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Synthesis, Structure, and Reactivity of a Remarkable Iron Sulfide: (TACN)$_2$Fe$_2$S$_6$

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Of all the sulfides, those of iron have received the most intense scrutiny. Molecular iron sulfido complexes can be roughly divided into two families on the basis of their magnetic properties. The inorganic Fe−S−SR clusters are characteristically high spin and do not typically display strong Fe−Fe bonding.[1] Organometallic iron sulfides, i.e., those with Cp, CO, and related π-ligands,[2] are generally spin-paired and often feature Fe−Fe bonds.[3] New classes of Fe−S compounds should be found at the interface, so to speak, of the organometallic and inorganic Fe−S families. To this end, we examined the preparation of Fe−S compounds containing the facially coordinating triamine 1,4,7-triazacyclononane (TACN).[4] It is known that TACN and η^5-C$_5$R$_5^-$ can afford analogous pairs of complexes, e.g., (TACN)ReO$_3^+$/Cp*ReO$_3$ and (TACN)Re(CO)$_3^+$/Cp*Re(CO)$_3$.[5] This parallel has not, however, been observed for first row metals.

The reaction of FeCl$_3$(TACN)[6] with Na$_2$S·9H$_2$O was found to produce mainly an insoluble black species with the formula FeS$_x$(TACN) (**1**).[7] The sulfidation reaction also affords trace amounts of a CH$_2$Cl$_2$-soluble violet compound (**2**). Initial characterization of crystals grown from CH$_2$Cl$_2$ indicated that **2** has the formula Fe$_2$(S$_2$)$_3$(TACN)$_2$; the persulfide is assumed to arise by the oxidation of sulfide by some of the Fe(III). With this information, we revised the synthesis of **2** by using anhydrous Na$_2$S$_2$[8] according to the stoichiometry shown in eq 1.

$$2(\mathrm{TACN})\mathrm{FeCl_3} + 3\mathrm{Na_2S_2} \xrightarrow[-6\mathrm{NaCl}]{} \underset{\mathbf{2}}{(\mathrm{TACN})_2\mathrm{Fe_2(S_2)_3}} \quad (1)$$

Crystallographic characterization of **2**, using crystals obtained from 1,2-dichloroethane and Et$_2$O, confirmed the stoichiometry shown in eq 1.[9,10] The new compound, which has idealized C_{3h} symmetry, is a confacial bioctahedral species consisting of two Fe(TACN) units linked by three persulfido ligands (Figures 1 and 2). Each Fe atom is bound in an N$_3$S$_3$ coordination sphere. The Fe atoms are separated by 2.546(2) Å, consistent with an Fe−Fe bond. The diamagnetism of this [Fe^{III}]$_2$ species is evidenced by the well-resolved ^{1}H and ^{13}C NMR spectra.

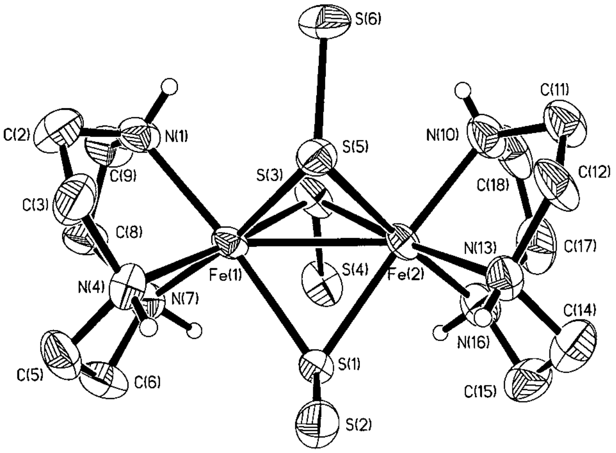

Figure 1. Structure of Fe$_2$(S$_2$)$_3$(TACN)$_2$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Important distances (Å): Fe(1)−Fe(2), 2.546(2); S(1)−S(2), 2.04(2); S(5)−S(6), 1.968(14); S(3)−S(4), 2.107(14); S(1)−Fe(1), 2.19(2); S(1)−Fe(2), 2.21(2); S(3)−Fe(1), 2.20(2); S(3)−Fe(2), 2.21(2); S(5)−Fe(1), 2.25(2); S(5)−Fe(2), 2.26(2); Fe(1)−N(7), 2.01(2); Fe(1)−N(4), 2.07(2); Fe(1)−N(1), 2.07(2).

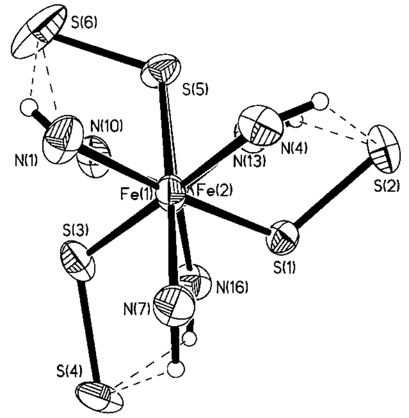

Figure 2. View of the NH···S hydrogen bonding network in **2**. Selected angles (deg): N1−H1−S6, 141.50 (7.31); N10−H10−S6, 136.21 (8.89); N4−H4−S2, 127.40 (5.66); N13−H13−S2, 136.96 (6.68). Selected distances (Å): H1−S6, 2.596 (0.084); H10−S6, 2.529 (0.091); H4−S2, 2.556 (0.086); H13−S2, 2.617 (0.087).

