

Metal-metal Bonded Fe₄ Clusters with Slow Magnetic Relaxation

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Abstract

Reaction of FeBr_2 with $\text{Li}(\text{N}=\text{C}^t\text{Bu}_2)$ (0.5 equiv) and Zn^0 (2 equiv) results in the formation of the formally mixed-valent cluster $[\text{Fe}_4\text{Br}_2(\text{N}=\text{C}^t\text{Bu}_2)_4]$ (**1**) in moderate yield. Subsequent reaction of **1** with $\text{Na}(\text{N}=\text{C}^t\text{Bu}_2)$ results in formation of $[\text{Fe}_4\text{Br}(\text{N}=\text{C}^t\text{Bu}_2)_5]$ (**2**), also in moderate yield. Both **1** and **2** were characterized by zero-field ^{57}Fe Mössbauer spectroscopy, X-ray crystallography, and SQUID magnetometry. Their tetrahedral $[\text{Fe}_4]^{6+}$ cores feature short Fe-Fe interactions (ca. 2.50 Å). Additionally, both **1** and **2** display $S = 7$ ground states at room temperature and slow magnetic relaxation with zero-field relaxation barriers of $U_{\text{eff}} = 14.7(4)$ and $15.6(7) \text{ cm}^{-1}$, respectively. Moreover, AC magnetic susceptibility measurements were well modelled by assuming an Orbach relaxation process.

Introduction

Transition metal clusters featuring direct metal-metal orbital overlap are emerging as a new class of single molecule magnets (SMMs).^{1,2} The metal-metal bonding present in these clusters can result in ferromagnetic (direct) exchange interactions and energetically isolated magnetic ground states,^{3–11} often leading to complexes with high relaxation barriers and long lived magnetization.^{1,12–19} For example, $[\text{Bu}_4\text{N}][(\text{H}^{\text{L}})_2\text{Fe}_6(\text{py})_2]$ ($\text{H}^{\text{L}}\text{H}_6 = \text{MeC}(\text{CH}_2\text{NHPH-}o\text{-NH}_2)_3$) features an $S = 19/2$ ground state and a relaxation barrier of $U_{\text{eff}} = 42.5(8) \text{ cm}^{-1}$.³ This cluster exhibits an octahedral arrangement of six Fe atoms, with relatively short Fe-Fe bonds (ca. 2.61 Å), and its magnetic properties are thought to be a consequence of its well-isolated, giant-spin ground state, which suppresses magnetization tunneling. Similarly, $[\text{Co}_4(\text{N}=\text{P}^t\text{Bu}_3)_4]^+$ exhibits a giant-spin $S = 9/2$ ground state with $U_{\text{eff}} = 87 \text{ cm}^{-1}$.¹² Like $[\text{Bu}_4\text{N}][(\text{H}^{\text{L}})_2\text{Fe}_6(\text{py})_2]$, this cluster features a compact metal core with short Co-Co bonds (2.36 Å), which leads to slow magnetic relaxation. The Fe(II) chain clusters $[\text{Fe}_4(\text{tpda})_3\text{X}_2]$ ($\text{H}_2\text{tpda} = N,N\text{-bis}(\text{pyridin-2-yl})\text{pyridine-2,6-diamine}$; $\text{X} = \text{Cl}, \text{Br}$) and $[\text{Fe}_3(\text{DpyF})_4][\text{BF}_4]_2$ ($\text{DpyF} = \text{dipyridylformamide}$) also exhibit ferromagnetic exchange and slow magnetic relaxation,^{19–21} although in these examples the Fe-Fe distances are relatively long ($>2.8 \text{ Å}$). Several other Fe-Fe bonded complexes also feature high spin ground states as a consequence of direct exchange interactions, including $[\text{Na}_6\text{Fe}_3(\text{tris-cyclo-salophen})(\text{py})_9]$,⁴ $[\text{Fe}(\text{PrNPPH}_2)_3\text{Fe}(\text{PMe}_3)]$,⁵ $[\text{Fe}_2(\text{DPhF})_3]$, and $[\text{Fe}_2(\text{DPhF})_4]$ ($\text{DPhF} = \text{diphenylforamidinate}$).^{22–25} While the magnetic relaxation in these examples was not explicitly measured, the observation that direct M-M bonding can lead to ferromagnetic exchange further highlights the value of this design feature.

Recently, we reported the synthesis and characterization of the ketimide-supported Fe_4 cluster, $[\text{Fe}_4(\text{N}=\text{CPh}_2)_6]$.¹³ This complex features relatively short Fe-Fe bonds within its tetrahedral

Fe₄ core and an $S = 7$ ground state that persists at room temperature. Additionally, it exhibits good SMM properties, including a relaxation barrier of $U_{\text{eff}} = 29 \text{ cm}^{-1}$ and relatively long relaxation times (up to $t = 34 \text{ s}$ at $T = 1.8 \text{ K}$). More remarkably, we observe no evidence for through-barrier relaxation in its AC relaxation measurements. We hypothesized that its good SMM performance was due to direct exchange-mediated ferromagnetic coupling amongst the four Fe centers, which was promoted by the ketimide group. In fact, the ketimide ligand is known for its ability to promote both metal-metal bonding and magnetic communication, as shown by the isolation of the [Cu(N=C^tBu₂)]₄, which is stabilized by cuprophilic interactions,²⁶ and [Pd₇(N=C^tBu₂)₆],²⁷ which features an unusual hexagonal planar Pd₇ core. Also notable are the bimetallic ketimide complexes, [Li(12-crown-4)₂][M₂(N=C^tBu₂)₅] (M = Mn, Fe, Co),²⁸ [Fe₂(N=C^tBu₂)₅],²⁸ and [Li][Cr₂(N=C₁₀H₁₄)₇],²⁹ which feature varying degrees of magnetic communication as assayed by SQUID magnetometry.

In an effort to test the effect of the ketimide substituents on the magnetic properties of [Fe₄(N=CPh₂)₆], we endeavored to synthesize an Fe₄ cluster supported by the bis(*tert*-butyl) ketimide ligand, which has much different electronic and steric properties than the di(phenyl) ketimide ligand employed previously. Herein, we report the synthesis and magnetic characterization of [Fe₄Br₂(N=C^tBu₂)₄] and [Fe₄Br(N=C^tBu₂)₅]. Despite having fairly short relaxation times, these complexes show no evidence of relaxation by quantum tunneling, cementing the role that direct-exchange interactions can play in generating SMMs.

