solution at −40 °C to form the Co(III)-peroxo complex $[Co(L)_2(O_2)]^+$ (**2**). The addition of NO gas to the freshly generated solution of the complex **2** led to the formation of the Co(II)-nitrato complex **3** through the putative formation of a Co(II)-peroxynitrite intermediate **2a**. The intermediate **2a** was found to mediate the nitration of the externally added phenol resembling the nitration of tyrosine in biological systems.



(L)

Figure 1. Ligand used in the present work.

■ RESULTS AND DISCUSSION

The ligand **L** (**L** = bis(2-ethyl-4-methylimidazol-5-yl)methane) was synthesized by following the earlier reported procedure.[23] The Co(II) complex **1**, $[Co^{II}(L)_2]Cl_2$, was prepared by stirring a mixture of cobalt(II) chloride hexahydrate with 2 equiv of the ligand in methanol (Experimental Section). The complex **1** was characterized by spectroscopic analyses such as UV−visible, Fourier transform infrared (FT-IR), electron paramagnetic resonance (EPR), and electrospray ionization (ESI) mass spectrometry (Experimental Section). The formation of the complex was further confirmed by the single-crystal X-ray structure determination. The crystallographic data and other metric parameters listed in Tables S1−S3 (Supporting Information). The ORTEP diagram of the complex **1** is shown in Figure 2. The crystal structure revealed that the Co(II) center is coordinated by the four nitrogen atoms from two units of the ligand in an overall distorted tetrahedral geometry. The presence of two chloride ions outside of the coordination sphere satisfied the charge of the central metal ion. The average Co−N distance (1.982 Å) was found to be within the range of analogous reported complexes.[24]

In methanol solution, complex **1** exhibited the absorptions at 515 nm (ε, 323 M^{-1} cm^{-1}) 559 nm (ε, 494 M^{-1} cm^{-1}), and 581 nm (ε, 490 M^{-1} cm^{-1}) along with the other intraligand transitions at lower wavelengths (Figure 3). These absorption bands in the visible region of the spectrum are attributed to the $^4A_2 \rightarrow {}^4T_1(F)$, $^4A_2 \rightarrow {}^4T_1(P)$, $^4A_2 \rightarrow {}^4T_2$ transitions, respectively, in tetrahedral Co(II) (d^7) system.[25] The crystalline complex **1** was dissolved in methanol, EPR was recorded at 77 K (Figure S7, Supporting Information). The observed g_{av} was 2.29. The observed magnetic moment was found to be 4.32 μ_B, which is comparable with the other reported Co(II) tetrahedral complexes.[26]

The addition of 5 equiv of H_2O_2 and 2 equiv of NEt_3 to the methanol solution of complex **1** at −40 °C afforded a pink color intermediate, which was thermally unstable and decomposed readily at room temperature (Scheme 1). In the

