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Published in:
Journal of the American Chemical Society

DOI:
10.1021/jacs.7b04158

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Download date: 06-09-2019
Transient Formation and Reactivity of a High-Valent Nickel(IV) Oxido Complex

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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)2(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)2(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)2(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)2(μ-X)3]X·(H2O)n (where X = Cl (1) or Br (2), n = 5 or 7) 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.
RESULTS AND DISCUSSION

Complexes 1 and 2 were prepared by methods analogous to those reported earlier (see SI for details). The 1H NMR spectrum of ZORA13 relativistic effects, Table S2), in excellent agreement with experiment. In this state, the locally spin-polarized triplet (S = 1) Ni(II) ions couple antiferromagnetically (AFM) to reach overall an open-shell singlet state. As a result, spin-up spin-density is observed around one Ni and spin-down around the other (Figure 1). This AFM state is only 0.3 kcal mol⁻¹ lower than the ferromagnetically (FM) coupled (S = 2) state (see SI section 7 for the corresponding spin-density plot). Both states would be consistent with the paramagnetic 1H NMR shifts (vide supra), but the AFM state is found to be slightly lower by both theory and experiment. The diamagnetic closed-shell singlet state, in which the Ni(II) ions are now locally in a closed-shell (S = 0) state, is higher in energy than the AFM state by 37.7 kcal mol⁻¹ (1) and 35.0 kcal mol⁻¹ (2). Finally, also an overall intermediate spin state (S = 1) was obtained, 25.5 kcal mol⁻¹ (1) and 23.4 kcal mol⁻¹ (2) higher in energy than the AFM state, where spin-density corresponding to the single occupation of an antibonding dₓ²−ᵧ² orbital was observed on 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).

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 t₁/₂ 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 H₂O₂ or purging with O₂ (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 t₁/₂ 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.,
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 energy shift 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_{3d,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., $\text{CH}_3\text{CN}$ 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 KPF_6 yielded the mononuclear Ni(III) compound ([(L)Ni(III)(CH_3CN)]_2Cl_2 (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\(^-\)/CH_3CN) 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 NiCl_2 and the ligand (L) in acetonitrile results in the appearance of the bands at $\lambda_{\text{max}}$ 363 and 612 nm (Figure S24), consistent with a maximum 50% conversion to 3. In the absence of ligand (i.e., only NiCl_2·6H_2O) 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)(CH2CN)]2+ (155.9 m/z), [Ni(II)-(L)(CH2CN)2]2+ (1763. m/z), [Ni(II)(L) (Cl)]+ (2641. m/z), and [Ni(II)-(L)(Cl)]+ (5652. m/z) (Figure S27). The spectrum obtained from a solution containing 3 shows an additional strong signal at 253.3 m/z with an isotope distribution consistent with two Ni centers (Figure S28), regardless of whether it was generated with NaOBr or NaOCl and with 2 in place of 1 (Figures S29–S33). Notably, however, the signal increased by 3 m/z units with Na18OCl (Figure S31). The m/z signal at 253.3 is therefore consistent with structures such as the peroxy-bridged 3a,20 [(L)2Ni(III)-(μ-O)(μ-O)]2+, the mono-μ-oxo-bis-terminal-oxo 3b, [(L)-(O)≡Ni-(IV)-(O)-Ni(IV)≡(O)-L]2+, and the tri-μ-oxido-bridged 3, [(L)2Ni(IV)-(μ-O)]2+ (Scheme 3), with the latter structure 3 favored on the basis of Raman spectroscopy (vide infra) and DFT.21

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(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.

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)-(μ-O)]2+,22 are found to be somewhat different. The most prominent feature in [(L)2Mn-(IV)-(μ-O)]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 [L2MnIV2(O)2(μ-O)2] (2.62 Å).22 Furthermore, the NiIV–N distance of 2.02 Å in 3 is substantially shorter than in [(L)2Mn(IV)-(μ-O)]2+ (2.11 Å). The NiIV–(μ-O) distance in 3 of 1.85 Å is however similar to that in the MnIV analogue (1.82 Å). Overall, the DFT structure for 3 and the X-ray structure for [(L)2Mn(IV)-(μ-O)]2+ are similar, which is apparent when superimposed (Figure S34).

The Raman spectrum of 3, with excitation resonant with the visible absorption band, shows enhanced Raman scattering at 801, 631, and 521 cm−1 (Figure 3), with only the band at 631 cm−1 (Δ[18O] = 32 cm−1) affected by the use of Na18OCl. The bands are unaffected by use of OBr− in place of OCl−. The DFT-calculated Raman spectrum for [(L)2Ni-(IV)-(μ-O)]2+ (3) shows a penta-atomic symmetric stretching Ni=O(3)=Ni mode at 638 cm−1, which shifted to 609 cm−1 upon isotope labeling (i.e., Δ[18O] = 29 cm−1, Figure S35). Mixed labeling (i.e., varying ratios of 16O and 18O) experiments show the series of four bands expected for the four isotopologues and correspond well with the DFT-calculated shifts (Figure 5).

The band at 801 cm−1 corresponds to a symmetric Ni=O=O stretching (calcd by DFT at 782 cm−1), at the same position upon 18O labeling, while the band at 521 cm−1 involves mainly a combination of Ni=O and Ni=O(3) stretching (calcd by DFT at 517 cm−1 and at 516 cm−1 upon 18O labeling). All of the
The Ni–O–O–Ni stretching modes in 3a are expected to be facile given the rapid exchange of Cl between the Ni–O–O−Ni bridging ligand and the xanthene moiety. Therefore, although the ESI mass spectral data could correspond also to a peroxy-bridged (3a) or the mono-μ-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 [(L)NiO3]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., [(L)Ni(II)(CH3CN)2]+ (4) and [(L)Ni(II)(CH3CN)2]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 3, 3a, or 3b (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 18O (3:0), pure 16O (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 [(L)NiIV3(μ-18O)]2+. The mechanism by which 3 forms from Ni(II) complexes undoubtedly involves multiple elementary steps. However, the coordination of OCl− to Ni(II) is expected to be facile given the rapid exchange of Cl−, Br−, and CH3CN 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 μ-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 fluorescein) resulted in a complete loss of absorbance at 612 nm within ca. 6 min (70, 150, and 350 s, respectively, Figure S37). At −15 °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 fluorescein 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04158.

Notes

The authors declare no competing financial interest.

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(15) At Si2g/TZ2P//BP86-D3/TZ2P.
(19) In the absence of Ni(II) or NaOCl is stable in CH3CN.
(21) The formation of species such as O=N=N=O−O=N=N=O is highly unlikely, as it is calculated to lie 45 to 58 kcal mol−1 (depending on functional used, e.g., BP86-D3 and Si2g) higher in energy than even the peroxo species 3a. Furthermore, DFT calculations indicate a high tendency for a species to converge to the structure of the 3a species. In addition ligand hydroxylolation can be discounted on the basis of the recovery of the Ni(II) complexes, e.g., 1 and 4, once 3 has reacted with solvent or substrate.


