Double exchange in a mixed-valent octanuclear iron cluster, \([\text{Fe}_8(\mu_4-O)_4(\mu_4-\text{Cl-pz})_{12}\text{Cl}_4]^-\)"}

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A combination of SQUID and pulsed high-field magnetometry is used to probe the nature of mixed valency in an \(\text{Fe}^{II}\text{Fe}^{III}\) cluster. DFT-computed spin Hamiltonian parameters suggest that antiferromagnetic coupling dominates, and that electron transfer both between the four iron of the cubane core (\(t_0\)) and between a cubane and three neighboring iron (\(t_3\)) is significant. Simulations using the computed parameters are able to reproduce the key features of the measured effective magnetic moment, \(\mu_{\text{eff}}(T)\), over the \(2 < T < 300\ \text{K}\) temperature range. In contrast, the field dependence of the molar magnetization, \(M_{\text{mol}}\), measured at 0.4 K is inconsistent with substantial electron transfer: only values of \(t_2 \sim 0\) place the separation between ground and first excited states in the region indicated by experiment. The apparent quenching of the cubane–outer electron transfer at very low temperatures indicates that vibronic coupling generates one or more shallow minima on the adiabatic potential energy surfaces that serve to trap the itinerant electron in the cubane core.

Introduction

The magnetic properties of clusters of transition metals with partially filled paramagnetic d shells are dominated by Mott physics in the sense that on-site Coulomb repulsion dominates direct overlap between the metal centers, such that the salient material properties can be described by magnetic exchange interactions between localized electron spins. Antiferromagnetic coupling between the moments then leads to a complex hierarchy of spin states and associated structure (steps and plateaux) in the field dependence of the magnetization. In contrast, mixed-valent clusters, where isotropic exchange and electron transfer, 1–3 intrinsic site asymmetry (e.g., in the ligand environment) 1,3 and/or intercenter Coulomb repulsion 1 and vibronic coupling 4–5 all play a significant role, are rather less well understood. These clusters exhibit spin-dependent electron transfer, which can be formulated as double exchange: the interaction between the localized electron spins through the itinerant electrons. 6–13 The majority of studies of double exchange have focused on binuclear \(d^{n+1}d^{n}\) complexes where eigenvalues take the form: 1–3

\[
E_{\pm}(S) = -(1/2)JS(S + 1) \pm \sqrt{\Delta^2/4 + B^2(S + 1/2)^2}
\]

with \(\Delta = E_A - E_B, B = t/(2S^0 + 1)\) for \(n < 5\) and \(t/(2S^0)\) for \(n \geq 5\), and \(S^0 = S_A^0 = S_B^0\) is the core spin. Vibronic coupling presents a further complication: in the limit of weak coupling, the adiabatic potential surfaces feature a single minimum corresponding to a delocalized state, but stronger coupling leads to two minima on the lower of the adiabatic potential surfaces (for any value of \(S\)), both corresponding to localized states. 1–5

Whilst double exchange in binuclear cases is reasonably well understood, 14–18 there remains a paucity of experimental and theoretical work dealing with the phenomenon in polynuclear,
mixed-valent, exchange-coupled \( \{\text{Pd}^{n+1} + (N - P)\text{d}^n \} \) systems (where \( N \) is the number of metal centers and \( P \) is the number of itinerant electrons).\(^2,19\text{-}24\) Expressions for the matrix elements of the transfer Hamiltonian have been derived and, unlike the binuclear analogues, they depend not only on the total spin but also on the intermediate spins resulting from the spin coupling scheme, which in turn are dictated by the cluster topology.\(^25,26\) Vibronic coupling also plays an important role in these cases, localizing the itinerant electrons on specific domains.\(^2,23,24\)