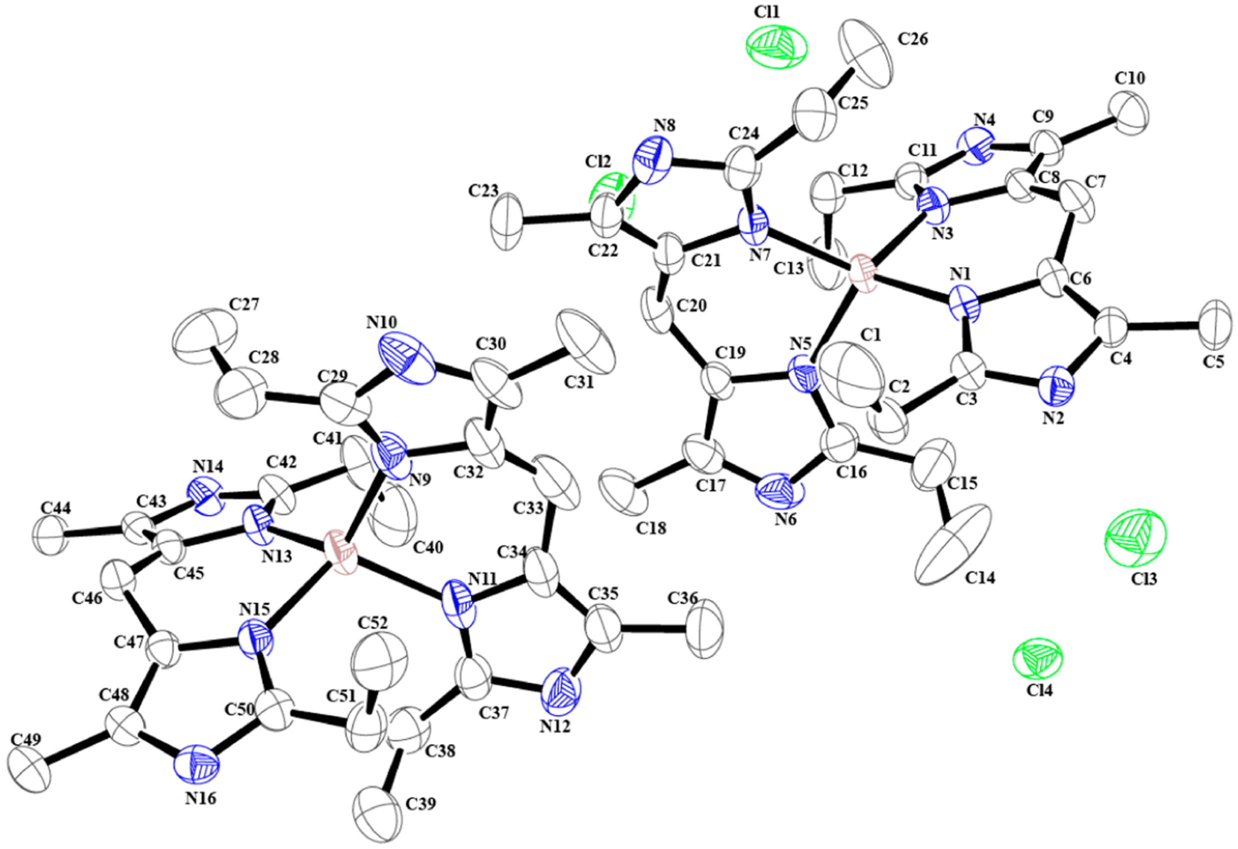


Figure 2. ORTEP diagram of complex **1** (30% thermal ellipsoid plot, H atoms and solvent molecules are not shown for clarity).

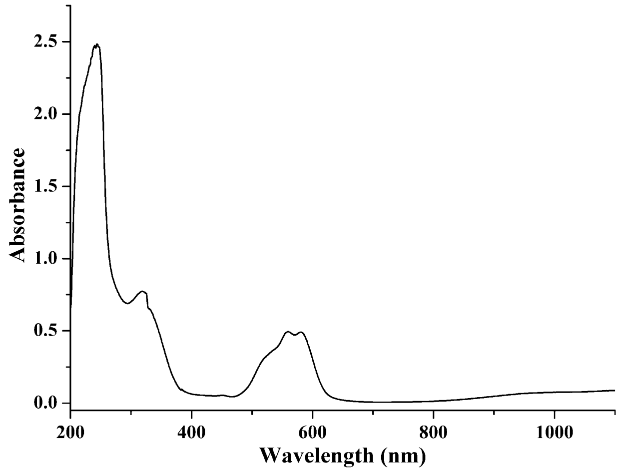


Figure 3. UV−visible spectrum of complex **1** in methanol at 298 K.

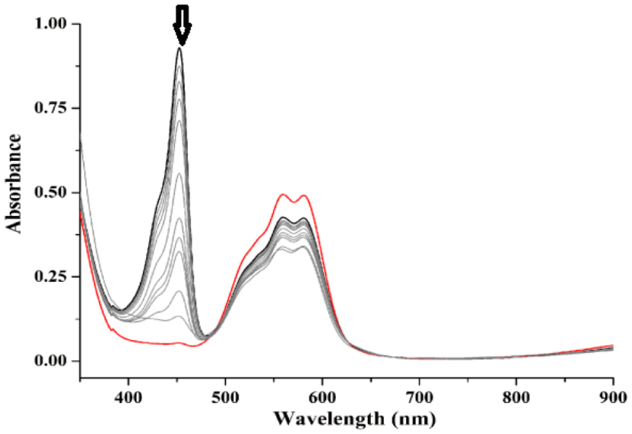


Figure 4. UV−visible spectra of complex **1** (red), after addition of H_2O_2\{complex **2**\} (gray), in methanol at −40 °C.

