

Probing Edge/Support Electronic Cooperativity in Single Edge Fe/Co₆Se₈ Clusters

Benjamin S. Mitchell¹, Andrei Chirila¹, Kevin Anderton², Werner Kaminsky¹, and Alexandra Velian^{1*}

¹Department of Chemistry, University of Washington, Seattle, Washington, 98195. ²Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, 02138.

Supporting Information Placeholder

Abstract. This study provides insights into the electronic structure of an atomically precise Fe/Co₆Se₈ cluster and the extent of redox cooperativity between the Fe active site and the non-innocent Co₆Se₈ support. Chemical oxidation studies enable the isolation of two types of oxidized Fe/Co₆Se₈ clusters, in which the counterion is either directly coordinated to the Fe, or completely dissociated. Experimental characterization by single crystal X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy, and ³¹P NMR spectroscopy is complemented by computational analysis. In aggregate, the study reveals that upon oxidation, the charge is shared between the Fe edge site and the Co₆Se₈ core, and that anion coordination perturbs the density of unpaired electrons on Co₆Se₈.

Multimetallic cooperativity holds the promise of imbuing base metals with the ability to achieve desirable multielectron transformations that are uncharacteristic of a single metal.¹ The power of multi-site cooperativity is illustrated by nature's reliance on base metal clusters to carry out some of the most complex and energetically difficult processes, such as cleaving dinitrogen during ammonia biosynthesis.^{2,3} Although the mode of operation and electronic structure of the FeMo cofactor are still topics of debate,⁴⁻⁶ this polymetallic cluster provides the active site for substrate binding and reduction, and mediates the transfer of the electrons required for nitrogen fixation.^{3,7-9}

Molecular clusters have the synthetic tunability to systematically probe and ultimately control how multiple metals interact to achieve complex redox transformations.¹⁰⁻¹⁶ Towards this goal, chemical oxidation studies provide valuable insights and can reveal how the metal identity,¹¹ ligand binding^{17,18} or the ligand framework impact charge distribution within a multimetallic platform.¹⁹⁻²² For example, inner-sphere oxidation of an all-ferrous Fe₃ cluster was shown to result in anion coordination at one Fe center, and localization of the generated charge on the two distal sites.¹⁷ On the contrary, outer-sphere oxidation of a Cu₄S cluster results in complete charge delocalization between the four Cu centers.¹⁸ The Fe₃ and Cu₄S clusters illustrate instances of distinct regimes for multi-site electronic interactions in structurally unrelated platforms. By anchoring base metals on the surface of a redox-noninnocent cluster (Co₆Se₈), our group introduced a modular platform that enables access to a range of redox regimes within the same framework that is also catalytically competent.²³⁻²⁵ Recently, we have shown that the identity of the edge metal M in the single edge clusters MCo₆Se₈(PEt₃)₄L'₂ (**1**-M, M = Cr, Mn, Fe, Co, Cu, Zn; L' = PPh₂N⁽⁻⁾Tol; Tol = 4-Tolyl, Ph = phenyl, Et = ethyl) determines the extent to which the active site and the support interact electronically, and have begun elucidating the consequences of the ensuing cooperativity in catalysis.^{25,26}

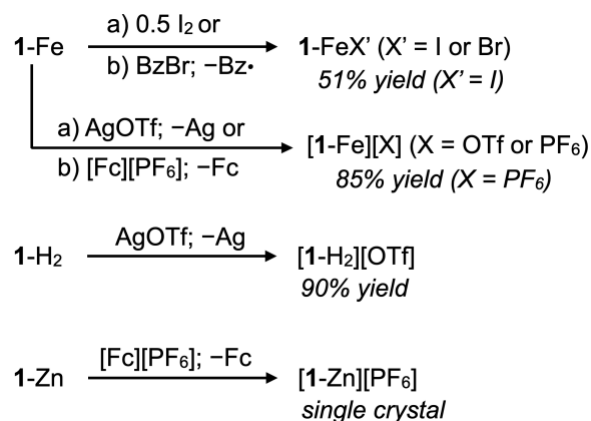
In this study, we investigate the chemical oxidation of the single-edge cluster **1**-Fe to elucidate the extent of edge/support electronic interactions in localizing the resulting charge. Single crystal X-ray diffraction studies, ⁵⁷Fe Mössbauer and ³¹P NMR spectroscopic analyses, as well as DFT calculations suggest that upon

mono-oxidation the Fe edge and the Co₆Se₈ core share the burden of the charge, and that the relative distribution of charge is perturbed by anion coordination.

