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# Multi-electron Activation of Dioxygen on Zirconium(IV) to Give an Unprecedented Bisperoxo Complex

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In nature multi-electron redox processes are carried out by complex multicomponent reaction centers as in cytochrome *c* oxidase ($O_2$ fixation) and photosystem II ($O_2$ evolution). Chemists often harness the diversity of transition metals to carry out multi-electron reactions.[1] In this study, we report the synthesis and structural characterization of an unprecedented $\eta^2$-bisperoxo $Zr^{IV}$ coordination complex supported by two bulky bidentate diimine ligands. The source of the peroxo ligands is oxygen, which we propose is activated on $Zr^{IV}$ with the necessary four electrons (two per $O_2$) originating from the ligand. The recent work of Wieghardt, Chirik, and Heyduk on redox active ligands is worthy of special mention.[2,3]

As often-postulated oxidants in industrial and biological processes, transition metal peroxo complexes are of special interest, particularly when formed from molecular oxygen because of the push for "green" oxidations.[4] Formation of peroxo complexes from reaction of early transition metals in low oxidation states with dioxygen is rare because their oxo complexes are stable and tend to form readily.[5] Despite the growing number of heterogeneous zirconium catalysts that utilize hydrogen peroxide in selective oxidations,[6] virtually nothing is known about the peroxo complexes of zirconium.[7−9]

A recent report on the reduction of glyoxal-bis(2,6-diisopropylphenyl)imine to afford the first boryl anion[10] prompted us to investigate this diamido ligand for the preparation and potential stabilization of low valent $Zr^{II}$.[11] Reaction of reduced diamido ligand with $ZrCl_4(THF)_2$ afforded the tetrahedral bis(diamido) $Zr^{IV}$ cleanly (Scheme 1). The molecular structure of **1** (Figure 1) shows a tetrahedral geometry around zirconium (∠N(21)−Zr−N(14) = 116.02°), $Zr-N_{av}$ distance of 2.068 Å, $C_{bridge}-N_{av}$ = 1.405 Å, C(12)−C(13) = 1.37 Å, and C(22)−C(23) = 1.36 Å. The olefinic $\pi$-bonds appear to exert some electron donation into zirconium. The average $Zr-C(sp^2)$ distance is 2.513 Å, which is shorter than van der Waals interactions. Another explanation may involve $\pi$ donation from the nitrogen lone pair, which folds the ligand forcing the C═C double bond closer to the metal.[12] Nonetheless, the crystal structure is in full agreement with a $Zr^{4+}$ bis(diamido) formulation.[13]

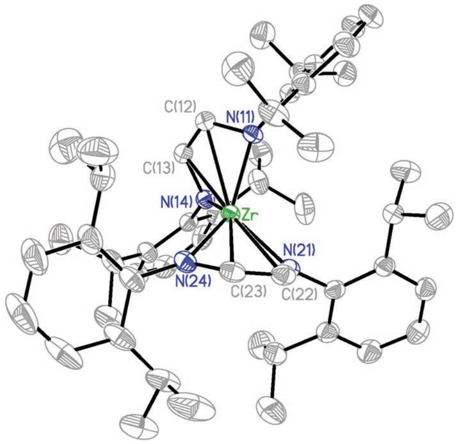


***Figure 1.*** Crystal structure of **1**: 50% ellipsoids, hydrogens omitted for clarity. Selected bond lengths in angstrom and angles in degrees: Zr−N21 = 2.0485(19), Zr−N24 = 2.091(2), Zr−C22 = 2.512(2), Zr−C23 = 2.532(3), N21−C22 = 1.405(3), C22−C23 = 1.359(4), N21−Zr−N11 = 117.08(7), N21−Zr−N24 = 86.77(8), and N21−C22−C23 = 122.1(2).

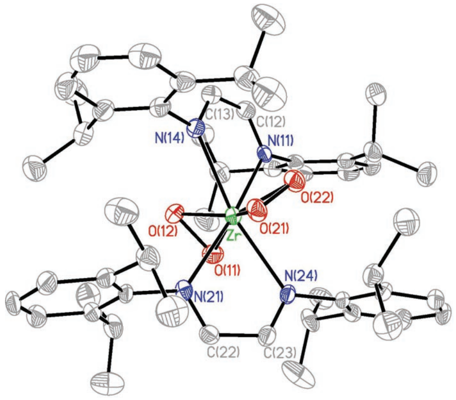
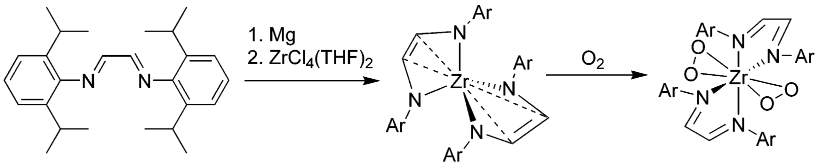


***Figure 2.*** Crystal structure of $\eta^2$-bisperoxo zirconium(IV), **2**: 50% ellipsoids, hydrogens and solvent molecules omitted. Selected bond lengths in angstrom and angles in degrees: Zr−O21 = 2.038(3), Zr−O22 = 2.034(3), Zr−N24 = 2.433(4), Zr−N21 = 2.438(4), O21−O22 = 1.504(4), N24−C23 = 1.271(6), C22−C23 = 1.478(6), N11−Zr−N24 = 114.01(12), O21−Zr−N24 = 79.57(13), and N24−C23−C22 = 119.6(4).

