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Electronic Structure of a Formal Iron(0) Porphyrin Complex Relevant to CO₂ Reduction

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Supporting Information

ABSTRACT: Iron porphyrins can act as potent electrocatalysts for CO₂ functionalization. The catalytically active species has been proposed to be a formal Fe(0) porphyrin complex, $[Fe(TPP)]^{2-}$ (TPP = tetraphenylporphyrin), generated by two-electron reduction of $[Fe^{II}(TPP)]$. Our combined spectroscopic and computational investigations reveal that the reduction is ligand-centered and that [Fe- $(TPP)]^{2-}$ is best formulated as an intermediate-spin Fe(II) center that is antiferromagnetically coupled to a porphyrin diradical anion, yielding an overall singlet ground state. As such, $[Fe(TPP)]^{2-}$ contains two readily accessible electrons, setting the stage for CO₂ reduction.

■ INTRODUCTION

Primarily because of the vast use of carbon-based fuels in combustion processes, the amount of CO_2 in the atmosphere has increased by almost 40% over the past 100 years, contributing significantly to global warming. Therefore, to cope with present environmental and energy issues, the reconversion of CO₂ into building blocks that can be employed for further use like formaldehyde, formic acid, oxalic acid, methanol, and CO has attracted much interest. Because of its thermodynamic stability and kinetic inertness, facile CO₂ reduction requires not only high energy input but also suitable catalysts.² One area of growing interest is electrochemical CO₂ functionalization, in part because such processes could be powered by renewable energy from wind and solar power plants.³ In addition to transition metal complexes based on cyclam⁴ or bipyridine⁵ ligands, iron porphyrins are known to act as potent catalysts for activating CO_2 .⁶ Iron(II) tetraphenylporphyrin ([Fe(TPP)]⁰), featuring a triplet ground state, can undergo two reversible single-electron reductions, yielding formal iron(I) ([Fe- $(TPP)]^{-}$ and iron(0) complexes ([Fe(TPP)]²⁻). The latter has been proposed to be the catalytically active species for CO₂ reduction.^{6,7} In the presence of external or internal proton sources, [Fe(TPP)]²⁻ and its derivatives have been reported to exhibit one of the highest catalytic activities and turnover frequencies observed so far.^{6a,b,d,e} To pinpoint the pivotal features responsible for the high efficiency of $[Fe(TPP)]^{2-}$, understanding its electronic structure is a prerequisite.



There is, however, controversy about the exact nature of the electronic ground states of $[Fe(TPP)]^-$ and $[Fe(TPP)]^{2-}$, because the reductions can be either metal- or ligand-centered. A variety of spectroscopic studies, including ⁵⁷Fe Mössbauer,⁸ electron paramagnetic resonance (EPR),^{8,9} resonance Raman,¹⁰ nuclear magnetic resonance (NMR),^{9a,11} X-ray diffraction,⁸ and ultraviolet/visible (UV/vis)^{9b,10a,11a,12} experiments, have been undertaken. Interestingly, different techniques seem to support distinct electronic structure descriptions of the ground state, and no consensus has yet been reached. Herein, we present a detailed electronic structure investigation of $[FeTPP]^{2-}$ by using a combined spectroscopic and computational approach.

EXPERIMENTAL DETAILS

Synthesis. All reactions were performed in an inert glovebox argon atmosphere. Stabilizer-free tetrahydrofuran (THF) was purchased from Acros Organics, stirred over sodium for 2 days, and stored over molecular sieves (4 Å). Stabilizer-free 2-MeTHF was purchased from Acros Organics. Before use, it was degassed by a freeze–pump–thaw technique (three cycles), stirred over sodium for 2 days, and stored over molecular sieves (4 Å). Heptane was purchased from Acros Organics, degassed by being bubbled with argon for 1 h, and stored over molecular sieves (4 Å). FeCITPP was purchased from Sigma-Aldrich with 95% purity (porphyrin residue). Sodium anthracenide was prepared by a previously described procedure.¹³ If reactions were performed in THF, 0.2 M sodium anthracenide in THF was used as a

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reducing agent. If reactions were performed in MeTHF, 0.2 M sodium anthracenide in MeTHF was used as a reducing agent. After reduction, all samples were stored at -40 °C inside the glovebox. All iron porphyrin species were prepared according to the published procedure.⁸

