Transient Formation and Reactivity of a High-Valent Nickel(IV) Oxido Complex

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Supporting Information

ABSTRACT: A reactive high-valent dinuclear nickel(IV) oxido bridged complex is reported that can be formed at room temperature by reaction of [(L)2Ni(II)(μ-X)3]X (X = Cl or Br) with NaOCl in methanol or acetonitrile (where L = 1,4,7-trimethyl-1,4,7-triazacyclononane). The unusual Ni(IV) oxido species is stabilized within a dinuclear tris-μ-oxido-bridged structure as [(L)2Ni(IV)(μ-O)3]2+. Its structure and its reactivity with organic substrates are demonstrated through a combination of UV−vis absorption, resonance Raman, 1H NMR, EPR, and X-ray absorption (near-edge) spectroscopy, ESI mass spectrometry, and DFT methods. The identification of a Ni(IV)-O species opens opportunities to control the reactivity of NaOCl for selective oxidations.

INTRODUCTION

Metalloenzymes are central to the functioning of biological systems, especially in oxidative transformations and protection against reactive oxygen species.1 Fe-, Cu-, and Mn-dependent metalloenzymes have been studied extensively and have stimulated the design and synthesis of structural and functional model complexes, especially in the search for synthetic analogues of reactive bioinorganic intermediates.2 Recently, attention has turned to synthetic nickel-based complexes due to both enzymes such as NOD (nickel oxide dismutase)3 and their potential in the activation of small molecules, including H2O2,4 mCPBA,5 and NaOCl.6 In the latter case, such complexes open the possibility to achieve selective alkane chlorination and alkane and alkene oxygenation.

Recently, several high-valent (Ni(III))4,7 and Ni(IV)6c,8 intermediates were identified spectroscopically. In contrast to organometallic Ni(IV) complexes,8 the formation of Ni(III) and, more so, Ni(IV) oxido complexes, although inferred, is controversial due to the implications of the oxo-wall premise.9 Nevertheless, several Ni(II) and Ni(III) oxido or peroxido complexes, formed with O2 and H2O2, have been characterized already at low temperature.24−27

Here we show that a novel room-temperature-stable dinuclear Ni(IV) oxido complex (3), [(L)2Ni(IV)(μ-O)3]2+ (where L = 1,4,7-trimethyl-1,4,7-triazacyclononane), can be generated by reaction of the Ni(II) complexes (1, 2) with NaOCl (Scheme 1). The high oxidation state of 3 is stabilized by the tris-μ-oxido-bridged dinuclear structure. Furthermore, the reactivity of 3 toward direct C−H oxidation of organic substrates is demonstrated.

Complex 3 is obtained within seconds of addition of near stoichiometric amounts of NaOCl to [(L)2Ni(II)(μ-X)3]X·(H2O)n (where X = Cl (1) or Br (2), n = 5 or 7)10 in methanol or acetonitrile at room temperature. The structure of 3 was elucidated through a combination of UV−vis absorption and resonance Raman spectroscopy and ESI mass spectrometry.

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Scheme 1. Formation of 3 from 1 and NaOCl

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RESULTS AND DISCUSSION

Complexes 1 and 2 were prepared by methods analogous to those reported earlier (see SI for details).\(^{10}\) The Raman spectra of 1 in the solid state (Figure S1) and in solution (i.e., methanol, acetonitrile, Figure S2) indicate that the complexes retain their structure; that is, the ligand (L) remains bound to Ni(II) upon dissolution. However, ESI mass spectrometry indicates that 1 can form mononuclear complexes with three \((176.3 \text{ m/z})\) or two acetonitrile ligands \((155.9 \text{ m/z})\) by substitution of the chlorido ligands (Figure S3). Indeed, mixtures of 1 and 2 show rapid exchange of Cl\(^-\) and Br\(^-\) ligands (Figure S4). The \(^1\)H NMR spectrum of 1 in acetonitrile shows paramagnetically shifted and broadened signals at ca. 60, 90, and 120 ppm (Figure S5), and its UV-vis absorption spectrum in methanol and acetonitrile (Figure S6) shows bands at 384, 635, and 1014 nm. The DFT data (vide infra) indicate that the ligand (L) remains bound to both Ni ions. Finally, the experimental NMR and UV-vis absorption spectra of the AFM state are similar to those of related Ni(II) complexes (Figure S7).\(^{16}\)

