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Mononuclear nickel(II)-superoxo and nickel(III)-peroxo complexes bearing a common macrocyclic TMC ligand

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Abstract

Mononuclear metal-dioxygen adducts, such as metal-superoxo and -peroxo species, are generated as key intermediates in the catalytic cycles of dioxygen activation by heme and non-heme metalloenzymes. We have shown recently that the geometric and electronic structure of the Ni-O₂ core in [Ni(*n*-TMC)(O₂)]⁺ (*n* = 12 and 14) varies depending on the ring size of the supporting TMC ligand. In this study, mononuclear Ni(II)-superoxo and Ni(III)-peroxo complexes bearing a common macrocyclic 13-TMC ligand, such as [Ni^{II}(13-TMC)(O₂)]⁺ and [Ni^{III}(13-TMC)(O₂)]⁺, were synthesized in the reaction of [Ni^{II}(13-TMC)(CH₃CN)]²⁺ and H₂O₂ in the presence of tetramethylammonium hydroxide (TMAH) and triethylamine (TEA), respectively. The Ni(II)-superoxo and Ni(III)-peroxo complexes bearing the common 13-TMC ligand were successfully characterized by various spectroscopic methods, X-ray crystallography, and DFT calculations. Based on the combined experimental and theoretical studies, we conclude that the superoxo ligand in [Ni^{II}(13-TMC)(O₂)]⁺ is bound in an end-on fashion to the nickel(II) center, whereas the peroxo ligand in [Ni^{III}(13-TMC)(O₂)]⁺ is bound in a side-on fashion to the nickel(III) center. Reactivity studies performed with the Ni(II)-superoxo and Ni(III)-peroxo complexes toward organic substrates reveal that the former possesses an electrophilic character, whereas the latter is an active oxidant in nucleophilic reaction.

Introduction

Mononuclear metal-dioxygen species (M-O₂) have been implicated as key intermediates in the catalytic cycles of dioxygen activation by heme and non-heme metalloenzymes.¹ A number of metal complexes binding an O₂ unit, such as metal-superoxo and -peroxo species, have been synthesized as chemical models of the M-O₂ intermediates,² and the binding modes of the O₂ unit (e.g., end-on (η^1) vs side-on (η^2) and superoxo vs peroxo) and the electronic nature of metal ions in the synthetic M-O₂ complexes have been intensively investigated with various spectroscopic methods and X-ray crystallography.³ The reactivity of M-O₂ complexes in electrophilic and nucleophilic reactions has also been the subject of

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intense scrutiny. For example, side-on synthetic iron(III)-peroxo complexes with heme and non-heme ligands have been structurally and spectroscopically characterized and investigated in oxidative nucleophilic reactions (e.g., aldehyde deformylation).^{4,5} As biomimetic compounds of copper-containing enzymes, a number of synthetic side-on and end-on copper(II)-superoxo and side-on copper(III)-peroxo complexes have been structurally and spectroscopically characterized and investigated in oxidative electrophilic reactions.⁶ It was also shown that the electronic nature of the copper-O₂ core (e.g., copper(II)-superoxo vs copper(III)-peroxo) varies depending on the supporting ligands of the copper complexes.^{3b,7}

Recently, we have reported the synthesis, spectroscopic and structural characterization, and reactivities of metal complexes with O₂-derived ligands bearing *N*-tetramethylated cyclam (TMC) chelates.⁸ In these studies, the ring size of the TMC ligands is shown to be an important factor in regulating the geometric and electronic structures of the M-O₂ complexes (e.g., side-on M⁽ⁿ⁺¹⁾⁺-peroxo vs end-on Mⁿ⁺-superoxo).^{9,10} One notable example is the finding that a side-on Ni(III)-peroxo complex is formed with a 12-TMC ligand (Scheme 1, blue-colored species),^{9b} whereas 14-TMC ligand affords an end-on Ni(II)-superoxo complex (Scheme 1, red-colored species).^{9a} Similarly, the formation of an end-on Cr(III)-superoxo complex and a side-on Cr(IV)-peroxo complex has been reported in the reactions of [Cr^{II}(14-TMC)]²⁺ and [Cr^{II}(12-TMC)]²⁺ with O₂, respectively.¹⁰

