

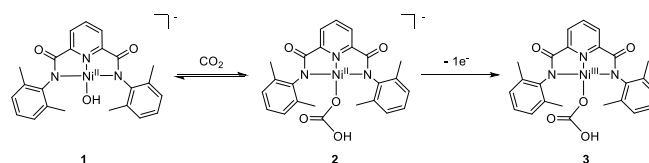
Characterization and Reactivity of a Terminal Nickel(III)-Oxygen Adduct

Paolo Pirovano,^[a] Erik R. Farquhar,^[b] Marcel Swart,^[c] Anthony J. Fitzpatrick,^[d] Grace G. Morgan,^[d] Aidan R. McDonald*^[a]

Abstract: High-valent terminal metal-oxygen adducts are hypothesized to be the potent oxidising reactants in late transition metal oxidation catalysis. In particular, examples of high-valent terminal nickel-oxygen adducts are sparse, meaning there is a dearth in the understanding of such oxidants. In this study, a monoanionic Ni^{II}-bicarbonate complex was found to react in a 1:1 ratio with the one-electron oxidant tris(4-bromophenyl)ammoniumyl hexachloroantimonate, yielding a thermally unstable intermediate in high yield (~95%). Electronic absorption, electronic paramagnetic resonance and X-ray absorption spectroscopies and density functional theory calculations confirm its description as a low-spin (*S* = 1/2), square planar Ni^{III}-oxygen adduct. This rare example of a high-valent terminal nickel-oxygen complex performs oxidations of organic substrates, including 2,6-ditertbutylphenol and triphenylphosphine, which are indicative of hydrogen atom abstraction and oxygen atom transfer reactivity, respectively.

Nature employs Fe- and Cu-containing oxygenases to perform hydrocarbon oxidation and Mn-containing photosystem II to perform water oxidation.^[1] Similarly, many synthetic Mn, Fe, Co, Ni, and Cu-containing catalysts are capable of both hydrocarbon and water oxidation.^[2] In most of these natural and non-natural first-row transition metal catalysed conversions, terminal high-valent metal-oxygen adducts, such as metal-oxo (M=O), metal-oxyl (M-O·) or metal-hydroxo (M-OH) intermediates, have been implicated as the reactive oxidants. These oxidants are potent hydrogen atom abstraction (HAA) or oxygen atom transfer (OAT) reagents, capable of activating some of the most inert of substrates. Many examples of enzymatic and synthetic terminal oxomanganese and oxoiron species have arisen in the past 10 years,^[3] however there remains a dearth in the number of terminal late transition metal-oxygen adducts (metal = Co, Ni, Cu). Ray/Nam and Tolman have recently made great strides in preparing the first examples of scandium(III)oxocobalt(IV) and hydroxocopper(III) species, respectively.^[4] However, well-characterized high-valent terminal nickel-oxygen adducts remain elusive.

Synthetic nickel containing complexes have been exploited as catalysts for the oxidation of hydrocarbons^[5] and water.^[6] Similarly, nickel-containing films and nanoparticles have been employed as oxidation catalysts.^[2b,7] Terminal high-valent nickel-oxygen adducts (Ni^{III/IV}-OX) have been postulated as the active oxidant in these systems, however, very few such species have been isolated and well-characterized to date.^[5,8] Interestingly, computational studies have forecast that a Ni^{III}=O species would be capable of the activation of the strongest of C-H bonds (CH₄, bond dissociation energy (BDE) = 104 kcal/mol).^[9] Some groups have attempted to prepare high-valent nickel-oxygen adducts, for example Ray reported that the oxidation of [Ni^{II}(TMG₃tren)(OTf)](OTf) (TMG₃tren = tris[2-(N-tetramethylguanidyl)ethyl]amine, OTf = trifluoromethanesulfonate) with 3-chloroperoxybenzoic acid produced two species claimed to be Ni^{III}-O(X) complexes.^[10] However, the low yield (15%) of Ni^{III} and identification of at least two Ni^{III} species in the reaction mixture hampered their characterization. Latos-Grażyński reacted a Ni^{III}-Br complex with hydroxide to yield a new species that was claimed to be a Ni^{III}-OH complex.^[11] However, this species was only characterized using EPR spectroscopy, and no reactivity studies were performed. Liaw prepared Ni^{III}-OR (R = Me, Ph) species, but did not report any HAA or OAT reactivity.^[12] Interestingly, several μ-oxo-dinickel(III)^[13] and nickel-containing heterobimetallic μ-oxo-complexes^[14] have been isolated and found to be effective HAA reagents. In contrast, there remains a lack of suitable high-valent terminal nickel-oxygen adducts that could help us understand further the reactivity properties of late transition metal oxidants. With this in mind, we set out to prepare, characterize and investigate the reactivity of such complexes. We identified Holm's [Ni^{II}(OH)(pyN₂^{Me2})]⁻ (**1**, Scheme 1) and [Ni^{II}(OCO₂H)(pyN₂^{Me2})]⁻ (**2**, Scheme 1) complexes (pyN₂^{Me2} = bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate) as excellent candidates for the generation of high-valent terminal nickel-oxygen adducts.^[15] Using similar 2,6-pyridinedicarboxamidate ligands, thermally stable Ni^{III} and Ni^{IV} complexes,^[16] as well as Cu^I-superoxide,^[17] and Cu^{III}-OH^[4c,18] entities have been isolated. Herein, we describe the oxidation of **2** (which is formed from the reaction between **1** and CO₂, Scheme 1), to yield a metastable Ni^{III}-OR species that displays the ability to perform HAA and OAT.



