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# Two-Electron Three-Centered Bond in Side-On ($\eta^2$) Uranyl(V) Superoxo Complexes

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Theoretical calculations suggest a novel two-electron three-atom bonding scheme for complexation of $O_2$ with U(V) compounds, leading to the stabilization of superoxo complexes in the side-on ($\eta^2$) configuration. This binding motif is likely to play an important role in the oxidative processes involving *trans*-uranium compounds having valence $5f_\varphi$ electrons.

## Introduction

Mononuclear dioxygen−metal compounds, such as $FeO_2$ complexes with Schiff base and porphyrin ligands, play an essential role in the chemistry of an array of molecules including oxyhemoglobin, cytochrome P-450, and cytochrome oxidase. It is well-known that the superoxo complexes of these molecules have end-on ($\eta^1$) coordination geometries with O−O bond lengths of ~1.30 Å, Fe−O−O bond angles of ~135°, and vibrational frequencies of ~1150 $cm^{-1}$,[1] which reflect a formal change of the oxidation state from $M^{n+}$ to $M^{n+1}$. In addition, there are side-on ($\eta^2$) peroxo-species, such as $[Fe(porphyrin)(O_2)]^-$, in which the O−O bond lengths are ~1.46 Å with vibrational frequencies of ~820 $cm^{-1}$.[1] These reflect a formal change of the oxidation state from $M^{n+}$ to $M^{n+2}$.

We report here computed structures for dioxygen metal compounds in which $O_2$ is strongly bound side-on ($\eta^2$), as it would be in a peroxide but with an O−O bond length of ~1.30 Å and frequency of ~1200 $cm^{-1}$, as it would in a superoxide. The systems exhibiting this behavior are dioxouranium(V) complexes in which strongly bound 5f electrons are available for binding of $O_2$. Addition of $O_2$ is consistent with condensed-phase studies that suggested that dioxygen complexes are intermediate in the oxidation of U(V) species.[2] Recently, gas-phase studies have been reported in which $O_2$ adds to $[UO_2(L)_n]^+$ coordination complexes, where L are $\sigma$-donor ligands.[3] Serial dissociation reactions of the resulting $[UO_2(L)_3(O_2)]^+$ complex showed an unusual pattern with initial elimination of neutral L, followed by loss of $O_2$, even though there were still $\sigma$-donors available for elimination. It was hypothesized that dioxygen was oxidizing the U(V) center, forming a U(VI)−superoxide complex whose formation and stability was in some way influenced by the number of donor ligands. However, these earlier studies had no direct experimental structural data supporting this idea. Here, we employ quantum chemical calculations to understand these spectroscopic observations.

To probe the nature and magnitude of these interactions, we used the relativistic effective core potential (RECP) density functional theory (DFT)[4] to calculate the geometries, frequencies, and electronic binding energies for 1:1 complexes of U(VI), U(V), and U(IV) dioxo monocations with dioxygen in the two binding motifs (Figure 1 and Table 1). This does not include spin−orbit effects, which we expect not to alter the conclusions of this study.[5]

We first consider the $UO_2^+$ cation, which has strong $\sigma$ and $\pi$ bonds to both axial oxygen atoms leaving a single electron in one of the $5f_\varphi$ orbitals ($^2\Phi$ state).[6] Dioxygen binding in an $\eta^2$ fashion (complex **1**) results in a strong bond (19.4 kcal/mol) between the singly occupied uranyl $5f_\varphi$ orbital and the $O_2$ $\pi^*$ orbital in the equatorial plane ($\pi^*_{xy}$) leaving the second $\pi^*$ singly occupied ($\pi^*_{yz}$). The O−O bond length of 1.29 Å and O−O stretching frequency of 1243 $cm^{-1}$ in complex **1** are consistent with formal reduction of coordinated dioxygen to superoxide.[1]

It has been suggested[3] that side-on binding of $O_2$ to U(V) complexes might occur through coupling uranyl $5f_\delta$ with the dioxygen $\pi^*_{yz}$ orbital (perpendicular to the equatorial plane). However, we find that this coupling leads to a bond strength of ~4 kcal/mol and requires a $5f_\varphi \rightarrow 5f_\delta$ promotion energy of ~5 kcal/mol. Thus, these orbitals do not participate in bonding. We were also able to find a stable end-on complex **2**, but this was bound by only 8.5 kcal/mol at the B3LYP level.

