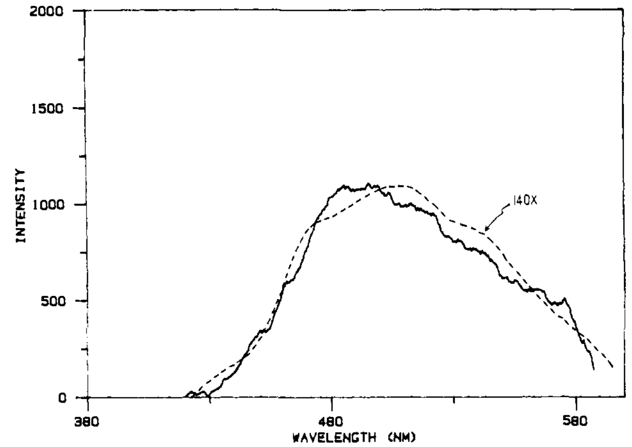
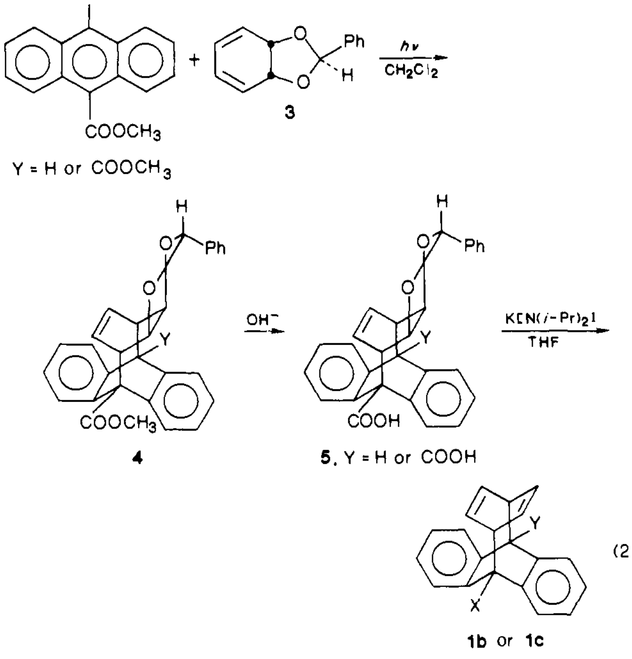


Figure 2. Chemiluminescence spectrum of **1b** at 150 °C (---) and the fluorescence spectrum of solid 9-anthroic acid at 125 °C (—).

we have succeeded in the synthesis of **1b** and **1c** according to eq 2.[3] The gap between the energy level of the radical ions formed and that of excited 9-anthroic acid may be estimated from polarographic measurements[4] and spectroscopic data of the products to be approximately 15 kcal/mol. Thermolyses of these compounds in the solid state at 150 °C are distinctively chemiluminescent,[5] and the presence of air or oxygen has no effect on the luminescence. The chemiluminescence spectrum of thermolysis of **1b** was found to be virtually identical with the fluorescence spectrum of 9-anthroic acid (Figure 2),[6] in agreement with our prediction.



Since the fluorescent state of 9-anthroic acid (0 → 0 band at 388 nm) is red-shifted from that of anthracene (0 → 0 band at 376 nm), the formation of excited anthroic acid in the thermolysis of **1b** may also be due to a more favorable energy factor. To explore this further, **1d** carrying an electron-releasing methyl group was synthesized.[2] The thermolysis of **1d** will yield 9-methylanthracene which exhibits a fluorescent state (0 → 0 band at 388 nm)[7] isoenergetic with that of 9-anthroic acid. However, the result from the thermolysis of **1d** was not detectably different from that of **1a**. Therefore, in contrast to the carboxyl group, an electron-releasing methyl group at the same position exerts no detectable effect on the probability of chemiluminescence of the parent compound.

In conclusion, the pericyclic dissociation of energy-rich dimers of aromatic compounds with appropriate substituents represents a new type of chemiluminescence. These compounds apparently exhibit more desirable handling characteristics in the laboratory for mechanistic studies than chemiluminescent peroxides, such as dioxetanes. The synthesis and thermolysis of compounds related to **1** are actively being pursued in our laboratory in order to probe into the mechanism of chemiluminescence.