Compound **1** reacts with dry dioxygen to give the $\eta^2$-bisperoxo $Zr^{IV}$ complex **2** (Scheme 1). The crystal structure of **2** is shown in Figure 2. The geometry around zirconium is octahedral with each peroxo ligand counted as occupying a single coordination site. For example, the angles ∠N(11)−Zr-center of O(11)−O(12) = 80.89°, ∠N(11)−Zr−N(14) = 68.82°, ∠center of O(11)−O(12)−Zr-center of O(21)−O(22) = 179.55°. The key bond lengths of the molecule are as follows: O−O = 1.508(av) Å, $Zr-O_{peroxo}$ = 2.034(av) Å, $Zr-N_{av}$ = 2.44 Å, $N-C_{bridge}$ = 1.265(av) Å, C(12)−C(13) = 1.47

***Scheme 1***



**1**

**2**

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Å, and C(22)−C(23) = 1.48 Å.[14] All of this data is in agreement with a $Zr^{IV}$ bisperoxo bis(diimine) complex. Hence, dioxygen is reduced to peroxo and the ligand is oxidized from diamido to diimine, a net four-electron process! The reaction of **1** with $O_2$ to give **2** is quite remarkable because it constitutes a rare activation of dioxygen by high valent $d^0$ transition metal.[15] While **2** is the first structurally characterized bisperoxo complex of Zr, bisperoxo complexes of other heavy transition metals including Mo, W, and Re are plentiful.[16]

The two peroxo ligands in compound **2** do not lie in the same plane. Instead they are virtually orthogonal (perpendicular) toward each other with a torsion angle O(11)−O(12)−O(21)−O(22) of 78°, constituting the first example of this geometry for any bisperoxo metal complex. The principal interaction of a $\eta^2$-peroxo (or oxygen) ligand with transition-metal *d*-orbitals involves the degenerate $\pi^*$ orbitals on peroxo and the metal $\pi$-orbitals.[17] The orthogonal geometry of the peroxo ligands on zirconium in **2** reduces the competition for metal *d*-orbitals and thus maximizes the bonding (Supporting Information). It is remarkable that complex **2** is stable enough to be isolated and characterized because it contains strictly $\sigma$-donor diimine ligands. Most likely the bulky isopropylphenyl substiuents on the ligand provide significant shielding which protects the peroxo groups.

In addition to structural characterization, compounds **1** and **2** were characterized by proton and carbon NMR as well as by infrared spectroscopy. The bis(diamido) species **1** is diamagnetic and displays in the $^1H$ NMR spectrum two almost overlapping doublets centered at 5.86 and 5.88 ppm (due to the dissymmetry of the molecule). These correspond to the protons of the two ethylenic bridges. A coupling constant $^3J_{H-H}$ of about 15 Hz is in good agreement with a *cis*-orientation of the protons. In $^{13}C$ NMR the ethylenic carbons show two resonances at 110.3 and 110.4 ppm, which further confirms carbon−carbon double bonds. Upon reaction with dry oxygen and formation of **2**, the signals at 5.86 and 5.88 ppm completely disappear and a new resonance at 8.21 ppm becomes evident. This piece of data along with the appearance of a new peak at 163.5 ppm in the $^{13}C$ NMR of **2** suggests the diimine character gained by the aromatic ligand, as opposed to the *cis*-ethylenic features present in **1**.[18] The infrared spectra provide additional evidence for the diimine character of the two aromatic ligands in the bisperoxo compound **2.** A very characteristic medium to strong intensity absorption band at 1618 $cm^{-1}$ proves the presence of a C═N group in the molecule. This absorption band is absent from the IR spectrum of **1**. Instead the characteristic C═C stretching vibration at 1670 $cm^{-1}$, along with the HC═ bending at 800 $cm^{-1}$ and the cis HC═CH out-of-plane bending at 680 $cm^{-1}$ is observed for the bis(diamido) complex **1**.

While strongly reducing (low-valent) organometallic complexes of zirconium are known to bind/activate dinitrogen,[19] **1** does not react with $N_2$, as all manipulations were carried out under $N_2$ atmosphere. The electron deficient and highly oxophilic Zr in **1** may form a weak adduct with dioxygen. Subsequently $O_2$ on zirconium is reduced by electron transfer from the diamido ligand to afford the peroxo complex. An alternative mechanism would be the interaction of $O_2$ directly with the ligands followed by peroxide coordination to Zr.[20] Attempts to prepare the potential monoperoxo intermediate under limiting $O_2$ were not successful. The only tractable product was bisperoxo **2**. Under inert atmosphere in the glovebox, bisperoxo **2** in the solid-state reverts back to **1** over a period of 7−10 days.[21]

Further spectroscopic, reactivity, and kinetic studies aimed at better understanding the formation of $Zr^{IV}$ bis(peroxide) are in progress in our laboratory. Also, we are testing the glyoxal-bis-(2,6-diisopropylphenyl)imine ligand for generation of other amido species of heavy transition metals.

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**Supporting Information Available:** Materials and methods, schematic MO diagram, and X-ray tables and figures, complete X-ray data for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Also when a solution of **2** is degassed under vacuum, it reverts to complex **1**. The details of this reaction to yield $O_2$ and complex **1** in the solid state as well as in solution will be reported elsewhere.

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