

Nickel Intermediates

Reactivity of a Nickel(II) Bis(amidate) Complex with *meta*-Chloroperbenzoic Acid: Formation of a Potent Oxidizing Species

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Abstract: Herein, we report the formation of a highly reactive nickel–oxygen species that has been trapped following reaction of a Ni^{II} precursor bearing a macrocyclic bis(amidate) ligand with *meta*-chloroperbenzoic acid (H*m*CPBA). This compound is only detectable at temperatures below 250 K and is much more reactive toward organic substrates (i.e., C–H bonds, C=C bonds, and sulfides) than previously

Introduction

The study of high-valent nickel complexes in particular and the redox chemistry of nickel species in general has attracted the attention of the bioinorganic-chemistry community, thus providing models of nickel-containing enzymes that catalyze redox processes.^[1] Enzymes with redox-active nickel sites include [NiFe] hydrogenases,^[2] CO dehydrogenase,^[3] acetyl-coenzyme A (CoA) synthase,^[4] and nickel superoxide dismutase.^[5] Moreover, high-valent nickel species have been frequently postulated to be key reaction intermediates in the catalytic cycle of oxidation reactions^[6,7] and in coupling reactions.^[8,9]

In the field of oxidation chemistry, nickel-oxygen species are perceived to be formed upon homolytic or heterolytic O–O bond cleavage of the terminal oxidant bound to a Ni^{II} precursor. For example, alkane oxidation catalyzed by the

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201501841. reported well-defined nickel-oxygen species. Remarkably, this species is formed by heterolytic O–O bond cleavage of a Ni–H*m*CPBA precursor, which is concluded from experimental and computational data. On the basis of spectroscopy and DFT calculations, this reactive species is proposed to be a Ni^{III}-oxyl compound.

 $[Ni^{II}(tpa)(OAc)(H_2O)]^+$ ion (tpa=tris(pyridylmethyl)amine) and related systems that use the oxidant *meta*-chloroperbenzoic acid (HmCPBA) occurs through Ni^{III}-oxo or Ni^{II}-oxyl intermediate species.^[10-12] Furthermore, experimental and theoretical studies have indicated that a $[Ni^{III}-O]^+$ species is a potent oxidant in the gas phase for the conversion of methane into methanol.^[13,14] However, the evidence available for Ni^{IV}-oxygen intermediates is limited.^[7]

In contrast to the large number of mononuclear Mn-oxygen and Fe-oxygen species reported over the past decade,^[15] relatively few examples of such species based on late-transition metals such as nickel have been described. Recently, Ray and co-workers have shown that a Ni^{II}-acylperoxo species coordinated to tris[2-(N-tetramethylguanidyl)ethyl]amine (TMG₃tren) is the precursor to a Ni^{III}-oxo/hydroxo compound that can perform an oxo transfer and C-H activation with a rate-determining hydrogen-atom abstraction.^[16] Moreover, Hikichi and coworkers reported the selective hydroxylation of cyclohexane catalyzed by tris(pyrazolyl)borate-based Ni^{II} complexes with HmCPBA.^[17] For these latter systems, thermally stable Ni^{II}-acylperoxo species were spectroscopically detected and crystallographically characterized.^[17] Evidence for the formation of a transient [Ni^{IV}(OH)(cyclam)]²⁺ species (cyclam = 1,4,8,11-tetraazacyclotetradecane) competent to epoxidize olefins was gathered for the reaction of the corresponding Ni^{II} precursor with H₂O₂ in acidic media.^[7] Most recently, McDonald and coworkers reported the characterization and reactivity of a terminal Ni^{III}–oxygen adduct, which could perform hydrogen-atom abstraction of weak C-H bonds and oxygen-atom transfer to triphenylphosphine.^[18]

There are precedents that show that pincerlike tridentate 2,6-pyridinecarboxamidate ligands can support well-defined Ni^{III} or Ni^{IV} complexes^[19] (including a Ni^{III}–OCOOH species^[18]) and a highly reactive Cu^{III}–OH motif, as reported by Tolman

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Figure 1. a) Schematic representation of H_2L . b) X-ray structure and selected bond lengths [Å] and angles [°] of $1\cdot NaCF_3SO_3$. Hydrogen atoms and cocrystallized NaCF_3SO₃ have been omitted for clarity.

and co-workers.^[20] Herein, we show that the reaction of $[Ni^{II}(L)]$ (1; L is a tetradentate dianionic macrocyclic ligand with two amidate, one pyridine, and one aliphatic amine groups; Figure 1 a) with HmCPBA forms a transient nickel–oxygen species 2, which has been spectroscopically characterized. Compound 2 is only stable at subambient temperatures (<250 K) and is more reactive toward organic substrates (C–H bonds, C=C bonds, and sulfides) than the previously reported well-defined nickel–oxygen species. Experimental and computational methods indicate that this species is formed by heterolytic O–O bond cleavage.

Results and Discussion

The ligand H₂L was synthesized following a four-step synthetic route (see Scheme S1 in the Supporting Information). Selective methylation of the central amine group of the commercially available N-(2-aminoethyl)-1,3-propanediamine required prior protection of the two terminal amine functionalities with phthalic anhydride. After methylation and amine deprotection with hydrazine, [1+1] cyclization with 2,6-pyridinedicarbonyl chloride yielded H₂L. This step was the most critical due to the formation of [2+2] macrocyclic byproducts. Thus, the reaction was carried out under high-dilution conditions to obtain the desired [1+1] product in at least modest yields (see the Supporting Information). The reaction of equimolar amounts of H₂L and [Ni^{II}(CF₃SO₃)₂(CH₃CN)₃] with two equivalents of NaH under anaerobic conditions in acetonitrile afforded complex [Ni^{II}(L)], which cocrystallizes with NaCF₃SO₃ in 72% yield as 1-NaCF₃SO₃. The nickel center is present in a square-planar geometry with coordination to the pyridine ring, an aliphatic tertiary amine group, and two amidate units trans to each other (Figure 1 b). The bond lengths Ni-N_{py} Ni-N_{CH2}, and Ni-N_{amide} (i.e., 1.80, 1.93, and 1.85–1.87 Å, respectively) are consistent with previously reported Ni^{II} square-planar complexes with pyridine, amine, or amidate-based ligands.[21-23] The geometry renders the complex diamagnetic, thus enabling characterization by using 1D and 2D ¹H and ¹³C NMR spectroscopy (see Figures S1-S4 in the Supporting Information). As expected, the complex does not present C_2 symmetry and the β protons of the pyridine ring appear as two well-resolved doublets at $\delta =$ 7.43 and 7.36 ppm. Analysis with high-resolution QTOF-MS showed a major peak at m/z 341.053, with an isotopic pattern fully consistent with $\{[Ni(L)] + Na\}^+$.