Acknowledgment. We acknowledge the generous support from the National Institute of General Medical Sciences and the partial support from the National Science Foundation. We also express our appreciation for the assistance of Professor G. R. Fleming and Scott Courtney in the construction of the chemiluminescence spectrometer, and thank the NSF Instrumentation Program and the National Cancer Institute via The University of Chicago Cancer Research Center (CA-14599) for the NMR instruments used in this work.

Supplementary Material Available: Text consisting of experimental details (2 pages). Ordering information is given on any current masthead page.

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[3] Correct spectral and elemental analyses were obtained for all intermediates, and correct spectral analyses were obtained for **1b–d**. Elemental analyses for **1b–d** were not attempted because of their low thermal stability.

[4] (a) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124–2130 and references therein. (b) Klemm, L. H.; Kohlik, A. J.; Desai, K. B. *J. Org. Chem.* **1963**, *28*, 625–630. Klemm, L. H.; Kohlik, A. J. *Ibid.* 2044–2049.

[5] The luminescence yield is estimated to be <0.001.

[6] The chemiluminescence spectrometer used in this investigation consists of a UFS-200 flat field spectrograph (Instrument SA, Inc., F/3, 200–800 nm), a DIDA-512G reticon detector head (set at 330–650 nm), and an OMSA ST-110 detector controller (Princeton Instruments, Inc.). The slit of the spectrograph was set at 250 μm, and the resolution was ± 5 nm.

[7] Rice, J.; McDonald, D. B.; Ng, L.-K.; Yang, N. C. *J. Chem. Phys.* **1980**, *73*, 4144–4146.

[8] The amount of energy required to form a 9-methylanthracene radical cation and benzene radical anion may be extrapolated from the polarographic oxidation potential of 9-methylanthracene and polarographic reduction potentials of aromatic compounds (ref 4) to be 4.5 eV or 103.5 kcal/mol. Therefore, their formation is unlikely.

Evidence for the Formation of a $ZnFe_3S_4$ Cluster in *Desulfovibrio gigas* Ferredoxin II

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The electron-transport protein ferredoxin II (Fd II) from *Desulfovibrio gigas* contains an Fe_3S_4 cluster[1] which reacts readily with Fe^{2+} to form the cubane Fe_4S_4 complex.[2] This conversion suggested that the Fe_3S_4 core of Fd II can serve as a precursor for the formation of novel clusters of the MFe_3S_4 type. Indeed, we have demonstrated[3] the formation of $[CoFe_3S_4]^{1+,2+}$. The Fe_3S_4

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[1] Huynh, B. H.; Moura, J. J. G.; Moura, I.; Kent, T. A.; LeGall, J.; Xavier, A. V.; Münck, E. *J. Biol. Chem.* **1980**, *255*, 3242–3244.

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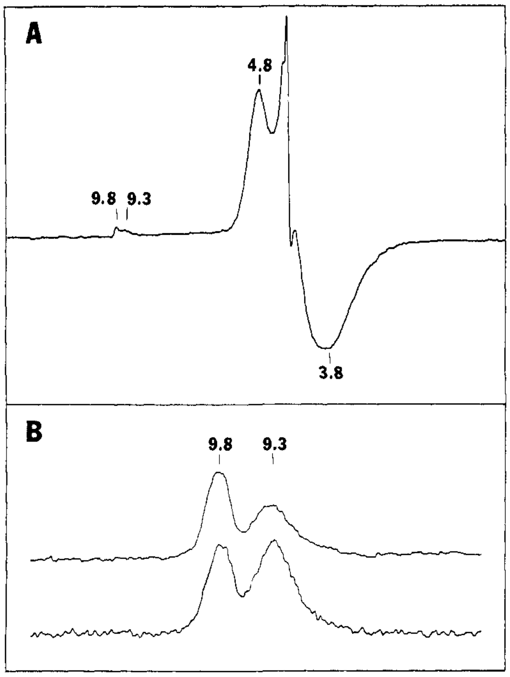

Figure 1. EPR spectra, 9.22 GHz, of I. (A) Spectrum recorded at $T \approx 8$ K; microwave power, 0.1 mW; modulation amplitude, 10 G. (B) Expanded region around g = 9–10. Upper trace: $T \approx 8$ K, 1 mW, 10-G modulation amplitude. Lower trace: $T \approx 15$ K, 1 mW, 10-G modulation amplitude.

cluster is also interesting from a standpoint of magnetism because the reduced cluster (spin $S = 2$) is a mixed-valence system with one localized Fe^{3+} and one delocalized Fe^{3+}/Fe^{2+} pair. Thus, Fd II has features (delocalization) typical of Fe_4S_4 cubanes. We have recently described the spin coupling in reduced Fd II with a Hamiltonian which takes into account Heisenberg exchange as well as electron delocalization.[4] This Hamiltonian holds promise for the description of Fe_4S_4 clusters. Since spin coupling in the latter is exceedingly complex, it is desirable to incorporate a diamagnetic metal, rather than Co^{2+}, into the Fe_3S_4 core and thus produce a cubane with only three paramagnetic sites. Here we report evidence for the formation of a cluster with novel features, most probably $ZnFe_3S_4$.