Chemical Oxidation

Electrochemical measurements have previously revealed that the single edge cluster **1**-Fe can be oxidized reversibly multiple times.²⁵ Here, the chemical mono-oxidation of **1**-Fe is accomplished using a series of inner and outer sphere oxidants of appropriate oxidative strength,²⁷ such as iodine, benzyl bromide,^{28,29} silver triflate (AgOTf), and ferrocenium hexafluorophosphate ([Fc][PF₆]; Scheme 1). The resulting mono-oxidized clusters are therefore obtained either as salts [**1**-Fe][X] (X = OTf, PF₆), with the counterion dissociated from Fe as in [**1**-Fe][OTf] or [**1**-Fe][PF₆], or as neutral species with the anion directly bound to the edge

Scheme 1. Chemical oxidation of **1**-Fe and **1**-H₂.



site, as in **1**-FeX' (X' = Br, I). From a synthetic standpoint, [Fc][PF₆] and I₂ are more convenient reagents, and enable the isolation of [**1**-Fe][PF₆] and **1**-FeI as analytically pure compounds (85% and 51% yield, respectively). While [**1**-Fe][OTf] and **1**-FeBr are not isolated pure, they are characterized in the solid state (Figure 1). The similar spectroscopic signatures of the [**1**-Fe][PF₆] and [**1**-Fe][OTf] salts suggests that the solid state of the latter is also representative of the former, and the two compounds are considered interchangeable in this text. Likewise, ¹H and ³¹P NMR spectroscopy indicates that the identity of the anion has only a minor impact on the structure of the **1**-FeX' clusters (Figure S11, Table S1).

The solubility properties of the oxidized clusters align with the extent of anion association at Fe. In contrast to the **1**-FeX' clusters, the hexafluorophosphate salt [**1**-Fe][PF₆] is insoluble in non-polar solvents (i.e. toluene, benzene). Interestingly, [**1**-Fe][OTf] readily dissolves in benzene, suggesting a closer association of the ions occurs in this solvent. ¹⁹F NMR spectroscopy indicates that while the triflate ion remains completely dissociated from the Fe edge in polar solvents (δ = -78 ppm in acetonitrile-*d*₃), it is weakly associated in non-polar ones (δ = -60 ppm in benzene-*d*₆).³⁰

To compare the structural and electronic changes incurred in the Fe/Co₆Se₈ cluster upon oxidation, **1**-Zn and **1**-H₂ which feature either a redox inactive edge metal (Zn) or no edge metal at all are also oxidized and analysed. The cluster ligand salt [**1**-H₂][OTf] is produced in good yield (90%) upon treatment with AgOTf. X-ray quality crystals of [**1**-Zn][PF₆] are grown from a crude reaction mixture between **1**-Zn and [Fc][PF₆] (Section S5).

Structural Analysis

Diffraction quality crystals of [**1**-Fe][OTf] and **1**-FeBr are obtained from layered solutions of toluene/*n*-pentane stored at -35 °C (Figure 1). Their analysis illustrates the dynamic ligand/active site/support interactions, and shines light on the structural changes incurred at the Fe edge upon oxidation of **1**-Fe.²⁵ Table 1 summarizes key interatomic distances of the clusters discussed in this section.

Binding an exogenous ligand at Fe can occur when the incoming ligand has sufficient coordinative strength to outcompete Se. In turn, the nucleophilicity of the Se sites and the Fe—Se bond strength is not a static quantity, but is responsive to redox changes of the Co₆Se₈ core, the ligand framework, or binding activity at neighboring edge sites when they are present.^{26,31} The structures of [1-Fe][OTf] and 1-FeBr capture a switching point: bromide is sufficiently nucleophilic to break an Fe—Se bond and give rise to a κ³-Fe edge in 1-FeBr. In contrast, triflate remains an outer sphere counterion as it cannot outcompete Se coordination. In [1-Fe][OTf], the κ⁴-Fe edge site retains the two Fe—Se bonds of the parent complex 1-Fe, previously characterized in the solid state and depicted in Figure 1a for comparison.²⁵