As our ongoing efforts to elucidate the ring size effect of TMC ligands on the geometric and electronic structure of the Ni-O₂ core in [Ni(*n*-TMC)(O₂)]⁺ (*n* = 12 – 14), we synthesized [Ni(13-TMC)(O₂)]⁺ and compared its structure with those of the previously reported [Ni^{III}(12-TMC)(O₂)]⁺ and [Ni^{II}(14-TMC)(O₂)]⁺ complexes (see Scheme 1). Interestingly, we observed the formation of two different intermediates, an end-on Ni(II)-superoxo complex (**2**, [Ni^{II}(13-TMC)(O₂)]⁺) and a side-on Ni(III)-peroxo complex (**3**, [Ni^{III}(13-TMC)(O₂)]⁺), depending on the base used in the reaction (Scheme 2, reaction *a* with tetramethylammonium hydroxide (TMAH) and reaction *b* with triethylamine (TEA)).¹¹ These Ni(II)-superoxo and Ni(III)-peroxo complexes bearing a common 13-TMC ligand were characterized with various spectroscopic methods and X-ray crystallography, and their reactivities were compared in electrophilic and nucleophilic reactions.

Results and discussion

Synthetic procedures for Ni-O₂ complexes bearing a 13-TMC ligand are depicted in Scheme 2. The starting material, [Ni^{II}(13-TMC)(CH₃CN)]²⁺ (**1**), was prepared by reacting Ni(ClO₄)₂·6H₂O and 13-TMC in CH₃CN under an inert atmosphere and characterized with various spectroscopic methods, such as UV-vis absorption spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and X-ray crystallography (see ESI†, Experimental Section, Figs. S1 – S3, Tables S1 and S2).

2 was prepared by adding 2 equiv. of H₂O₂ to a reaction solution containing **1** in the presence of 1.3 equiv. of TMAH in CH₃CN at –40 °C (Scheme 2, reaction *a*); the color of the solution changed from purple to yellowish green. A UV-vis spectrum of **2** shows an intense band at 339 nm (ϵ = 800 M^{–1} cm^{–1}) and two weak bands at 416 nm (ϵ = 130 M^{–1} cm^{–1}) and 684 nm 50 (ϵ = 60 M^{–1} cm^{–1}) (Fig. 1a), which is similar to that of the previously reported nickel(II)-superoxo complex bearing a 14-TMC ligand, [Ni^{II}(14-TMC)(O₂)]⁺ (see Fig. 1a).^{9a} Although we were not able to obtain an ESI-MS of **2** due to its thermal instability, the resonance Raman spectrum of **2** was successfully collected using 413-nm excitation in CH₃CN at 77 K (Fig. 1b). **2** prepared with H₂ ¹⁶O₂ exhibits an isotopically sensitive band at 1130 cm^{–1}, which shifts to 1070 cm^{–1} when H₂ ¹⁸O₂ is used. The observed isotopic shift of –60 cm^{–1} with ¹⁸O-substitution is in agreement with the calculated value

($\Delta\nu_{\text{calc}} = -64 \text{ cm}^{-1}$) for the O-O diatomic harmonic oscillator. The observed O-O frequency at 1130 cm^{-1} is comparable to those reported for end-on metal-superoxo complexes bearing 14-TMC, such as $[\text{Ni}^{\text{II}}(14\text{-TMC})(\text{O}_2)]^+$ (1131 cm^{-1})^{9a} and $[\text{Cr}^{\text{III}}(14\text{-TMC})(\text{O}_2)(\text{Cl})]^+$ (1170 cm^{-1}),^{10a} indicating the superoxo character of the O_2 unit in **2**. The electron paramagnetic resonance (EPR) spectrum of a frozen CH_3CN solution of **2** at 5 K exhibits a rhombic signal with g values of 2.25, 2.21, and 2.06 (Fig. 1c), which is a typical (d_z^2)¹ electron configuration observed for Ni(II)-superoxo^{9a,12} and Ni(III) complexes.¹³

