Synthesis, Structural, and Spectroscopic Characterization and Reactivities of Mononuclear Cobalt(III)–Peroxo Complexes

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Abstract: Metal–dioxynen adducts are key intermediates detected in the catalytic cycles of dioxygen activation by metalloenzymes, including heme and nonheme iron and copper enzymes. As chemical models of the enzymes, a number of metal–O2 complexes have been synthesized and characterized with various spectroscopic techniques and X-ray crystallography, and their reactivities have been extensively investigated in electrophilic reactions. In particular, heme and nonheme iron(III)–O2 complexes have been synthesized as chemical models of dioxygen-carrying enzymes, such as cytochrome P450 aromatases and Rieske dioxygenases, respectively, and have shown reactivities in nucleophilic reactions such as aldehyde deformylation. Mononuclear Cu–O2 complexes have been synthesized as chemical models of copper-containing enzymes, such as peptidylglycine alpha-hydroxylating monoxygenase (PHM) and dopamine beta-monoxygenase (DβM), and their reactivities have been investigated in electrophilic reactions.

The chemistry of cobalt–O2 complexes bearing salen, porphyrin, and tetraazamacrocycle ligands has been extensively investigated as chemical models of dioxygen-carrying proteins, such as hemoglobin and myoglobin, and as active site models of cytochrome P450 and Rieske dioxygenases. The activities in nucleophilic reactions such as aldehyde deformylation.

1. Introduction

Mononuclear metal–dioxynen adducts, M–O2, are generated as key intermediates in the catalytic cycles of dioxygen activation by metalloenzymes, including heme and nonheme iron and copper enzymes. As chemical models of the enzymes, a number of metal–O2 complexes have been synthesized and characterized with various spectroscopic techniques and X-ray crystallography, and their reactivities have been extensively investigated in electrophilic and nucleophilic oxidation reactions.

For example, heme and nonheme iron(III)–O2 complexes were synthesized as chemical models of Cytochrome P450 aromatases and Rieske dioxygenases, respectively, and have shown reactivities in nucleophilic reactions such as aldehyde deformylation.

Mononuclear Cu–O2 complexes have been synthesized as chemical models of copper-containing enzymes, such as peptidylglycine alpha-hydroxylating monoxygenase (PHM) and dopamine beta-monoxygenase (DβM), and their reactivities have been investigated in electrophilic reactions.

The chemistry of cobalt–O2 complexes bearing salen, porphyrin, and tetraazamacrocycle ligands has been extensively investigated as chemical models of dioxygen-carrying proteins, such as hemoglobin and myoglobin, and as active site models of cytochrome P450 and Rieske dioxygenases. The activities in nucleophilic reactions such as aldehyde deformylation.


oxidants in the oxidation of organic substrates. As a result, structural and spectroscopic characterization of the cobalt–O₂ complexes has been well established in the 1970s. The structural analysis of the cobalt–O₂ complexes by X-ray crystallography revealed that the O₂ group in the intermediates has superoxo character with an end-on (\(\eta^1\)) binding mode. Co(III)-(O₂)-,\(^{7,8}\) have also been reported,\(^{10}\) such as [Co{(2-phos)O(O₂)}]\(^2-\) (2-phos = cis-[C(C₂H₅)₂PCH₂CH₂C₆H₄]\(^2-\)),\(^{10a}\) Co{(TP))O(O₂)} (TP = hydridotris(3-tert-butyl-5-methylpyrazolyl)borate),\(^{10b}\) [Co{(imen)O(O₂)}]\(^2-\) (imen = tetramethylethenediamine),\(^{10c}\) [Co{(TIMEN)(O₂)}]\(^2-\) (TIMEN = tris[2-(3-xenyleneimidozil-2-ylidine)ethyl]amine).\(^{10d}\) The oxidation of organic substrates, such as phenols and olefins, by Co(II) Schiff base complexes, such as phenols and olefins, by Co(II) Schiff base complexes, has also been reported,\(^{10}\) such as [Co{(2-TMC)(O₂)}]+ (2-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane), [Mn{(14-TMC)(O₂)}]\(^2+\) (14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), [Mn{(13-TMC)(O₂)}]\(^3+\) (13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane), and [Cr{(14-TMC)(O₂)}(Cl)]\(^2-\) have also been reported along with their reactivities in aldehyde deformation and C–H bond activation reactions.\(^{14,15}\) Herein we report the synthesis, structural and spectroscopic characterization, and reactivities of side-on cobalt(III)–peroxo complexes bearing tetraaza macrocyclic ligands, [Co{(12-TMC)(O₂)}]\(^2+\) (2) and [Co{(13-TMC)(O₂)}]\(^2+\) (4).\(^{16}\) We have also shown that reactivities of metal–peroxo intermediates in O₂-transfer and oxidative nucleophilic reactions are markedly affected by the central metal ions and the ring size of the macrocyclic ligands.