Monitoring the reaction of **1** with three equivalents of HmCPBA in acetonitrile at -30 °C by means of UV/Vis absorp-



Figure 2. UV/Vis absorption spectroscopic changes observed upon the reaction of 1 (dotted line) with 3 equivalents of HmCPBA in CH₃CN at -30 °C to form 2 (dashed line). Inset: kinetic trace at $\lambda = 420$ nm.

tion spectroscopy indicated the formation of the metastable dark-yellow species **2** with an absorption band at $\lambda = 420$ nm ($\varepsilon > 7000 \text{ m}^{-1} \text{ cm}^{-1}$) and a shoulder at $\lambda = 580$ nm ($\varepsilon > 800 \text{ m}^{-1} \text{ cm}^{-1}$; Figure 2). The half-life of this species at $-30 \,^{\circ}\text{C}$ was 4.5 hours. Compound **2** was not detected when the reaction was carried out at room temperature.

Compound 2 reacts with various substrate classes. Indeed, the decay of 2 was accelerated substantially by the addition of thioanisole, which was ascertained by UV/Vis absorption spectroscopic analysis (see Figure S5 in the Supporting Information). Under conditions of excess substrate, the decay in absorbance showed pseudo-first-order behavior and could be fitted with a monoexponential function. The value of k_{obs} varied linearly with the thioanisole concentration, thus affording a second-order rate constant (k) of $0.56 \text{ m}^{-1} \text{ s}^{-1}$ at $-30 \degree \text{C}$ (see Figure S6 in the Supporting Information). Reaction rates were dependent on the substituent at the para positon to the sulfide group. The logarithm of the second-order rate constants of a series of para-substituted methylphenyl sulfides, namely, para-X-thioanisoles (k_X ; X = Me, Cl, CN), showed a correlation with the Hammett parameter ($\sigma_{\rm p}$) with a reaction constant (ρ) of -0.86 (Figure 3a). The negative ρ value indicates a buildup of positive charge in the transition state; hence, 2 has an electrophilic character in these reactions. Moreover, a plot of $log(k_x)$ against the one-electron oxidation potentials of each para-X-thioanisole species (E°_{ox}) afforded a linear correlation with a slope of -1.84 (see Figure S7 in the Supporting Information), thus indicating that the oxidation of sulfides by 2 occurs through direct oxygen-atom transfer rather than electron-transfer oxidation.[24]

Compound **2** also behaves as an electrophilic oxygen-atom transfer reagent toward alkenes. Thus, under pseudo-first-order reaction conditions, a second-order rate constant of $k = 0.18 \text{ m}^{-1} \text{ s}^{-1}$ was obtained for the oxidation of cyclooctene, whereas this value decreased to $k = 0.04 \text{ m}^{-1} \text{ s}^{-1}$ for 1-octene. The reaction of **2** with a series of *para*-substituted styrenes, namely, *para*-Y-styrenes (Y=OMe, Me, H, Cl, and NO₂), further evidences the electrophilic character of **2** as it affords a negative reaction constant of $\rho = -0.86$ (Figure 3 b). Analysis of the final oxidation products for the reaction of **2** with alkenes at



Figure 3. The Hammett plot $\log(k_{x}/k_{H})$ versus the Hammett parameter σ_{p} for the reaction of **2** in acetonitrile at -30 °C with a) *para*-X-thioanisoles and b) *para*-Y-styrenes.

-30°C indicates the formation of the corresponding epoxides with yields that range from 140% for cyclooctene oxide and styrene oxide to 50% for 1,2-epoxyoctane (with respect to the nickel complex). Despite the fact that peracids are well known to be capable of directly oxidizing alkenes without the mediation of a metal complex,^[25] control experiments (in the absence of a nickel complex) indicated that no epoxide was formed by direct reaction of HmCPBA with the alkene substrate under the current reaction conditions (i.e., the reaction mixture was quenched with excess NaHSO₃ after full decay of **2** at -30 °C). These results suggest that the slight excess of oxidant necessary to maximize the formation of 2 triggered a catalytic reaction as a background, which explains the yields of over 100% obtained for some of the substrates tested. Thus, the combination of 1 and HmCPBA might afford an efficient catalytic system for the oxidation of selected substrates (see below).

Compound **2** could perform hydrogen-atom abstraction from O–H bonds by reacting with 2,4,6-tri-*tert*-butylphenol to quantitatively form the corresponding phenoxyl radical, which manifested in the appearance of the intense absorption band at $\lambda = 626$ nm that is characteristic of this radical (see Figure S11 in the Supporting Information).^[26] Remarkably, **2** was also reactive toward hydrocarbon substrates with activated methylene C–H bonds, such as fluorene, 1,4-cyclohexadiene, 9,10-dihydroanthracene, and xanthene, again obeying pseudofirst-order kinetics under conditions with excess substrate and k_{obs} values linearly dependent on substrate concentration (see Figure S13 in the Supporting Information). The obtained second-order rate constants were adjusted for the reaction stoichiometry to yield the corrected rate constants (*k*'). As expect-



Figure 4. Plot of log(k') (determined at -30 °C) against the C–H BDE for the oxidation of alkanes with activated C–H bonds by **2**.

