

Structural Characterization of a Hydroperoxo Nickel Complex and Its Autoxidation: Mechanism of Interconversion between Peroxo, Superoxo, and Hydroperoxo Species**

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In memory of Jack Lewis

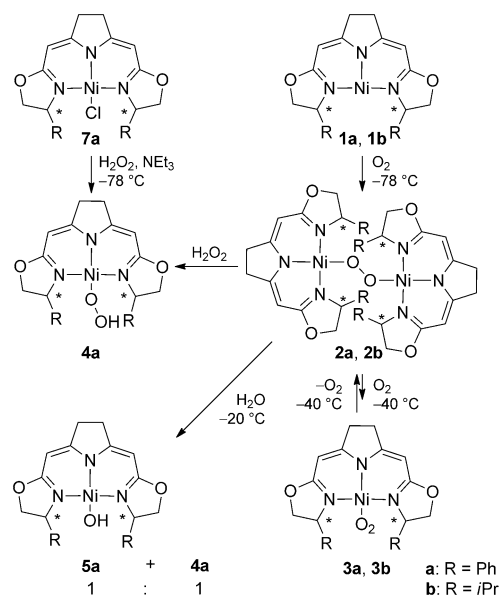
Abstract: Pincer-stabilized nickel(I) complexes readily react with molecular oxygen to form dinuclear 1,2- μ -peroxo-bridged nickel(II) complexes, which are the major components of a dynamic equilibrium with the corresponding mononuclear superoxo species. The peroxo complexes further react with hydrogen peroxide to give the corresponding nickel(II) hydroperoxides. One of these hitherto elusive species was characterized by X-ray diffraction for the first time [O–O bond length: 1.492(2) Å].

Transition-metal hydroperoxo complexes play an important role in enzymatic activation and the transport of dioxygen^[1] as well as as reactive intermediates in catalytic oxygenations.^[2] Although great efforts have been made to synthesize such metal complexes, only a limited number have been described^[3] with a handful having been structurally characterized.^[4] For over a decade, nickel hydroperoxo species have been considered to be a deactivated form of [NiFe] hydrogenase generated by oxygen.^[5] Yet, essentially no well characterized nickel hydroperoxo complexes can be found in the literature,^[6] despite recent work on the oxidation of water^[7] and on miscellaneous oxygenation reactions catalyzed by nickel,^[8] which demonstrate the potential of reactive nickel oxygen compounds.

The treatment of metal precursors with hydrogen peroxide solution, which is a suitable method for the synthesis of Fe^[9] and Cu^[4b,10] hydroperoxo complexes, usually leads to over-oxidized products with nickel precursors. Nevertheless, the latter method together with the direct reaction of low-valent nickel complexes with dioxygen has recently been used to obtain very exciting superoxo,^[11] peroxo,^[12] and oxo^[13] complexes depending on the ligand system employed. Riordan et al. observed an interesting reactivity pattern in the reaction of oxygen with the nickel(I) tmc complex. In this system, the nickel(I) fragment reacts with a molecule of oxygen most likely via a superoxo intermediate to give the

only peroxo-bridged nickel complex characterized to date.^[12a] In the presence of O₂, the peroxo complex is slowly converted into the mononuclear end-on superoxo species.^[14]

Recently, we developed a family of chiral pincer ligands, the iso-pmbox^[15] and boxmi ligands,^[16] which have displayed considerable potential in asymmetric catalysis^[17] and the stabilization of reactive T-shaped nickel(I) complexes, in particular.^[18] These iso-pmbox nickel(I) complexes **1** were found to react readily with molecular oxygen at low temperatures to form dinuclear 1,2- μ -peroxo-bridged nickel(II) complexes **2** (Scheme 1), similar to Riordan's previously described nickel tmc system.^[14] For the latter system, the



Scheme 1. Interconversions between the peroxo, superoxo and hydroperoxo complexes.

superoxo complex is the final thermodynamic product of the reaction of the Ni^I complex with an excess of O₂, whereas in our case, 1,2- μ -peroxo complex **2** was found to be the major component in a dynamic, oxygen-pressure-dependent equilibrium with what appears to be an end-on coordinated superoxo species **3**, as reported for palladium.^[19]

Peroxo complex **2a** further reacted with hydrogen peroxide to give the corresponding hydroperoxo nickel(II) complex **4a**, whereas controlled hydrolysis at low temperature gave

