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Fe–Fe Dimer with Redox-Active Ligands

[{Fe(tim)}$_2$]: An Fe–Fe Dimer Containing an Unsupported Metal–Metal Bond and Redox-Active N_4 Macrocyclic Ligands[**]

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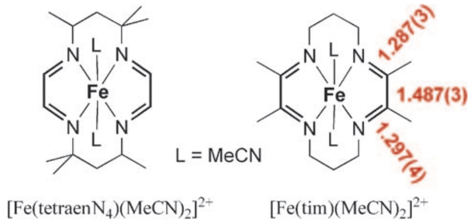
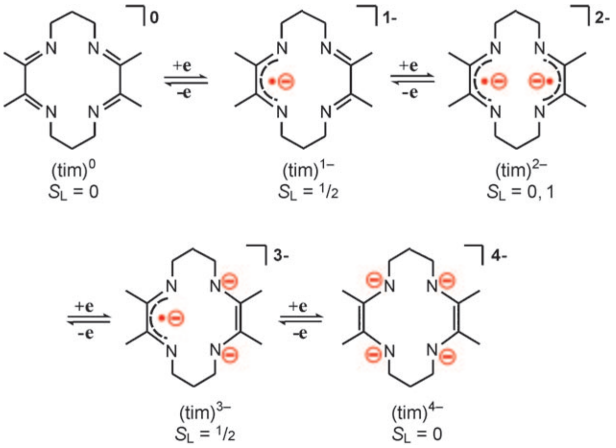
Dedicated to Professor Daryle H. Busch

The development of low-valent iron compounds has been newly prompted by the implication of such species in the catalytic cycle of carbon monoxide dehydrogenase as well as by their potential for nitrogen fixation chemistry.[1,2] Recent synthetic strategies have focused on the use of low-coordinate P, N, and S donor ligands to stabilize the low oxidation states of iron.[3–6] A few Fe^I and Fe^0 complexes coordinated by macrocyclic tetradentate N_4 ligands have also been reported; the best characterized examples are found in the porphyrin family.[7,8] However, the demonstrated redox participation of the porphyrin ligand has complicated the assignment of low-valent metal oxidation states in these systems.[7]

A low-spin Fe^I complex was reported by Rakowski and Busch using the macrocyclic tetraeneN_4 ligand (Scheme 1, left); additionally, formation of an Fe^0 species was implicated.[9] Redox participation of the macrocycle was not considered in this system. Recent work in our group demonstrating the redox non-innocence of α-diimine ligands suggested that extended α-diimine-based macrocycles, such as the tetraeneN_4 ligand, are also likely susceptible to reduction. In fact, Rose and co-workers had speculated that low-lying α-diimine π* orbitals of a structurally analogous [Fe^{II}(tim)(NCS)$_2$] complex[10] (Scheme 1, right, L = NCS) might favor ligand radical formation upon reduction.[11] The theoretical four-electron redox series available to both macrocyclic N_4 ligand systems (Scheme 2) suggests that an alternate description of Busch's [Fe^I(tetraeneN_4)]$^+$ complex as [Fe^{II}(L^-)]$^+$, containing the macrocyclic radical anion, is equally viable.[12–14]



Scheme 1. Fe^{II} compounds coordinated by tetraeneN_4 (left) and tim ligands (right). Bond lengths in red with estimated standard deviations.



Scheme 2. Four-electron redox series of the tim ligand. S_L = ligand spin.

We have now investigated the redox chemistry of the [Fe^{II}(tim)(MeCN)$_2$](PF$_6$)$_2$ complex (Scheme 1, right)[15a] to establish the unsaturated N_4 macrocyclic ligands. The crystal structure of [Fe^{II}(tim)(MeCN)$_2$](PF$_6$)$_2$ was redetermined at 100 K; the average diimine C–C bond length (1.487(3) Å) and the average C–N (1.292(4) Å) bond length typify the respective single and double bond length values expected for the fully oxidized, neutral ligand (tim^0) in the diamagnetic ferrous complex. The cyclic voltammogram of [Fe^{II}(tim)(MeCN)$_2$](PF$_6$)$_2$ exhibits two quasi-reversible one-electron reduction processes at $E_{1/2} = -1.16$ and -1.64 V versus ferrocenium/ferrocene. The potentials are slightly more negative than for the corresponding electron-transfer processes in [Fe^{II}(tetraeneN_4)(MeCN)$_2$]$^{2+}$, which were formerly assigned as metal-centered reductions to generate the Fe^I and Fe^0 species.[9] Chemical reduction of [Fe^{II}(tim)(MeCN)$_2$]$^{2+}$ required a greater than twofold excess of sodium in THF and yielded bronze–purple crystals of the reduced product, [{Fe(tim)}$_2$].

