ChemComm

This article is part of the

Porphyrins & Phthalocyanines web themed issue

Guest editors: Jonathan Sessler, Penny Brothers and Chang-Hee Lee

All articles in this issue will be gathered together online at <u>www.rsc.org/porphyrins</u>



Cite this: Chem. Commun., 2012, 48, 3730-3732

COMMUNICATION

Spectroscopic capture and reactivity of S = 1/2 nickel(III)–oxygen intermediates in the reaction of a Ni^{II}-salt with *m*CPBA[†][‡]

Florian Felix Pfaff,§ Florian Heims,§ Subrata Kundu, Stefan Mebs and Kallol Ray*

Received 1st February 2012, Accepted 23rd February 2012 DOI: 10.1039/c2cc30716b

Ni(III)-intermediates are trapped by EPR and UV/Vis spectroscopy in the reaction of a Ni(II) salt with *m*CPBA. On the basis of their oxo-transfer and hydrogen-atom abstraction abilities the intermediates are assigned as the elusive terminal Ni(III)–oxo/ hydroxo species. The findings suggest that Ni(III)–O(H) moieties are viable reactants in oxidation catalysis.

Metal complexes with terminal oxo or hydroxo ligands have been implicated in a variety of oxidative transformations. For instance, monomeric oxoiron units are proposed to be the competent oxidants in many mono- and dioxygenases.^{1,2} Similarly, numerous synthetic oxo- or hydroxo-metal complexes have been shown to be involved in either C-H bond cleavage or O-atom transfer reactions.^{2,3} High-valent nickel-oxo or -hydroxo complexes have also attracted much attention as they have shown promise as plausible intermediates in a number of nickel based oxidation reactions.^{4,5} For example, in the [Ni^{II}(TPA)]²⁺ [TPA: tris(2-pyridylmethyl)amine] based catalytic alkane hydroxylation reaction in the presence of *m*CPBA (*meta*-chloroperbenzoic acid), $^{4a-c}$ a [Ni^{III}–O]⁺ species is proposed as the active oxidant. Additionally, the [Ni^{III}–O]⁺ species is also suggested as the most potent oxidant for the chemically challenging conversion of methane to methanol in the gas phase based on experimental⁶ and theoretical studies.⁷ However, no direct spectroscopic evidence for a high-valent nickel-oxo species has been reported till date, leaving the assignment ambiguous.

Our understanding of the nickel based C–H hydroxylation and oxo-transfer reactions in the presence of *m*CPBA has stagnated for want of a system in which high valent nickel–oxygen intermediates could be trapped in significant yields. Here, we report a progress on this front. We have used the tetradentate tripodal ligand TMG₃tren⁸ (tris[2-(*N*-tetramethylguanidyl)ethyl] amine),



which has recently found application in the successful stabilization of superoxocopper(II),⁹ high-spin (S = 2){Fe^{IV}=O},¹⁰ and (S = 3/2){Co^{IV}-O(Sc³⁺)}¹¹ complexes. We have found that reaction of [Ni^{II}(TMG₃tren)]²⁺ with *m*CPBA at low temperature allows the unprecedented trapping of nickel(III)-oxygen species in approximately 15% yield. In what follows, we detail the spectroscopic and kinetic characterization of the metastable nickel(III)-oxygen complexes.

Reactions of equimolar amounts of TMG3tren and Ni^{II}(OTf)₂ in dichloromethane/toluene afforded the brown $[Ni^{II}(TMG_3 tren) (OTf)]^+$ (1-OTf) complex in 65% yield; the crystal structure (Scheme 1) exhibits the expected TBP geometry $(\tau = 0.82)$. **1-OTf** is paramagnetic (S = 1) as demonstrated by the ¹H NMR resonances spread over a chemical shift range of -50 to +50 ppm (Fig. S1, ESI^{\dagger}). Reaction of **1-OTf** (4 mM) with 1 eq. mCPBA at -30 °C resulted in the generation of two metastable intermediates (from EPR analysis) 2a and 2b $(t_{1/2} \approx 1 \text{ h at } -30 \text{ °C})$ with absorption maxima centered at 464 nm, 520 nm and 794 nm (Fig. 1 top). Interestingly, the spectral changes associated with the formation of 2a (and 2b) are found to be similar to that previously observed during the formation of the high-valent terminal metal-oxo complexes of iron¹⁰ and cobalt¹¹ supported by the TMG₃tren ligand (Fig. S2, ESI[‡]). The formation of the oxoiron(IV) complex involved development of bands at 400 nm and 825 nm and for that of the oxocobalt(IV) species the corresponding bands were observed at 489 and 810 nm, respectively.