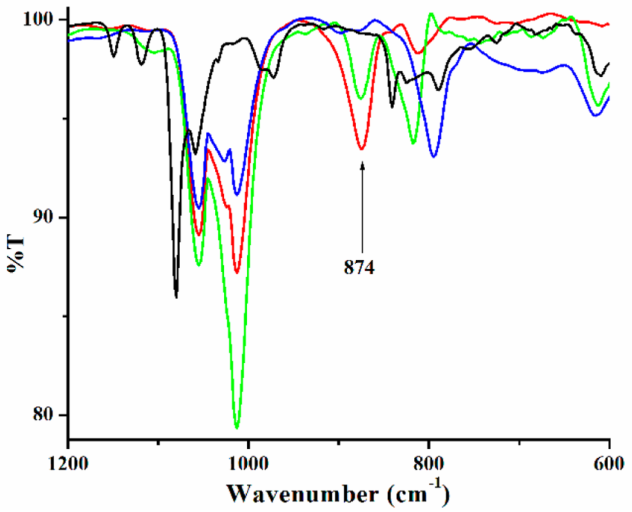
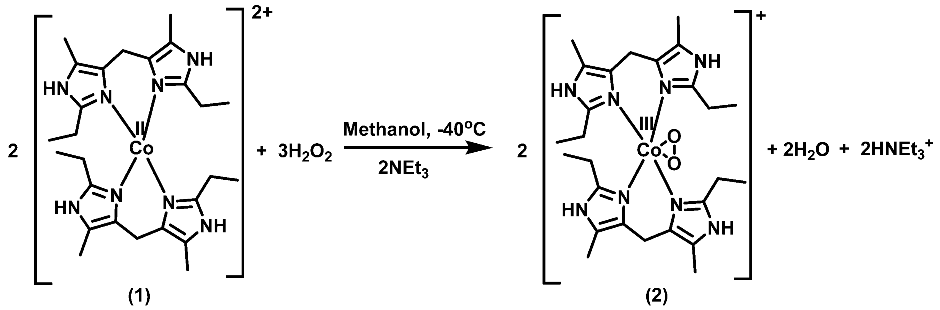


Figure 5. Solution FT-IR spectra of complexes **1** (black) and **2** (red) in methanol. Green and blue traces represent the gradual decomposition of complex **2** at room temperature.

visible region of the spectrum, the intermediate displayed a new absorption band at 452 nm (ε, 890 M^{-1} cm^{-1}; Figure 4). This was attributed to the formation of corresponding Co(III)-peroxo complex. The Nam group has reported a number of transition metal side-on peroxo complexes, where the absorption band in the visible region appeared in the range from 340 to 470 nm.[27] For example, the side-on peroxo complexes [Co^{III}(TMC)(O$_2$)]$^+$, [Co^{III}(15-TMC)(O$_2$)]$^+$, and [Co^{III}(12-TMC)(O$_2$)]$^+$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were reported to absorb at 436 nm (ε, 254 M^{-1} cm^{-1}), 464 nm (ε, 120 M^{-1} cm^{-1}), and 350 nm (ε, 450 M^{-1} cm^{-1}), respectively.[27,28] On the other hand, the end-on peroxo complexes of Co(III) displayed absorption bands in the range from 485 to 580 nm.[29]