In a series of recent papers, we have discussed the structural, spectroscopic and magnetic properties of a family of octanuclear iron \( \mu \) complexes of the general formula \( \text{[Fe}_8(\mu_{4-R-pz})_{12}X_4] \) \( \{=\text{[Fe}_8]^3 \} \) and their redox-modified, mixed-valent \( \text{[Fe}_8]^{n+} \) derivatives, where \( R = \text{H}, \text{Me}, \text{Cl}, \text{Br}, I, X = \text{Cl}, \text{Br}, \text{NCS}, n = 1\text{-}4.\)\(^2,27\text{-}29\) All of these complexes contain an \( \text{Fe}_8(\mu_{4-})\text{O}_4 \) core featuring an \( \text{Fe}_2\text{O}_4 \) cubane unit and four outer iron centers (\( \text{Fe}_c \) and \( \text{Fe}_o \), respectively, Fig. 1). The \( \text{Fe}_8(\mu_{4-})\text{O}_4 \)-motif is identical to that found in the structures of the minerals maghemite,\(^30\) magnetite\(^31\) and ferrihydrite\(^32\) and has also recently been proposed as the cluster motif produced at the oxireductase site of ferritin, prior to storage as ferrihydrite in the ferritin central cavity.\(^23,24\) SQUID magnetometry and density functional theory indicate that antiferromagnetic coupling between the cubane and outer iron centers dominates in these all-ferric clusters. The corresponding anionic \( \text{[Fe}_8]^{n+} \) complexes with \( n = 1\text{-}4 \) are all accessible electrochemically, and the singly-reduced anions of the \( R = \text{H}, \text{Cl} \) and \( X = \text{Cl} \) species have also been prepared chemically via reduction with a stoichiometric amount of \( [\text{BH}_4]^- \).\(^2,28\) The picture of mixed valency that has emerged depends strongly on the timescale of the chosen experiment.\(^2,28\) X-ray crystallography \( (293 \text{ K}) \) indicates that the structure of the \( \text{Fe}_8 \) cluster is almost totally unaffected by reduction: the bond lengths of neutral and anionic species are identical within experimental error. Analysis of \( \text{^{57}Fe-Mössbauer} \) spectra \( (78 \text{ K}) \) offers a different perspective, suggesting that the reduction is delocalized over all four \( \text{Fe}_c \) sites of the \( \text{Fe}_2\text{O}_4 \)-cubane, although a detailed comparison of observed and DFT-computed \( \text{^{57}Fe-Mössbauer} \) parameters was unable to rule out partial delocalization onto the \( \text{Fe}_o \) sites.\(^2^9\) On the very short timescale of X-ray photoelectron spectroscopy \( (10^{-17} \text{ s}) \), however, the electron appears localized. The profile of the near-infrared intervalence charge transfer (IVCT) band confirms that the \( \text{[Fe}_8(\mu_{4-4-Cl-pz})_{12}\text{Cl}_4]^- \) cluster is an example of a Robin–Day Class II complex.\(^3^4\) In this paper, we report magnetic measurements for the \( \text{[Fe}_8(\mu_{4-4-Cl-pz})_{12}\text{Cl}_4]^- \) cluster performed at both low and high fields. Pulsed high magnetic field measurements have proved to be a powerful tool for the study of multinuclear homovalent complexes, including octanuclear ferric species.\(^3^5\text{-}3^8\) We also use density functional theory (DFT) to develop a spin Hamiltonian including the effects of isotropic exchange \( (J) \), electron transfer \( (t) \) and intrinsic site asymmetry \( (\delta) \). The computation of isotropic exchange using DFT is a well-established discipline, and there is an extensive body of literature on the extent to which values depend on methodology. The computation of transfer parameters is, in contrast, less common and the performance of different functionals is therefore less certain.\(^3^9\) A particularly well-studied example is the Class III delocalized iron \( \mu(\text{m}) \) complex, \( \text{[LFe(\mu-\text{OH})_2FeL]}^{10} \) \( (L = \text{N}_2\text{N}_2\text{N}_2\text{N}_2\text{-trimethyl-1,4,7-triazacyclononane}) \), which has \( J < 0 \), but an \( S = 9/2 \) ground state as a result of the effect of double exchange. The value of \( B = 1366 \text{ cm}^{-1} \) computed by Barone and co-workers using the VWN-Stoll functional is very similar to experiment \( (1350 \text{ cm}^{-1}) \).\(^1^7\) Shoji and co-workers have also shown that the computed value of \( B \) for sulphide-bridged \( \text{Fe(μ-S)}_2\text{Fe} \) clusters was largely unaffected by the amount of exact Hartree–Fock exchange used in the functional.\(^4^0\)

