Iron–Sulfur Clusters

DOI: 10.1002/anie.201401018

Low-Spin Pseudotetrahedral Iron(I) Sites in $Fe_2(\mu\text{-}S)$ Complexes**

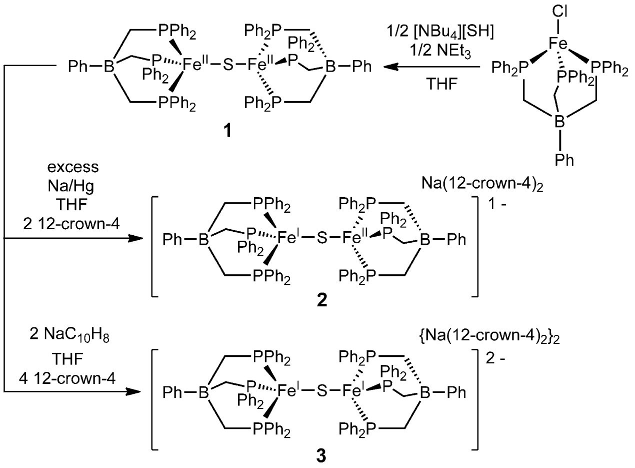
*John S. Anderson and Jonas C. Peters**

Dedicated to Professor Gregory L. Hillhouse

Abstract: *Fe^I centers in iron–sulfide complexes have little precedent in synthetic chemistry despite a growing interest in the possible role of unusually low valent iron in metalloenzymes that feature iron–sulfur clusters. A series of three diiron $[(L_3Fe)_2(\mu\text{-}S)]$ complexes that were isolated and characterized in the low-valent oxidation states Fe^{II}–S–Fe^{II}, Fe^{II}–S–Fe^I, and Fe^I–S–Fe^I is described. This family of iron sulfides constitutes a unique redox series comprising three nearly isostructural but electronically distinct $Fe_2(\mu\text{-}S)$ species. Combined structural, magnetic, and spectroscopic studies provided strong evidence that the pseudotetrahedral iron centers undergo a transition to low-spin $S = 1/2$ states upon reduction from Fe^{II} to Fe^I. The possibility of accessing low-spin, pseudotetrahedral Fe^I sites compatible with S^{2-} as a ligand was previously unknown.*

Fe–S–Fe linkages are common to a host of metalloenzymes that mediate metabolic transformations central to life. Iron–sulfur clusters composed of these linkages frequently perform roles associated with electron transfer and redox processes,[1] and research into the synthesis and characterization of model complexes of these clusters featuring Fe^{II} and Fe^{III} has been an area of intense study.[2] Holm and co-workers pioneered the synthesis of Fe–S clusters featuring exclusively Fe^{II} centers.[3] However, although unusually low formal oxidation states of Fe (e.g., Fe^I and Fe^0) have been implicated in the function of hydrogenase and nitrogenase enzymes, in which bridging sulfur atoms are present,[4,5] low-valent Fe species bound to two-coordinate sulfide are without ample precedent in synthetic coordination chemistry. It is therefore of interest to understand whether the sulfide structural unit is compatible with unusually low valent Fe centers, and if so, what electronic structures and reactivity patterns might be expected.

In this context, Holland and co-workers recently reported the singular example of a synthetic complex featuring Fe^I centers ligated to sulfide (S^{2-}). The complex was formed by the reduction of $[\{(HC(CMeN(2,6\text{-diisopropylphenyl}))_2)Fe\}_2\text{-}\{\mu\text{-}S\}]$ to a doubly reduced diiron(I) species.[6] Our research group has also had an interest in the study of unusually low valent Fe–X–Fe linkages, for example, in which the bridging X unit is either imide (NH^{2-}) or nitride (N^{3-}).[7] Herein, we describe a series of diiron $Fe_2(\mu\text{-}S)$ complexes in the formal oxidation states Fe^{II}–S–Fe^{II}, Fe^{II}–S–Fe^I, and Fe^I–S–Fe^I (Scheme 1). This family of iron sulfide complexes constitutes a unique set of three isolable and nearly isostructural, but electronically distinct, low-valent $Fe_2(\mu\text{-}S)$ species. Additionally, combined structural, magnetic, and spectroscopic studies provided strong evidence that the Fe centers undergo a transition to low-spin $S = 1/2$ states upon reduction. The possibility of accessing low-spin, pseudotetrahedral Fe^I sites compatible with S^{2-} as a ligand was previously unknown.