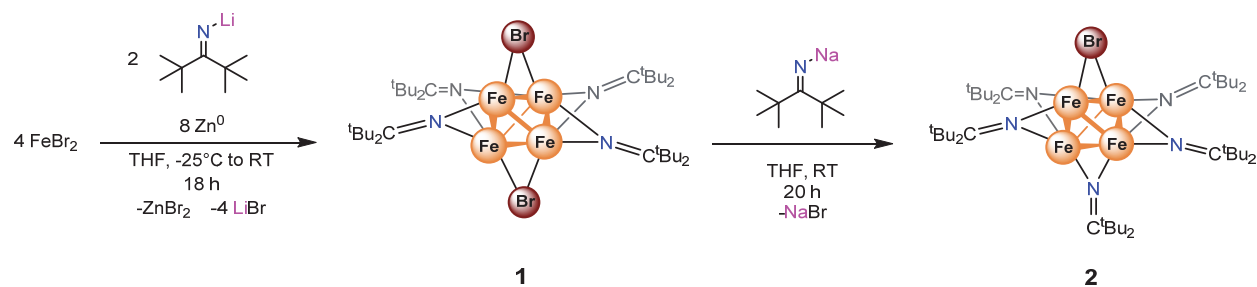
Results and Discussion

In an effort to synthesize [Fe₄(N=C^tBu₂)₆], we applied the same synthetic protocol used to generate [Fe₄(N=CPh₂)₆].¹³ Thus, reaction of FeBr₂ with 1.5 equiv of Li(N=C^tBu₂) and 2 equiv of Zn powder in THF at room temperature for 18 h results in the self-assembly of [Fe₄Br₂(N=C^tBu₂)₄]

(**1**), which could be isolated as deep purple blocks in low yield. Complex **1** is also formed using the rational stoichiometry of 1 equiv of FeBr₂ and 1 equiv of Li(N=C^tBu₂); however, the highest yields were achieved upon reaction of FeBr₂ with 0.5 equiv of Li(N=C^tBu₂) and 2 equiv of Zn powder in THF at room temperature for 18 h, which provided **1** in 45% yield (based on Li(N=C^tBu₂)) after work-up (Scheme 1). Curiously, complex **1** is still formed, albeit in low yields, when excess Li(N=C^tBu₂) (up to 2 equiv per FeBr₂) is employed in the reaction, suggesting that its two bromide ligands are relatively resistant to salt metathesis. Treatment of other ferrous salts (e.g., FeCl₂, FeI₂, Fe(OAc)₂) with Li(N=C^tBu₂) (1.5 equiv) and Zn⁰ (2 equiv) also failed to generate the desired [Fe₄(N=C^tBu₂)₆].

As a solid, **1** is stable under an inert atmosphere at -25 °C for several months. However, it rapidly decomposes on exposure to air, in both the solid state and solution. Complex **1** is slightly soluble in pentane, and very soluble in Et₂O, THF, benzene, and CH₂Cl₂. It is insoluble in acetonitrile and decomposes on dissolution in pyridine. Its ¹H NMR spectrum in C₆D₆ features a broad resonance at 120.8 ppm assignable to the single ^tBu environment (Figure S2), consistent with the idealized *D*_{2d} symmetry observed in the solid state (see below).

Scheme 1. Synthesis of Complexes **1** and **2**



Complex **1** crystallizes in the monoclinic space group *P*2₁/*c* (Figure 1). Its solid-state molecular structure reveals a tetrahedral [Fe₄]⁶⁺ core, wherein four edges are bridged by μ-N=C^tBu₂ ligands and two are bridged μ-bromide ligands. The two bromide ligands feature *trans* stereochemistry,

generating a complex with idealized D_{2d} symmetry. The average Fe–Fe distance is 2.50 Å (range = 2.4193(9) – 2.5510(9) Å; Table 1), which corresponds to a formal shortness ratio of $r = 1.07$, suggesting the presence of weak single bonds between the Fe centers.^{30,31} The Fe-Fe bonds in **1** are slightly shorter than the Fe–Fe bonds reported for [Fe₄(N=CPh₂)₆] (average = 2.56 Å; $r = 1.10$; range = 2.504(4) – 2.621(4) Å),¹³ suggesting that the bis(*tert*-butyl)ketimide ligands does promote stronger metal-metal bonding than the di(phenyl)ketimide; however, these shorter bonds do not result in better SMM performance (see below). For further comparison, its Fe-Fe distances are similar to the Fe-Fe distances in [Fe₂(N=C^tBu₂)₅][–] (2.443(1) Å; $r = 1.05$) and [Fe₄(μ-C₆H₄-4-Me)₆(THF)₄] (average = 2.47 Å; $r = 1.06$).^{22,28,32} Finally, the average Fe–Br distance in **1** is 2.51 Å (range = 2.4937(8) – 2.5331(8) Å) and the average Fe-N distance is 1.98 Å. The latter parameter compares well to the average Fe-N distance in [Fe₄(N=CPh₂)₆] (1.95 Å).¹³