Humboldt Universität zu Berlin, Department of Chemistry, Brook-Taylor Strasse 2, 12489, Berlin, Germany.

E-mail: kallol.ray@chemie.hu-berlin.de; Fax: +49 3020937387; Tel: +49 3020937385

[†] This article is part of the ChemComm 'Porphyrins and phthalocyanines' web themed issue.

[‡] Electronic supplementary information (ESI) available: Experimental section and X-ray crystallographic data. CCDC 865217. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc30716b

[§] Equal contribution of the two authors.



Fig. 1 Top: UV/vis spectral changes associated with the reaction of **1-OTf** (4 mM) with 1 eq. *m*CPBA at -30 °C in CH₂Cl₂ and the time trace for the development of the absorption band at 520 nm (inset); bottom: the X-band EPR spectrum (black trace) of the reaction product of **1-OTf** with *m*CPBA in CH₂Cl₂ at -30 °C and then frozen to 10 K (frequency 9.43479 GHz, power 0.20 mW, modulation 0.75 mT). The simulated spectrum is shown in blue. Simulation parameters for **2a** (85% yield; red trace): $g_1 = 2.05$, $g_2 = 2.16$, $g_3 = 2.31$; **2b** (15% yield, green trace): $g_1 = 2.13$, $g_2 = 2.17$, $g_3 = 2.26$. In the inset is shown the time trace for the development of the S = 1/2 EPR signals.

The reactions of peracids with transition metal centers in the +2 oxidation state have been studied in detail before.^{4,12} The initially formed acylperoxometal(II) intermediate (1-mCPBA in Scheme 1) can undergo O-O bond homolysis or heterolysis to generate the oxometal(III) or oxometal(IV) complexes. respectively (Scheme 1). The EPR spectrum of a sample frozen to 10 K after mixing 1-OTf with mCPBA at -30 °C shows signals of two rhombic S = 1/2 species; a major species (2a, 85%) with $g_1 = 2.05, g_2 = 2.16$, and $g_3 = 2.31$ and a minor species (**2b**, 15%) with $g_1 = 2.13$, $g_2 = 2.17$, and $g_3 = 2.26$ (Fig. 1B). These EPR properties, *i.e.* $g_{av} = 2.17$ for **2a** and 2.19 for **2b**, and $g_{\parallel} > g_{\perp}$, are indicative of Ni(III) with distorted square planar, trigonal bipyramidal, or compressed octahedral coordination with the unpaired electron in d(xy) or $d(x^2 - y^2)$ orbital.¹³ The maximum concentration of Ni(III) amounts to 15% of the total nickel concentration. The time trace of the development of the S = 1/2 Ni(III) EPR signals (Fig. 1 bottom inset) in the time-range of 0-2000 seconds is found to be similar to the time trace for the development of the 520 nm band in the

absorption spectra (Fig. 1 top inset). This indicates that the absorption spectral changes associated with the reaction of **1-OTf** with *m*CPBA can be attributed to the formation of the Ni(III) products. Thus, homolytic O–O cleavage (pathway A, Scheme 1) takes place in **1-m**CPBA to yield the Ni(III) products, **2a** and **2b**, as proposed before^{4a,c} for the corresponding [(TPA)Ni^{II}(OOC(O)C₆H₄Cl)]¹⁺ complex. This notion is also corroborated by gas chromatographic analysis of the peracid derived products in the reaction of **1-OTf** with 1 eq. *m*CPBA at –30 °C in CH₂Cl₂. Observed were 0.25 eq. chlorobenzene, 0.10 eq. 1,3-dichlorobenzene and 0.1 eq. 3-chlorophenol. These products are formed from the chlorophenyl radical (pathway A, Scheme 1) that is derived from the O–O bond homolysis process.