The addition of 5 equiv of H_2O_2 and 2 equiv amount of NEt$_3$ in methanol solution of complex **1** resulted in the appearance of a new stretching band at 874 cm^{-1} in the FT-IR spectrum (Figure 5). The intensity of the band was found to diminish with time suggesting the unstable nature of the intermediate (Figure 5). The band appeared to be sensitive to ^{18}O labeling and shifted to 826 cm^{-1} when $H_2{}^{18}O_2$ was used. Thus, it was assigned to the O−O stretching frequency in the Co(III)-peroxo intermediate. Note that, in cases of transition metal peroxo complexes, the O−O stretching frequency that appeared in the range of 830−900 cm^{-1} is designated for side-on (η^2) peroxo mode for 1:1 metal/O$_2$ species.[30] In case of structurally characterized side-on [Co^{III}(tmen)$_2$(O$_2{}^{2-}$)]$^+$ (tmen = tetramethylethylenediamine), the O−O stretching appeared at 861 cm^{-1} in KBr disc.[30b] In addition, the O−O stretching in side-on [Co(Ph$_2$PCH=CHPPh$_2$)$_2$(O$_2$)]$^+$ and [Rh(PhP(CH$_2$CH$_2$PPh$_2$)$_2$]Cl(O$_2$) appeared at 909 and 862 cm^{-1}, respectively.[31] Thus, it is logical to believe that addition of H_2O_2 to the methanol solution of complex **1** at −40 °C resulted in the formation of the corresponding Co(III)-peroxo intermediate, where the peroxo group is bonded to the metal ion in a side-on fashion. Though the resonance Raman study of the oxygenated intermediate gives a more accurate picture of peroxo binding mode in metal−peroxo complexes, the

Scheme 1. Reaction of Complex 1 with H_2O_2 in Methanol at −40 °C



photodecomposition of the intermediate in the present case precluded its study.

As expected for a Co(III)-peroxo species, the intermediate was silent in X-band EPR study (Figure 6).[27,28] The ESI-mass spectrum of the intermediate was populated by a peak at m/z 555.28, which is assignable to the mass of $[Co(L)_2(O_2)]^+$ (calculated m/z 555.26; Figure 7). The peak was sensitive toward ^{18}O labeling and found to appear at m/z 559.41 when $H_2{}^{18}O_2$ was used (Figures 7 and S9, Supporting Information). The upshift of mass by 4 units upon substitution of ^{16}O by ^{18}O suggests the presence of O_2 unit in complex **2**. The observed isotopic distribution pattern was in good agreement with the simulated one (Figure S17, Supporting Information).

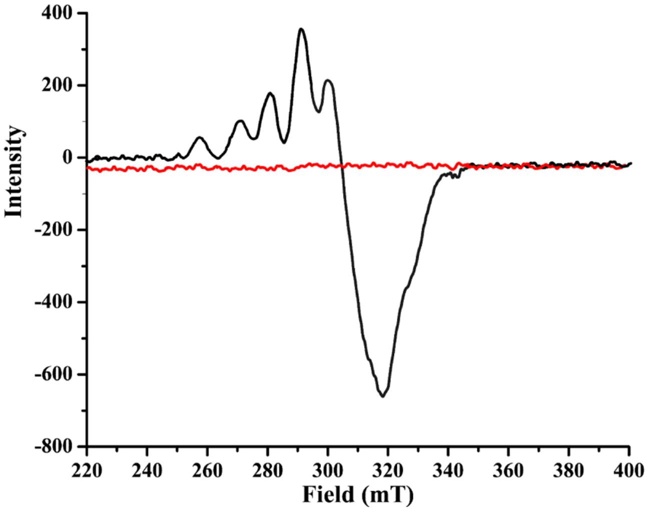


Figure 6. X-band EPR spectra of complexes **1** (black) and **2** (red) in methanol at 77 K.