Scheme 1. Synthesis of an $[(L_3Fe)_2(\mu\text{-}S)]^{n-}$ redox series ($n = 0, 1, 2$).

Use of $[NBu_4][SH]$ as a sulfur source enabled the synthesis of $[([PhBP_3]Fe)_2(\mu\text{-}S)]$ (**1**) as a dark-brown powder in moderate yield (51% isolated; Scheme 1) from the chloride precursor $[PhBP_3]FeCl$ ($[PhBP_3] = [PhB(CH_2PPh_2)_3]$).[8] The cyclic voltammogram of **1** (see the Supporting Information) displayed two reversible reductions that were assigned as the $Fe^{II}Fe^{II}/Fe^{II}Fe^I$ and $Fe^{II}Fe^I/Fe^IFe^I$ couples at −1.52 and −2.30 V versus Fc/Fc^+, respectively. Chemical reduction of **1** with Na/Hg amalgam resulted in a color change from dark brown to a deep green. Addition of [12]crown-4 and crystallization provided $[([PhBP_3]Fe)_2(\mu\text{-}S)][Na([12]crown\text{-}4)_2]$ (**2**) as a nearly black solid in 76% yield. When **1** was instead exposed to $NaC_{10}H_8$ (2 equiv), an almost black

---

[*] J. S. Anderson, Prof. J. C. Peters
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125 (USA)
E-mail: jpeters@caltech.edu

[**] This research was supported by the NIH (GM 070757). J.S.A. gratefully acknowledges a GRFP award from the NSF. Po-Heng Lin, Jay Winkler, Bruce Brunschwig, Harry Gray, and Dave Harris are thanked for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201401018.

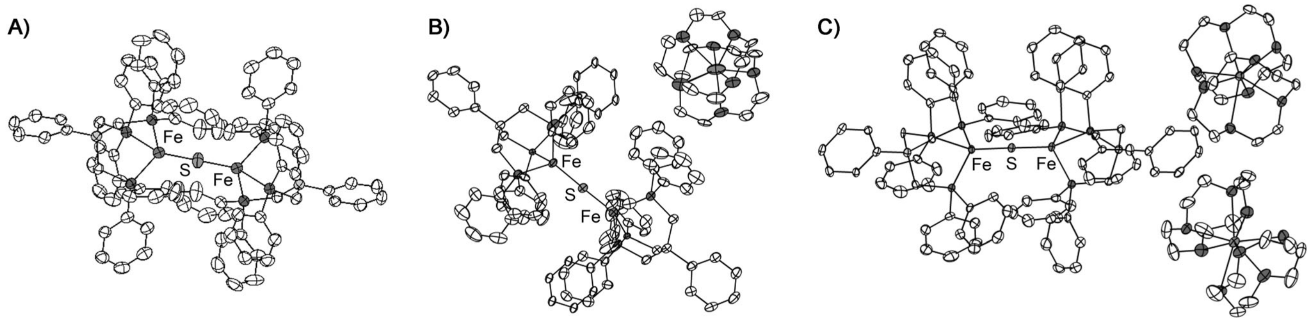


Figure 1. XRD structures of complexes A) **1**, B) **2**, and C) **3**, shown with ellipsoids at 50% probability and hydrogen atoms omitted for clarity.

solution resulted; this solution could be treated with [12]crown-4 and crystallized in an analogous manner to yield [([PhBP$_3$]Fe)$_2$(μ-S)][Na(12-crown-4)$_2$]$_2$ (**3**) as a black solid in 49% yield.

Species **1**, **2**, and **3** are an unusual iron–sulfide redox series, and hence more thorough characterization was undertaken, including single-crystal XRD studies (Figure 1). The Fe–S bond lengths in **1**–**3** are short when compared with previously reported Fe–S bond lengths for bridging sulfides (avg. 2.22 Å).[9] In fact, the Fe–S bond length of 2.071(1) Å in **3** is within error the shortest bond between Fe and sulfide reported in the CSD, with a close value of 2.078(8) Å for [Fe$_2$S$_2$(C$_4$H$_4$N)$_4$][NBu$_4$]$_2$ reported by Coucouvanis and co-workers.[10] The short Fe–S distances in **1**–**3** suggest an appreciable amount of multiple bonding between Fe and S, as has been observed in other linear sulfide-bridged complexes of mid to late first-row transition metals.[11] The Fe–S bond distances in **1**, **2**, and **3** differ only by 0.032 Å, suggesting little perturbation of the bonding in the Fe–S–Fe manifold upon reduction (Table 1).

