

## Research Article

# 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 ( $[\text{TM}-\text{O}_2]^{2+}$ ; 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  $[\text{Sc}-\text{O}_2]^{2+}$ ,  $[\text{V}-\text{O}_2]^{2+}$ ,  $[\text{Co}-\text{O}_2]^{2+}$ , and  $[\text{Ni}-\text{O}_2]^{2+}$ , all  $[\text{TM}-\text{O}_2]^{2+}$  molecules take on a high-spin state.  $[\text{Sc}-\text{O}_2]^{2+}$  adopts a trigonal structure, while  $[\text{Ti}-\text{O}_2]^{2+}$ ,  $[\text{Mn}-\text{O}_2]^{2+}$  are essentially linear and  $[\text{Fe}-\text{O}_2]^{2+}$ ,  $[\text{Zn}-\text{O}_2]^{2+}$  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<sub>2</sub> bond lengths fluctuate between values of 182.2 pm for  $[\text{Ni}-\text{O}_2]^{2+}$  and 232.2 pm for  $[\text{Zn}-\text{O}_2]^{2+}$ .

## 1. Introduction

Transition metals (TMs) bound to an O<sub>2</sub> molecule are the chemically active site in many industrial [1–5] and biological [1, 2, 6–10] molecules. Considering the TM–O<sub>2</sub> bond to lie along the  $z$ -axis of a Cartesian coordinate system, in TM–O<sub>2</sub> complexes, bonds can form by the interactions of TM  $3d_{z^2}$ ,  $3d_{yz}$ , and  $3d_{xz}$  atomic orbitals with suitable orbitals on the O<sub>2</sub> ligand in order to make  $\sigma$  ( $3d_{z^2}$ ) or  $\pi$  ( $3d_{yz}$  and  $3d_{xz}$ ) bonds (Scheme 1). While there have been numerous studies of neutral TM–O<sub>2</sub> [11, 12] complexes, in many TM–O<sub>2</sub> containing molecules of biological and industrial importance, the TM is bound to a porphyrin ring in the 2<sup>+</sup> oxidation state. Therefore,  $[\text{TM}-\text{O}_2]^{2+}$  molecules are the simplest approximations to this important class of TM–O<sub>2</sub> containing molecules.

Probably the most studied TM–O<sub>2</sub> bond is the Fe–O<sub>2</sub> 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 O<sub>2</sub> forming the  $\sigma$  bond, while donating an electron pair to oxygen to form a  $\pi$  bond. An alternative view involves Fe(III) interacting with

O<sub>2</sub><sup>2-</sup>. In a third possibility, triplet Fe(II) couples with triplet O<sub>2</sub> 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 O<sub>2</sub> → Fe and Fe → O<sub>2</sub>  $\sigma$  and  $\pi$  electron transfer.

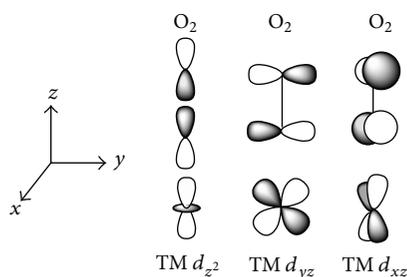
Further complicating matters, the number of near degenerate TM  $d$ -orbitals leads to the possibility of many low lying spin states. In addition, there are a number of different ways that the O<sub>2</sub> unit can be arranged relative to the TM. Herein, we seek to determine the lowest energy electronic and geometric states of  $[\text{TM}-\text{O}_2]^{2+}$  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–O<sub>2</sub> bond.

## 2. Theoretical Methods

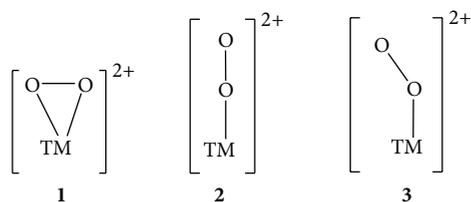
In order to locate the lowest energy geometrical configuration, B3LYP [17–19] geometry optimizations were performed using the LANL2DZ [20–22] effective core potential basis

TABLE 1: Lowest energy spin states and geometric parameters of  $[\text{TM}-\text{O}_2]^{2+}$  molecules. Bond lengths in pm and bond angles in degree.