Addition of NaOCl to 1 or 2 in methanol or in acetonitrile leads to a rapid increase in absorbance at 363 and 612 nm due to formation of 3 (Figure 1). In methanol, the visible absorption band decreases with a \(t_{1/2}\) of ca. 50 s at 20 °C (Figure S8), and the absorption spectrum after 20 min is similar to the initial spectrum, with only a minor shift from 388 to 378 nm (Figure 2). Notably, the rate of decay of 3 in methanol was substantially lower than the rate of the direct reaction of NaOCl with methanol in the absence of 1 (Figure S8), indicating that the formation of 3 competes with oxidation of methanol by NaOCl and that 3 is less reactive in the oxidation of methanol than NaOCl.

In both the presence and absence of 1, near-quantitative (cf. NaOCl) oxidation of methanol to formaldehyde occurs (1.5:1, Figure S9), indicating that although at least 2 equiv of NaOCl are consumed in forming 3 from 1, these oxidation equivalents are still available for subsequent oxidation of methanol. Further additions of NaOCl in the presence of 1 resulted in the reappearance of the 612 nm absorption (Figure S10), confirming the integrity of the catalyst under reaction conditions. Similar changes were observed with NaOBr (Figure S11), which indicates that the same intermediate is formed with both oxidants (vide infra). Addition of \(\text{H}_2\text{O}_2\) or purging with \(\text{O}_2\) (Figures S12 and S13) did not result in the appearance of 3.

Intermediate 3 forms upon addition of NaOCl to 1 also in acetonitrile (absorbance band at 612 nm), but persists for a substantially longer time period than in methanol, with a \(t_{1/2}\) of ca. 10 min at 20 °C and over 6 h at −15 °C (Figures S14 and S15), enabling characterization by resonance Raman spectroscopy, XANES, XES, and ESI mass spectrometry and reactivity with other substrates to be studied (vide infra). The maximum transient absorbance at 612 nm was obtained with 3–4 equiv of NaOCl (Figure S16) and is accompanied by an increase in oxidation state as confirmed by XANES and XES (Figure 3 and Figure S17).

The Ni K edge X-ray absorption near edge structure (XANES) as well as the X-ray emission (XES) spectra were recorded for 1 (30 mM) in acetonitrile before and after addition of NaOCl. Spectra were acquired over 5 min after addition when the concentration of 3 (generated from 1) was substantial, although Ni(II) species are present also. The Ni K edge XANES spectra of both 1 and the mixture of species formed after addition of NaOCl show a nondescript edge, i.e.,

Figure 1. Spin-density plot (S12g/T2ZP) for (antiferromagnetically coupled) 1 with spin-up spin-density shown in blue (around Ni\(_a\), left) and spin-down spin-density in red (around Ni\(_b\), right).

Figure 2. UV-vis absorption spectrum of 1 (3.5 mM) in methanol before (black) and after (red 6 s, blue 48 s, green 463 s) addition of 11 equiv of NaOCl(aq) at 293 K. Inset: Expansion of the NIR region. The data indicate that for 3 \(\epsilon_{612 \text{ nm}} > 715 \text{ M}^{-1}\text{cm}^{-1}\).
no significant pre-edge features, which indicates a near-octahedral, six-coordinated, geometry around the Ni center for all species present (consistent with the structures 1, 3, and 3a).

The edge position is a function of the ligands present and geometry as well as oxidation state, and hence a direct conclusion based on XANES alone cannot be drawn. For example, for purely oxidic Ni systems, an energy shift of about 1.8 eV per oxidation state is reported, with a much lower shift for sulfur-based systems. A conclusive statement as to the oxidation state requires the availability of a series of reference compounds with similar ligands and geometries (data for closely related structures are not yet available in the literature).

The energy shift of about 2 eV observed in the experimental spectra is consistent with an increase in oxidation state, but it will also reflect the change from chlorido to oxido ligands. Furthermore, the mixture of species available (including Ni(II)) reduces the magnitude of the observed shift and complicates interpretation.