ed, the rate constants decreased with an increase of C–H bond-dissociation energy (BDE). More interestingly, $\log(k')$ values correlated linearly with BDE with a slope of -0.23 (Figure 4). Such a linear relationship between the reaction rates and BDE provides strong evidence for hydrogen-atom abstraction as the rate-determining step for the oxidation. Parallel reactions with deuterated 9,10-dihydroanthracene ([D₄]DHA) yielded a kinetic-isotope effect (KIE) of 4 (see Figure S14 in the Supporting Information), which is a value consistent with C–H bond cleavage as the rate-determining step.^[27,28]

The reaction of **2** with substrates bearing stronger C–H bonds was also examined. The addition of alkanes, such as toluene, ethylbenzene, or cyclohexane (300 equiv), to a solution of **2** in CH₃CN at -30 °C caused the decay of its characteristic band at $\lambda = 420$ nm with significantly higher rates than in the absence of these substrates (see Figure S15 in the Supporting Information). However, the decay of **2** did not follow simple single-exponential functions, most probably because the background catalytic reaction significantly interferes with the kinetic trace. Analysis of the final organic products showed the formation of oxidized products (i.e., benzaldehyde, acetophenone, or cyclohexanone, respectively) in yields from 21 to 47% with respect to **1**.

The oxidizing power of 2 was compared with the previously spectroscopically characterized Ni^{II}-acylperoxo complex [Ni^{ll}(Tp^{CF₃Me})(*m*CPBA)] (Tp^{CF₃Me} = hydrotris(3-trifluoromethyl-5methylpyrazolyl)borate)^{[29]} and Ni^{III}-hydroxo(oxo) compound $[Ni^{III}{O(H)}(TMG_3 tren)]^{n+[16]}$ obtained by the reaction of the Ni^{II} precursors with HmCPBA (Table 1). Interestingly, ${\bf 2}$ reacts more than 200 times faster with C-H bonds than $[Ni^{III}{O(H)}(TMG_3 tren)]^{n+}$ at the same temperature (-30 °C). The same reaction is up to three orders of magnitude faster relative to $[Ni^{II}(Tp^{CF_3Me})(mCPBA)]$, whereas the reaction toward the para-Y-styrenes proceeds about 50 times faster. However, the much higher temperature (+70 °C) used for the reactivity studies with the Tp-based system indicates that differences with respect to 2 are indeed much greater. Overall, compound 2 is significantly more active than previously reported well-defined nickel-oxygen species. A comparison with the reactivity of the Ni^{III}-oxygen adduct recently reported by McDonald and coworkers^[18] was hampered because studies with this last compound are limited to substrates containing weaker O-H and



The EPR spectrum of a sample

frozen to 77 K after mixing

1 and HmCPBA at -30 °C shows signals of two rhombic S = 1/2species: a major species (95%) with $g_1 = 2.03$, $g_2 = 2.22$, and $g_3 =$ 2.24 and a minor species (5%) with $g_1 = 2.02$, $g_2 = 2.19$, and $g_3 =$ 2.31 (Figure 5). These EPR properties, that is, $g_{av} = 2.16$ and 2.18 for the major and minor species, respectively, and $g^{\parallel} > g^{\perp}$ are indicative of a Ni^{|||} species with dis-

Table 1. Second-order rate constants $(k, m^{-1}s^{-1})$ for the oxidation of different substrates by **2**, $[Ni^{III}[O(H)](TMG_3 tren)]^{n+}$, and $[Ni^{II}(Tp^{CF_3Me})(mCPBA)]$.

	2 (−30 °C)	[Ni ^{ll{} {O(H)}(TMG₃tren)] ^{<i>n</i>+} (−30 °C) ^[16]	[Ni ^{III} (Tp ^{CF₃Me})(<i>m</i> CPBA)] (+ 70 °C) ^[29]
xanthene	2.93	0.0131	0.0018
9,10-dihydroanthracene	2.62	0.0125	0.00051
1,4-cyclohexadiene	1.69	0.0073	0.019
fluorene	0.28	_	0.0010
styrene	0.45	-	0.0088
4-methylstyrene	0.69	_	0.017
4-methoxystyrene	1.51	-	0.022

C–H bonds (i.e., 2,6-di-*tert*-butylphenol and 1-benzyl-1,4-dihy-dronicotinamide, respectively; $BDE = 64 \text{ kcal mol}^{-1}$) or triphe-nylphosphine.

Given the high reactivity of compound **2** toward several substrate classes, including alkanes bearing strong C–H bonds, we tested the ability of **1** to act as a catalyst in the oxidation of cyclohexane with HmCPBA as oxidant. The slow addition of HmCPBA (150 equiv) to a solution containing **1** and cyclohexane (15000 equiv) afforded a mixture of cyclohexanol (A) and cyclohexanone (K) with a total turnover number of 100 and a product ratio of A/K \approx 1:1, with an overall 67% yield based on the oxidant. Blank experiments in the absence of the nickel catalyst showed the formation of only trace amounts of oxidized products (<0.5% yield).

Further insight into the nature of the oxidizing species was gained through the oxidation of *cis*-1,2-dimethylcyclohexane and adamantane. The oxidation of this substrate (150 equiv) by **1** (1 equiv) with HmCPBA (150 equiv) as an oxidant afforded the corresponding tertiary alcohol product with 84% retention of configuration (RC) of the tertiary carbon atoms. Under similar experimental conditions, adamantane was oxidized with a high preference for the tertiary carbon atom with a tertiary/ secondary ratio of 18:1 (corrected according to the number of equivalent secondary and tertiary C–H bonds). Much lower RC values and tertiary/secondary ratios would be obtained if freely diffusing radicals (i.e., hydroxyl or alkoxyl) were involved.^[30] This data indicates that a metal-based oxidant, most likely the spectroscopically detected species **2** (see below), is mainly responsible for the observed oxidation reactions.

The characterization of **2** with cryospray ionization mass spectrometry (CSI-MS) at -30° C revealed a clean spectrum with a major peak at m/z 318.0605, with an isotopic pattern fully consistent with the [Ni^{III}(L)]⁺ ion. Interestingly, monitoring the reaction of **2** with 1-octene by means of CSI-MS showed the progressive formation of the Ni^{II} species (m/z 355.0319). However, no Ni^{II} species was formed during the reaction with 9,10-dihydroanthracene, and only a Ni^{III} species was observed (m/z 318.0605; see Figures S20–S21 in the Supporting Information). In any case, the mass spectra of the reaction mixture obtained upon warming to room temperature, either in the presence or absence of the substrate, only exhibited signals that corresponded to Ni^{III} species with an oxidized/dehydrogenated ligand (m/z 355.0319).



