

Dioxygen Activation

A New Domain of Reactivity for High-Valent Dinuclear [M(μ-O)₂M'] Complexes in Oxidation Reactions

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Abstract: The strikingly different reactivity of a series of homo- and heterodinuclear $[(M^{III})(\mu-O)_2(M^{III})']^{2+}$ (M = Ni;M' = Fe, Co, Ni and M = M' = Co) complexes with β -diketiminate ligands in electrophilic and nucleophilic oxidation reactions is reported, and can be correlated to the spectroscopic features of the $[(M^{III})(\mu-O)_2(M^{III})']^{2+}$ core. In particular, the unprecedented nucleophilic reactivity of the symmetric $[Ni^{III-}(\mu-O)_2Ni^{III}]^{2+}$ complex and the decay of the asymmetric $[Ni^{III}(\mu-O)_2Co^{III}]^{2+}$ core through aromatic hydroxylation reactions represent a new domain for high-valent bis(μ -oxido)dimetal reactivity.

The synthesis and investigation of heterobimetallic bis(μ -oxido) complexes with $[M(\mu-O)_2M']^{n+}$ cores are of particular interest for modeling the structures and reactivities of active sites in chemically related metalloenzymes containing two different metal ions.^[1] Moreover, such studies can lead to the discovery of novel species^[2] exhibiting reactivity patterns different from their homodinuclear counterparts. The illustrative example (Scheme 1 inset) is the recently reported $[L^1Ni(\mu-O)_2Cu(MeAN)]^+$ (**1**; $L^1 = [HC(CMeNC_6H_3(Pr)_2)_2]$; MeAN = *N*,*N*,*N'*,*N''*,*N''*-pentamethyl dipropylenetriamine)^[3] complex, which, in sharp contrast to the presence of electrophilic oxido groups in symmetric $[M_2(\mu-O)_2]^{n+}$ (M = Ni, Co, Fe and Mn) analogues,^[4] possesses nucleophilic oxido ligands and deformylates aldehydes.

The unprecedented nucleophilic reactivity of **1** may be attributed to the asymmetric nature of the $bis(\mu-oxido)dime-$ tal core. Alternatively, the nature of the ancillary ligand may

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Scheme 1. Generation and self-decay of the heterodinuclear $[Ni^{||}(\mu - O)_2 Co^{||}]^{2+}$ complex **2** and its homodinuclear $[M^{|||}(\mu - O)_2 M^{|||}]^{2+}$ analogues **3** and **4** (M = Ni, Co). Inset: The structure of the previously reported^[3] asymmetric bis(μ -oxido)Ni^{|||}Cu^{|||} compound with nucleophilic oxido ligands.

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also play a vital role; notably, **1** possesses a dangling amine group, which may induce the change in reactivity, leading to the observed nucleophilicity. Understanding the origin of the nucleophilicity in **1**, therefore, warrants a systematic comparison of the reactivity of a series of symmetric and asymmetric dinuclear bis(μ -oxido) complexes involving similar ancillary ligands, which preferably lack any dangling basic/nucleophilic group that could affect the reactivity.

In our continuous effort to uncover structure–reactivity relationships of dinuclear metal–dioxygen intermediates, we now demonstrate spectroscopic trapping of a series of homoand heterodinuclear $[M^{III}(\mu-O)_2(M^{III})']^{2+}$ (M = Ni; M' = Co, Ni and M = M' = Co) complexes of β -diketiminate ligands. A comparison of the reactivity of these complexes in various oxidation reactions reveals a distinct reactivity pattern dependent on the spectroscopic properties of the bis(μ -oxido)dimetal core. Furthermore, the fully symmetric [L¹Ni^{III}-

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[[]L¹Ni^{II}O₂] -78 [(C7H8)CoL3] 2 [L¹Ni^{II}O₂] -78 °<u>C</u> toluene 'nΑ΄ Àr [(C7H8)(NiL1)2] 3 [L¹Ni^{II}O₂] -78 °<u>C</u> toluene A [(C₇H₈)FeL³] not isolated $Ar = 2,6^{-i}Pr_2C_6H_3$ 5 .78 °℃ [(C₇H₈)CoL³] + O₂ toluene

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 $(\mu$ -O)₂Ni^{III}L¹]²⁺ (**3**) complex demonstrates a nucleophilic property, which is in contrast to the observed electrophilic behavior of all homodinuclear bis(μ -oxido) cores reported to date.^[4] This, together with the self-decay of the heterodinuclear [L¹Ni(μ -O)₂CoL³] species **2** (L³ = [HC(CHNC₆H₃-([†]Pr)₂)₂]) by an unprecedented hydroxylation-mediated 1,3migration of an aryl nitrogen atom, represents a novel domain for high-valent bis(μ -oxido)dimetal reactivity.