The simulated XANES for complexes 1, 3, and 3a are displayed in Figure 3. All XANES spectra have only a pre-edge feature at low energy and an otherwise featureless edge, consistent with six-coordinated geometries. A clear difference in the spectra of the Ni(II) 1 of 5 eV with the Ni(III) 3a and Ni(IV) 3a species is calculated, i.e., upon oxidation and change of ligands from Cl to O. It is, however, also clear that XANES data will not allow for distinguishing the Ni(III) and Ni(IV) species, i.e., complexes 3 and 3a. Furthermore, the Ni K edge XANES of 1 undergoes only a few electronvolts shift in the presence of NaOCl and not the full 5 eV shift, as it is a mixture of Ni(II) and nickel in higher oxidation states, resulting in only an average shift, i.e., between 2 and 3 eV, reflecting an overall average increase in oxidation state. The XES data at the K_{Ni,3} edge also display an overall shift of a few electronvolts; however, the emission lines are sensitive to both oxidation state and ligand type also.

The three broad signals in the ¹H NMR spectrum of 1 in acetonitrile decrease upon addition of NaOCl, suggesting the formation of a diamagnetic species, and then recover concomitant with the increase and decrease in absorbance at 612 nm (Figure S18). Samples flash frozen to 77 K at any time, however, did not indicate the presence of a mononuclear Ni(III) species by X-band EPR spectroscopy.

Generation of 3 by electrochemical oxidation of 1 was also explored. The cyclic voltammetry of 1 shows irreversible redox waves at 1.52, 1.35, and 1.05 V and an irreversible redox wave at 0.58 V on the return cycle. At higher scan rates (up to 10 V s⁻¹) the initial oxidation wave at 1.05 V shows some evidence of chemical reversibility; however, the shifts in I_p,a (which are corrected for I_R,a) indicate that the oxidation is electrochemically irreversible also (Figure S19). Addition of NaOCl to 1 results (after 2 min) in a shift in the oxidation wave to 1.16 V, indicative of ligand exchange, e.g., CH₃CN replacing Cl⁻. It should be noted, however, that the redox chemistry of NaOCl, concentration polarization, and the likely complex series of dis- and comproportionation reactions between 1 and 3 preclude the observation of a redox wave assignable to 3. One hour after addition of NaOCl, a further shift is observed, indicating ligand exchange to form a Ni(II) complex similar to 4 (Figure S20). Notably the voltammetry and spectroelectrochemistry were not affected substantially by the addition of water and NaCl (i.e., at concentrations present under reaction conditions).

The spectroelectrochemistry of 1 in acetonitrile shows that oxidation at 1.2 V leads to essentially no change in the UV absorption (Figure S21a). On the second cycle the redox wave is shifted to >1.58 V; again relatively little change in absorbance is observed, and after reduction below 0.86 V only minor shifts in absorbance at ca. 300 nm are observed, consistent with ligand exchange (Figure S21b). Bulk electrolysis of 1 shows an increase in absorption at 344 nm; however, the EPR spectrum (X-band 77 K) of this sample was silent, and hence oxidation leads to ligand exchange to a Ni(II) complex with a more positive redox potential rather than formation of a Ni(III) or Ni(IV) complex.

Attempts to isolate 3 by flash precipitation with KPF₆ yielded the mononuclear Ni(III) compound [(L)Ni(III)(CH₃CN)]³⁺ (4) instead, reported earlier by Tak et al. as the B(Ph)₄ salt, in which the chlorido ligands are replaced by acetonitrile ligands to form a mononuclear complex (see the SI and Scheme 2). Notably, addition of NaOCl to 4 in acetonitrile results in the same visible absorption spectrum as obtained with 1 (Figure S23), indicating that the formation of 3 is not dependent on the initial form of the LNi(II) complex (with Cl⁻/Br⁻/CH₃CN) and is consistent with the rapid equilibration of these species in solution. Furthermore, addition of NaOCl (4–10 equiv) to a 1:1 mixture of NiCl₂ and the ligand (L) in acetonitrile results in the appearance of the bands at λ_{max} 363 and 612 nm (Figure S24), consistent with a maximum 50% conversion to 3. In the absence of ligand (i.e., only NiCl₂·6H₂O) the band at 612 nm was not observed (Figure S25).