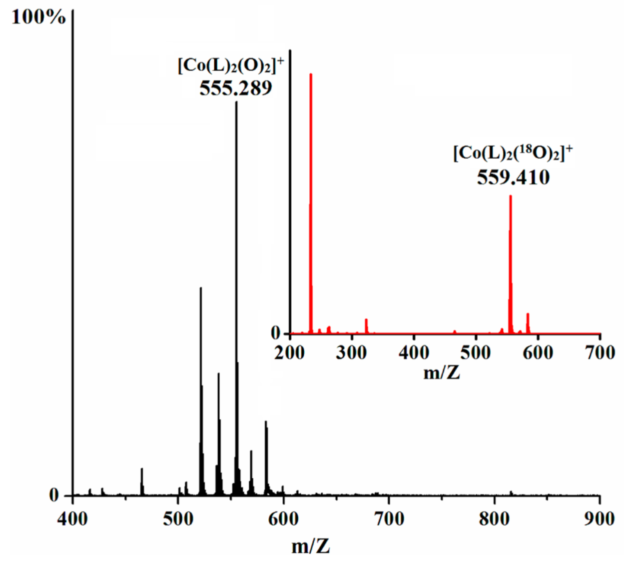


Figure 7. ESI-Mass spectra of complex **2** obtained from the reaction of complex **1** and $H_2{}^{16}O_2$ in methanol. (inset) The same when the reaction was carried out with $H_2{}^{18}O_2$.

Thermal instability of the intermediate precluded its isolation as solid and further characterization.

NO Reactivity of the Co(III)-Peroxo Intermediate. The addition of NO gas (ca. 5 equiv) to the freshly generated complex **2**, $[Co(L)_2(O_2)]^+$, in methanol at −40 °C followed by warming at room temperature resulted in the formation of complex **3** $\{[Co^{II}(L)_2(NO_3)]Cl\}$. It was isolated and characterized by elemental and spectroscopic analyses (Experimental Section and Supporting Information). It was further characterized by the single-crystal X-ray structure determination. The crystallographic data and important bond angles and distances are listed in Tables S1, S2, and S3, respectively, in the Supporting Information. The ORTEP diagram of the complex **3** is shown in Figure 8. The crystal structure revealed that the Co(II) center is bonded with two units of the ligand and a nitrate (NO_3^-) anion in a distorted octahedral geometry. An κ^2-O coordination mode of NO_3^- to the Co(II) center was observed. The Co−$O_{nitrato}$ bond distance is 2.287(4) Å, and Co−O−N bond angle is 94.08°. The N−O bond distances are 1.273(5) and 1.15(1) Å. In the FT-IR spectrum, complex **3** displayed a strong band at 1384 cm^{-1}, which is assignable to the $NO_3{}^-$ stretching frequency.[20] Note that the complex **3** with NO_3^- as counteranion was reported earlier by Sun and coworkers.[32]

