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Spin Isolation of the [3Fe–4S] Fragment of a [4Fe–4S] Cluster: Electronic Properties of the $[3Fe–4S]^0$ Cluster

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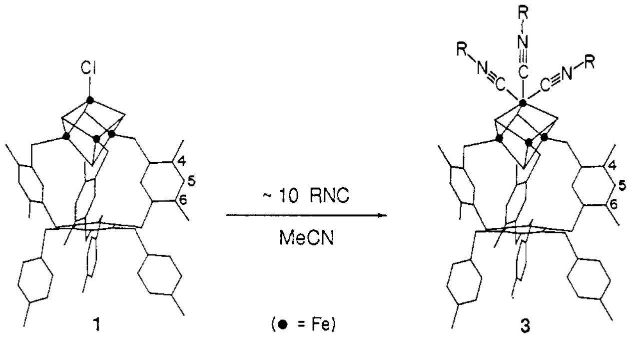
The cluster $[Fe_4S_4(LS_3)Cl]^{2-}$ (**1**), designed for investigation of subsite-specific properties of biological [4Fe–4S] clusters,[1] undergoes stoichiometric Cl^-/RS^- substitution reactions at the unique subsite only.[1,2] Changes in the highly sensitive ^{1}H NMR isotropic shifts[1-3] have demonstrated subsite-specific substitution reactions of **1** with a wide variety of ligands.[4] All spectra are consistent with cluster products of effective trigonal symmetry. In nearly all cases, isotropic shifts are sufficiently similar to demonstrate a common $S = 0$ ground state, a behavior exemplified by **1** and $[Fe_4S_4(LS_3)CN]^{2-}$ (**2**) whose [4-Me, 5-H, 6-Me] shifts (ppm, Me_2SO-d_6, 297 K) are as follows: **1** [−1.98, −1.43, −1.86] and **2** [−2.00, −1.31, −1.77]. However, this is not the case with clusters obtained from reactions with the stronger π-acid ligands RNC.[4]

In an equilibrium system with 10 equiv of t-BuNC, substitution of **1** yields $[Fe_4S_4(LS_3)(t\text{-}BuNC)_3]^{1-}$ (**3**), whose ^{1}H NMR spec- NMR spectrum indicates trigonal symmetry and demonstrates from signal integrations the indicated composition. The isotropic shifts of **3** [−9.09, −9.65, −12.98 ppm; Me_2SO-d_6, 297 K] are 5–8 times larger than those of **1** and **2**, indicating a $S > 0$ ground state. The solution moment $\mu_{eff} = 5.35\ \mu_B$ (Me_2SO, 297 K) is consistent with $S = 2$. The nature of this unprecedented spin change was clarified by Mössbauer spectra of an isolated salt of **3**.[5]



1 (● = Fe) **3**

The Mössbauer properties of **3** are best understood with reference to the spectra of *Desulfovibrio gigas* ferredoxin II (Fd II) in the $[Fe_3S_4]^0$ state[6,7] (Figure 1A), which has $S = 2$ and a subsite-voided cubane-type structure.[8] The zero-field spectrum of Fd II at 4.2 K consists of two quadrupole doublets in a 2:1 area ratio. Indistinguishable subsites 1 and 2 are a Fe^{3+}/Fe^{2+} delocalized pair ($Fe^{2.5+}$) with magnetic hyperfine coupling constant $A < 0$, whereas site 3 is trapped-valence Fe^{3+} with $A > 0$.[7] These features are an unambiguous signature of all $[Fe_3S_4]^0$ clusters studied thus far.[6,7,9-13] The 4.2 K spectrum of **3** (Figure 1B) can be deconvoluted into four doublets of equal area (Table I). Three of the doublets have parameters similar to those of Fd II, whereas the fourth, undoubtedly from the unique subsite, has parameters typical of low-spin Fe(II). Applied field spectra (Figure 2) confirm this interpretation.