Table 1: Selected bonding metrics for complexes **1**–**3**.

Complex	Fe–S [Å]	Fe–S–Fe [°]	Avg. Fe–P [Å]	Δ Fe–P [Å]
1	2.079(8)	180	2.393	0.04
2	2.1035(3)	173.18(5)	2.215	0.19
3	2.077	178.83(6)	2.170	0.04

All three complexes display nearly, or perfectly in the case of **1**, linear Fe–S–Fe bond angles. Fe–S–Fe linkages are more typically bent, as in the example reported by Coucouvanis and co-workers.[10] The steric profile of [PhBP$_3$] allows for a significantly bent Fe–X–Fe angle, as exemplified in a structurally related Fe$_2$(μ-N) nitride complex previously characterized by our research group.[7] This consideration suggests an electronic origin of the linearity of the Fe–S–Fe linkages in **1**–**3**. Whereas the bond distances in **1** are consistent with previously synthesized high-spin phosphine-ligated Fe^{II} complexes from our laboratory,[8,12] a contraction of 0.22 Å in the average Fe–P bond length is apparent upon reduction from **1** to **3** and results in an unusually short average Fe–P bond distance of 2.17 Å in **3** (the average Fe–*P*R$_3$ distance from the CSD is 2.24 Å).[9] Increased back-bonding into the phosphine ligands would explain some contraction in these lengths, but the magnitude of the change suggests that there may be additional factors involved, such as a spin-state change. To probe this possibility, we acquired variable-temperature magnetic-susceptibility data on **1**–**3** by SQUID magnetometry.

At room temperature, complex **1** displays a magnetic moment of 2.0 μ_B, which is much smaller than the spin-only value of 6.9 μ_B that is predicted for two noninteracting high-spin Fe^{II} centers.[13] The variable-temperature magnetic-susceptibility data for **1** from 2 to 300 K are shown in Figure 2 and show a decrease in the magnetic moment upon cooling. This phenomenon is consistent with antiferromagnetic coupling between the two Fe centers, and a simulation with a coupling constant of $J = -154$ cm^{-1} provided a reasonable fit to the data (Figure 2). Antiferromagnetic coupling through a linear one-atom bridge is common, and this behavior has been observed in other Fe–S–Fe complexes.[6b,14]

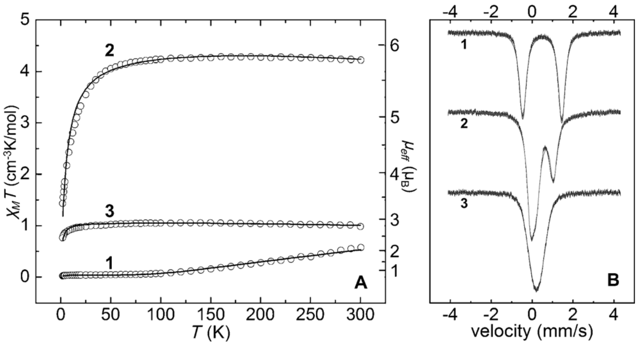


Figure 2. A) Variable-temperature magnetic-susceptibility data for **1**–**3** at a field of 0.5 T, and fits shown as solid lines with the parameters shown in the Supporting Information. B) Mössbauer data for **1**–**3** at 80 K, and fits shown as solid lines with the parameters shown in the Supporting Information.

