

pseudotetrahedral halo complexes of Co<sup>II</sup> and Ni<sup>II</sup> much greater reductions of the spin-orbit coupling constant, below the free-ion value, were observed for the latter than for the former, in studies of the anisotropic magnetic susceptibilities. Since the magnetic behavior is dominated by the nature of the ground state, which for d<sup>7</sup> Co<sup>II</sup> is the inactive <sup>4</sup>A<sub>2</sub> state but for d<sup>8</sup> Ni<sup>II</sup> is the potentially active (T ⊗ τ<sub>2</sub> + ε) <sup>3</sup>T<sub>1</sub>(F) state, the results were interpreted to support the operation of a significant Ham effect in the Ni<sup>II</sup> species, partially quenching the spin-orbit coupling. However, apart from [CuCl<sub>4</sub>]<sup>2-</sup>, the largest calculated E<sub>JT</sub> values of Table II are generally comparable with the spin-orbit coupling constant (ξ being 410, 533, and 649 cm<sup>-1</sup> for Fe<sup>II</sup>, Co<sup>II</sup>, and Ni<sup>II</sup>, respectively<sup>9</sup>) so that any calculations of the Ham reduction factors could not use simple perturbation techniques and full diagonalization

in the spin-orbit basis of the appropriate weak-field-state vibronic manifolds would be necessary.

There do however exist extensive data for M<sup>2+</sup> 3d ions doped into tetrahedral sites in hosts such as CdS, and for these systems Sturge<sup>24</sup> concluded that in most cases T ⊗ ε coupling would predominate. However, for the <sup>4</sup>T<sub>1</sub>(F) state of Co<sup>2+</sup>/CdS a substantial Ham effect is observed, reflected in an anomalously small spin-orbit splitting, which was analyzed by Sturge<sup>24</sup> in terms of a mainly T<sub>1</sub> ⊗ τ<sub>2</sub> coupling, with some T<sub>1</sub> ⊗ ε contribution. This accords strikingly with the present predictions, and it would thus appear eminently worthwhile for further studies to be made of 3d [MCl<sub>4</sub>]<sup>2-</sup> species and of other T<sub>d</sub> systems, especially for the <sup>3</sup>T<sub>1</sub>(F) and <sup>4</sup>T<sub>1</sub>(F) states of Ni<sup>II</sup> and Co<sup>II</sup>, with a view toward identifying any further situations in which T ⊗ τ<sub>2</sub> coupling might be dominant.

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## Chemistry of [Fe<sub>6</sub>S<sub>6</sub>]<sup>3+</sup> Prismatic Cages. Synthesis, Structural Characterization, and Electronic Structures of the [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>] Clusters (L = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, Br<sup>-</sup>)

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The syntheses of the [Cat]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>] clusters (L = Br<sup>-</sup>, cat = [Et<sub>3</sub>MeN]<sup>+</sup>; L = ArS<sup>-</sup>, Cat = [Et<sub>4</sub>N]<sup>+</sup>) are reported. The crystal and molecular structures of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>] (I) and of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]·CH<sub>3</sub>CN (II) are described in detail. I and II crystallize in the monoclinic space groups *P*<sub>2</sub><sub>1</sub>/*a* and *P*<sub>2</sub><sub>1</sub>/*n*, respectively, with two molecules in the unit cell. The cell dimensions in I are *a* = 13.173 (5) Å, *b* = 19.848 (10) Å, *c* = 14.304 (4) Å, and β = 98.05 (3)°. In II, *a* = 14.531 (3) Å, *b* = 11.028 (2) Å, *c* = 17.566 (3) Å, and β = 100.69 (1)°. Intensity data for both I and II were collected with a four-circle computer-controlled diffractometer with use of the θ-2θ scan technique. Both structures were solved by conventional methods from 3461 and 2516 reflections for I and II, respectively. The structures were refined by full-matrix least-squares techniques (283 parameters for I and 213 parameters for II) to final *R* values of 0.075 and 0.049, respectively, for I and II. The anions in I and II contain the [Fe<sub>6</sub>S<sub>6</sub>]<sup>3+</sup> hexagonal-prismatic core, which consists of alternating tetrahedral Fe and triply bridging S atoms. Three of the Fe coordination sites are occupied by core sulfide atoms while the fourth coordination site is filled by the terminal RO<sup>-</sup> and Br<sup>-</sup> ligands. There are two sets of Fe-Fe distances in the Fe<sub>6</sub>S<sub>6</sub> cores with mean values of 2.761 (5), 2.749 (4) Å and 3.80 (4), 3.81 (2) Å, respectively, for I and II. Similarly, two sets of Fe-S-Fe angles are found for I and II at 74.6 (2) and 74.3 (1)° and 113.8 (2) and 114.2 (9)°. The Fe-S bonds in I and II are 2.276 (5) and 2.274 (4) Å. The Fe-O bond in I is 1.880 (11) Å, and the Fe-Br bond in II is 2.366 (9) Å. The reactivity, cyclic voltammetry, and isotropically shifted NMR spectra of I and II are discussed in detail.

### Introduction

The importance of Fe/S centers in the function of the non-heme iron-sulfur proteins (ferredoxins)<sup>1</sup> has generated great interest in Fe/S coordination chemistry. As a result of extensive synthetic, structural, and spectroscopic studies, nearly exact analogues for the 1Fe, 2Fe, and 4Fe centers in the Fe/S proteins are presently available.<sup>2</sup> These synthetic analogues have contributed substantially to our understanding of the biologically occurring Fe/S centers and include the following compounds: [Fe(SR)<sub>4</sub>]<sup>n-</sup> (*n* = 1, 2, (SR)<sub>2</sub> = S<sub>2</sub>-*o*-xyl;<sup>3</sup> *n* = 2, R = Ph;<sup>4</sup> *n* = 1, 2, R = Et, Ph<sup>5</sup>);

[Fe<sub>2</sub>S<sub>2</sub>L<sub>4</sub>]<sup>2-</sup> (L = EtS<sup>-</sup>, *p*-MeC<sub>6</sub>H<sub>4</sub>S<sup>-</sup>;<sup>6a</sup> L = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>;<sup>6b,c</sup> L<sub>2</sub> = S<sub>3</sub><sup>2-</sup>;<sup>7</sup> L = *p*-MeC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, C<sub>4</sub>H<sub>4</sub>N<sup>-</sup>; L<sub>2</sub> = *o,o'*-C<sub>12</sub>H<sub>8</sub>O<sub>2</sub><sup>2-8</sup>); [Fe<sub>4</sub>S<sub>4</sub>L<sub>4</sub>]<sup>n-</sup> (L = aryl, alkanethiolates, *n* = 2, 3;<sup>2c</sup> L = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, *n* = 2;<sup>6b,c</sup> L = 2,4,6-*i*-Pr-C<sub>6</sub>H<sub>2</sub>S<sup>-</sup>, *n* = 1;<sup>9</sup> L = PhO<sup>-</sup>, *p*-

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MeC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>,  $n = 2^{10}$ ); [Fe<sub>4</sub>S<sub>4</sub>L<sub>2</sub>L'<sub>2</sub>]<sup>2-</sup> (L = C<sub>6</sub>H<sub>5</sub>S<sup>-</sup>, L' = *p*-MeC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>; L = Cl<sup>-</sup>, L' = C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>; L = Cl<sup>-</sup>, L = C<sub>6</sub>H<sub>5</sub>S<sup>-11</sup>); [Fe<sub>4</sub>S<sub>4</sub>L<sub>n</sub>L'<sub>4-n</sub>]<sup>2-</sup> (L = Et<sub>2</sub>Dtc,  $n = 2$ ; L = Cl<sup>-</sup>, L' = Et<sub>2</sub>Dtc,  $n = 2, 3^{12}$  (Dtc = dithiocarbamate)).