In the context of metal sulfide chemistry, the M$_2$S$_6$ core of **2** is unusual in several respects. There is only one previous example of a complex with the μ-η^1-S$_2$ ligand, Cp*$_2$Cr$_2$S$_5$, i.e., Cp*$_2$Cr$_2$(μ-S)(μ-η^1-S$_2$)(μ-η^2:η^2-S$_2$).[11] The occurrence of a M$_2$(S$_2$)$_3$ core is without precedent−most dinuclear metal sulfides have M$_2$S$_3$ or M$_2$S$_4$ cores.[1,2] Three structures have been observed for the related (C$_5$R$_5$)$_2$Fe$_2$S$_4^{n+}$ system: two isomers[12] of (C$_5$R$_5$)$_2$Fe$_2$(S$_2$)$_2$ and the doubly oxidized species[13] Cp*$_2$Fe$_2$(μ-η^2:η^2-S$_2$)$_2^{2+}$ (Scheme 1).

As is illustrated in Figure 2, the coordinated sulfur atoms in **2** are pyramidal such that the sum of the angles at these S atoms is 293.2−298.0°.[14]

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[1] Beinert, H.; Holm, R. H.; Münck, E. *Science* **1997**, *277*, 653.

[2] Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28* , 1613. Recent work is summarized in: Inomata, S.; Hiyama, K.; Tobita, H.; Ogino, H. *Inorg. Chem.* **1994**, *33*, 5337.

[3] Crystallographic results on the Fe−Mo−S site in nitrogenase indicates Fe−Fe bonding: Rees, D. C.; Y., H.; Kisker, C.; Schindelin, H. *J. Chem. Soc., Dalton Trans.* **1997**, 3909. Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.

[4] Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329. The reaction FeCl$_3$(Me$_3$TACN) + Na$_2$S$_x$ produced no soluble species; it is known that TACN and Me$_3$TACN, which have very different steric properties, often give rise to structurally disparate complexes.

[5] Herrmann, W. A.; Serrano, R.; Bock, H. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 5, 383. Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527. Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659.

[6] Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 9, 727.

[7] Hydrolysis of **1** with 12 M HCl liberates H$_2$S, giving Fe(TACN)(H$_2$O)$_{3-x}$Cl$_x^{(3-x)+}$ whose UV−vis spectrum matches that for samples obtained by dissolution of FeCl$_3$(TACN) in 12 M HCl.

[8] Synthesis of **2**: A 3:2 mixture of Na$_2$S$_2$ and FeCl$_3$(TACN) was stirred in absolute EtOH for 2 h. The precipitate was extracted into CH$_2$Cl$_2$ and crystallized by the addition of Et$_2$O. Yield: 83%.

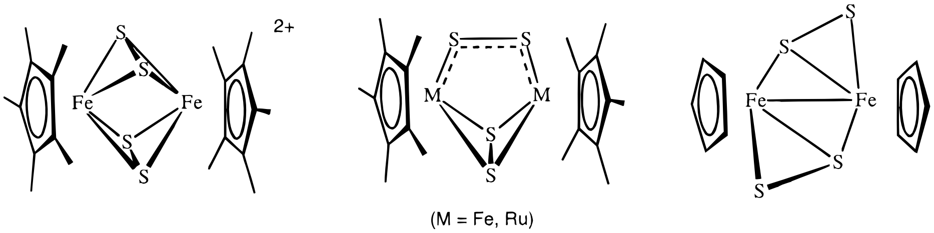
[9] Anal. Calcd (found) for **2**· CH$_2$Cl$_2$: C, 24.12 (23.75); H, 4.98 (5.19); N, 12.98 (12.90); Fe, 17.25 (17.47); S, 29.72 (29.62). ^{1}H NMR (CH$_2$Cl$_2$): δ 3.52 (NH), 2.97, 3.47, 3.11, 3.81. $\lambda_{\max}$, (CH$_2$Cl$_2$) nm (ϵ, L.mol^{-1} cm^{-1}): 308 (13300), 376 (8500), 548 (3350).

[10] C$_{16}$H$_{38}$Cl$_4$Fe$_2$N$_6$S$_6$ (0.09 × 0.12 × 0.20 mm crystal, data ($\lambda = 0.71073$ Å) collected over 2.24−28.29° at 198(2) K); tetragonal: $P4_12_12$, $a = b = 9.43630(10)$ Å, $c = 33.9780(7)$ Å; $V = 3025.53(8)$ Å^3, $Z = 4$; $\rho_{\mathrm{calc}} = 1.669$ g/m^3; abs coef = 1.746 mm^{-1}; rfxns = 19862 [R(int) = 0.0740], indep rfxns = 3722 [2899 obs, $I > 2\sigma(I)$]. Data/restraints/parameters = 3717/132/308; GOOF (on F^2) = 1.149. For obs data, $R_1 = 0.0435$, $wR_2 = 0.0685$; for all data, $R_1 = 0.0723$, $wR_2 = 0.0788$; largest diff peak = −0.315 e·Å^{-3}.