Comparison with the new experimental data shows that the temperature dependence of \( \mu_{\text{eff}} \) can only be reproduced if electron transfer between the cubane and outer iron centers \( (t_2) \) is included in the spin Hamiltonian. The field dependence of \( M_{\text{mol}} \) \( (\text{measured at } 0.4 \text{ K}) \), in contrast, can only be reproduced if \( t_2 \) is close to zero, suggesting that localization of the itinerant electron at low temperatures effectively quenches the cubane–outer electron transfer.

**Materials and methods**

\([\text{Bu}_4\text{N}][\text{Fe}_8(\mu_{4-})\text{O}_4(\mu-4-\text{Cl-pz})_{12}\text{Cl}_4] \) was prepared by reduction of its all-ferric precursor with a stoichiometric amount of \([\text{Bu}_4\text{N}][\text{BH}_4] \), as described previously.\(^2,28\) The identity of the sample of \([\text{Bu}_4\text{N}][\text{Fe}_8(\mu_{4-})\text{O}_4(\mu-4-\text{Cl-pz})_{12}\text{Cl}_4] \) used here was confirmed by satisfactory elemental analysis, infrared and \( \text{^{57}Fe-Mössbauer} \) spectroscopy.

**SQUID magnetometry**

The temperature dependent magnetization was measured with an MPMS XL-7 Quantum Design SQUID magnetometer on the polycrystalline sample in the range of \( T = 2 \) to 300 K at \( B = 0.1 \text{ T} \), and the isothermal magnetization was measured at \( T = 2 \) and \( 4.6 \text{ K up to magnetic field } B = 7 \text{ T} \). Experimental data were corrected for the diamagnetism of the constituent atoms by using the Pascal constants and for the diamagnetism of the sample holder.
Pulsed magnetic field measurements

Pulsed high-field magnetization measurements were performed using a 1.5 mm long susceptometer coil with a 1.5 mm diameter bore made of 50 gauge, high-purity copper wire of approximately 1500 turns. Approximately the first 1000 inner turns are in the opposite direction to the final outer 500 turns such that the coil is compensated, and when a magnetic field is passed through the coil with sample absent, the induced.emf and current in the inner turns is cancelled by that induced in the outer turns. The sample is placed inside the coil in a 1.3 mm diameter ampoule and the induced voltage

\[ \frac{dM}{dt} = \frac{dM}{dt}. \]

Numerical integration with respect to time, \( t \), yields \( M \). In order to ensure accurate values of \( M \), the sample can be moved in and out of the coil, allowing empty coil data to be subtracted from sample data under identical conditions. Samples are placed within a \(^{3}\)He cryostat to allow low-temperature studies down to approximately 0.4 K to be performed. A ten-turn coil accompanies the susceptometer into the cryostat to measure the applied field, \( B \). The voltage induced in this coil is \( \propto \frac{dB}{dt} \) and numerical integration yields \( B \). Calibration of the instruments is accomplished using the de Haas–van Alphen oscillations of the belly orbits of the copper of the susceptometer. The method has been calibrated using all-ferric [Fe\(_{5}\)] compounds (ESI, S5†).

