

A Square-Planar Tetracoordinate Oxygen-Containing Ti_4O_{17} Cluster Stabilized by Two 1,1'-Ferrocenedicarboxylato Ligands**

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Abstract: By introducing steric constraints into molecular compounds, it is possible to achieve atypical coordination geometries for the elements. Herein, we demonstrate that a titanium-oxo cluster $[\{\text{Ti}_4(\mu_4\text{-O})(\mu_2\text{-O})_2(\text{OPr})_6(\text{fdc})_2\}]$, which possesses a unique edge-sharing Ti_4O_{17} octahedron tetramer core, is stabilized by the constraints produced by two orthogonal 1,1'-ferrocenedicarboxylato (fdc) ligands. As a result, a square-planar tetracoordinate oxygen (ptO) can be generated. The bonding pattern of this unusual anti-van't Hoff/Le Bel oxygen, which has been probed by theoretical calculations, can be described by two horizontally σ -bonded $2p_x$ and $2p_y$ orbitals along with one perpendicular nonbonded $2p_z$ orbital. While the two ferrocene units are separated spatially by the ptO with an $\text{Fe}\cdots\text{Fe}$ separation of 10.4 Å, electronic communication between them still takes place as revealed by the cluster's two distinct one-electron electrochemical oxidation processes.

One of the most promising approaches for constructing unusual coordination geometries^[1] in molecular compounds and coordination polymers is the incorporation of steric constraints by means of multivalent ligands, which overcome the inherent preferences for normal bonding geometries. Oxygen—one of the most abundant elements on earth—is capable of forming ubiquitous oxides in which most O atoms are tetrahedrally tetracoordinated. In contrast, planar tetracoordinate oxygen (ptO), like planar tetracoordinate carbon^[2] and other nonmetal atoms,^[3] are considered to be energetically highly unfavorable. As a result, such a planar tetracoordinate geometry is difficult to achieve within unconstrained molecules on account of the fact that this anti-van't Hoff/Le Bel configuration^[4] contradicts valence shell electron pair repulsion (VSEPR) and classical molecular

orbital theories. Despite considerable efforts towards the synthesis of ptO species, only a very few examples^[5] have been reported in the literature. One salient feature in most of these species is that four MOL_5 octahedra (M = octahedrally coordinated metal, L = ligand) are held together in a face-sharing manner to form a square-planar M_4OL_{12} octahedron tetramer, in the center of which a ptO atom is embedded (see the Supporting Information, SI, Figure S1). In this type of arrangement, where the ptO atom acts as a 4-fold axial ligand shared by four octahedra, a total of 13 ligands is required. From a geometric point of view, however, it is easy to envisage that four MOL_5 octahedra can be arranged such that, by sharing two adjacent equatorial edges and one corner O atom with each other, a square-planar M_4OL_{16} octahedron tetramer is built up (SI, Figure S1). The central ptO atom is therefore achieved through an edge-sharing arrangement. In contrast to the case of the face-sharing arrangement, the ptO atom in this case acts as a 4-fold equatorial ligand shared by four octahedra, and a total of 17 ligands is required. The pursuit of the ptO species within an edge-sharing arrangement continues to be challenging, presumably because its compact structure cannot provide enough steric constraints for the stabilization of the ptO atom. The key to success in stabilizing the ptO atom in the edge-sharing arrangement is to provide additional steric constraints to the unshared eight axial ligands. 1,1'-Ferrocenedicarboxylic acid (fdcH_2) is a unique pivoted tetradentate ligand^[6] which is ideal for fulfilling this requirement on account of its ability to provide two carboxylato ligands simultaneously to coordinate with four in-plane metal ions. Additionally, ferrocene (Fc) and its derivatives are widely employed as redox-active species on account of the desirable stability of the Fc/Fc^+ redox couple. The Fc moiety has been integrated into numerous elaborate bridged bis-^[7]

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[**] We thank Amy A. Sarjeant and Charlotte L. Stern for carrying out single-crystal and powder XRD analysis. In the Stoddart laboratory, this research is part (Project 34-944) of the Joint Center of Excellence in Integrated Nano-Systems (JCIN) at King Abdulaziz

City of Science and Technology (KACST) and Northwestern University (NU). The authors would like to thank both KACST and NU for their continued support of this research. J.L. acknowledges the Chinese Scholarship Council for providing financial support during her stay at Northwestern University. M.F., X.L., and G.C.S. were supported by the Non-Equilibrium Energy Research Center (NERC), which is an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Basic Energy Sciences (DOE-BES) under Award DESC0000989. D.C. acknowledges the National Science Foundation for a Graduate Research Fellowship and the International Institute for Nanotechnology (IIN) at NU for a Ryan Fellowship. S.T.S. thanks the IIN at NU for an IIN Postdoctoral Fellowship.

