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"HIGH-VALENT" FERRYL-OXO COMPLEXES: HOW "HIGH" ARE THEY REALLY?

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ABSTRACT. S=1 $[FeO]^{2+}$ complexes are implicated in key biological oxidations with heme and non-heme enzymatic systems. These complexes are unanimously described as S=1 Fe(IV) covalently bound to O^{2-}. Reported here are UMP2/6-311+G** results for S=1 $[FeO]^{2+}$ in an octahedral ligand field, intriguingly suggesting that (1) the degree of iron-oxygen covalence may have previously been overestimated, and (2) the limiting description as {S=1/2 Fe(III) + S=1/2 $O^{\cdot-}$} is more suitable than {Fe(IV) + O^{2-}}.

INTRODUCTION

S=1 $[FeO]^{2+}$ complexes have been implicated in key biological oxidations with heme and non-heme enzymatic systems.[1-3] These complexes are unanimously described as S=1 Fe(IV) covalently bound to O^{2-} (cf Scheme 1).[1, 3-11] As reviewed in Ref[10], such description is consistent with extensive experimental data, including magnetic susceptibility, Mossbauer, EPR, NMR, resonance Raman, EXAFS, and X-ray crystallography. Further, semiempirical,[12-14] X-α,[15] DFT,[6, 8, 9] UHF,[16] RHF and CASSCF[11] calculations yielded pictures consistent with a strongly covalent Fe(IV)-oxo unit.

The main two lines of evidence supporting the Fe(IV)-oxo description come from Mössbauer spectroscopy and computational chemistry. Mössbauer parameters for biologically relevant S=1 $[FeO]^{2+}$ complexes were found to be more consistent with an Fe(IV) description than with Fe(II) or Fe(III).[17-23] While Mössbauer spectroscopy is generally assumed to be an infallible tool for pinpointing iron oxidation states, examples are known to the contrary. For instance, a recent exemplary synergy of spectroscopic, structural, and computational data on S=1/2 $[FeNO]^{7}$ complexes has shown that in a series of ferrous complexes, changes in the identity of one ligand altered Mössbauer parameters to extents similar to those observed upon a change in formal iron oxidation state.[24]

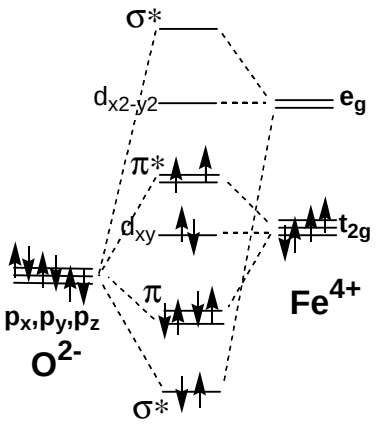
Kohn-Sham (DFT)[6, 8, 9] as well as RHF-CASSCF[11] orbitals computed by various groups have yielded a picture of the Fe-O interaction in S=1 $[FeO]^{2+}$ complexes, consistent with strong Fe(IV)-oxo covalence. The two unpaired electrons were found to be evenly delocalized onto the iron and oxygen atoms, within π^*_{xz} and π^*_{yz} orbitals. The convergence of CASSCF and DFT results on this issue provides a strong theoretical foundation for interpreting the available experimental data.

Previous attempts to provide a detailed molecular orbital description of S=1 $[FeO]^{2+}$ either relied on DFT, or on restricted Hartree-Fock based approaches. Seeking to further our understanding of bonding in these important biological

complexes, we report here on the molecular orbital picture in an octahedral S=1 $[FeO]^{2+}$, obtained with an unrestricted MP2 approach. Intriguingly, we find that (1) the degree of iron-oxygen covalence may have previously been overestimated, and (2) the limiting description as {S=1/2 Fe^{3+} + S=1/2 O^{-}} is more suitable than {Fe(IV) + O^{2-}}.

RESULTS AND DISCUSSION

Scheme 2 shows the UMP2/6-311+G** molecular orbital diagram for a S=1 $[FeO]^{2+}$ complex in an octahedral environment (for reference, the equivalent diagram obtained with a standard density functional, UBP86, is shown as Supporting Information; the latter agrees entirely with previous RHF/CASSCF and DFT results).[25, 26] First, we note that, as expected (cf. Scheme 1), the iron d_{xy} orbital (38α, 37β) is doubly-occupied, while the d_{z2} and d_{x2-y2} (essentially, 43α, 44α, 44β, 42β) are empty. In the iron-oxygen σ molecular orbital (40α, 39β), the oxygen contribution appears stronger than the iron contribution. This is consistent with a picture where the σ bond is dative (O:→Fe), rather than covalent (O· + ·Fe).