Mössbauer Spectroscopy. Mössbauer spectra were recorded on a conventional spectrometer with alternating constant acceleration of the γ -source. The minimum experimental line width was 0.24 mm/s (full width at half-height). The sample temperature was kept constant in an Oxford Instruments Variox or in an Oxford Instruments Mössbauer-Spectromag. The latter is a split-pair superconducting magnet system for applied fields up to 8 T where the temperature of the sample can be varied in the range of 1.5–250 K. The field at the sample is perpendicular to the γ -beam. The ⁵⁷Co/Rh source (1.8 GBq) was positioned at room temperature inside the gap of the magnet system at a zero-field position, by using a re-entrant bore. Isomer shifts are quoted relative to iron metal at 300 K. Magnetic Mössbauer spectra of fully reduced compound **4b** were simulated with the program MX (by E.B.) by using the usual nuclear Hamiltonian with an applied field only and zero internal field due to electronic spin S = 0.¹⁴

Zero-field spectra were measured at 80 K. For solid-state measurements, the obtained solid was filled into a self-sealing Delrin capsule in the glovebox. The capsule was additionally wrapped airtight in aluminum foil and placed in liquid nitrogen directly after being discharged from the glovebox. Handling and mounting of the samples were performed under liquid nitrogen. For solution measurements, the preparation of the reduced species was performed according to the previously described procedures. The starting compound was enriched with 20% [⁵⁷Fe(TPP)Cl]. The reaction solution was filtered and directly used for Mössbauer experiments. The solution capsule was placed in a Schlenk flask, discharged from the glovebox, and placed in liquid nitrogen until the solution was frozen. Handling and mounting of the samples were performed under liquid nitrogen.

UV/Vis. All UV/vis experiments were performed in MeTHF. Preparation as well as measuring of the samples was performed inside the glovebox with an optical fiber, using a 1 mm cuvette. Handling of the samples has to be performed without delay because of the high reactivity of the samples in solution. UV/vis spectra were recorded on a HP 8453 Diode Array system (190–1100 nm).

X-ray Absorption Spectroscopy (XAS). For solid-state XAS experiments, the samples were diluted in boron nitride, sealed in an aluminum spacer (1 mm layer thickness) between 38 μ m Kapton tape windows, and stored in liquid nitrogen. Handling and transportation of the samples were performed under a nitrogen atmosphere. XAS measurements were performed on ESRF beamline BM23, which is equipped with a liquid N2-cooled Si(111) double-crystal monochromator, which was used for energy selection. Energy calibration was performed by setting the first inflection of an Fe foil to 7111.2 eV. A beam size of 500 μ m \times 3 mm was used. A continuous flow dualchamber liquid He cryostat at 10 K was used. All samples were continuously monitored for signs of radiation damage throughout the course of data collection. Data were measured over an energy range of 7056-7970 eV. Data calibration and averaging were performed using Athena from the IFEFFIT package. Peak positions of the pre-edge and rising edge were determined by calculating the center of mass of the second-derivative minima of five-point smoothed spectra.

Theoretical Calculations. All calculations were performed with the ORCA program package.¹⁵ Geometry optimizations were performed on experimental X-ray structures using the BP86 functional¹⁶ with TZVP¹⁷ and ZORA-TZVP basis sets¹⁸ on all atoms. To accelerate calculations, the resolution of identity (RI) approximation is used in combination with the TZVP auxiliary basis set.¹⁹ Calculations of Mössbauer parameters were then performed using the B3LYP functional²⁰ together with the TZVP auxiliary basis set. The isomer shift was predicted by employing the calibration parameters previously published for a given combination of functionals and basis sets.²¹ An example of the input file for geometry optimization and parameter calculations is given in the Supporting Information. For XAS, calibration calculations were conducted on a series of literature known and measured iron complexes according to a previously published procedure.²² The list of complexes together with their experimental pre-edge energies as well as the herein calculated energies (shifted by a constant value of 22.37 eV for the used functional/basis set) is given in Table S1. Geometry optimizations of all iron complexes were performed on the basis of experimental X-ray structures employing the B3LYP functional with def2-TZVP basis sets,²³ followed by time-dependent density functional theory (TD-DFT) calculations using the CAM-B3LYP functional²⁴ together with the def2-TZVP auxiliary basis set.²⁵ During integral generation and transformation, the R1^{19a} and chain-of-sphere (COSX)²⁶ approximations were applied for Coulomb and exchange integrals, respectively.