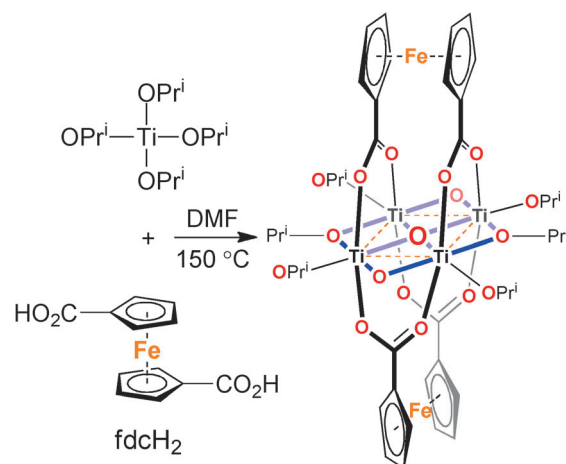


Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201402603>.

and multi-Fc^[8] systems wherein the electronic communication between Fc units can be finely tuned. Continuing research of long-range electronic communication between redox sites in molecular systems is vital not only to understanding chemical and biological processes but also for the design of molecular electronic devices. A bis-Fc system constructed from two fdc^{2-} groups with a square-planar $\{\text{M}_4(\mu_4\text{-O})\}$ species as a linker is appealing because both Fc moieties would be connected through metal ions, while, at the same time, isolated spatially by a ptO atom.

Herein, we present an experimental and computational study on a Ti-O cluster $[\{\text{Ti}_4(\mu_4\text{-O})(\mu_2\text{-O})_2\}(\text{OPr}^i)_6(\text{fdc})_2]$ (**1**, Scheme 1). A ptO atom is embedded in the core of this finite molecular cluster—a square-planar Ti_4O_{17} octahedron tetramer—which is composed of four edge-sharing TiO_6 octahedra by cooperative stabilization of two fdc^{2-} ligands. The electrochemical behavior of **1** has been studied in relation to the electronic interaction between the two Fc sites separated by over 10 Å by this unusual ptO atom.

The solvothermal reaction (Scheme 1) of $\text{Ti}(\text{OPr}^i)_4$ and fdcH_2 in DMF at 150 °C gives orange single-crystals of **1**. The cluster **1** is modestly soluble and stable for over 12 h in solvents such as DMF, CHCl_3 , and CH_2Cl_2 at room temperature. The ^1H NMR spectrum of **1** shows two sets of signals



Scheme 1. Synthesis and structural formula of **1**, $[\{\text{Ti}_4(\mu_4\text{-O})(\mu_2\text{-O})_2\}(\text{OPr}^i)_6(\text{fdc})_2]$.

for protons in the two Fc groups (**Fc** and **Fc'**; Figure 1 a). This observation suggests that the two Fc groups have different relative orientations with respect to the OPr^i groups. In agreement with this observation, the ^{13}C NMR spectrum (SI, Figure S2) also shows two sets of resonances for the two fdc^{2-}