Scheme 1. Complexes **1**^[15a], **2**^[15a], and **3**. Schematic representation of the preparation of **2** and **3**.

In acetone, at -80 °C, **2** was reacted with the organic oxidant tris(4-bromophenyl)ammoniumyl hexachloroantimonate^[19]

[a] P. Pirovano, Dr. A. R. McDonald
School of Chemistry and CRANN/AMBER Nanoscience Institute,
The University of Dublin, Trinity College, College Green, Dublin 2,
Ireland. E-mail: aidan.mcdonald@tcd.ie

[b] Dr. E. R. Farquhar
Case Western Reserve University Center for Synchrotron
Biosciences, National Synchrotron Light Source, Brookhaven
National Laboratory, Upton, NY 11973, USA

[c] Prof. M. Swart
Institut de Química Computacional i Catàlisi, Universitat de
Girona, Facultat de Ciències, Campus Montilivi, 17071 Girona,
Catalunya, Spain

[d] A. J. Fitzpatrick, Dr. G. G. Morgan
School of Chemistry & Chemical Biology, University College Dublin,
Science Centre, Belfield, Dublin 4, Ireland

('Magic-Blue', dissolved in CH_3CN , $E^\circ = 0.70 \text{ V vs Fc}^+/\text{Fc}^{[20]}$). An instantaneous reaction was observed as evidenced by the appearance of two intense features in the electronic absorption spectrum ($\lambda_{\text{max}} = 520$ and 790 nm , Figure 1), assigned to a novel species **3**. A titration of Magic Blue against **1** showed that the intensity of the new features reached a maximum after the addition of one equivalent of Magic Blue (Figure 1, inset). The addition of greater than one equivalent of Magic Blue did not cause a further change in the new features, while the presence of excess unreacted Magic Blue in the reaction mixture was observed in the electronic absorption spectrum (Figure S1). Initial indications thus suggested that **2** had been oxidized by one electron yielding a novel species, **3**, that we postulate is a $\text{Ni}^{\text{III}}-\text{OCO}_2\text{H}$ complex.

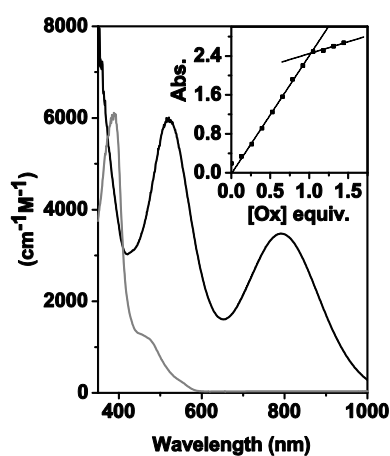


Figure 1. UV-vis spectrum of **2** (grey trace, 0.4 mM in acetone) that was reacted with Magic Blue at $-80 \text{ }^\circ\text{C}$ to yield **3** (black trace). Inset: Titration of Magic Blue with **2** monitored by plotting the intensity of the $\lambda_{\text{max}} = 520 \text{ nm}$ feature versus equivalents of Magic Blue.

The intense absorption features in the visible and near-IR (NIR) regions of the UV-vis spectrum, observed upon the reaction between **2** and Magic Blue to yield **3**, suggest a change in the oxidation state of the Ni center. Many of the Ni^{III} complexes reported to date display similarly intense chromophores in the visible and NIR regions of their absorption spectra.^[10,12,16,21] Intermediate **3** could be generated in acetone or THF. The features associated with **3** are the same in both solvents. Likewise, when **3** was prepared in the presence or absence of excess CH_3CN (acetone or CH_3CN can be used as the solvent for Magic Blue) no difference in the electronic absorption features was noted. These observations are important as they demonstrate that solvent is not coordinating to the Ni^{III} center in **3**. Should solvent coordinate to the Ni^{III} center in **3**, one would anticipate different UV-vis characteristics of the oxidized product in different solvent media.

