Measuring Metal–Metal Communication in a Series of Ketimide-bridged $[Fe_2]^{6+}$ Complexes

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ABSTRACT: Reaction of $Fe(acac)_3$ with 3 equiv of $Li(N{=}C(R)Ph)$ (R = Ph, ^{t}Bu) results in formation of the $[Fe_2]^{6+}$ complexes, $[Fe_2(\mu\text{-}N{=}C(R)Ph)_2(N{=}C(R)Ph)_4]$ (R = Ph, **1**; ^{t}Bu, **2**), in low to moderate yields. Reaction of $FeCl_2$ with 6 equiv of $Li(N{=}C_{13}H_8)$ ($HN{=}C_{13}H_8$ = 9-fluorenone imine) results in formation of $[Li(THF)_2]_2[Fe(N{=}C_{13}H_8)_4]$ (**3**), in good yield. Subsequent oxidation of **3** with ca. 0.8 equiv of I_2 generates the $[Fe_2]^{6+}$ complex, $[Fe_2(\mu\text{-}N{=}C_{13}H_8)_2(N{=}C_{13}H_8)_4]$ (**4**), along with free fluorenyl ketazine. Complexes **1**, **2**, and **4** were characterized by ^{1}H NMR spectroscopy, X-ray crystallography, ^{57}Fe Mössbauer spectroscopy, and SQUID magnetometry. The Fe–Fe distances in **1**, **2**, and **4** range from 2.803(7) to 2.925(1) Å, indicating that no direct Fe–Fe interaction is present in these complexes. The ^{57}Fe Mössbauer spectra for complexes **1**, **2**, and **4** are all consistent with the presence of symmetry-equivalent, high-spin Fe^{3+} centers. Finally, all three complexes exhibit a similar degree of antiferromagnetic coupling between the metal centers (J = -23 to -29 cm^{-1}), as ascertained by SQUID magnetometry.

Introduction

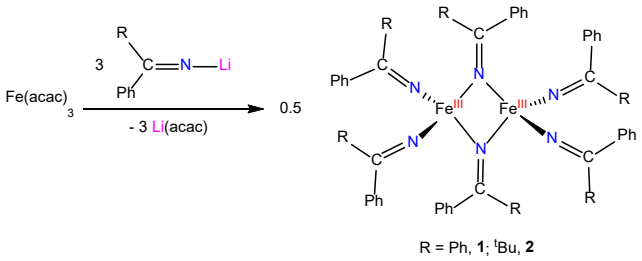
Metal–metal communication can play a key role in the emergence of single-molecule magnetism, which has potential applications in data storage and quantum computing.[1–9] For example, Long and co-workers isolated a series of phosphinimide-bridged $[M_4]^{5+}$ clusters, $[M_4(NP^tBu_3)_4]^+$ (M = Ni, Co) that feature high spin ground states and slow magnetic relaxation. The latter observation was attributed to direct exchange interactions,[10–12] which were thought to be a consequence of the relatively short M–M bonds imposed by the bridging phosphinimide ligand. The pyridin-2-yl-amide class of ligands can also promote strong metal–metal interactions, specifically in extended metal atom chains (EMACs).[13–20] For example, $[Cr_5(tdpa)_4X_2]$ (X = Cl^-, SCN^-; H_2tdpa = N^2,N^6-di(pyridine-2-yl)pyridine-2,6-diamine) exhibits strong antiferromagnetic coupling between metal centers, as well as single-molecule magnet behavior at low temperatures.[21] Metal–metal communication can also influence spin crossover (SCO) behavior in multi-metallic complexes,[22–29] which have potential applications in molecular electronics and sensors.[27,30,31] For example, the pyrazolate-bridged $[Fe_2]^{4+}$-containing polymer, $[\{Fe_2(NCS)_2(\mu\text{-bpypz})_2\}(\mu\text{-4,4′-bipy})]$ (Hbpypz = 3,5-bis(2-pyridyl)-pyrazole) exhibits a sharp SCO transition, due, in part, to the *minimal* magnetic exchange coupling between Fe centers.[32] Importantly, each of these examples relies on the ability of ligands to control the magnetic interactions between metal ions.