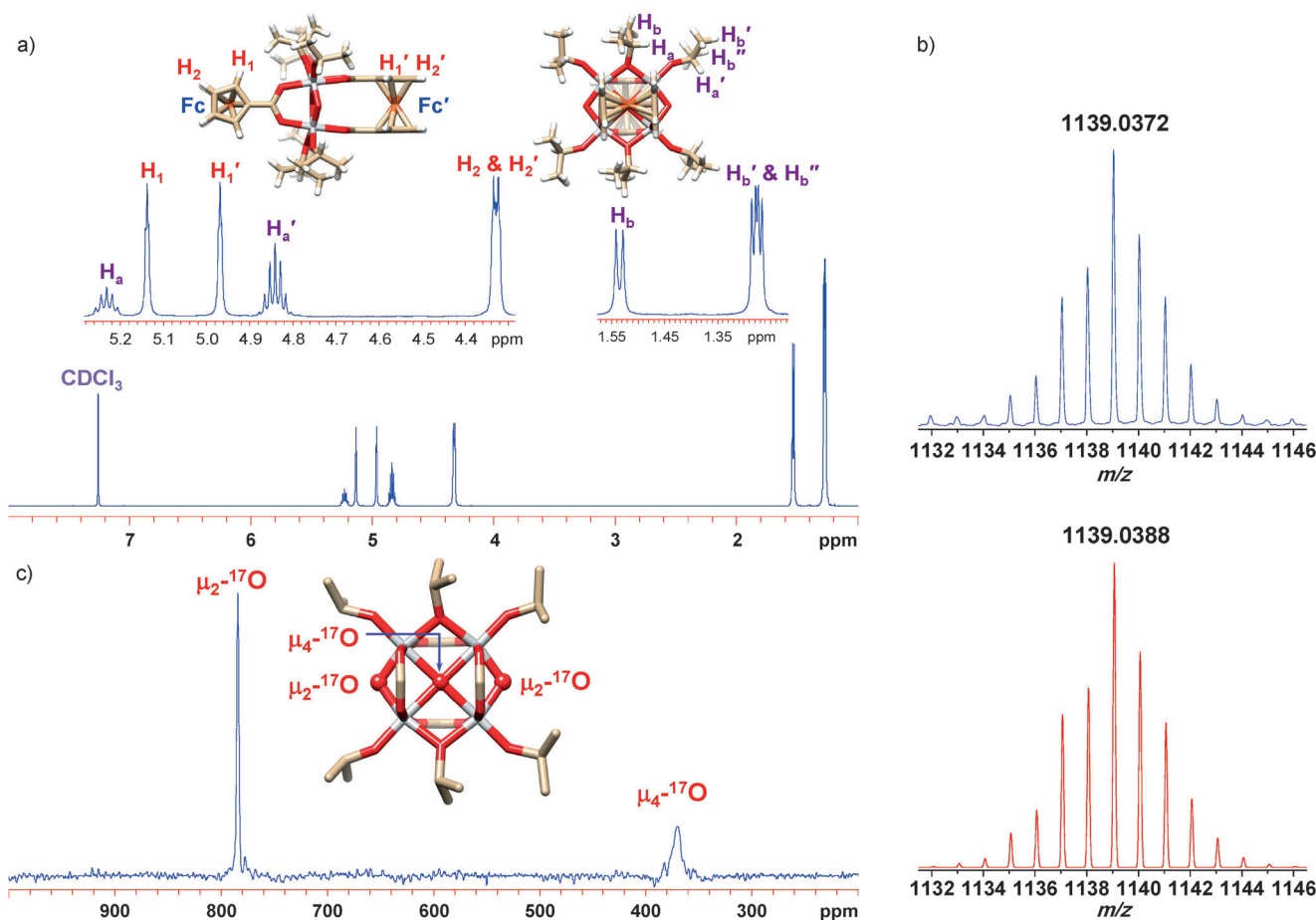


Figure 1. a) The ^1H NMR spectrum (CDCl_3 , 500 MHz) and b) HRESI-MS of **1**. The experimentally obtained isotopic distribution pattern (blue) for $[\text{M}+\text{H}]^+$ correlates well with the calculated pattern (red). c) ^{17}O NMR spectrum (CDCl_3 , 54.27 MHz) of the ^{17}O -enriched **1**. Red balls represent μ_2 - and μ_4 - ^{17}O atoms. Fc groups are omitted for clarity.

ligands. Furthermore, the ^{13}C NMR spectrum also contains two resonances for the CH_3 substituents on the $\mu_2\text{-OPr}^i$ groups, an indication that the rotation of the $\mu_2\text{-OPr}^i$ is constrained by the crowded arrangement of the six OPr^i groups in the equatorial plane. High-resolution electrospray ionization mass spectrometric (HRESI-MS) analysis of **1** shows a peak at m/z 1139.0372 (theoretical 1139.0388), corresponding to $[\text{M}+\text{H}]^+$, and the experimental isotopic pattern matches exactly with the simulated pattern of **1** (Figure 1b).