To investigate whether these results depend on the flavor of the DFT theory, we calculated the relative bond energies for the side-on coordination geometry, **1**, relative to the end-on, **2**. In all cases, complex **1** appears to be the most stable, by 17.6 (LDA), 15.4 (PBE), 15.5 (PW91), and 10.9 kcal/mol (B3LYP).

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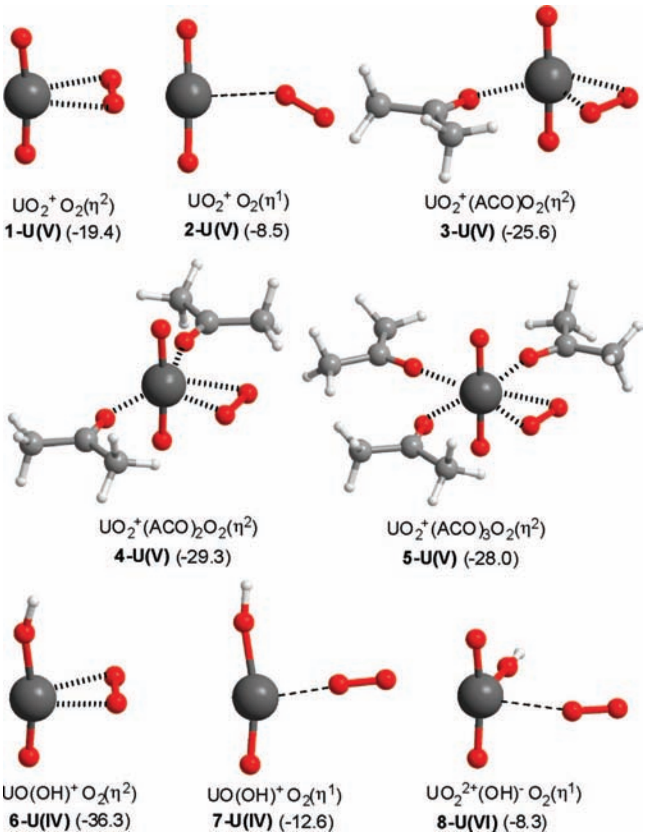

**Figure 1.** Structures and binding energies (kcal/mol) for ground-state dioxygen−uranium complexes **1**−**8**. The weaker interaction is indicated by the thinner dashed line.

**TABLE 1: Electronic Binding Energies (BE), Selected Geometric Parameters, and Frequencies for Complexes 1−8**[a]

| system | sym | state | BE kcal/mol | U···$O_2$ Å[c] | O−O Å | $\nu_{O-O}$ cm$^{-1}$ |
|---|---|---|---|---|---|---|
| **1** | $C_{2v}$ | $^2A_2$ | 19.4 | 2.293 | 1.290 | 1243 |
| **2** | $C_s$ | $^2A'$ | 8.5 | 2.613 | 1.205 | 1609 |
| | | $^4A'$ | 7.7 | 2.717 | 1.203 | 1637 |
| **3** | $C_1$ | $^2A$ | 25.6 | 2.318 | 1.298 | 1233 |
| **4** | $C_1$ | $^2A$ | 29.3 | 2.338 | 1.305 | 1225 |
| **5** | $C_1$ | $^2A$ | 28.0 | 2.369 | 1.301 | 1240 |
| **6** | $C_s$ | $^1A'$ | 36.3[b] | 2.238 | 1.318 | 1173 |
| | | $^1A'$ | 34.0 | 2.066 | 1.400 | 981 |
| | | $^3A''$ | 33.0 | 2.287 | 1.307 | 1212 |
| **7** | $C_s$ | $^1A'$ | 12.6[b] | 2.209 | 1.242 | 1291 |
| | | $^3A''$ | 11.9 | 2.083 | 1.282 | 1220 |
| **8** | $C_s$ | $^3A''$ | 8.3 | 2.661 | 1.202 | 1645 |

[a] B3LYP/SSC(2g)/6-311++G(3dp,3df) single-point energies on B3LYP/SSC/6-311++G** optimized geometries.[4] [b] This ground-state wave function has $M_s = 0$ (equal number of α- and β-spins), in which there is an α-spin on the U $5f_\delta$ orbital and a β-spin on the $O_2$ $\pi^*_{yz}$ orbital. These orbitals overlap slightly, so the corresponding triplet state is slightly higher within the chosen scalar relativistic approximation. [c] An average of two U−O distances for the side-on ($\eta^2$) bound oxygen.

