



Theoretical study of the effect of ligand topology on Fe(IV)O and Ru(IV)O complex reactivities



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ABSTRACT

Density functional theory calculations were carried out to clarify the effect of ligand topology on the stability and reactivity of $\text{cis-}\alpha\text{-[Fe}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ (Fe-2a), $\text{cis-}\beta\text{-[Fe}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ (Fe-2b), $\text{cis-}\alpha\text{-[Ru}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ (Ru-2a) and $\text{cis-}\beta\text{-[Ru}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ (Ru-2b) (BQCN = N,N'-dimethyl-N,N'-bis(8-quinolyl)-cyclohexanediamine). All the iron and ruthenium isomers possess the triplet ground states. The relative stability between the two iron isomers follows the order of Fe-2a > Fe-2b, which is in agreement with the conclusions of Hong et al. Moreover, the trend of the relative stability of the two ruthenium isomers is Ru-2a > Ru-2b. The Density-of-States spectrums represent that the contribution of BQCN ligand to ${}^3\text{Fe-2b}$ is more than the corresponding contribution to ${}^3\text{Fe-2a}$. The iron isomers react with isopropylbenzene via a two-state reactivity pattern on competing triplet and quintet spin states, while the ruthenium isomers react with isopropylbenzene by a single-state mechanism, only on the triplet spin state. The H-abstraction is affected by the tunneling contribution, which can decrease the reaction barriers. By adding the ZPE correction, PCM model assessed by DFT-D3 (BJ) and the tunneling correction, the analysis of the trend of the hydrogen-abstraction reactions barriers shows that Fe-2a is the more reactive than Fe-2b with the higher $\text{Fe}^{\text{IV/III}}$ redox potential. Moreover, for the ruthenium complexes, although Ru-2a is the more reactive than Ru-2b, only 0.6 kcal/mol lower. Above all, the ligand topology has little effect on the reactivities of the $[\text{Ru}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ complexes.

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1. Introduction

Oxygen-activating enzymes with mononuclear non-heme iron active sites participate in many metabolically important reactions that have environmental, pharmaceutical, and medical significance [1]. Over the past 15 years, studies have demonstrated that the iron (IV)-oxo state is accessible synthetically in a non-heme ligand environment [2]. Since the first crystal structure of a synthetic mononuclear non-heme iron(IV)-oxo complex was reported in a chemical model of non-heme iron enzymes in 2003 [3], a variety of mononuclear non-heme iron(IV)-oxo complexes bearing tetradentate N4 and pentadentate N5 and N4S ligands have been synthesized and characterized using various techniques, such as Mössbauer resonance and Raman and X-ray absorption spectroscopy, and density functional theory calculations [3–45]. In the biomimetic field, the reactivity and stability of non-heme iron(IV)-oxo complexes are sensitive to the ligand structure [40,46]. A number of important factors control the reactivities of

non-heme iron complexes in oxidation reactions. One such factor that determines the reactivities of iron catalysts is the ligand structure around the iron center [47].

Linear tetradentate N4 ligands can form around an octahedral iron center in three different topologies: $\text{cis-}\alpha$, $\text{cis-}\beta$, and trans forms [47]. The $\text{cis-}\alpha$ labile exchangeable sites which could affect the mechanism of the oxidation in iron(IV)-oxo complex have been studied by Prat I et al. [48]. Until 2011, the effect of topology on non-heme iron(IV)-oxo complex reactivity had not been explored. Mononuclear non-heme iron(IV)-oxo complexes with two different topologies have been synthesized and characterized using various spectroscopic methods by Hong et al. [47]. The complexes are $\text{cis-}\alpha\text{-[Fe}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ (Fe-2a) and $\text{cis-}\beta\text{-[Fe}^{\text{IV}}\text{(O)(BQCN)]}^{2+}$ (Fe-2b), in which the N-methyl groups are anti-aligned and aligned, respectively, (BQCN = N,N'-dimethyl-N,N'-bis(8-quinolyl)-cyclohexanediamine). The ${}^1\text{H}$ NMR spectra of Fe-2a and Fe-2b exhibit distinct peaks, which indicates that they each retain their respective ligand topologies in solution [47]. The $\text{Fe}^{\text{IV/III}}$ redox potential of Fe-2a is 0.11 V higher than Fe-2b, and both of them are more reactive than $[\text{Fe}^{\text{IV}}\text{(O)(N4Py)]}^{2+}$ (N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine), $[\text{Fe}^{\text{IV}}\text{(O)}$

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(Bn-TPEN)]²⁺ (Bn-TPEN = N-benzyl-N,N',N'-tris(2-pyridylmethyl)-1,2-diaminoethane), and [Fe^{IV}(O)(TMC)(NCMe)]²⁺ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [3,12,13,46].

Ligand topology is therefore an important factor that affects oxidizing power of the non-heme iron (IV)O complexes. However, little is known about it to date, except the theoretically-reported reaction barrier of Fe-2a [24]. The fundamental reasons for the different stability and reactivity of Fe-2a relative to Fe-2b are of great significance for the better understanding of the topological effects of equatorial ligands. Nonetheless, the detailed theoretical study on the effect of ligand topology on the non-heme Fe(IV)O complex reactivity remains vacant until now. In order to determine the ligand structures around the ruthenium center, a hypothetical [Ru^{IV}(O)(BQCN)]²⁺ complex, which contains two isomers Ru-2a and Ru-2b, was theoretically designed. Therefore, we have performed a density functional theory (DFT) calculation of the geometric and electronic structures, the tunneling effect, the Fe^{IV/III} redox potentials, and the isopropylbenzene hydrogen abstraction by the iron and ruthenium complexes.

