

Article

Mixed N₃S₂-Ligated Nonheme Fe(IV)=O Species Balancing Stability and Oxidation Reactivity as a Platform for Nonheme Iron Oxidation Catalysis

Hanaa Mansour¹, Ahmed M. Albasiony¹, Safaa N. Abdou², Mohamed M. Ibrahim¹ , Rudi van Eldik^{3,4} 
and Shaban Y. Shaban^{1,*} 

¹ Chemistry Department, Faculty of Science, Kafrelsheikh University, Kafrelsheikh 33516, Egypt; mansourhanaa@yahoo.com (H.M.); albasiony@sci.kfs.edu.eg (A.M.A.); mohamed.ibrahim@sci.kfs.edu.eg (M.M.I.)

² Chemistry Department, Al-Khurmah University College, Taif University, Al-Khurmah 21985, Saudi Arabia; s.nabeh@tu.edu.sa

³ Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, 91058 Erlangen, Germany; rudi.vaneldik@fau.de

⁴ Faculty of Chemistry, Nicolaus Copernicus University in Torun, 87-100 Torun, Poland

* Correspondence: shaban.shaban@sci.kfs.edu.eg

Abstract

Mononuclear nonheme iron(IV)–oxo species supported by mixed nitrogen–sulfur (N/S) ligands remain scarce, despite the prevalence of sulfur donors in biological iron sites and their expected impact on ferryl reactivity and catalyst design. In this work, a seven-coordinate iron(II) complex, [(N₃S₂)Fe^{II}(ClO₄)₂], bearing a rigid 15-membered N₃S₂ macrocycle, is shown to rapidly generate a mononuclear nonheme Fe^{IV}=O intermediate upon reaction with *m*-chloroperbenzoic (*m*-CPBA) acid in acetonitrile. The Fe^{IV}=O species forms within ≤2 s and is thermally persistent (*t*_{1/2} = 4.3 h at 25 °C), albeit in partial yield (~39% Fe^{IV}=O by Mössbauer spectroscopy), placing it in an intermediate regime between highly reactive but short-lived ferryl species and more inert, long-lived analogues. The intermediate is characterized by Mössbauer spectroscopy ($\delta = 0.35 \text{ mm s}^{-1}$, $\Delta E_Q = 0.90 \text{ mm s}^{-1}$, $\Gamma_{FWHM} = 0.30 \text{ mm s}^{-1}$, relative area = 39.4%), EPR silence, a UV–vis absorption band at 428 nm, and cryogenic high-resolution ESI–MS (*m/z* 223.510, (N₃S₂)Fe^{IV}=O²⁺). Stopped-flow kinetic studies reveal saturation behavior that is well described by a pre-equilibrium oxidant-association model and subsequent O–O bond activation, with apparent activation parameters of $\Delta H^\ddagger = 17.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -155 \text{ J mol}^{-1} \text{ K}^{-1}$, indicating a highly ordered transition state within the seven-coordinate N₃S₂ framework under the conditions employed. Functionally, the Fe^{IV}=O species mediates clean oxygen-atom transfer to triphenylphosphine (*k*₂ = $8.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) with an effective turnover number of ~12 after correction for the Fe^{IV}=O yield, establishing that this mixed N/S platform is catalytically competent under mild conditions, though less reactive than state-of-the-art all-nitrogen systems. Collectively, these findings identify the seven-coordinate N₃S₂ macrocycle as a mixed-donor platform that moderately extends ferryl lifetime while retaining measurable oxo-transfer reactivity, providing mechanistic guidance for the development of nonheme iron oxidation catalysts that incorporate sulfur donors.



Academic Editors: Lingbo Qu, Bing Yu, Rui Li and Kai Sun

Received: 31 May 2026

Revised: 6 July 2026

Accepted: 11 July 2026

Published: 13 July 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

Keywords: nonheme iron; iron(IV)–oxo; mixed N/S ligands; seven-coordinate macrocycle; oxidation catalysis; oxygen-atom transfer; stopped-flow kinetics; mössbauer spectroscopy

1. Introduction

Mononuclear nonheme iron(IV)–oxo species are central to a wide range of biological and synthetic oxidation reactions, including C–H bond hydroxylation, oxygen-atom transfer, and epoxidation. Their ability to mediate these transformations has made them important targets in bioinorganic chemistry, both as mechanistic probes for enzymatic oxygen activation and as platforms for developing nonheme oxidation catalysts [1–4]. In many nonheme systems, these transformations proceed through high-valent ferryl intermediates that serve as key oxidizing species in enzymes such as taurine/alpha-ketoglutarate dioxygenase, isopenicillin N synthase, and bleomycin [1–4]. Accordingly, the synthesis and characterization of discrete $\text{Fe}^{\text{IV}}=\text{O}$ complexes continues to be an active area of research, with broad implications for understanding both biological oxygen activation and the design of new oxidation catalysts [5–7].

Over the past two decades, a large number of mononuclear nonheme $\text{Fe}^{\text{IV}}=\text{O}$ complexes supported by nitrogen-donor ligands have been isolated and studied in detail. These systems include tetradentate and pentadentate ligand frameworks that provide strong, tunable coordination environments capable of stabilizing high-valent iron centers across a range of spin states and lifetimes [5–15]. Small changes in ligand basicity, denticity, and geometry can markedly influence ferryl reactivity and hence catalytic performance. For example, Pal et al. showed that substitution of pyridyl donors by less basic pyrazolyl groups in a pentadentate ligand framework dramatically enhances hydrogen-atom transfer reactivity, underscoring how subtle ligand modifications can alter the balance between stability and oxidizing power [5]. At the same time, highly reactive ferryl complexes often exhibit shorter lifetimes, highlighting the persistent challenge of designing systems that combine high reactivity with sufficient stability for mechanistic study and catalytic turnover [5,8–15].

In contrast, mononuclear $\text{Fe}^{\text{IV}}=\text{O}$ complexes supported by mixed nitrogen–sulfur ligand sets remain comparatively rare. This scarcity is notable because sulfur-containing donors are common in biological coordination environments and are expected to exert a significant influence on iron redox chemistry, ligand-field strength, and oxo-transfer reactivity. Sulfur ligation can modulate the electrophilicity of the ferryl unit, but it can also introduce synthetic and mechanistic complications, including ligand oxidation, sulfur labilization, and altered redox potentials relative to all-nitrogen systems [6,9,10,16–18]. As a result, the extent to which mixed N/S coordination can support a well-defined, mononuclear ferryl intermediate remains limited, and systematic insight into how such ligand environments affect O–O bond activation and oxygen-atom transfer chemistry at iron is still incomplete. In particular, there are only a few examples in which N/S-ligated $\text{Fe}^{\text{IV}}=\text{O}$ species have been characterized by a full suite of spectroscopic and kinetic methods, so the position of mixed-donor ferryl complexes on the stability–reactivity landscape is much less well defined than for the extensively studied all-nitrogen N_4 and N_5 ligand frameworks. Clarifying how sulfur incorporation shifts the balance between ferryl stability (lifetime, spectroscopic tractability) and oxidative reactivity (O–O bond cleavage and oxo-transfer) is therefore essential for developing rational ligand-design strategies in nonheme iron–oxo chemistry and for exploiting mixed N/S environments in oxidation catalysis.

To address this gap, we turned to seven-coordinate iron(II) complex $[(\text{N}_3\text{S}_2)\text{Fe}^{\text{II}}(\text{ClO}_4)_2]$ (1), which was previously synthesized and reported by us [18]. Complex 1 contains a rigid 15-membered N_3S_2 macrocycle and, by single-crystal X-ray diffraction, adopts distorted pentagonal–bipyramidal geometry: three nitrogen and two sulfur donors occupy the equatorial plane while two weakly bound perchlorate ligands occupy the axial positions (Figure 1). This seven-coordinate N/S framework is unusual among nonheme iron systems and offers an attractive platform for exploring whether mixed-donor coordination can

stabilize a high-valent iron–oxo intermediate while retaining sufficient robustness and oxo-transfer reactivity for oxidation catalysis [19,20]. In the present work, we show that oxidation of **1**, via its solvated dication $[(N_3S_2)Fe^{II}(CH_3CN)_2]^{2+}$, with *m*-chloroperbenzoic acid (*m*-CPBA) in acetonitrile rapidly generates a mononuclear $Fe^{IV}=O$ intermediate (Figure 1). We combine Mössbauer spectroscopy, EPR, UV–vis spectroscopy, high-resolution ESI–MS, and stopped-flow kinetics to define its electronic structure, formation mechanism, thermal stability, and oxygen-atom transfer reactivity. Together, these studies provide new insight into how a seven-coordinate N/S ligand environment modulates the balance between stability and reactivity in nonheme ferryl chemistry and demonstrate that this mixed-donor platform can support a catalytically competent nonheme iron oxidation system.