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a 1:1 mixture of **4a** and hydroxo complex **5a**. Hydroperoxide **4a** could also be synthesized by the direct reaction of an aqueous hydrogen peroxide solution with chlorido precursor **7a** in the presence of triethylamine and was isolated and structurally characterized by X-ray diffraction (Figure 1).^[20] A notable spectroscopic feature is the ¹H NMR chemical shift

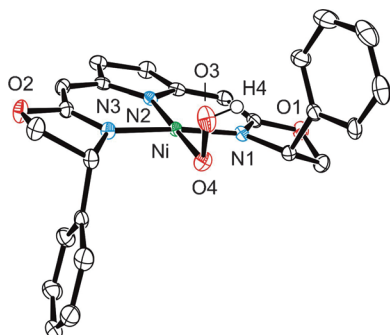


Figure 1. Molecular structure of **4a**. Hydrogen atoms were removed for clarity (except for H4). Selected bond lengths [Å] and angles [°]: O3–O4 1.492(2), Ni–O 1.8456(16), Ni–N1 1.8962(18), Ni–N3 1.8889(19), Ni–N2 1.9264(18); N3–Ni–N1 174.22(8), N1–Ni–N2 92.22(8), N3–Ni–N2 92.70(8), Ni–O3–O4 107.90(12), Ni–O3–O4–H4 –89.42(3.05).

of the hydroperoxo proton, which was observed at 3.62 ppm (CD₂Cl₂, 295 K). In accordance with the observed diamagnetism of the compound, the molecular structure determined by single-crystal X-ray structure analysis is characterized by a square-planar-coordinated nickel(II) center.

The central Ni–N2 bond [1.926(2) Å] is elongated compared to Ni–N_{oxazoline} bonds [Ni–N1: 1.896(2) Å; Ni–N3: 1.889(2) Å] leading to a slight distortion from a square-planar coordination geometry [N–Ni–N and O–Ni–N bond angles of 92.46(8)° and 87.54(8)°, respectively]. The O–O distance of 1.492(2) Å is in the range of the O–O bond lengths of other metal hydroperoxo complexes (1.397–1.549 Å)^[4b–c] and significantly longer than expected for a superoxo species^[14] (a value of 1.307 Å was calculated for end-on complex **3a**, see below). The crystallographic data were of sufficient quality to refine the position of the hydrogen atom, which was found to point towards the face of one of the phenyl substituents of the pincer ligands with a torsion angle Ni–O–O–H of –89(3)°. This stabilizing interaction was also observed in the DFT optimized structure (B3LYP/6-311G(d,p))^[21] and thus estimated to correspond to an energy difference of approximately 5 kcal mol^{–1} (ΔE , see the Supporting Information). Resonance Raman spectra of the compound that were recorded using a 632 nm or a 473 nm laser displayed only very weak bands, and neither the assignment of the Ni–O nor of the O–O vibrational modes was possible by labeling experiments using H₂¹⁸O₂. Complex **4a** was found to slowly oxygenate PPh₃ similar to other nickel oxygen compounds.^[11c]

The novel dinuclear 1,2- μ -peroxo-bridged complexes **2a** and **2b** contain two square-planar-coordinated nickel centers linked by a peroxo group and therefore exhibit diamagnetic NMR spectra, which could be fully assigned. The low-temperature FAB⁺ mass spectra revealed the corresponding

molecular ion peaks for **2a** and **2b** at m/z 916 and 780 with their characteristic isotope pattern. The UV/Vis spectrum of **2a** displayed an absorption band at 531 nm (ϵ = 5380 M^{–1} cm^{–1}) similar to the spectral band found for the nickel tmc system (465 nm), which was assigned to a peroxo $\rightarrow$ Ni charge transfer (CT) excitation.^[12a] DFT modeling (B3LYP/6-311G(d,p))^[21] allowed for a detailed picture of the structures of these compounds. Two energetically low-lying conformers (ΔG = 3.5 kcal mol^{–1}) that differ in the sense of the Ni–O–O–Ni torsion (125.6° and –112.1° for **2b**) with a calculated transition barrier of 8.2 kcal mol^{–1} were found (Figure 2). Owing to the chirality of the pincer ligands, these rotamers around the O–O bond are diastereomeric and therefore expected to display different properties. Indeed,