	Spin state	O-O	TM-O <sub>2</sub>	∠TMOO
$[\text{ScO}_2]^{2+}$	Doublet	130.0	195.4	70.6
$[\text{TiO}_2]^{2+}$	Triplet	124.2	176.5	180.0
$[\text{VO}_2]^{2+}$	Doublet	121.0	197.1	180.0
$[\text{CrO}_2]^{2+}$	Triplet	120.9	193.4	180.0
$[\text{MnO}_2]^{2+}$	Quartet	120.7	200.6	175.4
$[\text{FeO}_2]^{2+}$	Triplet	120.2	196.3	161.9
$[\text{CoO}_2]^{2+}$	Doublet	120.0	198.3	144.4
$[\text{NiO}_2]^{2+}$	Singlet	116.3	182.2	127.7
$[\text{CuO}_2]^{2+}$	Quartet	124.4	196.7	137.5
$[\text{ZnO}_2]^{2+}$	Triplet	118.1	232.2	126.0



SCHEME 1



SCHEME 2

set with an additional  $d$ -type polarization function ( $\zeta = 0.9610$ ) on the O atoms [23]. Optimizations began with trigonal, linear, and bent starting structures as shown in Scheme 2. Optimizations at all three starting geometries were performed for singlet, triplet, and quintet spin states for  $[\text{TM}-\text{O}_2]^{2+}$  molecules with an even number of electrons (TM = Ti, Cr, Fe, Ni, and Zn) and doublet, quartet, and sextet spin states for molecules with an odd number of electrons (TM = Sc, V, Mn, Co, and Cu).

In order to further verify the spin state of each molecule, CASSCF [24–29] energy point calculations were performed for the various different spin states at the lowest energy B3LYP conformation. The CASSCF active space consisted of nine orbitals: the 5 TM  $d$ -type orbitals along with the  $\pi$  and  $\pi^*$  O<sub>2</sub> combinations (Scheme 3). Six electrons were placed into this active space from the O<sub>2</sub> $\pi$  and  $\pi^*$  orbitals, along with the TM  $d$  electrons (i.e., 1 for Sc, 2 for Ti, etc.).

All calculations were carried out with the Gaussian 03 [30] suite of programs.

### 3. Results and Discussion

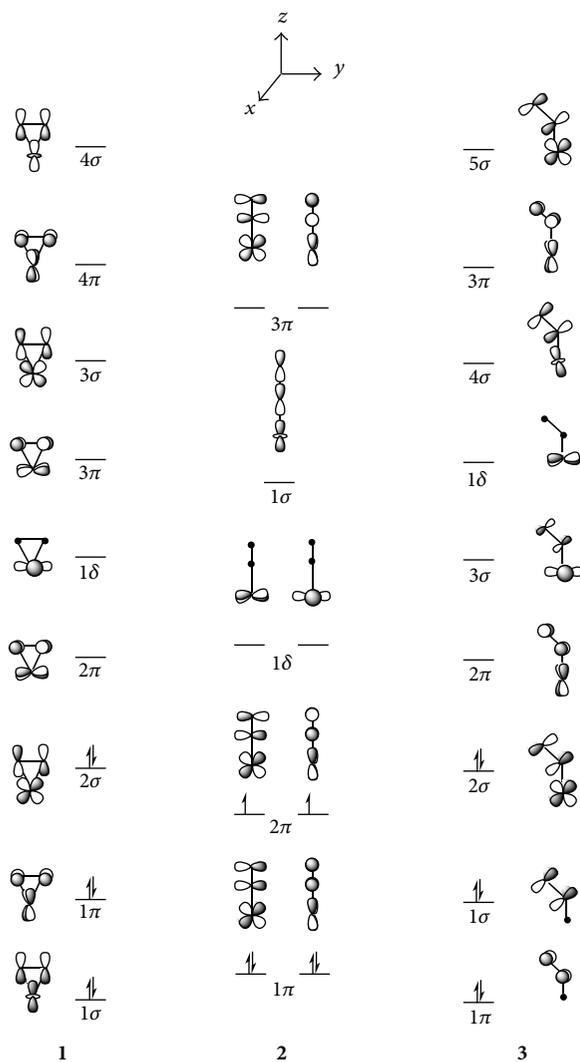
The geometric parameters and spin states of the lowest energy structures of all  $[\text{TM}-\text{O}_2]^{2+}$  molecules studied herein are reported in Table 1.

$[\text{Sc}-\text{O}_2]^{2+}$  adopts a trigonal structure as in **1** of Scheme 2. This can be thought of as the Sc<sup>2+</sup> atom bonding to the  $\pi$  system of O<sub>2</sub>. The single  $d$  electron of Sc<sup>2+</sup> spin pairs with the single electron in the  $\pi^*_z$  MO of O<sub>2</sub> as depicted in Scheme 3 (MO 2 $\sigma$ , **1**), while one electron remains in the  $\pi^*_x$  MO of O<sub>2</sub> (MO 2 $\pi$ , **1**) resulting in a doublet ground state.

