of a room-temperature solution of **4** in CO_2-saturated benzene or hexafluorobenzene (medium-pressure Hg lamp, Vycor filter).

The reactivity and the spectroscopic properties outlined above clearly indicate that **1** is more highly strained than **2**, in agreement with MNDO calculations (Table I). The opposite ordering of strain energies has been suggested on qualitative grounds.[2,13]

Although **1** and **2** are the only major photoproducts of **4** initially detectable by UV and IR, traces of two triplet products are readily detected by ESR. The ESR signal at 0.8143 T (9.3 GHz) identifies one of these species as a triplet nitrene, assigned as **3**.[14] The other triplet has $|D/hc| = 0.091$ cm^{-1} and $|E/hc| = 0.022$ cm^{-1}, compatible[15] with a localized 1,3-biradical structure. It might originate in a 1,2-H shift to the nitrogen in **1**, but a positive identification has yet to be accomplished.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 81-21122).

Registry No. 1, 85616-65-5; **2,** 85616-66-6; **3,** 93184-35-1; **4,** 85616-64-4; **8,** 93184-36-2; CO_2, 124-38-9.

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[14] (a) Assuming $E = 0$, one calculates[14b] $|D/hc| = 1.66$ cm^{-1}. (b) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964,** *41,* 1763. Wasserman, E. *Prog. Phys. Org. Chem.* **1971,** *8,* 319. (c) The ESR signal appears to correlate with a weak, sharp UV absorption peak at 302 nm. (d) The structure assignment is supported by a photochemical trapping experiment; in a CO-doped Ar matrix **1-3** are still formed from **4** and are stable in the dark, but subsequent irradiation (254 nm) at 36 K, where CO is mobile, produces a weak peak at 2265 cm^{-1} in the IR spectrum. Authentic 1-noradamantyl isocyanate has its strongest peak at 2265 cm^{-1} in Ar matrix. Precedent for photochemical addition of CO to a nitrene is found in ref 9b and: Dunkin, I. R.; Thompson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1982,** 1192.

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Oxidative Transformation of the $[Fe_4S_4X_4]^{2-}$ "Cubanes" to the $[Fe_6S_6X_6]^{2-}$ "Prismane" Clusters (X = Cl, Br). The Crystal and Molecular Structure of $[(C_6H_5)_4P]_2Fe_6S_6Cl_6$

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The existence of 3Fe centers in a number of Fe/S proteins is now well documented.[1] Identification of such centers is based on their characteristic "signatures" in the Mössbauer,[2] magnetic circular dichroism, (MCD),[3] and EPR[4] spectra. The exact nature of the Fe/S cores in the 3Fe ferredoxins is not entirely clear. The spectroscopic data on a number of these proteins and X-ray absorption fine structure (EXAFS) analyses on *D. gigas* FdII[5] and aconitase[6] suggest the presence of 3Fe-4S cores with structural features (Fe–Fe, ~2.70 Å) similar to those found in "conventional" 2Fe or 4Fe ferredoxins. An X-ray structure determination of FdI from *A. vinelandii* shows,[7] however, a 3Fe-3S core with a slightly puckered hexagonal ring structure and "unorthodox" structural features (Fe–Fe, ~4.1 Å; Fe–S–Fe, 126°, 131°, and 113°). These rather unique features had not been found previously in any of the synthetic Fe/S molecular clusters.

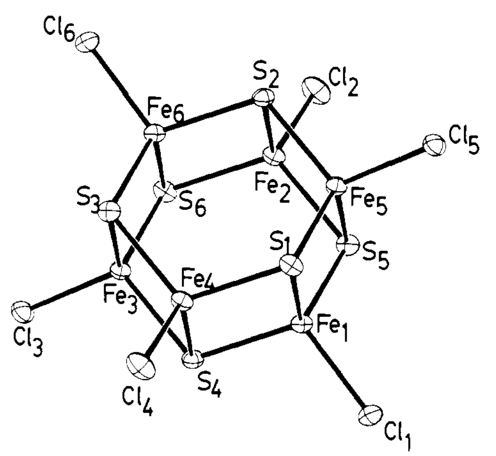

Figure 1. Structure and labeling of the anion in III. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces.

Recently we reported[8] on the synthesis, structural characterization, and electronic properties of the new, apparently metastable, $(Fe_6S_6Cl_6)^{3-}$ "prismane" cluster (I). At approximately the same time the structural characterization of the analogous I^- cluster in a higher oxidation level, $(Fe_6S_6I_6)^{2-}$ (II), was reported.[9] In both of these clusters the Fe_6S_6 cores contain two Fe_3S_3 puckered ring units with long (~3.8 Å) distances and large (~114°) Fe–S–Fe angles. The core in II represents the first example of a Fe/S cluster with a Fe/S ratio of 1 and a formal Fe oxidation state of 2.67. With the anticipation that appropriate cleavage of the $(Fe_6S_6)^{4+}$ core may result in possible synthetic analogues for the reduced form of the 3Fe centers, we proceeded with studies on the reactivity of the $(Fe_6S_6L_6)^{2-}$ dianions.