Reaction of equimolar amounts of the isolable Ni^{II}superoxo complex [L¹NiO₂]^[5] with the Co^I precursor [L³Co- $(C_7H_8)^{[6]}$ at -78 °C in toluene leads to immediate formation of the intermediate 2 (Figure 1A and Scheme 1) with absorption maxima λ_{max} (ϵ ; M^{-1} cm⁻¹) centered at 576 (1651) and 834 nm (2700). Notably, the near-IR absorption feature of 2 at 834 nm is blue-shifted relative to 1 (Table 1).^[3] Moreover, the thermal stability of 2 ($t_{1/2} = 245$ s in toluene at -50 °C) is significantly lower than that of 1 ($t_{1/2} = 900$ s in CH₂Cl₂ at -50°C).^[3] The electrospray mass spectrum (ESI-MS; Figure S1 in the Supporting Information) of 2 exhibits the most prominent peak at m/z = 955.4904, with a mass and isotope distribution pattern corresponding to $[L^1Ni(\mu-O)_2CoL^3]$. The rRaman spectrum of 2 using 413 nm laser excitation supports the $[Ni(\mu-O)_2Co]^{2+}$ assignment of **2** (Figure 1 C). The band at $v = 634 \text{ cm}^{-1} \text{ of } 2^{-16} \text{O}^{16} \text{O} \text{ shifts down to } 600 \text{ cm}^{-1} [v(2^{-18} \text{O}^{18} \text{O})]$ in the corresponding ¹⁸O₂-substituted complex **2**. The X-band EPR spectrum (Figure S2) shows a rhombic S = 1/2 signal



Figure 1. A) Absorption spectra of **2–4** at -78 °C in toluene. B– D) rRaman spectra (413 nm excitation) of **2–4** in toluene at -90 °C: B) **3**-¹⁶**O**₂ in [D₈]toluene (solid trace) and **3**-¹⁸**O**₂ in toluene (dash-dotted trace). C) **2**-¹⁶**O**₂ in [D₈]toluene (solid trace) and **2**-¹⁸**O**₂ in toluene (dash-dotted trace). D) **4**-¹⁶**O**₂ in [D₈]toluene (solid trace) and **4**-¹⁸**O**₂ in [D₈]toluene (dash-dotted trace). See also Figure S22.

Table 1: Spectroscopic and reactivity properties of 1-4.

	<i>t</i> _{1/2} [s]	$\nu_{(M-O)} \\ [cm^{-1}]$	λ_{\max} [nm]	$k_{2(PhCOCI)}^{[d]}$ [×10 ⁻⁴ m ⁻¹ s ⁻¹]	$k_{2(CHD)}^{[d]}$ [×10 ⁻⁴ m ⁻¹ s ⁻¹]
1 ^[a]	900 ^[b,c]	625	895	550	5
2	245 ^[b,d]	634	834	240	338
3	4200 ^[b,d]	632	853	305	97
4	stable ^[d]	647	582	52.2	60.9

[a] Ref. [3]. [b] -50 °C. [c] CH₂Cl₂. [d] Toluene.

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(75% yield based on spin-quantification) with $g_x = 1.98$, $g_y = 2.12$, $g_z = 2.76$, and observable ⁵⁹Co hyperfine splitting at g_x and g_z . The electronic structure of **2** is thus best represented as $[L^1Ni^{III}(\mu-O)_2Co^{III}L^3]$, where antiferromagnetic coupling between Ni^{III} (3d⁷; S = 1/2) and Co^{III} (3d⁶; S = 1) ions leads to an S = 1/2 ground state.

