Probing Edge/Support Electronic Cooperativity in Single Edge Fe/Co$_6$Se$_8$ Clusters

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Supporting Information Placeholder

Abstract. This study provides insights into the electronic structure of an atomically precise Fe/Co$_6$Se$_8$ cluster and the extent of redox cooperativity between the Fe active site and the non-innocent Co$_6$Se$_8$ support. Chemical oxidation studies enable the isolation of two types of oxidized Fe/Co$_6$Se$_8$ clusters, in which the counterion is either directly coordinated to the Fe, or completely dissociated. Experimental characterization by single crystal X-ray diffraction, $^{57}$Fe Mössbauer spectroscopy, and $^{31}$P 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 Co$_6$Se$_8$ core, and that anion coordination perturbs the density of unpaired electrons on Co$_6$Se$_8$.

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 Fe$_3$ 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 Cu$_4$S cluster results in complete charge delocalization between the four Cu centers.$^{18}$ The Fe$_3$ and Cu$_4$S 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 (Co$_6$Se$_8$), 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 MCo$_6$Se$_8$(PEt$_3$)$_4$L$^-$ (I-M, M = Cr, Mn, Fe, Co, Cu, Zn; L$^-$ = PPH$_2$N($^-$)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 I-Fe to elucidate the extent of edge/support electronic interactions in localizing the resulting charge. Single crystal X-ray diffraction studies, $^{57}$Fe Mössbauer and $^{31}$P NMR spectroscopic analyses, as well as DFT calculations suggest that upon
mono-oxidation the Fe edge and the Co₅Se₈ 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]). 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 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-d₃), it is weakly associated in non-polar ones (δ = −60 ppm in benzene-d₆).³⁰

To compare the structural and electronic changes incurred in the Fe/Co₅Se₈ 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 Co₈Se₈ 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 Co₈Se₈ 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 Co₈Se₈ 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 Co₈Se₈ 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.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>intra-Co₈Se₈ (avg, Å)</th>
<th>MCo₈Se₈ edge unit (Å)</th>
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<tbody>
<tr>
<td>1-Fe⁺</td>
<td>Co-Se 2.35 Co-Co 2.94 Sc-Se 3.27</td>
<td>Co-Se 2.40 Co-Co 2.89(8) Sc-Se 3.50(8)</td>
</tr>
<tr>
<td>1-Fe(Br)</td>
<td>Co-Se 2.35 Co-Co 2.92 Sc-Se 3.26</td>
<td>Co-Se 2.36 Co-Co 2.786(5) Sc-Se 3.444(3)</td>
</tr>
<tr>
<td>[1-Fe][OTf]</td>
<td>Co-Se 2.35 Co-Co 2.92 Sc-Se 3.27</td>
<td>Co-Se 2.42 Co-Co 2.85(1) Sc-Se 3.58(1)</td>
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<tr>
<td>1-Zn⁺</td>
<td>Co-Se 2.35 Co-Co 2.94 Sc-Se 3.27</td>
<td>Co-Se 2.38 Co-Co 2.895(6) Sc-Se 3.432(5)</td>
</tr>
<tr>
<td>[1-Zn][PF₆]</td>
<td>Co-Se 2.34 Co-Co 2.90 Sc-Se 3.26</td>
<td>Co-Se 2.37 Co-Co 2.88(1) Sc-Se 3.44(1)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Co₈Se₈(L)₆⁺</th>
<th>Co₈Se₈(L)₆[OTf]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₈Se₈(L)₆⁺</td>
<td>Co-Se 2.35 Co-Co 2.94 Sc-Se 3.25</td>
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<tr>
<td>Co₈Se₈(L)₆[OTf]⁺</td>
<td>Co-Se 2.34 Co-Co 2.90 Sc-Se 3.25</td>
<td>-</td>
</tr>
</tbody>
</table>

³Previously reported structures in ref. 23 and 25.