3 was further characterized using X-band electron paramagnetic resonance (EPR) spectroscopy. An acetone solution of **3** was frozen in liquid nitrogen and an axial spectrum

was obtained at 113 K (Figure 2, $g = 2.25, 2.02$). The yield of Ni^{III} was calculated to be $95\% (\pm 15\%)$ by double integration of the signal of **3** against that of a radical standard (TEMPO (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl)). The obtained g -values are consistent with an $S = \frac{1}{2}$ (low-spin) $d^7 \text{ Ni}^{\text{III}}$ species,^[21d,22] and the average g -value ($g_{\text{av.}} = 2.17$) is indicative of the unpaired electron sitting on the Ni-center, rather than being a ligand-based radical. Importantly, $g_{\perp} \gg g_{\parallel}$ which is typical for axially elongated octahedral complexes or square planar complexes.^[21b,21d,22-23] The most likely configurations for a low-spin d^7 ion in pseudo-tetragonal symmetry involve the unpaired electron density being located in an orbital of predominant d_{z^2} or d_{xy} character. Instances where $g_{\perp} \gg g_{\parallel}$ have been usually understood to correspond to a d_{z^2} singly-occupied orbital.^[21b,21d,22,23b,23d] In all, the EPR analysis suggests that oxidation of the square-planar precursor **2** resulted in the loss of an electron yielding a square-planar $S = \frac{1}{2} d^7 \text{ Ni}^{\text{III}}$ species, **3**, with a metal-based d_{z^2} -like SOMO. Density functional theory (DFT) Mulliken spin density calculations were performed in order to further probe the location of the unpaired electron density in **3**. These calculations supported the experimental observations that the unpaired spin predominantly resides in a metal-based molecular orbital. The DFT calculations predict that either metal-based d_{z^2} - or d_{xy} -like molecular orbitals are the likely locations of the unpaired electron density (Figure 3 displays spin density plot for d_{z^2} occupancy). The DFT calculations thus support the EPR determined electronic structure of **3**.

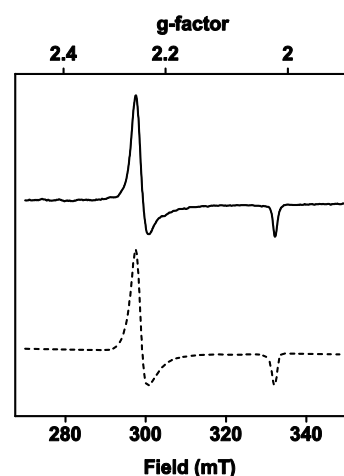


Figure 2. Solid trace: X-band EPR spectrum of **3** in a frozen acetone solution. Measured at 113 K ; microwave power = 31.6 mW ; modulation amplitude = 0.5 mT ; $g_{\perp} = 2.25$, $g_{\parallel} = 2.02$, $g_{\text{av.}} = 2.17$. Dashed trace: simulated spectrum for **3**. The system was modelled as an $S = \frac{1}{2}$ electron spin with axial g tensor, and inhomogeneous line broadening. The greater line broadening in the x and y directions is possibly due to unresolved hyperfine coupling with the ^{14}N nuclei of the ligand.

X-ray absorption spectroscopy (XAS) was employed to analyse the electronic and structural properties of **3**. The XAS edge energy measured for **3** (8345 eV) lies in the expected range for Ni^{III} complexes.^[14,24] Interestingly, there is only a very minor shift in the K-edge energy compared to the K-edge energy

measured for Ni^{II}-containing **2** (Figure S2). This is not unusual for Ni (and indeed Cu) K-edge analysis, several groups have made similar observations when comparing Ni^{II/III} species within comparable coordination environments.^[24a,25] Contributions to the edge from 1s → 4p absorption features distort the edge and prevent accurate assessment of the edge shift upon oxidation of **2** to yield **3**. The derivatives of the normalized X-ray absorption near-edge spectrum (XANES) indicate a modest edge shift of 0.1 - 0.2 eV when comparing the 1s → 3d pre-edge transition of **2** to **3**, in accord with increased oxidation of the Ni center in **3**. Although there appears to be negligible change in the edge energy between **2** and **3**, the shape of the edge and relative intensities of features in the edge are markedly different. Such differences are indicative of the distinct electronic environments of the Ni-center in complexes **2** and **3**.