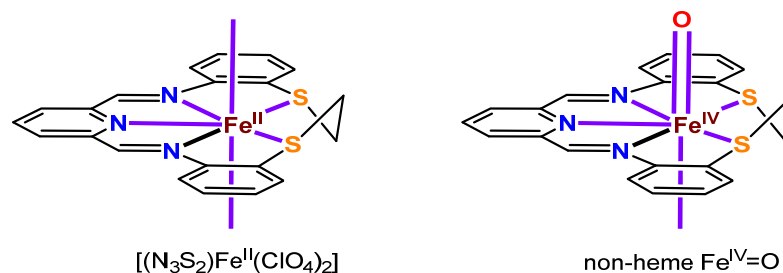


Figure 1. Depiction of the X-ray structure of precursor **1** and a schematic representation of the proposed non-heme $Fe^{IV}=O$ intermediate **2**.

2. Results

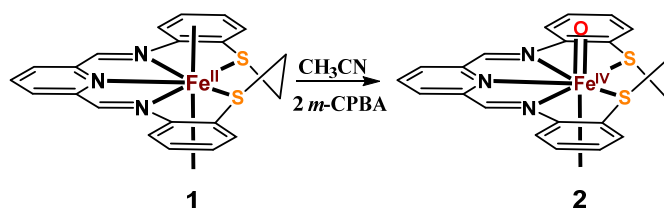
2.1. Synthesis and Characterization

The seven-coordinate iron(II) complex **1** was prepared by template condensation of pyridine-2,6-dicarbaldehyde and 1,2-bis(o-aminophenylthio)ethane in methanol in the presence of iron(II) perchlorate, following a previously reported procedure with minor modifications to the reaction scale and workup [18]. The complex was isolated as a light green solid in 67% yield and was found to be stable in air in the solid state for several weeks at room temperature. Molar conductivity measurements in acetonitrile were consistent with 1:2 electrolyte behavior, supporting dissociation of the two axial perchlorate anions and formation of the solvated dicationic species in solution. The infrared spectrum of **1** showed the expected bands for aromatic and aliphatic C–H stretching vibrations, as well as characteristic perchlorate absorptions in the fingerprint region. Elemental analysis was in good agreement with the proposed formulation, further supporting the identity of the isolated complex. Together, these data confirm successful preparation of the precursor and are consistent with the previously reported coordination environment of the complex.

Cyclic voltammetry of **1** in acetonitrile revealed a chemically reversible one-electron redox process at $E_{1/2} = -0.89$ V vs. Ag/AgCl, which was assigned to a ligand-centered oxidation of the macrocyclic framework. The large peak-to-peak separation relative to the ideal Nernstian value indicates quasi-reversible electron transfer, likely reflecting substantial structural reorganization at the seven-coordinate iron center upon oxidation. The electrochemical behavior therefore suggests that the precursor is sufficiently robust in solution to undergo controlled redox chemistry, while also highlighting the sensitivity of the coordination environment to oxidation. Overall, the synthesis and characterization data establish **1** as a well-defined, air-stable, seven-coordinate NS-ligated iron(II) complex suitable for probing high-valent iron–oxo formation. Its mixed donor set and accessible axial sites make it an attractive platform for investigating how sulfur incorporation influences ferryl generation, stability, and reactivity.

2.2. Formation of the Fe^{IV}=O Intermediate

Addition of excess *m*-CPBA (≥ 2 equiv) to a solution of **1** (0.5 mM) in acetonitrile at 23 °C results in rapid formation of a pale green species, as observed by UV-vis spectroscopy. We refer to this species as Fe^{IV}=O **2** (Scheme 1). On the basis of spectroscopic data and the NSFe^{IV}=O mass assignment, we depict **2** as a seven-coordinate species analogous to **1**, but we emphasize that the coordination number and axial ligation in solution are not directly established and may change upon oxidation. Under the conditions used here, the transformation was essentially complete within 2 s, and the resulting intermediate displayed a distinct absorption maximum at 428 nm (Figure 2A). In analogy to well-characterized nonheme Fe^{IV}=O complexes supported by N-donor ligands, the 400–500 nm region often exhibits ligand-to-metal or oxo-to-Fe^{IV} charge-transfer (LMCT) transitions that provide a characteristic spectroscopic handle for ferryl species [21,22]. Titration experiments showed that approximately two equivalents of *m*-CPBA were required to reach maximal absorbance at 428 nm (Figure 2B). The isosbestic point near 568 nm indicates spectrally clean interconversion between the precursor and the ferryl species under the titration conditions. This behavior suggests that oxidant stoichiometry is important for efficient ferryl formation and is consistent with a multistep oxidation process rather than a simple one-step conversion. However, the fact that full conversion was not achieved under these conditions indicates that the Fe^{IV}=O species is formed only in partial yield, with the remainder of the iron present as other species in solution or after freezing.



Scheme 1. Schematic depiction of Fe(IV)=O intermediate **2** generated from **1** upon reaction with *m*-CPBA in acetonitrile. The structure of **2** is drawn as a seven-coordinate species by analogy to **1**; however, the actual coordination number and axial ligation in solution are not directly established.

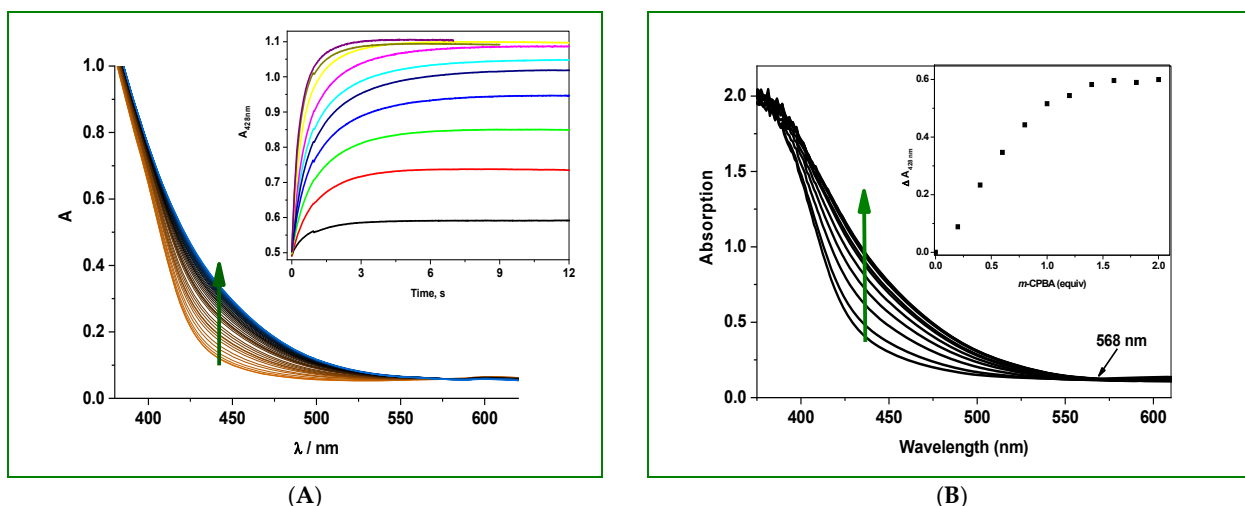


Figure 2. (A) Rapid-scan UV-vis spectra showing conversion of **1** to Fe^{IV}=O (**2**) upon *m*-CPBA addition in CH₃CN at 23 °C (inset: kinetic trace at 428 nm). (B) Titration spectra with incremental *m*-CPBA addition (0–2 equiv); inset shows ΔA_{428} vs. equivalents.

2.3. Spectroscopic Assignment

The identity of the pale green species formed upon oxidation of **1** was examined further by EPR and Mössbauer spectroscopy. X-band EPR spectra of the oxidized samples are silent at 77 K under perpendicular-mode conditions, indicating the absence of readily detectable $S = 1/2$ or $3/2$ signals. This observation is consistent with an integer-spin ferryl species and/or EPR-silent dimeric species, but does not by itself exclude high-spin Fe^{III} or μ -oxo-bridged intermediates. To better constrain the electronic speciation, we recorded ^{57}Fe Mössbauer spectra on samples prepared under the same conditions as the UV–vis ferryl-formation experiments (1.5 mM of **1**, 10 equiv *m*-CPBA in dry acetonitrile at 23 °C, freeze-quenched within a defined time window). The resulting spectra are well fitted with only two doublets, attributable to high-spin Fe^{II} and a minor Fe^{IV} component, and we do not resolve additional doublets consistent with Fe^{III} species within our experimental sensitivity, making such alternatives less likely under the present conditions.