To gain further insight into the coordination environment of the ptO atom in **1**, ^{17}O NMR spectroscopy on ^{17}O -labeled **1** was carried out. The ^{17}O -labeled **1** was conveniently prepared (see SI) in a manner in which the oxo-ligands were selectively enriched in ^{17}O , whereas the isopropoxo and carboxylato ligands remained unchanged. The ^{17}O NMR spectrum of **1** shows only two resonances related to the oxo-ligands (Figure 1c). The resonance located at 370.5 ppm is assigned to the central ptO ($\mu_4\text{-O}$) atom and the one at 784.0 ppm to the two $\mu_2\text{-O}$ atoms. The upfield-shifted resonance of the ptO atom relative to those of the $\mu_2\text{-O}$ atoms can be attributed to the stronger shielding effect originating from the weaker bond between Ti and ptO compared to the bond between Ti and $\mu_2\text{-O}$.

Single-crystal X-ray diffraction (XRD) analysis of **1** (Figure 2) shows that it crystallizes in the monoclinic space group $P2_1/c$ with eight formula units per cell (SI, Figure S5). The experimental powder XRD pattern of **1** is in agreement with the pattern derived from the crystal data (SI, Figure S4), confirming the purity of the bulk crystalline phase of **1**. The structure consists of a Ti_4O_{17} octahedron tetramer having a square-planar $\{\text{Ti}_4\text{O}\}$ core that is achieved by displaying four TiO_6 octahedra in a square-planar edge-sharing manner (SI, Figure S6). This Ti_4O_{17} octahedron tetramer is stabilized by the orthogonal blockage of the two fcd^{2-} groups at the eight axial vertices on both sides of the Ti_4 square plane. Although many TiO octahedron tetramers adopting various arrangements have been identified^[5e,9] in TiO -based clusters, such a square-planar edge-sharing arrangement with a bridging central ptO atom is sufficiently exceptional. The entire capping structure of **1** can be visualized as two sawhorse-shaped trestles that straddle four Ti atoms of the square-planar $\{\text{Ti}_4\text{O}\}$ core orthogonally from top and bottom. While this type of orthogonally straddled stabilization leads to the nonequivalent chemical environments of the two opposing Fc groups, as evidenced by NMR spectroscopy, it also eliminates the presence of other isomers of **1** and provides an extremely rigid Ti_4 square that stabilizes the ptO atom. Aside from the eight axial O atoms belonging to the two fcd^{2-} groups, the remaining nine equatorial O atoms—that is, 2 $\mu_2\text{-O}$, 4 $\mu_2\text{-OPr}^i$, 2 $\mu_3\text{-OPr}^i$, as well as 1 $\mu_4\text{-O}$ (ptO) at the center of the $\{\text{Ti}_4\text{O}\}$ core—are ligated with four Ti atoms to form a two-dimensional Ti–O sheet. The $\{\text{Ti}_4\text{O}\}$ core is a rectangle that is almost a square and is completely planar (Figure 2): 1) the mean length of the long sides ($\text{Ti1}\cdots\text{Ti2}$ and $\text{Ti3}\cdots\text{Ti4}$) is 3.11 Å, whereas the one of the short sides ($\text{Ti2}\cdots\text{Ti3}$ and $\text{Ti1}\cdots\text{Ti4}$) is 2.91 Å; 2) the deviations of all inner angles from 90° are $<0.3^\circ$; 3) the deviations of all atoms from the mean plane are <0.02 Å. The lengths of the four Ti–ptO