The edge/support interaction strength (Fe—Se bonds), and the Co…Co distances within the Co₈Se₈ cluster inform on the localization of the charge within the Fe/Co₈Se₈ constructs. We hypothesize that if oxidation is localized on the Co₈Se₈ 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 [1-Zn][PF₆]₆, where the charge is unambiguously confined on Co₈Se₈, and the Zn—Se contacts elongate from an average of 2.55 in 1-Zn to 2.64 Å (Figure S17). Instead, the opposite is observed when oxidizing 1-Fe: the two Fe—Se bonds contract from an average of 2.50 to 2.40 Å in [1-Fe][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 Co₈Se₈ core. When oxidation is strictly confined to the Co₈Se₈ core, as is the case in [1-Zn][PF₆]₆, 1-Cu²⁺ or [Co₈Se₈L¹₁]₆[OTf]²⁻ the Co…Co average distance consistently contracts from 2.94 to 2.90 avg. Å. Two limiting scenarios using Evans method confirm, as expected, that [1-Fe][OTf] and 1-FeI have five unpaired electrons each, but do not report on the location of the unpaired electron gained upon oxidation of 1-Fe. To experimentally probe these possibilities, 1-Fe, [1-Fe][PF₆], and 1-FeI are analysed using zero-field ⁵⁷Fe Mössbauer spectroscopy (Figure 2a). While the neutral 1-Fe cluster has an isomer shift most consistent with a high spin Fe(II) edge (δ = 0.72 mm/s), the oxidized clusters [1-Fe][PF₆] and 1-FeI have isomer shifts (δ = 0.43, 0.40 mm/s, respectively) typically associated with high spin Fe²⁺ or Fe³⁺ centers. Although the coordination environments of the two κ⁴-Fe edges in 1-Fe and 1-Fe⁺ are nearly identical (τ₄ = 0.78 and 0.77, respectively), the shortened Fe—Se bonds, decreased <N-Fe-N angle, and electronic changes at Fe give rise to significantly different quadrupole splitting (|ΔE₉| = 0.76, 1.01 mm/s, respectively). The quadrupole splitting of 1-Fe⁺ is nearly identical to that of 1-FeI (|ΔE₉| = 1.08 mm/s; τ₄ = 0.82), perhaps a reflection of their similar oxidation states and comparable polarization of Se and I.

In contrast to the tri-Fe clusters Fe₃Co₈Se₈L₆ (Fe₃) characterized previously by our group, the mono-Fe clusters discussed here incur a significantly stronger response in the ⁵⁷Fe Mössbauer isomer shifts upon

**Electronic Investigations Using Mössbauer Spectroscopy**

Two limiting scenarios would localize the charge in [1-Fe][X] and 1-FeX⁺ either on the Co₈Se₈ core (Fe²⁺/[Co₈Se₈]¹⁻), or on the iron edge site (Fe³⁺/[Co₈Se₈]⁰). Structural analysis, discussed in the previous section, suggests the charge is distributed between Fe and Co₈Se₈. Solution phase magnetic measurements and the Co…Co distance contracts only halfway from 2.94 Å in 1-Fe, to 2.92 Å in 1-FeBr and [1-Fe][OTf], foreshadowing that the positive charge is shared between the Fe and the Co₈Se₈ core.

![Figure 2](image-url) a) ⁵⁷Fe Mössbauer spectra of 1-Fe, 1-FeI, and [1-Fe][PF₆]. b) Comparison of ⁵⁷Fe Mössbauer isomer shifts between monoiron (1-Fe, 1-FeI, [1-Fe][PF₆]), and triiron (Fe₃, Fe₃L₆, [Fe₃L₆][PF₆], [TBA][Fe₃]; L = CNBu) 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 $\text{Co}_8\text{Se}_8$ core, giving rise to a redox regime wherein the edge sites remain isovalent ($\text{Fe}^{2+}$) upon chemical mono-oxidation or monoreduction.\textsuperscript{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”.\textsuperscript{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 Fe₃ in an intermediate, and dynamic edge/support redox regime.\textsuperscript{25}

\textbf{\textsuperscript{31}P 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.\textsuperscript{25} In particular, the \textsuperscript{31}P NMR chemical shifts of the phosphines are sensitive reporters for electronic and chemical changes occurring at the edge site ($\text{PPh}_2\text{NTol}$) or the $\text{Co}_8\text{Se}_8$ core ($\text{PEt}_3$). Here, we set out to investigate if the \textsuperscript{31}P NMR chemical shifts of 1-Fe, 1-FeI and [1-Fe][PF₆] shine light on the relative distribution of charge between the edge and the $\text{Co}_8\text{Se}_8$ core, and corroborate the findings with electronic structure calculations (Figure 3). Additionally, variable temperature NMR spectroscopy measurements, previously reported\textsuperscript{25} for \textsuperscript{31}P and appended here for \textsuperscript{1}H signals, reveal a Curie behaviour for 1-Fe, whereas inversion recovery experiments enable the complete assignment of the \textsuperscript{31}P and \textsuperscript{1}H NMR signals in 1-Fe (Figure S13-16).\textsuperscript{41,42} Figure 3a compares the \textsuperscript{31}P NMR of three pairs of compounds: the $\kappa^4$-complexes 1-Fe/[1-Fe][X], the $\kappa^3$-complexes 1-Fe(py)/1-FeX, and the parent cluster ligands 1-H₂/[1-H₂][OTf]. The \textsuperscript{31}P NMR chemical shifts are also summarized in Table S1.

