A Computational Determination of the Lowest Energy Electronic and Geometric States of First Row Transition Metal Dioxygen Dications

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The lowest energy geometric structures and electronic spin states of first row transition metal (TM) dioxygen dication molecules ([TM–O₂]²⁺; TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) have been determined at the B3LYP/LANL2DZ level of theory (along with an extra 𝑑-type polarization function added to the O atoms). In order to further verify the spin states, CASSCF(6 + 𝑛, 9) energy points were determined (𝑛 = number of TM 𝑑 electrons). It has been found that with the exception of [Sc–O₂]²⁺, [V–O₂]²⁺, [Co–O₂]²⁺, and [Ni–O₂]²⁺, all [TM–O₂]²⁺ molecules take on a high-spin state. [Sc–O₂]²⁺ adopts a trigonal structure, while [Ti–O₂]²⁺–[Mn–O₂]²⁺ are essentially linear and [Fe–O₂]²⁺–[Zn–O₂]²⁺ are bent. It is further noted that the O–O bond decreases from 130.0 pm to 118.1 pm as the TM changes from Sc to Zn. However, the TM–O bond lengths fluctuate between values of 182.2 pm for [Ni–O₂]²⁺ and 232.2 pm for [Zn–O₂]²⁺.

1. Introduction

Transition metals (TMs) bound to an O₂ molecule are the chemically active site in many industrial [1–5] and biological [1, 2, 6–10] molecules. Considering the TM–O₂ bond to lie along the 𝑧-axis of a Cartesian coordinate system, in TM–O₂ complexes, bonds can form by the interactions of TM 3dᵢ, 3dⱼ, and 3dᵣ atomic orbitals with suitable orbitals on the O₂ ligand in order to make 𝜋(3dᵢ, j, r) or 𝜎(3dᵢ, j, r) bonds (Scheme 1). While there have been numerous studies of neutral TM–O₂ [11, 12] complexes, in many TM–O₂ containing molecules of biological and industrial importance, the TM is bound to a porphyrin ring in the Z− oxidation state. Therefore, [TM–O₂]²⁺ molecules are the simplest approximations to this important class of TM–O₂ containing molecules.

Probably the most studied TM–O₂ bond is the Fe–O₂ bond due to its role in heme-containing proteins [13–16]. This bond has been described as low-spin Fe(II) accepting an electron pair from excited singlet-state O₂ forming the 𝜎 bond, while donating an electron pair to oxygen to form a 𝜋 bond. An alternative view involves Fe(III) interacting with O²⁻. In a third possibility, triplet Fe(II) couples with triplet O₂ to form a closed shell singlet. Computational results vary depending on the extent of electron correlation and basis set size. It is clear, however, that the overall bonding scheme involves some degree of both O₂ → Fe and Fe → O₂ 𝜎 and 𝜋 electron transfer.

Further complicating matters, the number of near degenerate TM 𝑑-orbitals leads to the possibility of many low lying spin states. In addition, there are a number of different ways that the O₂ unit can be arranged relative to the TM. Herein, we seek to determine the lowest energy electronic and geometric states of [TM–O₂]²⁺ molecules (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) as a precursor to a more in-depth study of the TM–O₂ bond.

2. Theoretical Methods

In order to locate the lowest energy geometrical configuration, B3LYP [17–19] geometry optimizations were performed using the LANL2DZ [20–22] effective core potential basis
Table 1: Lowest energy spin states and geometric parameters of [TM–O₂]^{2+} molecules. Bond lengths in pm and bond angles in degree.

<table>
<thead>
<tr>
<th>Spin state</th>
<th>O–O</th>
<th>TM–O₂</th>
<th>ζTMOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ScO₂]^{2+}</td>
<td>Doublet</td>
<td>130.0</td>
<td>195.4</td>
</tr>
<tr>
<td>[TiO₂]^{2+}</td>
<td>Triplet</td>
<td>124.2</td>
<td>176.5</td>
</tr>
<tr>
<td>[VO₂]^{2+}</td>
<td>Doublet</td>
<td>121.0</td>
<td>1971</td>
</tr>
<tr>
<td>[CrO₂]^{2+}</td>
<td>Triplet</td>
<td>120.9</td>
<td>193.4</td>
</tr>
<tr>
<td>[MnO₂]^{2+}</td>
<td>Quartet</td>
<td>120.7</td>
<td>200.6</td>
</tr>
<tr>
<td>[FeO₂]^{2+}</td>
<td>Triplet</td>
<td>120.2</td>
<td>196.3</td>
</tr>
<tr>
<td>[CoO₂]^{2+}</td>
<td>Doublet</td>
<td>120.0</td>
<td>198.3</td>
</tr>
<tr>
<td>[NiO₂]^{2+}</td>
<td>Singlet</td>
<td>116.3</td>
<td>182.2</td>
</tr>
<tr>
<td>[CuO₂]^{2+}</td>
<td>Quartet</td>
<td>124.4</td>
<td>196.7</td>
</tr>
<tr>
<td>[ZnO₂]^{2+}</td>
<td>Triplet</td>
<td>118.1</td>
<td>232.2</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The geometric parameters and spin states of the lowest energy structures of all [TM–O₂]^{2+} molecules studied herein are reported in Table 1. [Sc–O₂]^{2+} adopts a trigonal structure as in 1 of Scheme 2. This can be thought of as the Sc^{2+} atom bonding to the π system of O₂. The single d electron of Sc^{2+} spin pairs with the single electron in the π^*_x MO of O₂ as depicted in Scheme 3 (MO 2σ, 1), while one electron remains in the π^*_x MO of O₂ (MO 2π, 1) resulting in a doublet ground state.