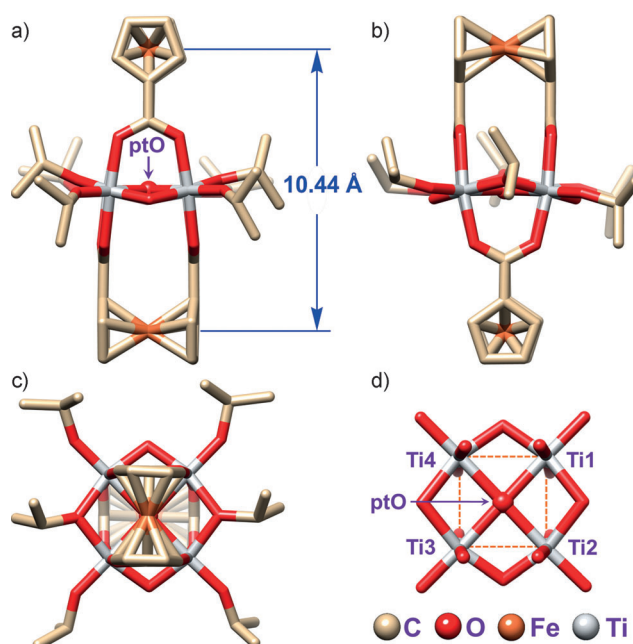


Figure 2. X-ray crystal structure of **1**. a) Front, b) side, and c) top views. d) Top view of the Ti_4O_{17} octahedron tetramer after omitting two Fc groups and all the Pr^i groups. The ptO atom is depicted as a red ball. The blue arrow indicates the Fe...Fe distance. H atoms are omitted for clarity. Selected distances [Å] and angles [°]: Ti1–ptO 2.14(4), Ti2–ptO 2.12(4), Ti3–ptO 2.13(4), Ti4–ptO 2.14(4), Ti1...Ti2 3.11(1), Ti2...Ti3 2.90(2), Ti3...Ti4 3.12(1), Ti4...Ti1 2.92(2); Ti1–ptO...Ti2 93.9(2), Ti2–ptO...Ti3 86.0(1), Ti3–ptO...Ti4 93.8(2), Ti4–ptO...Ti1 86.3(1), Ti1...Ti2...Ti3 90.3(4), Ti2...Ti3...Ti4 90.1(4), Ti3...Ti4...Ti1 89.8(4), Ti4...Ti1...Ti2 89.7(4).

bonds—varying from 2.12(4) to 2.14(4) Å (Figure 2)—are (SI, Table S2) much longer than those of other Ti–O bonds, thus providing evidence for weaker bonding between Ti and the ptO, an observation, which is consistent with the results obtained by ^{17}O NMR spectroscopy.

The bonding interactions between four Ti^{4+} and one ptO^{2-} were investigated by DFT calculations (ORCA 2.9.1/B3LYP/def2-svp; SI, Methods).^[10] The level of consistency between the DFT-optimized geometries for **1** and its oxidation states $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ with the original X-ray structure provides further evidence for the structural rigidity and stability of **1** (SI, Table S2). Two pairs of e_g -symmetric Ti–O σ -bonds, formed through overlapping the two horizontally orthogonal $2p_x$ and $2p_y$ orbitals of the ptO^{2-} with the 3d orbitals of four Ti^{4+} , are found in molecular orbitals (MOs) 257 and 258 (Figure 3). The remaining perpendicular $2p_z$ “lone-pair” orbital of the ptO^{2-} is not involved in bonding as observed in MO 287 (Figure 3). Regardless of the oxidation state (**1**, $\mathbf{1}^+$, or $\mathbf{1}^{2+}$), similar bonding patterns between the ptO^{2-} and Ti^{4+} are present. A related type of unusual bonding has been accounted for previously by Hoffmann’s hypothesis^[11] in relation to the bonding of the square-planar methane. Natural population analysis (NPA) shows (SI, Tables S3–S5) that the ptO atom is negative with an atomic charge of -1.01 e, which is significantly more negative than the average atomic charge of around -0.7 e found for the other 16 O atoms. This result is in good agreement with the nature of the weak bonding

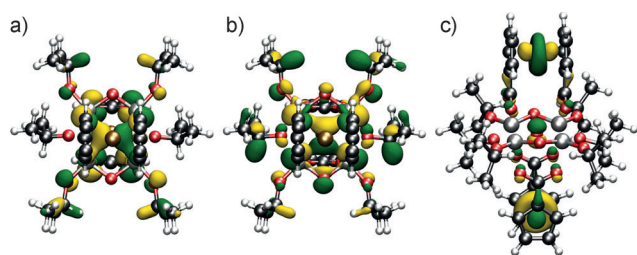


Figure 3. The calculated MOs, a) MO 257 (−8.542 eV) and b) MO 258 (−8.412 eV), that involve the bonding between the ptO atom and the four Ti atoms, as well as c) MO 287 (−6.577 eV), which involves only the ptO atom. Isosurface value: 0.030 au. Color code: carbon, dark gray; oxygen, red; hydrogen, white; titanium, light gray; iron, golden.