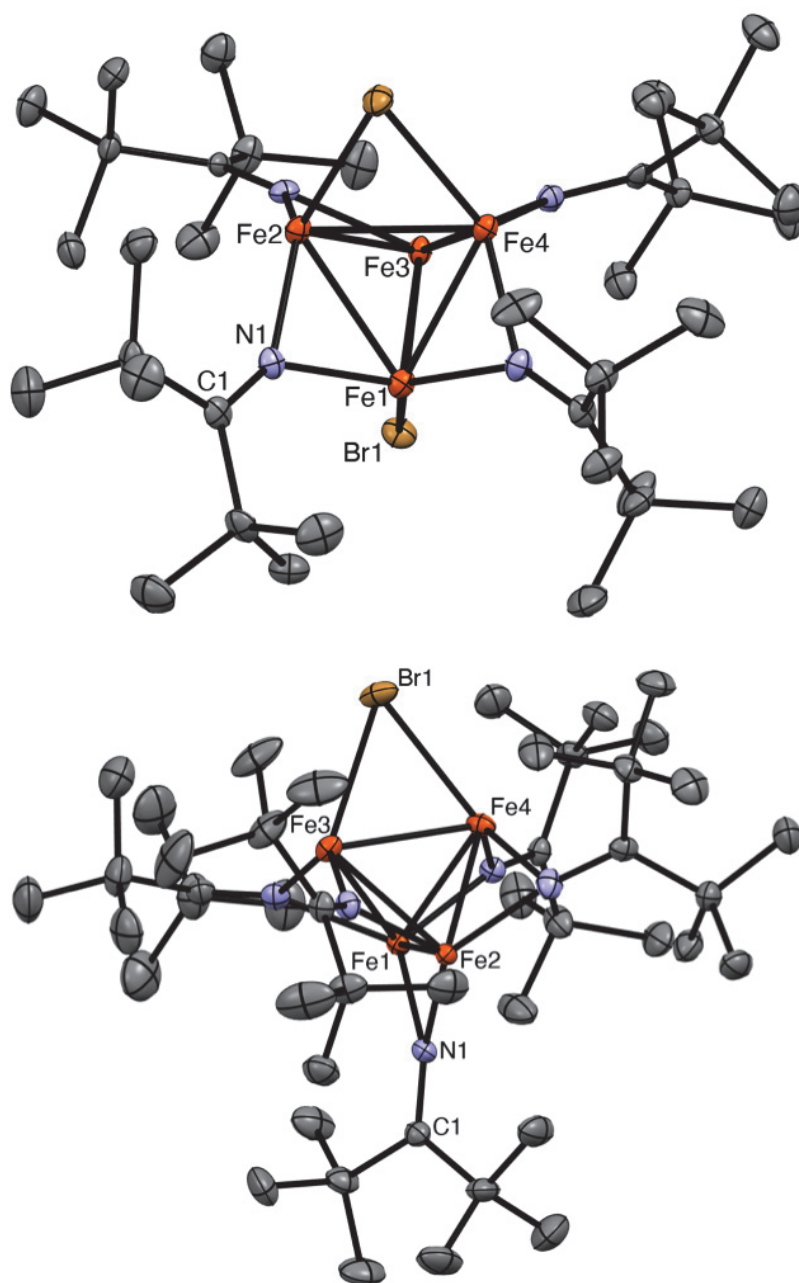


Figure 1. Solid-state molecular structures of **1** (top) and **2** (bottom), shown with 50% probability ellipsoids. Hydrogen atoms and alternate position of the Fe₄ core in **2** are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

Complex	1	2
Fe–Fe	2.4856(9)	2.5238(6)
	2.5293(9)	2.5648(6)
	2.4193(9)	2.4376(6)

	2.5510(9) 2.5296(9) 2.4736(8)	2.4651(6) 2.4525(6) 2.4658(7)
Fe–N	1.962(3) 1.982(3) 1.998(3) 1.999(3) 1.982(3) 1.990(3) 1.964(3) 1.969(3)	1.996(2) 2.012(2) 1.990(2) 2.004(2) 2.025(2) 1.897(2) 1.975(2) 1.953(2) 1.979(2) 2.015(2)
Fe–Br	2.5331(8) 2.4974(7) 2.4937(8) 2.5085(7)	2.5213(5) 2.5271(5)
C=N	1.278(5) 1.260(5) 1.268(5) 1.264(5)	1.265(3) 1.268(3) 1.271(3) 1.273(3) 1.270(3)
Fe–N–Fe	78.07(13) 75.14(12) 77.27(13) 79.92(12)	78.06(7) 76.57(8) 80.27(8) 77.58(8) 75.77(7)
Fe–Br–Fe	60.75(2) 60.36(2)	58.474(16)

In an effort to replace the two bromide ligands in **1** with ketimide moieties, we studied the reactivity of **1** with other ketimide sources. Thus, reaction of **1** with 2 equiv of Na(N=C^tBu₂) in THF for 20 h at room temperature results in formation of [Fe₄Br(N=C^tBu₂)₅] (**2**), which could be isolated in low yield after work-up. Complex **2** could be isolated in better yields upon reaction of **1** with only 1 equiv of Na(N=C^tBu₂) in THF (Scheme 1). Under these conditions, **2** can be isolated in 49% yield as deep red-black needles. Surprisingly, even with heating and longer reaction times, metathesis of the final bromide ligand could not be achieved. Additionally, reaction of **1** with 2

equiv of $\text{Li}(\text{N}=\text{C}^t\text{Bu}_2)$ only resulted in formation of the previously reported monometallic Fe(II) complex, $[\text{Li}(\text{THF})]_2[\text{Fe}(\text{N}=\text{C}^t\text{Bu}_2)_4]$,³³ as assayed by ^1H NMR spectroscopy (Figure S3).

The ^1H NMR spectrum of **2** in C_6D_6 features broad resonances at 98 ppm and 79 ppm, which are assignable to the methyl groups of the equatorial and axial ketimide ligands, respectively (Figure S4). The ESI-MS of **2**, recorded in THF in the positive ion mode, features a major peak at 1003.3074 m/z , corresponding to $[\text{Fe}_4\text{Br}(\text{N}=\text{C}^t\text{Bu}_2)_5]^+$ (calcd 1003.3762 m/z) (Figures S11-S12), further confirming its formulation.

Complex **2** crystallizes in the monoclinic space group $P2_1/c$ (Figure 1). Its solid-state molecular structure reveals a tetrahedral Fe_4 core ligated by one μ -bromide ligand and by five μ -ketimide ligands, generating a complex with idealized C_{2v} symmetry. The $[\text{Fe}_4]^{6+}$ core is disordered over two sites, which were modelled in 90:10 ratio; however, there is no apparent disorder of either the bromide or ketimide ligands. The average Fe–Fe distance is 2.48 Å (range = 2.4376(6) – 2.5648(6) Å) (Table 1), which corresponds to a formal shortness ratio of $r = 1.06$.^{30,31} This value is comparable to that found in **1**, and is indicative of the presence of weak Fe-Fe bonding. The Fe-Br and Fe-N distances in **2** are also comparable to those found in complex **1**.