[Ti–O₂]^{2+}, [V–O₂]^{2+}, [Cr–O₂]^{2+}, and [Mn–O₂]^{2+} are essentially linear with the O₂ binding end-on to the TM^2+. The slight bending in [Ti–O₂]^{2+} breaks the degeneracy of the 2σ and 1δ MOs. The observed triplet is the result of the subtle balance between orbital energies and favorable electron exchange. Doublet [V–O₂]^{2+} has one electron in the 1σ MO, and triplet [CrO₂]^{2+} has one electron in each of the degenerate 1δ MOs (Scheme 3, 2). In order for the high spin quartet to be the lowest energy state of [Mn–O₂]^{2+}, one electron must remain in each of the 1δ MOs, while another single electron occupies the 1σ MO (Scheme 3, 2). This situation is only possible if the 1σ and 1δ MOs are close enough in energy that exchange stabilization outweighs the destabilization introduced by placing an electron in the higher energy 1σ MO.

Upon examination of Scheme 3, it would appear that [Fe–O₂]^{2+} should continue the trend of linearity by completely filling the 1δ MO thus forming a stable singlet. Indeed, a stable linear singlet was found; however, it was 18.2 kJ/mol above the bent triplet ground state. Upon bending, the linear 1δ MO (Scheme 3, 2) splits into the bent 3σ and 1δ MOs (Scheme 3, 3). This results in a stabilization of the 3σ MO due to increased bonding interaction, while the 1δ MO experiences little change energetically. The triplet is then formed by placing a single electron in the 1δ and 4σ MOs. The bent triplet is favored over the bent singlet due to favorable exchange between electrons in these energetically close orbitals.

Adding more electrons causes [Co–O₂]^{2+}, [Ni–O₂]^{2+}, [Cu–O₂]^{2+}, and [Zn–O₂]^{2+} to become increasingly more bent. For [Co–O₂]^{2+} and [Ni–O₂]^{2+}, the 1δ and 4σ MOs...
are filled one at a time resulting in doublet and singlet ground states, respectively. On the other hand, [Cu–O$_2$]$^{2+}$ and [Zn–O$_2$]$^{2+}$ adopt high spin quartet and triplet ground states, respectively, indicating that the 4σ, 3π, and 5σ MOs (Scheme 3) are close in energy.

It is interesting to note that the O–O bond length decreases from a value of 130.0 pm in [Sc–O$_2$]$^{2+}$ to 118.1 pm in [Zn–O$_2$]$^{2+}$ (Table 1). Such a decrease could be caused by increasing the electron density in O–O bonding MOs or decreasing electron density in O–O antibonding MOs. This range is both above and below the O–O bond distance in O$_2$ (121 pm [31]), but within the limits of O$_2^-$ (135 pm [31], an extra electron in the π* antibonding MO) and O$_2$ (112 pm [31], one less electron in the π* antibonding MO). However, the TM–O$_2$ bond lengths are not so consistent and fluctuate between values of 182.2 pm in [Ni–O$_2$]$^{2+}$ and 232.2 pm in [Zn–O$_2$]$^{2+}$ (Table 1).

4. Conclusions

In the current study, we present the lowest energy geometrical conformations and spin states of first row [TM–O$_2$]$^{2+}$ molecules. [Sc–O$_2$]$^{2+}$ is trigonal, while [Ti–O$_2$]$^{2+}$–[Mn–O$_2$]$^{2+}$ are linear and [Fe–O$_2$]$^{2+}$–[Zn–O$_2$]$^{2+}$ are bent. The O–O bond length decreases as the TM goes from Sc to Zn, whereas the TM–O$_2$ bond length fluctuates. For [Mn–O$_2$]$^{2+}$, [Fe–O$_2$]$^{2+}$, [Cu–O$_2$]$^{2+}$, and [Zn–O$_2$]$^{2+}$ molecules, high spin states are lowest in energy indicating degenerate or near-degenerate orbitals.

Although it is clear that there is some level of electron transfer from the O$_2$ to the TM as well as some degree of TM to O$_2$ back donation, a more detailed analysis is required in order to fully understand the bonding in these unique molecules and how that extends to larger molecules of biological and industrial importance. Furthermore, we have shown that while the current results can be used as a starting point for studies of TM–O$_2$ containing molecules with σ donor and π acceptor ligands, caution must be exercised as both high- and low-spin ground states are possible.

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References