RESULTS AND DISCUSSION

Preparation of all reduced species was performed by previously published procedures (for further details, see the Supporting Information).⁸ Specifically, sequential reduction of the Fe(III) precursor, [Fe(TPP)Cl] (1), leads to isolation of ferrous $[Fe(TPP)(THF)_2]$ (2a) (S = 2), [Fe(TPP)] (2b) (S = 1), and the two- and three-electron-reduced sodium solvate complexes, $[Fe(TPP)][Na(THF)_3]$ (3a) (S = 1/2) and $[Fe(TPP)][Na(THF)_3]_2$ (4a) (S = 0), respectively. The crystal structure⁸ of 4a shows the coordination of two $[Na(THF)_3]^+$ moieties to a pyrrole nitrogen on each side of the porphyrin plane. To circumvent the complexity arising from this additional interaction, we prepared solution samples of $[Fe(TPP)]^-$ (3b) and $[Fe(TPP)]^{2-}$ (4b) by using 18-crown-6 to trap Na⁺ and dissolving 3a and 4a into an essentially noncoordinating solvent, 2-methyl-THF.

Iron K-edge X-ray absorption spectroscopy (XAS) provides an experimental means of assessing changes in the iron oxidation state within a series of related complexes. Figure 1A shows the normalized XAS spectra for solid samples of all complexes under investigation. The XAS spectra are comprised of three primary features: (1) weak 1s to 3d pre-edge feature in the \sim 7111–7113 eV region, (2) a rising edge shoulder at \sim 7118 eV, and (3) the rising edge inflection point (at \sim 7123 eV). Complex 1 clearly has the highest-energy pre-edge feature (Figure 1A and Table 1) and the highest-energy rising edge position (Figure 1A), consistent with ferric iron.²⁷ In contrast, complexes 2-4 have lower-energy pre-edges [with the lowest 1s to 3d feature at \sim 71111 eV (Table 1)] and a lower-energy rising edge position. These observations suggest that the iron centers in complexes 2-4 feature the same valence state (ferrous iron), thus pointing to ligand-centered reductions for complexes 3 and 4. We note, however, that significant changes are observed in the spectra of 2-4 in the \sim 7118 eV region. In the case of complex 2b, this feature can be attributed to a lowlying 1s to $4p_z$ transition due to the four-coordinate environment at the Fe. Similar features are also observed for complexes 3 and 4, reflecting the fact that $[Na(THF)_3]$ is only weakly interacting. In contrast, for six-coordinate complex 2a, this feature is absent as the $4p_z$ orbital is shifted to higher energies because of axial coordination. Using TD-DFT calculations, we are able to generally reproduce the trends observed in the energies and intensities of both the lowest-lying 1s to 3d pre-edge transitions (Figure 1B) and the \sim 7118 eV 1s to 4p feature (see Figure S4). As shown in Table 1, the calculations indicate similar pre-edge transition energies for 2a, 2b, 3a, and 4a and a considerably higher pre-edge transition energy for 1, consistent with the experimental observations. We note that the additional feature at ~7113.5 eV observed in the XAS spectrum of 2a is not predicted computationally. This may suggest that this feature originates from charge transfer processes, which are not well modeled by TD-DFT approaches.



Figure 1. (A) Experimental XAS spectra of iron tetraphenylporphyrins in all known oxidation states with an enlarged pre-edge region shown. (B) Calculated pre-edge features of 1–4.

Table 1. Experimental (exp.) and Calculated (calcd) Pre-Edge Energies (eV)

complex	S	exp.	calcd	bonding ^a			
1	⁵ / ₂	7112.9	7113.2	HS-Fe(III)(TPP) ²⁻			
2a	2	7110.5	7111.1	$HS-Fe(II)(TPP)^{2-}$			
2b	1	7110.5	7111.3	IS-Fe(II)(TPP) ²⁻			
3a	¹ / ₂	7110.5	7111.6	IS-Fe(II)(TPP) ^{3−•}			
4a	0	7110.1	7111.6	IS-Fe(II)(TPP) ^{4−••}			
^a Abbreviations: HS, high spin; IS, intermediate spin.							