2. Results and Discussion

2.1. Synthesis of Co–O₂ Complexes

Synthetic procedures for cobalt(III)–peroxo complexes are depicted in Scheme 1. The starting materials, [Co{(12-TMC)(CH₃CN)}]\(^2+\) (1) and [Co{(13-TMC)(CH₃CN)}]\(^2+\) (3), were prepared by reacting CoCl₂·6H₂O with the corresponding 12-TMC and 13-TMC ligands, respectively. The cobalt(III)–peroxo complexes were then synthesized as follows: Addition of 5 equiv of H₂O₂ to a reaction solution containing 1 and 2 equiv of triethylamine (TEA) in CH₃CN at 0 °C afforded a purple intermediate, [Co{(12-TMC)(O₂)}]\(^2+\) (2). 2 was then isolated at a temperature below −20 °C. Similarly, [Co{(13-TMC)(O₂)}]\(^2+\) (4) was obtained by reacting 3 with 5 equiv of H₂O₂ in the presence of 2 equiv of TEA in CH₃CN at 0 °C and isolated at a temperature below −40 °C. The intermediates, 2 and 4, persisted for several days.
at 0 °C. The greater thermal stability of 2 and 4 allowed us to use isolated cobalt-peroxo intermediates in spectroscopic and reactivity studies.

2.2. Structural and Spectroscopic Characterization. 2.2.1. X-ray Crystallography. Complexes 1–4 were successfully characterized by X-ray diffraction analyses. The molecular structures of the complex cations of 1–4 are shown in Figure 1 and Supporting Information (SI), Figure S1, and selected bond distances and angles are listed in Table 1 and Table S1 in the Supporting Information (SI). Complex 1 has a five-coordinate cobalt(II) ion with four nitrogens of the macrocyclic 12-TMC ligand in equatorial positions and one nitrogen of CH3CN in an axial position (SI, Figure S1a), as found in a nickel(II) analog, [Ni(12-TMC)(CH3CN)]2+.

Complex 3 has a coordination geometry similar to that of 1 (SI, Figure S1b). The average Co–N-equatorial bond distance of 3 (2.068 Å) is longer than that of 1 (1.988 Å), but the Co–N-axial bond distance of 3 (2.015 Å) is slightly shorter than that of 1 (2.036 Å).

The X-ray structures of 2 and 4 revealed a mononuclear side-on cobalt–O2 complex in a distorted octahedral geometry arising from the triangular CoO2 moiety with a small bite angle of 45.36(5)° for 2 and 45.16(12)° for 4 (Figure 1). The O–O bond lengths of 1.4389(17) Å for 2 and 1.4384(4) Å for 4, which are comparable to those in [Co(men)$_2$(O2)]$^{2+}$ (1.457 Å) and [Co(TIMEN)$_3$)$_2$(O2)]$^{2+}$ (1.429 Å), are indicative of the peroxo character of the O2 group, as assigned by resonance Raman data (vide infra). The average Co–O bond distance of 4 (1.856 Å) is slightly shorter than that of 2 (1.866 Å). Further, the O–O bond distances of 2 and 4 are longer than that of [Ni(12-TMC)(O2)]$^{2+}$ (1.386 Å), whereas the average Co–O bond distances of 2 (1.866 Å) and 4 (1.856 Å) are shorter than the average Ni–O bond distance of [Ni(12-TMC)(O2)]$^{2+}$ (1.889 Å).

Finally, all four N-methyl groups of the 12-TMC and 13-TMC ligands point toward the peroxo group, as observed in other metal(III)–peroxo complexes bearing tetraazamacrocyclic ligands, such as [Ni(12-TMC)(O2)]$^{2+}$, [Mn(14-TMC)(O2)]$^{2+}$ and [Mn(13-TMC)(O2)]$^{2+}$.