Fd II was purified as described.[2] Typically 0.5 mL of dithionite-reduced Fd II, 0.5 mM in Fe_3S_4, was anaerobically incubated for 2 h with 15 mM $Zn(NO_3)_2$ and 7 mM dithiothreitol. Excess reagents were removed with an anaerobic Sephadex G-25 column. Plasma emission spectroscopy yielded 4.2 Zn, 3.0 Zn, and 1.3 Zn per 3 Fe for three preparations;[5] the latter sample was enriched in ^{57}Fe. Except for ^{57}Fe hyperfine broadening for the 1.3 Zn per 3 Fe sample, the EPR spectra of the three samples were the same. We refer to the dithionite-reduced cluster as I.

Figure 1 shows X-band EPR spectra of I. Prominent resonances are observed at g = 4.8 and 3.8 and at g = 9.8 and 9.3. These signals are typical of an $S = {}^5\!/_2$ system described by the Hamiltonian

$$\hat{H}_e = D[S_z^2 - {}^{35}\!/_{12} + (E/D)(S_x^2 - S_y^2)] + g_0\beta\vec{H}\cdot\vec{S} \qquad (1)$$

for $\beta H \ll |D|$ and $g_0 \approx 2$. In fact, for $D < 0$ and $E/D = 0.25$, eq 1 predicts three Kramers doublets with the following sets of g values: $g_{x,y,z}$ = (0.5, 0.4, 9.8) for the ground doublet, $g_{x,y,z}$ (4.1, 3.8, 4.8) for the middle doublet, and $g_{x,y,z}$ = (1.4, 9.4, 0.9) for the upper doublet. Variable temperature (8–15 K) studies showed that the g_z = 9.8 resonance belongs to the ground state (see Figure 1B) and that $D \approx (-2.7 \pm 0.5)$ cm^{-1}. Upon mild oxidation with gallocyanin ($E_m \approx 30$ mV vs. NHE) the EPR signals dissappeared; they reappeared quantitatively upon rereduction with dithionite.

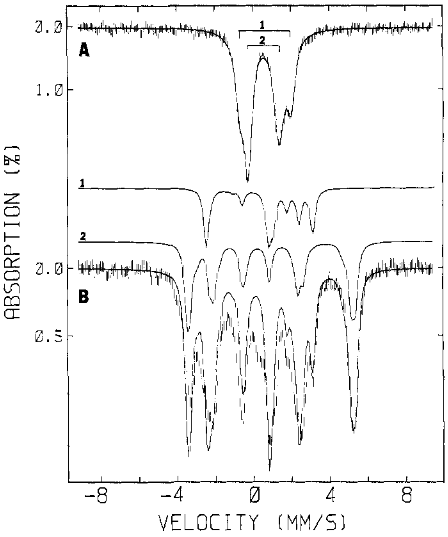

Figure 2. Mössbauer spectra of ^{57}Fe-enriched cluster I. (A) Spectrum recorded at 50 K. Solid line is the result of a least-squares fitting the spectrum to two doublets. The fit yielded an area ratio of 1.97:1 for sites 1 and 2. (B) 4.2 K spectrum recorded in a magnetic field of 0.05 T applied parallel to the γ-radiation. Solid lines are spectral simulations using the parameters of Table I. Spectral decomposition into components 1 and 2 is shown above the data; vertical scale of curves 1 and 2 is compressed by a factor of 2.

Table I. Hyperfine Parameters of I Used To Simulate the Spectrum of Figure 2B[a]

site	A_z, MHz	δ, mm/s	ΔE_Q, mm/s	η	β, deg
1	+6.6	0.62	−2.7	0.8	30
2a	−14.0	0.51	+1.6	0.5	33
2b	−14.8	0.54	+1.6	−2	15

[a] Zero-field splitting parameters used were$D = -2.7$ cm^{-1} and E/D = 0.25. The z-axes of the electric field gradient tensors (V_{xx}, V_{yy}, V_{zz}; $\eta = (V_{xx} - V_{yy})/V_{zz}$) are tilted by an angle β relative to the z-axis of the zero field splitting tensor. For the electronic system at hand, the values of η and β are not unique; see ref 7.

