COMMENTARY

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Valence electron delocalization in polynuclear iron-sulfur clusters

Abstract This commentary assesses the evidence for valence electron delocalization in dinuclear and polynuclear iron-sulfur clusters. We outline a simple Hamiltonian model that contains the important physical interactions and briefly review the experimental and computational tools that can be used to distinguish between valence electron delocalization and electron trapping and to assess likely magnitudes of resonance interactions.

General framework

When considering electron delocalization or localization between a pair of iron sites, both the shape of the potential well and the dependence of the potential energy surface on the alignment of the site spins are important. A good overview of these subjects is found in the review by Blondin and Girerd [1].

We shall consider a mixed-valence pair of Fe sites with spin-coupled Fe^{2+}–Fe^{3+} ions, where each site is internally high spin ($S_i = 2$ or 5/2). Such mixed-valence pairs occur for reduced 2Fe2S centers, for reduced 3Fe4S centers, and for all three observed oxidation states of 4Fe4S centers, as well as in mixed metal M3Fe4S systems. The presence of two possible sites for the "extra" sixth Fe(3d) electron suggests a simplified model Hamiltonian as illustrated in Fig. 1. This is a slight generalization of Fig. 3 of Blondin and Girerd [1], and we follow their notation. In the absence of a reson-
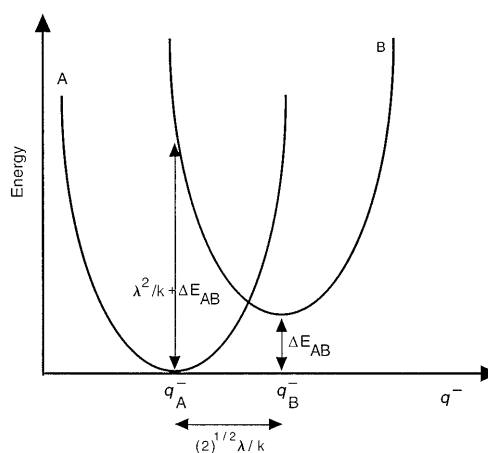
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Fig. 1 Schematic vibronic model for a mixed-valence dimer. Curves A and B are the diabatic energies (in the absence of resonance interaction) for localized states, as a function of a nuclear distortion parameter q^-. Notation is from [1]; see text for discussion

ance interaction between the two sites, this model has two "diabatic" surfaces, labeled A and B, that correspond to adding the extra electron to one of the two sites. The vibrational distortion parameter q^- represents changes that take place in the site environment on going from oxidized to reduced localized wavefunctions; these include changes in iron-sulfur bond lengths and rearrangements of the protein/solvent environment. This model is characterized by three parameters: the curvature k of the curves about the oxidized and reduced minima, the separation of these minima along the q^- coordinate (which is $(2)^{1/2} \lambda/k$ in this notation), and a shifting of the relative energies of curves A and B by ΔE_{AB}, reflecting a "static" preference (arising from an asymmetric environment) for the extra electron to reside on one site rather than the other. At the minimum of the A curve (point q_A^- in Fig. 1), state A has energy 0 and state B has energy $\Delta E = \lambda^2/k + \Delta E_{AB}$, where the first term can be considered a vibronic con-

Fig. 2 Squares of state coefficients for a mixed-valence pair, as a function of $\Delta E/B$. Curves are plotted for $S_{34} = 1/2$, 3/2, 5/2, 7/2 and 9/2, for the mixed-valence pair within a tetramer, and are the same for the total spin $S_{ij} = 1/2$, 3/2, 5/2, 7/2, and 9/2 of a dimer system
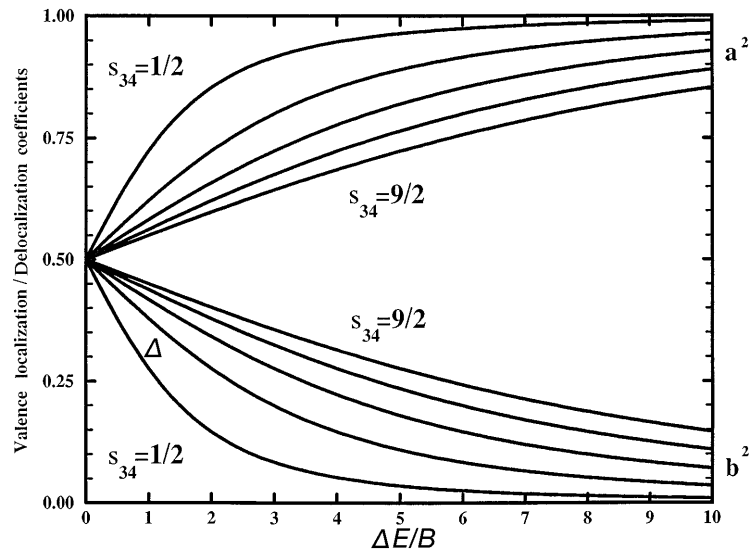
tribution and the second a static asymmetric contribution to a total "localization energy." This expression for ΔE corresponds to the situation where vibronic coupling dominates (Fig. 1), so the geometry of the system stays close to q_A^-. When resonance becomes substantial, ΔE is found from the minimum point of the total energy matrix (Eq. 1) (see Fig. 3 of [1]).