The minor component, which accounts for 39.4% of the total spectral area, exhibits an isomer shift of $\delta = 0.35 \text{ mm s}^{-1}$ and a quadrupole splitting of $\Delta E_{\text{Q}} = 0.90 \text{ mm s}^{-1}$, with a narrow linewidth ($\Gamma_{\text{FWHM}} = 0.30 \text{ mm s}^{-1}$). These values fall within, but toward the upper end of, the range reported for nonheme $\text{Fe}^{\text{IV}}=\text{O}$ complexes supported by N-donor ligands; typical integer-spin ferryl species show $\delta \approx 0.00\text{--}0.30 \text{ mm s}^{-1}$ and $\Delta E_{\text{Q}} \approx 0.5\text{--}1.5 \text{ mm s}^{-1}$, as illustrated by $\text{Fe}^{\text{IV}}(\text{O})(\text{N}_5)$ and $\text{Fe}^{\text{IV}}(\text{O})(\text{N}_4\text{Py})$ derivatives in Table 1 [11,12,14,23,24]. In contrast, assigning this doublet to Fe^{III} or Fe^{II} would require isomer shifts that deviate substantially from our observed value: low-spin Fe^{III} species typically display $\delta \approx 0.3\text{--}0.6 \text{ mm s}^{-1}$ with smaller quadrupole splittings, whereas high-spin Fe^{II} complexes exhibit $\delta \approx 1.0 \text{ mm s}^{-1}$. We therefore assign this minor doublet to the desired $\text{Fe}^{\text{IV}}=\text{O}$ intermediate **2**, while noting that the mixed NS donor set and the proposed seven-coordinate environment may shift the isomer shift slightly upward relative to classical all-nitrogen frameworks.

Table 1. Selected ^{57}Fe Mössbauer parameters (δ , ΔE_{Q}) for **2** and representative nonheme $\text{Fe}^{\text{IV}}=\text{O}$, Fe^{III} , and Fe^{II} complexes.

Species/Complex	Assignment	$\delta \text{ (mm s}^{-1}\text{)}$	$\Delta E_{\text{Q}} \text{ (mm s}^{-1}\text{)}$	T (K)	Ref.
2 (minor doublet)	$\text{Fe}^{\text{IV}}=\text{O}$ (integer-spin)	0.35	0.90	77	This work
2 (major doublet)	High-spin Fe^{II}	1.22	3.11	77	This work
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N}_5)]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	~ 0.03	0.85–1.38	80	[14]
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N}_4\text{Py})]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	-0.04	0.93	80	[11]
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N}_2\text{Py}_2\text{B})]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	-0.02	1.34	80	[12]
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N}_3\text{Py-NMB})]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	-0.03	1.10	80	[12]
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{CH}_3\text{CN})]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	0.14	0.78	80	[23]
$[\text{Fe}^{\text{IV}}(\text{O})(\text{Bn-tpen})]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	0.01	0.87	80	[11]
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N}_2\text{Py}_2\text{Qn})]^{2+}$	$\text{Fe}^{\text{IV}}=\text{O}$	0.03	0.56	80	[24]
$[\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})(\text{N}_5)]^{2+}$	Low-spin Fe^{II}	0.38–0.45	0.17–0.36	80	[14]
$[\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})(\text{N}_5)]^{2+}$	High-spin Fe^{II}	0.98–1.19	1.78–2.88	80	[14]

The major Mössbauer doublet, representing 60.6% of the spectral area, shows $\delta = 1.22 \text{ mm s}^{-1}$ and $\Delta E_{\text{Q}} = 3.11 \text{ mm s}^{-1}$, with a broader linewidth ($\Gamma_{\text{FWHM}} = 0.46 \text{ mm s}^{-1}$). These parameters fall squarely within the window characteristic of high-spin Fe^{II} species in distorted six- or seven-coordinate environments and are inconsistent with low-spin Fe^{III} , which typically displays substantially lower isomer shifts ($\delta \approx 0.3\text{--}0.6 \text{ mm s}^{-1}$) and different quadrupole splittings (Table 1). We therefore assign this dominant doublet to a high-spin Fe^{II} species derived from the precursor under the reaction conditions. While the Mössbauer parameters clearly support a high-spin Fe^{II} assignment, the present data do not

establish its precise molecular identity. Accordingly, we cannot distinguish between residual precursor-derived species, kinetically accumulated resting states, or Fe^{II}-containing products generated through nonproductive reaction pathways.

The persistence of a substantial high-spin Fe^{II} fraction in the presence of excess *m*-CPBA indicates that ferryl formation is incomplete under the conditions employed. Spectrophotometric titrations show that only ~2 equiv of oxidant are required to maximize the 428 nm absorbance, whereas additional oxidant leads to bleaching and evidence for competing oxidant-consumption pathways. The major Fe^{II} Mössbauer component is therefore best viewed as a precursor-derived Fe^{II} species that accumulates during turnover. Although its exact identity remains unresolved, it may arise from nonproductive reaction channels, ligand modification, or decomposition processes that divert oxidant away from productive ferryl formation. The present data do not support a simple reversible equilibrium between Fe^{II} and Fe^{IV}=O as the sole origin of the observed Fe^{II} population.

At higher *m*-CPBA loadings, solution bleaching and evidence for ligand-oxidation/over-oxidation processes further divert oxidant away from productive Fe^{II} → Fe^{IV}=O conversion. Together, these observations explain why high-spin Fe^{II} remains the dominant Mössbauer component under our conditions and highlight the intrinsic difficulty of achieving quantitative ferryl formation in mixed NS ligand environments.

Taken together, the EPR silence at 77 K, the two-doublet Mössbauer pattern, and the comparative data in Table 1 support a simple two-species description of the oxidized sample: an Fe^{IV}=O intermediate **2** in partial yield and a high-spin Fe^{II} species, with no spectroscopic evidence for significant amounts of Fe^{III} byproducts or μ-oxo dimers under the present conditions. We note that nonheme Fe^{IV}=O complexes may adopt either *S* = 1 or *S* = 2 ground states, and that both can be EPR-silent at 77 K under standard X-band conditions. The Mössbauer parameters of **2** ($\delta = 0.35 \text{ mm s}^{-1}$, $\Delta E_Q = 0.90 \text{ mm s}^{-1}$) and its modest oxygen-atom-transfer reactivity align more closely with established *S* = 1 ferryl systems (Table 1), but a definitive distinction between *S* = 1 and *S* = 2 would require high-field Mössbauer or magnetization measurements.

Cryogenic high-resolution ESI-MS provided complementary support for the ferryl assignment. Spectra were collected in positive-ion mode at −40 °C to suppress thermal decomposition and redox back-reaction pathways. Under these conditions, a prominent isotopic cluster centered at *m/z* 223.5 is observed and matches the calculated mass and isotopic pattern for the doubly charged [(N₃S₂)Fe(IV)=O]²⁺ ion closely (Figure 3C). The spectrum (Figure 3C) shows only minor additional signals, and we do not detect intense peaks corresponding to sulfoxidized or sulfonylated macrocycle fragments (e.g., *M* + 16, *M* + 32). The agreement between the experimental isotopic cluster and the calculated pattern, together with the absence of strong *M* + 16/*M* + 32 signals, provides positive evidence that the dominant ferryl species retains the intact N₃S₂ ligand under these conditions. Although low-level ligand oxidation at higher [*m*-CPBA] cannot be rigorously excluded, these data indicate that the N₃S₂ framework remains largely intact during formation of **2** and that the bleaching observed at [*m*-CPBA] > 0.01 M is more likely associated with secondary decomposition pathways [13,25].