As suggested by cyclic voltammetric measurements on CH_2Cl_2 solutions of I,[10] the chemical oxidation of the trianion should be readily accomplished in nonpolar solvents. Indeed, the reaction of CH_2Cl_2 solutions of I with a stoichiometric amount of ferrocenium hexafluorophosphate resulted in the clean quantitative oxidation of I as evidenced by characteristic spectral changes.[11] Unfortunately, this synthetic procedure predicates the use of the $(Fe_6S_6Cl_6)^{3-}$ trianion, which is metastable and is obtained in crystalline form only as the Et_4N^+ salt.[8]

In search of a general procedure[12] for the synthesis of the $(Fe_6S_6X_6)^{2-}$ dianions from readily available reagents, the oxidation of the $(Fe_4S_4X_4)^{2-}$ clusters was attempted in CH_2Cl_2 according to the reaction

$$3(Fe_4S_4X_4)^{2-} + 2(Fe(C_5H_5)_2)^+ \rightarrow 2(Fe_6S_6X_6)^{2-} + 2Fe(C_5H_5)_2 \quad (1)$$

The reaction proceeds cleanly at ambient temperature and for X = Cl and Br (eq 1) the oxidative transformation of the $(Fe_4S_4X_4)^{2-}$ clusters to the $(Fe_6S_6X_6)^{2-}$ "prismanes" is quantitative. Crystalline Ph_4P^+ or R_4N^+ salts can be isolated in excellent yields; however, solutions of these compounds in polar solvents (CH_3CN,

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[10] On a Pt electrode, 10^{-3} M, with Bu_4NClO_4 as the supporting electrolyte; $E_{1/2} = +0.300$ V.

[11] In CH_2Cl_2 solution the $(Fe_6S_6X_6)^{3-}$ (X = Cl, Br) anions show electronic transitions at 270 and 306 nm, respectively. The oxidized $(Fe_6S_6X_6)^{2-}$ show transitions at 287 and 326 nm, respectively.

[12] We have been unable to repeat the reported synthesis[9] of the $(Fe_6S_6I_6)^{2-}$ cluster in our laboratory. The synthetic procedure as outlined in ref 9 in our hands afforded $(FeI_4)^-$ salts in excellent yields. We suspect that the $[Fe_6S_6I_6]^{2-}$ cluster that allegedly is obtained by the published[9] procedure is only a minor reaction byproduct.

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Table I. Interatomic Distances[a] (Å) and Angles (deg) in the $(Fe_6S_6Cl_6)^{2-}$ (A) and $(Fe_6S_6Cl_6)^{3-}$ (B) Anions

	A[b]	B[c]
	Distances	
Fe–Fe[d]	3.791 (6,5)	3.790 (3,7)
Fe–Fe[e]	2.757 (6,5)	2.765 (3,3)
Fe–S[d]	2.268 (6,8)	2.284 (3,3)
Fe–S[e]	2.254 (12,8)	2.272 (6,2)
Fe–Cl	2.189 (6,8)	2.224 (3,2)
S–S[d]	3.743 (6,8)	3.801 (3,8)
S–S[e]	3.585 (6,8)	3.618 (3,5)
	Angles	
S–Fe–S[d]	112.0 (6,9)	113.7 (3,3)
S–Fe–S[e]	104.8 (12,5)	105.2 (6,2)
Fe–S–Fe[d]	114.5 (6,6)	113.2 (3,3)
Fe–S–Fe[e]	75.1 (12,4)	74.8 (6,2)
Fe–Fe–Fe[d]	60.0 (6,4)	60.0 (3,2)
Fe–Fe–Fe[e]	86.9 (6,5)	86.5 (3,3)

[a] See Figure 1 for the labeling scheme. The mean values of chemically equivalent bonds are given. In parenthesis the first entry represents the number of independent distances or angles averaged out, the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation: $\sigma = [\sum^{N}_{i=1}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [b] This work. [c] From ref 8. [d] Distances or angles within the Fe_3S_3 structural units. [e] Distances or angles within the Fe_2S_2 rhombic units.

DMF) are unstable and the transformation of the $(Fe_6S_6X_6)^{2-}$ anions to the $(Fe_4S_4X_4)^{2-}$ clusters and unidentified byproducts is evident in electronic spectra changes. In the presence of excess X^- the transformation occurs quantitatively[13] according to eq 2.

$$(Fe_6S_6X_6)^{2-} + 2X^- \rightarrow (Fe_4S_4X_4)^{2-} + (Fe_2S_2X_4)^{2-} \qquad (2)$$

The convenient, reliable synthesis of the $(Fe_6S_6X_6)^{2-}$ dianions allows for a new route for the synthesis of the corresponding trianions. The latter can be obtained in excellent yields by the $(R_4N)^+BH_4^-$ reduction of the dianions in CH_2Cl_2 solution (R = C_2H_5).

Single crystals of $(Ph_4P)_2(Fe_6S_6Cl_6)$ (III) were obtained by the slow diffusion of ether to a CH_2Cl_2 solution of this complex. In the crystal structure of III[14] the anion shows the same hexagonal prismatic Fe_6S_6 core reported for I[8] and II (Figure 1).[9] Selected structural parameters for the anion in III are compared to corresponding parameters in the anion of I (Table I).