In earlier reports, the presence of acetic acid was necessary for the formation of high-valent nickel complexes with NaOCl. Addition of acetic acid (4.5 equiv) to 3 in acetonitrile (generated by addition of 4.5 equiv of NaOCl to 1 (0.9 mM)) did not affect the absorbance at 612 nm significantly (Figure S26a). In contrast, addition of acetic acid (4.5 equiv)
prior to addition of NaOCl to 1 (0.9 mM) precluded the appearance of the 612 nm band and hence formation of 3 (Figure S26b).19

The ESI mass spectra of 1 in acetonitrile show signals (m/z) assignable to [Ni(II)(L)(CH3CN)]2+ (155.9 m/z), [Ni(II)-(L)(CH3CN)]2+ (176.3 m/z), [Ni(II)(L)(Cl)]2+ (264.1 m/z), and [Ni(II)(L)(Cl)]3+ (565.2 m/z) (Figure S27). The spectrum obtained from a solution containing (L)Ni(III)2(L)2(Cl)3+ (565.2 m/z; the latter distance is more similar to the bis-μ-oxo variant [L2MnIV-μ-O)2]2+ (2.62 Å).22 Furthermore, the NiIV−N distance of 2.02 Å in 3 is substantially shorter than that in the MnIV analogue (1.82 Å). Overall, the DFT structure for 3 and the X-ray structure for [(L)2Mn(IV)2(μ-O)3]2+ are similar, which is apparent when superimposed (Figure S34).

Scheme 3. Structures (3, 3a, 3b) Consistent with ESI Mass Spectral Data and Calculated Driving Forces for Their Formation from 1

All possible spin states were explored by DFT methods for 3, 3a, and 3b. As expected for the d7 Ni(III) ions in 3a, the lowest energy15 state corresponds to a doublet on each of the metals, which can be FM (S = 1) or AFM (open-shell singlet) coupled. The latter open-shell singlet state is lower in (Gibbs free) energy than the triplet by 2.1 kcal·mol−1, and 5.1 kcal·mol−1 lower than the diamagnetic closed-shell singlet state. All other spin states for 3a are >10 kcal·mol−1 higher in (Gibbs free) energy. The lowest energy for the d6 Ni(IV) ions in 3b corresponds to an AFM state, where each of the Ni(IV) ions is found locally in a triplet (S = 1) state. The AFM state is lower than the FM state in 3b by 1.2 kcal·mol−1, with the other spin states higher in energy by >10 kcal·mol−1.

The geometrical parameters for compound 3, which although isostuctural to [(L)2Mn(IV)2(μ-O)3]2+,22 are found to be somewhat different. The most prominent feature in [(L)2Mn(IV)2(μ-O)3]2+ is a short Mn(IV)−Mn(IV) distance of 2.30 Å, which is absent in 3, where the Ni(IV)−Ni(IV) is instead 2.46 Å; the latter distance is more similar to the bis-μ-oxo variant [L2MnIV-μ-O)2]2+ (2.62 Å).22 The NiIV−N distance of 2.02 Å in 3 is substantially shorter than in the MnIV analogue (1.82 Å). Overall, the DFT structure for 3 and the X-ray structure for [(L)2Mn(IV)2(μ-O)3]2+ are similar, which is apparent when superimposed (Figure S34).