2.2.2. Co K-Edge X-ray Absorption and EXAFS. The normalized Co K-edge X-ray absorption data for 2 and 4 are presented in SI, Figure S2. The inset shows the pre-edge transition, which is the result of an electric dipole forbidden, quadrupole allowed 1s→3d transition. The pre-edge energy position dominantly reflects the ligand-field strength at the absorbing metal center. The pre-edge transition for both 2 and 4 occurs at ~7710.1 eV. The intense step-function-like feature to higher energy (~7712 to 7728 eV) is the rising edge, which occurs due to dipole-allowed 1s→4p continuum transitions. The rising edge inflection energy reflects the charge at the absorbing metal center. This inflection point occurs at ~7721.0 eV for both 2 and 4, an energy typical for Co(III) systems.

The similarity in the pre-edge energy and the rising edge inflection points indicates that 2 and 4 are both Co(III)–O2$^{2-}$ complexes.

Co K-edge extended X-ray absorption fine structure (EXAFS) data were collected on 2 and 4 to evaluate the geometric structure of the O2 bound adducts of 1 and 3 in solution and compare them to the crystal structures. The k$^3$ weighted Co K-edge EXAFS data (SI, Figure S3, inset), non-phase-shift-corrected Fourier transform (k = 2–14 Å$^{-1}$) and the corresponding FEFF fits for 2 and 4 are shown in SI, Figure S3a and S3b, respectively. Numerical fits are presented in Table S2. FEFF fits to the data for 2 are consistent with 2 Co–O interactions at 1.85 Å and 4 Co–N interactions at 1.99 Å. The second shell for 2 was fit with 8 Co–C single-scattering and 24 Co–C–N multiple-scattering components from the 12-TMC ligand backbone carbons. FEFF fits to the data for 4 resulted in structural parameters similar to those for 2. The first shell was fit with 2 Co–O contributions at 1.85 Å and 4 Co–N contributions at 2.0 Å. The second shell was fit with 8 Co–C single-scattering and 24 Co–C–N multiple-scattering compo-

![Figure 1. X-ray crystal structures of (a) [Co(12-TMC)(O2)]$^{2+}$ (2) and (b) [Co(13-TMC)(O2)]$^{2+}$ (4) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.](image-url)
The resonance Raman spectrum of 13-TMC (CH3CN)2+ (1) with a value of 56 cm−1 was recorded in CD3CN and CH3CN, respectively, owing to a significant overlap with intense solvent bands. The peaks marked with “s” are ascribed to acetonitrile and d3-acetonitrile solvents. See SI, Figure S4 for resonance Raman spectra of 2 recorded under various conditions.

2.2.2. Spectroscopic Characterization. 2.2.2.1. [Co(12-TMC)(CH3CN)]4+ (2). The electronic spectrum of 2 shows distinct absorption bands at 350 (ε = 450 M−1 cm−1) and 560 nm (ε = 180 M−1 cm−1) and shoulders at ~500 (ε = 150 M−1 cm−1) and ~710 nm (ε = 90 M−1 cm−1) (Figure 2a). The electrospay ionization mass spectra (ESI-MS) of 2 exhibits a prominent signal at m/z 319.1 (Figure 2b), whose mass and isotopic distribution pattern correspond to [Co(12-TMC)(O2)]4+ (calculated m/z 319.2) (Figure 2b, inset). When the reaction was carried out with isotopically labeled H218O2, a mass peak corresponding to [Co(12-TMC)(18O2)]4+ appeared at m/z of 323.1 (calculated m/z 323.2) (Figure 2b, inset). The observation of the 4-mass-unit upshift upon the substitution of 16O with 18O indicates that 2 contains an O2 unit.

The resonance Raman spectrum of 2 obtained upon 442-nm excitation in CD3CN at 0 °C exhibits two isotopically sensitive bands at 902 and 538 cm−1 that shift to 845 and 516 cm−1, respectively, in samples of 2 prepared with H218O2 in CH3CN (Figure 2c and SI, Figure S4). The higher energy feature (902 cm−1) with a 16∆−18∆ value of 57 cm−1 (16∆−18∆ (calcd) = 51 cm−1) is ascribed to the O−O stretching vibration of the peroxo ligand, and the lower-energy feature (538 cm−1) is assigned to the Co−O stretching vibration (16∆−18∆ (calcd) = 24 cm−1).19 In addition, we have observed a good correlation between the O−O stretching frequency and the O−O bond length in 2 (Figure 3).17

The X-band EPR spectrum of the starting complex, [Co(12-TMC)(CH3CN)]4+ (1), at 4.3 K contains features at γg = 2.31 and γl ≈ 2.07, which are typical for a low-spin (S = 1/2) cobalt(II) complex (SI, Figure S5). The EPR spectrum of 2 is silent at 4.3 K (SI, Figure S5), suggesting that 2 is either a low-spin (S = 0) or an integer spin (S = 1, 2) cobalt(III) d6 species. The 1H NMR and COSY spectra of 2 recorded in d3-acetonitrile at −40 °C show sharp features in the 0−10 ppm region (SI, Figure S6), indicating that 2 is, in fact, a low-spin (S = 0) cobalt(III) d6 species at −40 °C.