Interestingly, when the reaction was performed in the presence of TEA instead of TMAH, a different species was produced (Scheme 2, reaction *b*). The reaction of **1** with 10 equiv. of H_2O_2 in the presence of 2 equiv. of TEA in CH_3CN at 10°C produces a green intermediate **3**, which shows distinct absorption features that are different from those of **2** but similar to those of the recently reported nickel(III)-peroxo complex bearing 12-TMC, $[\text{Ni}^{\text{III}}(12\text{-TMC})(\text{O}_2)]^+$ (Fig. 2a). The ESI-MS of **3** exhibits a prominent signal at a mass-to-charge (m/z) ratio of 332.0 (Fig. 2b), whose mass and isotope distribution pattern correspond to $[\text{Ni}(13\text{-TMC})(\text{O}_2)]^+$ (calculated m/z 332.2) (Fig. 2b, inset). When **3** was prepared with isotopically labelled $\text{H}_2^{18}\text{O}_2$, the mass peak corresponding to **3** shifted to m/z 336.0 (Fig. 2b, inset). The shift in four mass units upon substitution of ^{16}O with ^{18}O indicates that **3** contains an O_2 unit. On 458-nm excitation at 77 K, the resonance Raman spectrum of ^{16}O -labelled **3** in CH_3CN shows an isotopically sensitive band at 1008 cm^{-1} , which shifts to 950 cm^{-1} on ^{18}O -substitution (Fig. 2c). The O-O stretch of **3** is lower than those of Ni(II)-superoxo complexes, such as **2** (1130 cm^{-1}) and $[\text{Ni}^{\text{II}}(14\text{-TMC})(\text{O}_2)]^+$ (1131 cm^{-1}),^{9a} but similar to that of the Ni(III)-peroxo complex, $[\text{Ni}^{\text{III}}(12\text{-TMC})(\text{O}_2)]^+$ (1002 cm^{-1}).^{9b} The EPR spectrum of a frozen CH_3CN solution of **3** measured at 5 K exhibits an axial signal with g values of 2.19 and 2.07 (Fig. 2d). The room temperature magnetic moment of $2.1 \mu_{\text{B}}$, determined using the ^1H NMR Evans method,¹⁴ is consistent with an $S = 1/2$ ground state.

The single crystal structure of **3** revealed the mononuclear side-on Ni-peroxo complex in a distorted octahedral geometry (Fig. 3). The O-O bond length ($1.383(4) \text{ \AA}$) of **3** is comparable to that of $[\text{Ni}^{\text{III}}(12\text{-TMC})(\text{O}_2)]^+$ ($1.386 \text{ \AA}$). In addition, a good correlation was observed when the O-O bond length and O-O stretching frequency of **3** was fitted in the plot of O-O stretching frequency vs O-O bond length for side-on metal- O_2 complexes (ESI†, Fig. S4).^{3,8}

Ni K-edge XAS data on **2** and **3** are presented in Fig. 4. The inset shows the expanded pre-edge region. The pre-edge features arise due to electric dipole-forbidden quadrupole-allowed $1s \rightarrow 3d$ transitions.¹⁵ The pre-edge for **2** and **3** is at 8331.6 and 8332.3 eV, respectively (ESI†, Table S3). The $\sim 0.7 \text{ eV}$ shift reflects a significant increase in ligand field in **3** relative to **2**, attributable to the side-on (η^2) binding of O_2 in **3** in contrast to the end-on (η^1) binding expected in **2**. To higher energy is the intense, dipole-allowed $1s \rightarrow 4p$ continuum transitions. A shift in the rising-edge to high energies indicates an increase in oxidation state. For Ni compounds, typically, a small shift in edge energies is observed with oxidation.¹⁶ The rising-edge for **2** and **3** is at 8331.4 and 8331.7 eV, respectively, consistent with their respective Ni^{II} and Ni^{III} assignment. Based on the X-ray crystallography and spectroscopic data, **3** is assigned unambiguously as a side-on Ni(III)-peroxo complex.