Recently, the existence of a new "non conventional" Fe/S center in certain ferredoxins (Fd) has been revealed by spectroscopic studies in such proteins as *Azotobacter vinelandii* Fd I,<sup>13</sup> *Desulfovibrio gigas* Fd II,<sup>14</sup> *Aconitase*,<sup>15</sup> *Thermus thermophilus* Fd,<sup>16</sup> and others.<sup>17</sup> Most of the available data suggest the presence of a nonlinear, cubane-type Fe<sub>3</sub>S<sub>4</sub> core for this center. At variance with the analytical and spectroscopic studies is a crystallographic study of *A. vinelandii* Fd I that shows<sup>18</sup> a Fe<sub>3</sub>S<sub>3</sub> center with a puckered hexagonal ring structure, unusually long Fe-Fe distances (~4.0 Å), and oblique Fe-S-Fe angles (~118°). The Fe<sub>3</sub>S<sub>3,4</sub> centers appear to be stable only within the protein environment and do not maintain their integrity upon extrusion from the protein matrix. Core extrusion reactions<sup>19</sup> that employ aryl thiols allow for the isolation of Fe<sub>2</sub>S<sub>2</sub> and Fe<sub>4</sub>S<sub>4</sub> centers from conventional ferredoxins. Similar reactions with proteins that contain the Fe<sub>3</sub>S<sub>3,4</sub> centers result in the isolation of the thermodynamically more stable Fe<sub>2</sub>S<sub>2</sub> and Fe<sub>4</sub>S<sub>4</sub> cores.<sup>20,17b</sup>

The principle and practice of spontaneous-assembly synthesis<sup>21</sup> have proven successful in the synthesis and isolation of analogue clusters that contain the Fe<sub>2</sub>S<sub>2</sub> and Fe<sub>4</sub>S<sub>4</sub> cores. Clusters that contain nonlinear Fe<sub>3</sub>S<sub>3,4</sub> centers are not obtained in spontaneous-assembly reactions. It appears likely that these and other metastable Fe/S species may be obtained only fortuitously (in crystalline form) as a result of favorable lattice energies and/or reaction conditions (media dielectric, temperature).

Recently, we have reported the synthesis, structural characterization, chemical properties, and spectroscopic characteristics of a new class of Fe/S clusters that contain the [Fe<sub>6</sub>S<sub>6</sub>]<sup>4+3+</sup> prismatic cores. The [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>n-</sup> clusters (L = Cl<sup>-</sup>,  $n = 3$ ;<sup>22</sup> L = Cl<sup>-</sup>,  $n = 2$ ;<sup>23</sup> L = *p*-MeC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>,  $n = 3^{24}$ ) are characterized by paramagnetic,  $S = 1/2$  ( $n = 3$ ), and diamagnetic,  $S = 0$  ( $n = 2$ ), ground states. These clusters contain Fe<sub>3</sub>S<sub>3</sub> fragments similar to the center in Fd I from *A. vinelandii*<sup>18</sup> and, with the exception of [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>3+</sup>, are metastable and transform to conventional clusters that contain the [Fe<sub>4</sub>S<sub>4</sub>]<sup>2+</sup> or [Fe<sub>2</sub>S<sub>2</sub>]<sup>2+</sup> cores.

In this paper we report on the electronic, nuclear magnetic resonance, and electrochemical properties of the [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>3-</sup> and [Fe<sub>6</sub>S<sub>6</sub>(SAR)<sub>6</sub>]<sup>3-</sup> clusters (Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>), and the detailed crystal and molecular structures of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>] and [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-MeC<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>].

## Experimental Section

(1) **Synthesis.** All procedures were carried out in an inert atmosphere using a Vacuum-Atmospheres Dri-Lab glovebox filled with prepurified nitrogen. The chemicals in this research other than solvents were used as purchased. Acetonitrile (CH<sub>3</sub>CN) was distilled from calcium hydride (CaH<sub>2</sub>) before use. Diethyl ether and methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) were distilled after refluxing with CaH<sub>2</sub> for ~2 h. Sodium aryl phenoxides were obtained by the reaction of sodium metal dispersion and the appropriate aryl phenols in diethyl ether under nitrogen.

(2) **Physical Methods.** Visible and ultraviolet spectra were obtained on a Cary Model 219 spectrophotometer. Proton NMR spectra were obtained on a Bruker 360-MHz Pulse FT NMR spectrometer with Me<sub>4</sub>Si as internal standard. Chemical shifts are reported in parts per million (ppm). The following convention is used whenever isotropically shifted NMR spectra are reported. A positive sign is assigned to a resonance appearing downfield from Me<sub>4</sub>Si. A negative sign is given to absorptions occurring upfield from Me<sub>4</sub>Si.

Electrochemical measurements were performed with a PAR Model 173 potentiostat/galvanostat and a PAR Model 175 universal programmer. The electrochemical cell used had platinum working and auxiliary electrodes. As reference electrode a saturated calomel electrode was used. All solvents used in the electrochemical measurements were properly dried and distilled, and tetra-*n*-butylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) was used as the supporting electrolyte. Normal concentrations used were ~0.001 M in electroanalyte and 0.1 M in supporting electrolyte. Purified argon was used to purge the solutions prior to the electrochemical measurements.

**Preparation of Compounds.** [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]. The procedure for the synthesis of one member of the series of these compounds (Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (I)) has been described<sup>22b</sup> elsewhere. Pure, crystalline compounds also are obtained with Ar = *p*-C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub> and 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> in 75% and 68% yield, respectively, by using an identical procedure. The [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(OC<sub>6</sub>H<sub>5</sub>)<sub>6</sub>] homologue consistently was obtained as an oil ( $\lambda_{\max} = 420$  nm).

[Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]-CH<sub>3</sub>CN (II). The procedure for the synthesis of this compound has been described earlier.<sup>22b</sup>

[Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(SAR)<sub>6</sub>]. The thiolate compounds were prepared in a high-vacuum line with Schlenk glassware and at -23 °C (CCl<sub>4</sub>/liquid nitrogen slurry). In a typical preparation 0.49 g (0.42 mmol) of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>] and 0.37 g (2.53 mmol) of NaSC<sub>6</sub>H<sub>4</sub>-*m*-CH<sub>3</sub> were dissolved in ~40 mL of cold CH<sub>3</sub>CN. The solution was stirred for 30 min at ~-23 °C, and the ensuing purple solution was filtered to remove NaCl. To the filtrate was added diethyl ether to incipient crystallization. The solution was cooled to -24 °C, and when the mixture was allowed to stand overnight, 0.51 g (0.31 mmol) of black microcrystalline material was obtained. The product could not be obtained acceptably pure for a meaningful elemental analysis.