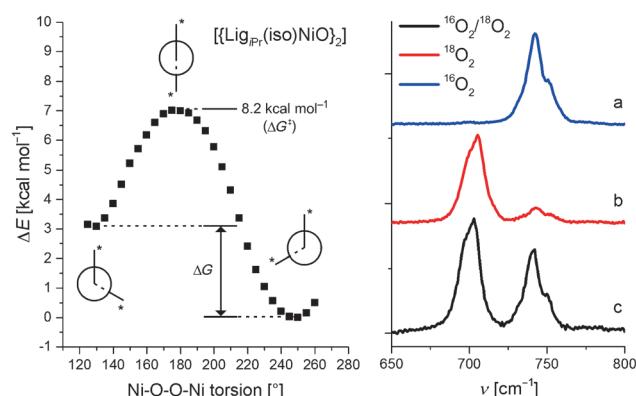


Figure 2. Left: Relaxed PES scan obtained by varying the Ni–O–O–Ni torsion angle in **2b** and ΔG values of both minimum-energy conformers and the transition state as determined by DFT calculations on the B3LYP/6-311G(d,p) level of theory. Right: Solid-state resonance Raman spectra (λ = 632 nm) of **2b** (blue), [¹⁸O]-**2b** obtained after stirring **2b** under an ¹⁸O₂ atmosphere (red), and a mixture of **2b** and [¹⁸O]-**2b** obtained by stirring **2b** under an ¹⁶O₂/¹⁸O₂ atmosphere. Additional signals that would correspond to the mixed species [¹⁶O, ¹⁸O]-**2b** were not observed (black).

a closer inspection of the resonance Raman spectra (λ = 632 nm) recorded for microcrystalline samples of **2b** revealed a shoulder at 752 cm^{–1} associated with the intense ν (O–O) band at 742 cm^{–1} for **2b**. The latter was shifted to 706 cm^{–1} in the ¹⁸O-labeled compound ([¹⁸O]-**2b**) with a corresponding shoulder at 699 cm^{–1} (Figure 2). Chemical exchange between both conformers is rapid on the NMR timescale, and spectral patterns remained in the high-temperature limit upon cooling to 180 K in THF for both the ¹H and ¹³C NMR spectra, which is consistent with the computed activation barrier of less than 10 kcal mol^{–1} (see below). The assignment of **2a** as a peroxo complex was corroborated by the resonance Raman band at 742 cm^{–1} (**2b**), which differs substantially from values observed for superoxo nickel complexes (971–1131 cm^{–1}).^[11] In comparison with the previously reported 1,2- μ -peroxo nickel(II) tmc complex, the O–O resonance Raman vibrational bands for **2a** and **2b** were found at lower wavenumbers.^[12a]

As mentioned above, the dinuclear 1,2- μ -peroxo-bridged complexes **2a** and **2b** are the major components of a dynamic

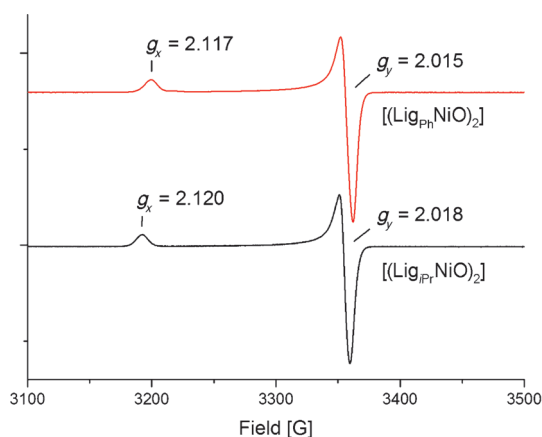


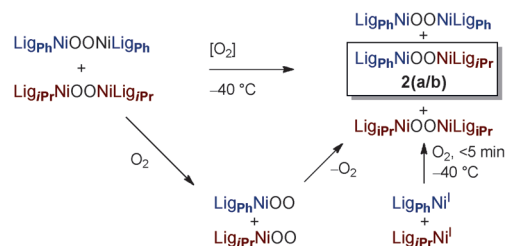
Figure 3. EPR spectra of **3a** (red) and **3b** (black), which are the minor components of the oxygen-dependent equilibria with the EPR-silent **2a** and **2b** in frozen toluene at 120 K.