In any case, the similarity in the lowest-energy 1s to 3d transitions supports a similar electronic structure at the iron in complexes 2-4, providing experimental evidence of ligand-centered reductions across this series.

In addition to our XAS studies, Mössbauer studies were performed on the complete series of complexes and further correlated to computations. The experimental Mössbauer parameters for the solid samples of **2a**, **2b**, **3a**, and **4a** have been previously reported;^{8,28} however, to the best of our knowledge, a detailed correlation of the experimental Mössbauer parameters to the electronic structures has not been made. Our Mössbauer measurements (Table 2) reproduced all previously published data. The measured isomer shifts for complexes **2b**–**4** all cluster around a remarkably low value of ~0.5 mm/s, having only small differences of ~0.1 mm/ s. In contrast, six-coordinate complex **2a** has a significantly

Table 2. Experimental (exp.) and Calculated (calcd) Isomer Shifts, δ (millimeters per second), and Quadrupole Splittings, ΔE_Q (mm/s), of Iron Tetraphenylporphyrin Species under Investigation

complex	δ exp.	δ calcd	$ \Delta E_{\rm Q} $ exp.	$ \Delta E_Q $ calcd			
2a ³²	0.95	0.90	2.64	2.34			
2b ^{28a,b}	$0.57^a (0.50^b)$	0.55	$2.21^{a} (1.51^{b})$	1.11			
3 ⁸	$0.65^c (0.52^d)$	0.48	$2.23^{c} (2.21^{d})$	0.32			
4 ⁸	$0.49^{e} (0.45^{f})$	0.59	$1.35^{e} (1.50^{f})$	0.75			
Values for 2b with a saddled core. ^{<i>b</i>} Values for 2b with a ruffled core.							

^cValues for 3a. ^dValues for 3b. ^eValues for 4a. ^fValues for 4b.

more positive isomer shift of 0.95 mm/s that is typical for sixcoordinate high-spin ferrous porphyrin complexes.²⁹ This experimental finding provides strong support for the notion that the iron centers in 2b, 3b, and 4b feature not only the identical oxidation state, consistent with the XAS results, but also the same local spin state ($S_{\text{Fe}} = 1$), as previously assigned for four-coordinate Fe(II) porphyrins.^{8,28,29} Should the reduction be iron-centered, the changes in the isomer shift should be more pronounced than what is found for 3b and 4b, because the isomer shift is a sensitive probe of the local electronic structure change at the iron center. The somewhat different isomer shifts between the measurements performed on the solid samples and the frozen solutions found for complexes 3 and 4 may be attributed to the weak coordination of $[Na(THF)_3]^+$ to the porphyrin ring in the solid state.⁸ For all investigated systems, the DFT-computed isomer shifts match the experimental values (in solution) reasonably well within the well-established uncertainty range ($\sim 0.1 \text{ mm/s}$).²¹ According to our earlier experiences,³⁰ the large deviations (>1 mm/s) between computed quadrupole splittings and experimental values are not unusual, especially for compounds involving a flexible first coordination sphere, such as porphyrin complexes, for which porphyrin may adopt several nearly isoenergetic core conformations.³¹ Such different core geometries may manifest themselves in the quadrupole splittings, as found for the two conformers of complex 2b (Table 2), whereas the influence on the isomer shift is insignificant. This may explain the particularly large error in the calculated quadrupole splitting of complex 3.

The magnetic Mössbauer spectrum of complex **4b** recorded at 4.2 K with an applied magnetic field of 4 T (Figure 2) confirms the diamagnetic ground state of this compound.⁸ In light of the consistent Mössbauer data of complex **2b**, we suggest that the S = 0 ground state of complex **4b** arises from a strong antiferromagnetic intramolecular exchange coupling of an intermediate-spin iron(II) ($S_{\text{Fe}} = 1$) with a porphyrin triplet anion diradical ($S_{\text{TPP}} = 1$).