The non-phase shift corrected Fourier transforms and the corresponding EXAFS data for **2** and **3** are presented in Fig. 5a. Their respective FEFF fits are presented in Figs. 5b and 5c and ESI†, Tables S4 and S5. The data show a large change in the first shell between **2** and **3**. The first shell of **2** is fit with 1 Ni-O at $1.91 \text{ \AA}$ and 5 Ni-O at $2.10 \text{ \AA}$. A three shell fit with 1 Ni-O at $1.90 \text{ \AA}$, 4 Ni-O at $2.07 \text{ \AA}$, and 1 Ni-O at $2.17 \text{ \AA}$ is also consistent with the data (Fig. 5b); this supports an end-on (η^1) O_2 binding in **2**. The presence of a sixth ligand could indicate trans-axial Ni-N(MeCN) ligation. The first shell of **3** is fit with 2 Ni-O at $1.89 \text{ \AA}$, 2

Ni-O at 2.05 Å, and 2 Ni-O at 2.16 Å (Fig. 5c), which is in excellent agreement with the crystal structure. Thus, the large difference in the first shells between **2** and **3** reflects the presence of the additional short Ni-O bond in **3**.

Density functional theory (DFT) calculations were performed to evaluate the geometric and electronic structures of **2** and **3**. The calculated metrical and electronic parameters of **3** are consistent with the experimental data presented here and support the side-on (η^2) bound Ni^{III}-peroxide complex (ESI†, Table S6). DFT calculations of **2** show 1 short Ni-O distance at 1.95 Å and 4 longer Ni-O distances at ~2.13 Å. No evidence of a trans axial MeCN ligation was found, although EXAFS data indicate the presence of a weakly bound sixth ligand. The Mulliken spin density analysis indicates two unpaired spin up electrons on Ni and one unpaired spin down electron on O₂ indicating a Ni^{II} (d^8 , $S = 1$) antiferromagnetically coupled with an O₂⁻ ($S = 1/2$) system, resulting in the d_z^2 doublet ground state in **2**. These results are consistent with the end-on (η^1) bound Ni^{II}-superoxo assignment of **2**. The calculated O-O bond distance for **2** is 1.32 Å, while that of **3** is 1.39 Å. This increase in O-O bond distance is typical on going from superoxo to peroxo complexes.

Finally, it is of interest to note that the interconversion between **2** and **3** does not occur. This is surprising since DFT calculations show that interconversion energy is low (~3 kcal/mol; see ESI†, Fig. S5). For example, since the only difference in the synthetic procedures for the generation of **2** and **3** was the base (e.g., TMAH for **2** and TEA for **3**, as shown in Scheme 2), we added TEA and TMAH to the solutions of **2** and **3** after these intermediates were generated. In these reactions, we did not observe the interconversion between them (Scheme 2, reactions *c* and *d*). One plausible explanation for no interconversion between **2** and **3** is that the *N*-methyl groups in **2** and **3** have a different orientation in the superoxo and peroxo moieties (e.g., *anti* to the superoxo moiety in **2** vs *syn* to the peroxo moiety in **3**, as proposed in Scheme 2). This is consistent with known crystal structures of metal-superoxo and -peroxo complexes bearing TMC ligands.⁸ *N*-methyl groups in the Cr-superoxo complex are oriented *anti* to the superoxo group,^{10a} whereas those in the metal-peroxo complexes are pointed *syn* to the peroxo moiety.^{5,10c,17} In contrast to this theory, DFT calculations show that the *anti* structure of **2** is energetically unfavorable (ESI†, Table S7). An alternative possibility, based on the EXAFS data, is the presence of a sixth ligand (a solvent, MeCN, water or OH⁻ (from TMAH)), which ligates axially to the Ni in **2** and precludes the interconversion; however, DFT calculations do not support trans-axial coordination in **2**. Nonetheless, the role of the bases for the formation of different Ni-O₂ intermediates is not clear at this moment and remains elusive.

We then examined the reactivities of **2** and **3** in oxidative electrophilic and nucleophilic reactions. Since it has been shown that metal-superoxo species are active oxidants in electrophilic reactions,^{6,9a,10a,18} the reactivity of **2** was first investigated in the oxidation of triethylphosphine (PEt₃) in CH₃CN:CH₃OH (1:1) at -40 °C. As shown in Fig. 6a, the characteristic UV-vis absorption band of **2** disappeared with a pseudo-first-order decay, and product analysis of the reaction solution revealed the formation of OPEt₃ in a quantitative yield. The pseudo-first-order rate constants increased proportionally with the increase of the concentration of PEt₃ (Fig. 6b), giving a second-order rate constant (k_2) of $3.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at -40 °C.