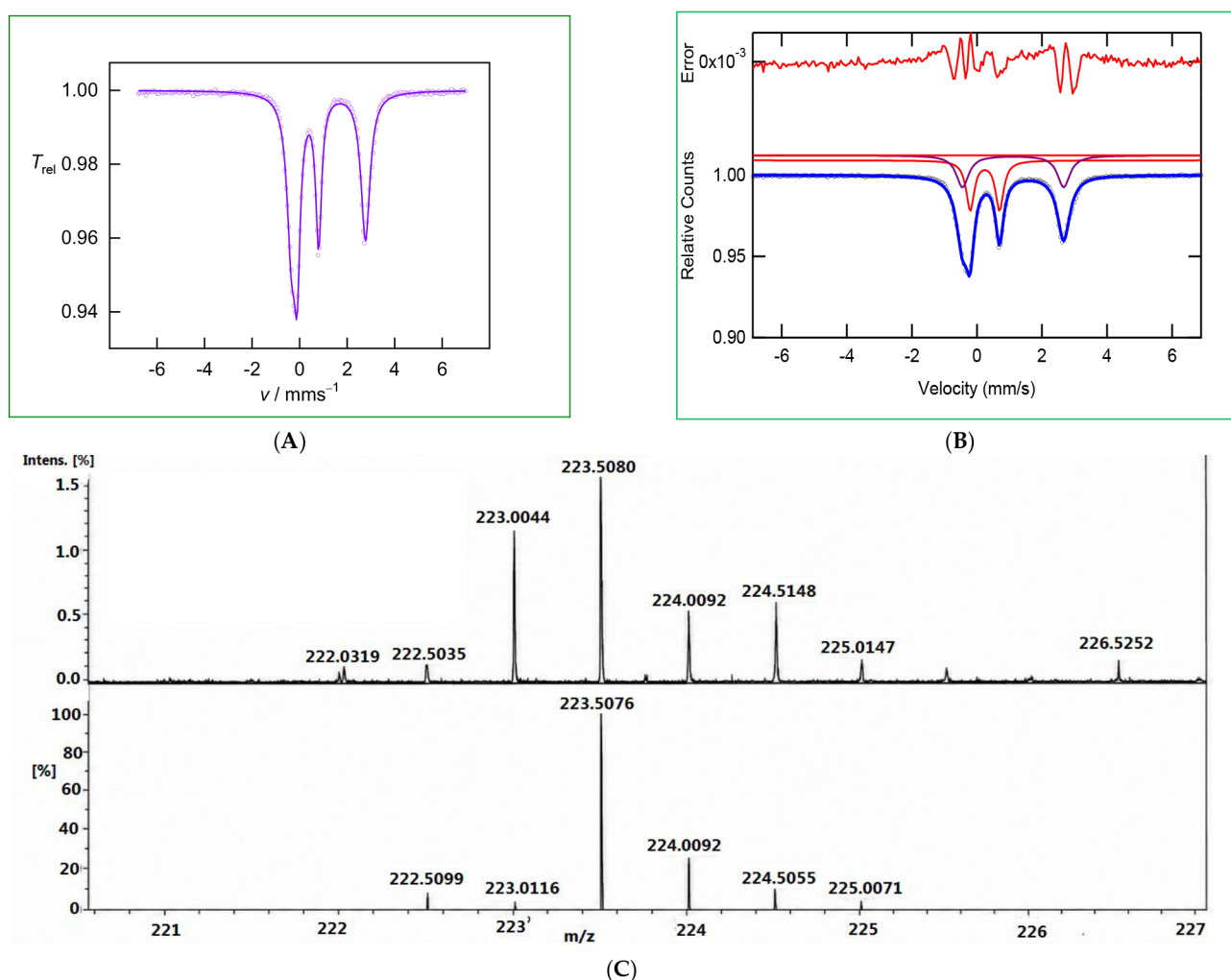


Figure 3. (A) ^{57}Fe Mössbauer spectrum of the green product (containing $[(\text{N}_3\text{S}_2)\text{Fe}^{\text{IV}}=\text{O}]$) recorded at 77 K. (B) The experimental data (black dots) are overlaid with the total fit (solid line), showing two doublets corresponding to distinct iron species. The first doublet (red) is assigned to the $\text{Fe}^{\text{IV}}=\text{O}$ complex ($\delta = 0.35(1) \text{ mm s}^{-1}$, $\Delta E_Q = 0.90(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.30(1) \text{ mm s}^{-1}$, relative area = 39.4%), and the second doublet (blue) corresponds to a high-spin Fe^{II} species ($\delta = 1.22(1) \text{ mm s}^{-1}$, $\Delta E_Q = 3.11(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.46(1) \text{ mm s}^{-1}$, relative area = 60.6%). Velocity scale is referenced to metallic α -iron at 77 K. (C) High-resolution ESI-MS at -40°C showing $[(\text{N}_3\text{S}_2)\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ (m/z 223.510) with matching isotopic pattern.

Taken together, the Mössbauer and mass-spectrometric data provide strong convergent evidence that oxidation of **1** generates a discrete mononuclear $\text{Fe}^{\text{IV}}=\text{O}$ species. The partial ferryl yield observed by Mössbauer spectroscopy is important for interpreting the kinetic and reactivity data discussed below, but it does not weaken the assignment of the detected minor component as a bona fide ferryl intermediate; rather, it highlights the intrinsic difficulty of achieving quantitative ferryl formation in mixed N/S ligand environments [20,25,26].

2.4. Kinetic Analysis of Ferryl Formation

The formation of the ferryl intermediate was investigated by stopped-flow UV–vis spectroscopy under pseudo-first-order conditions, with *m*-CPBA present in excess relative to **1**. Monitoring the growth of the 428 nm absorption band revealed single-exponential behavior at each oxidant concentration, indicating that ferryl formation proceeds through a kinetically well-defined process. Rapid-mixing conditions confirmed that the intermediate forms on the timescale of seconds, consistent with the static UV–vis observations described

above. The observed first-order rate constants increased with oxidant concentration and showed clear saturation behavior at higher *m*-CPBA loadings (Figure 4A). Under these conditions, simple linear rate laws fail to capture the pronounced curvature and yield systematically biased residuals (see Figure S1 in Supporting Information). In contrast, the pre-equilibrium oxidant-binding model (Equation (1)) affords an excellent global fit across the entire concentration range, with fit parameters, associated uncertainties, and goodness-of-fit values (R^2) summarized in Table 2. In keeping with the presence of competing oxidant-consumption pathways, the parameters extracted from Equation (1) are treated as apparent empirical fitting parameters that describe the observed saturation kinetics under the experimental conditions, rather than as rigorous thermodynamic equilibrium constants or intrinsic heterolysis rate constants.

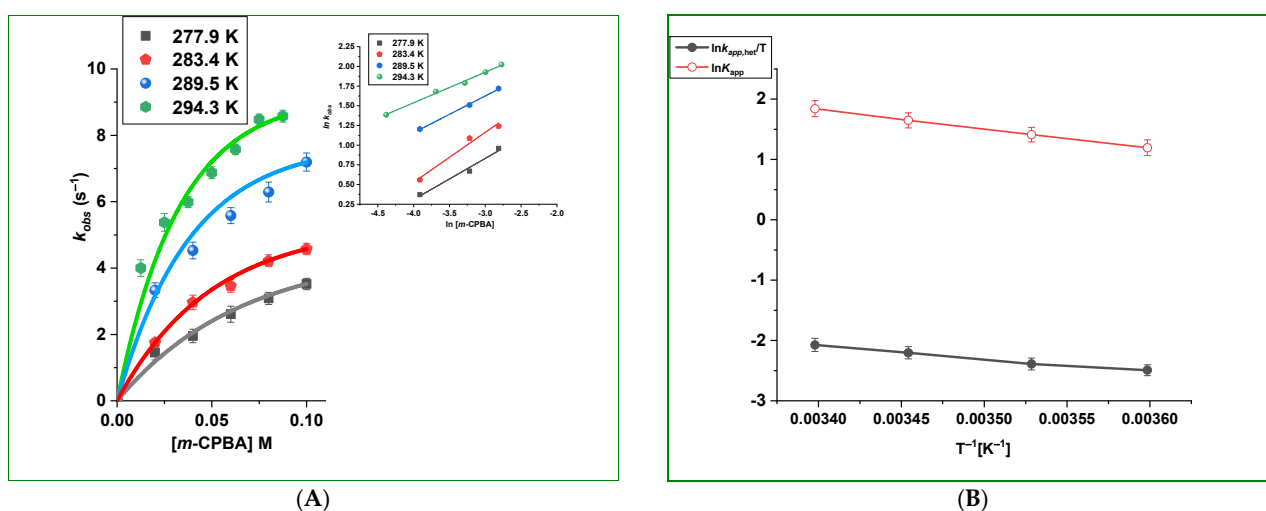


Figure 4. (A) Dependence of the observed first-order rate constant k_{obs} on $[m\text{-CPBA}]$ for formation of **2** at 277.9, 283.4, 289.5, and 294.3 K. Data points represent mean values of k_{obs} at each oxidant concentration; error bars correspond to one standard deviation from at least three independent measurements. Solid curves show global fits to the pre-equilibrium binding model (Equation (1)). Inset: $\ln(k_{\text{obs}})$ versus $\ln[m\text{-CPBA}]$ at low oxidant concentrations. (B) Eyring plots for $\ln(k_{\text{het}}/T)$ (●) and $\ln K$ (○).

Table 2. Apparent oxidant-association (K_{app}) and apparent heterolysis ($k_{\text{het,app}}$) parameters obtained from fitting Equation (1).

T (K)	K_{app} (M^{-1})	$k_{\text{app,het}}$ (s^{-1})	R^2
277.9	3.3 ± 1	23 ± 3	0.990
283.4	4.1 ± 1	26 ± 4	0.997
289.5	5.2 ± 0.5	32 ± 1	0.992
294.3	6.3 ± 0.2	37 ± 2	0.986
	$\Delta H^\ddagger$ (kJ mol^{-1}) = 26.8 ± 0.4	$\Delta H^\ddagger$ (kJ mol^{-1}) = 17.7 ± 1.0	
	$\Delta S^\ddagger$ ($\text{J mol}^{-1} \text{K}^{-1}$) = -91.7 ± 1.3	$\Delta S^\ddagger$ ($\text{J mol}^{-1} \text{K}^{-1}$) = -155.0 ± 5.0	
	$\Delta G^\ddagger$ (kJ mol^{-1}) = 53.7 ± 0.4	$\Delta G^\ddagger$ (kJ mol^{-1}) = 63.6 ± 1.4	