The ketimide anion, $[N{=}CR_2]^-$, is another ligand class that is adept at promoting metal–metal interactions,[33–35] as shown by the multimetallic complexes, $[Li(12\text{-crown-}4)_2][M_2(\mu\text{-}N{=}C^tBu_2)_3(N{=}C^tBu_2)_2]$ (M = Mn, Fe, Co), $[Fe_2(\mu\text{-}N{=}C^tBu_2)_2(N{=}C^tBu_2)_3]$, $[Fe_4(\mu\text{-}N{=}CPh_2)_6]$, and $[Fe_4(\mu\text{-Br})_2(\mu\text{-}N{=}C^tBu_2)_4]$.[36–38] In the case of $[Fe_4(\mu\text{-}N{=}CPh_2)_6]$ and $[Fe_4(\mu\text{-Br})_2(\mu\text{-}N{=}C^tBu_2)_4]$, metal–metal communication occurs via direct exchange, which leads to ferromagnetic coupling between metal centers.[37,38] In contrast, for $[Fe_2(\mu\text{-}N{=}C^tBu_2)_2(N{=}C^tBu_2)_3]$, metal–metal communication likely occurs via superexchange, which leads to anti-ferromagnetic coupling.[36] While the ability of the ketimide ligand to mediate metal–metal communication is reasonably well established,[33,36,37] the role that the ketimide substituents play in mediating these interactions is not well understood. In fact, the diversity of known ketimide substituents is relatively low and the most common substituents, by a substantial margin, are Ph and ^{t}Bu.[39–54] In this regard, we recently reported the syntheses of two "tied-back" ketimides, 2-adamantyl ketimide and 9-fluorenyl ketimide, in an effort to increase this substituent diversity.[33] The latter example, with its conjugated π-system, could be especially good at promoting metal–metal communication. Herein, we evaluate the magnetic properties of a series of $[Fe_2]^{6+}$ dimers with varying ketimide substituents, including the fluorenyl substituent, in an effort to tune the magnetic interactions between iron centers.

Results and Discussion

Synthesis. The reaction of $Fe(acac)_3$ with 3 equiv of $Li(N{=}CPh_2)$ in tetrahydrofuran (THF) at room temperature for 20 h resulted in the formation of $[Fe_2(\mu\text{-}N{=}CPh_2)_2(N{=}CPh_2)_4]$ (**1**), which was isolated as black needles in 40% yield after work-up (Scheme 1). Similarly, reaction of $Fe(acac)_3$ with 3 equiv of $Li(N{=}C(^tBu)Ph)$ in diethyl ether (Et_2O) at room temperature for 18 h resulted in the formation of $[Fe_2(\mu\text{-}N{=}C(^tBu)Ph)_2(N{=}C(^tBu)Ph)_4]$ (**2**), which was isolated as a black crystalline material in 35% yield after work-up. Complex **1** is soluble in THF, and somewhat soluble in toluene, benzene, and Et_2O, whereas complex **2** is soluble in THF, Et_2O, benzene, and hexanes. As solids, both **1** and **2** are stable under inert atmosphere at -25 °C for several months; however, they decompose rapidly upon exposure to air in both the solid and solution states.

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



The ^{1}H NMR spectrum of **1** (Figure S5) in C_6D_6 is consistent with the idealized D_{2h} symmetry observed in the solid state (see below). The spectrum exhibits two resonances at 19.52 and 13.49 ppm assignable to the *m*-Ar protons of the terminal and bridging ketimide ligands, respectively, and two resonances at -0.37 and -4.26 ppm assignable to the *p*-Ar protons of the bridging and terminal ketimide ligands. The *o*-Ar proton resonances were not observed, likely due to paramagnetic broadening. The ^{1}H NMR spectrum of **2** in C_6D_6 features seven broad and paramagnetically shifted resonances (Figure S6). There are two resonances in an approximately 18:36 ratio at 19.27 and 16.40 ppm, assignable to the bridging and terminal ^{t}Bu resonances, respectively. An additional three resonances at 18.17, 12.79, and 1.36 ppm, in an approximately 8:8:4 ratio, are assignable to the three expected terminal ketimide aryl resonances, and two resonances at 2.49 and 10.79 ppm are assignable to the *p*-Ar and either the *m*- or *o*-Ar protons of the bridging ketimide ligands. One resonance is not observed, presumably because it is too broad. These assignments are consistent with the idealized C_{2h} symmetry expected for the complex.