![Figure 3](image-url)

Figure 3. a) \textsuperscript{31}P NMR chemical shifts of amidophosphate $\text{PPh}_2\text{NTol}$ (triangles) and triethylphosphine $\text{PEt}_3$ (circles) groups in the neutral clusters 1-H₂, 1-Fe, and 1-Fe(py) (filled), and mono-oxidized clusters 1-[H₂]+, 1-[Fe]+, and 1-FeX (X = Br, I) (hollow). b) Relationship between the calculated Mulliken spin density calculated for the core or edge, and \textsuperscript{31}P NMR chemical shift of $\text{PEt}_3$ and $\text{PPh}_2\text{NTol}$. c) Mulliken spin density (α-β) plots of 1-Fe, [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 $\text{PEt}_3$ groups in the $\kappa^4$-Fe complexes 1-Fe/[1-Fe][X], indicating that $\text{Co}_8\text{Se}_8$ gains unpaired electron density. Indeed, the $\text{PEt}_3$ groups shift from −113 ppm in 1-Fe to −632 ppm in the [1-Fe]+ cation, whereas the $\text{PPh}_2\text{NTol}$ groups, already proximal to a paramagnetic center, are minimally affected. The oxidized metalloligand, [1-H₂][OTf], which confines the charge exclusively to the $\text{Co}_8\text{Se}_8$ core, exhibits a ca. 400 ppm negative shift for both the $\text{PEt}_3$ and the $\text{PPh}_2\text{NTol}$ groups compared to the neutral cluster 1-H₂.

The transition from $\kappa^4$ to $\kappa^3$ coordination at Fe is also associated with diagnostic changes in the \textsuperscript{31}P NMR chemical shifts, as seen comparing the [1-Fe]+/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.\textsuperscript{25} For example, ligand coordination leads to shifts of ca. 200 ppm to higher frequencies for the \textit{PPh}_2\textit{NTol} groups in both the neutral and the oxidized clusters. Although distal to the Fe site, the \textit{PET}_3 are especially sensitive to anion coordination. Two distinct \textit{PET}_3 signals are resolved for the \textit{I-FeX}’ clusters, marking their permanent desymmetrization. Their dramatic shifts from \(-633\) ppm in \([\textit{I-Fe}]^+\) to \(-351\) and \(-168\) ppm in \textit{I-FeI} are attributed to changes in the relative unpaired electron density on the \textit{Co}_6\textit{Se}_8 core due to anion coordination.

To probe how the electronic structure of \textit{I-Fe} is impacted by oxidation and anion coordination, we turned to DFT calculations (\textit{uB3LYP+/ccpVTZ}). Figure 3c depicts the Mulliken spin density (\(\alpha-\beta\)) plots for \textit{I-Fe},\textsuperscript{25} \textit{I-FeBr}, \([\textit{I-Fe}]^+\), and indicate that the spin density on the \textit{Co}_6\textit{Se}_8 core more than doubles upon oxidizing the neutral \textit{I-Fe} (0.31) to \([\textit{I-Fe}]^+\) (0.77). These calculations corroborate the conclusion that the charge is shared between the edge and the \textit{Co}_6\textit{Se}_8 support in \([\textit{I-Fe}]^+\). Interestingly, calculations also suggest that anion binding at Fe relieves spin density from the \textit{Co}_6\textit{Se}_8 core by localizing part of the spin on the halide, leading to a spin of only 0.46 for the \textit{Co}_6\textit{Se}_8 support in \textit{I-FeBr}.

Since the phosphines report on the electronic structure of \textit{Fe/Co}_6\textit{Se}_8 construct, their \textsuperscript{31}P NMR chemical shifts were plotted against the spin densities calculated for edge and support (Figure 3b,c). The \textsuperscript{31}P NMR chemical shifts of the \textit{PET}_3 groups on the neutral \textit{I-H}_2 were used as a reference point for a completely diamagnetic cluster. The linear correlation between the calculated spin density on the \textit{Co}_6\textit{Se}_8 support and experimental \textsuperscript{31}P NMR data for the \textit{PET}_3 groups reaffirms the conclusions that upon oxidation of \textit{I-Fe} the charge is delocalized between the Fe and the \textit{Co}_6\textit{Se}_8 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 \textit{PPh}_2\textit{NTol} groups in \textit{I-Fe}, \textit{I-Fe(Br)}, and \([\textit{I-Fe}]^+\) where the most significant variation occurs as a result of the \(\kappa^4\) to \(\kappa^3\) 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 \textit{I-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 \textit{Co}_6\textit{Se}_8 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data_request@ccdc.cam.ac.uk](mailto: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.

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Notes

The authors declare no competing financial interests

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