equilibrium with the corresponding superoxo species **3a** and **3b**. In the presence of O_2 , an axially symmetric EPR signal was observed in frozen toluene at 120 K (X-band, $g_{||} = 2.117$, $g_{\perp} = 2.015$ for **3a**; Figure 3), indicating a partially ligand-located spin density as would be expected for a superoxo complex.^[11c,19,22]

Quantitative analyses using 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as the internal standard indicated the presence of approximately 2% of such a species (**3b**) under an O_2 pressure of 8 bar. This species was found to be depleted and reformed reversibly upon removal of or pressurization with oxygen at $-20^\circ C$ (see the Supporting Information). DFT modeling (B3LYP/6-311G(d,p)) of **3a** for the $S = 1/2$ and $S = 3/2$ spin states established two isoenergetic isomers [$\Delta G(\text{low-high}) = 1.8 \text{ kcal mol}^{-1}$], a low-spin end-on and a high-spin side-on superoxo complex, respectively. The g_{iso} values computed for both structures [2.023 ($S = 1/2$) and 2.078 ($S = 3/2$)] would be consistent with the experimentally observed value of 2.050 (**3a**), whereas the other characteristics of the EPR spectra displayed in Figure 3 (sharp resonances and the absence of half-field transitions with $g \approx 4$) appear to favor the presence of a species with a doublet ground state.

Labeling experiments were performed to clarify the process involved in the equilibrium between superoxo complexes **3** and dinuclear 1,2- μ -peroxo complexes **2** (Scheme 1). In a first experiment, $^{16}O_2$ peroxo complex **2b** was stirred under an atmosphere of $^{18}O_2$, which led to a complete exchange of the dioxygen moiety at $-15^\circ C$ (Figure 2b). Repetition of this experiment with a mixture of $^{16}O_2$ and $^{18}O_2$ gave the ^{18}O , ^{18}O - and ^{16}O , ^{16}O -labeled peroxo complexes in the corresponding ratio, but no ^{16}O , ^{18}O -labeled species (Figure 2c).^[23]

Furthermore, cross-over experiments were carried out at $-40^\circ C$ by mixing two solutions that contained dinuclear 1,2- μ -peroxo complexes with differently substituted pincer ligands (Ph and *i*Pr; Scheme 2). In the absence of dioxygen, the symmetric complexes proved to be remarkably stable, and the formation of the cross-over product **2(a/b)** occurred only very slowly (on a timescale of days, Scheme 2). However, under an atmosphere of dioxygen, the exchange of complex

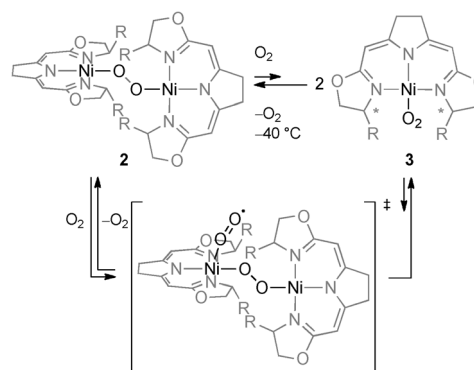


Scheme 2. Processes involved in the formation of scrambled product **2(a/b)**.

fragments was enhanced dramatically and steady-state concentrations of the nonsymmetric peroxo complexes **2(a/b)** were reached within 20 hours (see the Supporting Information).

The formation of the mixed product was confirmed by LT-MS (FAB⁺) in addition to the 1H NMR spectral analysis. The symmetric and nonsymmetric complexes were formed at the same steady-state ratio immediately after subjecting a mixture of **1a** and **1b** to an atmosphere of oxygen at $-40^\circ C$ (Scheme 2).

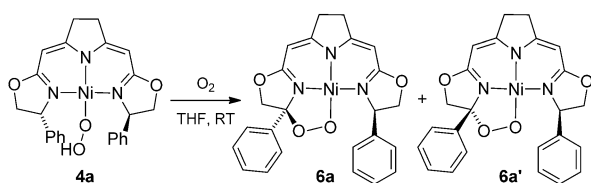
These observations are consistent with an associative mechanism for the interconversion of 1,2- μ -peroxo complex **2** and superoxo species **3** (Scheme 3). In such a scenario, the coordination of a molecule of dioxygen initiates the cleavage of the Ni– O_2 bond in complexes **2a** and **2b**, thereby reversibly generating two molecules of nickel superoxo species **3**. In the



Scheme 3. Mechanistic proposal for the interconversion between **2** and **3**.

case of two superoxo complexes bearing differently substituted pincer ligands, the reverse reaction then leads to the scrambled 1,2- μ -peroxo complex **2(a/b)** along with the symmetric dinuclear species **2a** and **2b**. In the absence of oxygen, on the other hand, no fragmentation takes place, and consequently, no nonsymmetric 1,2- μ -peroxo complexes are formed when the solutions of the two different peroxo complexes are combined, as was observed.