**Tris(triethylmethylammonium) Hexabromohexakis(μ<sub>3</sub>-sulfido)hexaferrate(III,III), [Et<sub>3</sub>MeN]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>].** A mixture of anhydrous FeBr<sub>2</sub> (1.00 g, 4.63 mmol), NaSPh (0.92 g, 6.97 mmol), Et<sub>3</sub>MeNBr (0.45 g, 2.29 mmol), and elemental sulfur (0.39 g, 12.2 mmol) was stirred for ca. 9 min in 40 mL of CH<sub>2</sub>Cl<sub>2</sub>. The brown solution that developed was filtered, and the precipitate that formed was collected and thoroughly washed with CH<sub>2</sub>Cl<sub>2</sub> until the washings were colorless. This crude product was contaminated with NaBr and unreacted elemental sulfur. It was recrystallized from a mixture of CH<sub>3</sub>CN-diethyl ether. Yield: 0.50 g, 48%. The product possessed properties identical with those of the tetraethylammonium salt described before.<sup>22b</sup> Anal. Calcd for Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>N<sub>3</sub>C<sub>21</sub>H<sub>54</sub> ( $M_r = 1354.9$ ): N, 3.10; C, 18.60; H, 3.99. Found: N, 3.00; C, 18.77; H, 3.72.

**Reaction of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>] with PhCOCl.** A 0.40-g (0.26-mmol) sample of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(O-C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>6</sub>] was dissolved in 55 mL of CH<sub>3</sub>CN. To that was added a solution of 0.178 mL (1.54 mmol) of PhCOCl in 15 mL of CH<sub>3</sub>CN. The resulting reaction mixture was stirred for ca. 20 min. A gradual color change from brown-red to brown occurred upon mixing. The solution was then filtered and to the filtrate was added 100 mL of diethyl ether. When the mixture was allowed to stand for 10 h, a black microcrystalline product formed, which was isolated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.17 g, 57%.

The UV-visible spectrum of the product taken in CH<sub>3</sub>CN confirmed the identity of the latter as [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>].

**X-ray Diffraction Measurements. Collection and Reduction of Data.** Single crystals of [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>] (I) and [Et<sub>4</sub>N]<sub>3</sub>-

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[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>] (II) were obtained by the slow diffusion of diethyl ether into CH<sub>3</sub>CN solutions of the complexes. The crystals used for data collection were sealed in glass capillaries. Details concerning crystal characteristics are shown in Table I. Intensity data for I and II were collected on Syntex P2<sub>1</sub> and Nicolet P3/F four circle diffractometers, respectively. Detailed descriptions of both instruments and data acquisition procedures have been described earlier.<sup>25</sup> Due to diffuse diffraction characteristics and rapid decomposition on the X-ray beam at ambient temperature, intensity data for I were collected at -123 °C by passing a stream of boil-off nitrogen over the crystal. The cell dimensions for I and II were refined with 25 machine-centered reflections with 2θ values between 25 and 40°.

The raw data were reduced to net intensities, estimated standard deviations were calculated on the basis of counting statistics, Lorentz-polarization corrections were applied, and equivalent reflections were averaged. The estimated standard deviation of the structure factor was taken as the larger of that derived from counting statistics and that derived from the scatter of multiple measurements.

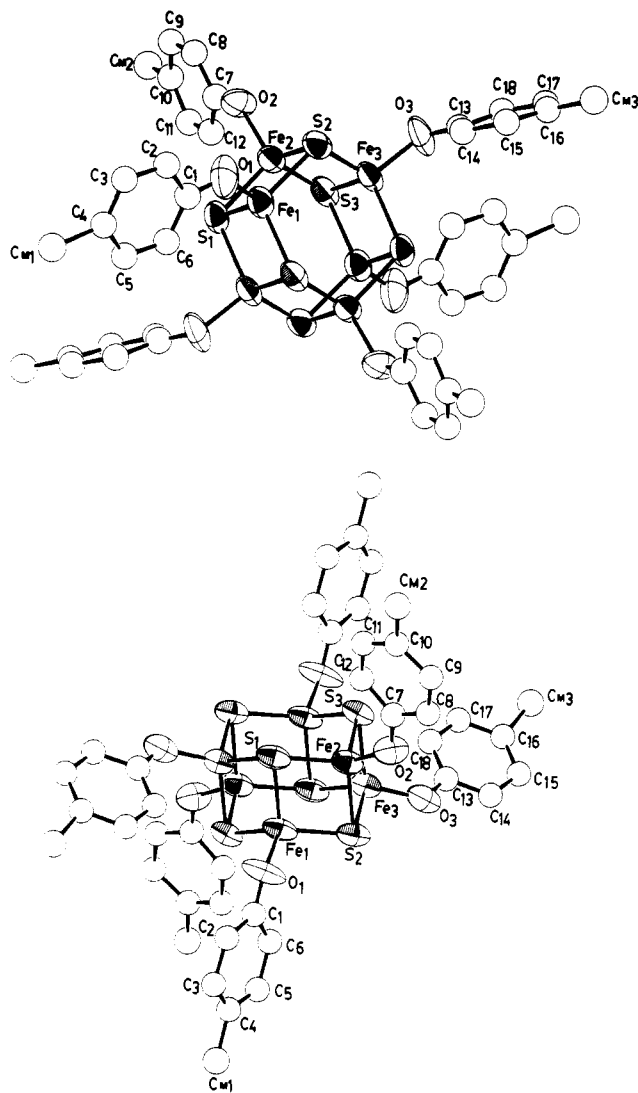
The least-squares program used minimizes  $\sum w(\Delta|F|)^2$ . The weighting function used throughout the refinement of the structure gives zero weight to those reflections with  $F^2 \leq 3\sigma(F^2)$  and  $w = 1/\sigma^2(F)$  to all others [ $\sigma^2(F^2) = (0.06F^2)^2 + \sigma^2(F^2)$  (from counting statistics)].

The procedures, atomic scattering factors, and anomalous dispersion corrections were used as previously described.<sup>25</sup> The refinement calculations were carried out on the University of Michigan Amdahl 800 computer using the locally adapted SHELX76 crystallographic program package. No absorption correction was applied to the data set from I ( $\mu = 13.3 \text{ cm}^{-1}$ ). For the intensity data from II an analytical absorption correction was applied by using the ABSC instruction in the SHELX76 package. The minimum and maximum absorption corrections were 0.558 and 0.401, respectively.