Table 1. Nickel-ligand bond distances (Å) for **2** and **3** as determined using: ^aXRD; ^bEXAFS; and ^cDFT

| | Ni-OCO ₂ H | Ni-N(py) | Ni-N(amid) |
|-----------------------------|-----------------------|----------|------------|
| 2 ^a [15a] | 1.871 | 1.817 | 2 @ 1.895 |
| 2 ^b | | 4 @ 1.87 | |
| 2 ^c | 1.90 | 1.80 | 2 @ 1.90 |
| 3 ^b | 2 @ 1.84 | | 2 @ 1.99 |
| 3 ^c | 1.96 | 1.84 | 2 @ 1.93 |

Extended X-ray absorption fine structure (EXAFS) analysis of **3** yielded a disordered first coordination shell of 4 O/N donors (Figure S3, Table S1). This shell could be split into two components with two scatterers at ~ 1.84 Å and two scatterers at ~ 1.99 Å giving the best fit of the experimental data obtained for **3** (Table 1). These observations suggest that a single-bonded oxygen ligand is present in **3**, i.e. the bicarbonate remains intact. Attempts to fit the data containing a very short Ni-O bond (~1.65 Å) resulted in very poor fits, ruling out the possibility of **3** being a Ni^{III}=O species. Comparison of the EXAFS fits for **2** and **3** suggests there are little to no structural differences in the two complexes. The fits acquired for **2** match well with the X-ray diffraction determined bond distances obtained for **2**.^[15a] We have employed DFT to further understand the structural properties of **3** (Table 1, Figure 3). The DFT predictions indicate that the bicarbonate ligand in **3** would remain bound in a monodentate fashion, in good agreement with the EXAFS analyses of a first coordination sphere of 4 donors. Furthermore, the computational analyses predicted that the *d*⁷ Ni^{III} ion in **3** would remain in a square planar coordination environment analogous to that seen for **2**, in good agreement with the EPR measurements that indicate the Ni^{III} ion sits in a square planar environ. DFT also predicted that the Ni-OCO₂H and Ni-N(py) bond distances in **3** would be 1.96 Å and 1.84 Å (Table 1), respectively, in reasonably good agreement with the EXAFS analyses showing two O/N scatterers at ~1.84 Å. The

combination of EXAFS and DFT predictions shows that the Ni center in **3** has remained 4-coordinate, in a square planar environment, and that the bicarbonate ligand is present.

It is important to note that the obtained EXAFS data could also be reasonably well fit with a -OH ligand (in place of -OCO₂H). Holm et al demonstrated that **2** reversibly binds CO₂, and it is reasonable to suggest the affinity of **3** for CO₂ may be less than for **2**.^[15a,15b,15d] We endeavored to probe **3** using Raman spectroscopy, but failed to identify peaks that confirmed the presence of either -OH or -OCO₂H ligands. We were hampered by the rich Raman spectrum of the acetone support medium. We also failed in our efforts to obtain mass spectrometric evidence for the molecular formula of **3**, presumably as a result of the low thermal stability of **3**. It is important to note that oxidation of **1** with Magic Blue does *not* yield the same spectroscopic features attributed to **3**, but in fact yields an as yet unidentified species. We therefore conclude that **3** maintains the coordinated -OCO₂H ligand.

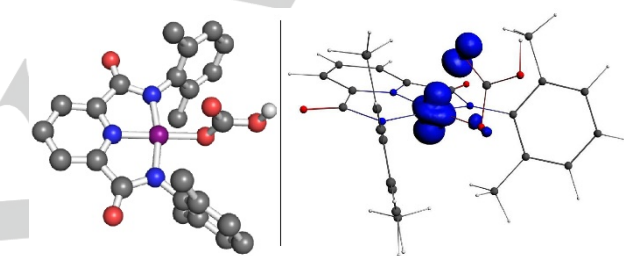


Figure 3. Left: DFT optimized structure of **3**. Hydrogen atoms (except bicarbonate proton) have been excluded for clarity. Right: DFT optimized spin density plot of **3**.

3 was stable at -80 °C, but decayed upon warming above -40 °C. After thermal decay and acidic workup of the reaction mixture, the protonated ligand (H₂pyN₂^{Me2}) was recovered without any indications of ligand oxidation (no evidence for ligand hydroxylation or oxidative decomposition was obtained by mass spectrometry or ¹H NMR spectroscopy). Interestingly, ESI-MS analysis showed the presence of trace amounts of hydroxyacetone, pyruvic acid and acetic acid.^[26] Importantly, at -40 °C, the half-life of **3** in acetone-*H*₆ was 5600 s whereas in acetone-*D*₆ it was found to be 6800 s (kinetic isotope effect (KIE) = 1.2). The observation of such acetone-derived products and an extended lifetime in perdeuterated solvent supports the postulate that **3** oxidizes acetone by rate-limiting HAA during its thermal decay.