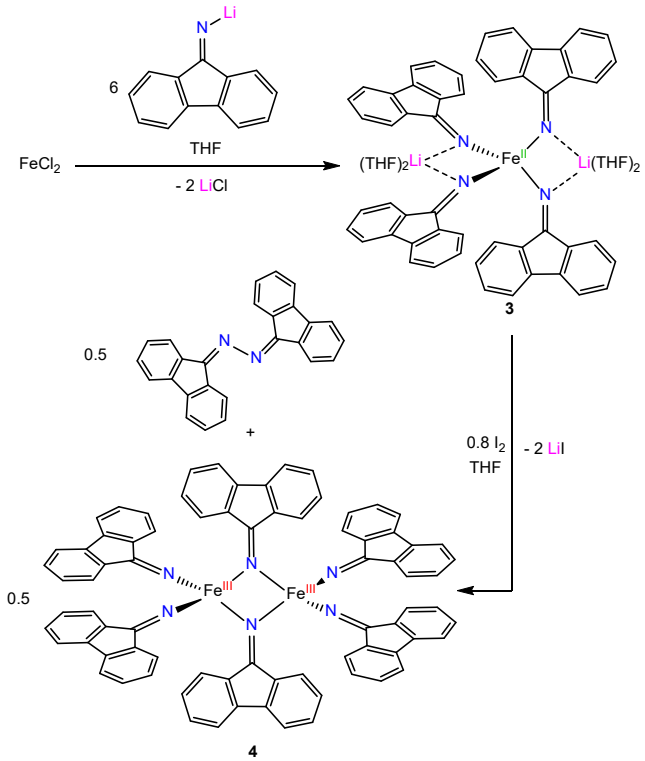
In contrast to relatively straight-forward syntheses of **1** and **2** from $Fe(acac)_3$, the reaction of 3 equiv of $Li(N{=}C_{13}H_8)$ ($HN{=}C_{13}H_8$ = 9-fluorenone imine) with $Fe(acac)_3$ results in formation of a complex reaction mixture, according to ^{1}H NMR spectroscopy. However, a two-step synthetic approach involving salt metathesis with Fe^{2+}, followed by oxidation to $[Fe_2]^{6+}$, proved to be successful. In particular, reaction of $FeCl_2$ with 6 equiv of $Li(N{=}C_{13}H_8)$ resulted in formation of $[Li(THF)_2]_2[Fe(N{=}C_{13}H_8)_4]$ (**3**), which was isolated as dark green blocks in 70% yield after work-up (Scheme 2). Complex **3** is soluble in THF and somewhat soluble in Et_2O, but insoluble in hexanes, pentane, and benzene. It is stable under an inert atmosphere at -25 °C for several months. Unfortunately, due to their similar solubilities, we could not completely separate complex **3** from the LiCl by-product. In addition, the highest yields of **3** were achieved when an excess of $Li(N{=}C_{13}H_8)$ was used. If lower amounts of $Li(N{=}C_{13}H_8)$ are employed, then the yields of **3** were reduced and ^{1}H NMR spectra showed the presence of several unidentified Fe-containing products.

The ^{1}H NMR spectrum of **3** in THF-d_8 exhibits four resonances at 31.45, 18.82, 14.27, and 12.52 ppm, in an approximately 1:1:1:1 ratio (Figure S8). The observation of four resonances are consistent with the single ligand environment expected for this complex, while the large chemical shifts are consistent with the anticipated open shell ground state.[55] The ^{7}Li NMR spectrum of **3** exhibits a highly-downfield resonance at 211 ppm, also consistent with a paramagnetic ground state (Figure S9). Additionally, its formulation was confirmed by X-ray crystallography (Figure S3). To our knowledge, **3** is the first fluorenyl ketimide complex to be prepared by salt metathesis. Previously reported fluorenyl ketimide complexes we prepared by disproportionation of 9-diazofluorene or by activation of the N–H bond of 9-fluorenone imine.[56–59]