X-ray absorption spectroscopy (XAS) studies were performed at the Ni and Co K-edges to directly probe the metal oxidation states in 2. Notably, the Ni K-edge spectrum of 2 is virtually indistinguishable to that reported previously for 1 (where the oxidation state of Ni has been unambiguously determined to be +3; Figure S3A),^[3] although the pre-edge is slightly more intense and sharper in 2 (Figure S3A inset). The higher pre-edge intensity (Table S1) of 2 (6.6 units) relative to 1 (5.4 units) at the Ni K-edge may originate from the larger deviation from the ideal square (sq) planar geometry^[7] at the Ni center of **2** (dihedral angle $\theta = 172^\circ$; Table S2) relative to 1 ($\theta = 178.1^\circ$; Table S2) in the optimized structures derived from density functional theory (DFT) calculations. In addition, a comparison of the Co K-edge spectrum of 2 with that of $[L^{3}Co(C_{7}H_{8})]$ shows a blue-shift in the edge energy (Figure S3B) together with an upshift (from 7709 eV in $[L^{3}Co(C_{7}H_{8})]$ to 7709.8 eV in 2; Table S1) and intensity increase in the pre-edge peak of 2 (16.9 units) vs. [L³Co- (C_7H_8)] (6.2 units). This strongly suggests a change in Co oxidation from +1 to +3 during the conversion of [L³Co- (C_7H_8)] to 2. Thus XAS data also are consistent with a $[L^1Ni^{III}(\mu-O)_2Co^{III}L^3]$ assignment for 2.

Extended X-ray absorption fine structure (EXAFS) analyses revealed further structural details. For **2** a shell of four N/O scatterers at 1.86 Å is obtained from Ni EXAFS (Table S3–1, Figure S4A), which is in excellent agreement with the DFT calculated average Ni–N/O distance of 1.88 Å for **2**. In addition, a peak at 2.78 Å corresponding to the Co scatterer is observed, thereby strongly supporting the presence of a heterodinuclear Ni…Co center in **2**. Further support for a Ni…Co separation of ca. 2.78 Å comes from Co EXAFS (Table S3–2, Figure S4B), which detects a Ni scatterer at 2.72 Å. In addition the best fit of the Co EXAFS can be obtained with four N/O scatterers at 1.82 Å. Notably, the DFT calculated average Co–N/O and Co–Ni distances of 1.87 and 2.77 Å, respectively, are again in reasonable agreement with the experiment.

The $[L^1Ni^{III}(\mu-O)_2Ni^{III}L^1]^{2+}$ (3) and $[L^3Co^{III}(\mu-O)_2 Co^{III}L^{3}]^{2+}$ (4) complexes, which are homometallic (symmetric) analogues of 2, have also been synthesized by reacting $[L^1Ni^{II}O_2]$ with $[(L^1Ni)_2(C_7H_8)]$ and $[L^3Co(C_7H_8)]$ with dioxygen, respectively, in toluene at -78 °C (Scheme 1). Table 1 lists rRaman, absorption spectra and $t_{1/2}$ data for 1–4. Notably, complex 4 is unique in the series with a significantly blueshifted absorption band (Figure 1 a), higher energy metal-oxo $(v_{(M-O)})$ stretching vibration frequency and higher stability relative to 1-3. Thermal stability of 4 at room temperature enabled its isolation as dark blue crystals in 80% yields; the X-ray crystal structure (Scheme 1, Figure S5, Table S4) consists of two L³Co–O fragments (Co–O distance of 1.786(1) Å) related by inversion and separated by Co - Co = 2.6715(5) Å. The short metal-metal and metal-oxo distances found in 4 compare favorably to those in related "diamond core" structures.^[4] A solution magnetic moment (μ_{eff} , C₆D₆, 298 K) of 2.55 µB for 4 suggests population of a higher spin state at elevated temperatures. The Ni sites in 3 are, however, antiferromagnetically coupled at 298 K stabilizing the singlet (S=0) state. DFT calculations provide some insight into the differences in the magnetic properties of 4 and 3. The parallel spin coupling in 4 can be ascribed to the slightly folded Co_2O_2 structure, in which two cobalt planes make an angle (ϕ) of 178° (calculated $\phi = 171.7^{\circ}$; Table S2) and initiates ferromagnetic interaction due to loss of orbital overlap. In contrast, a nearly planar Ni₂O₂ structure ($\phi = 179.8^{\circ}$; Table S2) is predicted by DFT for 3, which may explain the strong antiferromagnetism leading to an S = 0 ground state. Similar diminution of antiferromagnetic couplings due to a folded Co₂O₂ core have been observed earlier.^[4g,h] Moreover, the Co-Co separation of 2.6715 Å (DFT: 2.66 Å) in 4 is significantly shorter than the DFT calculated Ni-Ni separation of 2.77 Å (Table S9) for 3. This reduction favors the direct interaction, increasing also the ferromagnetic contribution.