Figure 5. Top: EPR spectrum of the reaction of 1 (1.9 mM) with 3 equivalents of HmCPBA in acetonitrile at -30 °C after 60 seconds under argon. Bottom: Simulated EPR spectrum (black line), which accounts for a major species (95%, dotted line) $g_1 = 2.03$, $g_2 = 2.22$, and $g_3 = 2.24$ (anisotropic broadening: $H_1 = 200$, $H_2 = 235$, and $H_3 = 100$ MHz) and a minor species (5%, dashed line) with $g_1 = 2.02$, $g_2 = 2.19$, and $g_3 = 2.32$ (anisotropic broadening $H_1 = 50$, $H_2 = 180$, and $H_3 = 180$ MHz).

torted-square-planar, trigonal-bipyramidal, or compressed-octahedral coordination and the unpaired electron in the d_{xy} or $d_{x^2-y^2}$ orbitals.^[31-34] The maximum concentration of the Ni^{III} species, however, amounts to only 16%. Moreover, the time dependence of the change in the intensity of the EPR signal did not directly correlate with that of the UV/Vis absorbance at $\lambda =$ 420 nm (or its shoulder at $\lambda =$ 580 nm) assigned to **2**. The concentration of the Ni^{III} species steadily increased over time, even after the disappearance of the chromophore (see Figure S22 in the Supporting Information). These data indicate that the signal of the Ni^{III} species corresponds to a decayed species of **2** that is not responsible for the observed oxidation chemistry.

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Indeed, the addition of 1 to preformed 2 causes the immediate decay of the latter species, as followed by using UV/Vis absorption spectroscopy (see Figure S19 in the Supporting Information). The EPR spectrum of the resultant solution shows the formation of the Ni^{III} species in a much higher yield of 35% (relative to the total nickel concentration after adding 2.75 equivalents of the Ni^{III} complex to the preformed solution of **2**; note that the maximum possible yield is 53%; see Figure S23 and Scheme S2 in the Supporting Information). Analysis of the reaction mixture by means of ESI-MS also shows the presence of a Ni^{III} species, thus further suggesting that comproportionation occurred between **2** (possibly a formal Ni^{IIV} species; see below) and **1** (a Ni^{III} species) to give the [Ni^{III}(L)]⁺ ion (*m/z* 318.0617; see Figure S18 in the Supporting Information).

To help further characterize the Ni center of 2, XAS was applied at the metal K-edge. The pre-edge of 2, associated with $1s \rightarrow 3d$ transitions, occurs at approximately 8333.5 eV and has a normalized area of 0.16, thus indicating the presence of a high-valence Ni species (see Figure S24 in the Supporting Information). Generally for Ni^{II} complexes, the $1s \rightarrow 3d$ transitions occur at around 8332 eV and are 2-3-fold less intense.[35] A higher oxidation state for 2 is further emphasized by a higher rising-edge energy determined by using the half-height method. This energy in 2 is at approximately 8343.4 eV, which is between 1.5 and 2 eV higher in energy than reported for a Ni^{II} species^[35] and is consistent with a Ni^{III} species.^[36-38] Previous studies on Ni-oxido and Ni-cyclam derivatives show a shift of 1.5-2 eV on going from Ni^{II} to Ni^{III} species, whereas a shift of approximately 4 eV would be expected for a Ni^{IV} species.^[36-38] Relative to Ni foil, this translates to a shift of approximately 4 eV for a Ni^{III} center, whereas a Ni^{IV} species would be expected to have a shift of approximately 6 eV to higher energy (see Figure S24 in the Supporting Information).^[37] Therefore, the X-ray absorption near-edge structure (XANES) spectra of 2 is most consistent with a Ni^{III} oxidation of the metal center. The Fourier-transformed EXAFS spectra of 2 is shown in Figure 6. Three scattering shells are implied by the features at 1.4, 1.8, and 2.2 Å. Single-scatter fits are consistent with the first two peaks that correspond to two N/O scattering shells (see Table S4 in the Supporting Information). On the other hand, the feature at 2.2 Å is consistent with contributions from multiple scattering of the pyridine ring. Several multiple scattering models were attempted (see Table S5 in the Supporting Information), and the EXAFS analysis converged on a model with two longer metal-N/O bonds of approximately 2.12 Å, and three shorter N–O bonds of approximately 1.88 Å, including the pyridine ligand (Table 2).

DFT calculations were carried out to explore the possible nature of **2**. Previous reports on related systems indicate four distinct mechanistic scenarios for the reaction of **1** with HmCPBA (reactions A-D; Scheme 1). Pathway A involves the formation of the Ni^{II}–acylperoxy [(L)Ni^{II}-mCPBA]⁻ species. However, this process was considered to be kinetically and thermodynamically unfeasible due to the high free-energy difference of the [(L)Ni^{II}-mCPBA]⁻ ion relative to the starting reactants ($\Delta G^{\circ} = +47.7$ kcal mol⁻¹). This difference may be rationalized





Figure 6. Fourier-transformed EXAFS spectra of **2** (no phase correction, FT window = $2-12 \text{ Å}^{-1}$): dotted line = data, black line = best fit. Inset: k^3 -weighted unfiltered EXAFS spectra: dotted line = data, black line = best fit.