Given the likely (and potentially variable) presence of LiCl in isolated samples of complex **3**, we performed the oxidation by titration with I_2 in THF, and monitored the conversion to the product by ^{1}H NMR spectroscopy. Formally, this transformation requires two oxidizing equivalents: one to form Fe^{3+} and one to convert the redox-active ketimide ligand to ketazine.[59–61] Typically, the highest yields of **4** were achieved upon addition of ca. 0.8 equiv of I_2 to the reaction mixture (Scheme 2). Consistent with the reaction scheme, ^{1}H NMR spectra of the crude reaction mixtures do contain resonances assignable to free fluorenyl ketazine (Figure S10).[59–61]

Work-up the resulting reaction mixture, followed by storage at -25 °C for 24 h, resulted in the deposition of $[Fe_2(\mu\text{-}N{=}C_{13}H_8)_2(N{=}C_{13}H_8)_4]$ (**4**), as a black crystalline solid in good yields. Separation of any remaining ketazine by-product was achieved by quickly rinsing the isolated material with a small portion of THF. Complex **4** is somewhat soluble in THF, but insoluble in Et_2O, hexanes, pentane, and benzene. Its ^{1}H NMR spectrum in THF-d_8 exhibits four resonances at 15.19, 11.93, 0.15, and -0.39 ppm, which are assignable to the four expected CH environments of the bridging ketimide ligand (Figure S11). Additionally, we observe three resonances at 23.55, 16.04, and -3.67 ppm, which are assignable to three of the terminal ketimide CH resonances. One terminal ketimide CH environment was not observed. Importantly, this spectral signature is consistent with the expected idealized D_{2h} symmetry, and suggests that the bimetallic structure of **4** is maintained in donor solvents. The UV-vis spectrum of **4** is also qualitatively similar to that observed for **1** (Figures S16 and S18), suggesting similar structures in solution. For comparison, oxidation of $[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$ with 1 equiv of I_2 results in formation of the stable Fe(IV) complex, $[Fe(N{=}C^tBu_2)_4]$,[55] demonstrating the greater redox stability of bis(*tert*-butyl)ketimide vs. fluorenyl ketimide.

Scheme 2. Synthesis of complexes **3** and **4**



X-ray crystallography. Complexes **1**, **2**, and **4** all crystallize in the triclinic space group *P*-1 (Figures 1, S1, S2, and S4). Complex **1** crystallizes as a toluene solvate, **1**·C_7H_8 with two

independent molecules in the asymmetric unit, whereas **4** crystallizes as a THF solvate, **4**·2THF. All three complexes feature two pseudotetrahedral iron centers bound by two bridging and four terminal ketimide ligands. The Fe–Fe distances are 2.8639(12) and 2.8278(12), 2.9245(13), and 2.803(7) Å for **1**, **2**, and **4**, respectively (Table 1). These values correspond to formal shortness ratios of 1.23 and 1.21, 1.26, and 1.20, respectively,[62,63] and suggest the absence of a direct M–M bonding interaction.[64] For comparison, the imido-bridged $[Fe_2]^{6+}$ complex reported by Holland and co-workers, $[L^{Et}Fe(\mu\text{-}NPh)_2FeL^{Et}]$ (L^{Et} = {(2,6-$Et_2C_6H_3$)NC(Me)}$_2$CH), features a significantly shorter Fe–Fe bond length of 2.5648(4) Å.[65] The Fe–Fe distances in **1**, **2**, and **4** are also much longer than those of the $[Fe_2]^{4+}$ ketimide complex, $[Li(12\text{-crown-}4)_2][Fe_2(\mu\text{-}N{=}C^tBu_2)_3(N{=}C^tBu_2)_2]$ (2.443(1) Å), and the $[Fe_2]^{5+}$ ketimide complex, $[Fe_2(\mu\text{-}N{=}C^tBu_2)_3(N{=}C^tBu_2)_2]$ (2.5468(14) Å).[36] The Fe–Fe distances in **1** are also slightly longer than that of its isostructural $[Fe_2]^{4+}$ congener, $[K(18\text{-crown-}6)]_2[Fe_2(\mu\text{-}N{=}CPh_2)_2(N{=}CPh_2)_4]$ (2.7936(9) Å).[66] As expected, the Fe–$N_{terminal}$ distances are shorter than the Fe–$N_{bridging}$ distances. Finally, the Fe–N–C angles of the terminally-bound ketimide ligands are generally linear, suggesting the presence of π-donation from ketimide to metal (Table 1).