Table 1 (see also Figure S6 and Table S5) also compares the kinetic data for the four complexes with respect to their rates of nucleophilic and electrophilic reactions. In one set of experiments, the nucleophilic oxidation of benzoyl chloride (PhCOCl) by **2–4** was investigated in toluene solutions, resulting in about 80% yield of benzoic acid (Figure 2 and



Figure 2. Reactivity studies of complexes **2–4**. Yields are given relative to the metal complexes.

Figure S7). Comparison of the reaction rates with that reported previously for $\mathbf{1}^{[3]}$ reveals a reactivity order of $\mathbf{1}$ > 3 > 2 > 4. This trend is also found to be valid for reactions with 2-phenylpropionaldehyde (2-PPA), to form acetophenone and formate (Figure 2, Figure S8, Table S5). Furthermore, when the logarithms of the second order rate constants $(\log k_2)$ were plotted versus λ_{max} or $v_{(M-O)}$, an excellent linear correlation was observed (Figure 3), demonstrating that λ_{max} or $v_{(M-O)}$ reflect the relative nucleophilicities of the bis(μ oxido)dimetal units in 1-4. The reactivity of 2 and 3 was further investigated using a series of para substituted benzaldehydes (Figure S9). Positive ρ values of 1.33 and 2.26 in the Hammett plots were obtained for 2 and 3, respectively (Figure S10), which, when compared to the ρ value of 2.83 reported previously for $\mathbf{1}$,^[3] again supports the nucleophilicity order of 1 > 3 > 2. These results demonstrate that the bis(μ -oxido)dimetal cores of 2 and 3 are active nucleophilic oxidants, similar to that reported previously for **1**.



Figure 3. Linear correlation of the logarithms of $k_{2(PhCOCI)}$ vs. λ_{max} (filled circles and dashed line) or $v_{(M-O)}$ (filled squares and solid line) of the bis(μ -oxido)dimetal units in **1-4**.

For comparison, the hydrogen atom abstraction (HAT) rates of 1-4 were also investigated with 1,4-cyclohexadiene (CHD) and substituted phenols. They follow the reactivity order 2 > 3 > 4 > 1 (Figure S11, Table S5). Interestingly, the linear correlation observed for the $\log k_2$ values for PhCOCl oxidation versus λ_{max} or $\nu_{(M\text{-}O)}$ values does not extend to HAT rates of 1-4 (Figure S12B, Table S5). While the respective rate values associated with 1-3 for the oxidation of CHD follow a linear correlation similar to that observed for PhCOCl, 4 deviates significantly from this pattern and exhibits HAT rates that are few orders of magnitude below what are predicted by these lines. Clearly, the nucleophilic and electrophilic oxidation reactions are not governed by a common set of factors. Based on the observed HAT rates 2 can be considered as the most electrophilic of all the complexes 1-4. Replacement of the Co atom in $[L^1Ni(\mu-O)_2CoL^3]$ with Fe further increases the electrophilicity of the bis(µ-oxido)dimetal core to an extent that the $[L^1Ni(\mu-O)_2FeL^3]$ (5) complex becomes extremely unstable against self-decay by an intramolecular ligand hydroxylation pathway (Scheme 1). Thus, monitoring of the reaction of $[L^1Ni^{II}O_2]$ with $[L^3Fe(C_7H_8)]^{[8]}$ in toluene by means of UV/Vis spectroscopy (Figure S13) at -90 °C did not lead to the observation of any intermediate species. The molecular structure of the resultant product 6 (>90 % vields: Figure S14, Table S7) reveals the presence of β -diketiminatoligated Ni^{II} and Fe^{II} centers^[9] in sq planar and tetrahedral (T_d) coordination environments, respectively. The two metals are bridged by µ-hydroxido (Figure S15) and µ-alkoxido units derived from C-H activation of an isopropyl (*i*Pr) group belonging to the β -diketiminato-ligand bound at the nickel site.