Table 2. EX/ lengths and	AFS multiple the coordina	-scattering tion number	model showing for complex 2 . ^[a]	Ni—ligand	bond		
Model	Path	Δr [Å]	$\sigma^2 [\times 10^3 \text{ Å}^2]$	R [%]	χ^2_v		
N ₂ N ₃ (Pyr)	2 N ^{2.0} 3 N ^{1.8} 1 Pyr ^[b]	0.12(1) 0.08(1) 0.08(1)	1.9(6) 1.9(6) 6(2)	8.7	7.2		
[a] E_0 = 8344.2 eV and S_0 = 0.9. [b] The pyridine scattering paths do not in-							



Scheme 1. Possible pathways (A–D) studied by DFT that correspond to the reaction of 1 with HmCPBA in acetonitrile. Free energies are given in kcal mol⁻¹ at -30 °C.

by the acidity of HmCPBA ($pK_a=31$), which was computed to be much lower than that of $1-H^+$ ($pK_a=7$) in acetonitrile, so that proton transfer from HmCPBA to 1 is unfavorable. An al-

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ternative mechanism involves the formal oxidation of Ni^{II} to Ni^{III} (accompanied by the 1e⁻ reduction of HmCPBA to give the radical anion), and the subsequent coordination of another HmCPBA or mCPBA molecule to the +3 metal center. However, DFT calculations suggest the thermodynamic unviability of these two processes (pathway B: $\Delta G^{\circ} = +30.0 \text{ kcal mol}^{-1}$; pathway C: $\Delta G^{\circ} = +13.5 \text{ kcal mol}^{-1}$). This result is in agreement with the EPR data, which indicated that the Ni^{III} species is not related to chromophore **2**.

Instead, the complexation of 1 with HmCPBA is thermodynamically reasonable with a ΔG° value of +4.4 kcal mol⁻¹ (pathway D, Scheme 1). Complex [Ni^{II}(L)]–HmCPBA may evolve through two different reaction pathways as previously postulated for other nickel systems (Scheme 1): 1) homolytic O-O bond cleavage to form a Ni^{III}-hydroxo species and a carboxyl radical, which decomposes to give chlorobenzene and carbon dioxide or 2) heterolytic O-O bond cleavage to form a Ni^{IV}oxo/hydroxo intermediate and the corresponding benzoic acid (HmCBA). Computational studies indicate that the homolytic pathway is kinetically unfavorable by +30.0 kcal mol⁻¹ (Scheme 2). Instead, the O-O heterolysis shows a lower barrier of only +9.0 kcal mol⁻¹ to afford a nickel-oxygen species. Interestingly, chromatographic analysis of the reaction mixture after the self-decay of 2 did not show the presence of chlorobenzene or CO₂, but the formation of quantitative amounts of HmCBA was ascertained instead by using NMR spectroscopy

and GC-MS, thus indicating that an O–O heterolysis pathway is followed under the experimental conditions (see Figure S17 in the Supporting Information). Thus, both experimental and theoretical data point toward an O–O heterolytic pathway as the most plausible mechanism. According to DFT calculations, the terminal oxygen atom of the Ni product **2** formed after O–O heterolysis bears an interaction with the acidic proton of the acid byproduct (i.e., HmCBA). This compound would carry out the oxidation of the substrate.

Analysis of the Hirshfeld spin density on the nickel center $(\rho(Ni) = 0.66)$ and the oxo moiety $(\rho(O) = 1.29)$ suggests that 2 is best described as a Ni^{III}-O⁻ species (see Tables S6 and S7 and Figure S26 in the Supporting Information). Interestingly, inspection of the spin natural orbitals (SNOs) of complex 2 shows two single occupied orbitals: 1) $\sigma^*(d_z^2/p_z)$ distributed between the Ni and O centers and 2) p_v orbital centered on the terminal oxygen atom (see Figure S27 in the Supporting Information). This electron distribution may be responsible for the weakening of the Ni–O bond (1.95 Å) and the significant oxyl character of the oxygen group. Moreover, the Mayer index for the Ni-O bond is about 0.6, which is in agreement with the half broken σ bond and the lack of π bonding showed in the SNOs. Finally, an atoms-in-molecules (AIM) analysis was performed on 2 to better understand the nature of the Ni-O bond. We found negative but close to zero values of $\nabla^2 \rho(r)$ and H(r), which suggests a very weak Ni-O interaction with almost no



Scheme 2. Energetic profile of pathway D for the reaction of 1 with HmCPBA in CH₃CN (homolytic and heterolytic O–O bond cleavage). Free energies are given in kcalmol⁻¹ at -30 °C. ΔE_{ZPE} values in kcalmol⁻¹ are shown in parentheses (ZPE=zero-point energy).

covalent character (see Figure S28 in the Supporting Information). Therefore, the DFT analysis of the electronic structure of $[Ni^{III}(L)(O)]$ reveals that the Ni and O atoms are weakly connected, thus making the terminal oxygen atom highly reactive.

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The experimental extended X-ray absorption fine structure (EXAFS) distances of **2** are consistent with the Ni^{III}–oxyl radical theoretical model, with three shorter and two longer N–O bonds. The Ni^{III}–oxyl radical model predicts a pyridine–Ni bond of 1.85 Å, with the two proximal Ni–N bonds of 1.86 and 1.90 Å, which is consistent with the N/O scattering shell of 1.88 Å. The Ni^{III}–oxyl radical model also predicts two longer bonds for Ni–O and Ni–N (1.95 and 1.96 Å, respectively), thus corresponding to the two longer N–O distances of 2.12 Å derived from EXAFS analysis. This finding is well within the resolution of the EXAFS single-scatter fits (ca. 0.14 Å) for the long Ni–N/O distances.

Resonance Raman spectroscopic analysis of **2** in frozen acetonitrile (77 K) showed enhancement of two sets of bands at $\tilde{\nu}$ = 450 and 477 cm⁻¹ and $\tilde{\nu}$ = 736 and 879 cm⁻¹, which appear concomitantly with the absorbance of **2** (Figure 7). Simulation



Figure 7. Resonance Raman spectra (λ_{ex} =457 nm) in frozen acetonitrile (77 K) of a) **2** formed after the reaction of **1** (0.24 mM) with 3 equivalents of HmCPBA at -30 °C, b) HmCPBA (0.72 mM), c) **1** (0.25 mM), and d) decomposed **2**.

of the Raman spectra of $[Ni^{III}(L)(O\cdot)]$ –H*m*CBA by using DFT methods predicted a Ni–O vibration at $\tilde{\nu} = 433 \text{ cm}^{-1}$ and a ligand-based stretching vibration at $\tilde{\nu} = 443 \text{ cm}^{-1}$ (see Figure S29 in the Supporting Information). Thus, within error, the experimental and theoretical results are in agreement for the first set of bands at $\tilde{\nu} = 450$ and 477 cm^{-1} . The bands at $\tilde{\nu} = 736$ and 879 cm^{-1} are tentatively assigned to O–O stretching modes from a byproduct, most likely a Ni^{III}–peroxy species.