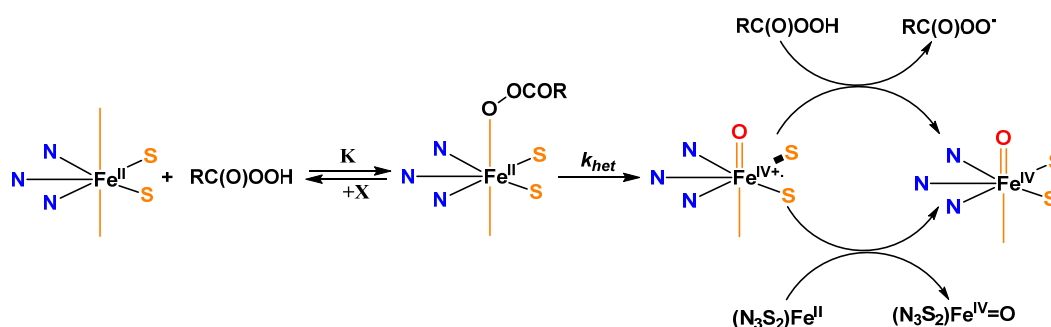
At low *m*-CPBA, plots of $\ln k_{\text{obs}}$ vs. $\ln [m\text{-CPBA}]$ at four temperatures (277.9–294.3 K) are approximately linear, with slopes in the range 0.53–0.74 and R^2 values of 0.975–0.998 (Figure 4A inset, Table S1 in Supporting Information). This behavior supports near-first-

order dependence on oxidants in this regime and is consistent with rapid pre-equilibrium oxidant binding followed by rate-limiting O–O bond heterolysis.

$$k_{obs} = \frac{2 k_{app,het} K_{app} [m - CPBA]}{1 + K_{app}[m - CPBA]} \quad (1)$$

where K_{app} is an apparent oxidant-association parameter and $k_{het,app}$ is an apparent heterolysis rate parameter derived from fitting the observed saturation behavior. The factor of 2 in Equation (1) reflects an idealized dual-oxidant disproportionation pathway and is intended as a formal upper-bound stoichiometry rather than the experimental oxidant-to-iron ratio. In practice, ~2 equiv *m*-CPBA are needed to maximize the 428 nm band and Mössbauer spectroscopy shows only partial ferryl formation, indicating substantial non-productive oxidant consumption and limited driving force for $Fe^{IV}=O$ accumulation. The pre-equilibrium model is used here as a phenomenological description of the observed saturation kinetics. Because competing oxidant-consumption pathways are not explicitly included in Equation (1), the extracted parameters should be regarded as apparent fitting parameters rather than rigorous thermodynamic or mechanistic constants [26]. The apparent kinetic parameters obtained from fitting Equation (1) are summarized in Table 2. Both K_{app} and $k_{app,het}$ increase modestly with temperature, indicating that oxidant binding is thermodynamically accessible but entropically disfavored.

Eyring analysis of $k_{app,het}$ yields an activation enthalpy $\Delta H^\ddagger = 17.7 \pm 1.0 \text{ kJ mol}^{-1}$ and a strongly negative activation entropy $\Delta S^\ddagger = -155 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ (Figure 4B). The large negative $\Delta S^\ddagger$ is diagnostic of a highly ordered transition state, consistent with substantial O–O polarization and heterolytic cleavage within a constrained coordination environment. At lower *m*-CPBA concentrations, the near-linear dependence of k_{obs} on oxidant concentration suggests that alternative single-oxidant pathways may also contribute (pathway b, Scheme 2), whereas saturation behavior at higher oxidant loadings favors the dual-oxidant disproportionation pathway embodied in Equation (1).



Scheme 2. Minimal mechanism for $Fe(IV)=O$ formation from 1, showing pre-equilibrium oxidant binding (K), O–O heterolysis (k_{het}), and secondary pathways. X denotes a generic ligand or counteranion (e.g., MeCN or ClO_4^-) occupying an axial coordination site.

At *m*-CPBA concentrations above ca. 0.01 M, bleaching of the solution prevents reliable determination of kinetic parameters, likely due to ligand-oxidation or over-oxidation side reactions rather than decomposition of the $Fe^{IV}=O$ intermediate itself. Attempts to determine the activation volume $\Delta V^\ddagger$ by high-pressure stopped-flow methods were unsuccessful due to the very rapid O–O heterolysis rates ($k_{obs} \gtrsim 10 \text{ s}^{-1}$). Nevertheless, the low activation enthalpy and highly ordered transition state are comparable to values reported for well-established N_4 - and N_5 -ligated $Fe^{IV}=O$ systems, indicating that incorporation of thioether sulfur donors does not impose a significant kinetic penalty on O–O bond cleavage, despite the increased redox lability associated with mixed N/S coordination. Overall, the

kinetic data show that **1** undergoes rapid but mechanistically organized conversion to the $\text{Fe}^{\text{IV}}=\text{O}$ intermediate. The saturation behavior and activation parameters support a pre-equilibrium oxidant-binding model followed by rate-limiting O–O heterolysis, reinforcing the view that the seven-coordinate NS framework influences both the efficiency and the mechanism of ferryl formation [19,20,25,26].

The incomplete ferryl yield (~39% by Mössbauer spectroscopy) indicates that productive $\text{Fe}^{\text{IV}}=\text{O}$ formation competes with additional oxidant-consumption and decomposition pathways. Consequently, the apparent parameters extracted from Equation (1) should not be interpreted as defining a simple thermodynamic equilibrium between Fe^{II} and $\text{Fe}^{\text{IV}}=\text{O}$. Rather, they provide a compact empirical description of the observed concentration dependence of ferryl formation under the experimental conditions employed.

2.5. Oxygen-Atom Transfer Reactivity

The reactivity of the $\text{Fe}^{\text{IV}}=\text{O}$ intermediate toward oxygen-atom transfer was evaluated using triphenylphosphine (PPh_3) as a benchmark substrate. Upon addition of PPh_3 to solutions containing the ferryl species, the characteristic absorption band at 428 nm decayed cleanly with single-exponential kinetics (Figure 5A). This clean spectral change is consistent with direct oxygen-atom transfer from the ferryl center to the phosphine and supports the assignment of the detected species as a bona fide oxidant (Figure 5B).

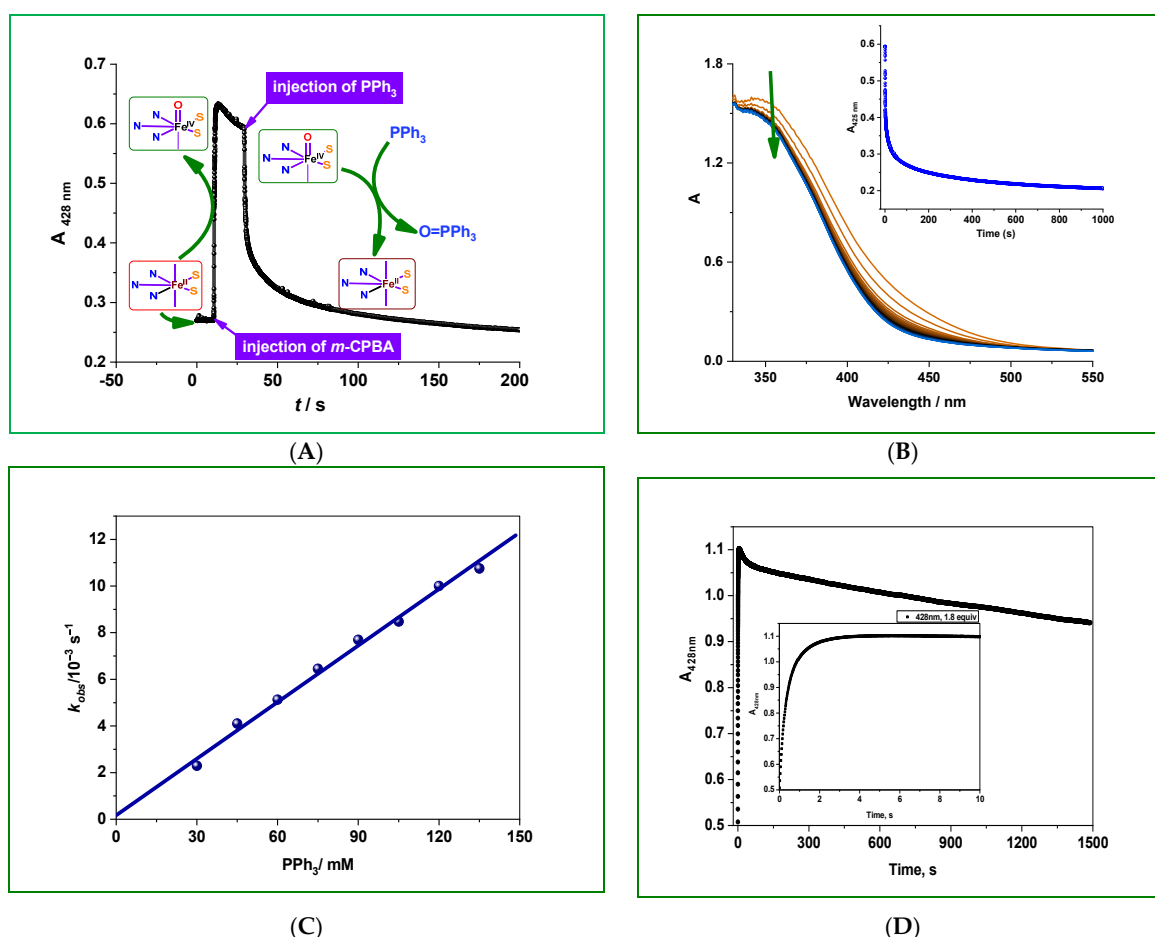


Figure 5. (A) Stability of $\text{Fe}^{\text{IV}}=\text{O}$ intermediate ($t_{1/2} = 4.3 \text{ h}$) (inset is the $\text{Fe}^{\text{IV}}=\text{O}$ formation); (B) UV-vis spectra of $\text{Fe}^{\text{IV}}=\text{O}$ intermediate decay during the reaction with PPh_3 (inset is the kinetic trace at 428 nm); (C) reaction of $\text{Fe}^{\text{IV}}=\text{O}$ intermediate with PPh_3 ; (D) linear k_{obs} vs. $[\text{PPh}_3]$; slope = k_2 .