We investigated further the HAA reactivity of **3** towards external substrates by reacting it with molecules containing weak X-H bonds (X = C, O). At -40 °C, **3** reacted with 100 equiv. of 2,6-ditertbutylphenol (DTPB), as evidenced by the disappearance (600 s) of the electronic absorption features attributed to **3** (Figure S4). This resulted in the appearance of a new band at λ_{max} = 555 nm, which we attribute to the formation of the phenoxyl radical as a result of HAA from DTBP by **3**.^[27] EPR analysis confirmed the formation of a phenoxyl radical (Figure S11). After warming to room temperature, 3,3',5,5'-tetra-

tert-butyl-[1,1'-bi(cyclohexane)]-2,2',5,5'-tetraene-4,4'-dione and traces of 2,6-diterbutylquinone were detected using GC-MS. Such products form by radical coupling or thermal decomposition (Scheme S1), respectively, of the parent 2,6-diterbutylphenoxy radical. A pseudo first-order rate constant (k_{obs}) for this reaction was determined by plotting the change in absorbance features for **3** against time and fitting the resulting curve (Figure S5). A second-order rate constant (k_2) was calculated from the slope of a linear plot of k_{obs} -values determined under a series of substrate concentrations (Figure S6). The k_2 -value determined for the reaction between **3** and DTBP was $0.1040 \text{ M}^{-1}\text{s}^{-1}$, while for deuterio-DTBP a k_2 -value of $0.0503 \text{ M}^{-1}\text{s}^{-1}$ was determined, yielding a KIE value of 2.1. This KIE value is consistent with **3** performing HAA on the DTBP O–H bond, and with HAA being rate-limiting. **3** was found to also react with 1-benzyl-1,4-dihydropyridinamide (BNAH, C–H bond dissociation energy (BDE) = 68 kcal/mol) at $-80 \text{ }^\circ\text{C}$, as evidenced by a rapid disappearance of the visible absorption features attributed to **3** (Figure S7). The product of this reaction was identified by ^1H NMR as 1-benzyl-1-pyridinium-3-carboxamide, which typically forms as a result of HAA from the C–H bond of BNAH. In summary, **3** was found to be a quite reactive HAA reagent capable of activating relatively weak O–H and C–H bonds at low temperatures.

We also probed the capacity of **3** to carry out OAT. **3** was reacted with triphenylphosphine (PPh_3 , 50 equiv.) at $-80 \text{ }^\circ\text{C}$ resulting in the formation of triphenylphosphine oxide (O=PPh_3 , detected by ESI-MS and ^{31}P NMR) in near quantitative yields (Figure S8). A second-order rate constant (k_2) for the reaction between **3** and PPh_3 was determined ($5.3 \text{ M}^{-1}\text{s}^{-1}$, Figures S9 & S10). This k_2 -value for PPh_3 oxidation is quite high compared to values determined for some Fe=O and Mn=O complexes in the same reaction.^[3] We believe it is quite significant that the nickel-containing species displayed such a high rate constant, an outcome that merits considerable future attention. **3** thus represents an exciting example of a terminal Ni-oxygen adduct that is capable of HAA and OAT.

In summary, the one-electron oxidation of **2** at low temperature generates a Ni^{III} complex, **3**. EPR spectroscopy suggested the oxidation was borne principally by the central metal atom, yielding a low-spin $d^7 \text{ Ni}^{\text{III}}$ ion, sitting in a square planar coordination environment. XAS analysis provided further support for this indicating that **3** contained a Ni^{III} center coordinated by four N/O donor ligands. DFT calculations on the structure and Mulliken spin density supported these experimental conclusions further. **3** was capable of oxidizing organic substrates including DTPB, BNAH, and PPh_3 . This constitutes the first example of a terminal $\text{Ni}^{\text{III}}\text{-O(X)}$ species that is sufficiently well-behaved to allow thorough structural, spectroscopic, and reactivity investigations. This is an important step towards the elucidation of the properties of late transition metal-oxygen adducts and their role in oxidation catalysis.

Acknowledgements

This publication has emanated from research supported in part by the European Union (FP7-333948, AMcD), a research grant from Science Foundation Ireland (SFI/12/RC/2278, AMcD), and COST Action CM1305 (ECOSTBio). MS acknowledges MINECO (CTQ2011-25086/BQU), DIUE of the Generalitat de Catalunya (2014SGR1202), MICINN (Ministry of Science and Innovation, Spain), the FEDER fund (UNGI08-4E-003) and CESCA. Operation of NSLS X3B is supported by NIH grant P30-EB-009998. The NSLS is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

Keywords: reactive intermediates • oxidation catalysis • metal-oxo • high-valent nickel • model complexes