The formulation of **2** as a Ni^{III}–oxyl species is consistent with the DFT calculations and with the fact that a heterolytic O–O bond cleavage is experimentally observed (i.e., the formation of HmCBA as a reaction byproduct). This formulation would also be in agreement with the EPR and NMR silence of **2** and with the EXAFS data. Analysis by CSI-MS that showed the lack of signals with intensity–time profiles similar to those observed by UV/Vis absorption spectroscopic analysis agrees with the neutral character of **2**. Finally, the reaction of **2** with 1-octene (100 equiv) in CH₃CN and in the presence of ¹⁸O-labeled water at -30 °C affords 7% of the corresponding ¹⁸O-labeled epoxide product. This data indicates that water exchange can occur prior to reaction with substrates, as previously observed for other metal–oxo species.^[39]

The formulation of **2** as a Ni^{III}–oxyl species is controversial. To date, metal–oxyl species have been postulated several times, but have been scarcely directly detected.^[40,41] A possible alternative to this mechanism would be the formulation of **2** as the [Ni^{II}(L)]–H*m*CPBA adduct, a precursor to the high-valent nickel species (Scheme 3). However, this possibility would not



Scheme 3. Schematic representation of the nickel species formed upon the reaction of 1 with HmCPBA.

agree with the data from X-ray absorption spectroscopy (XAS), which supports a metal center with a higher valence. Moreover, the reaction of 1 with an aliphatic peracid, such as pernonanoic acid, under the same conditions as those used for the generation of 2 (3 equivalents of peracid, CH₃CN, -30 °C) affords a UV/Vis absorption spectrum almost identical to 2, with a characteristic absorption band centred at $\lambda = 416$ nm (see Figure S25 in the Supporting Information). Given the different nature of the two peracids (i.e., pernonanoic acid and HmCPBA), markedly different UV/Vis absorption spectra would be expected for both systems if the peracid unit was coordinated to the nickel center in 2, which is not the case. Moreover, the formation of a Ni^{III}-oxyl species by heterolytic O-O bond cleavage is in agreement with the much higher reactivity of the present system relative to the previously reported and well-defined Ni-mCPBA species.[16,29]

Conclusion

The Ni^{II} complex of the bis(amidate) macrocyclic ligand (L) has been shown to react with HmCPBA at low temperatures to form compound **2**, which has been spectroscopically trapped. This species is kinetically competent enough to carry out the oxidation of different substrates, such as olefins, sulfides, and C–H bonds. Remarkably, the activity of **2** is much higher than that previously established for well-defined nickel–oxygen systems, which may indicate that an alternative mechanism occurs in the present system. A combination of experimental and theoretical results have suggested that a heterolytic O–O bond cleavage in a Ni–HmCPBA adduct occurs, thus giving rise to the formation of a high-valent nickel–oxygen species that is best formulated as a Ni^{III}–oxyl complex. This work suggests that the use of a dianionic ligand may lead to alternative reaction pathways relative to previous systems, thus favoring the



formation of high-valent nickel species that behave as strong oxidants. In this line of research, work in our group is aimed at ligand tuning and the use of alternative oxidants to increase the reactivity of the nickel species further.

Experimental Section

Materials and methods

The reagents and solvents used are commercially available and were purchased from Panreac, Scharlau, and Aldrich. The preparation and handling of air-sensitive materials were carried out in a N₂ drybox (MBraun ULK 1000) with O₂ and H₂O concentrations of <1 ppm. Commercially available 70% *meta*-chloroperbenzoic acid was purified prior to use by following a reported procedure.^[42] The deuterated substrate [D₄]-9,10-dihydroanthracene was prepared from 9,10-dihydroanthracene by following previously reported procedures.^[43]

Elemental analyses of C, H, and N were performed on a PerkinElmer EA2400 series II elemental analyzer. Mass spectrometric analysis was performed by electrospray ionization (ESI) on a high-resolution Bruker micrOTOF QII (Q-TOF) mass spectrometer with a quadrupole analyzer and positive and negative ionization modes. ¹H NMR, ¹³C NMR, COSY, and HSQC spectra were performed on Bruker Ultrashield Avance III400 and Ultrashield DPX300 spectrometers. UV/Vis absorption spectra were performed on a diode-array Agilent Cary 60 spectrophotometer and low-temperature control was maintained with a cryostat from Unisoku Scientific Instruments. X-ray analyses were carried out on Bruker Smart Apex CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) from an X-ray tube. GC analyses were carried out on an Agilent 7820A gas chromatograph (HP5 column, 30 m) with a flame-ionization detector. GC-MS was performed on an Agilent 7890A gas chromatograph interfaced with an Agilent 5975c mass spectrometer with a triple-axis detector. The identification of CO₂ was carried out on an Agilent 7820A GC system equipped with three columns, washed molecular sieves (5 Å; outside diameter (OD) = $2 \text{ m} \times 1/$ 8 inch, mesh 60/80 SS; Porapak Q, OD = 4 m×1/8 inch, mesh 80/ 100 SS), and a thermal-conductivity detector. Raman spectra were recorded in NMR tubes (diameter=5 mm) at 77 K in a liquid-nitrogen-filled quartz dewar. Spectra were collected in the back-scattering mode (135°) with excitation at $\lambda =$ 457 nm (Cobolt Lasers, 50 mW) and planoconvex lens (diameter = 25 mm) to collect and collimate the Raman scattering, which was passed through the long pass cutoff filter (Semrock). The scattering was focused at the entrance slits of a Shamrock 303i spectrograph with a grating of 1200 $L\,mm^{-1}$ blazed at $\lambda\!=\!500\,nm$ and a iDUS-420-BRDD CCD detector (Andor Technology). Spectral calibration was carried out in acetonitrile and toluene (1:1 v/v). The spectra were processed on Andor Solis and Spectrum 10 (PerkinElmer). Cyclic voltammetry (CV) was performed by using a potentiostat from CHInstruments with a three-electrode cell. The working electrode was a glassy carbon disk from BAS (0.07 cm²), the reference electrode was a saturated KCl calomel electrode, and the auxiliary electrode was a platinum wire. CV was carried out with nBu₄NPF₆ (TBAP) as a supporting electrolyte (0.1 M). The EPR spectra were recorded on an ESP 300 X-Band EPR spectrometer from Bruker with a TE011 superhigh Q microwave resonator. The samples were cooled to 77 K in a liquid-nitrogen Dewar. Spin quantifications were calculated on the basis of double integrals of the recorded spectra relative to a measured standard of Cu^{\parallel} ions of a given concentration. Sample tubes were filled higher than the cavity dimension to guarantee an equally filled cavity for all the measured samples. Spin quantifications were additionally corrected for volume errors, thus resulting in slight differences in tube diameter. EPR simulation was performed by using EASYSPIN.^[44]