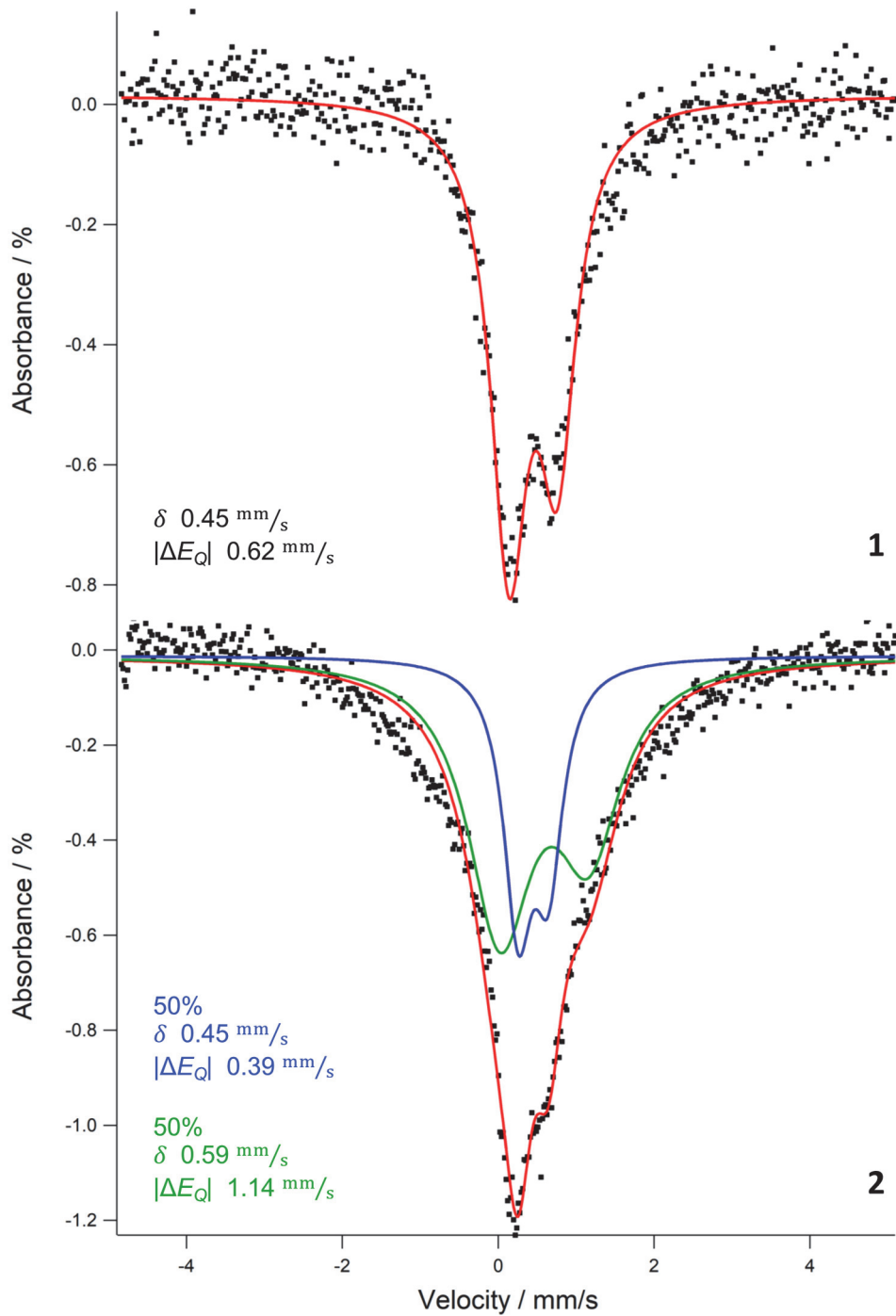


Figure 2. Zero-field ^{57}Fe Mössbauer spectra of **1** (top) and **2** (bottom) collected at $T = 90$ K. The red traces correspond to the overall fit, while the blue and green traces correspond to the two doublets employed to fit **2**.

The ^{57}Fe Mössbauer spectrum of **1** taken at $T = 90$ K reveals a single asymmetric doublet indicative of a single iron environment (Figure 2), consistent with the idealized D_{2d} symmetry of the complex, which should result in a single Fe environment. The doublet has an isomer shift of $\delta = 0.45$ mm/s and a quadrupole splitting of $|\Delta E_Q| = 0.62$ mm/s. For **2**, the zero-field ^{57}Fe Mössbauer spectrum at $T = 90$ K displays a broad signal consistent with two overlapping asymmetric doublets. One doublet has an isomer shift of $\delta = 0.45$ mm/s and a quadrupole splitting of $|\Delta E_Q| = 0.39$ mm/s, whereas the second doublet has an isomer shift of $\delta = 0.59$ mm/s and a quadrupole splitting of $|\Delta E_Q| = 1.14$ mm/s. The spectrum is consistent with the idealized C_{2v} symmetry of the complex, which should result in two different Fe environments in a 1:1 ratio. These spectra are similar to those reported for other Fe(I)/Fe(II) mixed-valent clusters. For example, the mixed-valent Fe(I)/Fe(II) species $[\text{MgCl}(\text{THF})_5][\text{Fe}_8\text{Me}_{12}]$ exhibits a broad doublet with an isomer shift of $\delta = 0.30$ mm/s and a quadrupole splitting of $\Delta E_Q = 0.85$ mm/s,³⁴ $[\text{Fe}_4(\mu\text{-Ph})_6(\text{THF})_4]$ features parameters of $\delta = 0.6$ and $|\Delta E_Q| = 0.84$ mm/s, and $[\text{Fe}_4(\text{N}=\text{CPh}_2)_6]$ features parameters of $\delta = 0.34$ mm/s and $|\Delta E_Q| = 0.79$ mm/s.^{13,32} The UV-vis-NIR spectrum of **1** in THF at 298 K (Figure S7) exhibits a broad absorption band at 827 nm ($\epsilon = 1200 \text{ L mol}^{-1} \text{ cm}^{-1}$), which we tentatively assign to an intervalence charge transfer (IVCT). Similarly, the UV-vis-NIR spectrum of **2** in THF at 298 K (Figure S8) exhibits a broad band at 923 nm ($\epsilon = 1100 \text{ L mol}^{-1} \text{ cm}^{-1}$). The appearance of IVCT bands for both complexes is evidence for electron delocalized Class II- or Class III-type behavior,^{7,35–37} and is consistent with our Mössbauer results.