The electrospray mass (ESI-MS) spectrum of the reaction mixture of 1-OTf with mCPBA at -30 °C in CH₂Cl₂ shows a peak at m/z = 513.352 (Fig. S3, ESI[‡]). By simulation of the observed isotope distribution patterns this peak is formulated as {[Ni^{II}(O)(TMG₃tren-H)]}⁺ and is derived from the alkoxonickel(II) product resulting from the self-hydroxylation of the ligand. Such a decay pathway has also been reported previously for the corresponding [(TMG₃tren)- $Fe^{IV}(O)$ ²⁺ and $[(TMG_3tren)Co^{IV}(O)]^{2+}$ complexes.^{10,11} The ESI-MS spectrum also features two intense peaks at m/z =663.321 and 803.328 corresponding to {[Ni^{IV}(O)(TMG₃tren)](OTf)}⁺ and [(TMG₃tren)Ni^{II}(HOC(O)C₆H₄Cl)](OTf)⁺, respectively. We propose that these peaks derive from the heterolytic cleavage of the residual [(TMG₃tren)Ni^{II}- $(OOC(O)C_6H_4Cl)]^+$ species under the conditions of ESI-MS experiments (pathway B, Scheme 1). In solution only homolysis occurs as evident from the GC-MS analysis of the peracid derived products; no chlorobenzoic acid was obtained, which is expected to result from O-O bond heterolysis (Scheme 1).

Compounds 2a and 2b display the signature reactivity features^{2,3,12} of oxidizing metal-oxo (or -hydroxo) complexes. Rate constants for oxo-transfer to PPh3 or C-H activation of 9,10-dihydroanthracene (DHA), 1,4-cyclohexadiene, xanthene, and 1-benzyl-1.4-dihydronicotinamide (BNAH)¹⁴ in CH₂Cl₂ at -30 °C were obtained from the pseudo-first order fit (Fig. S4–S8, ESI[±]) of the decay of the absorption band at 520 nm. Second order rate constants (Table 1) were then determined from the dependence of the first-order rate constants on substrate concentrations, which were found to decrease with an increase in the C-H bond dissociation energy (BDE) of the substrates (Fig. 2A). Additionally, a deuterium kinetic isotope effect (KIE) of 3.9 was obtained in the oxidation of 9,10dihydroanthracene- d_4 (Fig. 2B). Interestingly, a comparable KIE of 2.8 has been reported^{4a} for the $[Ni^{II}(TPA)]^{2+}$ catalyzed oxidation of cyclohexane, for which a Ni(III)-oxo intermediate has been proposed as the active oxidant in the catalytic cycle. These confirm H-atom abstraction as the rate-determining step in the C-H activation reactions. Furthermore, the involvement of the Ni(III)-oxidant in the oxo-transfer and H-atom abstraction

Table 1 Second order rate constants determined for the different substrates by kinetic studies using UV-Vis spectroscopy

Substrate	PPh ₃ (-30 °C)	1,4-CHD (-30 °C)	DHA (-30 °C)	Xanthene (-30 °C)	BNAH (-60 °C)
$\frac{\text{BDE/kcal mol}^{-1}}{k_2/\text{M}^{-1} \text{ s}^{-1}}$	$\overline{5.49} \times 10^{-3}$	$78 \\ 7.26 \times 10^{-3}$	77 1.25×10^{-2}	$75.5 \\ 1.31 \times 10^{-2}$	67.9 1.53



Fig. 2 Reactivity of 2 in oxo-transfer and C-H activation reactions. (A) Plot of $\log k'_2$ of **2a** (**2b**) at -30 °C against C–H BDE of substrates. Second-order rate constants, k_2 , were determined at -30 °C and then adjusted for reaction stoichiometry to yield k'_2 based on the number of equivalent target C-H bonds of substrates. The reaction with BNAH was found to be too fast to be followed at -30 °C. Thus k_2 for BNAH was determined at -60 °C and adjusted for -30 °C by multiplying k_2 by 8; the rate is considered to be doubled for every 10 °C rise in temperature; (B) plots of the first-order rate constant (k_{obs}) against the concentration of DHA and DHA-d4; the point at zero-substrate concentration corresponds to the rate-constant for the self-decay of 2a (2b) $(1.89 \times 10^{-4} \text{ s}^{-1})$; (C) decay of the Ni(III) EPR feature at -30 °C upon addition of PPh₃ {[1-OTf]: 4 mM; [mCPBA]: 4 mM; [PPh₃]: 1.0 M}. In the inset is given the relative concentration of Ni(III) (C/C_0) vs. time calculated from the decay of EPR signals. The pseudo-first order fit ($k_{obs} = 0.05 \text{ s}^{-1}$) of the decay is shown as a bold line.