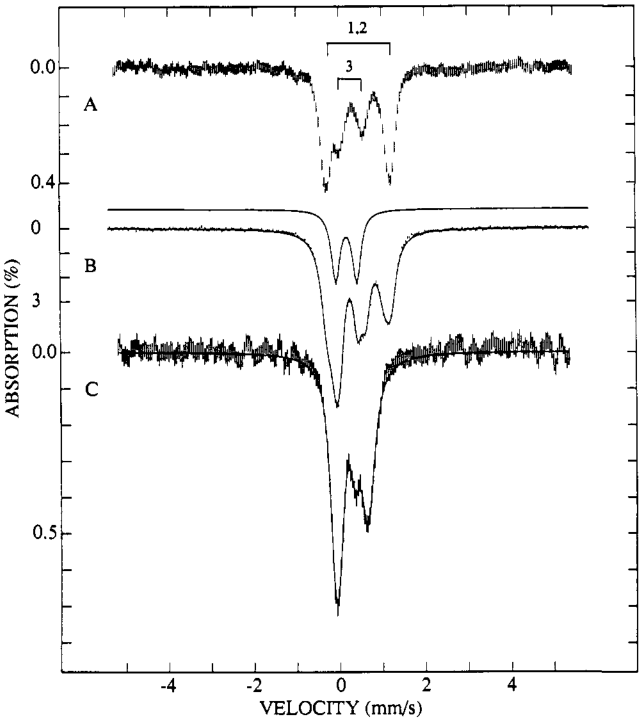


Figure 1. Zero-field Mössbauer spectra of reduced *D. gigas* Fd II[6] (A) and $(Ph_4P)[3]$ (B, C) at 4.2 K (A, B) and 260 K (C). The doublets of Fd II subsite 3 (Fe^{3+}) and delocalized pair subsites 1 and 2 ($Fe^{2.5+}$) are marked by the brackets. The solid line in spectrum B is a least-squares fit to four distinct sites with 1:1:1:1 area ratios (Table I). The doublet of the low-spin Fe^{2+} subsite is drawn separately above spectrum B. The solid line in spectrum C is a least-squares fit to two doublets with a 1:3 area ratio.

Table I. Mössbauer Parameters of $(Ph_4P)[3]$ at 4.2 K

site	δ,[a] mm/s	ΔE_Q, mm/s	type
1	0.46	1.21	$Fe^{2.5+}$
2	0.47	1.49	$Fe^{2.5+}$
3	0.34	0.59	Fe^{3+}
4	0.20	0.50	low-spin Fe^{2+}

[a] Referenced to Fe metal at 300 K.

Spectra measured at 1–6 T contain a component with zero internal magnetic field ($A = 0$), which can be simulated (solid line in Figure 2C) with the δ and ΔE_Q values of the unique subsite. Subtraction of the simulated spectrum from the raw data affords the spectrum of Figure 2B, which is strikingly similar to that of Fd II. Indeed, the former consists of a Fe^{3+} component (subsite

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(1) Stack, T. D. P.: Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2484. LS_3 = 1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(p-tolylthio)benzene(3−).

(2) Stack, T. D. P.; Carney, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1670.

(3) Holm, R. H.; Phillips, W. D.; Averill, B. A.; Mayerle, J. J.; Herskovitz, T. *J. Am. Chem. Soc.* **1974**, *96*, 2109. Isotropic shifts arise from population of states of the spin ladder with $S > 0$.

(4) Examples include CN^-, PhO^-, Me_3SiO^-, RNC (R = Me, Et, t-Bu, C_6H_{11}), $[H_2B(pz)_2]^{1-}$ (pz = 1-pyrazolyl), $[o\text{-}C_6H_4S_2]^{2-}$, $Et_2NCS_2{}^{1-}$, $[2\text{-}SC_5H_4N]^{1-}$, $Me_2PCH_2CH_2PMe_2$, $[HB(pz)_3]^{1-}$, $C_5H_5{}^{1-}$, and tacn (1,4,7-triazacyclononane).

(5) Addition of 1 equiv of $NaBF_4$ to an acetonitrile solution of $(Ph_4P)_2[1]$ followed by filtration (to eliminate NaCl) and removal of solvent from the filtrate containing 10 equiv of t-BuNC afforded $(Ph_4P)[3]$ as a black air-sensitive solid (ν_{NC} 2153, 2123 cm^{-1}, KBr; ν_{NC} (t-BuNC) 2140 cm^{-1}, CH_2Cl_2). Its ^{1}H NMR spectrum is identical with that of the product generated in solution.

(6) Moura, J. J. G.; Moura, I.; Kent, T. A.; Lipscomb, J. D.; Huynh, B. H.; LeGall, J.; Xavier, A. V.; Münck, E. *J. Biol. Chem.* **1982**, *257*, 6259.

(7) Papaefthymiou, V.; Girerd, J.-J.; Moura, I.; Moura, J. J. G.; Münck, E. *J. Am. Chem. Soc.* **1987**, *109*, 4703.

(8) Kissinger, C. R.; Adman, E. T.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1988**, *110*, 8721.

(9) Kent, T. A.; Dreyer, J.-L.; Kennedy, M. C.; Huynh, B. H.; Emptage, M. H.; Beinert, H.; Münck, E. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1096.

(10) Kent, T. A.; Emptage, M. H.; Merkle, H.; Kennedy, M. C.; Beinert, H.; Münck, E. *J. Biol. Chem.* **1985**, *260*, 6871.