Under pseudo-first-order conditions, the observed rate constants increased linearly with increasing PPh_3 concentration, with no significant intercept ($R^2 > 0.99$; Figure 5C). This linear dependence confirms a bimolecular oxygen-atom transfer process and excludes substantial contributions from competing decomposition pathways on the timescale of the measurements [20,26]. From the slope of the linear fit, a second-order rate constant of $8.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ was obtained.

The thermal stability of the intermediate further supports its utility in reactivity studies. At 25°C , the $\text{Fe}^{\text{IV}}=\text{O}$ species exhibited a half-life of 4.3 h, corresponding to a decomposition rate constant $k_{\text{decomp}} \approx 4.5 \times 10^{-5} \text{ s}^{-1}$ (Figure 5D). This lifetime is sufficiently long to permit productive oxygen-atom transfer, yet remains within the moderate stability regime typical of reactive nonheme ferryl species [5,8,9,13–15,20,25,26].

Catalytic experiments showed that repeated oxidant addition regenerates the ferryl intermediate and enables multiple turnovers. After correcting for the partial yield of ferryl formation ($\sim 39\%$), an effective turnover number of approximately 12 was obtained. Although modest, this level of activity is significant for a mixed N/S ligand system and demonstrates that the seven-coordinate framework can sustain more than a single oxidation event. Overall, the oxygen-atom transfer experiments demonstrate that the seven-coordinate N_3S_2 -ligated $\text{Fe}^{\text{IV}}=\text{O}$ intermediate combines measurable stability with genuine oxidizing power. Its ability to transfer oxygen to PPh_3 , together with its moderate lifetime and limited but reproducible catalytic turnover, places it in an intermediate regime between highly stable but less reactive ferryl systems and more aggressive species that decay rapidly.

2.6. Integrated Interpretation

Taken together, the spectroscopic, kinetic, and reactivity data demonstrate that the seven-coordinate iron(II) complex 1 provides access to a well-defined mononuclear $\text{Fe}^{\text{IV}}=\text{O}$ intermediate 2 in a mixed N/S ligand environment. Rapid formation of the ferryl species is observed by UV-vis spectroscopy, while Mössbauer spectroscopy and cryogenic high-resolution ESI-MS independently confirm its identity as a discrete high-valent iron-oxo complex. The data also reveal that ferryl formation occurs in only partial yield ($\sim 39\%$), indicating that the system supports high-valent oxidation but does not proceed quantitatively under the conditions employed. This incomplete conversion reflects both the intrinsic challenges associated with achieving full ferryl generation in mixed N/S systems and the delicate balance between oxidant strength, ligand robustness, and competing pathways. The observation of only partial ferryl yield ($\sim 39\%$) demonstrates that productive ferryl formation competes with additional oxidant-consumption and decomposition pathways under the reaction conditions employed. Under these conditions, the seven-coordinate N_3S_2 framework stabilizes the $\text{Fe}^{\text{IV}}=\text{O}$ species sufficiently to permit multiple oxygen-atom-transfer events but does not drive the system toward quantitative ferryl accumulation, which is reflected in the effective turnover number of 12.

Kinetic studies show that ferryl generation proceeds via a mechanistically well-defined pathway involving rapid pre-equilibrium binding of the oxidant (*m*-CPBA) followed by rate-limiting O–O bond heterolysis. The low activation enthalpy ($\Delta H^\ddagger = 17.7 \text{ kJ mol}^{-1}$) combined with a strongly negative activation entropy ($\Delta S^\ddagger = -155 \text{ J mol}^{-1} \text{ K}^{-1}$) points to a highly ordered transition state, highlighting the significant role of the seven-coordinate N_3S_2 framework in controlling oxidant activation. Thus, the ligand environment not only stabilizes the ferryl core but also actively shapes the pathway leading to its formation, enforcing a constrained geometry that facilitates O–O bond cleavage while helping to avoid rapid, uncontrolled decomposition of the high-valent species [14,27].

Once generated, the $\text{Fe}^{\text{IV}}=\text{O}$ intermediate exhibits sufficient persistence ($t_{1/2} = 4.3$ h at 25°C) to mediate clean oxygen-atom transfer to PPh_3 and to support modest catalytic turnover ($\text{TON} \approx 12$). This balance of moderate lifetime and retained reactivity positions the present system in an intermediate region of the stability–reactivity landscape: less persistent than the most stable N-only ferryl complexes, yet significantly more stable than highly activated systems that sacrifice lifetime for enhanced reactivity. In practical terms, the N_3S_2 -supported $\text{Fe}^{\text{IV}}=\text{O}$ species is long-lived enough to enable detailed mechanistic interrogation and repeated oxidant additions, while remaining sufficiently oxidizing to function as a competent oxygen-atom-transfer reagent.

Comparison with recent ligand-tuning strategies in all-nitrogen systems further underscores this point. For instance, Pal et al. demonstrated that replacing pyridyl donors with less basic pyrazolyl ligands in an N_5 framework yields an $\text{Fe}^{\text{IV}}=\text{O}$ species up to 5000-fold more reactive in hydrogen-atom transfer (HAT), with rate constants reaching 0.29 s^{-1} at 298 K [5]. However, this increased electrophilicity comes at the cost of a dramatically shortened lifetime (on the order of minutes). In contrast, the N_3S_2 -supported $\text{Fe}^{\text{IV}}=\text{O}$ intermediate reported here maintains a much longer lifetime (4.3 h at 25°C) while preserving measurable oxo-transfer reactivity, as reflected in a bimolecular OAT rate constant of $8.1 \times 10^{-2}\text{ M}^{-1}\text{ s}^{-1}$ and an effective turnover number of ~ 12 after correction for the partial ferryl yield. These findings illustrate that, whereas N-only ligand modifications often maximize reactivity through increased electrophilicity, mixed N/S coordination offers a complementary approach that enhances stability without fully compromising chemical competence.

Overall, incorporation of sulfur donors into a seven-coordinate nonheme iron platform modulates $\text{Fe}^{\text{IV}}=\text{O}$ behavior in a distinct manner compared to all-nitrogen systems. The N_3S_2 framework provides a balanced profile in which the high-valent species is readily accessible, spectroscopically characterizable, and catalytically competent under mild conditions, even though it is less reactive than state-of-the-art N-only nonheme $\text{Fe}^{\text{IV}}=\text{O}$ catalysts. In this sense, the present system is best viewed as a mechanistic platform that explicitly reveals the trade-offs imposed by sulfur donors—particularly partial ferryl yield and competing side reactions—rather than as a performance-maximized oxidation catalyst. Given the current scarcity of well-defined mononuclear N/S-supported $\text{Fe}^{\text{IV}}=\text{O}$ complexes, these results highlight the potential of mixed-donor ligands for fine-tuning the properties of high-valent iron–oxo intermediates and motivate further exploration of sulfur-containing ligand architectures in nonheme iron oxidation catalysis.

3. Materials and Methods

3.1. General Methods

All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Acetonitrile was dried and purified using a double-alumina solvent purification system (Innovative Technologies) and deoxygenated by argon sparging for 30 min prior to use. Air- and moisture-sensitive manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. *Caution:* Metal perchlorate salts are potentially explosive and should be handled in small quantities ($<1\text{ g}$) with appropriate shielding and standard safety precautions. *m*-CPBA, 75%, Acros Organics, was purified immediately before use by washing with phosphate buffer ($\text{pH } 7.4$, $3 \times 20\text{ mL}$), followed by water ($2 \times 20\text{ mL}$) to remove residual acids, and dried under reduced pressure.

3.2. Preparation of $[(\text{N}_3\text{S}_2)\text{Fe}^{\text{II}}(\text{ClO}_4)_2]$ (**1**)

Complex **1** was prepared according to a previously reported procedure with minor modifications [18]. Pyridine-2,6-dicarbaldehyde (0.27 g , 2.0 mmol) and 1,2-bis(o-

aminophenylthio)ethane (0.55 g, 2.0 mmol) were each dissolved in methanol (10 mL). $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.81 g, 2.1 mmol) was added to the dialdehyde solution, followed by the amine solution. The reaction mixture was stirred at room temperature for 5 h, affording an orange solution. The solvent volume was reduced to approximately 5 mL under reduced pressure, and diethyl ether (20 mL) was added to induce precipitation of a light-green solid. The product was collected by filtration, washed with diethyl ether (3×10 mL), and dried in vacuo to afford **1** as an air-stable solid (0.423 g, 67% yield). IR (KBr, cm^{-1}): 3050 (m, ν_{CH} , arom), 2985 (m, ν_{CH} , aliph), 1629 (s, $\nu_{\text{C}=\text{N}}$), 1587 (m, $\nu_{\text{C}=\text{C}}$, arom), 1099 (s, $\nu_{\text{ClO}_4^-}$), 624 (s, $\nu_{\text{ClO}_4^-}$). Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{FeN}_3\text{O}_8\text{S}_2$ (M.wt. = 698.35): C, 43.01; H, 3.47; N, 6.02. Found: C, 42.87; H, 3.52; N, 6.08 (air-stable solid).