Hydroperoxo species **4a** was found to be thermally unstable, and its decomposition under inert atmosphere led to a mixture of different unidentified compounds. However, when **4a** was kept at room temperature in the presence of O_2 , it was cleanly converted into the two diastereomers **6a** and **6a'** (Scheme 4).^[24]



Scheme 4. Aerobic autoxidation of hydroperoxo complex **4a**.

These alkylperoxometallacycles are most likely formed by radical C–H activation at the benzylic position of the ligand, which thereby loses its stereochemical information, leading to the inversion of the chiral center in **6a'**. The latter species is the major product of the reaction and could be isolated and characterized by X-ray diffraction (Figure 4).^[20]

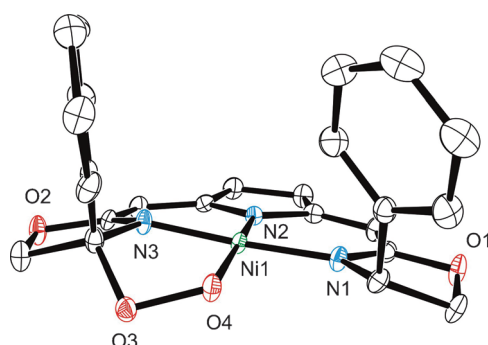
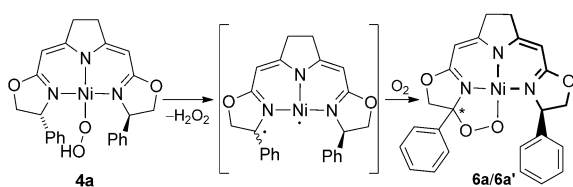


Figure 4. Molecular structure of **6a'**. Only one of the two independent molecules is shown. Hydrogen atoms were removed for clarity. Selected bond lengths [Å] and angles [°]: O3–O4 1.505(3), Ni–O4 1.850(3), Ni–N1 1.857(3), Ni–N3 1.803(3), Ni–N2 1.885(3); N3–Ni–N1 171.72(14), N1–Ni–O4 90.08(12), N3–Ni–O4 84.65(12), Ni–O4–O3 108.24(17).

The mechanism that we propose for the decomposition involves homolytic Ni–O and C–H bond scission and subsequent oxygen insertion leading to product **4a** (Scheme 5). In such a scenario, the hydroperoxo ligand



Scheme 5. Mechanistic proposal for the aerobic autoxidation of **4a**.

itself does not act as an oxidant, but as a hydrogen atom acceptor. The fact that the analogous reactivity was observed for hydroxo complex **5a**, which was found to slowly react to **6a/6a'** in the presence of oxygen at room temperature, supports the proposed mechanism.

In comparison to previously described systems, the bis(oxazolinyl)methylidenpyrrolidinato ligands uniquely stabilize the peroxo complexes with respect to further oxidation of either the metal center or the dioxygen moiety.

This allowed the systematic synthesis of hydroperoxo complex **4a**, the investigation of its interconversion with 1,2-μ-peroxo nickel(II) complex **2a** and transient superoxo complex **3a**, as well as the autoxidation to an alkylperoxometallacycle.