We now consider a resonance interaction between these localized states. According to the theory of "double exchange" (or "resonance delocalization coupling") developed by Anderson and Hasegawa [2] and applied to iron-sulfur systems by a number of groups, the energy of delocalization for a mixed-valence pair of transition metal sites depends on the alignment of the spins of the sites (i.e., on the pair spin quantum number S_{ij}) in a linear fashion: $E_{res} = \pm B(S_{ij} + 1/2)$, with the plus/minus sign representing the antibonding/bonding combination of orbitals associated with the delocalized electron. Then, if we focus on the minimum point of $q^- = q_{min}^-(A) = q_A^-$ (the last equality applying in the strong vibronic limit, and where the extra electron resides on site A) the energy matrix can be written:

$$\begin{bmatrix} 0 & -B\left(S_{ij}+\frac{1}{2}\right) \\ -B\left(S_{ij}+\frac{1}{2}\right) & \Delta E \end{bmatrix} \quad (1)$$

This is the model considered by Belinskii et al. [3] (their Eq. 4), and in the commentary by Kröckel et al. in this issue, but emphasizes the fact that ΔE contains both a static asymmetry ΔE_{AB} and a vibronic component λ^2/k (in the strong vibronic limit). In this model, these contributions are additive.

The properties of this simple resonance Hamiltonian model have been discussed in many places. Generally, valence trapping will occur unless $2|B(S_{ij} + 1/2)| > \Delta E$; as delocalization becomes important, the minimum in the ground state energy moves to $q^- = 0$ (see Fig. 3 of [1]). Asymmetries in site properties are governed by the ratio $R_{loc} = \Delta E/|B(S_{ij} + 1/2)|$, as shown in Fig. 2. For small values of this ratio, the system is almost com-

pletely delocalized: $R_{loc} \leq 0.4$ corresponds to $0.4 < c_A^2, c_B^2 \leq 0.6$, where c_A^2, c_B^2 are the weights of the local states. Large values of R_{loc} (>3) correspond to $c_A^2 > 0.9$, giving nearly complete localization. Some relevant examples for dimeric systems are presented in the commentary by Kröckel et al., while for reduced $[Fe_4S_4]^{1+}$ clusters, see Fig. 5 in [4], and [5].

Since different dimer spin states S_{ij} are possible, a Heisenberg term $(J/2)S_{ij}(S_{ij} + 1)$ can be added to the diagonal elements of Eq. 1. Qualitatively, the energies of various spin states are determined by the relative magnitudes of B and J (or with different J parameters for various pairwise interactions in polynuclear systems), whereas the extent of delocalization for a given spin state is determined by the ratio of B to ΔE.

In polynuclear systems, the solution depends on the equivalences among the sites and on which J_{ij} parameters are equal. We focus on $Fe_4S_4^{3+,1+}$, which display a variety of important phenomena. The Hamiltonian described by Eqs. 4 and 5 of the Bertini and Luchinat commentary in this issue follows earlier work [6] and gives Heisenberg energies added to the diagonal elements, $E_{heis}(S_{12},S_{34},S)$, where S_{12}, S_{34} and S are good quantum numbers. There are three different Heisenberg parameters in the problem, (J, ΔJ_{12}, ΔJ_{34}) in addition to B and ΔE. Again, the spin ground state and ordering of excited spin states depends on the B and multiple J parameters. While the primary effect of the ratio of B to ΔE is to affect the delocalization versus localization of the mixed-valence pair, an additional important result is that this ratio may affect the nature of the spin ground state and ordering of excited spin states as well [4, 5].