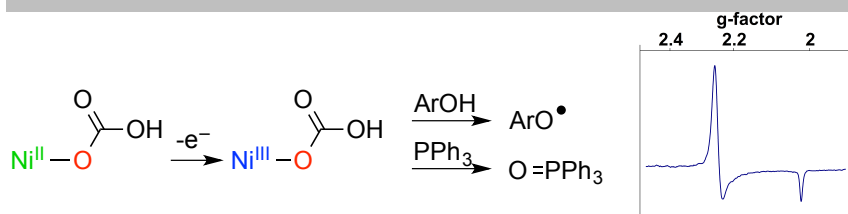
- 1] a) M. Sono, M. P. Roach, E. D. Coulter, J. H. Dawson, *Chem. Rev.* **1996**, *96*, 2841-2888; b) I. G. Denisov, T. M. Makris, S. G. Sligar, I. Schlichting, *Chem. Rev.* **2005**, *105*, 2253-2277; c) E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y.-S. Yang, J. Zhou, *Chem. Rev.* **2000**, *100*, 235-350; d) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, *Chem. Rev.* **2004**, *104*, 939-986; e) E. I. Solomon, D. E. Heppner, E. M. Johnston, J. W. Ginsbach, J. Cirera, M. Qayyum, M. T. Kieber-Emmons, C. H. Kjaergaard, R. G. Hadt, L. Tian, *Chem. Rev.* **2014**, *114*, 3659-3853; f) J. Yano, V. Yachandra, *Chem. Rev.* **2014**, *114*, 4175-4205.
- 2] a) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329-2363; b) A. Singh, L. Spiccia, *Coord. Chem. Rev.* **2013**, *257*, 2607-2622.
- 3] a) W. Nam, *Acc. Chem. Res.* **2007**, *40*, 522-531; b) C. Krebs, D. Galonić Fujimori, C. T. Walsh, J. M. Bollinger, *Acc. Chem. Res.* **2007**, *40*, 484-492; c) L. Que, *Acc. Chem. Res.* **2007**, *40*, 493-500; d) G. Yin, *Coord. Chem. Rev.* **2010**, *254*, 1826-1842; e) A. R. McDonald, L. Que, *Coord. Chem. Rev.* **2013**, *257*, 414-428; f) W. J. Song, M. S. Seo, S. D. George, T. Ohta, R. Song, M.-J. Kang, T. Tosha, T. Kitagawa, E. I. Solomon, W. Nam, *J. Am. Chem. Soc.* **2007**, *129*, 1268-1277; g) X. Wu, M. S. Seo, K. M. Davis, Y.-M. Lee, J. Chen, K.-B. Cho, Y. N. Pushkar, W. Nam, *J. Am. Chem. Soc.* **2011**, *133*, 20088-20091; h) T. Taguchi, R. Gupta, B. Lassalle-Kaiser, D. W. Boyce, V. K. Yachandra, W. B. Tolman, J. Yano, M. P. Hendrich, A. S. Borovik, *J. Am. Chem. Soc.* **2012**, *134*, 1996-1999.
- 4] a) F. F. Pfaff, S. Kundu, M. Risch, S. Pandian, F. Heims, I. Pryjomskaya-Ray, P. Haack, R. Metzinger, E. Bill, H. Dau, P. Comba, K. Ray, *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 1711-1715; *Angew. Chem.* **2011**, *143*, 1749-1753; b) S. Hong, F. F. Pfaff, E. Kwon, Y. Wang, M.-S. Seo, E. Bill, K. Ray, W. Nam, *Angew. Chem. Int. Ed.* **2014**, *53*, 10493-10407; *Angew. Chem.* **2014**, *126*, 10571-10575; c) P. J. Donoghue, J. Tehranchi, C. J. Cramer, R. Sarangi, E. I. Solomon, W. B. Tolman, *J. Am. Chem. Soc.* **2011**, *133*, 17602-17605.
- 5] a) J. D. Koola, J. K. Kochi, *Inorg. Chem.* **1987**, *26*, 908-916; b) R. Irie, Y. Ito, T. Katsuki, *Tetrahedron Lett.* **1991**, *32*, 6891-6894; c) T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, *Chem. Lett.* **1991**, *20*, 1-4; d) R. I. Kureshy, N. H. Khan, S. H. R. Abdi, P. Iyer, A. K. Bhatt, *J. Mol. Catal. A: Chem.* **1998**, *130*, 41-50; e) I. Fernández, J. Pedro, A. L. Rosello, R. Ruiz, X. Ottenwaelde, Y. Journaux, *Tetrahedron Lett.* **1998**, *39*, 2869-2872; f) T. Nagataki, Y. Tachi, S. Itoh, *Chem. Commun.* **2006**, *14*, 4016-4018; g) T. Nagataki, S. Itoh, *Chem. Lett.* **2007**, *36*, 748-749; h) T. Nagataki, K. Ishii, Y. Tachi, S. Itoh, *Dalton Trans.* **2007**, *21*, 1120-1128; i) M. Balamurugan, R. Mayilmurugan, E. Suresh, M. Palaniandavar, *Dalton Trans.* **2011**, *40*, 9413-9424; j) M. Sankaralingam, P. Vadivelu, E. Suresh, M. Palaniandavar, *Inorg. Chim. Acta* **2013**, *407*, 98-107.
- 6] a) G. Zhu, E. N. Glass, C. Zhao, H. Lv, J. W. Vickers, Y. V. Geletii, D. G. Musaev, J. Song, C. L. Hill, *Dalton Trans.* **2012**, *41*, 13043-13049; b) M.