To our astonishment, the crystal structure of the product revealed that the reduced iron species dimerizes to generate [{Fe(tim)}$_2$][15b] (Figure 1). The metal–metal bond in the

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[**] C.R.H. gratefully acknowledges the Max Planck Society for a postdoctoral fellowship. We are grateful to the Fonds der Chemischen Industrie for financial support of this work. tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

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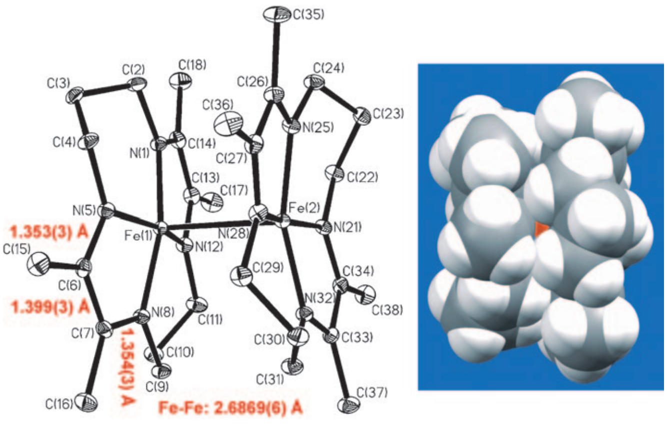

Figure 1. Crystal structure of [{Fe(tim)}$_2$] and space-filling representation of the molecule (right). Selected bond lengths: C(6)–N(5) 1.353(3) Å, C(6)–C(7) 1.399(3) Å.

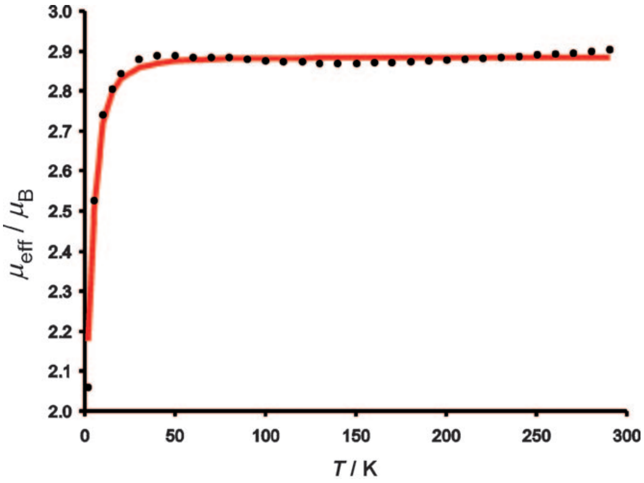

Figure 2. Magnetic susceptibility μ_{eff} of solid [{Fe(tim)}$_2$] at 1 T and 2–300 K (●). Fit of the data (—) with $S=1$, $g=2.04$, $|D|=12.4$ cm^{-1}, TIP $=141\times10^{-6}$ emu (TIP = temperature-independent paramagnetism).