(11) Emptage, M. H.; Kent, T. A.; Huynh, B. H.; Rawlings, J.; Orme-Johnson, W. H.; Münck, E. *J. Biol. Chem.* **1980**, *255*, 1793.

(12) Hille, R.; Yoshida, T.; Tarr, G. E.; Williams, C. H., Jr.; Ludwig, M. L.; Fee, J. A.; Kent, T. A.; Huynh, B. H.; Münck, E. *J. Biol. Chem.* **1983**, *258*, 13008.

(13) Huynh, B. H.; Patil, D. S.; Moura, I.; Teixeira, M.; Moura, J. J. G.; DerVartanian, D. V.; Czechowski, M. H.; Pickril, B. C.; Peck, H. D., Jr.; LeGall, J. *J. Biol. Chem.* **1987**, *262*, 795.

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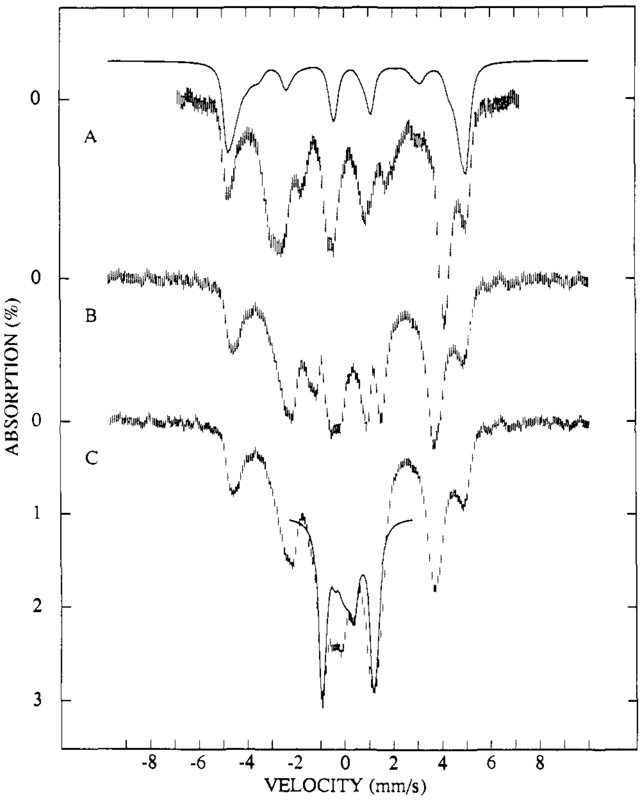

Figure 2. The Mössbauer spectra of *D. gigas* Fd II (A) and $(Ph_4P)[3]$ (C) recorded in a parallel field of 6.0 T at 4.2 K. Spectrum B was obtained by subtracting the theoretical spectrum of low-spin Fe^{2+} subsite 4 (solid line in spectrum C) from the data. The solid line above spectrum A is the contribution of Fe^{3+} subsite 3 in the $[3Fe{-}4S]^0$ cluster of Fd II.

3) with $A > 0$ and two slightly inequivalent components (subsites 1 and 2) with $A < 0$.[14] Above 100 K, the intensities of doublets 1–3 decrease with concomitant appearance of a new doublet. At 260 K, the spectrum consists of *two* doublets with a 3:1 area ratio, with the new doublet having isomer shift $\delta_{av} = 0.32$ mm/s and quadrupole splitting $\Delta E_Q = 0.70$ mm/s. Correcting for a second-order Doppler shift (0.10 mm/s) and referring δ_{av} to 4.2 K yields $\delta_{av}(4.2\ K) = 0.42$ mm/s. This value corresponds closely to the mean shift of sites 1–3, plausibly suggesting that the new doublet represents a valence-detrapped or valence-delocalized state of these sites.