Unlike **2**, addition of PEt₃ to a solution of **3** in CH₃CN:CH₃OH (1:1) at 25 °C did not show any UV-vis spectral changes, and product analysis of the reaction solution did not reveal oxygenated products. These results indicate that **3** is not capable of conducting oxidative electrophilic reaction under the reaction conditions. In contrast, **3** is capable of deformylating aldehyde via nucleophilic reaction, as frequently observed in aldehyde deformylation reactions by metal-peroxo complexes.^{4b,9b,17} Kinetic studies of **3** with 2-

phenylpropionaldehyde (2-PPA) in CH₃CN at 25 °C show a first-order decay profile (Fig. 7a), and the pseudo-first-order rate constants increased proportionally with the aldehyde concentration ($k_2 = 4.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C) (Fig. 7b). Product analysis of the final reaction mixture revealed the formation of acetophenone ($85 \pm 10\%$).

Conclusions

Comparisons of the structure and reactivity of metal-O₂ complexes (i.e., metal-superoxo vs metal-peroxo species) are of importance in understanding intrinsic properties of these intermediates in dioxygen activation and oxidation chemistry. Although we have reported recently the synthesis of metal-superoxo and -peroxo complexes by changing the ring size of the supporting TMC ligands (e.g., [Ni(*n*-TMC)(O₂)]⁺ and [Cr(*n*-TMC)(O₂)]⁺ with *n* = 12 and 14),^{9,10} the synthesis of metal-superoxo and -peroxo complexes bearing a common TMC ligand has not been shown previously. In this work, we have shown the first successful synthesis of an end-on Ni(II)-superoxo complex, [Ni^{II}(13-TMC)(O₂)]⁺ (**2**), and a side-on Ni(III)-peroxo complex, [Ni^{III}(13-TMC)(O₂)]⁺ (**3**), bearing a common macrocyclic 13-TMC ligand. These intermediates were fully characterized with various spectroscopic techniques, X-ray crystallography, and DFT calculations. In particular, resonance Raman spectroscopy together with EXAFS clearly differentiates an end-on bound superoxo ligand of **2** (e.g., $\nu(\text{O-O})$ of 1130 cm⁻¹) and a side-on bound peroxo ligand of **3** (e.g., $\nu(\text{O-O})$ of 1008 cm⁻¹). The reactivities of **2** and **3** were also compared in electrophilic and nucleophilic reactions; **2** is capable of conducting oxidative electrophilic reaction, whereas **3** shows no electrophilic reactivity but is an active oxidant in nucleophilic reaction. Although we were successful in generating Ni(II)-superoxo and Ni(III)-peroxo complexes bearing a common supporting ligand in the presence of two different bases, the role of the bases and the exact mechanism of the formation of two different Ni-O₂ intermediates in the reactions of Ni(II) complex and H₂O₂ is not known at this moment and will be the subject of future studies.

Experimental Section

Generation and characterization of [Ni^{II}(13-TMC)(O₂)]⁺ (**2**)

Treatment of [Ni^{II}(13-TMC)(CH₃CN)](ClO₄)₂ (**1**, 2 mM) with 2 equiv. of H₂O₂ in the presence of 1.3 equiv. of TMAH in CH₃CN at -40 °C afforded the formation of a yellowish green solution. Spectroscopic data, including UV-vis, resonance Raman, and EPR, were reported in Fig. 1. [Ni^{II}(13-TMC)(¹⁸O₂)]⁺ was prepared by adding 2 equiv. of H₂ ¹⁸O₂ (14 μL , 90% ¹⁸O-enriched, 2% H₂ ¹⁸O₂ in water) in the presence of 1.3 equiv. of TMAH in CH₃CN (2 mL) at -40 °C.