Figure 2B shows a 4.2 K Mössbauer spectrum of I. The spectral pattern observed is typical for a Kramers doublet with $g_z \gg g_x$, g_y (the middle doublet is only ≈3% populated at 4.2 K). At 50 K the electronic spin relaxes fast, and the Mössbauer spectrum consists of two doublets with an area ratio ≃ 2:1. The values for ΔE_Q and δ (Table I) for site 1 (one Fe) suggest Fe^{2+} with tetrahedral sulfur coordination whereas those of site 2 remind us of the delocalized Fe^{2+}/Fe^{3+} pairs of $[Fe_4S_4]^{1+}$; see ref 6.

The spectrum of Figure 2B can be decomposed into essentially two components (the two Fe of site 2 are only slightly inequivalent; sites 2a and 2b). The rightmost absorption line in Figure 2B belongs entirely to sites 2a and 2b. By matching the theory to this line, we found that ≈60% of total Fe belongs to site 2 and about 30% to site 1; the remaining absorption is as yet unidentified. Six preparations gave identical spectra; none had detectable levels of adventitious Fe^{3+} or Fe^{2+}.

The spectrum of Figure 2B was analyzed by augmenting eq 1 with the hyperfine terms (i = 1, 2a, 2b).

$$\hat{H}_{hf} = \sum_i \vec{S}\cdot\tilde{A}(i)\cdot\vec{I}(i) - g_n\beta_n\vec{H}\cdot\vec{I}(i) + \hat{H}_{quad}(i) \qquad (2)$$

The spectral simulations are not perfect; however, the essential features of the data are well represented by the theory. Because of the uniaxial nature of the electronic ground doublet, the spectrum of Figure 2B is only sensitive to the z-components of the magnetic hyperfine tensors, A_z(i). From studies in applied

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(5) The protein seems to bind Zn^{2+} in variable amounts. In a related project, we have observed with EPR binding of two–three Cu^{2+} in sites other than the "vacant" site of Fe_3S_4.

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fields up to 6.0 T we found that $A_z(1) > 0$, $A_z(2a) < 0$, and $A_z(2b) < 0$.

Cluster I has unique spectroscopic features. Formally, it contains two Fe^{2+} and one Fe^{3+}; thus the three iron sites accommodate one more electron than those of reduced Fd II. Since we have no spectroscopic data on the Zn, our spectra could indicate the formation of a superreduced Fe_3S_4 cluster, the reduction being achieved, however, only in the presence of Zn (but not with Fe, Co, Cu, or V); Zn^{2+} would bind to the protein in the vicinity of the cluster stabilizing the superreduced state. The oxidized/reduced Fd II couple has $E_m = -130$ mV (vs. NHE); in the absence of Zn^{2+} we have never observed, even at −600 mV, any EPR feature indicative of the $S = {}^5/_2$ state (3% $S = {}^5/_2$ clusters would have been detected). A superreduced state has never been indicated for any protein containing an Fe_3S_4 cluster. More plausibly, therefore, Zn has been incorporated into the vacant site of the Fe_3S_4 cluster to form $ZnFe_3S_4$. This interpretation is suggested by our earlier work which has demonstrated facile formation of $[Fe_4S_4]^{1+}$ and $[CoFe_3S_4]^{1+}$ under similar incubation conditions. Since I has half-integer spin, the incorporated Zn must be Zn^{2+}, suggesting that I is $[ZnFe_3S_4]^{1+}$ and thus the analogue of $[Fe_4S_4]^{1+}$. In order to prove incorporation of Zn directly, EXAFS and ENDOR experiments are in preparation.

$[Fe_4S_4]^{1+}$ cores seem to consist of two spin-coupled pairs; see ref 8. For the postulated $[ZnFe_3S_4]^{1+}$ the replacement of one Fe^{2+} by Zn^{2+} has disrupted one pair and created the trapped Fe^{2+} of site 1. In order to exploit the cluster for the study of spin coupling of cubanes, A_x(i) and A_y(i) need to be determined. Such efforts are in progress.

Acknowledgment. This work was supported by the National Science Foundation, the National Institutes of Health, the Instituto de Investigacão Cientifica Technologica, the Junta Nacional de Investigacão Cientifica Tecnologica, the Agency for International Development, and a NATO Collaborator Research Grant.