2.2.2.2. [Co(13-TMC)(O2)]4+ (4). Spectroscopic properties of 4 are similar to those of 2. The electronic spectrum of 4 shows distinct absorption bands at 348 (ε = 620 M−1 cm−1) and 562 nm (ε = 210 M−1 cm−1) and shoulders at ~500 (ε = 170 M−1 cm−1) and ~710 nm (ε = 100 M−1 cm−1) (Figure 4a). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b), whose mass and isotopic distribution pattern correspond to those of [Co(13-TMC)(O2)]4+ (calculated m/z 333.2) (Figure 4b). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b), whose mass and isotopic distribution pattern correspond to those of [Co(13-TMC)(O2)]4+ (calculated m/z 333.2) (Figure 4b). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b), whose mass and isotopic distribution pattern correspond to those of [Co(13-TMC)(O2)]4+ (calculated m/z 333.2) (Figure 4b). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b), whose mass and isotopic distribution pattern correspond to those of [Co(13-TMC)(O2)]4+ (calculated m/z 333.2) (Figure 4b). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b), whose mass and isotopic distribution pattern correspond to those of [Co(13-TMC)(O2)]4+ (calculated m/z 333.2) (Figure 4b). The ESI-MS of 4 exhibits a prominent mass signal at m/z 333.1 (Figure 4b), whose mass and isotopic distribution pattern correspond to those of [Co(13-TMC)(O2)]4+ (calculated m/z 333.2). With the expected 4-mass-unit upshift upon the substitution of 16O by 18O (Figure 4b, inset).

The resonance Raman spectrum of 4, obtained upon 442-nm excitation in CD3CN at 0 °C, exhibits two isotopically sensitive bands at 902 and 542 cm−1 that shift to 846 and 520 cm−1, respectively, in samples of 4 prepared with H218O2 in CH3CN (Figure 4c and SI, Figure S7). The higher energy feature (902 cm−1) with a 16∆−18∆ value of 56 cm−1 (16∆−18∆ (calcd) = 51 cm−1) is ascribed to the O−O stretching vibration of the peroxo ligand, and the lower-energy feature (542 cm−1) is assigned to the Co−O stretching vibration (16∆−18∆ (calcd) = 24 cm−1).
close agreement with the data obtained from X-ray crystallography observed a good correlation between the O–O bond length (Figure 3). 17 Like 2, the relatively low O–O frequency is consistent with the O–O bond distance in 4, and we have observed a good correlation between the O–O stretching frequency and the O–O bond length (Figure 3). 17

The X-band EPR spectrum of [Co(13-TMC)(CH3CN)]2+ (3) at 4.3 K contains features at g∥ = 2.31 and g⊥) = 2.07, which are typical for a low-spin (S = 1/2) cobalt(II) species (SI, Figure S8). Complex 4 is EPR silent (X-band, 4.3 K) and exhibits a sharp 1H NMR spectrum in the 0–10 ppm region (data not shown), indicating that 4 is a low-spin (S = 0) cobalt(III) d6 species. Taken together, the spectroscopic data with the structural characterization demonstrate that 2 and 4 are low-spin (S = 0) cobalt(III)–peroxo complexes with the peroxo ligand bound in a side-on π2 fashion, [Co(III)(13-TMC)(O2)]2+ and [Co(III)(13-TMC)(O2)][], respectively.

2.2.4. DFT Calculations. Spin-unrestricted broken symmetry density functional theory (DFT) calculations were performed on the cationic moieties of [Co(12-TMC)(O2)]2+ and [Co(13-TMC)(O2)]2+. Obtained from the crystal structures of 2 and 4. The relevant bond distances are presented in SI, Table S3. The calculated Co–O, O–O, and average Co–N distances of 1.88, 1.44, and ~2.03 Å, respectively, are in close agreement with the data obtained from X-ray crystallography and Co K-edge EXAFS results for 2. The DFT optimized structure of 4 is qualitatively similar to that of 2, although there is a larger spread in the Co–N distances (see SI, Table S3). This is consistent with the slight decrease in the first shell intensity of the Fourier transform of 4 relative to 2 (see SI, Figure S3 for comparison). The average Co–O and O–O distances are 1.90 and 1.42 Å, which are in reasonable agreement with the experimental data. The calculated geometric and electronic structures for 2 and 4 are consistent with a low-spin [Co(III)–O22+] ground state as observed from the experimental data.