Keywords: autoxidation · hydroperoxides · nickel · peroxides · pincer ligand

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- [1] a) L. Que, Y. Dong, *Acc. Chem. Res.* **1996**, *29*, 190–196; b) L. Que, R. Y. N. Ho, *Chem. Rev.* **1996**, *96*, 2607–2624; 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) A. Decker, E. I. Solomon, *Curr. Opin. Chem. Biol.* **2005**, *9*, 152–163.
- [2] a) B. Meunier, *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*, Springer, Berlin, **2000**; b) K. Chen, L. Que, *J. Am. Chem. Soc.* **2001**, *123*, 6327–6337; c) C. Limberg, *Angew. Chem.* **2003**, *115*, 6112–6136; d) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, *Chem. Rev.* **2004**, *104*, 939–986; e) R. Mas-Ballesté, L. Que, *J. Am. Chem. Soc.* **2007**, *129*, 15964–15972; f) J. L. Fillol, Z. Codolà, I. Garcia-Bosch, L. Gómez, J. J. Pla, M. Costas, *Nat. Chem.* **2011**, *3*, 807–813; g) W. N. Olloo, A. J. Fielding, L. Que, *J. Am. Chem. Soc.* **2013**, *135*, 6438–6441; h) K. Ray, F. F. Pfaff, B. Wang, W. Nam, *J. Am. Chem. Soc.* **2014**, *136*, 13942–13958.
- [3] a) K. D. Karlin, P. Ghosh, R. W. Cruse, A. Farooq, Y. Gultneh, R. R. Jacobson, N. J. Blackburn, R. W. Strange, J. Zubieta, *J. Am. Chem. Soc.* **1988**, *110*, 6769–6780; b) P. Chen, K. Fujisawa, E. I. Solomon, *J. Am. Chem. Soc.* **2000**, *122*, 10177–10193; c) G. Roelfes, V. Vrajmasu, K. Chen, R. Y. N. Ho, J.-U. Rohde, C. Zondervan, R. M. la Crois, E. P. Schudde, M. Lutz, A. L. Spek, R. Hage, B. L. Feringa, E. Münck, L. Que, *Inorg. Chem.* **2003**, *42*, 2639–2653; d) M. M. Konnick, I. A. Guzei, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 10212–10213; e) L. Li, A. A. Narducci Sarjeant, M. A. Vance, L. N. Zakharov, A. L. Rheingold, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2005**, *127*, 15360–15361; f) T. Kitagawa, A. Dey, P. Lugo-Mas, J. B. Benedict, W. Kaminsky, E. Solomon, J. A. Kovacs, *J. Am. Chem. Soc.* **2006**, *128*, 14448–14449; g) D. Maiti, H. R. Lucas, A. A. N. Sarjeant, K. D. Karlin, *J. Am. Chem. Soc.* **2007**, *129*, 6998–6999; h) J. Cho, S. Jeon, S. A. Wilson, L. V. Liu, E. A. Kang, J. J. Braymer, M. H. Lim, B. Hedman, K. O. Hodgson, J. S. Valentine, E. I. Solomon, W. Nam, *Nature* **2011**, *478*, 502–505; i) F. Li, K. K. Meier, M. A. Cranswick, M. Chakrabarti, K. M. Van Heuvelen, E. Münck, L. Que, *J. Am. Chem. Soc.* **2011**, *133*, 7256–7259; j) L. V. Liu, S. Hong, J. Cho, W. Nam, E. I. Solomon, *J. Am. Chem. Soc.* **2013**, *135*, 3286–3299; k) H. So, Y. J. Park, K.-B. Cho, Y.-M. Lee, M. S. Seo, J. Cho, R. Sarangi, W. Nam, *J. Am. Chem. Soc.* **2014**, *136*, 12229–12232.
- [4] a) D. Carmona, M. P. Lamata, J. Ferrer, J. Modrego, M. Perales, F. J. Lahoz, R. Atencio, L. A. Oro, *J. Chem. Soc. Chem. Commun.* **1994**, 575–576; b) A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa, H. Einaga, *Angew. Chem. Int. Ed.* **1998**, *37*, 798–799; *Angew. Chem.* **1998**, *110*, 874–875; c) Y. Takahashi, M. Hashimoto, S. Hikichi, M. Akita, Y. Moro-oka, *Angew. Chem. Int. Ed.* **1999**, *38*, 3074–3077; *Angew. Chem.* **1999**, *111*, 3259–3262; d) D. D. Wick, K. I. Goldberg, *J. Am. Chem. Soc.* **1999**, *121*, 11900–11901; e) I. A. Guzei, A. Bakac, *Inorg. Chem.* **2001**, *40*, 2390–2393; f) M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammer, *Angew. Chem. Int. Ed.* **2005**, *44*, 6947–6951; *Angew. Chem.* **2005**, *117*, 7107–7111; g) M. C. Denney, N. A. Smythe, K. L. Cetto, R. A. Kemp, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 2508–2509; h) G. Katona, P. Carpentier,