All possible spin states were explored by DFT methods for 3, 3a, and 3b. As expected for the d7 Ni(IV) ions in 3, the lowest energy15 state corresponds to locally closed-shell singlet (S = 0) Ni(IV) ions. For consistency, we explored the possibility of other spin states and found several higher lying spin states, where, for example, the Ni(IV) ions had locally a triplet (S = 1) state that coupled to form overall a quintet (S = 2) state. However, these other spin states are >27 kcal·mol−1 higher in energy (see Table S2) and will not be discussed any further.
vibrations of the normal modes are available in the SL. The modes observed for 3 are similar in energy to those of the isostructural complex $$\left\{\left[(\text{L})\text{Mn(IV)}_2(\mu-O)_3]\right\}_2^+$$, which shows a \(\text{Mn} = (\text{O})_3 = \text{Mn}\) stretch at 701 cm\(^{-1}\) (\(\Delta^{18}\text{O} = 33\) cm\(^{-1}\)). Furthermore, the spectrum is similar to that reported by Riordan and co-workers for $$\left\{\left[\left((\text{PhTe})_{\text{Bu}}\text{Ni(III)}\right)_2(\mu-O)_3]\right\}_2^+$$, with a band at 585 cm\(^{-1}\) (\(\Delta^{18}\text{O} = 30\) cm\(^{-1}\)), and by Fukuzumi and co-workers for $$\left\{\left[(\text{L})\text{Ni(III)}_2(\mu-O)_3]\right\}_2^+$$, where \(\text{L} = \text{N,N-bis[2-(2-pyridyl)ethyl]2-phenylethylamine, with a band at 612 cm\(^{-1}\) (\(\Delta^{18}\text{O} = 32\) cm\(^{-1}\)). The higher Raman shift for 3 is consistent with an increase in the oxidation state from III to IV.

The \(\text{Ni} - \text{O} - \text{Ni}\) stretching modes in 3a are expected to be facile given the rapid exchange of Cl to form 3b (Figure S36), which shows an \(\text{O} - \text{O} - \text{Ni}\) stretching band (\(\Delta^{18}\text{O}\)) in parentheses) at 892 (841) cm\(^{-1}\), a \(\text{Ni} - \text{N}\) stretching mode at 768 (768) cm\(^{-1}\), and \(\text{Ni} - \text{O}\) bending/stretching modes at 633 (633), 601 (594), 585 (571), and 536 (516) cm\(^{-1}\). Of these modes, the 663 and 768 cm\(^{-1}\) modes are strongly IR active. Therefore, given that in the present system only the band at 631 cm\(^{-1}\) is affected by the use of \(^{18}\text{OCl}^-\) and that the DFT-calculated IR spectrum of 3a (Figure S36) indicates bands at ca. 660 and 770 cm\(^{-1}\) only and not a band at ca. 801 cm\(^{-1}\), the peroxy species can be discarded. The same is true for 3b, which shows terminal-oxo \(\text{Ni} - \text{O}\) stretches at 742 cm\(^{-1}\) (shifting to 718 cm\(^{-1}\) upon \(^{18}\text{O}\) labeling, i.e., \(\Delta^{18}\text{O} = 24\) cm\(^{-1}\)) and two bands at 689 cm\(^{-1}\) (\(\Delta^{18}\text{O} = 26\) cm\(^{-1}\)) and 668 cm\(^{-1}\) (\(\Delta^{18}\text{O} = 26\) cm\(^{-1}\)). The \(\text{Ni} - \text{O} - \text{Ni}\) stretch is found at 653 cm\(^{-1}\) (\(\Delta^{18}\text{O} = 17\) cm\(^{-1}\)). No bands are observed around 521 cm\(^{-1}\), and all bands show significant isotope effects. Therefore, although the ESI mass spectral data could correspond also to a peroxy-bridged (3a) or the mono-\(\mu\)-oxo species (3b), the most appropriate structural assignment for the high-valent nickel species is 3 based on the vibrational spectra.