2.3. Reactivities of Co–O2 Complexes. 2.3.1. Nucleophilic Reactions. The reactivity of the cobalt(III)–peroxo complexes was investigated in electrophilic and nucleophilic reactions. First, the electrophilic character of 2 and 4 was tested in the oxidation of thioanisole and cyclohexene. Upon addition of substrates to a solution of 2 and 4 in CH3CN at 25 °C, the intermediate remained intact without showing any absorption spectral change, and product analysis of the reaction solutions revealed that no oxygenated products were formed. These results demonstrate that the Co(III)–peroxo complexes are not capable of conducting electrophilic oxidation with the substrates under the reaction conditions.

The nucleophilic character of 4 was then investigated in aldehyde deformylation, with precedents that metal(III)–peroxo complexes with heme and nonheme ligands react with aldehydes to give corresponding deformylated products. 4,12a,14 Upon reacting 4 with cyclohexanecarboxaldehyde (CCA) in CH3CN at 25 °C, the characteristic UV–vis absorption bands of 4 disappeared with pseudo-first-order decay (Figure 5a), and product analysis of the reaction solution revealed that cyclohexene (80 ± 10%) was produced in the oxidation of CCA. 12a,14,20 The pseudo-first-order rate fitting of the kinetic data, monitored at 380 nm, yielded the kobs value of 1.6 × 10−2 s−1 (Figure 5a). The pseudo-first-order rate constants increased proportionally with the concentration of CCA, giving a second-order rate constant (k2) of 2.0 × 10−1 M−1 s−1 (Figure 5b). Similar results were obtained in the reactions of 2-phenylpropanaldehyde (2-PPA) but with a slower rate (k2 = 1.5 × 10−2 M−1 s−1 at 25 °C) (SI, Figure S9). The product analysis of the resulting solution revealed the formation of acetophenone (90 ± 10%). Activation parameters for the aldehyde deformylation of 4 between 278 and 308 K were determined to be ΔH° = 64 kJ mol−1 and ΔS° = −67 J mol−1 K−1 for CCA (Figure 5c) and ΔH° = 62 kJ mol−1 and ΔS° = −77 J mol−1 K−1 for 2-PPA (SI, Figure S9). Further, the reactivity of 4 was investigated with para-substituted benzaldehydes, para-X–Ph–CHO (X = OMe, Me, F, H), to investigate the effect of para-substituents on the benzaldehyde oxidation process by Co(III)-peroxo species. A Hammett plot of the pseudo-first-order rate constants versus σp gave a ρ value of 1.7 (Figure S10), which is consistent with the nucleophilic character of the Co-peroxo unit in the oxidation of aldehydes. 12d Finally, it is of interest to note that the reactivity of 2 is much lower than that of 4 in nucleophilic reactions; therefore, we were not able to obtain kinetic data for 2 under the reaction conditions. The latter result implies that the nucleophilic character of the peroxo ligand is influenced markedly by the ring size of tetraazaamacrocyclic ligands (i.e., [Co(13-TMC)(O2)]2+ > [Co(12-TMC)(O2)]2+).
2.3.2. O₂-Transfer Reactions. It has been shown that a mononuclear Ni(III)–peroxo complex, \([\text{Ni}(12\text{-TMC})(\text{O}_2)]^+\), is capable of transferring the peroxo group to a manganese(II) complex, thus affording the corresponding nickel(II) and manganese(III)–peroxo complexes (eq 1). We therefore attempted the intermolecular dioxygen transfer from the cobalt–peroxo complexes, 2 and 4, to the \([\text{Mn}(14\text{-TMC})]^{2+}\) complex. Interestingly, addition of \([\text{Mn}(14\text{-TMC})]^{2+}\) to a solution of 2 in CH₃CN at 25 °C resulted in the disappearance of 2 with a corresponding nickel(II) and manganese(III)–peroxo complexes (eq 1). We therefore attempted the intermolecular O₂-transfer from 2 to \([\text{Mn}(14\text{-TMC})]^{2+}\) was further confirmed by ESI-MS analysis of the reaction solution at different times, where the mass peak at \(m/z\) 319.1 corresponding to 2 disappeared with a concomitant appearance of the mass peak at \(m/z\) 343.2 corresponding to 5 (Figure 6b). Further, when the O₂-transfer reaction was carried out under an \(^{18}\text{O}_2\) atmosphere, the product 5 did not contain the isotopically labeled \(^{18}\text{O}_2\) group, demonstrating that molecular oxygen was not involved in the O₂-transfer reaction. Furthermore, we found that the reverse reaction, which is the peroxo ligand transfer from 5 to 2, does not occur.