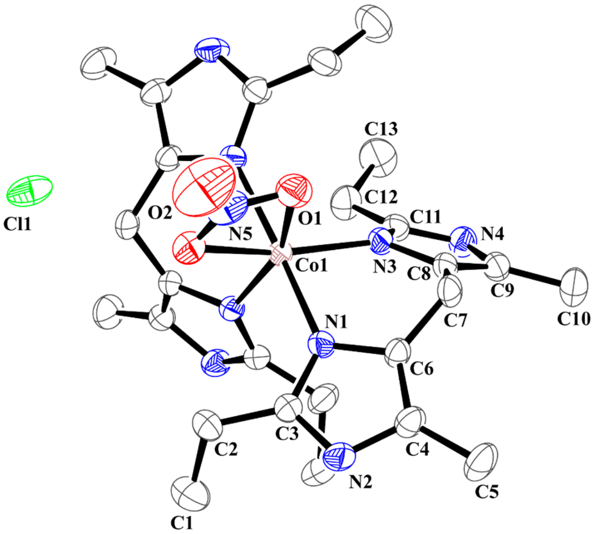
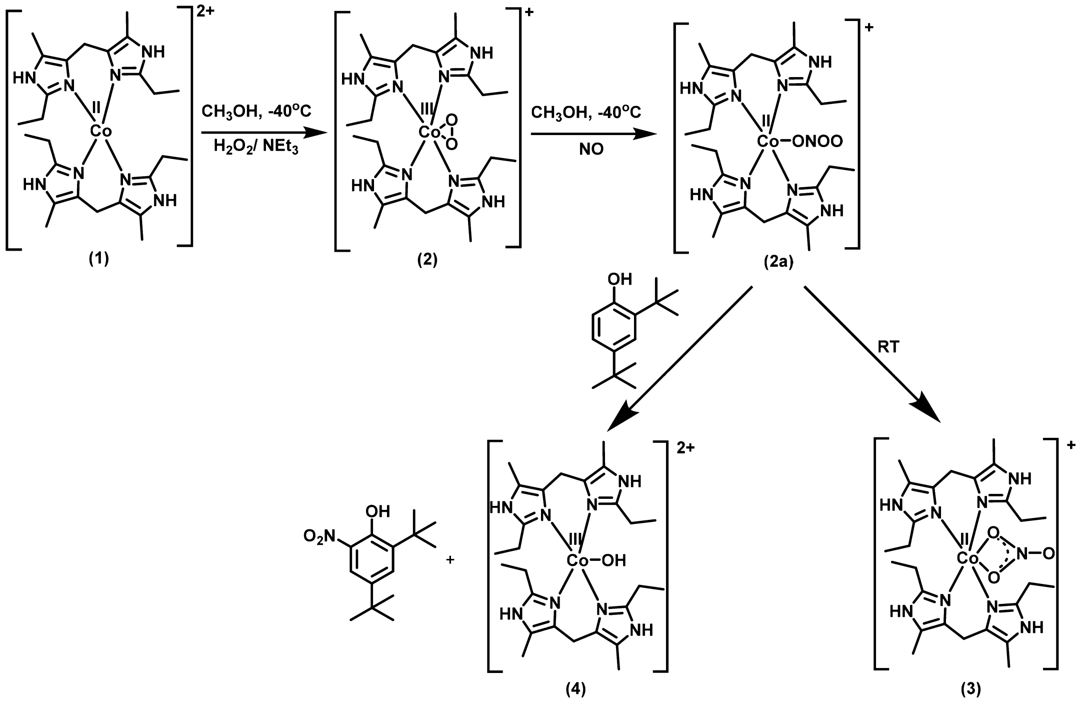


Figure 8. ORTEP diagram of complex **3** (30% thermal ellipsoid plot, H atoms and solvent molecule are not shown for clarity).

The formation of the complex **3** can be envisaged through the formation of a putative peroxynitrite intermediate (complex **2a**) in the course of the reaction (Scheme 2). Note that NO_3^- is the common decomposition or isomerization product of the peroxynitrite anion.[8] Since direct spectroscopic evidence of the peroxynitrite intermediate was not obtained owing to its unstable nature, we sought chemical evidence for the proposed intermediate. When the reaction of the peroxo complex **2** with NO was followed by the addition of 2,4-ditertiarybutylphenol (DTBP), the exclusive formation of the complex **3** was observed, and unreacted DTBP (ca. 95%) was recovered. However, when DTBP was added before the addition of NO (Scheme 2), an appreciable nitration (ca. 60%) was observed. Workup of the reaction mixture revealed the formation of the corresponding Co^{III}-hydroxo product, **4** (ca. 70%) along with 2,4-ditertiarybutyl-6-nitrophenol. The nitration of phenol ring by Co(II)-peroxynitrite intermediate is expected to result in the formation of corresponding Co(II)-hydroxide (Scheme 2).

Scheme 2



However, only Co(III)-hydroxide was isolated. This is perhaps because of the air sensitivity of the Co(II)-hydroxide. It has been found in a separate control experiment that in the reaction condition complex **3** does not induce phenol ring nitration, and this excludes the possibility of the formation of nitrophenol from the reaction of complex **3** with externally added phenol. Note that the phenol nitration has been used extensively as an evidence of the formation of metal-peroxynitrite intermediates.[9a,13,15] It is worth mentioning that even at −80 °C, no indication of formation of a new species was observed in the UV−visible spectroscopy.