between Ti and the ptO. Wiberg-type bond index calculations in the NPA were carried out (SI, Tables S6–S8) to probe the bonding pattern between the atoms in **1**. The overall bond index for the ptO atom is 1.73, which is significantly smaller than 2—a standard bond order which is followed nicely by the other 16 O atoms. A detailed scrutiny of the bond index between the ptO and all other atoms reveals that it is partially bonded to the surrounding four Ti atoms with an average ptO–Ti bond index 0.36. In addition, the short sides Ti2...Ti3 and Ti1...Ti4 of the {Ti₄O} core were found to have a non-negligible average bond index 0.06, suggesting that weak bonding exists between these two Ti atom pairs which also rationalizes the low bond index between the ptO and Ti atoms.

The two Fc groups and the ptO atom constitute a highly linear system (Fe...ptO...Fe angle of 179.8(9)°) with two Fe...ptO separations of 5.22(4) Å and a fixed Fe...Fe distance of 10.44(2) Å (Figure 2). Although both Fc sites are connected by the Ti₄ square, they are separated spatially by the ptO by over 10 Å. To shed light on the redox behavior of such a unique system, we investigated the electrochemical properties of **1** in CHCl₃ with the traditional supporting electrolyte [nBu₄N][PF₆] (Figure 4). The cyclic voltammogram (CV) of **1** is composed of two reversible one-electron oxidation processes (Figure 4a, upper part). In agreement with the CV, the differential pulse voltammogram (DPV) also shows

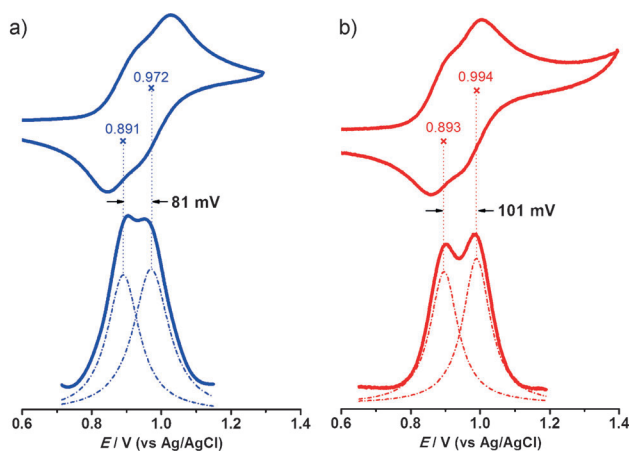


Figure 4. CV (upper part) and DPV (lower part) profiles of **1** in CHCl₃ with a) 0.1 M [nBu₄N][PF₆] and b) 0.02 M Na[B{C₆H₃(3,5-CF₃)₂]₄.

two peaks with similar intensity (Figure 4a, lower part). The half-wave potentials ($E_{1/2}$) for the two oxidation states **1**⁺ and **1**²⁺ are +0.891 and +0.972 V, respectively, corresponding to a $\Delta E_{1/2}$ value of 81 mV. On account of the fact that the ion-pairing interaction^[8f,12] between the [PF₆][−] electrolyte anion and the monocation product **1**⁺ may diminish the $\Delta E_{1/2}$ value, we have investigated the electrochemical behavior of **1** in CHCl₃ with sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (Na[B{C₆H₃(3,5-CF₃)₂]₄) as the supporting electrolyte. Indeed, when the electrolyte anion is changed to [B{C₆H₃(3,5-CF₃)₂]₄[−], the CV of **1** exhibits two reversible anodic waves (Figure 4b, upper part) and the DPV shows two well-separated peaks (+0.893 and +0.994 V) with a larger $\Delta E_{1/2}$ value of 101 mV (Figure 4b, lower part). In agreement with Geiger's results,^[12] the use of Na[B{C₆H₃(3,5-CF₃)₂]₄ as electrolyte provides a more reliable $\Delta E_{1/2}$ value for two reasons: 1) the weakly coordinating [B{C₆H₃(3,5-CF₃)₂]₄[−] electrolyte anion minimizes ion-pairing and 2) the small Na⁺ electrolyte countercation enhances competitive ion-pairing with the supporting salt anion. The presence of two well-separated one-electron oxidation processes is indicative of the existence of modest electronic communication between the two Fc sites in the mixed-valence state **1**⁺. The thermodynamic stability of **1**⁺ can be estimated from the comproportionation constant (K_c) for the process: **1** + **1**²⁺ ⇌ 2 (**1**⁺), which was found to be 51 using the equation $K_c = \exp(F\Delta E_{1/2}/RT)$.^[13] A detailed inspection (Figure 5) of the frontier MOs of