Temperature-dependent dc magnetization data were collected for a crystalline sample of **1** at $H = 5000$ Oe, revealing a μ_{eff} value of $16.18 \mu_B$ at $T = 300$ K ($\chi_M T = 32.73 \text{ cm}^3\text{K/mol}$), which corresponds to an $S = 7$ ground state (Figure 3a). Similarly, the magnetic susceptibility of **2**, under the same applied field, was found to be $\mu_{\text{eff}} = 16.15 \mu_B$ at $T = 300$ K ($\chi_M T = 32.61 \text{ cm}^3\text{K/mol}$). The

related $[\text{Fe}_4]^{6+}$ cluster, $[\text{Fe}_4(\text{N}=\text{CPh}_2)_6]$ features a comparable moment ($\mu_{\text{eff}} = 14.64 \mu_{\text{B}}$ at $T = 300 \text{ K}$),¹³ suggesting the same $S = 7$ ground state for all three complexes. Importantly, these room temperature moments imply strong spin delocalization across the $[\text{Fe}_4]^{6+}$ core. For comparison, a cluster with discrete Fe(I) and Fe(II) centers would exhibit a μ_{eff} value of $8.83 \mu_{\text{B}}$.¹³ We hypothesize that the ferromagnetic coupling observed in **1** and **2** is due to direct exchange; however, double exchange has also been used to explain ferromagnetic coupling in formally mixed-valent bimetallic iron complexes,^{38,39} and it could be operative here, as well.

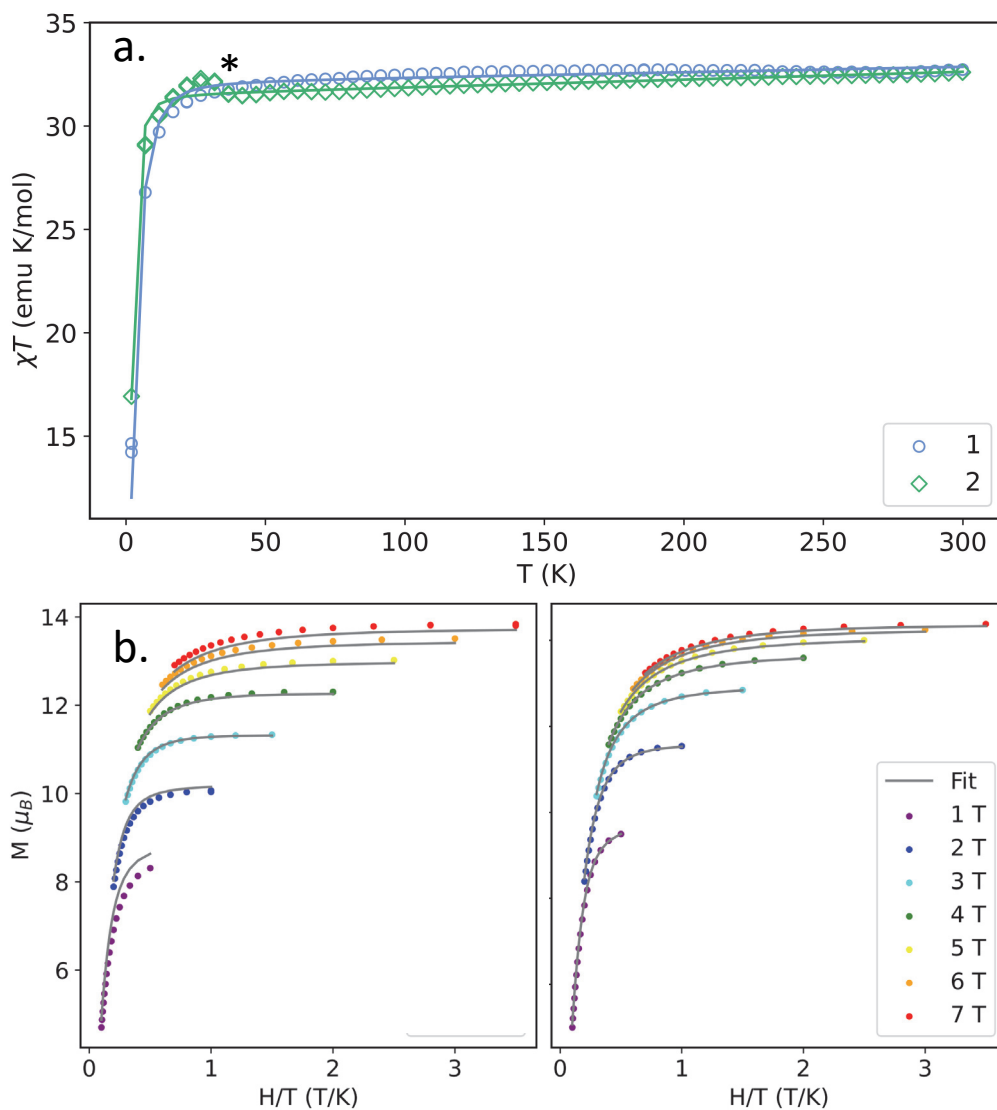


Figure 3. a. Magnetic susceptibility multiplied by temperature ($\chi_M T$) for **1** (blue circles) and **2** (green diamonds) collected under an applied magnetic field of $H = 5$ kOe from $T = 2$ K to $T = 300$ K. The solid lines represent fits to the spin Hamiltonian $\hat{H} = D\hat{S}_z^2 + g_{iso}\mu_B SH$, where $S = 7$, $D = -0.85$ cm⁻¹, $\chi_{TIP} = 0.0026$ cm³ mol⁻¹, and $g = 2.14$ for **1**, and $S = 7$, $D = -0.14$ cm⁻¹, $\chi_{TIP} = 0.0038$ cm³ mol⁻¹, and $g = 2.12$ for **2**. The asterisk indicates the antiferromagnetic transition of O₂. b. Variable-temperature, variable-field reduced magnetization data for **1** (left) and **2** (right). Data was collected at temperatures ranging from $T = 2$ to $T = 10$ K. Gray lines represent fits to the data, as described in the main text.