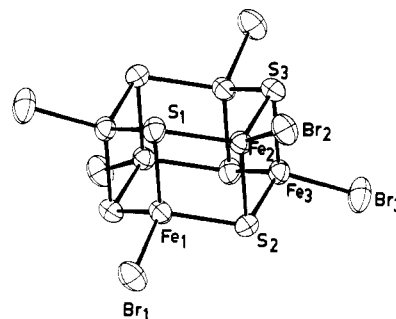
**Determination of Structures.** [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>] (I). The structure of I was solved with the use of a sharpened Patterson synthesis map calculated by the SHELX76 crystallographic package. The [Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>]<sup>3-</sup> anion is required by symmetry to reside on a crystallographic inversion center. The three unique iron atoms were initially determined from the Patterson map. A subsequent Fourier map calculation phased by three Fe atoms revealed the three crystallographically unique sulfur atoms. The rest of the oxygen and carbon atoms were located by successive electron density difference Fourier maps followed by full-matrix least-squares refinement. The refinement of all atoms in the asymmetric unit using isotropic temperature factors gave a conventional *R* value of 0.13. One of the tetraethyl ammonium cations resides on a general position and the other on a center of symmetry (0,0,0). As a result the latter is subject to a twofold disorder. Further refinement with anisotropic temperature factors for the non-hydrogen, nondisordered, atoms resulted in a *R* value of 0.079. At this stage the hydrogen atoms were introduced at their calculated positions (C-H = 0.95 Å). In the final refinement the hydrogen atoms were included<sup>26</sup> in the structure factor calculation but were not refined. The final *R* value was 0.075, and the weighted *R<sub>w</sub>* was 0.072. During the last cycle of refinement all parameter shifts were less than 10% of their esd.

[Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]·CH<sub>3</sub>CN. The structure of II was solved by the direct-methods routine SOLV of the SHELX76 package. Here too the [Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]<sup>3-</sup> anion is required by symmetry to reside on a crystallographic inversion center. After the heavy-atom fragment (Fe<sub>3</sub>S<sub>3</sub>) of the structure was located, the rest of the non-hydrogen atoms were found from subsequent Fourier electron density difference maps. In this structure as well, one of the [Et<sub>4</sub>N]<sup>+</sup> cations is required by symmetry to reside on a crystallographic inversion center and therefore it is disordered. The type of disorder is identical with the one described above for I, and its was treated similarly. The refinement of all atoms in the asymmetric unit using the isotropic temperature factor set gave a *R* value of 0.096. Anisotropic temperature factors were assigned to all non-hydrogen, nondisordered atoms, and refinement converged to *R<sub>w</sub>* = 0.051 and *R* = 0.047. At this stage the hydrogen atoms on the nondisordered carbon atoms were included in the structure factor calculation at their calculated positions but were not refined (C-H = 0.95 Å). A final cycle of least-squares refinement resulted in values of *R<sub>w</sub>* = 0.043 and *R* = 0.049. During the last cycle of refinement all parameter shifts were less than 10% of their esd.

**Crystallographic Results.** The final atomic positional and thermal parameters for [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>] and [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]·CH<sub>3</sub>CN with standard deviations derived from the inverse matrices of the least-squares refinements are compiled in Tables II and III, respectively. Intramolecular distance and angles for the anions in both structures are given in Table IV. The atom-labeling schemes are



**Figure 1.** Structure and labeling of the [Fe<sub>6</sub>S<sub>6</sub>(OC<sub>6</sub>H<sub>4</sub>Me)<sub>6</sub>]<sup>3-</sup> anion (two views). Thermal ellipsoids are drawn by ORTEP. The ellipsoids of the Fe<sub>6</sub>S<sub>6</sub>O<sub>6</sub> fragment represent 50% probability surfaces; the remaining carbon atoms were drawn with artificially small and uniform ellipsoids for clarity.



**Figure 2.** Structure and labeling of the [Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]<sup>3-</sup> anion.

shown in Figures 1 and 2. The atomic positional and thermal parameters and tables of interatomic distances and angles for the [Et<sub>4</sub>N]<sup>+</sup> cations in all structures have been deposited as supplementary material.

The generated atomic parameters of the hydrogen atoms have been deposited together with tables of the *F<sub>o</sub>* and *F<sub>c</sub>* values. (See paragraph at the end of this paper regarding supplementary material.)

## Results and Discussion

**Synthesis.** As described previously for the hexachloro homologue,<sup>22b</sup> the [Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]<sup>3-</sup> cluster can be obtained by a reaction that usually is employed for the synthesis of the [Fe<sub>4</sub>S<sub>4</sub>X<sub>4</sub>]<sup>2-</sup> cubanes. The latter are obtained in high yield when [Ph<sub>4</sub>P]<sup>+</sup> is

(25) Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1984**, *23*, 403.

(26) Cleland, W. E.; Averill, B. A. *Inorg. Chem.* **1984**, *23*, 4192.

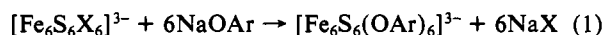
**Table I.** Summary of Crystal Data, Intensity Collection, and Structure Refinement

	[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ·(OC <sub>6</sub> H <sub>4</sub> Me) <sub>6</sub> ]	[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub> ·CH <sub>3</sub> CN]
formula	C <sub>66</sub> H <sub>102</sub> N <sub>3</sub> O <sub>6</sub> Fe <sub>6</sub> S <sub>6</sub>	C <sub>26</sub> H <sub>63</sub> N <sub>4</sub> Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub>
<i>M<sub>r</sub></i>	1560	1439
<i>a</i> , Å	13.173 (5)	14.531 (3)
<i>b</i> , Å	19.848 (10)	11.028 (2)
<i>c</i> , Å	14.304 (4)	17.566 (3)
α, deg	90.00	90.00
β, deg	98.05 (3)	100.69 (1)
γ, deg	90.00	90.00
<i>V</i> , Å <sup>3</sup> ; <i>Z</i>	3703 (3); 2	2766 (1); 2
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.42	1.73
<i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup>	1.34 <sup>a</sup>	1.78 <sup>b</sup>
space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
cryst dimens, mm	0.17 × 0.39 × 0.39	0.13 × 0.13 × 0.34
abs coeff μ, cm <sup>-1</sup>	13.26	59.82
temp, °C	-123	21
radiation	Mo (λ <sub>Kα</sub> = 0.71069 Å)	Mo (λ <sub>Kα</sub> = 0.71069 Å)
data collcd;	<i>h, k, ±l</i> ; 40; 3796	<i>h, k, ±l</i> ; 40; 4028
2θ, deg; no.		
scan speed	2–29.3	2–29.3
min–max, deg/min		
no. of unique data	3461	2516
no. of data used in refinement ( <i>F</i> <sub>o</sub> <sup>2</sup> > 3σ( <i>F</i> <sub>o</sub> <sup>2</sup> ))	2107	1874
no. of atoms in asymmetric unit	95	53
no. of variables	283	213
phasing technique	Patterson	direct methods
<i>R</i> , %	7.50	4.89
<i>R</i> <sub>w</sub> , %	7.22	4.35

<sup>a</sup> By flotation in CCl<sub>4</sub>/pentane mixture. <sup>b</sup> By flotation in CHBr<sub>3</sub>/pentane mixture. <sup>c</sup> *R* = Σ(*F*<sub>o</sub> - |*F*<sub>c</sub>|)/Σ*F*<sub>o</sub>; *R*<sub>w</sub> = [Σ*w*(*F*<sub>o</sub> - |*F*<sub>c</sub>|)<sup>2</sup>/Σ*wF*<sub>o</sub><sup>2</sup>]<sup>1/2</sup>.

present in the reaction medium as a counterion. The cluster assembly follows a different course in the presence of [Et<sub>4</sub>N]<sup>+</sup> where instead the hexanuclear prismanes form and can be isolated in excellent yields. At this stage we can only speculate that the [Et<sub>4</sub>N]<sup>+</sup> cation promotes the specific assembly of three [Fe<sub>2</sub>S<sub>2</sub>X<sub>2</sub>L<sub>2</sub>]<sup>-</sup> units (L = CH<sub>3</sub>CN) prior to the formation of the [Fe<sub>6</sub>S<sub>6</sub>X<sub>6</sub>]<sup>3-</sup> "prismanes". In the absence of the apparently specific ion pairing facilitated by the [Et<sub>4</sub>N]<sup>+</sup> cation, the [Fe<sub>2</sub>S<sub>2</sub>X<sub>2</sub>L<sub>2</sub>]<sup>-</sup> units dimerize to form the [Fe<sub>4</sub>S<sub>4</sub>X<sub>4</sub>]<sup>2-</sup> cubanes.