In contrast to **1**, **2** displayed a high magnetic moment of 5.8 μ_B at 300 K, and this moment remained nearly constant upon cooling to about 50 K before dropping at lower temperatures, presumably as a result of intermolecular antiferromagnetic interactions. For a high-spin $S_1 = 2$ and $S_2 = 3/2$ case, the spin-only moment for two noninteracting Fe centers is 6.2 μ_B,[13] which is higher than that observed for **2** above 50 K. Antiferromagnetic coupling seems unlikely, as the magnetic moment did not decrease upon cooling. An $S = 1/2$ ground state would also be expected from an antiferromagnetically coupled system, but the X-band EPR spectrum of **2** at 4 K (see the Supporting Information) shows a strong feature located near $g = 5$, inconsistent with an $S = 1/2$ ground state. Correspondingly, fits of the magnetic susceptibility for an $S_1 = 2$ and $S_2 = 3/2$ state with even modest negative values of J provided very poor fits to the data (see the Supporting Information). The 300 K moment of 5.8 μ_B is near the spin-only value of one $S = 5/2$ center (5.9 μ_B), thus suggesting that either an $S_1 = 2$ and $S_2 = 1/2$ or an $S_1 = 1$ and $S_2 = 3/2$ spin-state assignment with strong ferromagnetic coupling between the two metal centers could be an appropriate model. Simulations using either of these spin-state descriptions can provide a good fit to the susceptibility data (see Figure 2 and the Supporting Information). For the additional reasons given below, we prefer an $S_1 = 2$ and $S_2 = 1/2$ assignment for **2** with $J = 100\ \text{cm}^{-1}$.

An increase in magnetic moment is typically observed upon cooling in ferromagnetic systems.[13] It results from an increase in the population of higher spin states as the temperature is lowered. At sufficiently large ferromagnetic couplings, a high-spin ground state becomes thermally well separated from lower-spin excited states, and a plateau in the moment is observed. Such behavior has been observed in other strongly coupled systems.[15] The large coupling in **2** is thus in accord with the relatively temperature independent profile of its magnetic moment above 50 K. Whereas the fit of the susceptibility data of **2** requires the coupling constant to be large and positive, the magnitude of J is sensitive to minor perturbations in the fit and diamagnetic correction, thus implying substantial uncertainty in the value of J. The presence of coupling between the two Fe centers in **2** is further corroborated by an intervalence charge-transfer (IVCT) band at 6750 cm^{-1} in the near-IR spectrum of **2**. Analysis of this band (see the Supporting Information) suggests that **2** is well-described as a Class II mixed-valence species according to the Robin–Day classification scheme.[16]

The variable-temperature magnetic data for complex **3** also display a nearly flat moment upon cooling from 300 to 50 K. A similar analysis to that performed for **2** suggests that the high-spin $S_1 = S_2 = 3/2$ case should show a spin-only value of 5.5 μ_B for uncoupled Fe centers: much larger than that observed. If one assumes a low-spin configuration at both Fe centers and a ferromagnetic coupling constant of $J = 110\ \text{cm}^{-1}$, a satisfactory fit to the magnetic data is obtained. The assignment of **3** as a ferromagnetically coupled low-spin Fe^{I}/Fe^{I} complex suggests by extension that the assignment of **2** as an $S_1 = 2$ and $S_2 = 1/2$ species is plausible and is perhaps the best model of those we have considered. Such a low-spin assignment for **2** (and **3**), although highly unusual for an iron–sulfide complex, seems to us plausible by comparison with previous examples of low-spin pseudotetrahedral L$_3$Co^{II}X complexes of the same trisphosphine ligand scaffold.[17]

We turned to Mössbauer spectroscopy to further probe the Fe sites in **1**–**3** (Figure 2B). Complex **1** shows a quadrupole doublet (80 K) with an isomer shift of $\delta = 0.49\ \text{mm s}^{-1}$ and a quadrupole splitting of $\Delta E_q = 1.91\ \text{mm s}^{-1}$. These values are similar to data for related trisphosphine Fe^{II} complexes reported by our research group.[18] Upon reduction to **2**, the quadrupole doublet shifts slightly to $\delta = 0.47\ \text{mm s}^{-1}$ and contracts to $\Delta E_q = 1.14\ \text{mm s}^{-1}$. Additionally, a new feature in a 1:1 ratio with the doublet appears in the spectrum at $\delta = 0.16\ \text{mm s}^{-1}$, which can be fit with an almost negligible quadrupole splitting of $\Delta E_q = 0.01\ \text{mm s}^{-1}$. The two Fe sites in **2** are hence well-resolved on the Mössbauer timescale. The Mössbauer spectrum of **3** shows a single broad feature centered at $\delta = 0.22\ \text{mm s}^{-1}$ with quadrupole splitting that is too small to be resolved. Fe^{I} complexes structurally related to **2** and **3** that have been previously characterized by Mössbauer spectroscopy, for example, [[PhBP$_3$]Fe(PMe$_3$)], are high-spin, and have parameters that do not agree well with those obtained for the reduced sites in **2** and **3**, thus suggesting distinct electronic structures for the present case.[18] An increase in the isomer shift δ is most typically observed upon reduction of an Fe system, in contrast to the trend observed for **1**–**3**.[19] The negative shift that is instead observed presumably results from the high covalency present in these low-valent [(L$_3$Fe)$_2$(μ-S)] cores.