A sample of 2 (4 mm; prepared by reaction of 1 with 3 equivalents of HmCPBA in CH₃CN at -30° C) was loaded into a holder (2 mm) with Kapton tape windows and stored at liquid-nitrogen temperatures until run. Data was collected at the SOLEIL synchrotron SAMBA beamline equipped with a Si(220) double-crystal monochromator and a liquid-helium cryostat (20 K). X-ray absorption (XAS) was detected in fluorescence mode by using a Canberra 35element Ge detector and a Z-1 filter. An internal-energy calibration was performed by using the first inflection point of the XANES spectrum of nickel foil ($E_{cal} = 8331.6 \text{ eV}$). Data reduction and normalization was performed by using the Athena software package with the AUTOBK algorithm. To extract intensities and energy positions, the XANES pre-edge and edge were fit with pseudo-Voigt functions and the edge jump was modeled by using a cumulative Gaussian-Lorentzian sum function. EXAFS were extracted by using a $R_{\rm bkg}$ value of 1.05 Å and a spline between k=1 and 13.7 Å⁻¹. The Artemis software program with an IFEFFIT engine and FEFF6 code was used for EXAFS analysis.^[45-47] The k^3 -weighted data was fit in rspace over a range of k=2-12 Å⁻¹, with S₀=0.9 and a Kaiser-Bessel window (dk 2). The spectra were not phase corrected and a global ΔE_0 value was employed, with the initial E_0 value set to the inflection point of the rising edge at 8344.2 eV. Single-scatter paths for Ni–N with initial r_{eff} values of 1.8 and 2.0 Å and multiple scattering from pyridine (initial $r_{\rm eff}\!=\!$ 1.8 Å) were fit in terms of $\Delta r_{\rm eff}$ and σ^2 , as previously described.^[48-50] To assess the goodness of fit from different models, the R_{factor} (%R) and the reduced χ^2 (χ^2_{y}) were minimized. Although the R_{factor} is generally expected to decrease with the number of adjustable parameters, χ^2_{ν} may eventually increase, thus indicating that the model is overfitting the data.^[51]

Synthesis of [Ni^{II}(CF₃SO₃)₂(CH₃CN)₃]

NiCl₂ (2.36 g, 0.018 mmol) was suspended in dry acetonitrile (50 mL) in a Schlenk flask (100 mL). Me₃SiOTf (7.1 mL, 0.039 mmol) was added to the solution in an N₂ atmosphere. The skin-colored suspension was stirred vigorously at room temperature for 3 weeks while the color darkened to deep blue. The mixture was then filtered to remove the starting material, the solvent was evaporated under reduced pressure, and a purple precipitate was formed. The solid was collected, dissolved in acetonitrile (5 mL), and slow diffusion of diethyl ether at room temperature over the resulting solution afforded a purple solid, which was dried under vacuum to yield $[\mathrm{Ni}^{\mathrm{H}}(\mathrm{CF}_3\mathrm{SO}_3)_2(\mathrm{CH}_3\mathrm{CN})_3]$ as a pale-purple solid (5.43 g, 0.011 mmol, 63%). Elemental analysis (%) calcd for C₈H₉F₆N₃NiO₆S₂: C 20.02, H 1.89, N 8.75; found: C 19.76, H 1.97, N 8.63.

Synthesis of [Ni^{II}(L)] (1)

A solution of $[Ni^{II}(CF_3SO_3)_2(CH_3CN)_3]$ (32.09 mg, 0.057 mmol) in anhydrous acetonitrile (0.5 mL) in a glove box was added dropwise to a vigorously stirred suspension of H₂L (15.10 mg, 0.057 mmol) in anhydrous acetonitrile (0.5 mL). After a few seconds, the solution became colorless. The addition of NaH (2.71 mg, 0.11 mmol, 2 equiv) caused a further color change to orange. The reaction mixture was stirred for 3 h, the solvent was removed, and the resulting residue dissolved in methanol, filtered through celite, and concentrated. Slow diffusion of diethyl ether over the resulting solution afforded **1** in a few days as orange crystals (20.07 mg, 0.041 mmol, 72%). ESI-MS: m/z (%): 341.05 $[M+Na]^+$ (100), 659.12 $[2M+Na]^+$ (40); ¹H NMR (CD₃CN, 400 MHz, 298 K): δ = 7.95 (t, J = 7.6 Hz, 1H; H_a), 7.43 (dd, J = 7.6 Hz, 1H; H_b), 7.36 (dd, J = 7.6 Hz,

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1 H; H_c), 3.43–3.35 (m, 1 H; H_d), 3.33–3.20 (m, 3 H; H_e/t_f), 2.94–2.87 (m, 1 H; H_h), 2.82–2.74 (m, 1 H; H_i), 2.73–2.71 (m, 1 H; H_j), 2.69 (s, 3 H; CH₃), 2.50–2.45 (m, 1 H; H_k), 1.81–1.73 ppm (m, 2 H; H_l/m); ¹³C NMR (CD₃CN, 100 MHz, 298 K): δ = 169.39 (C₁₂ or C₁₃), 166.14 (C₁₂ or C₁₃), 153.54 (C₁₀ or C₁₁), 152.53 (C₁₀ or C₁₁), 141.27 (C₁), 121.72 (C₂), 121.60 (C₃), 65.38 (C₄), 58.28 (C₅), 41.54 (C₆), 41.23 (C₇), 40.90 (C₈), 26.21 ppm (C₉); elemental analysis (%) calcd for C₁₃H₁₆N₄NiO₂·NaCF₃SO₃: C 34.24, H 3.28, N 11.61; found: C 33.98, H 3.08, N 11.23; CV (CH₃CN vs. SCE): $E_{1/2}$ =0.96 V.