The aryloxy prismanes, [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>3-</sup>, are obtained by simple metathetical reactions from the halide analogues in CH<sub>3</sub>CN solution (eq 1). The crude products from such reactions contain



small amounts of [Fe<sub>4</sub>S<sub>4</sub>(OAr)<sub>4</sub>]<sup>2-</sup> (<8%) that very likely are due to the [Fe<sub>4</sub>S<sub>4</sub>X<sub>4</sub>]<sup>2-</sup> clusters that form slowly in CH<sub>3</sub>CN solutions of the [Fe<sub>6</sub>S<sub>6</sub>X<sub>6</sub>]<sup>3-</sup> "prismanes". The metastable nature and thermal transformations of the latter have been described previously.<sup>22b</sup>

By comparison to the [Fe<sub>6</sub>S<sub>6</sub>X<sub>6</sub>]<sup>3-</sup> metastable clusters (X = Cl, Br) the aryloxy-analogous compounds exhibit greater thermal stability. The conversion to the [Fe<sub>4</sub>S<sub>4</sub>(OAr)<sub>4</sub>]<sup>2-</sup> clusters (eq 2)



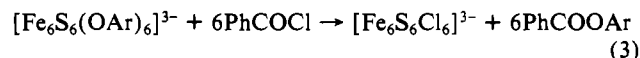
does not occur readily, and in refluxing CH<sub>3</sub>CN for ca. 30 min this transformation proceeds to only ~40% (monitored by NMR). The transformation indicated in eq 2 above is not reversible, and the two clusters are not at equilibrium. The wide difference in the chemical shifts of the isotropically shifted aromatic proton resonances in the two types of clusters allows for their unambiguous identification in solution by NMR spectroscopy. The relative intensities of the NMR signals from mixtures of the two clusters do not show reversible changes with changes in temperature, and solutions of pure [Fe<sub>4</sub>S<sub>4</sub>(OAr)<sub>4</sub>]<sup>2-</sup> exhibit only a single set of aromatic proton resonances.<sup>10</sup>

**Table II.** Fractional Atomic Coordinates and Thermal Parameters<sup>a</sup> and Their Standard Deviations<sup>b</sup> in [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>6</sub>]

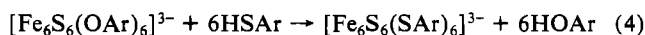
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Fe1	0.0617 (02)	0.0945 (01)	0.5975 (02)	0.0602
Fe2	0.0953 (02)	0.0681 (01)	0.4141 (02)	0.0643
Fe3	-0.1106 (02)	0.0390 (01)	0.3700 (02)	0.0632
S1	0.1950 (03)	0.0369 (02)	0.5489 (03)	0.0699
S2	-0.0383 (03)	0.1253 (02)	0.4618 (03)	0.0641
S3	0.0248 (03)	-0.0192 (02)	0.3252 (03)	0.0624
O1	0.1045 (08)	0.1676 (05)	0.6774 (08)	0.0753
O2	0.1598 (09)	0.1239 (05)	0.3359 (08)	0.0928
O3	-0.2046 (09)	0.0738 (06)	0.2692 (08)	0.0987
C1	0.0483 (15)	0.2157 (09)	0.7061 (13)	0.0816
C2	-0.0559 (15)	0.2221 (09)	0.6816 (12)	0.0256
C3	-0.1114 (14)	0.2791 (10)	0.7091 (13)	0.0304
C4	-0.0611 (16)	0.3284 (10)	0.7629 (13)	0.0311
C5	0.0422 (18)	0.3213 (11)	0.7948 (14)	0.0381
C6	0.0963 (15)	0.2635 (11)	0.7651 (14)	0.0330
CM1	-0.1221 (15)	0.3926 (10)	0.7899 (14)	0.0364
C7	0.2229 (14)	0.1060 (08)	0.2799 (12)	0.0668
C8	0.2362 (14)	0.1470 (09)	0.2017 (13)	0.0279
C9	0.3017 (15)	0.1279 (10)	0.1367 (13)	0.0331
C10	0.3592 (16)	0.0700 (11)	0.1498 (14)	0.0328
C11	0.3557 (16)	0.0316 (10)	0.2286 (15)	0.0362
C12	0.2862 (16)	0.0496 (10)	0.2930 (13)	0.0313
CM2	0.4355 (19)	0.0485 (11)	0.0811 (17)	0.0473
C14	-0.2767 (11)	0.1279 (09)	0.1313 (16)	0.0624
C15	-0.2664 (11)	0.1693 (09)	0.0544 (16)	0.0556
C16	-0.1731 (11)	0.2012 (09)	0.0484 (16)	0.0638
C17	-0.0902 (11)	0.1917 (09)	0.1193 (16)	0.0613
C18	-0.1006 (11)	0.1503 (09)	0.1962 (16)	0.0412
C13	-0.1939 (11)	0.1184 (09)	0.2022 (16)	0.0383
CM3	-0.1351 (31)	0.2455 (20)	-0.0523 (28)	0.1066
N1	0.1106 (11)	0.3325 (07)	0.4618 (13)	0.0773
C19	0.1513 (13)	0.2622 (08)	0.4752 (13)	0.0785
C20	0.2531 (15)	0.2507 (09)	0.4391 (16)	0.1191
C21	0.0143 (13)	0.3318 (09)	0.5066 (14)	0.0873
C22	-0.0397 (14)	0.3999 (11)	0.5022 (17)	0.1340
C23	0.1828 (19)	0.3837 (11)	0.5083 (22)	0.1275
C24	-0.2079 (19)	0.3770 (13)	0.6115 (22)	0.1490
C25	0.0932 (21)	0.3524 (11)	0.3627 (21)	0.1335
C26	0.0284 (19)	0.3038 (13)	0.3018 (16)	0.1325
N2	0.0	0.0	0.0	0.1220
CA1	0.0545 (41)	-0.0715 (29)	0.0186 (37)	0.0501
CA2	0.1341 (51)	0.9156 (31)	0.1123 (46)	0.0523
CA3	0.0575 (33)	0.0721 (23)	0.0013 (29)	0.0338
CA4	0.3795 (37)	0.5692 (24)	0.0914 (34)	0.0358
CB1	0.0761 (36)	0.0068 (24)	0.0922 (35)	0.0407
CB2	0.1454 (35)	-0.0508 (25)	0.1140 (31)	0.0267
CB3	0.0687 (34)	-0.0121 (22)	-0.0739 (31)	0.0374
CB4	0.1563 (37)	0.0389 (25)	-0.0787 (34)	0.0359

<sup>a</sup> The equivalent isotropic thermal parameters are in units of square angstroms. A table of anisotropic temperature factors has been deposited. <sup>b</sup> Calculated standard deviations are indicated in parentheses.