- Zhang, M.-T. Zhang, C. Hou, Z.-F. Ke, T.-B. Lu, *Angew. Chem. Int. Ed. Engl.* **2014**, DOI: 10.1002/anie.201406983.
- [7] a) G. Chen, L. Chen, S.-M. Ng, T.-C. Lau, *ChemSusChem* **2014**, *7*, 127-134; b) A. Singh, S. L. Y. Chang, R. K. Hocking, U. Bach, L. Spiccia, *Catal. Sci. Tech.* **2013**, *3*, 1725-1732; c) D. Hong, Y. Yamada, T. Nagatomi, Y. Takai, S. Fukuzumi, *J. Am. Chem. Soc.* **2012**, *134*, 19572-19575; d) M. Dincă, Y. Surendranath, D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 10337-10341; e) P. Boizumault-Moriceau, *Appl. Catal., A* **2003**, *245*, 55-67; f) X. Zhang, J. Liu, Y. Jing, Y. Xie, *Appl. Catal., A* **2003**, *240*, 143-150.
- [8] a) M. Sankaralingam, M. Balamurugan, M. Palaniandavar, P. Vadivelu, C. H. Suresh, *Chem. Eur. J.* **2014**, *20*, 11346-11361; b) J. F. Kinneary, J. S. Albert, C. J. Burrows, *J. Am. Chem. Soc.* **1988**, *110*, 6124-6129; c) H. Yoon, T. R. Wagler, K. J. O'Connor, C. J. Burrows, *J. Am. Chem. Soc.* **1990**, *112*, 4568-4570; d) D. K. Bediako, Y. Surendranath, D. G. Nocera, *J. Am. Chem. Soc.* **2013**, *135*, 3662-3674.
- [9] A. W. Pierpont, T. R. Cundari, *Inorg. Chem.* **2010**, *49*, 2038-2046.
- [10] F. F. Pfaff, F. Heims, S. Kundu, S. Mebs, K. Ray, *Chem. Commun.* **2012**, *48*, 3730-3732.
- [11] P. J. Chmielewski, L. Latos-Grażyński, *Inorg. Chem.* **1997**, *36*, 840-845.
- [12] T.-w. Chiou, W.-f. Liaw, *Inorg. Chem.* **2008**, *47*, 7908-7913.
- [13] a) K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, Y. Moro-oka, *J. Am. Chem. Soc.* **2000**, *122*, 254-262; b) S. Itoh, H. Bandoh, M. Nakagawa, S. Nagatomo, T. Kitagawa, K. D. Karlin, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 11168-11178; c) S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, Y. Moro-oka, M. Akita, *Chem. Eur. J.* **2001**, *7*, 5011-5028; d) S. Itoh, H. Bandoh, S. Nagatomo, T. Kitagawa, S. Fukuzumi, *J. Am. Chem. Soc.* **1999**, *121*, 8945-8946; e) R. Schenker, B. S. Mandimutsira, C. G. Riordan, T. C. Brunold, *J. Am. Chem. Soc.* **2002**, *124*, 13842-13855; f) K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer, C. G. Riordan, *Inorg. Chem.* **2004**, *43*, 3324-3326.
- [14] S. Kundu, F. F. Pfaff, E. Miceli, I. Zaharieva, C. Herwig, S. Yao, E. R. Farquhar, U. Kuhlmann, E. Bill, P. Hildebrandt, H. Dau, M. Driess, C. Limberg, K. Ray, *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 5622-5626; *Angew. Chem.* **2013**, *125*, 5732-5736.
- [15] a) D. Huang, R. H. Holm, *J. Am. Chem. Soc.* **2010**, *132*, 4693-4701; b) D. Huang, O. V. Makhlynets, L. L. Tan, S. C. Lee, E. V. Rybak-Akimova, R. H. Holm, *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 1222-1227; c) D. Huang, O. V. Makhlynets, L. L. Tan, S. C. Lee, E. V. Rybak-Akimova, R. H. Holm, *Inorg. Chem.* **2011**, *50*, 10070-10081; d) O. Troeppner, D. Huang, R. H. Holm, I. Ivanović-Burmazović, *Dalton Trans.* **2014**, *43*, 5274-5279.
- [16] A. K. Patra, R. Mukherjee, *Inorg. Chem.* **1999**, *38*, 1388-1393.
- [17] a) P. J. Donoghue, A. K. Gupta, D. W. Boyce, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2010**, *132*, 15869-15871; b) P. Pirovano, A. M. Magherusan, C. McGlynn, A. Ure, A. Lynes, A. R. McDonald, *Angew. Chem. Int. Ed. Engl.* **2014**, 5946-5950; *Angew. Chem.* **2014**, *126*, 6056-6060.