Generation of 2

In a typical experiment, a solution of 1 in acetonitrile (2.5 mL, 0.24 mM) was placed in a cuvette (pathlength = 1 cm; [1] = 0.6 µmol). The quartz cell was placed in the Unisoku cryostat of a UV/Vis absorption spectrophotometer and cooled to 243 K. After reaching thermal equilibrium, an UV/Vis absorption spectrum of the starting complex was recorded. Then, a solution of HmCPBA (3 equiv) in acetonitrile (105 µL, 17 mM) was added. The formation of a band at λ_{max} = 420 nm (ϵ > 7000 M⁻¹ cm⁻¹) and a shoulder at λ_{max} = 580 nm (ϵ > 800 M⁻¹ cm⁻¹) was observed. Compound **2** was fully formed within 100 s.

Analysis of the reaction of 2 with substrates

Once **2** was fully formed, an aliquot of a solution in acetonitrile (150 μ L) containing the corresponding equivalents of the desired substrate was added to the cuvette. The decay of the band at λ = 420 nm was monitored, and the reaction was quenched after complete decay by adding an excess of NaHSO₃ (0.1 mL of a commercially available 40% aqueous solution). Biphenyl was added as an internal standard, and the nickel complex was removed by passing the solution through a short plug of silica. The products were eluted with ethyl acetate and analyzed by using a gas chromatography flame-ionization detector (GC-FID). The organic products were identified by comparison with authentic compounds.

Catalytic experiments at room temperature with HmCPBA

In a typical reaction, a solution of HmCPBA (0.58 M, 0.5 mL, 290 µmol) in acetonitrile was delivered by syringe pump over 30 min at 25 °C to a vigorously stirred a solution of the nickel catalyst (2.0 µmol) and the substrate (1900 µmol) in acetonitrile (2.5 mL). The final concentrations of the reagents were 0.7 mm nickel catalyst, 97 mm HmCPBA, and 0.62 m substrate. After syringe-pump addition, the resulting solution was stirred for another 30 min. For the oxidation of cyclohexane, biphenyl was added as an internal standard and the nickel complex was removed by passing the solution through a short path of silica gel. The products were eluted with ethyl acetate and analyzed by using a GC-FID. The organic products were identified by comparison with authentic compounds.

Computational details

All DFT calculations were carried out by using the Gaussian09 set of programs.^[52] The X-ray diffraction structure of [Ni^{II}(L)] (1) was chosen as a starting point for geometry optimizations by using the B3LYP exchange-correlation functional^[53,54] and the TZVP basis set.^[55] Nickel species were considered in all possible spin states without symmetry constraints. The CH₃CN solvation and effects were included in the geometry optimizations through the solvent model D (SMD) polarizable continuum model.^[56] Dispersion effects were introduced through single-point calculations with the Grimme D_3 correction with Becke–Johnson damping.^[57] The connection between the transition states and minimum values was verified by using intrinsic reaction coordinate (IRC) calculations.

The Hirshfeld spin densities and charges, Mayer bond-order index,^[58,59] and spin natural orbitals (SNO) were computed to rationalize the electronic structure of intermediate **2**. A Bader AIM analysis^[60–62] was also conducted on **2** to elucidate the nature of the Ni–O bond.

Analytical frequency calculations were performed to evaluate the thermal corrections and entropic effects at 243.15 K and to characterize the located stationary points in the condensed phase. Raman spectra intensities of intermediate **2** were simulated at 77 K and with laser excitation at $\lambda = 457$ nm by using the GaussSum 3.0 software.^[63]

Final Gibbs energies (G) were evaluated by using the following equation:

$$G = E_{\text{TZVP}}(\text{SMD} + D_3) + G_{\text{corr}}$$
(1)

where $E_{\text{TZVP}}(\text{SMD} + D_3)$ was obtained by using single-point calculations with the TZVP basis set on equilibrium geometries, including solvation and dispersion effects, and G_{corr} is the thermal correction obtained from a thermostatistical analysis at the B3LYP/SMD level. The pK_a values were computed according to:

$$pk_{a} = \frac{\Delta G^{\circ}}{RT \ln(10)}$$
(2)

where *R* is the universal gas constant and *T* is the temperature.^[64] The standard dissociation free-energy change (ΔG°) between an acid (AH) and its conjugate base (A⁻) in the solvent phase may be calculated by using the following equations:

$$\Delta G^{\circ} = G(A_{sol}^{-}) + G(H_{sol}^{+}) - G(AH_{sol}^{-}) + \Delta G^{*}$$
(3)

$$G(H_{aq}^{+}) = G(H_{gas}^{+}) + \Delta G_{solv}^{H+}$$
(4)

where $G(AH_{sol})$ and $G(A_{sol}^{-})$ are the standard free energies of the acid and its conjugate base, respectively. The $G(H_{sol}^+)$ is the free energy of the proton in acetonitrile, obtained from the solvation free energy of a proton in acetonitrile ($\Delta G_{sol}^{H+} = -260.2$ kcal mol⁻¹)^[56] and its gas-phase free energy ($G(H_{gas}^+) = -6.3$ kcal mol⁻¹).^[57] ΔG^* is the standard-state thermodynamic correction associated with the conversion from a standard state of 1 M in the aqueous phase and 1 atm in the gas phase into 1 M in both phases, with a value of 1.54 kcal mol⁻¹ at 243.15 K.

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