In systems with more than two metal ions, there may be several sets of these parameters, and it can be difficult to estimate their magnitudes from experimental data, both because fits may be underdetermined, and because the simple model outlined in Fig. 1 (and its extensions to larger systems) may have limitations. Here we discuss the computational and experimental evi-

dence that we feel provides the strongest evidence for the relative magnitudes of J, B and ΔE in iron-sulfur clusters.

Computational results

In principle, each of the parameters in Fig. 1 could be assessed by appropriate electronic structure calculations. These have the advantage of allowing a detailed dissection of various contributions, but also two significant drawbacks: first, the accuracy and reliability of calculations on such large and complex systems is not well-established; second, computational techniques for including environmental effects (from the protein and solvent) are only in their infancy and are even less well tested. In spite of these drawbacks, we feel that quantum chemistry calculations can offer some important insights into the general nature of the parameters involved in spin Hamiltonian descriptions of iron-sulfur clusters.

We have reviewed such calculations elsewhere [7, 8], and will not repeat the arguments here. We have concentrated on estimates of J and B, and have not yet made calculations that directly relate to vibronic couplings or to static asymmetries. In general, our calculations are consistent with experimental measurements and suggest fairly large values for B in iron-sulfur mixed-valence $[Fe_2S_2(SR)_4]^{3-}$ dimers, in the range of 400–500 cm^{-1} [9, 10] and larger values for B for the mixed-valence pair (or pairs) in tetramers, 700–900 cm^{-1} [10, 11]. We would like to emphasize that our estimates for B arise in a direct way from the computations, and are independent of estimates of J: fundamentally, we estimate B from the splitting of the bonding and antibonding orbitals in a "high-spin" configuration in which both of the sites in the mixed-valence pair have parallel spins. The value one gets in this way is strongly dependent on the iron-iron distance, since it arises from overlaps of iron d on each site, as well as contributions from bridging sulfurs. Basically, a large value of B corresponds to the formation of a weak metal-metal bond between the iron sites. We use a very flexible (triple-ζ) set to describe the electron distribution around the iron sites and believe that the computational methods we are using should provide at least a qualitatively correct picture.

We have also made estimates of the extent to which Heisenberg coupling constants may vary from one iron-iron pair to another within a four-iron cluster. In the $[Fe_4S_4]^{3+}$ oxidation state, the Heisenberg interaction in the ferric pair is expected to be larger than that in the mixed-valence pair, and we have calculated a difference of about 160 cm^{-1} [11]. For the $[Fe_4S_4]^{2+}$ state, the variation in J is expected to be smaller, since the formal oxidation state is $+2.5$ for all iron sites, and there are only minor geometric distortions away from a "tetrahedral" geometry in which all iron sites are equivalent. In recent calculations [12] we have looked at a C_{2v} model

of $[Fe_4S_4(SCH_3)_4]^{2-}$, and find $|\Delta J|/B$ of about 0.13 and $|\Delta J|/J$ about 0.17.

Experimental approaches

Mössbauer and ENDOR spectroscopy

In favorable cases, Mössbauer spectroscopy can provide values for magnetic hyperfine couplings and iron quadrupole splittings and isomer shifts. Such measurements can confirm the equivalence or inequivalence of sites with respect to both the electron distribution and the spin distribution. When the sites have the same sign and magnitude for the Fe hyperfine coupling, the corresponding spin vectors are parallel, and a large total spin quantum number for S_{ij} is just the required condition to give a large resonance energy. For detrapping to occur at such extremely low temperatures (e.g., 3 K), the barrier to electron hopping must be extremely low or absent. Careful studies of such pairwise equivalence within the mixed-valence pair have been conducted for the high-potential (HP) iron-sulfur protein from *Chromatium vinosum* and a synthetic analogue [13].