The [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>3-</sup> clusters exhibit exceedingly high hydrolytic and solvolytic instability. Traces of water in CH<sub>3</sub>CN solutions of these compounds severely hinder their crystallization and eventually lead to decomposition. Similarly, a decomposition of these clusters takes place after prolonged periods of standing in DMF solution. This type of instability is typical for aryloxy Fe/S complexes and has been observed previously with the [Fe(OPh)<sub>4</sub>]<sup>-</sup>,<sup>5b</sup> [Fe<sub>2</sub>S<sub>2</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>4</sub>]<sup>2-</sup>,<sup>8,26</sup> and [Fe<sub>4</sub>S<sub>4</sub>(OAr)<sub>4</sub>L<sub>x</sub>]<sup>2-</sup> (*x* = 0;<sup>10</sup> *x* = 2, L = Cl, SPh<sup>11</sup>) complexes. The [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>3-</sup> clusters react rapidly with PhCOCl to afford the [Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>]<sup>3-</sup> prismane (eq 3) by a reaction similar to that reported previously<sup>5</sup> for the [Fe<sub>4</sub>S<sub>4</sub>(SR)<sub>4</sub>]<sup>2-</sup> cubanes.



The aryloxy prismanes also react instantly and quantitatively with either aliphatic or aromatic thiols to afford the analogous thiolate clusters. The reaction (eq 4) is accompanied by the development of a deep violet color and can be monitored by



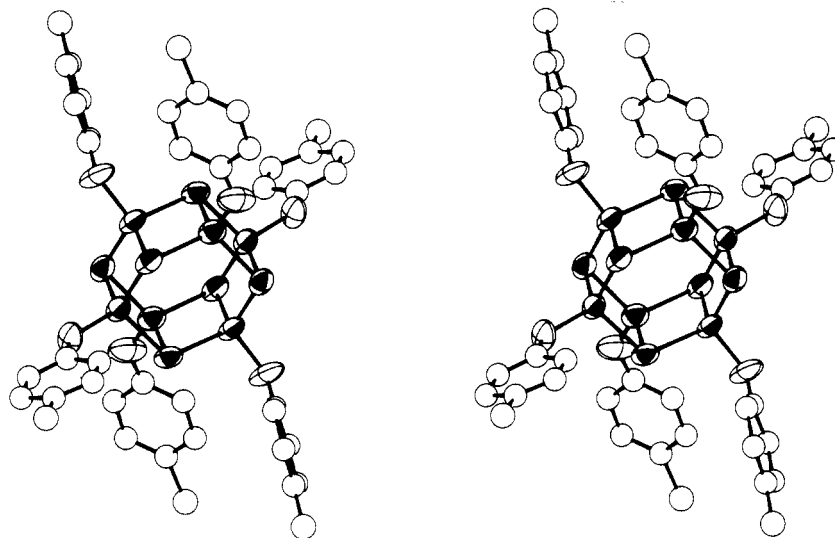


Figure 3. Perspective view of the  $[\text{Fe}_6\text{S}_6(\text{OC}_6\text{H}_4\text{-}p\text{-Me})_6]^{3-}$  anion as drawn by ORTEP.

Table III. Fractional Atomic Coordinates and Thermal Parameters<sup>a</sup> and Their Standard Deviations<sup>b</sup> in  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6\text{Br}_6]\cdot\text{CH}_3\text{CN}$

atom	x	y	z	U
Fe1	0.4362 (01)	-0.1297 (02)	0.0839 (01)	0.0434
Fe2	0.3610 (01)	-0.0789 (02)	-0.0675 (01)	0.0444
Fe3	0.4652 (01)	0.1152 (02)	0.1044 (01)	0.0427
Br1	0.4321 (01)	0.2339 (01)	0.2079 (01)	0.0726
Br2	0.2221 (01)	-0.1637 (01)	-0.1415 (01)	0.0596
Br3	0.3796 (01)	-0.2628 (02)	0.1688 (01)	0.0967
S1	0.3346 (02)	0.0226 (03)	0.0390 (02)	0.0484
S2	0.4649 (02)	-0.2278 (03)	-0.0228 (02)	0.0454
S3	0.5683 (02)	-0.0385 (03)	0.1451 (02)	0.0457
N1	0.2361 (07)	-0.0755 (09)	-0.3925 (06)	0.0459
C1	0.2667 (10)	-0.1963 (13)	-0.4178 (08)	0.0679
C2	0.3046 (10)	-0.2862 (12)	-0.3516 (09)	0.0712
C3	0.2141 (09)	0.0071 (11)	-0.4626 (07)	0.0546
C4	0.1367 (09)	-0.0349 (12)	-0.5267 (07)	0.0579
C5	0.3122 (10)	-0.0174 (12)	-0.3335 (08)	0.0599
C6	0.4045 (09)	0.0023 (14)	-0.3586 (08)	0.0693
C7	0.1485 (10)	-0.0956 (14)	-0.3572 (08)	0.0622
C8	0.1038 (10)	0.0125 (14)	-0.3322 (08)	0.0725
N2	0.0	0.0	0.0	0.1263
C9	0.0917 (33)	-0.0685 (48)	0.0025 (26)	0.0475
C10	0.0878 (35)	-0.1814 (49)	0.0278 (28)	0.0305
C11	-0.0873 (25)	-0.0780 (33)	-0.0437 (21)	0.0342
C12	-0.0856 (33)	-0.0557 (47)	-0.1337 (31)	0.0463
C13	-0.0084 (34)	-0.1369 (47)	0.0253 (26)	0.0467
C14	0.0846 (37)	-0.2218 (45)	0.0491 (29)	0.0439
C15	0.0290 (26)	0.0141 (35)	-0.0836 (22)	0.0378
C16	-0.0424 (32)	-0.0822 (42)	-0.1392 (26)	0.0368
NS	0.1210 (13)	0.3839 (16)	0.0761 (11)	0.0517
C1S	0.1581 (13)	0.4267 (17)	0.1309 (12)	0.0362
C2S	0.2077 (13)	0.4731 (17)	0.2040 (11)	0.0401

<sup>a</sup>The equivalent isotropic thermal parameters are in units of square angstroms. A table of anisotropic temperature factors has been deposited. <sup>b</sup>Calculated standard deviations are indicated in parentheses.

electronic absorption spectroscopy. Each of the two clusters shows a broad absorption band with  $\lambda_{\text{max}} = 427 \text{ nm}$  ( $\epsilon = 19\,720$ ) for  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_6]^{3-}$  and  $\lambda_{\text{max}} = 480 \text{ nm}$  ( $\epsilon = 21\,330$ ) for  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]^{3-}$ .