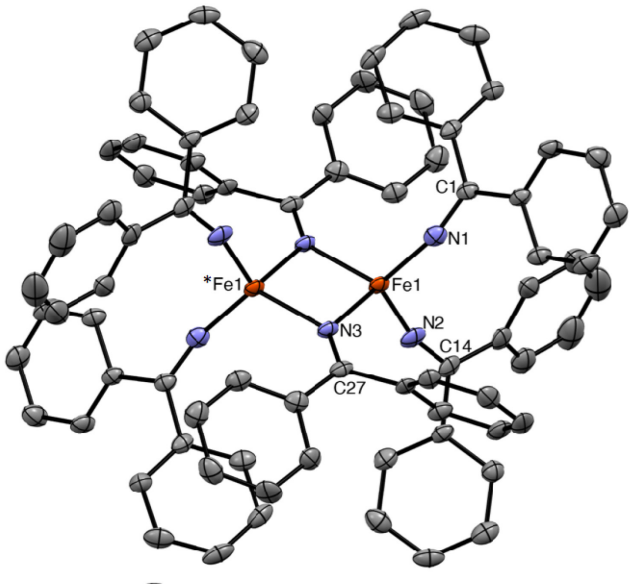


Figure 1. Solid-state molecular structure of **1**·C_7H_8 shown with 50% probability ellipsoids. Hydrogens atoms, second independent molecule, and the toluene solvate have been excluded for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (°) for Complexes **1**, **2**, **4**, and $[K(18\text{-crown-}6)]_2[Fe_2(\mu\text{-}N{=}CPh_2)_2(N{=}CPh_2)_4]$.

Parameter	**1**·C_7H_8	2	**4**·2THF	$[K(18\text{-crown-}6)]_2[Fe_2(N{=}CPh_2)_6]$[66]
Fe–Fe	2.8639(12), 2.8278(12)	2.9245(13)	2.803(7)	2.7936(9)
Formal shortness ratio[62]	1.23, 1.21	1.26	1.20	1.20
Fe–$N_{bridging}$	2.011(3), 2.037(4) 2.001(3), 2.026(3)	2.070(3) 2.085(3)	2.008(8) 2.021(9)	2.045(3) 2.000(3)
Fe–$N_{terminal}$	1.842(4), 1.857(4) 1.848(4), 1.869(3)	1.901(3) 1.927(3)	1.850(9) 1.851(9)	1.941(3) 1.864(3)
Fe–N–$C_{terminal}$	163.6(3), 163.9(3) 171.8(3), 144.6(3)	162.4(3) 167.7(3)	156.1(9) 169.2(9)	171.7(3) 144.3(3)