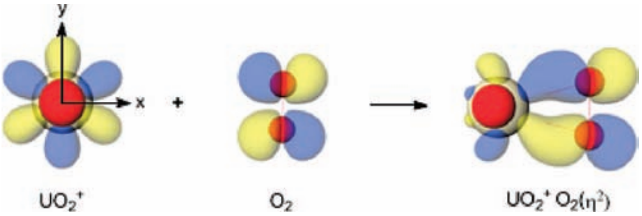

**Figure 2.** Frontier MOs of $UO_2^+$, $O_2$, and their $\eta^2$ complex, showing a significant overlap between the uranyl $5f_\varphi$ and $O_2$ $\pi^*_{xy}$ orbitals.

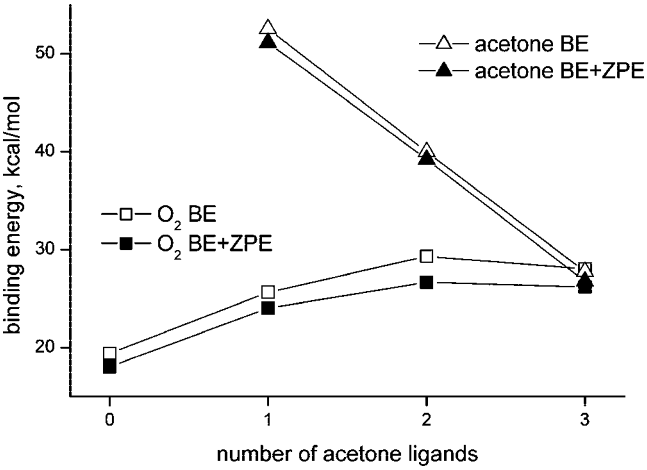

**Figure 3.** B3LYP ligand binding energies for $[UO_2(ACO)_n(O_2)]^+$ complexes (with and without zero-point energy (ZPE) corrections), where ACO = acetone and $n$ = 0−3.

We propose that symmetric side-on binding of the superoxo species is favored because the 60° angle between adjacent lobes of the U $5f_\varphi$ orbital gives an excellent overlap with adjacent lobes of the $O_2$ $\pi^*_{xy}$ orbital, as shown in Figure 2. This contrasts with the case of d orbitals, where the 90° angle between adjacent lobes leads to a less favorable overlap with the $O_2$ $\pi^*_{xy}$ orbital.[7]

The binding energy of dioxygen to U(V) systems is sensitive to the presence of electron-donating ligands that can increase the overall basicity of the uranium center, facilitating electron transfer to the $O_2$.[3] This phenomenon is illustrated by trends in binding energies calculated for the $[UO_2(ACO)_n(O_2)]^+$, where $n$ = 1−3 and ACO = acetone. Coordination of a single ACO causes *an increase* in $O_2$ binding of ∼ 5kcal/mol compared to $[UO_2(O_2)]^+$, and addition of a second ACO results in a further strengthening of $O_2$ by another 4 kcal/mol (Figure 3). Addition of the third ACO does not appreciably change the $O_2$ binding energy. However, calculated ACO BE values decrease in a nearly linear fashion on going from $n$ = 1−3[9] and become similar to the BE value for $O_2$ in the $[UO_2(ACO)_3(O_2)]^+$ complex. Collision-induced dissociation studies[3] showed that ACO is preferentially eliminated from $[UO_2(ACO)_3(O_2)]^+$, while $O_2$ is lost from $[UO_2(ACO)_2(O_2)]^+$. Thus, we expect the $O_2$ binding energies calculated with B3LYP to be slightly underestimated relative to the binding energies of acetone. (On the other hand, Table 2S and Figure 1S (Supporting Information) suggest that the LDA, PBE, and PW91 functionals yield $O_2$ binding energies that are too large. For example, in contrast to experiment,[3] these methods predict $O_2$ to be more strongly bound than the second acetone ligand.)

The calculated U═O, U−$O_2$, and U−ACO bond lengths increase progressively with increasing $n$, consistent with normal behavior seen in metal ion coordination complexes.[9] Interestingly, O−O bond lengths track the binding energy very closely, increasing as $n$ goes from 0 to 2 and then decreasing modestly.