Variable-temperature, variable-field (VTVF) reduced magnetization data for **1** and **2** both feature non-superimposable isocurves (Figure 3b), indicative of slow magnetic relaxation, as was observed for [Fe₄(N=CPh₂)₆].¹³ The VTVF data were fit with the PHI software package according to the spin Hamiltonian $\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g_{iso}\mu_B SH$, to give $D = -0.41$ cm⁻¹, $|E/D| = 0.002$, and $g = 2.07$ for **1**, and $D = -0.27$ cm⁻¹, $|E/D| = 0.02$, and $g = 2.09$ for **2** (Figure 3b).⁴⁰ These parameters are comparable to those observed for [Fe₄(N=CPh₂)₆], which exhibited values of $D = -0.75$ cm⁻¹, $|E/D| = 0.17$, and $g = 1.92$.¹³

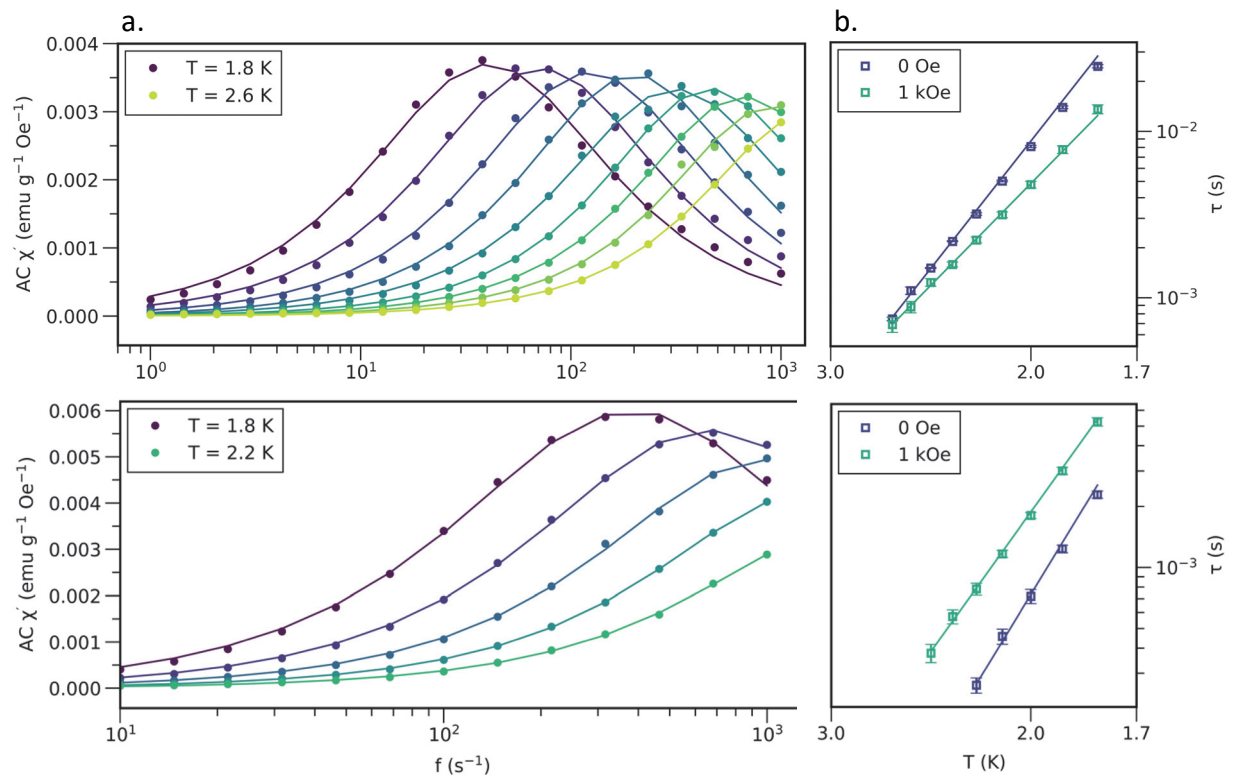


Figure 4. (a) Imaginary part of the AC susceptibility of **1** (top) and **2** (bottom) at zero field as a function of excitation frequency and temperature. The temperature was increased by 0.1 K increments between isotherms. The lines shown are fits to the generalized Debye model. (b) Arrhenius plot of the relaxation times of **1** (top) and **2** (bottom) in zero field (navy) and under $H = 1$ kOe applied field (teal). The fits shown are to eq 1.

Magnetic hysteresis measurements show waist-restricted $M(H)$ hysteresis loops at $T = 2$ K for both **1** and **2** (Figures S16 and S22), suggesting rapid relaxation of the magnetization when H approaches 0 Oe. To probe the mechanism(s) of magnetic relaxation, the relaxation dynamics of **1** and **2** were measured with ac magnetic susceptibility measurements. Data were recorded at $H = 0$ and $H = 1000$ Oe applied fields at temperatures between $T = 1.8$ K and $T = 2.6$ K and frequencies

between $f_{ac} = 1$ Hz and $f_{ac} = 1000$ Hz. For both **1** and **2**, the in-phase (χ_M') and out-of-phase (χ_M'') measurements were fit using a generalized Debye model, and relaxation times (τ) were extracted from these fits (Figure 4). A corresponding plot of $\ln(\tau)$ versus T^{-1} is linear for both complexes under both zero field and $H = 1000$ Oe applied field, consistent with an Orbach relaxation process, as described by the equation:

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{U_{eff}}{k_B T}\right) \quad (1)$$

Where τ is the observed relaxation time, U_{eff} is the effective spin-reversal barrier, k_B is the Boltzmann constant, and τ_0 is a pre-exponential factor. That said, we cannot exclude the possibility that Raman relaxation is also operative, given the narrow temperature range of our ac data.