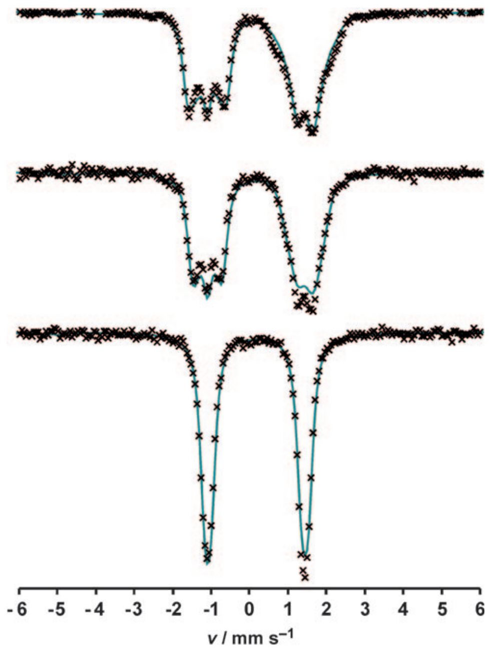

Figure 3. Applied-field Mössbauer spectra of [{Fe(tim)}$_2$] at 4 K and 1 T (bottom), 4 T (middle), 6 T (top). Blue lines represent the best fit obtained with $S_T=1$ (total spin state), $\delta=0.18$ mm s^{-1}, $\Delta E_Q=+2.54$ mm s^{-1}, $\eta=0.3$, $D=+13.01$ cm^{-1}, $E/D=0.08$, $g_x=g_y=g_z=2.00$, $[A/g_N\beta_N]$: $A_{xx}=-7.69$ T, $A_{yy}=-14.48$ T, $A_{zz}=-44.11$ T. Isomer shift relative to α-Fe at 298 K.

[{Fe(tim)}$_2$] dimer is not supported further by bridging ligands.[15c] The only other examples of Fe–Fe bonds in the absence of bridging ligands are found among Fe carbonyl compounds containing low-valent Fe^{I} or Fe^{0} centers.[16–19] Thus, [{Fe(tim)}$_2$] represents the only example, to our knowledge, of "untethered" metal–metal bonding in an iron complex comprised of Werner-type ligands.[20,21] The Fe–Fe bond of [{Fe(tim)}$_2$] is fairly weak; the two metal centers are separated by 2.69 Å.[22] Each square-pyramidal Fe center is displaced from the N$_4$ cavity plane by 0.26 Å. The two coordinated macrocycles are staggered with respect to their α-diimine units; the twist angle is approximately 15° shy of perpendicular. A significant shortening of all four diimine C–C bonds (C–C$_{av}$ 1.398(3) Å) is apparent compared to the analogous bond lengths of [Fe^{II}(tim)(MeCN)]$^{2+}$; the average diimine C–N bonds (1.355(3) Å) are consequently longer than in the starting compound. This change clearly demonstrates the reduction of all four diimine units, compatible with either tim^{2-} or tim^{3-} ligands. Concomitantly, the presence of a ferrous or a ferric ion is implied; both Fe^{II} and Fe^{III} would adopt an intermediate-spin ground state ($S_{Fe}=1$ or 3/2) in the square-planar N$_4$ donor environment.

Magnetic susceptibility data (Figure 2) for the Fe–Fe dimer affords $\mu_{\text{eff}}=2.9\,\mu_B$ (1 T, 2–300 K), consistent with an $S=1$ ground state for this compound. The applied-field Mössbauer spectra (Figure 3) are also consistent with the $S=1$ spin state of the molecule and yield an isomer shift of $\delta=0.18$ mm s^{-1} and a quadrupole splitting of $\Delta E_Q=+2.54$ mm s^{-1}. The Mössbauer data demonstrate the electronic equivalence of the two iron centers. The isomer shift and hyperfine coupling tensor (A) values are suggestive of intermediate-spin ferric compounds containing π-radical systems.[23] The electronic spectrum of [{Fe(tim)}$_2$] exhibits an absorption band at 598 nm ($\varepsilon\approx7000$ M^{-1} cm^{-1}) that mimics the characteristic chromophore in α-diimine-radical systems of iron.[14]

The spectroscopic data alone do not discriminate between the aforementioned [{Fe^{II}(tim^{2-})}$_2$] and [{Fe^{III}(tim^{3-})}$_2$] resonance structures. A viable electronic configuration can be envisioned for both an intermediate-spin ferrous or intermediate-spin ferric species (Figure S5 in the Supporting Information). However, neither formulation presents a convincing argument for the strongly energetically favorable $S=1$ ground state of the dimeric compound over its $S=0$ counterpart ($\Delta E>50$ kcal mol^{-1}, based on DFT calculations).