The thiolate prismanes,  $[\text{Fe}_6\text{S}_6(\text{SR})_6]^{3-}$  ( $\text{R} = \text{Et}; \text{CH}_2\text{Ph}; \text{Ph}; p\text{-}, m\text{-CH}_3\text{Ph}$ ), are highly metastable at ambient temperatures and in  $\text{CH}_3\text{CN}$  solution rapidly (<5 min) transform to the cubane homologues. The successful isolation of the  $[\text{Fe}_6\text{S}_6(\text{SAr})_6]^{3-}$  clusters can be accomplished only at low temperatures ( $\sim -20^\circ\text{C}$ ). The rate of transformation of these clusters to the corresponding  $[\text{Fe}_4\text{S}_4(\text{SAr})_4]^{2-}$  cubanes is considerably slower in relatively nonpolar solvents; however, even in  $\text{CH}_2\text{Cl}_2$  solution at ambient temperature, the transformation is nearly complete after ca. 1 h.

**Crystallographic Studies. Description of Structures.** The  $[\text{Et}_4\text{N}]^+$  cations and the  $[\text{Fe}_6\text{S}_6\text{L}_6]^{3-}$  anions are well separated

in the crystal structures of  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_6]$  (I) and  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6\text{Br}_6]$  (II). The  $\text{CH}_3\text{CN}$  molecule of solvation in II also is located on a general position away from the anion. The six  $[\text{Et}_4\text{N}]^+$  cations in each of the unit cells of both structures are divided in two crystallographically independent groups. Four of the cations are located on general positions, and the remaining two reside on inversion centers (0,0,0) and consequently are subject to a twofold positional disorder. The structures of the cations are unexceptional and will not be considered further. The  $[\text{Fe}_6\text{S}_6\text{L}_6]^{3-}$  anions in both structures are located on crystallographic centers of symmetry at 0, 0,  $1/2$  and  $1/2$ , 0, 0 for I and II, respectively. The  $[\text{Fe}_6\text{S}_6]^{3+}$  core in both structures defines a distorted hexagonal prism with idealized  $D_{3d}$  symmetry. The core polyhedron, which contains Fe and S atoms at alternate vertices, also can be described in terms of two ( $\text{Fe}_6$  and  $\text{S}_6$ ) concentric, interpenetrating, trigonally compressed octahedra. The  $\text{Fe}_6\text{S}_6$  units are inscribed in larger trigonally compressed octahedra defined by the six O atoms in I and the six Br atoms in II, (Figures 1, 2). The coordination geometry for the Fe atoms in both structures is distorted tetrahedral. The Fe–O bond length in I at 1.880 (11) Å (range 1.86 (11)–1.895 (12) Å) is similar to the corresponding bond lengths in  $[\text{Fe}_4\text{S}_4(\text{OC}_6\text{H}_5)_4]^{2-}$  at 1.865 (8) Å and in the  $[\text{Fe}_2\text{S}_2(o,o\text{-biphenolate})_2]^{2-}$  anion<sup>8</sup> at 1.893 (3) Å. A more detailed comparison of the Fe–O bond length in I to those observed in other Fe/S/OR complexes is not warranted in view of the fact that the data in I were obtained at  $-123^\circ\text{C}$ . The O–Fe–S angles in I range from 108.7 (4) to 115.0 (4)°. The orientation of the phenyl rings in the structure of I (Figure 3) and the distortions apparent in the  $\text{S}_3\text{FeO}$  sites can be attributed to intramolecular, ortho phenyl hydrogen–sulfur and metal interactions. A detailed discussion of these unique types of intramolecular interaction in the structures of the  $[\text{M}(\text{SPh})_4]^{2-}$  complexes has been given previously.<sup>27</sup>

The Fe–Br distance in II at 2.366 (9) Å (range 2.351 (2)–2.382 (2) Å) is comparable to the Fe–Br distance in  $[\text{Fe}_4\text{S}_4(\text{Br})_4]^{2-}$  at 2.341 (2) Å.<sup>28</sup> The Br–Fe–S angles in II also are similar to the cubane homologue and range from 110.4 (1) to 113.5 (1)°.

**Structures of the  $[\text{Fe}_6\text{S}_6]^{3+}$  Cores.** The hexagonal-prismatic  $[\text{Fe}_6\text{S}_6]$  cages in I and II are very similar and possess idealized  $D_{3d}$  symmetry. The  $\text{Fe}_6\text{S}_6$  polyhedra and the homologous  $\text{Fe}_4\text{S}_4$  cubanes are oligomers of the same  $\text{Fe}_2\text{S}_2$  rhombic unit. The fusion of three such units in the closed structure of the  $\text{Fe}_6\text{S}_6$  cage generates the new, cyclic,  $\text{Fe}_3\text{S}_3$  structural units. The latter possess a cyclohexane type chair conformation. The dihedral angles  $\text{Fe1S2Fe3/S1S3Fe1'Fe3'}$  and  $\text{S1S3Fe1'Fe3'/Fe1'S2'Fe3'}$  in the

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(28) Müller, A.; Schladerbeck, N.; Bögge, H. *Chimia* **1985**, *39*, 24.

Table IV. Selected Distances (Å) and Angles (deg) in the [Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>]<sup>3-</sup> and [Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>]<sup>3-</sup> Anions

Distances <sup>a</sup>						
	[Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ] <sup>3-b</sup>	[Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub> ] <sup>3-c</sup>	[Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ] <sup>3-b</sup>		[Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub> ] <sup>3-c</sup>	
Fe1-Fe2	2.771 (3)	2.743 (2)	Fe1...Fe2	3.824 (4)	3.797 (2)	
Fe2-Fe3	2.759 (3)	2.757 (2)	Fe2...Fe3	3.732 (4)	3.785 (2)	
Fe1-Fe3	2.753 (3)	2.748 (2)	Fe1...Fe3	3.857 (4)	3.853 (2)	
mean	2.761 (5)	2.749 (4)	mean	3.804 (37)	3.812 (20)	
Fe1-S1	2.285 (5)	2.281 (4)	Fe1-O1	1.883 (11)	Fe1-Br1	2.351 (2)
Fe2-S2	2.278 (5)	2.271 (4)	Fe2-O2	1.861 (11)	Fe2-Br3	2.382 (2)
Fe3-S3	2.291 (5)	2.289 (4)	Fe3-O3	1.895 (12)	Fe3-Br3	2.366 (2)
mean	2.285 (5)	2.280 (5)	mean	1.880 (11)	mean	2.366 (9)
Fe1-S2	2.272 (5)	2.272 (4)	S1-S2	3.608 (6)		3.630 (5)
Fe1-S3	2.259 (5)	2.258 (4)	S2-S3	3.630 (6)		3.621 (4)
Fe2-S1	2.263 (6)	2.277 (4)	S3-S1	3.634 (6)		3.626 (4)
Fe2-S3	2.268 (5)	2.264 (4)	mean	3.624 (8)		3.626 (5)
Fe3-S1	2.283 (5)	2.272 (4)	S1...S3	3.806 (6)		3.773 (5)
Fe3-S2	2.282 (5)	2.278 (4)	S2...S3	3.689 (6)		3.700 (5)
mean	2.271 (5)	2.270 (4)	S1...S2	3.814 (6)		3.746 (5)
mean of 9	2.276 (5)	2.274 (4)	mean	3.770 (40)		3.740 (21)
O1-C1	1.308 (19)		mean of 6	3.697 (37)		3.683 (27)
O2-C7	1.283 (18)					
O3-C13	1.328 (24)					
mean <sup>d</sup>	1.306 (20)					