Figures 4 and 5 show the expected decrease of antisymmetric ($\nu_a$) and symmetric ($\nu_s$) O═U═O stretching frequencies with the number of ACO ligands coordinated to $UO_2^+$ and $UO_2^{2+}$. There results confirm that the U(VI) species have higher uranyl stretching frequencies than the corresponding U(V) species ($\Delta\nu_a$ = ∼120 cm$^{-1}$, $\Delta\nu_s$ = ∼95 cm$^{-1}$). The binding of dioxygen to U(V) dioxo cations results in a blue shift of uranyl vibrational frequencies. The frequency shift increases progressively from $\Delta\nu_a$ = 38 cm$^{-1}$ and $\Delta\nu_s$ = 17 cm$^{-1}$ to $\Delta\nu_a$ = 64 cm$^{-1}$ and $\Delta\nu_s$

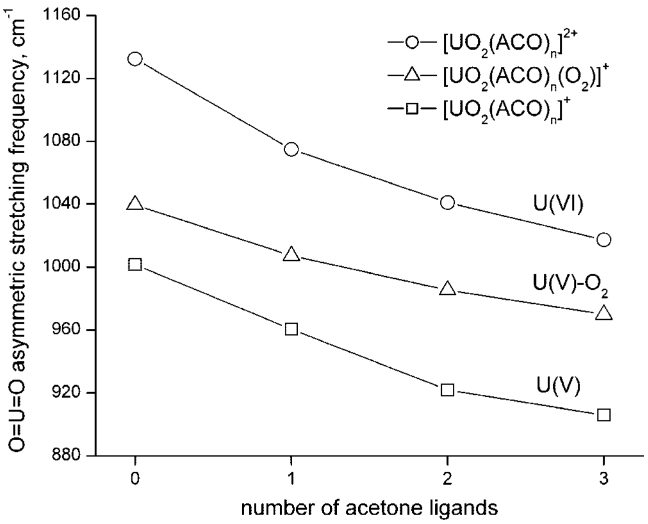

**Figure 4.** Comparison of asymmetric O═U═O stretching frequencies for $[UO_2(ACO)_n]^{2+}$, $[UO_2(ACO)_n]^{+}$, and $[UO_2(ACO)_n(O_2)]^{+}$ complexes.

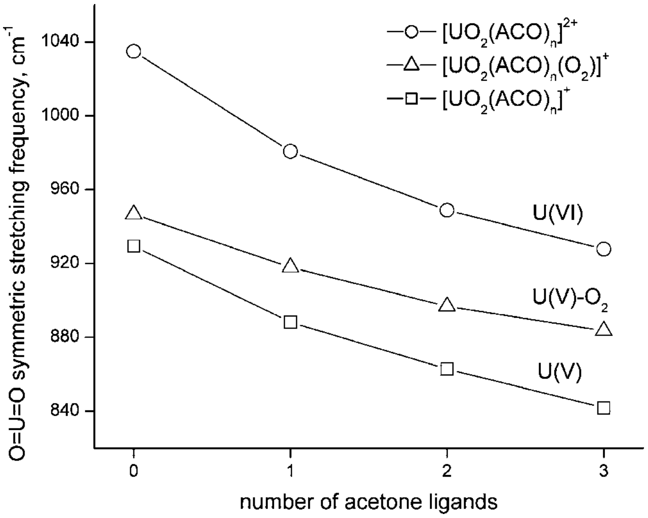

**Figure 5.** Comparison of symmetric O═U═O stretching frequencies for $[UO_2(ACO)_n]^{2+}$, $[UO_2(ACO)_n]^{+}$, and $[UO_2(ACO)_n(O_2)]^{+}$ complexes.

= 42 cm$^{-1}$ as the number of acetone donor ligands increases from zero to three. This is consistent with the oxidation of U(V) to U(VI). Indeed, the O═U═O stretching modes for $UO_2^+O_2(\eta^2)$ ($\nu_a$ = 1039 cm$^{-1}$, $\nu_s$ = 947 cm$^{-1}$) are slightly higher than those for an unambiguous U(VI) compound, $(UO_2)^{2+}(OH)^-$ ($\nu_a$ = 1017 cm$^{-1}$, $\nu_s$ = 937 cm$^{-1}$).