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Synthesis, Structural Characterization, and Electronic Structures of the $[Fe_6S_6(X)_6(Mo(CO)_3)_2]^{3-}$ Clusters (X = Cl, Br)

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In the last few years, work in our laboratory has been aimed toward the design and synthesis of structural analogues for the Fe/Mo/S center in nitrogenase[1] or the nitrogenase cofactor.[2] Our synthetic efforts are directed mainly by the data available for the Fe/Mo/S center, from analytical,[3] Mössbauer,[4] EXAFS,[5] and ENDOR[6] studies. These studies broadly define the heterometallic center as an asymmetric, spin-coupled, $S = {}^3/_2$ aggregate with a Fe/Mo/S ratio of 6-7/1/6-8.

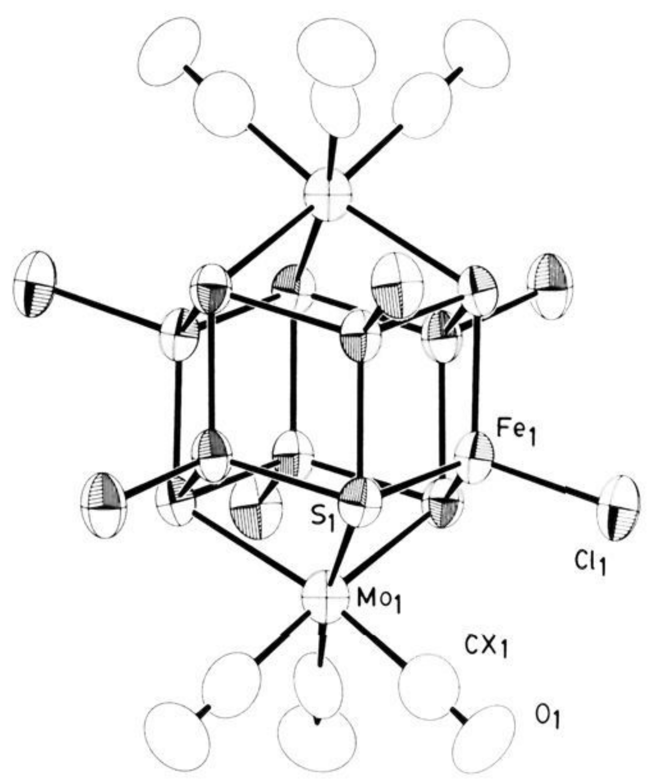

Figure 1. Structure and labeling of the anion in I. Thermal ellipsoids as drawn by ORTEP (Johnson, C. K. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces.

Recently, we reported on the synthesis spectroscopic properties and molecular structures of the $[Fe_6S_6(OR)_6(W(CO)_3)_2]^{3-}$[7] and $[Fe_6S_6(Cl)_6(Mo(CO)_3)_2]^{4-}$[8] complex anions and of the synthesis and spectroscopic properties of $[Fe_6S_6(OR)_6(Mo(CO)_3)_2]^{3-}$.[9] These clusters are obtained by the addition of two $M(CO)_3$ fragments (M = Mo, W) to the $[Fe_6S_6(L)_6]^{3-}$ prismanes[10] and adopt a heterometallic pentlandite type of structure with $[Fe_6M_2S_6]^{3+,2+}$ cubic cores. In this paper we report on the synthesis, crystal structures, and Mössbauer spectra of the trianionic $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{3-}$ clusters (L = Cl, Br).

The $[Fe_6S_6(L)_6(M(CO)_3)_2]^{n-}$ clusters display two reversible waves in cyclic voltammetry that correspond to the 3−/4− and 4−/5− couples. The low potentials of the 3−/4− couples, at +0.05 and +0.08 V ($E_{1/2}$ values in CH_2Cl_2 on a Pt electrode vs. SCE) for L = Cl and Br, respectively, suggest that the trianions would be susceptible to reduction under mildly reducing conditions. Indeed the adduct-forming reactions of the $[Fe_6S_6(L)_6]^{3-}$ prismanes with an excess of the mildly reducing $Mo(CO)_3(CH_3CN)_3$ reagent, in CH_3CN solution, produce primarily the $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{4-}$ tetraanions when L = Cl or Br. The $Mo(CO)_3(CH_3CN)_3$ complex ($E_{1/2}$ for the 0/+1 couple, +0.30 V

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