Mössbauer Spectroscopy and Magnetism. In an effort to confirm their oxidation states, zero-field ^{57}Fe Mössbauer spectroscopy was performed on complexes **1**, **2**, and **4** (Figure 2, Tables 2 and S2). The Mössbauer spectra of all three complexes are very similar. For example, the Mössbauer spectrum of **1** taken at T = 90 K exhibits a sharp asymmetric doublet, with an isomer shift of δ = 0.23 mm/s and quadrupole splitting of $|\Delta E_Q|$ = 0.71 mm/s. The Mössbauer spectrum of **2** features an isomer shift of δ = 0.26 mm/s and quadrupole splitting of $|\Delta E_Q|$ = 0.86 mm/s. Finally, the Mössbauer spectrum of **4** exhibits a sharp asymmetric doublet with an isomer shift of δ = 0.22 mm/s and quadrupole splitting of $|\Delta E_Q|$ = 0.72 mm/s. The presence of a single quadrupole doublet in all three spectra confirm that each complex contains symmetry-related iron environments, consistent with the NMR spectral and X-ray crystallographic data. Moreover, the observed isomer shifts are in line with those expected for high-spin Fe^{3+}.[65,67–72] A comparison with the reported ^{57}Fe Mössbauer parameters for other ketimide-supported clusters and complexes is also informative (Table 2). Generally speaking, there is a good correlation between oxidation state and isomer shift, with one exception. The Fe^{II}/Fe^{I} mixed-valent cluster, $[Fe_4(\mu\text{-}N{=}CPh_2)_6]$, exhibits an anomalously low isomer shift.[37] We do not have a good explanation for this discrepancy at the moment. Also of note, the monometallic Fe^{3+} ketimide, $[Li(12\text{-crown-}4)_2][Fe^{III}(N{=}C^tBu_2)_4]$, features a much larger quadrupole splitting ($|\Delta E_Q|$ = 3.56 mm/s) than those observed for complexes **1**, **2**, or **4**.[73] The large discrepancy is likely a result of the former complex's S = 3/2 spin state, which contrasts to the S = 5/2 spin states of **1**, **2**, and **4** (see below).[74–77]

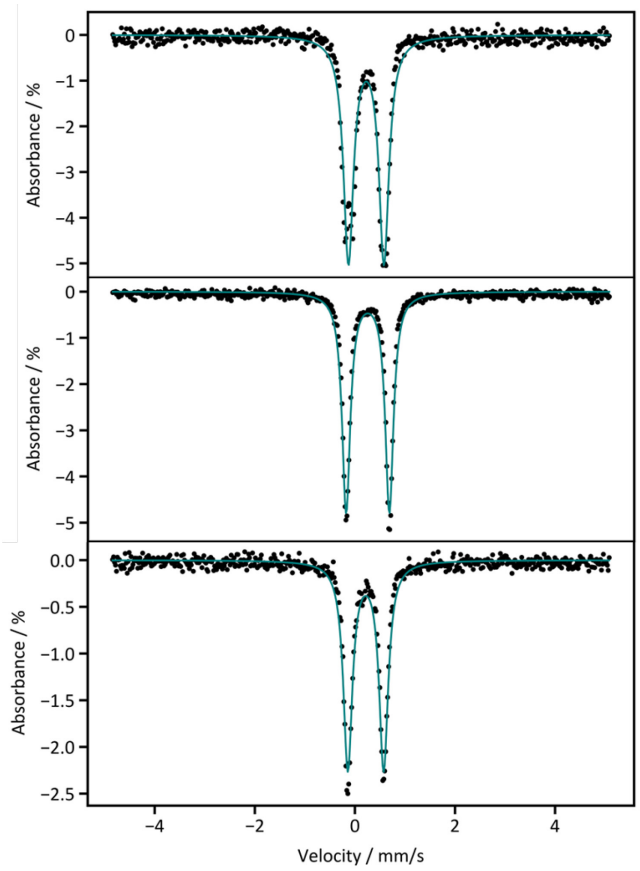


Figure 2. Zero-field ^{57}Fe Mössbauer spectra of **1** (top), **2** (middle), and **4** (bottom) collected at T = 90 K. The teal traces correspond to the overall fit.

Table 2. ^{57}Fe Mössbauer parameters for complexes **1**, **2**, and **4** along with other selected ketimide-supported complexes. O.S. = formal oxidation state.

Complex	δ (mm/s)	$\lvert\Delta E_Q\rvert$ (mm/s)	O.S.	Ref
1	0.23	0.71	3	This work
2	0.26	0.86	3	This work
4	0.22	0.72	3	This work
$[Fe_4(\mu\text{-}N{=}CPh_2)_6]$	0.34	0.79	1.5	[37]
$[Fe_4(\mu\text{-}Br)_2(\mu\text{-}N{=}C^tBu_2)_4]$	0.45	0.62	1.5	[38]
$[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$	0.44	0.85	2	[73]
$[Li(12\text{-crown-}4)_2][Fe(N{=}C^tBu_2)_4]$	0.19	3.56	3	[73]
$Fe(N{=}C^tBu_2)_4$	-0.15	1.62	4	[73]