Applying eq 1 to the relaxation data recorded for complex **1** at $H = 0$ Oe and $H = 1000$ Oe yields τ_0 values of $2.2(5) \times 10^{-7}$ s and $1.0(1) \times 10^{-6}$ s, and U_{eff} values of $14.7(4)$ cm⁻¹ and $11.8(2)$ cm⁻¹, respectively. The relaxation data for **2** at $H = 0$ Oe and $H = 1000$ Oe could also be fit to eq 1, yielding τ_0 values of $1.0(5) \times 10^{-8}$ s and $1.4(4) \times 10^{-7}$ s, and U_{eff} values of $15.6(7)$ cm⁻¹ and $13.2(4)$ cm⁻¹, respectively. The values of U_{eff} calculated for **1** and **2** using $U = |D|S^2$ are $U = 20.1$ cm⁻¹ and 13.2 cm⁻¹, respectively. The latter is in good agreement with that determined from the ac magnetic susceptibility measurements, but the former is larger, suggesting that Raman relaxation may also be occurring in this complex, which lowers the effective barrier.¹² For comparison, [Fe₄(N=CPh₂)₆] features a U_{eff} value of $29.1(1)$ cm⁻¹,¹³ whereas the tetrametallic SMMs [Ni₄(N=P^tBu₃)₄][B(C₆F₅)₄] and [Co₄(N=P^tBu₃)₄][B(C₆F₅)₄] feature U_{eff} values of $16.53(6)$ cm⁻¹ and 87 cm⁻¹, respectively.^{2,12} While it is difficult to extract structure-function relationships from this small series of complexes, it is heartening to observe that they universally exhibit slow magnetic relaxation, strengthening the argument that direct exchange will be an important criterion for the design of high-performing SMM in the years to come.

Conclusions

In summary, we report the synthesis of $[\text{Fe}_4\text{Br}_2(\text{N}=\text{C}^t\text{Bu}_2)_4]$ and $[\text{Fe}_4\text{Br}(\text{N}=\text{C}^t\text{Bu}_2)_5]$, two ketimide-supported $[\text{Fe}_4]^{6+}$ clusters. Both clusters exhibit $S = 7$ ground states at room temperature, which results from strong ferromagnetic coupling between the Fe(I) and Fe(II) centers within the $[\text{Fe}_4]^{6+}$ core. Additionally, both clusters exhibit slow magnetic relaxation with zero-field relaxation barriers of $U_{\text{eff}} \approx 14 \text{ cm}^{-1}$. While their barriers to magnetic relaxation are modest, we observe no evidence for relaxation via quantum tunneling, bolstering the use of ferromagnetic direct exchange to generate new, high-performing SMMs.⁴¹ Additionally, this work highlights the utility of the ketimide ligand to generate metal clusters with significant amounts of direct M-M bonding.

Experimental Details

General Procedures. All operations were performed in a glovebox under an atmosphere of N_2 . Diethyl ether (Et_2O) was dried by passage over activated molecular sieves using a Vacuum Atmospheres DRI-SOLV solvent purification system. Tetrahydrofuran (THF) was distilled over Na/benzophenone and stored over activated 3 Å molecular sieves for 24 h prior to use. Acetonitrile was stored over activated 3 Å molecular sieves for three days and degassed by sparging with N_2 prior to use. Pentane was dried on an MBraun solvent purification system. C_6D_6 and $^t\text{BuCN}$ were dried over activated 3 Å molecular sieves for 72 h prior to use. FeCl_2 was purchased from Strem and stirred in a mixture of diethyl ether and TMSCl for 18 h at room temperature prior to use. $\text{Li}(\text{N}=\text{C}^t\text{Bu}_2)$ was prepared according to published literature procedures.⁴² All other reagents were purchased from commercial suppliers and used as received.

All NMR spectra were collected at room temperature. ^1H NMR spectra were recorded on an Agilent Technologies 400-MR DD2 400 MHz or a Varian Unity Inova 500 MHz spectrometer. NMR spectra were referenced to external SiMe_4 using residual solvent resonances as internal standards. Electronic absorption spectra were recorded on a PerkinElmer Lambda 750 UV/Vis/NIR Spectrophotometer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. Mass spectra were collected at the Materials Research Laboratory Shared Experimental Facilities at UCSB, using an electrospray ionization (ESI) source in positive ion mode with a Waters Xevo G2-XS TOF Time-of-Flight mass spectrometer. Model mass spectra were generated in MassLynx V4.1 software with the isotope clusters displayed with a minimum abundance of 0.1%. Elemental analyses were performed by the Microanalytical Laboratory at the University of California, Berkeley, using a Perkin Elmer 2400 Series II combustion analyzer.

Zero-Field ^{57}Fe Mössbauer Spectroscopy. Data were collected on a SEECo Model W304 resonant gamma-ray spectrometer (activity = $50 \text{ mCi} \pm 10\%$), $^{57}\text{Co}/\text{Rh}$ source (manufactured by Ritverc) equipped with a Janis Research Model SVT-400 cryostat system. The source linewidth is $<0.12 \text{ mm/s}$ for the outermost lines of a 25 micron $\alpha\text{-Fe}$ foil standard. Isomer shifts are referenced to a $\alpha\text{-Fe}$ foil at room temperature. ^{57}Fe Mössbauer samples were prepared using 35 mg of crystalline **1** and 21 mg of crystalline **2** suspended in Paratone-N oil and measured at 90 K. The samples were loaded into a polypropylene capsule under inert atmosphere, which was subsequently sealed with vacuum grease to prevent exposure to air. The data were fit using a custom Igor Pro (Wavemetrics) macro package developed by the Betley group at Harvard University.

Magnetic Measurements. Magnetic properties were recorded using a Quantum Design Magnetic Property Measurement System SQUID vibrating sample magnetometer (MPMS3 SQUID-VSM).