Generation and characterization of [Ni^{III}(13-15 TMC)(O₂)]⁺ (**3**)

Treatment of **1** (4 mM) with 10 equiv. of H₂O₂ in the presence of 2 equiv. of triethylamine (TEA) in CH₃CN (2 mL) afforded the formation of a green solution at 25 °C. Spectroscopic data, including UV-vis, ESI-MS, resonance Raman, and EPR, were reported in Fig. 2. [Ni^{III}(13-TMC)(¹⁸O₂)]⁺ was prepared by adding 10 equiv. of H₂ ¹⁸O₂ (138 μL , 90% ¹⁸O-enriched, 2% H₂ ¹⁸O₂ in water) to a solution containing **1** (4 mM) and 2 equiv. of TEA in CH₃CN (2 mL) at ambient temperature. Crystals suitable for X-ray crystallography were obtained by slow diffusion of Et₂O into a solution of **3** in CH₃CN.

Reactivity studies

All reactions were run monitoring UV-vis spectral changes of reaction solutions, and rate constants were determined by fitting the changes in absorbance at 331 nm for [Ni^{II}(13-TMC)(O₂)]⁺ (**2**) and 413 nm for [Ni^{III}(13-TMC)(O₂)]⁺ (**3**). Reactions were run at least in triplicate, and the data reported represent the average of these reactions. *In situ*-generated **2**

and **3** were used in kinetic studies, such as the oxidation of PEt_3 in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ (1:1) at -40°C and 2-PPA in CH_3CN at 25°C , respectively. After completion of the reactions, pseudo-first-order fitting of the kinetic data allowed us to determine k_{obs} values. Products formed in the oxidation of PEt_3 by **2** in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ (1:1) at -40°C were analyzed by ^{31}P and ^1H NMR spectroscopy; OPEt_3 was formed as a sole product in the oxidation of PEt_3 by **2**. Products formed in the oxidation of 2-PPA by **3** in CH_3CN at 25°C were analyzed by injecting the reaction mixture directly into GC and GC-MS; acetophenone ($85 \pm 10\%$) was the sole product detected in this reaction.

X-ray crystallography

Crystal data for **1**-(ClO_4)₂: $\text{C}_{15}\text{Cl}_2\text{NiN}_5\text{O}_8$, Tetragonal, $P4/nmm$, $Z = 2$, $a = 9.2584(6)$, $b = 9.2584(6)$, $c = 14.1473(17)$ Å, $V = 1212.68(18)$ Å³, $\mu = 1.065$ mm⁻¹, $\rho_{\text{calcd}} = 1.391$ g/cm³, $R_1 = 0.0612$, $wR_2 = 0.1594$ for 912 unique reflections, 75 variables. CCDC reference number 729199.

Crystal data for **3**-(ClO_4)- CH_3CN : $\text{C}_{15}\text{H}_{33}\text{ClNiN}_5\text{O}_6$, Monoclinic, Pc , $Z = 2$, $a = 7.7299(2)$, $b = 7.7263(2)$, $c = 17.8514(5)$ Å, $\beta = 100.673(2)^\circ$, $V = 1047.70(5)$ Å³, $\mu = 1.095$ mm⁻¹, $\rho_{\text{calcd}} = 1.501$ g/cm³, $R_1 = 0.0360$, $wR_2 = 0.0762$ for 3604 unique reflections, 258 variables. CCDC reference number 900983.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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11. Irrespective of the kind of bases (e.g., TMAH and TEA), 14-TMC produced an end-on Ni(II)-superoxo species $[\text{Ni}^{\text{II}}(\text{O}_2)(14\text{-TMC})]^+$, whereas 12-TMC yielded a side-on Ni(III)-peroxo species $[\text{Ni}^{\text{III}}(\text{O}_2)(12\text{-TMC})]^+$.
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Fig. 1.

(a) UV-vis spectra of $[\text{Ni}^{\text{II}}(13\text{-TMC})(\text{O}_2)]^+$ (**2**) (red line) and $[\text{Ni}^{\text{II}}(14\text{-TMC})(\text{O}_2)]^+$ (black line) in CH_3CN at -40°C . (b) Resonance Raman spectra of **2** (16 mM) obtained upon excitation at 458 nm at 77 K; **2** prepared with $\text{H}_2\ ^{16}\text{O}_2$ (red line) and $\text{H}_2\ ^{18}\text{O}_2$ (blue line). The black line shows the difference of the spectra prepared with $\text{H}_2\ ^{16}\text{O}_2$ and $\text{H}_2\ ^{18}\text{O}_2$. (c) X-band EPR spectrum of **2** in frozen CH_3CN at 5 K. Instrumental parameters: microwave power = 0.989 mW, frequency = 9.646 GHz, sweep width = 0.25 T, modulation amplitude = 1 mT.