[11] Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1766.

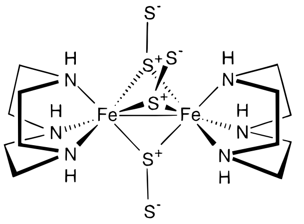
S0002-7863(98)01388-2 CCC: $15.00

Scheme 1



Solid state and solution measurements provide new insights into the μ-η^1-S_2 ligand. A band assigned as ν_{s-s} is found at 495 cm^{-1} in the IR spectrum of **2**; no absorptions in this range are seen in $FeCl_3$(TACN). One of the attractive features of the TACN ligand relative to Cp is that its NMR signals provide information about the local symmetry at the metal center. In particular, for **2** we observe two ^{13}C NMR signals at δ 50.13 and 53.34. This indicates that inversion at S is slow. Similarly, the ^{1}H NMR spectrum of **2** shows separate signals for each of four diastereotopic protons, an assignment supported by homonuclear correlation spectra. Considerable interest has been shown in related diiron derivatives of O_2 as models for the nonheme dioxygen carrier hemerythrin.[15,16] While models generally assume a terminally bound η^1-O_2, the present result suggests that alternative bonding modes merit consideration.[17]

The terminal S atoms in **2** are evidently nucleophilic as indicated by the following resonance description:



The crystallographic analysis (where (N)*H* atom positions were refined) reveals a network of intramolecular H···S bonds involving all six NH groups and all three terminal S atoms (Figure 2). This is a rare example of hydrogen bonding to an inorganic sulfur ligand.[18] Further evidence for NH···S bonding is provided by the sharp ν_{N-H} band at 3073 cm^{-1}, which is ~200 cm^{-1} lower than that for $FeCl_3$(TACN) (and other derivatives of **2**). The polarized nature of the persulfido ligands in **2** is also supported by reactivity studies. Treatment of **2** with MeI (0 °C, MeCN, 5 min) produces a green thermally labile ($t_{1/2} \sim 5$ min at 25 °C) precipitate assigned as $[(TACN)_2Fe_2(\mu\text{-}\eta^1{:}\eta^1\text{-}S_2Me)(\mu\text{-}\eta^1{:}\eta^1\text{-}S_2)_2]I$ (**3**) (eq 2).[19]

$$(TACN)_2Fe_2(S_2)_3 \xrightarrow{E} (TACN)_2Fe_2(S_2)_2(S_2E)^{z+} \quad \begin{array}{c}(E = Me, z = 1;\\ E = SO_3, z = 0;\\ E = H, z = 1)\end{array} \tag{2}$$

Protonation of **2** (1 equiv of HOTf, MeCN) generates a green species ($t_{1/2} \sim 10$ s at −10 °C), which is spectroscopically similar to the methylation product. Treatment of **2**H^+ with Et_3N (−10 °C) regenerates **2** in good yield. Spectroscopically similar adducts form when solutions of **2** are treated with SO_3·py.[20,21]

In summary, the use of TACN in place of Cp gives rise to an unprecedented type of metal sulfido complex, the novel structure of which encourages further exploration of the $[(TACN)M]_nS_y$ series. The reactivity characteristics of **2** suggest that it is a promising building block for the synthesis of new iron sulfido clusters.

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Supporting Information Available: Crystallographic data for **2** (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(14) Sum of ∠Fe1−S1−S2 + ∠Fe2−S1−S2 + ∠Fe1−S1−Fe2. For $SOCl_2$, the sum is 326° and for μ-η^1-S_2 in $Cp^*_2Cr_2S_5$, this angle is 281.6°.

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(16) Waller, B. J. L.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625.

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(18) Ueyama, N.; Okamura, T.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 8129 and references therein discuss NH···S (thiolate) bonding.

(19) Anal. Calcd (found) for $C_{13}H_{33}N_6Fe_2S_6I$: C, 22.17 (21.20); H, 4.72 (4.89); N, 11.93 (12.04). ^{1}H NMR (CD_3CN): δ 3.91, 3.85, 3.62, 3.56, 3.43, 3.28, 3.21, 3.10, 2.95, 2.79, 2.43, 2.36. IR: 3256 (ν_{NH}), 502 cm^{-1} (ν_{SS}). λ_{max} (MeCN) = 612 nm, ϵ = 1800 cm^{-1}·M^{-1}.

(20) UV−vis (CH_2Cl_2): λ_{max} = 604 nm. IR: ν_{S-O} = 1217, 1008, 615 cm^{-1}. Higher adducts, which are insoluble, also form.

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