3.3. Instrumentation and Measurements

Conductivity. Molar conductivity measurements were performed at 25 °C using a Jenway 4510 conductivity meter equipped with a platinum-black electrode. Solutions of **1** (1.0 mM) in acetonitrile exhibited $\Lambda_m = 260\text{--}280 \text{ S cm}^2 \text{ mol}^{-1}$, consistent with 1:2 electrolyte behavior.

UV-vis Spectroscopy. Static UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) using tandem quartz cuvettes (0.88 cm optical path length). Stopped-flow kinetic measurements were conducted on an Applied Photophysics SX-18MV spectrometer (Applied Photophysics Ltd., Leatherhead, Surrey, UK) with a 1.0 cm optical path length and a dead time <1.5 ms. The instrument temperature was controlled to ± 0.1 °C. $\text{Fe}^{\text{IV}}=\text{O}$ formation was monitored at 428 nm under pseudo-first-order conditions with *m*-CPBA in excess (0.1–1.0 mM). Reported rate constants represent averages of at least three independent measurements ($\pm 10\%$).

High-Resolution ESI-MS. High-resolution mass spectra were acquired on Bruker maXis UHR-QqTOF mass spectrometer equipped with a Dionex HPLC Cryospray source operating at -40 °C. Samples (0.5 mM **1**, 2 equiv *m*-CPBA in acetonitrile) were infused at $3 \mu\text{L min}^{-1}$. Data were processed using Compass DataAnalysis software (version 4.3, Bruker Daltonics GmbH, Bremen, Germany).

EPR Spectroscopy. X-band EPR spectra (9.38 GHz) were recorded at 77 K on a Bruker EMX spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) using modulation amplitude of 10 G, modulation frequency of 100 kHz, and microwave power of 20 mW. No EPR signals were detected for the oxidized species.

^{57}Fe Mössbauer Spectroscopy. Mössbauer spectra were recorded at 77 K using a conventional constant-acceleration spectrometer (MS1-Electronics) with a $^{57}\text{Co}/\text{Rh}$ source. Velocity calibration was performed using α -iron foil at room temperature. Spectral simulations were carried out using Mössbauer Studio (MS1-Electronics), assuming Lorentzian quadrupole doublet models.

3.4. Preparation of Mössbauer and EPR Samples

Mössbauer samples were prepared by mixing solutions of **1** (1.5 mM in dry, deoxygenated acetonitrile) with purified *m*-CPBA (10 equiv) at 23 °C under an inert atmosphere. The reaction mixtures were allowed to evolve for a defined time window corresponding to maximal absorbance at 428 nm in static UV-vis experiments, after which they were rapidly freeze-quenched in liquid nitrogen. The resulting frozen samples were transferred to Mössbauer sample holders under cold conditions and stored at liquid-nitrogen temperature until measurement at 77 K. EPR samples were prepared under identical conditions (same concentration range, oxidant equivalents, reaction temperature, and reaction time) and freeze-quenched on the same timescale. This protocol ensures that the Mössbauer and EPR

spectra correspond to the same oxidized species observed in the UV-vis and stopped-flow experiments used to monitor $\text{Fe}^{\text{IV}}=\text{O}$ formation.

4. Conclusions

In summary, we have synthesized and characterized a mixed-donor N_3S_2 nonheme iron complex **1** that can be oxidized by *m*-CPBA to give a pale-green high-valent intermediate **2**. Under carefully controlled conditions, this species displays a characteristic UV-vis band at 428 nm, Mössbauer parameters consistent with a nonheme $\text{Fe}^{\text{IV}}=\text{O}$ unit, and a cryogenic HR-ESI-MS signal assigned to $[(\text{N}_3\text{S}_2)\text{Fe}^{\text{IV}}=\text{O}]^{2+}$. Together with the kinetic and spectroscopic data, these observations support the formation of a discrete mononuclear ferryl intermediate rather than a mixture of ill-defined high-valent states.

The Mössbauer parameters and EPR silence at 77 K support assignment of **2** as an integer-spin nonheme $\text{Fe}^{\text{IV}}=\text{O}$ species. While comparison with related ferryl systems may favor an $S = 1$ description, the present data do not permit definitive discrimination between $S = 1$ and $S = 2$ ground states. Accordingly, the electronic-structure assignment remains tentative and will require future high-field Mössbauer spectroscopy and/or SQUID magnetometry for unambiguous resolution. The partial ferryl yield ($\approx 39\%$ by Mössbauer spectroscopy) and the persistence of a substantial high-spin Fe^{II} fraction indicate that productive ferryl formation competes with additional oxidant-consumption and decomposition pathways under the reaction conditions employed. The identity of the dominant Fe^{II} species remains unresolved and may reflect precursor-derived resting states and/or Fe^{II} -containing products formed through nonproductive reaction channels. Despite these limitations, the ferryl intermediate **2** mediates oxygen-atom transfer to triphenylphosphine with a measurable bimolecular rate constant ($k_2 = 8.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) and an effective turnover number of ~ 12 under mild conditions, after correction for the ferryl yield.

Although its OAT reactivity and catalytic performance fall below those of state-of-the-art nonheme $\text{Fe}^{\text{IV}}=\text{O}$ catalysts supported by all-nitrogen N_4/N_5 ligands, the present system extends ferryl lifetimes into the hours regime at 25°C while retaining oxo-transfer competence. We therefore view this N_3S_2 platform less as a performance-optimized oxidation catalyst and more as a mechanistic probe for how sulfur donors and seven-coordinate geometries modulate ferryl formation, stability, and reactivity. In this role, the complex demonstrates that mixed N/S coordination can moderately extend ferryl lifetime while preserving measurable oxo-transfer activity, explicitly revealing the trade-offs between ferryl accessibility, robustness, and oxidative power. More broadly, the present results highlight both the opportunities and limitations associated with sulfur incorporation into nonheme iron frameworks. While competing side reactions currently limit ferryl accumulation, the N_3S_2 platform nevertheless provides direct insight into how mixed-donor coordination environments influence high-valent iron-oxo chemistry. In future studies, we will combine ^{18}O -labeled oxidants and H_2^{18}O with cryogenic HR-ESI-MS to directly verify the origin of the ferryl oxygen and further refine the mechanistic picture developed here. These findings should aid the future design of mixed-donor ligands that more effectively balance ferryl accessibility, stability, and oxidation reactivity in nonheme iron catalysis.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16070631/s1>, Figure S1: Linear dependence of the observed first-order rate constant k_{obs} for formation of $\text{Fe}^{\text{IV}}=\text{O}$ intermediate **2** on the concentration of *m*-CPBA at four temperatures (277.9, 283.4, 289.5, and 294.3 K). Solid lines show linear least-squares fits with the indicated R^2 values; Table S1: Linear fits of $\ln k_{\text{obs}}$ vs. $\ln [m\text{-CPBA}]$ at low oxidant concentrations and extracted parameters.

Author Contributions: Conceptualization, S.Y.S. and R.v.E.; methodology, A.M.A., H.M. and S.Y.S.; software, S.Y.S.; validation, A.M.A., H.M. and S.Y.S.; formal analysis, S.Y.S.; investigation, A.M.A., H.M. and S.Y.S.; resources, M.M.I. and S.N.A.; data curation, H.M.; writing—original draft preparation, H.M., A.M.A., M.M.I., S.N.A., S.Y.S. and R.v.E.; writing—review and editing, H.M., A.M.A., M.M.I., S.N.A., S.Y.S. and R.v.E.; visualization, S.Y.S.; supervision, S.Y.S. and R.v.E.; project administration, S.Y.S. and R.v.E.; funding acquisition, S.N.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Deanship of Graduate Studies and Scientific Research, Taif University, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available from the corresponding author upon request.

