

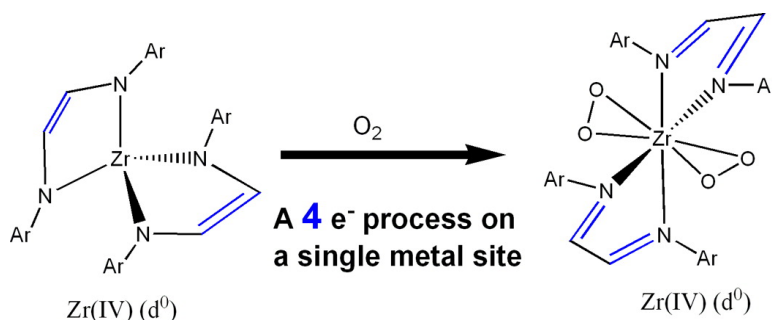
Communication

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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 (O₂ fixation) and photosystem II (O₂ 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 η^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 O₂) 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 anion¹⁰ 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 ZrCl₄(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 (\angle 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 π -bonds appear to exert some electron donation into zirconium. The average Zr–C(sp²) distance is 2.513 Å, which is shorter than van der Waals interactions. Another explanation may involve π 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 Zr⁴⁺ bis(diamido) formulation.¹³

Compound **1** reacts with dry dioxygen to give the η^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 \angle N(11)–Zr–center of O(11)–O(12) = 80.89°, \angle N(11)–Zr–N(14) = 68.82°, \angle center of O(11)–O(12)–Zr–center

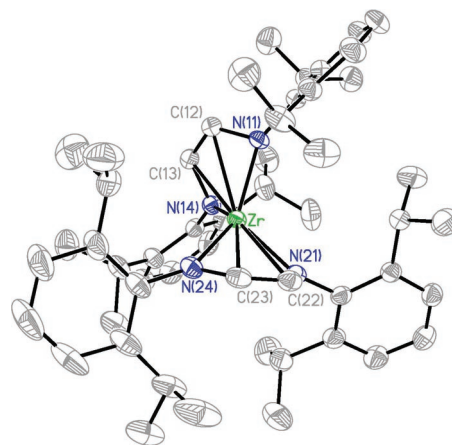


Figure 1. Crystal structure of **1**: 50% ellipsoids, hydrogens omitted for clarity. Selected bond lengths in angstrom and angles in degrees: Zr–N21 = 2.0485(19), Zr–N24 = 2.091(2), Zr–N2 = 2.512(2), Zr–C23 = 2.532(3), N21–C22 = 1.405(3), C22–C23 = 1.359(4), N21–Zr–N11 = 117.08(7), N21–Zr–N24 = 86.77(8), and N21–C22–C23 = 122.1(2).

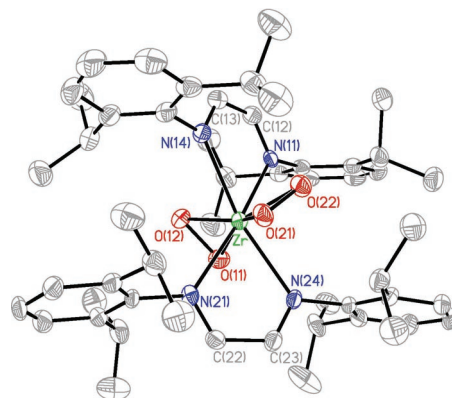
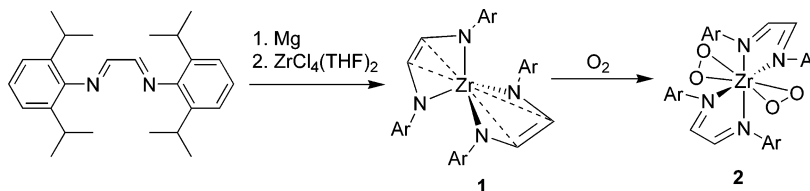


Figure 2. Crystal structure of η^2 -bisperoxo zirconium(IV), **2**: 50% ellipsoids, hydrogens and solvent molecules omitted. Selected bond lengths in angstrom and angles in degrees: Zr–O21 = 2.038(3), Zr–O22 = 2.034(3), Zr–N24 = 2.433(4), Zr–N21 = 2.438(4), O21–O22 = 1.504(4), N24–C23 = 1.271(6), C22–C23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

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



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 O₂ 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 η²-peroxo (or oxygen) ligand with transition-metal *d*-orbitals involves the degenerate π* orbitals on peroxo and the metal π-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 σ-donor diimine ligands. Most likely the bulky isopropylphenyl substituents 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 ¹³C 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 ¹³C 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=C 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 N₂, as all manipulations were carried out under N₂ atmosphere. The electron deficient and highly oxophilic Zr in **1** may form a weak adduct with dioxygen. Subsequently O₂ on zirconium is reduced by electron transfer from the diamido ligand to afford the peroxo complex. An alternative mechanism would be the interaction of O₂ directly with the ligands followed by peroxide coordination to Zr.²⁰ Attempts to prepare the potential monoperoxo intermediate under limiting O₂ 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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