The collection of data presented suggests that upon reduction of the high–spin Fe$_2$(μ-S) complex **1** to **2**, a reduced Fe^{I} center results that populates a low-spin $S = 1/2$ state instead of an $S = 3/2$ state akin to that of Fe sites in the diiron(I) sulfide system described by Holland and co-workers.[6] Further reduction to **3** provides two ferromagnetically coupled low-spin d^7 Fe^{I} centers. In addition to the susceptibility data presented, these conclusions are supported by the substantially shortened Fe–P bond distances observed upon successive reductions. The Mössbauer data collected on **1**–**3** are also consistent with this model, as they show values corresponding to high-spin Fe^{II} centers for complex **1** but new features that are distinct from those of previously reported high-spin Fe^{I} complexes of similar geometries supported by the [PhBP$_3$] ligand auxiliary.

The magnetic data associated with complexes **1**–**3** and the unusual observation of low-spin, tetrahedral Fe^{I} sites within an [(L$_3$Fe)$_2$(μ-S)] system deserves some additional comment. Analysis of a qualitative d-orbital-splitting diagram with no explicit coupling depicted helps to suggest an array of coupling interactions imposed by the spin-state change that may account for the observed magnetic behavior (Figure 3). In complex **1**, antiferromagnetic exchange is expected to

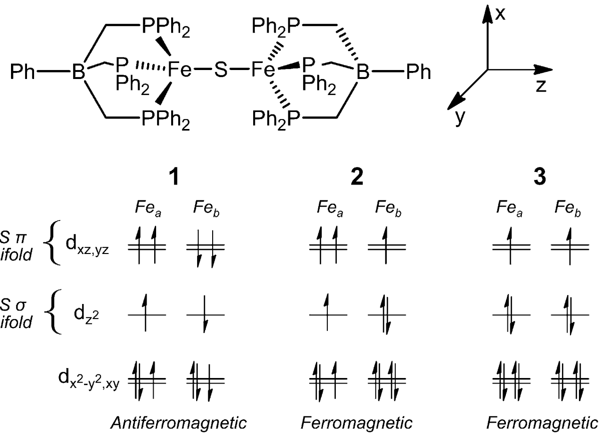


Figure 3. Qualitative d-orbital-splitting diagrams illustrating the orbitals involved in coupling in complexes **1**–**3**.

occur through both the σ and π manifolds via the half-populated d_{z^2} and $d_{xz,yz}$ orbitals. Upon reduction, and the double population of one d_{z^2} orbital as a result of a transition to a low-spin d^7 center, the coupling interaction mediated through the σ manifold, which should dominate, instead becomes ferromagnetic. Upon further reduction to **3**, the σ manifold becomes completely filled as a result of the presence of two low-spin d^7 centers. A ferromagnetic interaction is observed and results from the π manifold as required by the Hund rule.[20] Although speculative, this orbital picture provides a simple intuitive explanation for the observed magnetism in **1**–**3**. Further investigations, including theoretical calculations and variable-field magnetic studies, are warranted to more fully understand this electronically unusual iron–sulfide series.

Received: January 30, 2014

Keywords: diiron complexes · hydrogenases · iron–sulfur clusters · low-spin iron(I) · nitrogenases