ENDOR measurements can also provide an accurate assessment of magnetic hyperfine couplings. These are carried out at low temperature, so that only the ground spin state is usually occupied. ENDOR spectroscopy of γ-irradiated single crystals of a synthetic 4Fe4S cluster shows near but not exact equivalence of the magnetic hyperfine coupling on the mixed-valence pair, and approximate, but still less exact equivalence of the two sites of the ferric pair [14]. This is consistent with a delocalized mixed-valence pair, but where the sites experience slightly different environments. Similar conclusions come from analysis of the anisotropic part of the proton hyperfine in this system [15, 16]. Analysis of g tensors from single-crystal EPR spectroscopy shows that the mixed-valence pair can reside on different $Fe_2S *_2$ faces of the cubane at low temperatures [17]. Thermally dependent hopping of the mixed-valence pair is also inferred from analysis of NMR spectra of various oxidized HP proteins [18, 19]. Site equivalences over one specific pair have also been observed by Mössbauer spectroscopy in a number of Fe_3S_4, Fe_4S_4, and MFe_3S_4 systems, where equivalence by the isomer shift, quadrupole splitting, and magnetic hyperfine coupling for two sites are all simultaneously present [20, 21].

Optical measurements

In delocalized clusters, optical measurements of the resonance splitting energy (giving the energy difference between bonding and antibonding valence delocalization) are potentially feasible. If the resonance splitting is large and the system is "truly" delocalized, such measurements should be spin and dipole allowed, with

a specific polarization direction along the metal-metal axis of the delocalized mixed-valence pair and energies in the near-IR to optical range. Single-crystal polarized IR/optical spectroscopy would be particularly promising. Initial measurements with magnetic circular dichroism (MCD) have been made on both 2Fe2S and 4Fe4S systems [22]. Cysteine → serine mutants of $[Fe_2S_2]^{1+}$ ferredoxin display a mixture of $S = 1/2$ (localized) and $S = 9/2$ ground state species. For this Fe_2S_2 cluster, both the presence of an $S = 9/2$ ground state and the location of an intense MCD band at 700 nm suggest a large double-exchange interaction, equivalent to $B = 1400$ cm^{-1}. Similar MCD bands at 700–800 nm (equivalent to $B = 1250$–1400 cm^{-1}) are present in various polynuclear complexes, including $Fe_3S_4^0$, $[Fe_4S_4]^{1+}$, Fe_8S_8, and $MFe_3S_4^{2+,1+}$ [22]. Further studies with optical spectroscopy are important to confirm or modify these spectral assignments. For delocalized or weakly localized (low barrier) clusters with small resonance energy splittings, the appropriate near-IR or optical bands should be absent. If the system is trapped valence (Robin-Day class II) [23], then an intervalence charge transfer (IVCT) band should be measurable (for an initial assignment in localized $[Fe_2S_2]^{1+}$, see [24]) and, with modern methods, there are ways to readily distinguish trapped and fully delocalized valence (Robin-Day class III) [23] via the intensity, vibronic fine structure [1], and temperature dependence of the band [25, 26].

Magnetic susceptibility

Fits of magnetic susceptibility data to spin Hamiltonians generally provide less direct evidence of the magnitude of J and B parameters, both because only the total cluster spin states are involved and because there is often a family of parameter values that can fit the data. A significant illustration of the results of a $(J,B,\Delta J)$ model versus a $(J,\Delta J)$ model is provided by the work of Jordanov et al. [27]. They measured the magnetic susceptibility of a synthetic $[Fe_4S_4]^{3+}$ cluster and fit the data using both $(J,B,\Delta J_{12})$ and $(J,\Delta J_{12})$ models, where ΔJ_{12} refers to the ferric pair with spin S_{12}, and ΔJ_{34}, S_{34} refer to the mixed-valence pair. ΔJ_{ij} is the difference between J_{ij} within the ferric (12) and mixed-valence (34) pairs and the Heisenberg coupling parameter (J) linking each site of the mixed-valence pair with each site of the ferric pair. We consider the same temperature range, 30–320 K, the same number of magnetic microstates (27), and $g = 2.0$ for all states. Then the quality of the best fit to the $(J,B, \Delta J_{12})$ model (fit II, Table 2) is $(R)^{1/2} = 7.7 \times 10^{-5}$ where $(J,B, \Delta J_{12}) = (542, 553, 134$ cm$^{-1})$ while for the $(J,\Delta J_{12})$ model, $(R)^{1/2} = 15.4 \times 10^{-5}$ with $(J,\Delta J_{12}) = (397, 0$ cm$^{-1})$ (R = the normalized residual of the fit). (See footnote 12 of [27] for details.) Our best calculated results are $(J,B) = (673, 878$ cm$^{-1})$ with the ferric pair $\Delta J_{12} = 160$ cm^{-1}, so these parameters are reasonably comparable to the experi-