DFT computational analysis on [{Fe(tim)}$_2$] yields excellent agreement between the geometry-optimized and the crystallographically determined structures (Table S2 in the Supporting Information). The DFT-calculated Mössbauer

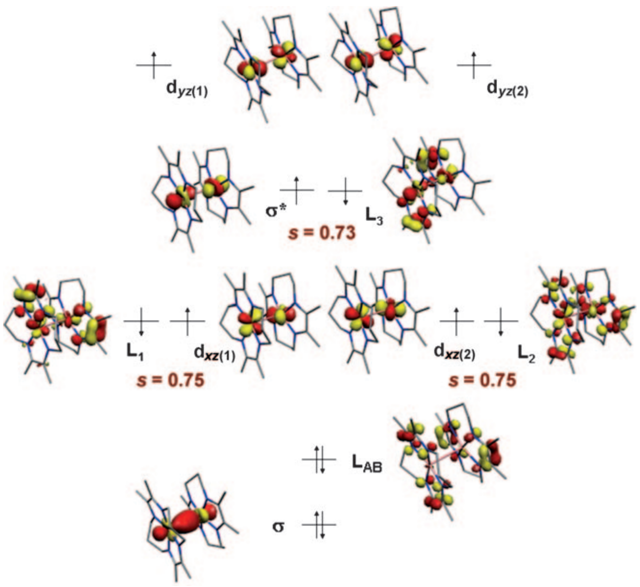

Figure 4. DFT-derived (B3LYP) qualitative MO diagram for $[\{Fe(tim)\}_2]$; spatial overlap (s) is indicated; z axis is along the Fe—Fe bond.

spectroscopy parameters are also in accord with experimental values (calculated: $\delta = 0.19\ mm\,s^{-1}$, $\Delta E_Q = 1.76$). The DFT calculations suggest that a more accurate electronic structure for the dimeric complex is represented by a mixed-valence species—with respect to both the metal and ligand—described as $[\{Fe^{2.5}(tim^{2.5-})\}_2]$. The DFT-derived qualitative molecular orbital (MO) scheme (Figure 4) depicts a doubly occupied σ orbital that stems from the d_{z^2}–d_{z^2} interaction between the two Fe ions and accounts for the metal–metal bond. A purely ligand-centered orbital (L_{AB}) signifies partial closed-shell, two-electron-reduced α-diimine character. Three additional ligand-centered singly occupied MOs (SOMOs) are also found, each antiferromagnetically coupled to corresponding metal-centered SOMOs ($d_{xz(1)}$, $d_{xz(2)}$, and σ*). The two remaining unpaired electrons on the metal center occupy degenerate near-orthogonal Fe d_{yz} orbitals and are responsible for the triplet ground state of the molecule.

Strong spatial orbital overlap ($s \approx 0.7$) is observed between three pairs of metal-centered and ligand-centered SOMOs, such that the total spin state $S_T = 1$. The singly occupied σ* orbital signifies an overall formal metal–metal bond order of 0.5 and explains the long Fe—Fe bond length. More importantly, the presence of one unpaired electron in the σ* orbital, delocalized over both metal centers, effects strong exchange interactions between the Fe centers and dictates the parallel alignment of the metal spins. Consequently, an $S = 1$ ground state results from the two unpaired, parallel spins in the Fe d_{yz} orbitals. Electron delocalization over the metal- and ligand-centered orbitals and significant covalent interactions, as denoted by the DFT calculations, illustrate the difficulty in assigning precise Fe and tim oxidation states. Thus, while the $[\{Fe^{2.5}(tim^{2.5-})\}_2]$ formulation readily accounts for the bonding and magnetism of the dimer, at present we cannot unequivocally exclude the alternate possibilities afforded by the resonant $[\{Fe^{II}(tim^{2-})\}_2]$ and $[\{Fe^{III}(tim^{3-})\}_2]$ structures.

The demonstrated redox non-innocence of the tim ligand in the $[\{Fe(tim)\}_2]$ complex is certain to be relevant to the chemistry of similar α-diimine-based macrocyclic ligands. The redox participation of such ligands has broad implications for the reactivity of metal compounds coordinated by unsaturated N_4 macrocycles, particularly given the breadth of redox and catalytic studies on reactions of these systems towards dioxygen and hydrogen activation.[24,25]

Experimental Section

All syntheses were carried out under an inert atmosphere using standard Schlenk and glovebox techniques. For details on physical methods, see the Supporting Information.

$[Fe(tim)(MeCN)_2](PF_6)_2$ was synthesized according to literature procedures.[15a]

$[\{Fe(tim)\}_2]$: A typical synthesis involved the addition of 2–3 equivalents Na (as 5% or 10% Na/Hg beads, 0.63 mmol Na) to a suspension of $[Fe(tim)(MeCN)_2](PF_6)_2$ (0.154 g, 0.228 mmol) in dry THF (10 mL). The solution was stirred overnight, during which time the solution became indigo in color. The solution was subsequently filtered over celite, and the product was recrystallized by vapor diffusion of diethyl ether into the THF solution (yield 0.05 g, 72%). The same method yielded single crystals suitable for X-ray analysis. Elemental analysis calcd for $C_{28}H_{48}N_8Fe_2$: C 55.27, H 7.95, N 18.42; found: C 55.31, H 7.93, N 18.40. UV/Vis: λ_{max} ($\varepsilon = M^{-1}cm^{-1}$) in THF: 578 (7000), 724 nm sh (2000).