- V. Nivière, P. Amara, V. Adam, J. Ohana, N. Tsanov, D. Bourgeois, *Science* **2007**, *316*, 449–453; i) D. Barats, G. Leitus, R. Popovitz-Biro, L. J. W. Shimon, R. Neumann, *Angew. Chem. Int. Ed.* **2008**, *47*, 9908–9912; *Angew. Chem.* **2008**, *120*, 10056–10060; j) R. Dragoş-Adrian, A. W. Joseph, L. H. David, B. Manfred, *Nat. Commun.* **2013**, *4*, 2167.
- [5] a) A. Abou Hamdan, B. Burlat, O. Gutiérrez-Sanz, P.-P. Liebgott, C. Baffert, A. L. De Lacey, M. Rousset, B. Guigliarelli, C. Léger, S. Dementin, *Nat. Chem. Biol.* **2013**, *9*, 15–17; b) W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, *Chem. Rev.* **2014**, *114*, 4081–4148.
- [6] a) R. Zell, H. Sigel, *Helv. Chim. Acta* **1966**, *49*, 870–875; b) T. Dhanasekaran, H. Prakash, P. Natarajan, *J. Photochem. Photobiol. A* **2001**, *141*, 17–24.
- [7] a) P. Du, R. Eisenberg, *Energy Environ. Sci.* **2012**, *5*, 6012–6021; b) A. Singh, L. Spiccia, *Coord. Chem. Rev.* **2013**, *257*, 2607–2622; c) D. Wang, G. Ghirlanda, J. P. Allen, *J. Am. Chem. Soc.* **2014**, *136*, 10198–10201.
- [8] a) S. Otsuka, A. Nakamura, Y. Tatsuno, M. Miki, *J. Am. Chem. Soc.* **1972**, *94*, 3761–3767; b) H. Yoon, T. R. Wagler, K. J. O'Connor, C. J. Burrows, *J. Am. Chem. Soc.* **1990**, *112*, 4568–4570; c) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329–2364; d) T. Nagataki, Y. Tachi, S. Itoh, *Chem. Commun.* **2006**, 4016–4018; e) K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.* **2008**, *252*, 1420–1450; f) A. Gunay, K. H. Theopold, *Chem. Rev.* **2010**, *110*, 1060–1081.
- [9] a) A. J. Simaan, F. Banse, J.-J. Girerd, K. Wieghardt, E. Bill, *Inorg. Chem.* **2001**, *40*, 6538–6540; b) V. Bolland, F. Banse, E. Anxolabéhère-Mallart, M. Ghiladi, T. A. Mattioli, C. Philouze, G. Blondin, J.-J. Girerd, *Inorg. Chem.* **2003**, *42*, 2470–2477; c) M. Martinho, F. Banse, J. Sainton, C. Philouze, R. Guillot, G. Blain, P. Dorlet, S. Lecomte, J.-J. Girerd, *Inorg. Chem.* **2007**, *46*, 1709–1717; d) M. Martinho, P. Dorlet, E. Rivière, A. Thibon, C. Ribal, F. Banse, J.-J. Girerd, *Chem. Eur. J.* **2008**, *14*, 3182–3188.
- [10] a) M. Koda, T. Kita, I. Miura, N. Nakayama, T. Kawata, K. Kano, S. Hirota, *J. Am. Chem. Soc.* **2001**, *123*, 7715–7716; b) T. Fujii, A. Naito, S. Yamaguchi, A. Wada, Y. Funahashi, K. Jitsukawa, S. Nagatomo, T. Kitagawa, H. Masuda, *Chem. Commun.* **2003**, 2700–2701; c) K. Itoh, H. Hayashi, H. Furutachi, T. Matsumoto, S. Nagatomo, T. Tosha, S. Terada, S. Fujinami, M. Suzuki, T. Kitagawa, *J. Am. Chem. Soc.* **2005**, *127*, 5212–5223; d) S. Kim, C. Saracini, M. A. Siegler, N. Driehko, K. D. Karlin, *Inorg. Chem.* **2012**, *51*, 12603–12605.
- [11] 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) K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer, C. G. Riordan, *Inorg. Chem.* **2004**, *43*, 3324–3326; c) S. Yao, E. Bill, C. Milsman, K. Wieghardt, M. Driess, *Angew. Chem. Int. Ed.* **2008**, *47*, 7110–7113; *Angew. Chem.* **2008**, *120*, 7218–7221.