reactions (and not the **1-***m***CPBA** species in Scheme 1) was confirmed from the disappearance of the EPR features of **2a** and **2b** with a pseudo-first order decay (Fig. 2C and Fig. S9, ESI‡) in the presence of PPh₃ and DHA. The product analysis of the resultant reaction solutions revealed that the decay of the EPR signal was associated with the formation of triphenyl-phosphineoxide (40%) from PPh₃ reaction, and anthracene (10%), and anthraquinone (10%) from DHA reaction.¹⁵

In conclusion, we have reported the generation of Ni(III)-oxygen intermediates, 2a and 2b, during the reaction of $[Ni^{II}(TMG_3 tren)]^{2+}$ with *m*CPBA at low temperature. Based on their ability to perform oxo-transfer reaction and C-H activation with a rate-determining H-atom abstraction process we propose a terminal Ni(III)-oxo/hydroxo assignment for 2a and 2b. Although a number of Ni-dioxygen adducts have been reported recently,¹⁶ high-valent nickel with a terminal oxo/hydroxo unit has remained elusive till date. The difference between 2a and 2b is, however, not clear at present. In spite of their different spectroscopic properties (as evident from EPR studies) the kinetics of their oxo-transfer and C-H activation reactions were found to be comparable in the time-scale of UV-Vis and EPR experiments. The difference in their EPR spectra may originate from the difference in the protonation state (oxo vs. hydroxo) of the terminal oxygen atom. However, further studies are needed for the

unambiguous assignment of 2a and 2b. Thus, despite the nature of these Ni(III)–oxygen species is not entirely clear, their key role in oxidation reaction has been clearly established.

We gratefully acknowledge financial support of this work from the *Cluster of Excellence "Unifying Concepts in Catalysis"* (*EXC 314/1*), *Berlin.* We also thank Dr E. Bill, Mr F. Reikowski, and Prof. Dr R. Stößer for measurement and interpretation of EPR data.