DFT calculations

All calculations described in this paper were done using spin-unrestricted DFT as implemented in the Gaussian 09 program. The B3LYP functional was used throughout, in conjunction with the TZV basis set of Ahlrichs et al. In all cases, the data correspond to single point calculations performed at the crystallographically determined geometry (293 K). In order to extract values of the various parameters in a spin Hamiltonian, we mapped DFT-computed energies of selected microstates onto their spin Hamiltonian counterparts. The set of single determinants in question (Scheme 1) represent a delocalized \( S = 39/2 \) state (HS) and localized and pair-delocalized broken-symmetry states (BS1–4 and BS5–6, respectively). Convergence on a given BS state was achieved using the converged all-ferric BS-state density as an initial guess and, in some cases, the guess = alter keyword.

The all-ferric BS-state density was obtained using the guess = alter keyword. In the HS state, there are no restrictions on the location of the itinerant electron (spin-\( \beta \) by construction). In the BS states, in contrast, the alignment of the spin vectors on the core electrons determines the localization of the itinerant electron (spin-\( \alpha \) by construction). Thus, in BS1 and BS2 (\( M_S = 31/2 \)), the itinerant spin-\( \alpha \) electron must be localized on the single iron center where the core electrons are spin-\( \beta \). For BS3 and BS4 (\( M_S = 21/2 \)), there is no direct spin block to delocalization over the two spin-\( \beta \) iron centers (centers 1 and 5 in Scheme 1), but the spatial separation between the two iron centers effectively prevents delocalization. There are, in principle, four versions of each of BS1, BS2, BS3 and BS4, generated by cyclic permutation around the cubane and outer iron centers (for example, BS1 could also be generated with the iron(II) site at center 2, 3 or 4). The energies of these differ only marginally due to the very slight differences between any two of these microstates, which are characteristics of localized configurations. The transfer parameters are estimated from the pair-delocalized BS states with \( M_S = 21/2 \), BS5 and BS6 (of which there are 6 and 12 almost identical versions, respectively, obtained by cyclic permutation) in Scheme 1, where the itinerant electron is

![Scheme 1](image-url)
trapped either in a single Fe₉–Fe₉ dimer unit or a single Fe₉–Fe₉ dimer unit. Complete trapping is guaranteed in BS5 and BS6 because the itinerant electron (spin-α by construction) must be localized on iron centers where the alignment of the other five electrons is spin-β.

Results and discussion

The results of the magnetometry experiments are shown in Fig. 2 and 3: the temperature dependence of the effective magnetic moment, μ_magnet, at a field of 0.1 T in Fig. 2 and the field dependence of the molar magnetization, M_mol, in Fig. 3 (an expanded view of the low-field region is shown on the right). In Fig. 3, circles show the data measured by SQUID magnetometry (2 K, 0 < B < 65 T) while triangles show the pulsed high-field data (0.4 K, 0 < B < 65 T). In Fig. 2, the sharp decrease in μ_magnet on cooling offers strong evidence for dominant antiferromagnetic exchange. Moreover, the low-temperature limit of μ_magnet = 2.34 μ_B is consistent with an S = 1/2 ground state as is the saturation value of 1.12 N₄μ_B for M_mol in the region 5–60 T in Fig. 3 (minor deviations from the spin-only values of 1.73 μ_B and 1.0 N₄μ_B being due to a very small amount of paramagnetic impurity). The pulsed high-field experiment, however, reveals a step in M_mol at ~63 T (the crossover field B_c, shown in Fig. 3) where the Zeeman splitting causes the M_S = −3/2 component of the first excited quartet state to cross the M_S = −1/2 component of S = 1/2. Assuming a value of 2.0 for g, the corresponding energy gap between the S = 1/2 and S = 3/2 states at zero field can be estimated as ΔE(1/2–3/2) = gμ_BB_c ~ 85 K (59 cm⁻¹).

The magnetic data can be interpreted in terms of an exchange + transfer Hamiltonian, H(8), summarized in eqn (2) and (3).

\[
H(8) = H_{ex} + H_{tr}
\]

Taking pairwise differences between the energies of these microstates gives rise to a system of linear equations, which can be solved for four unknowns, J₁, J₂, J₃, and Δ. Note that the four equations above in fact contain five unknowns, but J₄ appears with the same coefficient (+60/4) in all four expressions and can therefore be eliminated, allowing J₁, J₂, J₃, and Δ to be determined uniquely.