$[\text{Ti}-\text{O}_2]^{2+}$ ,  $[\text{V}-\text{O}_2]^{2+}$ ,  $[\text{Cr}-\text{O}_2]^{2+}$ , and  $[\text{Mn}-\text{O}_2]^{2+}$  are essentially linear with the O<sub>2</sub> binding end-on to the TM<sup>2+</sup>. The slight bending in  $[\text{Ti}-\text{O}_2]^{2+}$  breaks the degeneracy of the 2 $\pi$  and 1 $\delta$  MOs. The observed triplet is the result of the subtle balance between orbital energies and favorable electron exchange. Doublet  $[\text{V}-\text{O}_2]^{2+}$  has one electron in the 1 $\delta$  MO, and triplet  $[\text{CrO}_2]^{2+}$  has one electron in each of the degenerate 1 $\delta$  MOs (Scheme 3, **2**). In order for the high spin quartet to be the lowest energy state of  $[\text{Mn}-\text{O}_2]^{2+}$ , one electron must remain in each of the 1 $\delta$  MOs, while another single electron occupies the 1 $\sigma$  MO (Scheme 3, **2**). This situation is only possible if the 1 $\sigma$  and 1 $\delta$  MOs are close enough in energy that exchange stabilization outweighs the destabilization introduced by placing an electron in the higher energy 1 $\sigma$  MO.

Upon examination of Scheme 3, it would appear that  $[\text{Fe}-\text{O}_2]^{2+}$  should continue the trend of linearity by completely filling the 1 $\delta$  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 1 $\delta$  MO (Scheme 3, **2**) splits into the bent 3 $\sigma$  and 1 $\delta$  MOs (Scheme 3, **3**). This results in a stabilization of the 3 $\sigma$  MO due to increased bonding interaction, while the 1 $\delta$  MO experiences little change energetically. The triplet is then formed by placing a single electron in the 1 $\delta$  and 4 $\sigma$  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  $[\text{Co}-\text{O}_2]^{2+}$ ,  $[\text{Ni}-\text{O}_2]^{2+}$ ,  $[\text{Cu}-\text{O}_2]^{2+}$ , and  $[\text{Zn}-\text{O}_2]^{2+}$  to become increasingly more bent. For  $[\text{Co}-\text{O}_2]^{2+}$  and  $[\text{Ni}-\text{O}_2]^{2+}$ , the 1 $\delta$  and 4 $\sigma$  MOs



SCHEME 3

are filled one at a time resulting in doublet and singlet ground states, respectively. On the other hand,  $[\text{Cu-O}_2]^{2+}$  and  $[\text{Zn-O}_2]^{2+}$  adopt high spin quartet and triplet ground states, respectively, indicating that the  $4\sigma$ ,  $3\pi$ , and  $5\sigma$  MOs (Scheme 3, 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  $[\text{Sc-O}_2]^{2+}$  to 118.1 pm in  $[\text{Zn-O}_2]^{2+}$  (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  $\text{O}_2$  (121 pm [31]), but within the limits of  $\text{O}^{2-}$  (135 pm [31], an extra electron in the  $\pi^*$  antibonding MO) and  $\text{O}^{2+}$  (112 pm [31], one less electron in the  $\pi^*$  antibonding MO). However, the TM– $\text{O}_2$  bond lengths are not so consistent and fluctuate between values of 182.2 pm in  $[\text{Ni-O}_2]^{2+}$  and 232.2 pm in  $[\text{Zn-O}_2]^{2+}$  (Table 1).

## 4. Conclusions

In the current study, we present the lowest energy geometrical conformations and spin states of first row  $[\text{TM-O}_2]^{2+}$  molecules.  $[\text{Sc-O}_2]^{2+}$  is trigonal, while  $[\text{Ti-O}_2]^{2+}$ – $[\text{Mn-O}_2]^{2+}$  are linear and  $[\text{Fe-O}_2]^{2+}$ – $[\text{Zn-O}_2]^{2+}$  are bent. The O–O bond length decreases as the TM goes from Sc to Zn, whereas the TM– $\text{O}_2$  bond length fluctuates. For  $[\text{Mn-O}_2]^{2+}$ ,  $[\text{Fe-O}_2]^{2+}$ ,  $[\text{Cu-O}_2]^{2+}$ , and  $[\text{Zn-O}_2]^{2+}$  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  $\text{O}_2$  to the TM as well as some degree of TM to  $\text{O}_2$  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– $\text{O}_2$  containing molecules with  $\sigma$  donor and  $\pi$  acceptor ligands, caution must be exercised as both high- and low-spin ground states are possible.

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