Inspecting the FeCo₂Se₂ edge units indicates that anion coordination, as well as oxidation leads to significant restructuring that propagates through the entire cluster. For example, to accommodate a κ⁴-bound Fe edge on the Co₆Se₈ surface, the Co—Se bonds elongate from 2.36 Å in 1-FeBr, to 2.42 Å in [1-Fe]⁺, and the vicinal selenium atoms are pushed apart increasing the Se...Se interatomic distance from 3.44 Å to 3.58 Å. Since the average interatomic Co...Se and Se...Se distances of the Co/Se cores remain virtually unchanged, these local distortions are compensated by deformations in the rest of the Co/Se core. Inspecting the edge metrics of [1-Fe]⁺ also reveals that the “appended” Fe center becomes truly incorporated by the Co₆Se₈ cluster. This is reflected in Fe...Co distances of 2.754(6) and 2.805(6) Å that are notably shorter than the average Co...Co distances of the Co₆Se₈ core (2.92 Å).

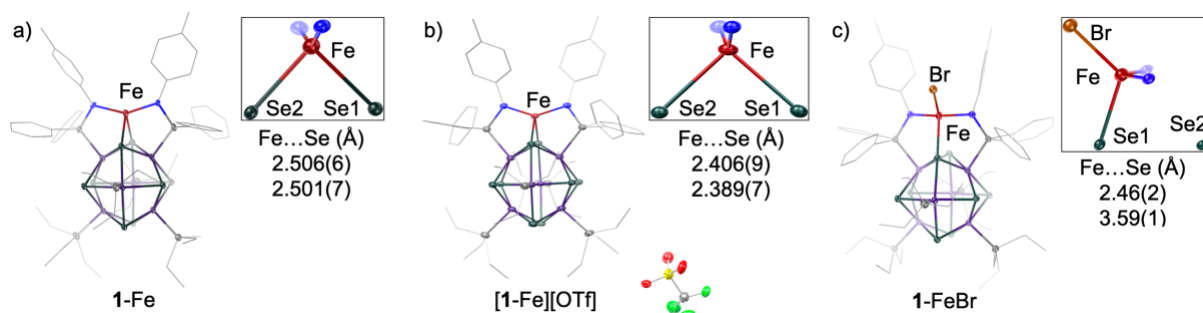


Figure 1. Comparison of bonding metrics at the Fe edge upon mono-oxidation. Single crystal X-ray diffraction of a) 1-Fe (from Ref 25), b) [1-Fe][OTf], and c) 1-FeBr. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

Table 1. Select interatomic distances (Å).

Compound	intra-Co ₆ Se ₈ (avg, Å)			MCo ₂ Se ₂ edge unit (Å)						
	Co—Se	Co...Co	Se...Se	Co—Se	Co...Co	Se...Se	M...Se	M...Se	M...Co	M...Co
1-Fe ⁱ	2.35	2.94	3.27	2.40	2.890(8)	3.504(8)	2.501(7)	2.506(6)	2.94(1)	2.937(5)
1-Fe(Br)	2.35	2.92	3.26	2.36	2.786(5)	3.444(3)	2.46(2)	3.59(1)	3.58(2)	3.694(7)
[1-Fe][OTf]	2.35	2.92	3.27	2.42	2.85(1)	3.58(1)	2.389(7)	2.406(9)	2.754(6)	2.805(6)
1-Zn ⁱ	2.35	2.94	3.27	2.38	2.895(6)	3.432(5)	2.537(7)	2.562(7)	3.069(8)	3.087(9)
[1-Zn][PF ₆]	2.34	2.90	3.26	2.37	2.88(1)	3.44(1)	2.615(8)	2.66(1)	3.104(9)	3.123(9)
Co ₆ Se ₈ (L ^H) ₆ ⁱ	2.35	2.94	3.25	-	-	-	-	-	-	-
[Co ₆ Se ₈ (L ^H) ₆][OTf] ⁱ	2.34	2.90	3.25	-	-	-	-	-	-	-

ⁱ Previously reported structures in ref. 23 and 25.