mental fit values [11]. The B value is smaller from the experimental fit than from the calculations, but large in both cases. As shown above, introducing the B term does improve the fit. As we show next, the three-parameter Heisenberg model $(J,\Delta J_{12},\Delta J_{34})$ should still differ in the quality of fit from the three-parameter $(J,\Delta J_{12},B)$, because the covariance between B and ΔJ_{34} is limited and depends on the spin state ordering.

The problem of the covariance of B versus ΔJ in the mixed-valence pair can be stated simply. Consider the solution to the spin Hamiltonian of the Bertini-Luchinat commentary in this issue:

$$E(S_{12},S_{34},S) = (\Delta J_{34}/2)[S_{34}(S_{34}+1)] \pm B(S_{34}+1/2) + (J/2)[S(S+1)] + (\Delta J_{12}/2)[S_{12}(S_{12}+1)] \quad (2)$$

(Note that S_{12} and S_{34} are ferric and mixed-valence pairs respectively, opposite to the definition in the Bertini-Luchinat commentary.) Only the first two terms have a dependence on S_{34}, and on B and ΔJ_{34} [we need to consider only the lower (–) root for the B term]. Since the magnetic susceptibility depends on the energies and total spin (S) of the excited spin states with respect to the spin ground state, we need to consider only energy differences involving these first two terms. Then if the mixed-valence pair spin of the ground state is $S_{34}^g = 9/2$ and we consider excited states where $S_{34}^e = 7/2$, the relative energies of the excited states are unchanged so long as

$$B - (9\Delta J_{34}/2) = \text{Constant} \quad (3)$$

This is the covariance relationship necessary to give the identical level structures (Fig. 2B Bertini-Luchinat commentary). When, however, there are also other low-lying spin states where $S_{34}^e = 5/2$ as well as $S_{34}^e = 7/2$, then no such covariance relationship is possible, because there are only two free parameters B and ΔJ_{34}. This is why in Fig. 2A, the level structures of the $Fe_3S_4^0$ are not identical. In the magnetic susceptibility fit of Jordanov et al. [27], there are three low-lying states, with mixed-valence pair spins $S_{34} = 9/2, 7/2, 5/2$ respectively, and so there is no covariance relation between B and ΔJ_{34}. The covariance relationship is essentially accidental, depending on the spin excited states having either the same or a single different S_{34} quantum number compared to the ground state. Where this does not occur, the two models are inequivalent. This is as expected, since a quadratic function $(\Delta J_{34}/2)[S_{34}(S_{34} + 1)]$ is fundamentally different from a linear function $-B(S_{34} + 1/2)$, even though the two curves may cross at two points. The inequivalence among sites (for example, in their oxidation states, and in electron densities by measures such as Mössbauer isomer shifts) is greater for $Fe_4S_4^{3+,1+}$ complexes than in $Fe_4S_4^{2+}$, and there are correspondingly larger variations in $\Delta J_{12}/J$ [Where 12 = ferric pair (in 3+), or ferrous pair (1+) in the former systems. As a consequence, the covariance of B and ΔJ_{34} in Eq. 3 applies far better for $[Fe_4S_4]^{2+}$, since only low-lying $S_{34} = 9/2, 7/2$ states are present.

An illustration of this effect can be found in fits of the ^{13}C isotropic chemical shifts seen by solid-state NMR-MAS spectroscopy on $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ and $(Et_4N)_2[FC_4S_4(S-tBU)_4]$ in the temperate range 150–350 K [12]. Here the constants in Eq. 3 were found to be $570\ cm^{-1}$ and $730\ cm^{-1}$, respectively, with J around $340\ cm^{-1}$. Taking the theoretical value cited above of 0.17 for $\Delta J/J$, we then have ΔJ of about $60\ cm^{-1}$ and B between 300 and $460\ cm^{-1}$. Other examples of this sort of covariance are discussed in the commentary by Bertini and Luchinat.