- [18] M. R. Halvagar, P. V. Solntsev, H. Lim, B. Hedman, K. O. Hodgson, E. I. Solomon, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2014**, *136*, 7269-7272.
- [19] F. A. Bell, A. Ledwith, D. C. Sherrington, *J. Chem. Soc. C* **1969**, 2719-2720.
- [20] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.
- [21] a) A. G. Lappin, M. C. M. Laranjeira, R. D. Peacock, *Inorg. Chem.* **1983**, *22*, 786-791; b) S. A. Jacobs, D. W. Margerum, *Inorg. Chem.* **1984**, *23*, 1195-1201; c) H. J. Kruger, R. H. Holm, *J. Am. Chem. Soc.* **1990**, *112*, 2955-2963; d) H. J. Kruger, G. Peng, R. H. Holm, *Inorg. Chem.* **1991**, *30*, 734-742; e) J. M. Corker, J. Evans, W. Levason, M. D. Spicer, P. Andrews, *Inorg. Chem.* **1991**, *30*, 331-334; f) T. Storr, P. Verma, Y. Shimazaki, E. C. Wasinger, T. D. P. Stack, *Chem. Eur. J.* **2010**, *16*, 8980-8983; g) Y.-M. Lee, S. Hong, Y. Morimoto, W. Shin, S. Fukuzumi, W. Nam, *J. Am. Chem. Soc.* **2010**, *132*, 10668-10670; h) T.-P.-A. Cao, G. Nocton, L. Ricard, X. F. Le Goff, A. Auffrant, *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 1368-1372; *Angew. Chem.* **2014**, *126*, 1192-1196.
- [22] a) F. V. Lovecchio, E. S. Gore, D. H. Busch, *J. Am. Chem. Soc.* **1974**, *96*, 3109-3118; b) R. I. Haines, A. McAuley, *Coord. Chem. Rev.* **1981**, *39*, 77-119; c) J. N. Stuart, A. L. Goerges, J. M. Zaleski, *Inorg. Chem.* **2000**, *39*, 5976-5984.
- [23] a) R. I. Haines, A. McAuley, *Inorg. Chem.* **1980**, *1109*, 719-723; b) P. J. Alonso, L. R. Falvello, J. Forniés, A. Martín, B. Menjón, G. Rodríguez, *Chem. Commun.* **1997**, *2*, 503-504; c) T. J. Collins, T. R. Nichols, E. S. Uffelman, *J. Am. Chem. Soc.* **1991**, *113*, 4708-4709; d) X. Ottenwaelder, R. Ruiz-García, G. Blondin, R. Carasco, J. Cano, D. Lexa, Y. Journaux, A. Aukauloo, *Chem. Commun.* **2004**, 504-505.
- [24] a) G. J. Colpas, M. J. Maroney, C. Bagyinka, M. Kumar, W. S. Willis, S. L. Suib, P. K. Mascharak, N. Baidya, *Inorg. Chem.* **1991**, *30*, 920-928; b) J. Cho, H. Y. Kang, L. V. Liu, R. Sarangi, E. I. Solomon, W. Nam, *Chem. Sci.* **2013**, *4*, 1502-1508.
- [25] a) M. Haumann, A. Porthun, T. Buhrke, P. Liebisch, W. Meyer-Klaucke, B. Friedrich, H. Dau, *Biochemistry* **2003**, *42*, 11004-11015; b) G. Davidson, S. B. Choudhury, Z. Gu, K. Bose, W. Roseboom, S. P. J. Albracht, M. J. Maroney, *Biochemistry* **2000**, *39*, 7468-7479; c) R. Sarangi, *Coord. Chem. Rev.* **2013**, *257*, 459-472.
- [26] T. Schaefer, J. Schindelka, D. Hoffmann, H. Herrmann, *J. Phys. Chem. A* **2012**, *116*, 6317-6326.
- [27] a) E. R. Altwickler, *Chem. Rev.* **1967**, *67*, 475-531; b) J. M. Wittman, R. Hayoun, W. Kaminsky, M. K. Coggins, J. M. Mayer, *J. Am. Chem. Soc.* **2013**, *135*, 12956-12959.

Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION



Paolo Pirovano, Erik R. Farquhar,
Marcel Swart, Anthony J. Fitzpatrick,
Grace G. Morgan, Aidan R. McDonald*

Page No. – Page No.

**Characterization and Reactivity of a
Terminal Nickel(III)-Oxygen Adduct**

A nickel(III)-bicarbonate complex was obtained in high yield by the oxidation of a nickel(II) precursor. The nickel(III) species readily performed hydrogen atom abstraction and oxygen atom transfer, demonstrating that it is a viable model for elusive high-valent terminal nickel-oxygen intermediates in oxidation catalysis.