Kinetic studies of the O₂-transfer from 2 to \([\text{Mn}(14\text{-TMC})]^{2+}\) were carried out in acetone at 0 °C (SI, Figure S11a). Addition of 15 equiv of \([\text{Mn}(14\text{-TMC})]^{2+}\) to a solution of 2 yielded a \(k_{\text{obs}}\) value of \(2.2 \times 10^{-3}\) s⁻¹ under pseudo-first-order conditions. The rate constant increased proportionally with the concentration of \([\text{Mn}(14\text{-TMC})]^{2+}\), giving a second-order rate constant of \(k_2 = 1.5 \times 10^{-1}\) M⁻¹ s⁻¹ at 0 °C (Figure 7a, red line). The reaction rate was dependent on temperature, and a linear Eyring plot was obtained between 0 and 25 °C to give the activation parameters of \(\Delta H^\ddagger = 65\) kJ mol⁻¹ and \(\Delta S^\ddagger = -63\) J mol⁻¹ K⁻¹ (Figure 7b, red line). The dependence of the rate constants on the concentration of reactants and the significant negative entropy value suggest that the O₂-transfer reaction proceeds via a bimolecular mechanism in which the formation of an undetected \([\text{Ni}(12\text{-TMC})(\text{O}_2)\text{Co}^{\text{II}}\text{Mn}(14\text{-TMC})]^{3+}\) intermediate is the rate-determining step (eq 2). It is of interest to note that the O₂-transfer from 2 to \([\text{Mn}(14\text{-TMC})]^{2+}\) is \(~1100\) times slower than that from \([\text{Ni}(12\text{-TMC})(\text{O}_2)]^{+}\) to \([\text{Mn}(14\text{-TMC})]^{2+}\) (e.g., \(k_2 = 1.9 \times 10^{-4}\) M⁻¹ s⁻¹ for the reaction of 2 and \(k_2 = 0.2\) M⁻¹ s⁻¹).
In this study, we synthesized and characterized mononuclear cobalt(III)–peroxo complexes bearing tetraaza macrocyclic ligands, [Co(12-TMC)(O2)]^2+ and [Co(13-TMC)(O2)]^2+. The structural and Co K-edge EXAFS spectroscopic characterization clearly showed that the peroxo ligand is bound in a side-on \eta^2 fashion. The cobalt(III)–peroxo complexes have shown reactivities in the oxidation of aldehydes and O2-transfer reactions. In the aldehyde oxidation reactions, the nucleophilic reactivity of metal(III)–peroxo complexes was found to depend significantly on the ring size of the macrocyclic ligands, with the reactivity order [Co(13-TMC)(O2)]^+ > [Co(12-TMC)(O2)]^+. In the O2-transfer reactions, the cobalt(III)–peroxo complexes were shown to transfer their peroxo ligand to a manganese(II) complex. The O2-transfer reactions were found to depend significantly on the central metal ions and the supporting ligands, showing the reactivity order [Ni(12-TMC)(O2)]^+ > [Co(13-TMC)(O2)]^+ > [Co(12-TMC)(O2)]^+.

3. Conclusions

The reactivity order of [Ni(12-TMC)(O2)]^+ > [Co(13-TMC)(O2)]^+ > [Co(12-TMC)(O2)]^+ is observed in O2-transfer reactions.

4. Experimental Section

Materials. All chemicals obtained from Aldrich Chemical Co. were of the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use.25 H2IO2 (90% 18O-enriched, 2% H218O in water) and 18O (95% 18O-enriched) were purchased from ICON Services Inc. (Summit, NJ, USA). The 12-TMC and 13-TMC ligands were prepared by reacting 1,4,7,10-tetraaza cyclooctadecane and 1,4,7,10-tetraazacyclododecane, respectively.23 All air-sensitive reactions were performed using either a glovebox or standard Schlenk techniques. [Ni(12-TMC)(O2)]^+ and [Co(13-TMC)(O2)]^+ were prepared according to the literature methods.12a,14a

Caution. Perchlorate salts are potentially explosive and should be handled with care!