Our spectroscopic results clearly evidence that complexes 3 and 4 contain intermediate-spin ferrous ions, the same as that found for 2b.^{28,33} In accordance with this conclusion, a computational attempt to locate a low-spin d⁷ Fe(I) state for 3b from different initial guesses failed, indicating that the Fe(I) state is much higher in energy. A low-spin d⁸ Fe(0) state for 4b can be obtained from the restricted Kohn–Sham calculations; however, this state is 58 kcal/mol above a broken-symmetry state discussed below. More importantly, our computed electronic structures also predict accurate spectroscopic parameters when compared to the experimental Mössbauer isomer shifts and XAS data, whereas the computed isomer shift for the hypothetical d⁸ Fe(0) species (0.38 mm/s) shows a



Figure 2. Applied magnetic field Mössbauer spectrum of $[FeTPP]^{2-}$ in MeTHF (4b) recorded at 4.2 K and 4 T. The green line shows a simulation of the target compound with S = 0 and $\delta = 0.45$ mm/s, $\Delta E_Q = +1.50$ mm/s, and asymmetry parameter $\eta = 0.1$ (see Table 2). The dotted line represents an unknown ferrous impurity (accounting for 10% of the total iron) with $\delta = 1.02$ mm/s, $\Delta E_Q = +3.61$ mm/s, and $\eta = 0.3$, which also could be simulated with an S = 0 ground state (we presume that the apparent diamagnetism may arise from an exceptionally large zero-field splitting rendering an isolated $m_s = 0$ ground sublevel, or from exchange coupling within a dimer). The red line is the superposition of both subspectra.

substantial deviation from the experiment. Similarly, the calculated pre-edge energy for the d⁸ Fe(0) state ($E_{\text{pre edge}} = 7112.1 \text{ eV}$) is distinctly different from that experimentally observed for complex **2b**. As depicted in Figure 3, the iron



Figure 3. Schematic molecular orbital diagram of 4.

center in complex 4 features a $d_{xy}^2 d_{z^2}^2 d_{xz}^{-1} d_{yz}^{-1}$ electron configuration that is antiferromagnetically coupled to a triplet porphyrin diradical tetra-anion. Because the singly occupied Fe d_{xz} and d_{yz} orbitals and the π^* orbitals of the porphyrin radical³⁴ transform as the same irreducible representation (e_g) in the effective D_{4h} point group, antiferromagnetic coupling is achieved by symmetry-allowed overlap as quantified by the large S values (Figure 3). It has been reported that complex 4 possesses a diamagnetic ground state even at room temperature.⁸ Remarkably, this exchange interaction fixes the iron electron configuration to be $d_{xy}^2 d_{z}^{22} d_{xz}^{-1} d_{yz}^{-1}$, consistent with the negligibly small asymmetry parameter (η) determined by applied field Mössbauer spectroscopy (Figure 2). In contrast, there remains intense debate about the exact electron configuration for the ground state of complex **2b**, for which two different states have been proposed, either $A_{2g}(d_{xy}^2 d_{z}^{2d} d_{xz}^{-1} d_{yz}^{-1})$ or $E_g(d_{xy}^2 d_{z}^{-21} (d_{xz} d_{yz})^3)$.^{28,33}

CONCLUSION

In summary, our combined experimental and theoretical investigations of the redox series of $[Fe(TPP)]^{0/1-/2-}$ show that the reductions are not metal- but ligand-centered. Analysis of the experimentally validated electronic structure of Fe- $(TPP)]^{2-}$, the putative species for CO₂ functionalization, reveals that the two additional reducing electrons reside in π^* orbitals of the porphyrin ligand. These electrons are likely to be responsible for CO₂ reduction in the catalytic process. As these electrons are delocalized onto the conjugated macrocycle, one can anticipate that the corresponding electron transfer involves marginal geometric distortions of the porphyrin ligand and hence a low reorganizational energy. This contrasts with metalcentered redox processes, which typically entail significant geometric adjustments in the first coordination sphere, especially for 3d transition metals. In other words, noninnocent ligands such as porphyrin may function as electron buffers to facilitate electron transfers in chemical transformations.³⁵ An analogous situation is found for N-H and O-H bond activation mediated by a related corrole system.³⁶ A detailed mechanistic study of CO_2 activation by $[Fe(TPP)]^{2-}$ is in progress.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00401.

Experimental procedures, details of sample preparation, spectroscopic measurements, theoretical calculations, and Mössbauer and XAS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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