The edge/support interaction strength (Fe—Se bonds), and the Co...Co distances within the Co₆Se₈ cluster inform on the localization of the charge within the Fe/Co₆Se₈ constructs. We hypothesize that if oxidation is localized on the Co₆Se₈ core, the Fe—Se bonds will elongate due to the decreased electron richness of

the Se sites. This scenario is clearly illustrated in the mono-oxidized zinc cluster $[\mathbf{1}\text{-Zn}][\text{PF}_6]$, where the charge is unambiguously confined on Co_6Se_8 , and the Zn—Se contacts elongate from an average of 2.55 in $\mathbf{1}\text{-Zn}$ to 2.64 Å (Figure S17). Instead, the opposite is observed when oxidizing $\mathbf{1}\text{-Fe}$: the two Fe—Se bonds contract from an average of 2.50 to 2.40 Å in $[\mathbf{1}\text{-Fe}][\text{OTf}]$, suggesting that unlike in the zinc congener, the edge site participates in localizing the charge.

Another empirical structural reporter supporting this claim is the average interatomic distance between neighboring Co atoms within the Co_6Se_8 core. When oxidation is strictly confined to the Co_6Se_8 core, as is the case in $[\mathbf{1}\text{-Zn}][\text{PF}_6]$, $\mathbf{1}\text{-Cu}$,²⁵ or $[\text{Co}_6\text{Se}_8\text{L}^{\text{H}}_6][\text{OTf}]$,²³ the Co...Co average distance consistently contracts from 2.94 to 2.90 avg. Å.^{23,32} Instead, the average Co...Co distance contracts only halfway from 2.94 Å in $\mathbf{1}\text{-Fe}$, to 2.92 Å in $\mathbf{1}\text{-FeBr}$ and $[\mathbf{1}\text{-Fe}][\text{OTf}]$, foreshadowing that the positive charge is shared between the Fe and the Co_6Se_8 core.

Electronic Investigations Using Mössbauer Spectroscopy

Two limiting scenarios would localize the charge in $[\mathbf{1}\text{-Fe}][\text{X}]$ and $\mathbf{1}\text{-FeX}'$ either on the Co_6Se_8 core ($\text{Fe}^{2+}/[\text{Co}_6\text{Se}_8]^{1+}$), or on the iron edge site ($\text{Fe}^{3+}/[\text{Co}_6\text{Se}_8]^0$). Structural analysis, discussed in the previous section, suggests the charge is distributed between Fe and Co_6Se_8 . Solution phase magnetic measurements using Evans method³³ confirm, as expected, that $[\mathbf{1}\text{-Fe}][\text{OTf}]$ and $\mathbf{1}\text{-FeI}$ have five unpaired electrons each, but do not report on the location of the unpaired electron gained upon oxidation of $\mathbf{1}\text{-Fe}$. To experimentally probe these possibilities, $\mathbf{1}\text{-Fe}$, $[\mathbf{1}\text{-Fe}][\text{PF}_6]$, and $\mathbf{1}\text{-FeI}$ are analysed using zero-field ^{57}Fe Mössbauer spectroscopy (Figure 2a). While the neutral $\mathbf{1}\text{-Fe}$ cluster has an isomer shift most consistent with a high spin Fe(II) edge ($\delta = 0.72$ mm/s), the oxidized clusters $[\mathbf{1}\text{-Fe}][\text{PF}_6]$ and $\mathbf{1}\text{-FeI}$ have isomer shifts ($\delta = 0.43$, 0.40 mm/s, respectively) typically associated with high spin $\text{Fe}^{2.5+}$ or Fe^{3+} centers.^{17,34–36} Although the coordination environments of the two $\kappa^4\text{-Fe}$ edges in $\mathbf{1}\text{-Fe}$ and $\mathbf{1}\text{-Fe}^+$ are nearly identical ($\tau_4 = 0.78$ and 0.77, respectively³⁷), the shortened Fe—Se bonds, decreased $\langle\text{N-Fe-N}\rangle$ angle, and electronic changes at Fe give rise to significantly different quadrupole splitting ($|\Delta E_Q| = 0.76$, 1.01 mm/s, respectively). The quadrupole splitting of $\mathbf{1}\text{-Fe}^+$ is nearly identical to that of $\mathbf{1}\text{-FeI}$ ($|\Delta E_Q| = 1.08$ mm/s; $\tau_4 = 0.82$), perhaps a reflection of their similar oxidation states and comparable polarizability of Se and I.³⁸