Temperature-dependent dc magnetization data were also collected for crystalline samples of **1**, **2**, and **4** at H = 1,000 Oe (Figure 3). Complex **1** exhibits a magnetic moment of $\chi_M T$ = 3.36 emuK mol^{-1} at T = 300 K (μ_{eff} = 5.18 μ_B), which drops precipitously to $\chi_M T$ = 0.003 emuK mol^{-1} at T = 2 K (μ_{eff} = 0.17 μ_B). Likewise, complex **2** exhibits a room-temperature moment of $\chi_M T$ = 3.24 emuK mol^{-1} (μ_{eff} = 5.09 μ_B), which drops to $\chi_M T$ = 0.023 emuK mol^{-1} at T = 2 K (μ_{eff} = 0.43 μ_B). Complex **4** features a higher room-temperature moment of $\chi_M T$ = 4.13 emuK mol^{-1} (μ_{eff} = 5.75 μ_B) that similarly drops to $\chi_M T$ = 0.101 emuK mol^{-1} at T = 2 K (μ_{eff} = 0.90 μ_B). To fit the magnetic data, the exchange Hamiltonian $\widehat{\boldsymbol{H}} = -2\boldsymbol{J}\widehat{\boldsymbol{S}}_{\boldsymbol{Fe}} \cdot \widehat{\boldsymbol{S}}_{\boldsymbol{Fe}}$ was employed. During the fitting process, J and % paramagnetic impurity (S = 5/2) were allowed to refine freely for all three complexes, while the Weiss constant (Θ) was allowed to refine for **4**. The g values were kept constant at $g_1 = g_2$ = 2.00 for **1** and **2**, and $g_1 = g_2$ = 2.10 for **4**, following past precedent.[78–81] D and χ_{TIP} were not included in the fits. Reasonable fits were obtained by assuming $S_1 = S_2$ = 5/2 (Table 3, Figure 3), although the fit for **4** shows small deviations at low and high temperatures (Figure 3 inset). The fits gave magnetic coupling constants of J = -29.0, -29.6, and -25.7 cm^{-1} for complexes **1**, **2**, and **4**, respectively, confirming the strong antiferromagnetic coupling between the Fe^{3+} centers in all three dimers. The magnetic communication in **1**, **2**, and **4** is likely facilitated through superexchange; however, based on the similar J coupling values uncovered for all three complexes, it is clear that the ketimide substituents have a minimal effect on the magnetic communication between metal centers.

Table 3. Hamiltonian parameters from fits to magnetic susceptibility data.

Complex	1	2	4
J (cm^{-1})	-29.0	-29.6	-25.7
g_1, g_2	2.00[a]	2.00[a]	2.10[a]
Paramagnetic Impurity[b] (%)	2.1	1.2	2.4
Θ (K)	--	--	-6.9

[a]Fixed

[b]S = 5/2

For comparison, the magnetic coupling constants in **1**, **2**, and **4** are much smaller than those measured for other ketimide-bridged dimers, such as $[Fe_2(\mu\text{-}N{=}C^tBu_2)_2(N{=}C^tBu_2)_3]$ (J = -235 cm^{-1}), $[Mn_2(\mu\text{-}N{=}C^tBu_2)_3(N{=}C^tBu_2)_2]^-$ (J = -78 cm^{-1}), and $[Li][Cr_2(\mu\text{-}N{=}C_{10}H_{14})_3(N{=}C_{10}H_{14})_4]$ (J = -200 cm^{-1}).[33,36] In the case of the $[Fe_2]^{5+}$ complex, $[Fe_2(\mu\text{-}N{=}C^tBu_2)_2(N{=}C^tBu_2)_3]$, the shorter Fe–Fe distance (2.547(1) Å) likely contributes to the larger coupling.[82,83] Similarly, the $[Fe_2]^{4+}$ complex, $[(PhCN)_2(Mes)_2Fe_2(\mu\text{-}N{=}C(Mes)(Ph))_2]$,[84] also features larger antiferromagnetic coupling (J = -63.7 cm^{-1}) than **1**, **2**, and **4**, likely for the same reason. Several chalcogenide-bridged $[Fe_2]^{6+}$ complexes have also been characterized by magnetometry.[81,85] These exhibit antiferromagnetic coupling constants ranging