15-25 mg samples of polycrystalline material were loaded into a glass NMR tube, which was subsequently flame sealed under static vacuum. For **1**, the solids were kept in place by adding eicosane wax (37 mg), which was subsequently melted into the sample to minimize torquing during measurements. For **2**, the solids were kept in place by quartz wool packed on either side of the sample. DC magnetic measurements were performed in VSM mode while sweeping either the applied magnetic field or temperature at controlled rates. Variable-temperature, variable-field magnetization data was collected under fields ranging from $H = 1$ to $H = 7$ T over the temperature range 2 to 20 K. The data was fitted using the program PHI.⁴⁰ AC susceptibility measurements were performed at fixed temperatures and fields in three-point measurement mode with an excitation field amplitude of 2 Oe. AC susceptibility data was fit using the generalized Debye model. For the magnetic susceptibility measurements, diamagnetic corrections ($\chi_{\text{dia}} = -5.37 \times 10^{-4}$ cm³/mol for [Fe₄Br₂(N=C^tBu₂)₄], $\chi_{\text{dia}} = -6.07 \times 10^{-4}$ cm³/mol for [Fe₄Br(N=C^tBu₂)₅]) were made using Pascal's constants.⁴³ The data was not corrected for the contributions from the sample holder, quartz wool, or eicosane.

Synthesis of [Fe₄Br₂(N=C^tBu₂)₄] (1**).** To a cold (-25 °C), stirring suspension of FeBr₂ (0.402 g, 1.86 mmol) in THF (3 mL) was added dropwise a cold solution of Li(N=C^tBu₂) (0.139 g, 0.94 mmol) in THF (5 mL), which resulted in a color change to deep red-brown. The reaction mixture was allowed to warm to room temperature, whereupon Zn⁰ powder (0.245 g, 3.74 mmol) was added, which resulted in a slow color change to deep purple-red. After 18 h, the volatiles were removed *in vacuo* resulting in formation of a deep purple solid. The solid was triturated with pentane (6 × 1 mL), extracted with pentane (10 mL), and filtered through a Celite column supported on glass wool (0.5 cm × 5 cm). The filtrate was concentrated *in vacuo* and transferred to a 5 mL vial, which was placed inside of a 20 mL scintillation vial. Isooctane (2 mL) was added

to the outer vial. Storage of this two-vial system at -25 °C for 48 h resulted in the deposition of large black-purple blocks. The crystalline material was isolated by decanting the supernatant and then washed with cold (-25 °C) pentane (2 × 1 mL). The washings were discarded and the crystals were dried *in vacuo*, yielding **1** (100 mg, 45% yield). Anal. Calcd for C₃₆H₇₂Br₂Fe₄N₄: C 45.80, H 7.69, N 5.93%. Found: C 45.62, H 7.52, N 5.82%. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ 120.8 (br s, 72 H). UV-vis/NIR (THF, 0.10 mM, 25 °C, L mol⁻¹ cm⁻¹): 527 nm (ε = 3700), 827 nm (ε = 1200). FT-IR (KBr pellet, cm⁻¹): 586 (s), 640 (s), 763 (m), 837 (m), 871 (w), 964 (s), 1037 (m), 1105 (w), 1141 (w), 1193 (s), 1209 (s), 1228 (m), 1361 (s), 1371 (s), 1400 (m), 1459 (m), 1479 (s), 1554 (m), 1575 (s), 1587 (m), 1648 (m), 1672 (w), 2233 (w), 2871 (m), 2962 (s). Zero-field ⁵⁷Fe Mössbauer [90 K]: δ = 0.45 mm/s, |ΔE_Q| = 0.62 mm/s, η = 0.573.

Synthesis of [Fe₄Br(N=C^tBu₂)₅] (2**).** To a stirring, deep red solution of **1** (0.103 g, 0.109 mmol) in THF (4.5 mL) at room temperature was added dropwise a yellow solution of Na(N=C^tBu₂) (0.018 g, 0.110 mmol) in THF (3 mL). After 20 h, the volatiles were removed *in vacuo* to provide a black solid. This solid was triturated with pentane (3 × 1 mL), extracted with pentane (6 mL), and filtered through a Celite column supported on glass wool (0.5 cm × 5 cm). The filtrate was concentrated *in vacuo*. Storage of this vial at -25 °C for 48 h resulted in the deposition of solid dark purple crystalline material, which was isolated by decanting the supernatant (54 mg, 49% yield). X-ray quality crystals were grown by storage of Et₂O/acetonitrile solution of **2** (3 mL:0.5 mL) at -25 °C for 12 h. Anal. Calcd for C₄₅H₉₀BrFe₄N₅: C 53.81, H 9.03, N 6.97%. Found: C 53.49, H 8.99, N 6.97%. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ 98.3 (br s, 72 H), 79.2 (br s, 18 H). ESI-MS: *m/z* 1003.3074 [M⁺] (Calcd *m/z* 1003.3762). UV-vis/NIR (THF, 0.10 mM, 25 °C, L mol⁻¹ cm⁻¹): 506 nm (ε = 4700), 923 nm (ε = 1100). FT-IR (KBr pellet, cm⁻¹): 584 (m), 644 (s), 765 (m), 842 (w), 877 (w), 973 (m), 1035 (w), 1192 (s), 1224 (m), 1240 (m), 1369 (s), 1373 (m), 1461

(m), 1481 (s), 1539 (w), 1602 (s), 1666 (m), 2233 (w), 2875 (m), 2964 (s). Zero-field ^{57}Fe Mössbauer [90 K]: $\delta = 0.45$ mm/s, $|AE_Q| = 0.39$ mm/s, $\eta = 0.558$; $\delta = 0.59$ mm/s, $|AE_Q| = 1.14$ mm/s, $\eta = 0.600$.

Associated Content

Supporting Information

The supporting information is available free of charge at <https://pubs.acs.org>.

- Experimental procedures and crystallographic, spectroscopic, and magnetic characterization details for **1** and **2** (PDF).

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Notes

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Table of Contents Graphic

The $[\text{Fe}_4]^{6+}$ -containing clusters, $[\text{Fe}_4\text{Br}_2(\text{N}=\text{C}^t\text{Bu}_2)_4]$ and $[\text{Fe}_4\text{Br}(\text{N}=\text{C}^t\text{Bu}_2)_5]$, feature $S = 7$ ground states and zero-field relaxation barriers of $U_{\text{eff}} \approx 14 \text{ cm}^{-1}$.