Within the accuracy of the structure determinations, the Fe_6 distorted octahedra in I and III have indistinguishable Fe–Fe distances and Fe–Fe–Fe angles. The Fe–S, Fe–Cl, and S–S distances in I, however, are slightly longer than those in III, and collectively these differences may be statistically significant. The shorter Fe–S distances in III possibly reflect the higher formal charge (evident in the Mössbauer spectra isomer shift (IS) values) for the iron atoms in this cluster.

The Mössbauer spectra of III at 125 K (vs. Fe) display one quadrupole doublet with IS and ΔE_Q values of 0.425 (1) and 0.616 (1) mm/s, respectively.[15] The IS value is somewhat smaller than the corresponding value observed for I under identical conditions (IS, 0.494; ΔE_Q, 1.095 mm/s; 125 K) and is consistent with the higher formal oxidation state for the iron atoms in III. The appearance of only one Fe site in the spectra suggests electron delocalization not unlike the one found in I and the Fe_4S_4 centers. The magnetic moment of III measured in solution by NMR (μ_{eff}^{corr} 3.1 μ_B at 296 K) suggests magnetic coupling between the iron atoms at this temperature. The absence of an EPR signal and the insensitivity of the Mössbauer spectra to a weak magnetic field at 7 K indicate that this coupling results in a $S = 0$ ground magnetic state.

The oxidative transformation of $(Fe_4S_4Cl_4)^{2-}$ to III should be contrasted with the oxidative transformation of the Fe_4S_4 centers to Fe_3S_4 centers in certain ferredoxins. The apparent structural difference of the oxidation products in the two systems may reflect the ability of the protein substrate to "capture" unstable intermediates and prevent subsequent rearrangements or higher order coupling reactions.

The facile reversible reduction of III at low potential ($E_{1/2}$, 0.32 V, in CH_2Cl_2 vs. SCE) reveals a new Fe/S redox couple and introduces the Fe_6S_6 core as a viable candidate for future consideration in the biochemistry of "unconventional" and perhaps hitherto unknown Fe/S proteins.

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Supplementary Material Available: Tables of structure factors and positional and thermal parameters (17 pages). Ordering information is given on any current masthead page.

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(14) Crystal and refinement data for $(Ph_4P)_2(Fe_6S_6Cl_6)$ (III): $a = 13.454$ (9) Å, $b = 13.528$ (8) Å, $c = 19.211$ (11) Å, $\alpha = 74.31$ (5)°, $\beta = 70.27$ (5)°, $\gamma = 61.51$ (4)°; space group $P\bar{1}$, $Z = 2$; $d_{calcd} = 1.65$, $d_{obsd} = 1.62$, $\mu = 22.8$ cm^{-1}, $2\theta_{max} = 41°$ (Mo, $\lambda(K\alpha)$, 0.71069 Å); Reflections collected 5824; unique reflections 5467 used in refinement $F_o^2 > 3\sigma(F_o^2)$, 2973; parameters 373; final $R = 0.06$.

(15) The IS and ΔE_Q values at 150 and 175 K are 0.41 and 0.66 mm/s and 0.44 and 0.72 mm/s, respectively. At 4.2 K the Mössbauer spectra of both $[Fe_6S_6Cl_6]^{2-}$ and $[Fe_6S_6Br_6]^{2-}$ show three quadrupole doublets in an approximate 1:1:1 ratio. The origin of this *reversible* change in the Mössbauer spectra at low temperatures presently is under study.

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cis-$(NH_3)_2Pt^{IV}$ Complexes of Uracil through Cl_2 Treatment of a Pt(II) Complex: Oxidative Addition to the Metal and Modification (Cl Substitution, HOCl Addition) of the Nucleobase

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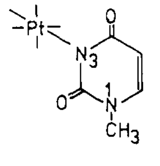
The role of metal ions in nucleic acid chemistry has evoked considerable interest in metal binding properties of nucleobases.[1] The coordination chemistry of the naturally occurring pyrimidine nucleobases uracil and thymine is, with metal coordination through the N(3) site, dominated by low coordination numbers of the metals bound, e.g., 2 for Ag[2] and Hg[3] and 4 for Pt.[4] Only one example with a five-coordinate metal, Cd,[5] has been structurally characterized as yet, but not a single example of a six-coordinate metal bound to N(3). The expected interference of the exocyclic oxygens at either side of N(3) with other ligands around the metal seems to be responsible for this lack.[6] We herewith wish to report the first examples of 1-methyluracil derivatives containing an octahedrally coordinated metal, Pt(IV), bound through N(3), *mer*-$(NH_3)_2PtCl_3L$ with L = $C_5H_5N_2O_2$ (**2**), $C_5H_4N_2O_2Cl$ (**3**), and $C_5H_5N_2O_3Cl_2$ (**4**).



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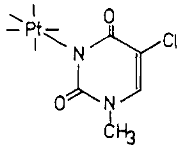

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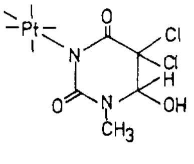

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