from J = -75 cm^{-1} (for [{Fe(salen)}$_2$S]) to -105 cm^{-1} (for [{Fe(bipy)$_2$}$_2$O]$^{4+}$).[85–88] The μ-imido complex, [L^{Et}Fe(μ-NPh)$_2$FeL^{Et}], also features a large antiferromagnetic coupling constant (J = -123 cm^{-1}).[65] In these cases, the superexchange is facilitated by the dianionic bridging ligands, which results in stronger magnetic coupling presumably due to the shorter Fe–$E_{bridging}$ bond lengths. In contrast, [Fe$_2$]$^{6+}$ complexes bridged by monoanionic ligands tend to feature weaker antiferromagnetic couplings,[89] ranging from J = -2.2 cm^{-1} for [Fe$_2$(bbpnol)$_2$] (H$_3$bbpnol = *N*,*N*'-bis(2-hydroxybenzyl)-2-ol-1,3-propanediamine) to J = -28.6 cm^{-1} for [Fe$_2$(chp)$_4$(OMe)$_2$(dmbipy)$_2$] (chp = 6-chloro-2-pyridone; dmbipy = 4,4'-dimethyl-2,2'-bipyridine).[89 90] In this regard, the antiferromagnetic coupling constants measured for **1**, **2**, and **4** are on the upper end of these values, demonstrating that, for monoanionic bridging ligands, ketimides can mediate amongst the strongest metal–metal communication.

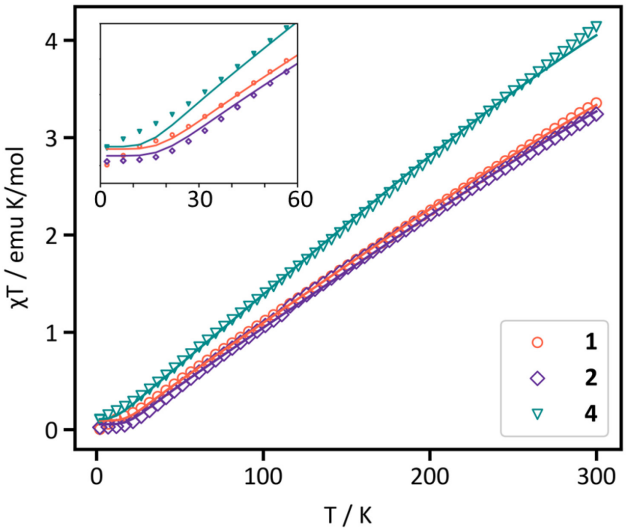


Figure 3. Solid-state magnetic susceptibility data (χ_MT vs. T) for 1 (orange circles), 2 (purple diamonds), and 4 (green triangles) collected under an applied magnetic field of H = 1 kOe from T = 2 to T = 300 K. The solid lines represent fits to the data, as described in the main text. Inset: Expansion of χ_MT vs. T, showing the low temperature data only.

Conclusions

We have synthesized three ketimide-bridged [Fe$_2$]$^{6+}$ complexes with varying substituents on the ketimide ligands. The Fe–Fe bond lengths are similar across the three complexes and do not indicate the presence of direct Fe–Fe interactions. Nonetheless, all three complexes exhibit robust antiferromagnetic communication between Fe centers, likely via superexchange. Surprisingly, however, there is minimal correlation between the substituent identity and the antiferromagnetic exchange coupling constant, even in the case of the fully-conjugated fluorenyl substituent. Despite the lack of any apparent correlation, this work nicely demonstrates the ability of ketimide ligands to generate multi-metallic metal complexes and to facilitate communication between metal centers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and crystallographic, spectroscopic, and magnetic characterization details for **1**, **2**, **3**, and **4**. (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

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A series of ketimide-bridged $[Fe_2]^{6+}$ complexes exhibit strong metal–metal communication, likely via superexchange.