EXPERIMENTAL SECTION

Materials and Methods. All reagents and solvents were purchased from commercial sources and were of reagent grade. HPLC grade methanol was used and dried by heating with iodine-activated magnesium with magnesium loading of ca. 5 g/L. The dried methanol was stored over 20% (m/v) molecular sieves (3 Å) for 3 d before use. Deoxygenation of the solvent and solutions was effected by repeated vacuum/purge cycles or bubbling with nitrogen or argon for 30 min. NO gas was purified by passing through KOH and P_2O_5 column. The dilution of NO was effected with argon gas using Environics Series 4040 computerized gas dilution system. UV−visible spectra were recorded on an Agilent HP 8454 spectrophotometer. FT-IR spectra were taken on a PerkinElmer spectrophotometer with either sample prepared as KBr pellets or in solution in a KBr cell. ^{1}H NMR spectra were obtained with a 400 MHz Varian FT spectrometer. Chemical shifts (ppm) were referenced either with an internal standard (Me_4Si) for organic compounds or to the residual solvent peaks. The X-band EPR spectra were recorded on a JES-FA200 ESR spectrometer, at room temperature or at 77 K. Spectra were recorded with all the samples prepared in methanol solution at 77 K. The experimental conditions [frequency, 9.136 GHz; power, 0.995 mW; field center, 336.00 mT, width, ±250.00 mT; sweep time, 30.0 s; modulation frequency, 100.00 kHz, width, 1.000 mT; amplitude, 1.0, and time constant, 0.03 s] were kept the same for all the samples. Mass spectra of the compounds were recorded in a Waters Q-Tof Premier and Aquity instrument. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. The magnetic moment of complexes was measured on a Cambridge Magnetic Balance. Elemental analyses were obtained from a PerkinElmer Series II Analyzer.

Single crystals were grown by 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 Mo Kα radiation (λ = 0.710 73 Å) at 273(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.[33] Data integration and reduction were undertaken with SAINT and XPREP software. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97.[34] Structural illustrations were drawn with ORTEP-3 for Windows.[35]

Synthesis of Ligand L. The ligand was prepared from the reaction of 2-ethyl-4-methyl imidazole (2.2 g; 20 mM) and formaldehyde (0.45 g; 15 mM) using the protocol reported earlier.[23] Yield: 1.97 g (ca. 85%).

Synthesis of Complex 1. A solution of $CoCl_2{\cdot}6H_2O$ (1.19 g; 5 mM) in methanol (20 mL) was added to a solution of the ligand (2.32 g, 10 mM) in methanol (15 mL) over a period of 10 min. The resulting violet solution was stirred for 3 h and then kept at room temperature for slow evaporation. After a few days, violet color crystals of complex **1** were obtained. Yield, ca. 82%. Elemental analyses for $C_{26}H_{40}Cl_2CoN_8$,: Calcd (%): C, 52.53; H, 6.78; N, 18.85, found (%): C, 52.47; H, 6.80; N, 18.93. UV−visible (methanol): λ_{max} (ε/M^{-1} cm^{-1}) at 515 nm (323), 559 nm (494), 581 nm (490) and 319 nm (772). FT-IR (KBr pellet): 2975, 1603, 1465, 1295, 1079, 825, 674 cm^{-1}. X-band EPR: g_{av} 2.29. Conductivity: 185 S cm^2 mol^{-1}. Magnetic moment: 4.32 μ_B ESI-Mass (m/z): Calcd: 261.63, found: 261.60.

Reaction of Complex 1 with H_2O_2. Complex **1** (1.18 g; 2 mM) was dissolved in 20 mL of dried and degassed methanol in a 50 mL Schlenk fask fitted with a rubber septum and connected to the Schlenk line. The solution was cooled at −40 °C. To this cold solution, precooled 5 equiv of hydrogen peroxide (37% v/v, 0.8 mL) and 2 equiv amount of NEt_3 were added, and the solution turned pink. It was then stirred for 10 min at −40 °C to afford complex **2**. The complex was found to be thermally unstable. So attempts were not made to isolate it. All the spectral characterization was done using freshly prepared complex **2** in methanol at −40 °C. UV−visible (methanol): λ_{max} (ε/M^{-1} cm^{-1}): 452 nm (890), 559 nm (419). FT-IR (in methanol): 1637, 1054, 874, 817 $\mathrm{cm^{-1}}$. ESI-Mass (m/z): Calcd: 555.28, found: 555.26.