In spite of this formal covariance, use of a fairly large value of B can result in a more robust spin Hamiltonian solution. Consider the $[Fe_4S_4]^{3+}$ cluster containing a mixed-valence pair and a ferric pair of irons (we use a C_{2v} model here). The corresponding spin Hamiltonian has exchange terms J, ΔJ_{12} (>0, for the ferric pair) and ΔJ_{34} (<0, for the mixed-valence pair) and a double-exchange term. The existence of the state $|7/2,3,1/2>$ (the state most consistent with the observed hyperfine properties for various synthetic centers) [14, 15] implies the set of conditions (with $x = |\Delta J_{34}/\Delta J_{12}|$):

$$3(1-x) < (B_{34}/\Delta J_{12}) + (x/2) < 4(1-x) \qquad (4)$$

If B_{34} is vanishingly small, this implies that x is in the narrow range from 6/7 to 8/9 (0.86 to 0.89). For the state $|9/2,4,1/2>$ to be the first excited state, rather than the state $|5/2,2,1/2>$, requires further that $0.875 < x < 0.889$. It does not seem reasonable to expect such requirements to be fulfilled over a wide range of systems [3, 28]. Moreover, this picture predicts very small energy gaps between the ground state and the first few excited states.

On the other hand, neglecting ΔJ_{34} ($x = 0$) yields

$$3 < (B_{34}/\Delta J_{12}) < 4 \qquad (5)$$

Since ΔJ_{12} is of the order of $100–150\ cm^{-1}$, B_{34} is consequently of the order of a few hundreds of cm^{-1}. The condition on $B_{34}/\Delta J_{12}$ is less stringent in this "B-only" model, and there is no necessary quasi-degeneracy at low energies. Moreover, since there is no strict covariance relation between B_{34} and ΔJ_{34} for $[Fe_4S_4]^{3+}$ systems, fits of magnetic susceptibility data within the two limiting approaches should help decide which is closer to reality.

Summary

In assessing the presence and magnitude of valence delocalization (double exchange) in iron-sulfur clusters, it is important to realize that different experimental methods give different types of information. Mössbauer [13, 20] and ENDOR [14] spectroscopy provide very good evidence for site equivalences within a mixed-valence pair (or pairs), and therefore for the presence of delocalized valence, but not directly for the magnitude of B, although the latter must be sufficient to overcome the total of all localizing forces. Magnetic susceptibility [29], and solid-state or solution NMR [19] can be fit with various spin coupling models. Fits may not be unique, but the covariance of B and ΔJ of the mixed-valence pair is approximate at best and depends on the system and its spin state ladder. Our current fits for $Fe_4S_4^{2+,3+}$ systems are consistent with large B values, $300–460\ cm^{-1}$ ($2+$), $550–600\ cm^{-1}$ ($3+$) [27] while directly calculated B values are higher: $800–900\ cm^{-1}$ (for $2+,3+$) [10, 11]. Belinskii et al. [3] have proposed setting an upper bound for B in $Fe_2S_2^{1+}$ dimers, based on magnetic susceptibility data and the presence of a trapped valence ground state. This depends on knowing ΔE, which is a sum of a static asymmetry energy ΔE_{AB} and vibronic (including additional solvation or protein) terms. Neither of these are known experimentally, and possible thermal measurements (by NMR, for example) can give only ΔE_{AB}. We suspect that ΔE may be considerably larger than the estimate of 100 mV by Belinskii et al. The experimental value of ΔE should be accessible using optical spectroscopy to determine the energy of the IVCT band in trapped $Fe_2S_2^{1+}$ dimers, following up on the initial assignment made with MCD [24]. In addition, our calculations predict larger B values in tetramers than in dimers, by a factor of 1.5–2.0. Initial spectroscopic measurements by MCD also suggest large resonance parameters in tetramers [22], and further work with optical methods should be more definitive. From our calculations [10], the B term plays an important role in oxidation/reduction thermodynamics, contributing about 1 eV to the higher redox potential of the HP couple versus the reduced 4Fe4S ferredoxin couple. This should be testable, for example, by measuring redox potentials after substitution of simpler metals for some Fe sites in 4Fe complexes so as to destroy the resonance interaction of specific mixed-valence pairs.

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