2. Computational methods

2.1. Standard methods

We considered the triplet and quintet spin states for Fe-2a and Fe-2b; and the triplet spin states for Ru-2a and Ru-2b. DFT calculations were performed with the GAUSSIAN 09 suite of a quantum chemical package [49], and the spin-unrestricted Becke, three-parameter, Lee–Yang–Parr (B3LYP) functional [50] as the method of choice. The geometries for the four non-heme complexes were fully optimized without symmetry constraints. The Lanl2DZ basis set [51] was used for iron and ruthenium, moreover 6-311G** [51c,52] for the other atoms. To save computational resources, for the reaction pathways, we used the Lanl2DZ basis set for iron and ruthenium, the 6-311G** basis set for electron-rich O atom, and the 6-31G** basis set for C, H, and N atoms (B1 in brief). This basis set is used to optimize transition states and minima. All transition states were confirmed by one imaginary mode from vibrational analysis calculations and the local minima described here only have real frequencies. Single-point energy calculations were performed with a larger basis set TZVP [53] for all atoms (B2 in brief) of iron complexes. For ruthenium complexes, the def2-TZVP [53] on Ru and TZVP for other atoms were used for single-point energy calculation (B2 in brief). To evaluate the solvent effect, acetonitrile was used in the self-consistent reaction field calculations according to the polarizable continuum model (PCM), and the PCM model was assessed by DFT-D3 (BJ) [54] (with Grimme's 2011 dispersion correction) and the SMD model. The mechanism of hydrogen abstraction reaction was determined using intrinsic reaction coordinate studies.

2.2. Tests of the functionals

It has been reported that the UB3LYP functional has verified the spin-state splitting of mononuclear non-heme iron complexes. However, in this work, the focus is on two iron complexes with triplet and quintet states, which are close in energy, so it is necessary to test the functionals. To determine the choice of UB3LYP, we used both of the UOPBE [55] and UTPSSh [56] functionals. For the two iron complexes, all three functionals predict that Fe-2a is the more stable than Fe-2b. Tests of the relative energy and geometric parameters of the transition states for the reactions of two iron isomers with isopropylbenzene were performed with the three functionals. Because the UTPSSh underestimates the relative energy of the quintet spin state, the O–H distance which is calculated by the

UTPSSh functional is shorter on the quintet spin state. As expected, the UOPBE/B2//UOPBE/B1, UTPSSh/B2//UTPSSh/B1, UOPBE/B2//UB3LYP/B1, and UTPSSh/B2//UB3LYP/B1 results are comparable with those obtained from UB3LYP/B2//UB3LYP/B1. Therefore, all functionals give the same ordering of species and we selected UB3LYP as the method of choice. The computational details are presented in the [Supplementary electronic material \(SI\)](#).

2.3. Tunneling corrections

Eckart tunneling calculations were performed using TheRate Program [57]. Due to the tunneling, the transmission coefficient κ , is calculated by integrating of the barrier “penetration” probability as a Boltzmann-averaged function of the energy [58]. The effect of the transmission coefficient on the barrier is calculated by the equation [59]:

$$\Delta\Delta E_{\text{tun}}^{\#} = -RT \ln \kappa(T) \quad (1)$$

where R denotes the universal gas constant and T is the absolute temperature. Generally, the experimental rate data were collected at 273 K.

2.4. Electronic structures of the Fe-2a and Fe-2b

In order to understand the ligand topology effect better, we calculated the electronic structures, including Orbital population, Wiberg bond order, Hirshfeld charge, Density-of-States (DOS) and Overlap Population Density-of-States (OPDOS) Spectrums. All the calculations were performed using Multiwfn program [60].

3. Results and discussion

3.1. Properties of the four complexes

Our computational study produced geometric and electronic structures of the two iron and ruthenium isomers. The two possible iron and two hypothetical ruthenium isomers, which have the same BQCN ligand but different ligand wrapping around the metal center, will be discussed in detail. Structurally, the N-methyl groups of the BQCN ligand have different configurations in the two topologies: anti-aligned in the cis- α isomer (2a) and aligned in the cis- β isomer (2b) [47]. The two ruthenium isomers followed by metal center exchange of the iron by ruthenium. We set z to be along the Fe–O axis, whereas x and y are along the equatorial nitrogens.

3.1.1. Properties of the two iron isomers

The geometric structures for the two iron isomers are shown in [Fig. 1](#), with the corresponding energies of the singlet, triplet and quintet spin states relative to the triplet state at the higher level, UB3LYP/B2//UB3LYP/B1. The key geometric and electronic parameters in the UB3LYP/B1 optimized geometries of the corresponding isomers are listed in [Table 1](#). The bond length and bond order reveal that the Fe–O bond typically has double bond character and the bond length does not change significantly from the triplet to the quintet spin state, because $\sigma_{x^2-y^2}^*$ is strongly Fe–N σ -antibonding and is perpendicular to the Fe–O bond. The calculated Fe–O bond lengths for the two isomers are 1.630 Å and 1.626 Å, respectively, which are similar to that in crystal structures of some other non-heme iron(IV)-oxo complexes with an $S = 1$ spin state [3,8]. On the triplet/quintet spin state, the Wiberg bond orders between the Fe fragment and the O fragment are 1.640/1.671 for Fe-2a and 1.649/1.686 for Fe-2b, respectively. The reason that we have chosen the Wiberg bond order and the Hirshfeld charge analyses has been noted in [SI](#).

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