DFT calculations provide further support for this assignment in the thermochemistry of the reaction of 1 and 2 with NaOCl to form 3. Mass spectral data indicate that the reactive intermediate 3 has the composition $$\left\{\left[(\text{L})\text{Ni}_{\text{II}}\text{O}\right]\right\}_2^+$$, and the absence of EPR (X-band) signals at 77 K at any time suggests that mononuclear Ni(III) complexes are not present to a significant extent. Hence, geometry optimizations were performed with all spin multiplicities for 1, 2, 3, and 3a, as well as possible mononuclear Ni(II) complexes, e.g., $$\left\{\left[(\text{L})\text{Ni} - \text{II}\right](\text{CH}_3\text{CN})_2\right\}_2^+$$ (4) and $$\left\{\left[(\text{L})\text{Ni} - \text{II}\right](\text{CH}_3\text{CN})_2\right\}_2^+$$ (5) (Table S2). Antiferromagnetically coupled dinuclear species were found as lowest energy for 1, 2, 3a, and 3b, while a closed-shell spin state was found for 3 (vide supra); a high-spin Ni(II) (\(S = 1\)) ground state was found for 4 and 5. The reactions of 1 with NaOCl to form 3a, 3b, or 3 (Scheme 3) were calculated to be exergonic by \(-92.5, -88.1, \) and \(-50.3\) kcal-mol\(^{-1}\), respectively; hence, 3 is 4.46 kcal-mol\(^{-1}\) more stable than 3a and 42.2 kcal-mol\(^{-1}\) than 3b, in terms of Gibbs energy (in electronic energy: 7.50 and 46.11 kcal-mol\(^{-1}\), respectively for 3a and 3b), Table S3.

Further spectroscopic evidence for the formation of 3, and not 3a or 3b, is obtained by mixed labeling experiments. In these experiments we applied ratios of pure \(^{16}\text{O}\) (3:0), pure \(^{18}\text{O}\) (0:3), and 1:2:2:1 mixtures of these, such that we would have four different distributions with on average the incorporation of 0, 1, 2, and 3 labeled oxygens into the complex. The observed isotope shifts observed in our Raman spectra with these mixed labeling experiments match perfectly with the corresponding DFT isotope shifts; that is, the 631 cm\(^{-1}\) peak (638 cm\(^{-1}\) DFT) shifts to 623 cm\(^{-1}\) (630 cm\(^{-1}\) DFT), to 613 cm\(^{-1}\) (622 cm\(^{-1}\) DFT), and finally to 599 (609 cm\(^{-1}\) DFT).

Overall, the spectroscopic and computational data are consistent with the assignment of the intermediate as 3 $$\left\{\left[(\text{L})\text{Ni(IV)}_2(\mu-18\text{O})_6]\right\}_2^+$$, which is obtained by mixed labeling experiments. In this mechanism which 3 forms from Ni(II) complexes undoubtedly involves multiple elementary steps. However, the coordination of \(\text{OCl}^-\) to Ni(II) is expected to be facile given the rapid exchange of Cl\(^-\), Br\(^-\), and CH\(_3\)CN ligands. Heterolytic cleavage of Ni(II)–O–Cl to form a transient intermediate Ni(IV) species and Cl\(^-\) is presumably followed by formation of a \(\mu-\text{O}\)-bridged Ni(IV) dimer, which does not show antiferromagnetic coupling, in contrast with the equivalent manganese complex, but instead corresponds to diamagnetic closed-shell Ni(IV) ions.

Finally, although 3 undergoes rapid self-decay in methanol to yield formaldehyde, in acetonitrile it is relatively stable, allowing for its reactivity with organic substrates to be assessed. The addition of ca. 4 equiv of substrate (e.g., xanthene, 9,10-dihydroanthracene, and fluorene) resulted in a complete loss of absorbance at 612 nm within ca. 6 min (70, 150, and 350 s, respectively, Figure S37). At \(-15^\circ\text{C}, 3\) is stable for over 6 h (Figure S38); however, addition of 4 equiv of xanthene resulted in a rapid loss in absorbance at 612 nm (within ca. 275 s, Figure S39). Addition of 50 equiv of fluorene to 3 resulted in the disappearance of the signal at \(m/z\) 253.3 and a recovery of the signals of 1 and 4 (Figure S40). Hence, although substrates react directly with NaOCl, 3 engages in C–H oxidation also (Figure S39).
CONCLUSIONS

Complex 3 represents the first example of a Ni(IV)-oxido-bridged dimer. Its generation from NaOCl and subsequent reaction with organic substrates opens up the possibility to use NaOCl as a terminal oxidant. The intermediary of a transition metal catalyst opens the possibility of engaging in selective oxidations, thereby taming the reactivity of this potent oxidant.

ASSOCIATED CONTENT

Supporting Information
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Notes
The authors declare no competing financial interest.

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