The pair-delocalized BS states with M_S = ±21/2 in BS5 and BS6 in Scheme 1, define ‘effective dimer’ models where the itinerant electron is trapped in a single Fe₉–Fe₉ dimer unit (BS5) or in a single Fe₉–Fe₉ dimer unit (BS6). In each case, there are two separate states where the itinerant electron occupies the in-phase (E_BΣ₉) and out-of-phase (E_BΣ₈) combinations of the d orbitals involved in the transfer pathway. The energies of these BS states can be associated with the eigenvalues of the [2 × 2] spin Hamiltonian matrices computed in two products of single-center spin functions (one where the itinerant electron is localized on the first
center of the pair, and the other on the second center of the pair). For the BS5 states, the matrix and its eigenvalues take the form:

\[
\text{BS5:} \begin{pmatrix} \frac{25}{4}J_1 + \frac{20}{4}J_2 - \frac{75}{4}J_3 + \frac{60}{4}J_4 & t_1 \\ \frac{25}{4}J_1 + \frac{20}{4}J_2 - \frac{75}{4}J_3 + \frac{60}{4}J_4 & \frac{25}{4}J_1 + \frac{20}{4}J_2 - \frac{75}{4}J_3 + \frac{60}{4}J_4 \end{pmatrix}
\]

\[
E_{\text{BS5}} = \frac{25}{4}J_1 + \frac{20}{4}J_2 - \frac{75}{4}J_3 + \frac{60}{4}J_4 \pm t_1
\]

\[
t_1 = \frac{E_{\text{BS5}+} - E_{\text{BS5}-}}{2}
\]

The expression for \(t_1\) is identical to the analytical form shown in eqn (1) for symmetric clusters \(t = \frac{E_+ - E_-}{2}\) where \(E_+\) and \(E_-\) are the eigenvalues corresponding to symmetric and antisymmetric combinations of basis functions. The energy difference \(E_+ - E_-\) can be approximated as the difference between the Kohn–Sham eigenvalues for the in-phase and out-of-phase combinations of the relevant d orbitals in the isovalent ferromagnetically coupled state (the all-ferric BS5 state in this case).\(^{40}\)

The corresponding matrix for \(t_2\) (using the BS6 states) is:

\[
\text{BS6:} \begin{pmatrix} \frac{75}{4}J_1 + \frac{60}{4}J_2 - \frac{125}{4}J_3 + \frac{20}{4}J_4 & t_2 \\ -\frac{125}{4}J_3 + \frac{20}{4}J_4 + \Delta & -\frac{125}{4}J_3 + \frac{20}{4}J_4 + \Delta \end{pmatrix}
\]

The eigenvalues of which are rather more complicated because the diagonal elements differ \(i.e.,\) the analytical form for symmetric cases in eqn (1) is no longer appropriate. \(E_+ - E_-\) in this case can be obtained from the separation of the Kohn–Sham eigenvalues in the neutral (all-ferric) BS6 state.

The full set of spin Hamiltonian parameters that emerges from this analysis is (further details are given in ESI, S2†):

\[
J_1 = -5.9 \text{ cm}^{-1}, \quad J_2 = -10.1 \text{ cm}^{-1}, \quad J_3 = -55.1 \text{ cm}^{-1},
\]

\[
\Delta = 0.7 \text{ cm}^{-1}, \quad t_1 = -1438 \text{ cm}^{-1}, \quad t_2 = 1784 \text{ cm}^{-1}
\]

The \(J_1\) and \(J_3\) values, corresponding to the \(\text{Fe}^{\text{III}}_{\text{c}}–\text{Fe}^{\text{III}}_{\text{c}}\) and \(\text{Fe}^{\text{III}}_{\text{c}}–\text{Fe}^{\text{II}}_{\text{o}}\) interactions, are very similar to those reported previously for the all-ferric analogue, both from DFT \((-6.3 \text{ cm}^{-1}, -52.8 \text{ cm}^{-1})\) and from best fit to the SQUID magnetometry data \((-2.1 \text{ cm}^{-1}, -50.6 \text{ cm}^{-1})\).\(^{27}\)