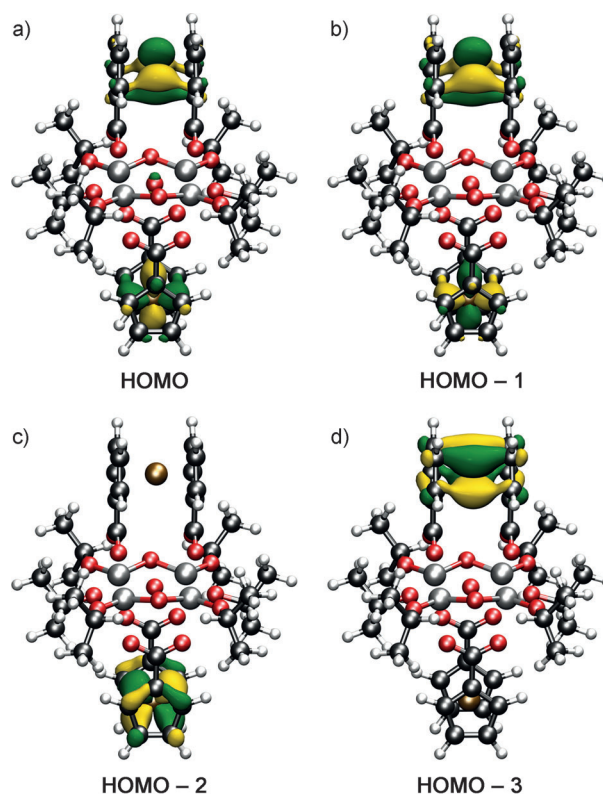


Figure 5. The calculated HOMOs a) MO 292 (−5.741 eV), b) MO 291 (−5.749 eV), c) MO 290 (−5.761 eV), and d) MO 289 (−5.762 eV) in the optimized geometry of **1**. Isosurface value: 0.030 au. Color code: carbon, dark gray; oxygen, red; hydrogen, white; titanium, light gray; iron, golden.

1 shows that the four highest-occupied MOs (HOMOs), HOMO-3 to HOMO, form two degenerate pairs with negligible energy differences and with major contributions from the 3d orbitals of Fe in the Fc groups. This observation suggests that the two Fc units are equivalent electronically in the ground state **1**⁰, although they are not equivalent symmetrically in space on account of their relative positions to the OPrⁱ groups. The two lowest-unoccupied MOs (LUMOs) near the HOMO–LUMO gap are the 3d orbitals on the four Ti atoms (SI, Figure S7). It should be noted that bis- or multi-Fc systems which exhibit electronic interaction over Fe...Fe distance of more than 10 Å are relatively rare.^[14] While a through-bond mechanism for electronic communication over an Fe...Fe separation of 10.4 Å in the mixed-valence state **1**⁺ cannot be ruled out, it is more likely that a through-space mechanism is operative.^[15]

In summary, a square-planar tetracoordinate oxygen atom can be stabilized in a Ti–O cluster **1** which has a unique Ti₄O₁₇ octahedron tetramer core constrained by two fdc²⁻ ligands. DFT calculations indicate that the ptO adopts an unusual bonding pattern with two horizontally σ -bonded 2p_x and 2p_y orbitals in addition to one perpendicular nonbonding 2p_z orbital. The two one-electron electrochemical oxidation processes suggest that modest electronic communication occurs between the two Fc sites even though they are spatially separated by the ptO with an Fe...Fe separation of 10.4 Å. This research, which has uncovered a unique example of an integrated molecular system incorporating a ptO atom and two Fc groups, advances our fundamental understanding of the relationship between electronic communication and molecular structure.

Received: February 21, 2014

Revised: May 20, 2014

Published online: July 2, 2014

Keywords: electrochemistry · ferrocene · oxido ligands · titanium-oxo clusters

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