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[1] D. C. Rees, *Annu. Rev. Biochem.* **2002**, *71*, 221.
[2] M. P. Hendrich, W. Gunderson, R. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu, J. C. Peters, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17107.
[3] N. P. Mankad, M. T. Whited, J. C. Peters, *Angew. Chem.* **2007**, *119*, 5870; *Angew. Chem. Int. Ed.* **2007**, *46*, 5768.
[4] C. C. Lu, C. T. Saouma, M. W. Day, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 4.
[5] S. Stoian, Y. Yu, J. M. Smith, P. L. Holland, E. L. Bominaar, E. Münck, *Inorg. Chem.* **2005**, *44*, 4915.
[6] J. L. Kisko, T. Hascall, G. Parkin, *J. Am. Chem. Soc.* **1998**, *120*, 10561.
[7] T. Mashiko, C. A. Reed, K. J. Haller, W. R. Scheidt, *Inorg. Chem.* **1984**, *23*, 3192.
[8] G. S. Srivatsa, D. T. Sawyer, N. J. Boldt, D. F. Bocian, *Inorg. Chem.* **1985**, *24*, 2123.
[9] M. C. Rakowski, D. H. Busch, *J. Am. Chem. Soc.* **1975**, *97*, 2570.
[10] tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.
[11] J. G. J. Norman, L. M. Chen, C. M. Perkins, N. J. Rose, *Inorg. Chem.* **1981**, *20*, 1403.
[12] C. C. Lu, E. Bill, T. Weyhermüller, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **2008**, *130*, 3181.
[13] N. Muresan, K. Chłopek, T. Weyhermüller, F. Neese, K. Wieghardt, *Inorg. Chem.* **2007**, *46*, 5327.
[14] K. Chłopek, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2005**, *44*, 7087.

[15] a) D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, N. J. Rose, *J. Am. Chem. Soc.* **1973**, *95*, 5152; b) CCDC 719467 ([{Fe(tim)}$_2$]) and 719468 ([Fe(tim)(MeCN)$_2$](PF$_6$)$_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. c) Residual densities in the crystal structure refinement were carefully checked, but no significant density was found between the Fe centers.

[16] C. F. Putnik, J. J. Welter, G. D. Stucky, M. J. J. D'Aniello, B. A. Sosinsky, J. F. Kirner, E. L. Muetterties, *J. Am. Chem. Soc.* **1978**, *100*, 4107.

[17] H. Deng, S. G. Shore, *Inorg. Chem.* **1992**, *31*, 2289.

[18] D. Luart, M. Sellin, P. Laurent, J.-Y. Salauen, R. Pichon, L. Toupet, H. Des Abbayes, *Organometallics* **1995**, *14*, 4989.

[19] T. M. Bockman, H.-C. Cho, J. K. Koch, *Organometallics* **1995**, *14*, 5221.

[20] F. A. Cotton, L. M. Daniels, J. H. Matonic, C. A. Murillo, *Inorg. Chim. Acta* **1997**, *256*, 277.

[21] C. A. Murillo, *Multiple Bonds Between Metal Atoms*, 3rd ed., Springer, New York, **2005**.

[22] Fe−Fe bond lengths in Fe carbonyl compounds (in the absence of bridging ligands) vary from 2.78–3.14 Å(see Ref. [16–19]). Single Fe−Fe bond lengths of 2.2–3.12 Å are reported for binuclear compounds containing tethered N donor and bridging carbonyl ligands (see Ref. [20,21]).

[23] K. Chłopek, N. Muresan, F. Neese, K. Wieghardt, *Chem. Eur. J.* **2007**, *13*, 8390.

[24] X. Hu, B. S. Brunschwig, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 8988.

[25] J. F. Endicott, B. Durham in *Coordination Chemistry of Macrocyclic Compounds* (Ed.: G. A. Melson), Plenum, New York, **1979**, pp. 393.