Clemente-Juan \textit{et al.} have noted that the exchange part of the \(H(8)\) Hamiltonian (eqn (2)) can be made independent of the position of the itinerant electron by assuming the isotropic exchange to be independent of the oxidation state \(i.e., J_4 = J_5 \text{ and } J_3 = J_6\).\(^{26}\) The values of \(J_4\) and \(J_5\) that emerge from our DFT analysis are indeed quite similar, fully justifying the first of these assumptions. As emphasized above, \(J_4\) is unavailable from our DFT analysis, so we are unable to assess the validity of the second approximation, which we nevertheless adopt in the subsequent modelling of the magnetic data. The imposed
symmetry of the isotropic exchange parameters does nothing, however, to alleviate the intrinsic problem that the dimension of the largest submatrix of $H(8)$ is such that exact diagonalization is intractable. This problem can be avoided if electron transfer between the cubane and outer iron centers is neglected ($t_2 = 0$ in eqn (3)), effectively localizing the itinerant electron on the cubane core and reducing the number of localized configurations to four (of the $\text{Fe}_4(\text{Fe awarded}, \text{Fe}^\text{III})_3(\text{Fe}^\text{II})_4$ type). Our computed value of $t_2 = 1784$ cm$^{-1}$, however, suggests that such an approximation will miss much of the important mixed valency physics. Alternatively, diagonalization of a model Hamiltonian, $H(6)$, based on a smaller hexanuclear cluster with an $\text{Fe}_6(\mu_3-\text{O})_3$ core and three pendant iron centers (ESI, S3, Scheme S1, eqn (S1) and (S2)†), is tractable even when $t_2 \neq 0$.$^{26}$ This model shares the same $n + n$ core/out topology as the parent $\text{Fe}_8$ cluster and, in the limiting case that $t_2 = 0$, the $H(8)$ and $H(6)$ Hamiltonians generate very similar eigenvalue patterns.$^{26}$ A comparison of the magnetic functions ($\mu_{\text{eff}}$ and $M_{\text{mol}}$) reconstructed using both $H(8)$ and $H(6)$ confirms that they are indeed almost identical in the limiting case of $t_2 = 0$ (ESI, S3, Fig. S3†). However, $H(6)$ (and therefore, by extension, $H(8)$) provides a very poor fit to the temperature dependence of $\mu_{\text{eff}}$ over the range $2 < T < 300$ K when $t_2$ is set to 0 (black line in Fig. 2). Moreover, we were unable to identify any physically reasonable combination of $J_{1-4}$ and $t_1$ that could reproduce the sharp rise in $\mu_{\text{eff}}$ between 0 and 100 K, suggesting that the separation between the ground doublet state and excited states with higher multiplicity is being systematically overestimated. When $t_2$ is increased (now by necessity using only $H(6)$), states with $S > 1/2$ are indeed stabilized, and values in the region of $1750$ cm$^{-1}$ provide a reasonable match to $\mu_{\text{eff}}$ over the entire temperature range ($2 < T < 300$ K). The data are therefore entirely consistent with our computed value of $t_2 = 1784$ cm$^{-1}$ (orange curve in Fig. 2). The influence of the dominant cubane–outer exchange interactions and the intrinsic site asymmetry on $\mu_{\text{eff}}$ is explored in Fig. S4 and S5 (ESI, S4†).