In contrast, decay of a solution of **2** led to the hydroxylation of one of the arene residues in the major (>75% yield relative to **2**) decay product **7** (Scheme 1, Figure S16, Table S7). The X-ray crystal structure analysis of **7** shows a heterodinuclear complex, with β -diketiminato-ligated Ni^{II} and Co^{II} centers in sq planar and T_d coordination environments, respectively. The oxidation state assignments are based on XANES studies (Figure S17); the Ni K-edge of **7** is nearidentical to that of the [L¹Ni^{II}O₂] precursor (consistent with sq planar Ni^{II}) and the Co K-edge of **7** reveals an edge energy intermediate between the Co¹ precursor, [L³Co(C₇H₈)], and **2** (consistent with Co^{II}). Notably, the metal atoms are bridged

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by μ-hydroxido and μ-phenoxido units (Figure S18) derived from hydroxylation induced 1,3-migration of the aryl nitrogen atom of the β-diketiminato ligand bound at the Ni site. The conversion of **2** to **7** is therefore reminiscent of the NIH shift reaction suggested for enzymatic aromatic hydroxylations.^[10] This involves 1,2-migration of an aryl-X (X = H, CH₃ or Cl) atom during rearomatization of an oxygenated intermediate (Figure S19A). The cleavage of the aromatic C–N bond during the conversion of **2** to **7** similarly suggests a decay mechanism (Scheme 2; also supported by DFT, Figure S19B)



Scheme 2. Self-decay of 2 by an electrophilic aromatic hydroxylation mechanism to form 7.

involving intramolecular electrophilic attack of the $[\mathrm{Ni}^{\mathrm{III}}(\mu\text{-}$ $O_{2}Co^{III}^{2+}$ core on an aromatic ring of the Ni-bound β diketiminato ligand leading to a cationic intermediate; the rearomatization process now involves cleavage of a C-N bond to form a Ni-nitrene species,^[11] which then effects Hatom abstraction from an isopropyl iPr group to yield 7. Thermal decay of a solution of 3 led to the isolation of crystals of the previously reported^[5] bis(hydroxido)dinickel(II) species in 15% yield (Figure S20). The formation of such doubly protonated reduced species has been previously observed in reactions of basic bis(u-oxido)dimetal cores^[12] with protons and is consistent with the presence of nucleophilic oxido ligands in 3. In contrast to the metastable properties of 2, 3 and 5, complex 4 is considerably more stable at 25 °C, and no significant decay was observed at this temperature over a period of 24 hours.

DFT calculations of 1–5 provided further insight into the different reactivity patterns of the homo and heterodinuclear bis(μ -oxido) cores. The geometry and the ground spin state of the complexes 1–4 are nicely reproduced in the calculation (Tables S8, S9). A quintet (S = 2) ground-state is predicted for 5 akin to 4, which is consistent with the predicted short Ni–Fe distance of 2.69 Å and a folded NiO₂Fe core ($\phi = 166.7^\circ$; Table S2). Furthermore, the calculated charge densities (Q_O) on the bridging O-atoms of 1–4 when plotted against the log k_2 for the PhCOCl oxidation reactions also fall on a line very similar to the linear correlation obtained from log k_2 vs. λ_{max} and $\nu_{(M-O)}$ plots (Figure S12A). This correlation is however not valid for electrophilic reactions. For example, the room temperature stability of 4 contrasts with the facile decay of 5 by an electrophilic intramolecular ligand hydroxylation step

(that prevents its isolation even at low temperatures), although identical $Q_{\rm O}$ values have been calculated in both cases (Table S10). For comparison calculations were also performed on the hypothetical [L¹Ni(μ -O)₂CuL³] complex (**8**)^[13] that unlike **1** contains a β -diketiminate ligand attached to the Cu center. A trend of increasing $Q_{\rm O}$ and decreasing covalency of the [Ni(μ -O)₂M] (M = Fe, Co, Ni, Cu) cores with increasing atomic weight of M is now obvious, as also evidenced by the decreasing M–O Mayer bond order and increasing Ni–M distances (Tables S9 and S10).