Synthesis of [Co(12-TMC)(CH3CN)](ClO4)2·12-TMC (0.50 g, 2.19 mmol) was added to an acetonitrile solution (50 mL) of Co(ClO4)2·6H2O. Yield: 0.88 g (76%). UV–vis (\(\varepsilon\), M\(^{-1}\) cm\(^{-1}\)) in CH3CN: \(345 \text{ nm (120), 451 \text{ nm (120), 520 \text{ nm (150).}}\) ESI-MS (in CH3CN): m/z 164.0 [Co(12-TMC)]^2+. Anal. Calcd for C14H28CoN4O8Cl2: C, 41.89; H, 5.86; N, 13.28. Found: C, 41.95; H, 5.90; N, 13.49. X-ray crystallographically suitable crystals were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution of [Co(12-TMC)(CH3CN)](ClO4)2·12-TMC. The structural and Co K-edge EXAFS spectroscopic characterization clearly showed that the peroxo ligand is bound in a side-on \eta^2 fashion. The cobalt(III)–peroxo complexes have shown reactivities in the oxidation of aldehydes and O2-transfer reactions. In the aldehyde oxidation reactions, the nucleophilic reactivity of metal(III)–peroxo complexes was found to depend significantly on the ring size of the macrocyclic ligands, with the reactivity order [Co(13-TMC)(O2)]^+ > [Co(12-TMC)(O2)]^+. In the O2-transfer reactions, the cobalt(III)–peroxo complexes were shown to transfer their peroxo ligand to a manganese(II) complex. The O2-transfer reactions were found to depend significantly on the central metal ions and the supporting ligands, showing the reactivity order [Ni(12-TMC)(O2)]^+ > [Co(13-TMC)(O2)]^+ > [Co(12-TMC)(O2)]^+.


samples directly into the source using a manual method. The spray voltage was set at 4.2 kV, and the capillary temperature at 80 °C. Resonance Raman spectra were obtained using a liquid nitrogen cooled CCD detector (CCD-1024 × 256-OPEN-ILS, HORIBA Jobin Yvon) attached to a 1-m single polychromator (MC-100DG, Ritsu Oyo Kogaku) with a 1200 grooves/mm holographic grating. An excitation wavelength of 441.6 nm was provided by a He–Cd laser (Kimmon Koha, IK5651R-G and KR1801C), with 15 mW of power at the sample point. All measurements were carried out with a spinning cell (1000 rpm) at 0 °C. Raman shifts were calibrated with indene, and the accuracy of the peak positions of the Raman bands was ±1 cm−1. EPR spectra were taken at 4 K using a X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperatures were achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. EPR spectra were obtained on a JEOL JES-FA200 spectrometer.

Recrystallization. Single crystals of 1-(ClO4)2, 2-(BPh3) ·CH3CN, 3-(ClO4)2, and 4-(ClO4)2 ·CH3CN were picked from solutions by a nylon loop (Hampton Research Co.) on a homemade cooper plate mounted inside a liquid N2 Dewar vessel at ca. −40 °C and mounted on a goniometer head in a N2 cryostream. Data collections were carried out on a Bruker SMART 1100 CCD diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHELXTL V 6.12. Hydrogen atoms were located in the calculated positions for 2-(BPh3) ·CH3CN and 4-(ClO4)2 ·CH3CN. Due to the high degree of disorder, however, hydrogen atoms could not be placed in ideal positions for 3-(ClO4)2 and the coordinated CH3CN of 1-(ClO4)2.

**Physical Methods.** UV–vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments for low-temperature experiments or with a circulating water bath. Electrospray ionization mass spectra were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ Advantage Max quadrupole ion trap instrument, by infusing
The structural parameters that varied during the fitting process were the bond distance (R) and the bond variance σ², which is related to the Debye–Waller factor resulting from thermal motion, and the static disorder of the absorbing and scattering atoms. The non-structural parameter E₀ (the energy at which k = 0) was also allowed to vary but was restricted to a common value for every component in a given fit. Coordination numbers were systematically varied in the course of the fit but were fixed within a given fit.