---

[1] a) H. Beinert, R. H. Holm, E. Münck, *Science* **1997**, *277*, 653–659; b) D. C. Johnson, D. R. Dean, A. D. Smith, M. K. Johnson, *Annu. Rev. Biochem.* **2005**, *74*, 247–281.
[2] a) R. H. Holm, P. Kennepohl, E. I. Solomon, *Chem. Rev.* **1996**, *96*, 2239–2314; b) P. V. Rao, R. H. Holm, *Chem. Rev.* **2004**, *104*, 527–559; c) Y. Ohki, M. Imada, A. Murata, Y. Sunada, S. Ohta, M. Honda, T. Sasamori, N. Tokitoh, M. Katada, K. Tatsumi, *J. Am. Chem. Soc.* **2009**, *131*, 13168–13178.
[3] a) T. A. Scott, C. P. Berlinguette, R. H. Holm, H. C. Zhou, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 9741–9744; b) L. Deng, R. H. Holm, *J. Am. Chem. Soc.* **2008**, *130*, 9878–9886; c) M. Chakrabarti, L. Deng, R. H. Holm, E. Münck, E. L. Bominaar, *Inorg. Chem.* **2009**, *48*, 2735–2747.
[4] a) D. J. Evans, C. J. Pickett, *Chem. Soc. Rev.* **2003**, *32*, 268–275; b) J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, *Chem. Rev.* **2007**, *107*, 4273–4303.
[5] a) O. Einsle, F. A. Tezcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard, D. C. Rees, *Science* **2002**, *297*, 1696–1700; b) P. C. Dos Santos, R. Y. Igarashi, H. I. Lee, B. M. Hoffman, L. C. Seefeldt, D. R. Dean, *Acc. Chem. Res.* **2005**, *38*, 208–214; c) L. C. Seefeldt, B. M. Hoffman, D. R. Dean, *Annu. Rev. Biochem.* **2009**, *78*, 701–722.
[6] a) J. Vela, S. Stoian, C. J. Flaschenriem, E. Münck, P. L. Holland, *J. Am. Chem. Soc.* **2004**, *126*, 4522–4523; b) M. M. Rodriguez, B. D. Stubbert, C. C. Scarborough, W. W. Brennessel, E. Bill, P. L. Holland, *Angew. Chem.* **2012**, *124*, 8372–8375; *Angew. Chem. Int. Ed.* **2012**, *51*, 8247–8250.
[7] a) S. D. Brown, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 1913–1923; b) S. D. Brown, M. P. Mehn, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 13146–13147.
[8] S. D. Brown, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 322–323.
[9] Cambridge Structural Database, 2011 update: F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380–388.
[10] A. Salifoglou, A. Simopoulos, A. Kostikas, R. W. Dunham, M. G. Kanatzidis, D. Coucouvanis, *Inorg. Chem.* **1988**, *27*, 3394–3406.
[11] a) C. Mealli, S. Midollini, L. Sacconi, *Inorg. Chem.* **1978**, *17*, 632–637; b) T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins, J. Trotter, *Inorg. Chem.* **1979**, *18*, 3543–3548; c) J. Mautz, G. Huttner, *Eur. J. Inorg. Chem.* **2008**, 1423–1434.
[12] a) T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 10782–10783; b) S. D. Brown, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 4538–4539; c) C. C. Lu, C. T. Saouma, M. W. Day, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 4–5.
[13] O. Kahn, *Molecular Magnetism*, Wiley, New York, **1993**.
[14] R. N. Mukherjee, T. D. P. Stack, R. H. Holm, *J. Am. Chem. Soc.* **1988**, *110*, 1850–1861.
[15] a) O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin, Y. Jeannin, *Inorg. Chem.* **1983**, *22*, 2877–2883; b) F. Birkelbach, M. Winter, U. Floerke, H.-J. Haupt, C. Butzlaff, M. Lengen, E. Bill, A. X. Trautwein, K. Wieghardt, P. Chaudhuri, *Inorg. Chem.* **1994**, *33*, 3990–4001; c) A. Escuer, M. A. S. Goher, F. A. Mautner, R. Vicente, *Inorg. Chem.* **2000**, *39*, 2107–2112.
[16] P. Schatz in *Inorganic Electronic Structure and Spectroscopy, Vol. II* (Eds.: A. B. P. Lever, E. I. Solomon), Wiley, New York, **1999**.
[17] a) D. M. Jenkins, A. J. Di Bilio, M. J. Allen, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2002**, *124*, 15336–15350; b) D. M. Jenkins, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 7148–7165.
[18] M. P. Hendrich, W. Gunderson, R. K. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu, J. C. Peters, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17107–17112.
[19] L. R. Walker, G. K. Wertheim, V. Jaccarino, *Phys. Rev. Lett.* **1961**, *6*, 98–101.
[20] G. F. Dionne, *Magnetic Oxides*, Springer Science + Business Media, LLC, **2010**, pp. 107–149.