In contrast to the tri-Fe clusters $\text{Fe}_3\text{Co}_6\text{Se}_8\text{L}_6'$ (Fe_3) characterized previously by our group,³⁹ the mono-Fe clusters discussed here incur a significantly stronger response in the ^{57}Fe Mössbauer isomer shifts upon

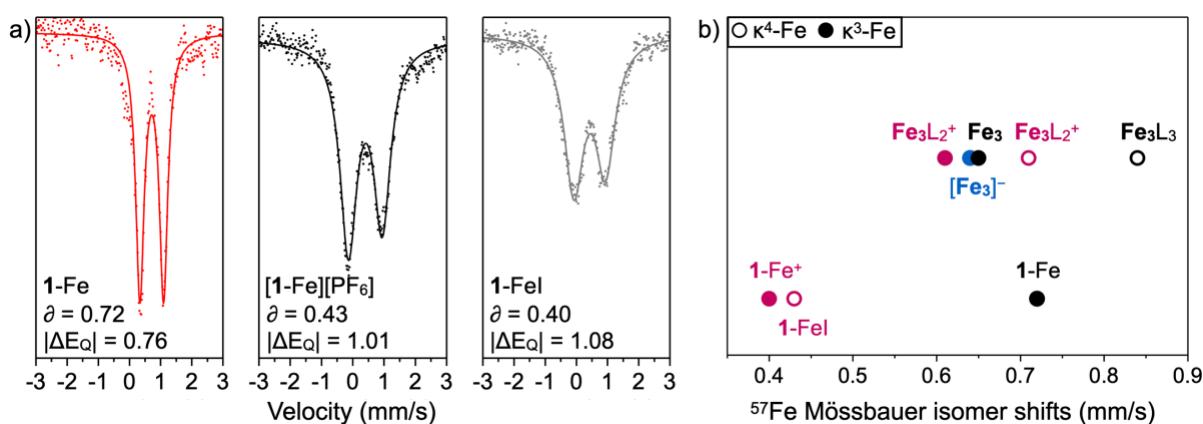


Figure 2. a) ^{57}Fe Mössbauer spectra of $\mathbf{1}\text{-Fe}$, $\mathbf{1}\text{-FeI}$, and $[\mathbf{1}\text{-Fe}][\text{PF}_6]$. b) Comparison of ^{57}Fe Mössbauer isomer shifts between monoiron ($\mathbf{1}\text{-Fe}$, $\mathbf{1}\text{-FeI}$, $[\mathbf{1}\text{-Fe}][\text{PF}_6]$), and triiron (Fe_3 , Fe_3L_3 , $[\text{Fe}_3\text{L}_2][\text{PF}_6]$, $[\text{TBA}][\text{Fe}_3]$; L = CN'Bu) clusters redox series. Mono-oxidized clusters are depicted pink, neutral in black, and monoreduced in blue.

oxidation (Figure 2b). Mössbauer and electrochemical measurements have previously led us to propose that the frontier orbitals of tri-Fe clusters are primarily localized on the Co_6Se_8 core, giving rise to a redox regime wherein the edge sites remain isovalent (Fe^{2+}) upon chemical mono-oxidation or monoreduction.²³ While limiting scenarios of localizing the charge on the iron or core are attractive in their simplicity, it is also possible, and likely, that “the distribution of electron density does not occur in $1e^-$ jumps”.⁴⁰ Instead, we propose that the charge is distributed between the Fe edge(s) and the cobalt core, to different extents depending on the number of edge sites and bound exogenous ligands, placing **1-Fe** and Fe_3 in an intermediate, and dynamic edge/support redox regime.²⁵

³¹P NMR Spectroscopy and DFT Calculations Inform on Edge/Core Charge Distribution