The $M_{\text{mol}}(B)$ curves measured using either SQUID or pulsed high-field magnetometry (Fig. 3) offer a rather different perspective: the agreement between experiment and the curve generated using $t_2 = 1784$ cm$^{-1}$ is strikingly poor. In the low-field region sampled by both the pulsed high-field measurements and SQUID magnetometry (up to 7 T, see the expanded plot), $M_{\text{mol}}$ is rather insensitive to the value of $t_2$ in the range 0–1500 cm$^{-1}$ because only the ground doublet state is appreciably populated under these conditions (the curves for values of $1250$ cm$^{-1}$ and smaller lie directly below the red curve at 1500 cm$^{-1}$). Based on the low-field data alone, therefore, we can do no more than place an upper limit of $\sim 1500$ cm$^{-1}$ on $t_2$ at 2 K. The high-field data, however, pinpoint the crossover field $B_{cs}$ to the point where the $S = 3/2$ state becomes the ground state, at $\sim 63$ T, a value that is consistent only with $t_2$ values approaching zero (where $B_{cs}$ is $60.6$ T). Values of $1500$ cm$^{-1}$, $1000$ cm$^{-1}$ and even $500$ cm$^{-1}$ for $t_2$, in contrast, generate much smaller crossover fields that are clearly inconsistent with the data. Indeed, no physically reasonable alternative combination of parameters with $t_2$ substantially greater than zero can reproduce the experimental data (ESI, S4, Fig. S6, S7†).

The fact that $t_2$ appears to be quenched at very low temperatures is indicative of significant vibronic coupling, which generates a number of distinct minima on the adiabatic potential surfaces that serve to localize the itinerant electron on the cubane core. Note that the localizing influence of vibronic coupling is particularly strong when $S$ is small. This assertion is consistent with the energy of the IVCT transition, which leads to an upper estimate of $\sim 6000$ cm$^{-1}$ for the reorganization energy, $\lambda$.$^{28}$ Based on the magnetic data alone, we are unable to distinguish between the alternative possibilities that it is localized on a single center ($t_1 = t_2 = 0$) or pairwise delocalized ($t_1 = -1438$ cm$^{-1}$, $t_2 = 0$): the predicted values of $B_{cs}$ are almost identical, 61.4 T and 61.1 T, respectively. The X-ray photoelectron spectroscopy data reported in ref. 28 are, however, more consistent with localization on a single center. The sharp increase in $\mu_{\text{eff}}$ in the low-temperature region suggests, however, that the barriers to delocalization are low.

**Conclusions**

In this paper, we have presented new magnetic data measured using both conventional SQUID and pulsed high-field magnetometry that reveal the nature of mixed valency in the $\text{Fe}_4\text{Fe}^\text{III}_8$ cluster, $[\text{Fe}_4(\mu_3-\text{O})_4(\mu-4-\text{Cl-pz})_2\text{Cl}_4]^{-}$. The isotropic exchange proves to be very similar to that in the parent all-ferric $\text{Fe}_8^\text{III}$ cluster, with a dominant antiferromagnetic coupling between the cubane and outer iron centers mediated by a $\mu_3$-oxo ligand. However, electron transfer, both within the cubane core ($t_1$) and between the cubane and outer iron centers ($t_3$), is an important component of the spin Hamiltonian. In particular, the $\mu_{\text{eff}}(T)$ curve cannot be fitted adequately over the entire temperature range ($2 < T < 300$ K) if the value of $t_2$ is smaller than $1750$ cm$^{-1}$. The picture that emerges from the molar magnetization data measured up to very high field at 0.4 K is, in contrast, rather different: the plateau in the region $5 < B < 60$ T is indicative of a large zero-field separation between ground doublet and first excited quartet states that is inconsistent with any value of $t_2$ substantially greater than zero. The striking discrepancy between values of $t_2$ that afford reasonable agreement with the low- and high-temperature data indicates that the measurements are sampling fundamentally different electronic distributions. The quenching of $t_2$ at low temperatures is consistent with the presence of significant vibronic coupling that localizes the itinerant electron on the cubane core.

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J.E.M. and R.G.R. conceived the project, designed the experiments and wrote the paper; E.M.Z. and W.M.C.S. carried out the computational work; E.M.Z. also contributed to the measurements and wrote the paper; E.M.Z. and W.M.C.S. carried out the computational work and wrote the paper.

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