In conclusion, this study presents the first example showing that a fully symmetric $bis(\mu$ -oxido)dimetal complex 3 can act as a nucleophilic oxidant in addition to demonstrating the typical HAT reactivities. 3 reveals a characteristic absorption band in the near infrared (IR) region, which acts as a spectroscopic marker for nucleophilic bis(µ-oxido)dimetal cores. Furthermore, the nature of the second metal ion (M) is shown to systematically modulate the electronic structure and reactivity of a series of β -diketiminate [Ni(μ -O)₂M]²⁺ complexes with M = Fe, Co Ni, and Cu. The combined experimental and computational evidences herein indicate that the decreasing nucleophlicity of the oxygen atoms in the order $[Ni^{III}(\mu - O)_2 Cu^{III}]^{2+} > [Ni^{III}(\mu - O)_2 Ni^{III}]^{2+} > [Ni^{III}(\mu - O)_2 Ni^$ $O)_2 Co^{III}]^{2+} > [Ni^{III}(\mu - O)_2 Fe^{III}]^{2+}$ correlates to the increasing covalency of the M-O bonds, owing to an increase in the extent of $O \rightarrow M \pi$ -backdonation (Figure S21). For M = Fe(d⁵) with half-filled $\pi^*(xz, yz)$ levels O \rightarrow M π -backdonation is maximum with the most electrophilic oxygen atoms. The additional electrons in the $Co(d^6)$, $Ni(d^7)$ and $Cu(d^8)$ complexes subsequently fill up the $\pi^*(xz, yz)$ levels and reduce the $O \rightarrow M$ π -backdonation to an extent that there is essentially no multiple bond character present in the [Ni^{III}- $(\mu$ -O)₂Cu^{III}]²⁺ complex. Additionally, with increasing oxido nucleophilicity, the energy of the oxygen based highest



Figure 4. Nature of the HOMOs and LUMOs and their absolute energies as obtained from DFT calculations on a series of $[L^1Ni(\mu-O)_2ML^3]$ (M = Fe, Co, Ni and Cu) complexes. ΔE represents the HOMO-LUMO energy gap.

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occupied molecular orbital (HOMO) is found to increase, thereby decreasing its energy separation from the metal/ β -diketiminate ligand-based lowest unoccupied molecular orbital (LUMO) in the order $[Ni^{III}(\mu-O)_2Fe^{III}]^{2+} > [Ni^{III}(\mu-O)_2Co^{III}]^{2+} > [Ni^{III}(\mu-O)_2Ni^{III}]^{2+} > [Ni^{III}(\mu-O)_2Cu^{III}]^{2+}$ (Figure 4). We tentatively assign the near IR absorption band of the $[Ni(\mu-O)_2M]^{2+}$ complexes to originate from this HOMO \rightarrow LUMO transition, which may explain the red shift of this band with increasing nucleophilicity of the oxido groups. Therefore, the present study highlights the importance of the interplay between metal centers and local environment in governing key physical and chemical properties of biologically relevant dinuclear metal–dioxygen intermediates.

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- a) V. R. Kaila, M. I. Verkhovsky, M. Wikström, *Chem. Rev.* 2010, 110, 7062–7081; b) J. P. Klinman, *Chem. Rev.* 1996, 96, 2541– 2562; c) Y. Matoba, T. Kumagai, A. Yamamoto, H. Yoshitsu, M. Sugiyama, *J. Biol. Chem.* 2006, 281, 8981–8990.
- [2] a) I. Garcia-Bosch, X. Ribas, M. Costas, *Eur. J. Inorg. Chem.* 2012, 179–187; b) N. P. Mankad, *Chem. Eur. J.* 2016, 22, 5822– 5829.
- [3] S. Kundu, F. F. Pfaff, E. Miceli, I. Zaharieva, C. Herwig, S. Yao, E. R. Farquhar, U. Kuhlmann, E. Bill, P. Hildebrandt, Angew.