Notes and references

- (a) C. Krebs, D. G. Fujimori, C. T. Walsh and J. M. Bollinger, Acc. Chem. Res., 2007, 40, 484; (b) J. T. Groves, J. Inorg. Biochem., 2006, 100, 434; (c) In Cytochrome P450 Structure Mechanisms and Biochemistry, ed. J. T. Groves, Y. Z. Han and P. R. Ortiz de Montellano, Plenum, New York, 1995, vol. 1, p. 3; (d) A. Decker and E. I. Solomon, Curr. Opin. Chem. Biol., 2005, 9, 152.
- 2 J. Hohenberger, K. Ray and K. Meyer, *Nat. Commun.*, 2012, DOI: 10.1038/ncomms1718.
- (a) L. Que, Jr., Acc. Chem. Res., 2007, 40, 493; (b) W. Nam, Acc. Chem. Res., 2007, 40, 522; (c) L. Que, Jr. and W. B. Tolman, Nature, 2008, 455, 333; (d) P. J. Donoghue, J. Tehranchi, C. J. Cramer, R. Sarangi, E. I. Solomon and W. B. Tolman, J. Am. Chem. Soc., 2011, 133, 17602; (e) G. Yin, A. M. Danby, D. Kitko, J. D. Carter, W. M. Scheper and D. H. Busch, J. Am. Chem. Soc., 2008, 130, 16245; (f) X. Wu, M. S. Seo, K. M. Davis, Y.-M. Lee, J. Chen, K.-B. Cho, Y. N. Pushkar and W. Nam, J. Am. Chem. Soc., 2011, 133, 20088; (g) W. J. Song, M. S. Seo, S. D. George, T. Ohta, R. Song, M.-J. Kang, T. Tosha, T. Kitagawa, E. I. Solomon and W. Nam, J. Am. Chem. Soc., 2007, 129, 1268; (h) T. Taguchi, R. Gupta, B. L. Kaiser, D. W. Boyce, V. K. Yachandra, W. B. Tolman, J. Yano, M. P. Hendrich and A. S. Borovik, J. Am. Chem. Soc., 2012, 134, 1996.
- 4 (a) T. Nagataki, Y. Tachi and S. Itoh, *Chem. Commun.*, 2006, 4016; (b) M. Balamurugan, R. Mayilmurugan, E. Suresh and M. Palaniandavar, *Dalton Trans.*, 2011, 40, 9413; (c) T. Nagataki, K. Ishii, Y. Tachi and S. Itoh, *Dalton Trans.*, 2007, 1120; (d) X. Solans-Monfort, J. L. G. Fierro, L. Hermosilla, C. Sieiro, M. Sodupe and R. Mas-Ballesté, *Dalton Trans.*, 2011, 40, 6868.
- 5 S. Yao and M. Driess, Acc. Chem. Res., 2012, 45, 276.
- 6 D. Schröder and H. Schwarz, Angew. Chem., Int. Ed., 1995, 34, 1973.
- 7 (a) A. W. Pierpont and T. R. Cundari, *Inorg. Chem.*, 2010, **49**, 2038; (b) Y. Shiota and K. Yoshizawa, *J. Am. Chem. Soc.*, 2000, **122**, 12317.
- 8 H. Wittmann, V. Raab, A. Schorm, J. Plackmeyer and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2001, 1937.
- 9 D. Maiti, D.-H. Lee, K. Gaoutchenova, C. Würtele, M. C. Holthausen, A. A. N. Sarjeant, J. Sundermeyer, S. Schindler and K. D. Karlin, *Angew. Chem., Int. Ed.*, 2008, 47, 82.
- (a) J. England, M. Martinho, E. R. Farquhar, J. R. Frisch, E. L. Bominaar, E. Münck and L. Que Jr., *Angew. Chem., Int. Ed.*, 2009, 48, 3622; (b) J. England, Y. Guo, E. R. Farquhar, V. G. Young Jr., E. Münck and L. Que Jr., *J. Am. Chem. Soc.*, 2010, 132, 8635.
- 11 F. F. Pfaff, S. Kundu, M. Risch, S. Pandian, F. Heims, I. Pryjomska-Ray, P. Haack, R. Metzinger, E. Bill, H. Dau, P. Comba and K. Ray, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 1711.
- 12 (a) K. Ray, S. M. Lee and L. Que, Jr., *Inorg. Chim. Acta*, 2008, 361, 1066; (b) M. R. Bukowski, K. D. Koehntop, A. Stubna, E. L. Bominaar, J. A. Halfen, E. Münck, W. Nam and L. Que, Jr., *Science*, 2005, 310, 1000.
- (a) Y.-H. Huang, J.-B. Park, M. W. W. Adams and M. K. Johnson, *Inorg. Chem.*, 1993, **32**, 375; (b) C.-M. Lee, C.-H. Chen, F.-X. Liao, C.-H. Hu and G.-H. Lee, *J. Am. Chem. Soc.*, 2010, **132**, 9256; (c) N. Yang, M. Reiher, M. Wang, J. Harmer and E. C. Duin, *J. Am. Chem. Soc.*, 2007, **129**, 11028; (d) M. Dey, J. Telser, R. C. Kunz, N. S. Lees, S. W. Ragsdale and B. M. Hoffman, *J. Am. Chem. Soc.*, 2007, **129**, 11030.
- 14 The reaction with BNAH was found to be too fast to be followed at -30 °C. Thus k_2 for BNAH was determined at -60 °C and adjusted for -30 °C by multiplying k_2 by 8. Rate is approximately considered to be doubled for every 10 °C rise in temperature.
- 15 Yields are reported based on the starting Ni(III) concentration.
- 16 (a) M. T. K. Emmons and C. G. Riordan, Acc. Chem. Res., 2007, 40, 618; (b) M. Suzuki, Acc. Chem. Res., 2007, 40, 609.