NMR spectroscopy furnishes detailed insights into the electronic and structural characteristics of the single edge clusters **1-M**.²⁵ In particular, the ³¹P NMR chemical shifts of the phosphines are sensitive reporters for electronic and chemical changes occurring at the edge site (PPh_2NTol) or the Co_6Se_8 core (PEt_3). Here, we set out to investigate if the ³¹P NMR chemical shifts of **1-Fe**, **1-FeI** and $[\mathbf{1-Fe}][\text{PF}_6]$ shine light on the relative distribution of charge between the edge and the Co_6Se_8 core, and corroborate the findings with electronic structure calculations (Figure 3). Additionally, variable temperature NMR spectroscopy measurements, previously reported²⁵ for ³¹P and appended here for ¹H signals, reveal a Curie behaviour for **1-Fe**, whereas inversion recovery experiments enable the complete assignment of the ¹H and ³¹P NMR signals in **1-Fe** (Figure S13-16).^{41,42} Figure 3a compares the ³¹P NMR of three pairs of compounds: the κ^4 -complexes **1-Fe**/ $[\mathbf{1-Fe}][\text{X}]$, the κ^3 -complexes **1-Fe(py)**/**1-FeX**, and the parent cluster ligands **1-H₂**/ $[\mathbf{1-H}_2][\text{OTf}]$. The ³¹P NMR chemical shifts are also summarized in Table S1.

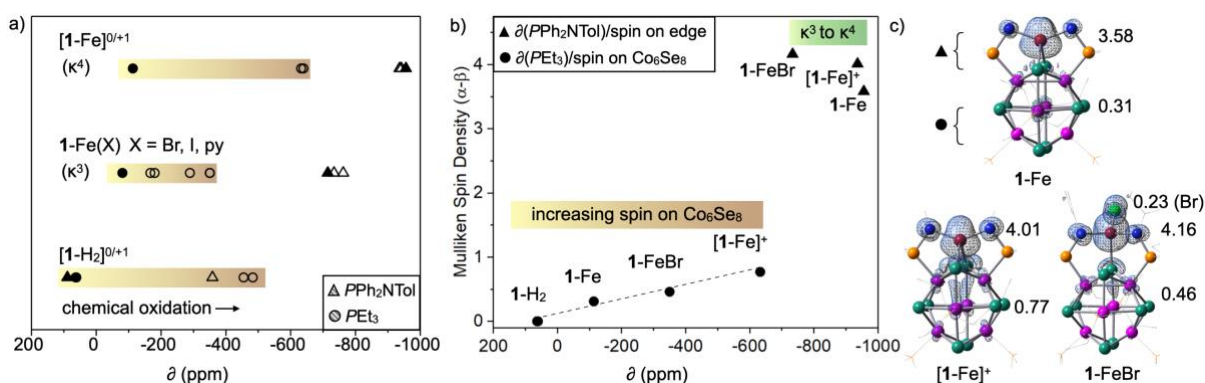


Figure 3. a) ³¹P NMR chemical shifts of amidophosphine PPh_2NTol (triangles) and triethylphosphine PEt_3 (circles) groups in the neutral clusters **1-H₂**, **1-Fe**, and **1-Fe(py)** (filled), and mono-oxidized clusters $[\mathbf{1-H}_2]^+$, $[\mathbf{1-Fe}]^+$, and **1-FeX** ($\text{X} = \text{Br}, \text{I}$) (hollow). b) Relationship between the calculated Mulliken spin density calculated for the core or edge, and ³¹P NMR chemical shift of PEt_3 and PPh_2NTol . c) Mulliken spin density (α - β) plots of **1-Fe**, $[\mathbf{1-Fe}]^+$, and **1-FeBr** calculated at the DFT uB3LYP+/cc-pVTZ level of theory.

Oxidation has a large impact on the chemical shift of the PEt_3 groups in the κ^4 -Fe complexes **1-Fe**/ $[\mathbf{1-Fe}][\text{X}]$, indicating that Co_6Se_8 gains unpaired electron density. Indeed, the PEt_3 groups shift from -113 ppm in **1-Fe** to -632 ppm in the $[\mathbf{1-Fe}]^+$ cation, whereas the PPh_2NTol groups, already proximal to a paramagnetic center, are minimally affected. The oxidized metalloligand, $[\mathbf{1-H}_2][\text{OTf}]$, which confines the charge exclusively to the Co_6Se_8 core, exhibits a ca. 400 ppm negative shift for both the PEt_3 and the PPh_2NTol groups compared to the neutral cluster **1-H₂**.