Chem. Int. Ed. 2013, 52, 5622–5626; Angew. Chem. 2013, 125, 5732–5736.

- [4] a) M. T. Kieber-Emmons, C. G. Riordan, Acc. Chem. Res. 2007, 40, 618-625; b) 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; c) S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, Y. Moro-oka, M. Akita, Chem. Eur. J. 2001, 7, 5011-5028; d) C. E. Tinberg, S. J. Lippard, Acc. Chem. Res. 2011, 44, 280-288; e) 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; f) C. Citek, S. Herres-Pawlis, T. D. P. Stack, Acc. Chem. Res. 2015, 48, 2424-2433; g) P. L. Larsen, T. J. Parolin, D. R. Powell, M. P. Hendrich, A. S. Borovik, Angew. Chem. Int. Ed. 2003, 42, 85-89; Angew. Chem. 2003, 115, 89-93; h) X. Dai, P. Kapoor, T. H. Warren, J. Am. Chem. Soc. 2004, 126, 4798-4799; j) L. Que, Jr., W. B. Tolman, Angew. Chem. Int. Ed. 2002, 41, 1114-1137; Angew. Chem. 2002, 114, 1160-1185.
- [5] S. Yao, E. Bill, C. Milsmann, K. Wieghardt, M. Driess, Angew. Chem. Int. Ed. 2008, 47, 7110–7113; Angew. Chem. 2008, 120, 7218–7221.
- [6] S. Yao, N. Lindenmaier, Y. Xiong, S. Inoue, T. Szilvási, M. Adelhardt, J. Sutter, K. Meyer, M. Driess, *Angew. Chem. Int. Ed.* **2015**, *54*, 1250–1254; *Angew. Chem.* **2015**, *127*, 1266–1270.
- [7] S. E. Shadle, J. E. Penner-Hahn, H. J. Schugaryl, B. Hedman, K. Hodgson, E. I. Solomon, J. Am. Chem. Soc. 1993, 115, 767–776.
- [8] S. Yao, T. Szilvási, N. Lindenmaier, Y. Xiong, S. Inoue, M. Adelhardt, J. Sutter, K. Meyer, M. Driess, *Chem. Commun.* 2015, 51, 6153–6156.
- [9] Assignment based on a previous study, see S. Yao, C. Herwig, Y. Xiong, A. Company, E. Bill, C. Limberg, M. Driess, Angew. Chem. Int. Ed. 2010, 49, 7054–7058; Angew. Chem. 2010, 122, 7208–7212.
- [10] a) G. Guroff, J. W. Daly, D. M. Jerina, J. Renson, B. Witkop, S. Udenfriend, *Science* **1967**, *157*, 1524–1530; b) A. Bassan, M. R. A. Blomberg, P. E. M. Siegbahn, *Chem. Eur. J.* **2003**, *9*, 4055–4067.
- [11] K. Ray, F. Heims, F. F. Pfaff, Eur. J. Inorg. Chem. 2013, 3784– 3807.
- [12] a) N. W. Aboelella, J. T. York, A. M. Reynolds, K. Fujita, C. R. Kinsinger, C. J. Cramer, C. G. Riordan, W. B. Tolman, *Chem. Commun.* **2004**, 1716–1717; b) J. T. York, A. Llobet, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2007**, *129*, 7990–7999.
- [13] 8 could not be synthesized owing to the lack of [L³Cu¹] precursor complex (see C. Shimokawa, Y. Tachi, N. Nishiwaki, M. Ariga, S. Itoh, *Bull. Chem. Soc. Jpn.* 2006, 79, 118–125).

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Communications



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Dioxygen Activation

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A New Domain of Reactivity for High-Valent Dinuclear $[M(\mu-O)_2M']$ Complexes in Oxidation Reactions



Unified in differences: The decisive effect of the second metal ion on the electronic structure and reactivity (from nucleophilic to electrophilic) of a series of $[Ni(\mu - O)_2 M]^{2+}$ complexes in oxidation reactions is reported. The observations underline the importance of subtle electronic differences in the reactivity of biologically relevant metal-dioxygen intermediates.

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