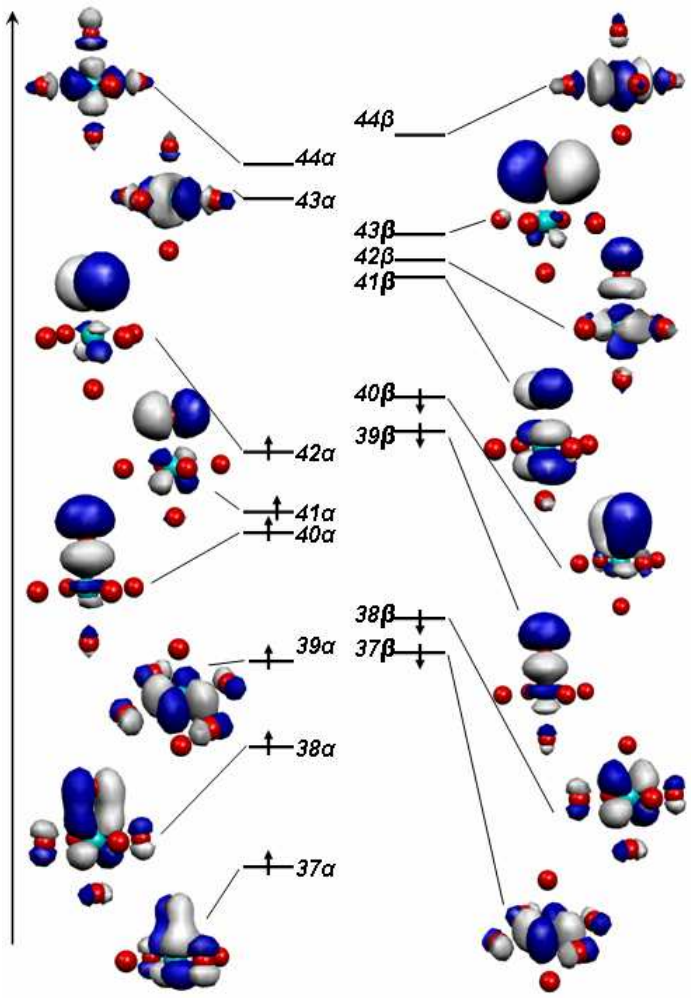


Scheme 1

Also consistent with expectations illustrated by Scheme 1, the two unpaired electrons in Scheme 2 are found to reside in the Fe-O π* molecular orbitals. Orbital 43β (formally π*) is empty, and is almost entirely localized onto the oxygen. The corresponding π orbital is accordingly localized on the iron. The other pair of π/π* orbitals, 40β and 41β, feature the inverse situation: the bonding (occupied) orbital is mainly oxygen-localized, and the anti-bonding (empty) orbital has significant iron character. Thus, the system appears best described as featuring one unpaired electron on the oxygen, and one on the iron – implying a Fe^{3+}-O^{-} description. Finally, notable as a general feature, is the significantly smaller covalence in the orbitals shown in Scheme 2, compared to orbitals obtained from DFT calculations (not shown).

The simplified model used here ignores covalence between iron and its other (“non-oxo”) ligands. Such covalence may lead to intricate orbital mixing, to the extent where the iron-oxygen interaction may appear entirely covalent. Furthermore,

non-covalent effects such as hydrogen bonding are known to affect the polarizability of the iron-oxygen interaction in S=1 $[FeO]^{2+}$ complexes.[9, 27] These effects may well be small, since, as shown in Supporting Information, the same "Fe^{3+}+O^{-}" description in fact applies to a more realistic, solvated, S=1 Fe(IV)=O model, $[Fe(NH_3)_4(CN)O]^{2+}$ (an adduct known to exist experimentally[1], albeit with aliphatic amine rather than ammonia equatorial ligands). Systems such as S=1 $[FeO]^{2+}$ are expected to have low-lying excited states, an issue not explicitly addressed by our computational approach. Thus, to conclude, our proposed "Fe^{3+}+O^{-}" description is simply a limiting structure. To verify to which extent this limiting structure would be more realistic than the traditional Fe(IV)-oxo limiting structure, more sophisticated treatments of S=1 $[FeO]^{2+}$ complexes and are underway.



Scheme 2

The key finding of our study appears to be that S=1 $[FeO]^{2+}$ complexes are far from being as covalent as previously assumed. This (together with the availability of low-lying excited states) differentiates S=1 $[FeO]^{2+}$ from S=1 O_2 (another diatomic featuring two singly-occupied π^* orbitals). Unlike molecular oxygen, $[FeO]^{2+}$ is known to be reactive as an oxygen transfer agent, performing oxygen *atom* insertion in aliphatic C-H bonds.[4] The latter reactivity is much more readily reconciled with our newly-proposed UMP2 description than with the classical "triplet dioxygen-like" description. Beyond this orbital argument, the reactivity of S=1 $[FeO]^{2+}$ (much like S=1 O_2) appears to also be governed by spin state conservation. Heme as well as non-heme mononuclear S=1 $[FeO]^{2+}$ complexes in fact exhibit significantly lower reactivity as oxygen transfer agents, compared to their one-electron oxidized counterparts. These latter complexes, known as Compound I in hemoproteins, feature a S=1/2 state when the axial ligand trans to the oxygen is a thiolate, and a S=3/2 state when the axial ligand is a histidine.[1, 2, 8] This difference in spin states is due to either ferromagnetic or antiferromagnetic coupling between S=1 $[FeO]^{2+}$ and the S=1/2 oxidized porphyrin in Compound I.[8] The reaction of Compound I with aliphatic hydrocarbons leads to a product-bound state which is S=1/2 Fe(III) with a thiolate ligand (i.e., ground state), but is S=3/2 Fe(III) with a histidine ligand (i.e., excited state). Consistently, thiolate-ligated hemoproteins are far more frequently involved in oxygen-transfer reactions than histidine-ligated hemoproteins.[2, 7] Similarly, di-iron non-heme S=1 $[FeO]^{2+}$ complexes are known to be more efficient oxygen atom-transfer reagents than their mononuclear counterparts,[1, 28, 29] with the second iron of the complex possibly playing the same role as the heme of Compound I in preserving spin state along the reaction coordinate. The extent of availability of excited states ([Fe(IV)-oxo], [Fe(II)-oxygen atom]) for $[FeO]^{2+}$ complexes is also a likely "switch" whereby the other iron ligands (heme or non-heme) may control oxygen-transfer reactivity.

EXPERIMENTAL

The Gaussian98 suite of programs was used for all calculations. Further details are provided in text.

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