The transition from κ^4 to κ^3 coordination at Fe is also associated with diagnostic changes in the ³¹P NMR chemical shifts, as seen comparing the $[\mathbf{1-Fe}]^+/\mathbf{1-FeX}$ and **1-Fe**/**1-Fe(py)** pairs (Figure 3a). The **1-Fe(py)**

adduct is presumed to form upon dissolving **1**-Fe in pyridine.²⁶ For example, ligand coordination leads to shifts of ca. 200 ppm to higher frequencies for the *PPh₂NTol* groups in both the neutral and the oxidized clusters. Although distal to the Fe site, the *PEt₃* are especially sensitive to anion coordination. Two distinct *PEt₃* signals are resolved for the **1**-FeX' clusters, marking their permanent desymmetrization. Their dramatic shifts from -633 ppm in [**1**-Fe]⁺ to -351 and -168 ppm in **1**-FeI are attributed to changes in the relative unpaired electron density on the Co₆Se₈ core due to anion coordination.

To probe how the electronic structure of **1**-Fe is impacted by oxidation and anion coordination, we turned to DFT calculations (uB3LYP+/ccpVTZ). Figure 3c depicts the Mulliken spin density (α - β) plots for **1**-Fe,²⁵ **1**-FeBr, [**1**-Fe]⁺, and indicate that the spin density on the Co₆Se₈ core more than doubles upon oxidizing the neutral **1**-Fe (0.31) to [**1**-Fe]⁺ (0.77). These calculations corroborate the conclusion that the charge is shared between the edge and the Co₆Se₈ support in [**1**-Fe]⁺. Interestingly, calculations also suggest that anion binding at Fe relieves spin density from the Co₆Se₈ core by localizing part of the spin on the halide, leading to a spin of only 0.46 for the Co₆Se₈ support in **1**-FeBr.

Since the phosphines report on the electronic structure of Fe/Co₆Se₈ construct, their ³¹P NMR chemical shifts were plotted against the spin densities calculated for edge and support (Figure 3b,c). The ³¹P NMR chemical shifts of the *PEt₃* groups on the neutral **1**-H₂ were used as a reference point for a completely diamagnetic cluster. The linear correlation between the calculated spin density on the Co₆Se₈ support and experimental ³¹P NMR data for the *PEt₃* groups reaffirms the conclusions that upon oxidation of **1**-Fe the charge is delocalized between the Fe and the Co₆Se₈ support, and that anion binding impacts the distribution of unpaired electron density by localizing some of the spin. At the same time, the relatively small change in the spin density at the edge sites is consistent with minor differences in the chemical shifts of the *PPh₂NTol* groups in **1**-Fe, **1**-Fe(Br), and [**1**-Fe]⁺ where the most significant variation occurs as a result of the κ^4 to κ^3 transition at Fe upon anion binding.

Conclusions

In conclusion, this study reveals atom level insights into the structural and electronic effects of chemical oxidation of **1**-Fe. Outer- and inner-sphere oxidation illustrates the versatility of the cluster construct to accommodate charge and ancillary ligands. The combination of experimental and computational methods highlights an interesting regime of redox delocalization where the charge is shared between the Fe edge and the Co₆Se₈ core.

ASSOCIATED CONTENT

Supporting Information

General experimental considerations, synthetic protocols, and experimental characterization including crystallographic data, NMR studies, and computational investigations are available online.

Accession Codes

CCDC 225100-225102 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Alexandra Velian – Department of Chemistry, University of Washington, Seattle, Washington 98195, United States; orcid.org/0000-0002-6782-7139; Email: avelian@uw.edu

Authors

Benjamin S. Mitchell - Department of Chemistry, University of Washington, Seattle, Washington 98195, United States; orcid.org/0000-0001-6585-2237

Andrei Chirila - Department of Chemistry, University of Washington, Seattle, Washington 98195, United States; orcid.org/0000-0001-9657-2334

Kevin Anderton - Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States; orcid.org/0000-0002-2599-9143

Werner Kaminsky - Department of Chemistry, University of Washington, Seattle, Washington 98195, United States; orcid.org/0000-0002-9100-4909

Notes

The authors declare no competing financial interests

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