Acknowledgments: The authors would like to acknowledge the Deanship of Graduate Studies and Scientific Research, Taif University, for funding this work.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Fagnano, A.; Fratello, F.; Paoloni, R.; Sappino, C.; Lanzalunga, O.; Costas, M.; Di Stefano, S.; Olivo, G. Proximity effects on the reactivity of a nonheme iron(IV)-oxo complex in C-H oxidation. *Angew. Chem. Int. Ed.* **2024**, *63*, e202401694. [\[CrossRef\]](#)
2. Srnec, M.; Iyer, S.R.; Dassama, L.M.K.; Park, K.; Wong, S.D.; Sutherlin, K.D.; Yoda, Y.; Kobayashi, Y.; Kurokuzu, M.; Saito, M.; et al. Nuclear resonance vibrational spectroscopic definition of the facial triad Fe(IV)=O intermediate in taurine dioxygenase: Evaluation of structural contributions to hydrogen atom abstraction. *J. Am. Chem. Soc.* **2020**, *142*, 18886–18896. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Solomon, E.I.; Deweese, D.E.; Babicz, J.T. Mechanisms of O₂ activation by mononuclear nonheme iron enzymes. *Biochemistry* **2021**, *60*, 3497–3506. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Nam, W. High-valent iron(IV)-oxo complexes of heme and nonheme ligands in oxygenation reactions. *Acc. Chem. Res.* **2007**, *40*, 522–531. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Pal, N.; Xiong, J.; Jahja, M.; Mahri, S.; Young, V.G., Jr.; Guo, Y.; Swart, M.; Que, L., Jr. A 5000-fold increase in the HAT reactivity of a nonheme Fe(IV)=O complex simply by replacing two pyridines of the pentadentate N₄Py ligand with pyrazoles. *Proc. Natl. Acad. Sci. USA* **2025**, *122*, e2414962122. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Satpathy, J.K.; Yadav, R.; Sahoo, L.; Uhlig, J.; Nordlander, E.; Sastri, C.V.; de Visser, S.P. Sulfur-ligated iron(IV)-imido and iron(IV)-oxo complexes: Which one is more reactive? *Chem. Sci.* **2026**, *17*, 1349–1364. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Paris, J.C.; Cheung, Y.H.; Zhang, T.; Chang, W.-C.; Liu, P.; Guo, Y. New frontiers in nonheme enzymatic oxyferryl species. *ChemBioChem* **2024**, *25*, e202400307. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Wang, D.; Ray, K.; Collins, M.J.; Farquhar, E.R.; Frisch, J.R.; Gómez, L.; Jackson, T.A.; Kerscher, M.; Waleska, A.; Comba, P.; et al. Nonheme oxoiron(IV) complexes of pentadentate N₅ ligands: Spectroscopy, electrochemistry, and oxidative reactivity. *Chem. Sci.* **2013**, *4*, 282–291. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Rohde, J.-U.; In, J.-H.; Lim, M.-H.; Brennessel, W.W.; Bukowski, M.R.; Stubna, A.; Münck, E.; Nam, W.; Que, L., Jr. Crystallographic and spectroscopic characterization of a nonheme Fe(IV)=O complex. *Science* **2003**, *299*, 1037–1039. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Annaraj, J.; Kim, S.; Seo, M.S.; Lee, Y.-M.; Kim, Y.; Kim, S.-J.; Kim, J.; Choi, Y.S.; Jang, H.G.; Nam, W. An iron(II) complex with an N₃S₂ thioether ligand in the generation of an iron(IV)-oxo complex and its reactivity in olefin epoxidation. *Inorg. Chim. Acta* **2009**, *362*, 1031–1034. [\[CrossRef\]](#)
11. Kaizer, J.; Klinker, E.J.; Oh, N.Y.; Rohde, J.-U.; Song, W.J.; Stubna, A.; Kim, J.; Münck, E.; Nam, W.; Que, L. Nonheme Fe^{IV}O Complexes That Can Oxidize the C-H Bonds of Cyclohexane at Room Temperature. *J. Am. Chem. Soc.* **2004**, *126*, 472–473. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Mitra, M.; Nimir, H.; Demeshko, S.; Bhat, S.S.; Malinkin, S.O.; Haukka, M.; Lloret-Fillol, J.; Lisensky, G.C.; Meyer, F.; Shteinman, A.A.; et al. Nonheme Fe(IV) Oxo Complexes of Two New Pentadentate Ligands and Their Hydrogen-Atom and Oxygen-Atom Transfer Reactions. *Inorg. Chem.* **2015**, *54*, 7152–7164. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Puri, M.; Que, L., Jr. Toward the synthesis of more reactive S = 2 nonheme oxoiron(IV) complexes. *Acc. Chem. Res.* **2015**, *48*, 2443–2452. [\[CrossRef\]](#) [\[PubMed\]](#)

14. Li, Y.; Singh, R.; Sinha, A.; Lisensky, G.C.; Haukka, M.; Nilsson, J.; Yiga, S.; Demeshko, S.; Gross, S.J.; Dechert, S.; et al. Nonheme Fe(IV)=O complexes supported by four pentadentate ligands: Reactivity toward H- and O-atom transfer processes. *Inorg. Chem.* **2023**, *62*, 18338–18356. [[CrossRef](#)] [[PubMed](#)]
15. Guo, M.; Zhang, J.; Zhang, L.; Lee, Y.-M.; Fukuzumi, S.; Nam, W. Enthalpy-entropy compensation effect in oxidation reactions by manganese(IV)-oxo porphyrins and nonheme iron(IV)-oxo models. *J. Am. Chem. Soc.* **2021**, *143*, 18559–18570. [[CrossRef](#)] [[PubMed](#)]
16. Pestovsky, O.; Bakac, A. Aqueous ferryl(IV) ion: Kinetics of oxygen atom transfer to substrates and oxo exchange with solvent water. *Inorg. Chem.* **2006**, *45*, 814–820. [[CrossRef](#)] [[PubMed](#)]
17. Chantarojsiri, T.; Sun, Y.; Long, J.R.; Chang, C.J. Water-Soluble Iron(IV)-Oxo Complexes Supported by Pentapyridine Ligands: Axial Ligand Effects on Hydrogen Atom and Oxygen Atom Transfer Reactivity. *Inorg. Chem.* **2015**, *54*, 5879–5887. [[CrossRef](#)] [[PubMed](#)]
18. Shaban, Y.S.; Ibrahim, M.M.; Heinemann, F.W.; van Eldik, R. Seven-coordinate iron(II) complexes of sulfur-based N3S2 macrocyclic ligands: Synthesis, properties, and crystal structure. *J. Coord. Chem.* **2012**, *65*, 934–944. [[CrossRef](#)]
19. Wu, C.; Chen, J.; Nam, W.; Wang, B. Heme and nonheme high-valent manganese(V)-oxo complexes: Synthesis, characterization, and reactivity. *Coord. Chem. Rev.* **2025**, *528*, 216429. [[CrossRef](#)]
20. Gong, Z.; Wang, L.; Xu, Y.; Xie, D.; Qi, X. Enhanced reactivities of iron(IV)-oxo porphyrin species in oxidation reactions promoted by intramolecular hydrogen bonding. *Adv. Sci.* **2024**, *11*, 2310333. [[CrossRef](#)] [[PubMed](#)]
21. Decker, A.; Rohde, J.U.; Klinker, E.J.; Wong, S.D.; Que, L., Jr.; Solomon, E.I. Spectroscopic and quantum chemical studies on low-spin FeIV=O complexes: Fe-O bonding and its contributions to reactivity. *J. Am. Chem. Soc.* **2007**, *129*, 15983–15996. [[CrossRef](#)] [[PubMed](#)]
22. Sastri, C.V.; Park, M.J.; Ohta, T.; Jackson, T.A.; Stubna, A.; Seo, M.S.; Lee, J.; Kim, J.; Kitagawa, T.; Münck, E.; et al. Axial Ligand Substituted Nonheme FeIV=O Complexes: Observation of Near-UV LMCT Bands and Fe=O Raman Vibrations. *J. Am. Chem. Soc.* **2005**, *127*, 12494–12495. [[CrossRef](#)] [[PubMed](#)]
23. Ray, K.; England, J.; Fiedler, A.T.; Martinho, M.; Münck, E.; Que, L., Jr. An Inverted and More Oxidizing Isomer of [Fe^{IV}(O)-(tmc)(NCCH₃)]²⁺. *Angew. Chem. Int. Ed.* **2008**, *47*, 8068–8071. [[CrossRef](#)] [[PubMed](#)]
24. Rana, S.; Biswas, J.P.; Sen, A.; Clémancey, M.; Blondin, G.; Latour, J.M.; Rajaraman, G.; Maiti, D. Selective C-H Halogenation over Hydroxylation by Non-Heme Iron(IV)-Oxo. *Chem. Sci.* **2018**, *9*, 7843–7858. [[CrossRef](#)] [[PubMed](#)]
25. Sastri, C.V.; Lee, J.; Oh, K.; Lee, Y.J.; Lee, J.; Jackson, T.A.; Ray, K.; Hirao, H.; Shin, W.; Halfen, J.A.; et al. Axial ligand tuning of a nonheme iron(IV)-oxo unit for hydrogen atom abstraction. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 19181–19186. [[CrossRef](#)] [[PubMed](#)]
26. Baglia, R.A.; Zaragoza, J.P.T.; Goldberg, D.P. Biomimetic Reactivity of Oxygen-Derived Manganese and Iron Porphyrinoid Complexes. *Chem. Rev.* **2017**, *117*, 13320–13352. [[CrossRef](#)] [[PubMed](#)]
27. Yokota, S.; Fujii, H. Critical Factors in Determining the Heterolytic versus Homolytic Bond Cleavage of Terminal Oxidants by Iron(III) Porphyrin Complexes. *J. Am. Chem. Soc.* **2018**, *140*, 5127–5137. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.