From the preceding results, we draw these conclusions. (1) The $[Fe_4S_4]^{2+}$ core of **3** contains a unique hexacoordinate Fe(II) subsite which is *low*-spin and thus is not spin-coupled[15] to the remaining $[Fe_3S_4]^0$ cluster fragment (subsites 1–3). (2) The Mössbauer spectra of the fragment convincingly resemble those of protein $[Fe_3S_4]^0$ clusters, and with reference to the spin-coupling correlation diagram for the cluster,[6] the spin of **3** must be $S = 2$. (3) From conclusion 2, the electronic ground state of the fragment consists of a trapped-valence Fe^{3+} ($S = {}^5/_2$) and a delocalized pair ($S = {}^9/_2$). The spectral pattern of Figure 2, parts A and B, has been observed for a variety of core units, viz., protein-bound $[Fe_3S_4]^0$,[9-13] $[Fe_3Se_4]^0$,[16] and $[ZnFe_3S_4]^{2+}$,[15b] as well as for **3**. These observations persuasively suggest that the delocalized pair/Fe^{3+} electronic ground state is intrinsic to a cuboidal $[Fe_3S_4]^0$ cluster and is not a protein-induced property. From the studies reported here and other observations, we anticipate that the synthetic cluster will provide further valuable insights into the static and dynamic properties of the Fe_3S_4 core. The $[Fe_3S_4]^{1+}$ and $[Fe_3S_4]^{1-}$ states are potentially available from chemically reversible redox reactions with $E_{1/2} = -0.18$ and -1.09 V (CH_2Cl_2) vs SCE, respectively. Lastly, the structure at the unique subsite of **3** is likely to be biased toward that at the $Fe(CO)_3$ subsites of $Fe_4S_4(CO)_{12}$.[17] If so, the longer Fe–Fe and Fe–S core distances may facilitate removal of the unique Fe atom to yield cuboidal Fe_3S_4, thus far structurally proven only in supportive protein environments.[8,18,19]

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[14] The main difference between the spectra can be attributed to the larger zero-field splitting parameter of **3** ($D \approx -8$ cm^{-1}) vs that of Fd II ($D = -2.5$ cm^{-1}).

[15] In this sense, low-spin Fe(II) has the same function as Zn(II) in the artificial $[ZnFe_3S_4]^{1+,2+}$ clusters of Fd II: (a) Surerus, K. K.; Münck, E.; Moura, I.; Moura, J. J. G.; LeGall, J. *J. Am. Chem. Soc.* **1987**, *109*, 3805. (b) Surerus, K. K. Ph.D. Thesis, University of Minnesota, 1989.

[16] Surerus, K. K.; Kennedy, M. C.; Beinert, H.; Münck, E. *Proc. Natl. Acad. Sci. U.S.A.*, in press.

[17] Nelson, L. L.; Lo, F. Y.-K.; Rae, A. D.; Dahl, L. F. *J. Organomet. Chem.* **1982**, *225*, 309.

[18] Stout, C. D. *J. Mol. Biol.* **1989**, *205*, 545.

[19] Robbins, A. H.; Stout, C. D. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 3639; *Proteins* **1989**, *5*, 289.

Para Photoaddition of *N*-Methyltriazolinedione to Benzene. Synthesis of Energy-Rich Azo Compounds Comprising Benzene + N_2

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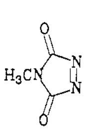
Photoadditions involving benzene have been extensively investigated, yet still attract considerable interest.[2] For simple olefins, 1,3-photoadditions or meta photoadditions to benzene generally dominate, although increasing charge-transfer character often leads to 1,2-additions.[2] On the other hand, 1,4-photoadditions to benzene are most rare and have been suggested in at least some cases to arise from secondary photolysis of ortho adducts[2b] or from stepwise processes.[3] We here report an unusual photochemical [4 + 2] addition to benzene and subsequent reactions of the product. Beyond the novelty of the photochemistry, the resulting adducts open the way to previously unknown energy-rich benzene + N_2 systems.

The wide variety of ground-state triazolinedione (TAD) additions has led to a profusion of interesting azo compounds.[4] To extend the utility of these versatile reagents, we[5,6] and others[7] have been exploring their photoadditions. We have reported that 4-methyl-1,2,4-triazoline-3,5-dione (MTAD, **1**) undergoes photochemical [4 + 2] additions to naphthalene[5] and phenanthrene[6] to give **2** and **3**, respectively. We have now observed a similar addition to the archetypal aromatic molecule, benzene.



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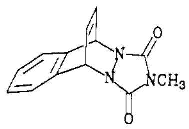

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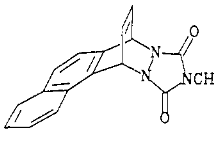

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[1] Fellow of the Alfred P. Sloan Foundation, 1986–1990.

[2] (a) Wender, P. A.; Von Geldern, T. W.; Levine, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 4858 and references therein. (b) Mattay, J. *J. Photochem.* **1987**, *37*, 167 and references therein.

[3] (a) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811 and references therein. (b) Yang, N. C.; Masnovi, J.; Chiang, W.; Wang, T.; Shou, H.; Yang, D. H. *Tetrahedron* **1981**, *37*, 3285.

[4] (a) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762. (b) Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325.

[5] (a) Kjell, D. P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 5368. (b) Kjell, D. P.; Sheridan, R. S. *J. Photochem.* **1985**, *28*, 205.

[6] Hamrock, S. J.; Sheridan, R. S. *Tetrahedron Lett.* **1988**, *29*, 5509.

[7] (a) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092. (b) Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090. (c) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 3927.

0002-7863/89/1511-9247$01.50/0