Our calculations also indicate that the presence of an additional 5f electron in the U(IV) complex (**6**), UOOH$^+$ ($^3$H state), further strengthens the interaction energy with dioxygen, leading to a bond energy of 36.3 kcal/mol (compared to 19.4 kcal/mol for the analogous U(V) complex **1**). Here, the $O_2$ is again bound side-on with the O−O bond length of 1.32 Å and O−O stretching frequency of 1173 cm$^{-1}$. Again, we find a stable end-on bonding motif (complex **7**), but it is 23.7 kcal/mol less stable. Interestingly, the reported[5a] B3LYP binding energy for a neutral $UO_2$ (71.0 kcal/mol) is nearly twice as large as that for UOOH$^+$ (Table 1). Although no dioxygen−U(IV) complexes containing intact $O_2$ ligands have been observed, the products of irreversible oxidation to $[UO_2(OH)]^+$ have been found in the gas phase.[3]

**TABLE 2: Natural Bond Order Analysis of Charge Transfer in 1−8**[a]

| system | U | $O_2$ | $O_2$, α-spin | $O_2$, β-spin |
|---|---|---|---|---|
| 1 | 0.191 | −0.443 | 0.247 | −0.690 |
| 2 | −0.022 | 0.007 | 0.023 | −0.015 |
| 3 | 0.156 | −0.496 | 0.231 | −0.727 |
| 4 | 0.133 | −0.533 | 0.218 | −0.751 |
| 5 | 0.097 | −0.543 | 0.212 | −0.755 |
| 6 | 0.234 | −0.564 | 0.218 | −0.782 |
| 7 | 0.145 | −0.328 | 0.086 | −0.414 |
| 8 | −0.044 | 0.041 | 0.030 | 0.011 |

[a] Obtained with B3LYP/SSC/6-311++G**.[4]

For the U(VI) complex $UO_2(OH)^+$ **8**, which lacks an available valence electron, we expect very weak binding to $O_2$. Indeed, we find complex **8** to yield a U···O bond length of 2.66 Å and a bond strength of 8.3 kcal/mol. Since the standard entropy change upon complex formation is −24.8 cal mol$^{-1}$ K$^{-1}$, this complex would not be expected to be observed at $T$ > 300 K. This is consistent with experiment.[3]

Natural bond order analysis[8] of charge transfer in complexes **1**−**8** confirms (Table 2) that $O_2$ behaves as a weak electron donor in **2** and **8**, whereas in **1**, **3**−**6**, and to some extent **7**, it acts as a strong electron acceptor. In the latter case, there is almost full β-spin electron transfer (0.69−0.78**e**) from U to $O_2$ and notably large α-spin electron transfer in the opposite direction (0.22−0.25**e**), which is fully compatible with a superoxo character of the complexes.

In summary, our calculations suggest a novel two-electron three-atom bonding scheme for complexation of $O_2$ with U(V) compounds leading to the stabilization of superoxo complexes in the side-on ($\eta^2$) configuration. This binding motif, which is expected to be prevalent in many actinide compounds having valence $5f_\varphi$ electrons, is likely to play an important role in the oxidative processes involving these species.

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**Supporting Information Available:** Table 1S provides additional information on geometric parameters and frequencies for U(IV), U(V), and U(VI) species and their complexes with $O_2$. Table 2S and Figure 1S compare electronic binding energies for complexes **1**−**8** calculated with B3LYP, LDA, PBE, and PW91 functionals, complete ref 4a, and Cartesian coordinates and absolute energies for optimized structures at the B3LYP/SSC/6-311++G** level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Electronic structure calculations were carried out using the NWChem program.[4a] Geometries were optimized at the B3LYP/SSC/6-311++G** level[4b,c] followed by single point energy calculations using the Stuttgart-SC basis set[4d] (SSC) augmented with the two g-functions of the Stuttgart-LC basis set on U and the 6-311++(3df,3pd) basis set on other elements. Control calculations for complex **1** show that this procedure leads to a small difference in binding energies (<0.5 kcal/mol) when compared to results obtained after full optimization at the B3LYP/SSC(3g,1h)/aug-cc-pVTZ level. A number of additional calculations were performed within the local density (LDA) and the generalized-gradient approximations (PBE[4e] and PW91[4f]). (a) Straatsma, T. P. et al. *NWChem, A Computational Chemistry Package for Parallel Computers, Version 5.0"*; Pacific Northwest National Laboratory: Richland, WA 99354−0999, USA, 2006. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Küsle, W,; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535. (e) Perdew, J. P.; Burke, K.; Emzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. (f) Perdew, J. P.; Wang, Y. *Phys Rev. B* **1992**, *46*, 12947.

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