Fig. 2.

(a) UV-vis spectra of $[\text{Ni}^{\text{III}}(13\text{-TMC})(\text{O}_2)]^+$ (**3**) (red line) and $[\text{Ni}^{\text{III}}(12\text{-TMC})(\text{O}_2)]^+$ (black line) in CH_3CN at 10°C . (b) ESI-MS of **3** in CH_3CN at 10°C . The minor peaks at m/z 300.0 (P1), 345.0 (P2), and 359.0 (P3) are assignable to $[\text{Ni}(13\text{-TMC})]^+$, $[\text{Ni}(13\text{-TMC})(\text{HCOO})]^+$, and $[\text{Ni}(13\text{-TMC})(\text{CH}_3\text{COO})]^+$, respectively. Insets show the observed isotope distribution patterns for $[\text{Ni}(13\text{-TMC})(^{16}\text{O}_2)]^+$ (lower) and $[\text{Ni}(13\text{-TMC})(^{18}\text{O}_2)]^+$ (upper) (c) Resonance Raman spectra of **3** (16 mM) obtained upon excitation at 458 nm at 77 K; **3** prepared with $\text{H}_2\ ^{16}\text{O}_2$ (red line) and $\text{H}_2\ ^{18}\text{O}_2$ (blue line). The black line shows the difference of the spectra prepared with $\text{H}_2\ ^{16}\text{O}_2$ and $\text{H}_2\ ^{18}\text{O}_2$. (d) X-band EPR spectrum of **3** in frozen CH_3CN at 5 K. Instrumental parameters: microwave power = 1.013 mW, frequency = 9.646 GHz, sweep width = 0.25 T, modulation amplitude = 1 mT.

Fig. 3. ORTEP plot of [Ni^{III}(13-TMC)(O₂)]⁺ (**3**) with 30% probability thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni-O1 1.897(3), Ni-O2 1.898(3), Ni-N1 2.046(3), Ni-N2 2.192(3), Ni-N3 2.076(3), Ni-N4 2.210(3), O1-O2 1.383(4); O1-Ni-O2 42.73(12), Ni-O1-O2 68.369(16), Ni-O2-O1 68.58(16).

Fig. 4. Normalized Ni K-edge X-ray absorption spectra for **2** (—) and **3** (—). The inset shows the expanded pre-edge region.

Fig. 5.

(a) Comparison of the nonphase-shift corrected Fourier Transforms (FT) for **2** (—) and **3** (—). The inset shows the corresponding EXAFS data. *FEFF* best-fit results for **2** and **3** are shown in (b) and (c), respectively; data (solid line) and fit (dashed line).

Fig. 6. Reactions of $[\text{Ni}^{\text{II}}(13\text{-TMC})(\text{O}_2)]^+$ (**2**) with PET_3 in $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ (1:1) at -40°C . (a) UV-vis spectral changes of **2** (2 mM) upon addition of 40 equiv. of PET_3 . Inset shows the time course of the absorbance at 331 nm. (b) Plot of k_{obs} against PET_3 concentration to determine a second-order rate constant.

Fig. 7. Reactions of $[\text{Ni}^{\text{III}}(13\text{-TMC})(\text{O}_2)]^+$ (**3**) with 2-PPA in CH_3CN at 25 °C. (a) UV-vis spectral changes of **3** (4 mM) upon addition of 100 equiv. of 2-PPA. Inset shows the time course of the absorbance at 413 nm. (b) Plot of k_{obs} against 2-PPA concentration to determine a second-order rate constant.

Scheme 1.

A schematic drawing showing the effect of the ring-size of macrocyclic TMC ligands on the formation of Ni-O₂ intermediates; 12-TMC, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane; 13-TMC, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane; 14-TMC, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

Scheme 2.

Synthetic routes for the preparation of **2** and **3**. The structure of the end-on Ni(II)-superoxo complex (**2**) was drawn based on the crystal structure of an end-on Cr(III)-superoxo complex, $[\text{Cr}^{\text{III}}(\text{O}_2)(14\text{-TMC})]^{2+}$.^{10a}