Synthesis of Complex 3. The peroxo complex **2** was prepared freshly in a 50 mL Schlenk flask under Ar atmosphere as stated above. To this freshly generated peroxo complex **2** in methanol at −40 °C, NO gas (ca. 5 equiv) was added through a gastight syringe fitted in the Schlenk line. The resulting solution was stirred for 10 min, then warmed to room temperature, and the excess of NO gas was removed by applying several cycles of vacuum and Ar purge. Then the solution was kept for slow evaporation in air. After a few days, crystals of complex **3** were obtained. Yield (ca. 72%). Elemental analyses for $C_{26}H_{40}ClCoN_9O_3$, Calcd (%): C, 50.28; H, 6.43; N, 20.29, found (%): C, 50.40; H, 6.44; N, 20.41. FT-IR (KBr pellet): 2975, 1634, 1580, 1470, 1384, 1319, 1086 $\mathrm{cm^{-1}}$. UV−visible (methanol): λ_{max} (ε/$\mathrm{M^{-1}\,cm^{-1}}$): 532 nm (190). Conductivity: 124 S $\mathrm{cm^2\,mol^{-1}}$. X-band EPR: g_{av}, 2.16. Observed magnetic moment, 1.81 μ_B

Nitration of 2,4-Ditertiarybutylphenol. Complex **1** (1.18 g; 2 mM) was dissolved in 20 mL of dried and degassed methanol under Ar atmosphere in a 50 mL Schlenk flask with a rubber septum and fitted in the Schlenk line, and the solution was cooled at −40 °C. To this cold solution, precooled hydrogen peroxide (37% v/v, 0.8 mL, 5 equiv) was added and stirred for 10 min at −40 °C to result in the formation of complex **2**. To this solution, the NO gas (ca. 5 equiv) was added through a gastight syringe fitted in the Schlenk line followed by a methanol (5 mL) solution containing 2,4-ditertiarybutylphenol (2.06 g; 10 mM) precooled at −40 °C, and the mixture was stirred for 0.5 h at −40 °C. The reaction mixture was then warmed to room temperature, and the excess of NO gas was removed by applying several cycles of vacuum and Ar purge. Then the solution was dried using rotavapor. The solid mass was then subjected to column chromatography using silica gel column. Pure 2,4-ditertiarybutyl-6-nitrophenol was eluted with 100% hexane (R_f, 0.46; yield: ca. 60%), and complex **4** was eluted with methanol (R_f, 0.24; ca. 70%). 2,4-ditertiarybutyl-6-nitrophenol: Elemental analyses for $C_{14}H_{21}NO_3$, Calcd (%): C, 66.91; H, 8.42; N, 5.57, found (%): C, 66.88; H, 8.44; N, 5.66. Other spectral data were compared with the earlier reported results to confirm the formation of the compound.

Complex 4. Elemental analyses for $C_{26}H_{41}Cl_2CoN_8O$, Calcd (%): C, 51.07; H, 6.76; N, 18.32, found (%): C, 51.01; H, 6.80; N, 18.38. FT-IR (KBr pellet): 3450, 2977, 1636, 1452, 1078, 920, 838 $\mathrm{cm^{-1}}$. UV−visible (methanol): λ_{max} (ε/$\mathrm{M^{-1}\,cm^{-1}}$): 507 (67), 565 (107) and 615 (90) nm.

■ CONCLUSION

In conclusion, the present study demonstrated an example of a Co(II) complex, **1**, which in methanol solution reacted with H_2O_2 at −40 °C to result in the corresponding Co(III)-peroxo complex, **2**. It was characterized by spectroscopic analyses. The peroxo intermediate **2**, upon reaction with NO, resulted in a Co(II)-nitrato complex, **3**, presumably through the formation of Co(II)-peroxynitrite intermediate. It was evidenced by the external phenol ring nitration reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01110.

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

Accession Codes

CCDC 1548490−1548491 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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