- [12] a) M. T. Kieber-Emmons, R. Schenker, G. P. A. Yap, T. C. Brunold, C. G. Riordan, *Angew. Chem.* **2004**, *116*, 6884–6886; b) S. Yao, Y. Xiong, M. Vogt, H. Grützmacher, C. Herwig, C. Limberg, M. Driess, *Angew. Chem. Int. Ed.* **2009**, *48*, 8107–8110; *Angew. Chem.* **2009**, *121*, 8251–8254; c) J. Cho, R. Sarangi, J. Annaraj, S. Y. Kim, M. Kubo, T. Ogura, E. I. Solomon, W. Nam, *Nat. Chem.* **2009**, *1*, 568–572; d) S. Hikichi, H. Okuda, Y. Ohzu, M. Akita, *Angew. Chem. Int. Ed.* **2009**, *48*, 188–191; *Angew. Chem.* **2009**, *121*, 194–197.
- [13] a) S. Hikichi, M. Yoshizawa, Y. Sasakura, M. Akita, Y. Moro-oka, *J. Am. Chem. Soc.* **1998**, *120*, 10567–10568; b) B. S. Mandimutsira, J. L. Yamarik, T. C. Brunold, W. Gu, S. P. Cramer, C. G. Riordan, *J. Am. Chem. Soc.* **2001**, *123*, 9194–9195.
- [14] M. T. Kieber-Emmons, J. Annaraj, M. S. Seo, K. M. Van Heuvelen, T. Tosha, T. Kitagawa, T. C. Brunold, W. Nam, C. G. Riordan, *J. Am. Chem. Soc.* **2006**, *128*, 14230–14231.
- [15] a) C. Mazet, L. H. Gade, *Chem. Eur. J.* **2003**, *9*, 1759–1767; b) F. Konrad, J. Lloret Fillol, C. Rettenmeier, H. Wadepohl, L. H. Gade, *Eur. J. Inorg. Chem.* **2009**, 4950–4961.
- [16] Q.-H. Deng, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2011**, *17*, 14922–14928.
- [17] Q.-H. Deng, R. L. Melen, L. H. Gade, *Acc. Chem. Res.* **2014**, *47*, 3162.
- [18] C. Rettenmeier, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2014**, *20*, 9657–9665.
- [19] R. Huacuja, D. J. Graham, C. M. Fafard, C.-H. Chen, B. M. Foxman, D. E. Herbert, G. Alliger, C. M. Thomas, O. V. Ozerov, *J. Am. Chem. Soc.* **2011**, *133*, 3820–3823.
- [20] CCDC 1041693 (**4a**) and 1041694 (**6a'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [21] a) A. J. H. Wachtters, *J. Chem. Phys.* **1970**, *52*, 1033–1036; b) P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377–4384; c) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; d) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648; e) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; f) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; g) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206; h) K. Raghavachari, G. W. Trucks, *J. Chem. Phys.* **1989**, *91*, 1062–1065; i) R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206–1216; j) M. P. McGrath, L. Radom, *J. Chem. Phys.* **1991**, *94*, 511–516; k) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; l) L. A. Curtiss, M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning, L. Radom, *J. Chem. Phys.* **1995**, *103*, 6104–6113; m) J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys.* **1997**, *107*, 5016–5021.
- [22] a) R. D. Jones, D. A. Summerville, F. Basolo, *Chem. Rev.* **1979**, *79*, 139–179; b) T. D. Smith, J. R. Pilbrow, *Coord. Chem. Rev.* **1981**, *39*, 295–383; c) B. Ramdhanie, J. Telser, A. Caneschi, L. N. Zakharov, A. L. Rheingold, D. P. Goldberg, *J. Am. Chem. Soc.* **2004**, *126*, 2515–2525.
- [23] D. Maiti, H. C. Fry, J. S. Woertink, M. A. Vance, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2007**, *129*, 264–265.
- [24] J. Cho, H. Furutachi, S. Fujinami, M. Suzuki, *Angew. Chem. Int. Ed.* **2004**, *43*, 3300–3303; *Angew. Chem.* **2004**, *116*, 3362–3365.

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