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Acknowledgment. The research was supported by NRF/MEST of Korea through the CRI, WCU (R31-2008-000-10010-0), and GRL (2010-00353) Programs (W.N.), the Ministry of Education,

### Table 2. Crystallographic Data and Structure Refinements for 1-(ClO₄)₂, 2-(BPh₄)·CH₃CN, 3-(ClO₄)₂, and 4-(ClO₄)·CH₃CN

<table>
<thead>
<tr>
<th></th>
<th>1-(ClO₄)₂</th>
<th>2-(BPh₄)·CH₃CN</th>
<th>3-(ClO₄)₂</th>
<th>4-(ClO₄)·CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₀H₈Cl₂CoN₈O₈</td>
<td>C₁₄H₂₀CoN₄O₂</td>
<td>C₁₀H₈Cl₂CoN₈O₈</td>
<td>C₁₄H₂₀CoN₈O₈</td>
</tr>
<tr>
<td>Weight</td>
<td>524.24</td>
<td>679.58</td>
<td>508.03</td>
<td>473.84</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298(2)</td>
<td>170(2)</td>
<td>298(2)</td>
<td>170(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>monoclinic</td>
<td>tetragonal</td>
<td>orthorhobic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>P4/nmm</td>
<td>Pm4/nmm</td>
<td>Pca2(1)</td>
</tr>
<tr>
<td>Cell dimensions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>14.718(2)</td>
<td>12.445(15)</td>
<td>9.2584(6)</td>
<td>12.168(18)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.9472(12)</td>
<td>27.912(3)</td>
<td>9.2584(6)</td>
<td>9.5673(18)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.5452(2)</td>
<td>11.1477(13)</td>
<td>9.2584(6)</td>
<td>17.218(3)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β (deg)</td>
<td>110.063(2)</td>
<td>14.1473(17)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>2310.4(5)</td>
<td>3577.9(7)</td>
<td>1212.68(18)</td>
<td>2106.7(7)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>d_{expt} (g/cm³)</td>
<td>1.507</td>
<td>1.262</td>
<td>1.391</td>
<td>1.494</td>
</tr>
<tr>
<td>µ (mm⁻¹)</td>
<td>1.022</td>
<td>0.520</td>
<td>0.972</td>
<td>0.982</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>13894</td>
<td>21911</td>
<td>7455</td>
<td>22983</td>
</tr>
<tr>
<td>Independent reflections [R(int)]</td>
<td>8229 [0.0688]</td>
<td>890 [0.0587]</td>
<td>3632 [0.0352]</td>
<td></td>
</tr>
<tr>
<td>Parameters</td>
<td>160</td>
<td>429</td>
<td>75</td>
<td>258</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.030</td>
<td>0.950</td>
<td>1.065</td>
<td>1.003</td>
</tr>
<tr>
<td>Final R ([F &gt; 2σ(I)])</td>
<td>0.0794</td>
<td>0.0365</td>
<td>0.0673</td>
<td>0.0345</td>
</tr>
<tr>
<td>Final wR ([I &gt; 2σ(I)])</td>
<td>0.2227</td>
<td>0.0481</td>
<td>0.1745</td>
<td>0.1164</td>
</tr>
</tbody>
</table>

The theoretical models were fit to the data using EXAFSPAK.\textsuperscript{30} The structural parameters that varied during the fitting process were the bond distance (R) and the bond variance σ², which is related to the Debye–Waller factor resulting from thermal motion, and the static disorder of the absorbing and scattering atoms. The non-structural parameter E₀ (the energy at which k = 0) was also allowed to vary but was restricted to a common value for every component in a given fit. Coordination numbers were systematically varied in the course of the fit but were fixed within a given fit.

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Culture, Sports, Science and Technology of Japan through the Global COE program and Priority Area (No. 20050029) (T.O.), and NIH Grant DK-31450 (E.I.S.). SSRL operations are funded by the Department of Energy, Office of Basic Energy Sciences. The SSRL Structural Molecular Biology program is supported by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and the Department of Energy, Office of Biological and Environmental Research. This publication was made possible by Award P41 RR001209 from the National Center for Research Resources (NCRR), a component of the National Institutes of Health (NIH).

Supporting Information Available: Non-phase-shift-corrected Fourier transform data, their corresponding EXAFS data, and FEFF best fit parameters for 2 and 4, X-ray crystal structures of 1 and 3, resonance Raman data of 2 and 4, EPR data of 1-4, COSY NMR spectrum of 2, kinetic data of the reactions of 4 with 2-PPA and para-X-Ph-CHO, UV-vis spectral changes of the O2-transfer reactions of 2 and 4, and X-ray crystallographic files of 1-4 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.