Angles						
	[Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ] <sup>3-</sup>	[Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub> ] <sup>3-</sup>		[Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ] <sup>3-</sup>	[Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub> ] <sup>3-</sup>	
S1-Fe1-S3	113.8 (2)	112.5 (1)	Fe2-S1-Fe3	110.4 (2)	112.6 (1)	
S1-Fe2-S3	114.3 (2)	112.4 (1)	Fe1-S2-Fe3	115.7 (2)	115.7 (1)	
S2-Fe3-S1	113.3 (2)	110.8 (1)	Fe2-S3-Fe1	115.3 (2)	114.2 (1)	
mean	113.8 (3)	111.9 (5)	mean	113.8 (2)	114.2 (9)	
S2-Fe1-S1	104.7 (2)	105.8 (1)	Fe1-S1-Fe2	75.1 (2)	74.0 (1)	
S3-Fe1-S1	106.2 (2)	106.1 (1)	Fe1-S1-Fe3	74.1 (2)	74.2 (1)	
S2-Fe2-S1	105.2 (2)	105.9 (1)	Fe1-S2-Fe2	75.0 (2)	74.3 (1)	
S2-Fe2-S3	106.0 (2)	106.0 (1)	Fe2-S2-Fe3	74.5 (1)	74.6 (1)	
S2-Fe3-S3	105.1 (2)	104.9 (1)	Fe1-S3-Fe3	74.5 (2)	74.3 (1)	
S1-Fe3-S3	105.2 (2)	105.3 (1)	Fe2-S3-Fe3	74.5 (1)	74.5 (1)	
mean	105.4 (2)	105.7 (2)	mean	74.6 (2)	74.3 (1)	
mean of 9	108 (2)	108 (1)	Fe1-Fe3-Fe2	87.8 (1)	87.2 (1)	
O1-Fe1-S1	113.1 (4)	Br1-Fe1-S1	113.5 (1)	Fe1-Fe2-Fe3	88.4 (1)	88.9 (1)
O2-Fe2-S2	108.7 (4)	Br2-Fe2-S2	110.4 (1)	Fe3-Fe1-Fe2	85.0 (1)	87.1 (1)
O3-Fe3-S3	115.0 (4)	Br3-Fe3-S3	112.7 (1)	mean	87.1 (1)	87.7 (6)
mean	112.3 (2.0)	mean	112.2 (9)	Fe2-Fe1-Fe3	58.1 (1)	59.3 (1)
O1-Fe1-S2	113.5 (4)	Br1-Fe1-S2	111.6 (1)	Fe1-Fe2-Fe3	61.4 (1)	61.1 (1)
O1-Fe1-S3	110.0 (4)	Br1-Fe1-S3	110.1 (1)	Fe2-Fe3-Fe1	60.5 (1)	59.6 (1)
O2-Fe2-S1	114.6 (4)	Br2-Fe2-S1	112.7 (1)	mean	60 (1)	60.0 (5)
O2-Fe2-S3	107.6 (4)	Br2-Fe2-S3	109.3 (1)	Fe1-O1-C1	128.1 (1)	
O3-Fe3-S2	109.9 (4)	Br3-Fe3-S2	111.3 (1)	Fe2-O2-C7	126.9 (1)	
O3-Fe3-S1	108.2 (4)	Br3-Fe3-S1	111.5 (1)	Fe3-O3-C13	132.0 (1)	
mean	110 (1)	mean	111.1 (5)	mean	129.0 (1.5)	
mean of 9	111 (1)	mean of 9	111.5 (5)			

<sup>a</sup> The standard deviation from the mean,  $\sigma$ , is reported;  $\sigma = [\sum_{i=1}^N (X_i - \bar{x})^2 / (N(N-1))]^{1/2}$ . <sup>b</sup> For the cations in [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>], the N-C bonds are within the range of 1.46 (3)-1.50 (2) Å with a mean value of 1.49 (3) Å for the cation of N1 and 1.51 (5)-1.62 (4) Å with a mean value of 1.57 (6) Å for the disordered [Et<sub>4</sub>N]<sup>+</sup> of N2. The six Ci-N1-Cj angles are found between 104 (1) and 113 (1)° with a mean value of 110 (2)°. <sup>c</sup> For the cations in [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Br<sub>6</sub>], the N-C bonds are within the range of 1.50 (2)-1.54 (2) Å with a mean value of 1.52 (2) Å for the cation of N1 and 1.53 (5)-1.61 (4) Å with a mean value of 1.58 (5) Å for the disordered [Et<sub>4</sub>N]<sup>+</sup> of N2. The six Ci-N1-Cj angles are found between 108 (1) and 111 (1)° with a mean value of 110 (1)°. For the cations the scatter estimate was obtained as  $S = [\sum_{i=1}^N (X_i - \bar{x})^2 / (N-1)]^{1/2}$ , where  $X_i$  is the value of an individual bond or angle and  $\bar{x}$  is the mean value for the  $N$  equivalent bond lengths or angles. <sup>d</sup> For the phenyl rings of the three phenoxy ligands in the [Fe<sub>6</sub>S<sub>6</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>6</sub>]<sup>3-</sup> anion, the C-C bonds are within the range of 1.359 (22)-1.817 (43) Å with a mean value of 1.432 (43) Å, and the C-C-C angles are found between 116 (2) and 123 (2)° with a mean value of 120 (2)°.

Fe<sub>3</sub>S<sub>3</sub> chairs are 132.5 and 134.8° in I and 135.3 and 133.7° in II. The S1S2S3 planes within a single Fe<sub>3</sub>S<sub>3</sub> unit are parallel to and lie above the Fe1'Fe2Fe3' planes. These elevations are 0.62 and 0.63 Å, respectively, for I and II.

The Fe<sub>2</sub>S<sub>2</sub> rhombic units are parallel to the idealized S<sub>6</sub> axis and are very nearly planar with a maximum deviation from the least-squares planes of 0.01 Å. The planarity of the Fe<sub>2</sub>S<sub>2</sub> units in the Fe<sub>6</sub>S<sub>6</sub> cages should be contrasted with the nonplanar geometry of the same units in the structures of the Fe<sub>4</sub>S<sub>4</sub> clusters. The three independent dihedral angles between the Fe<sub>2</sub>S<sub>2</sub> rhombi are 122.3, 116.2, and 121.5° in I and 121.8, 118.5, and 119.7° in II. The rather small, S1Fe2S2Fe1/S1Fe1Fe3'S3', dihedral

angle in I (116.2°) indicates a slight distortion (compression) of the prismatic core along a two-fold axis perpendicular to the idealized S<sub>6</sub> axis. This twofold axis passes through the centers of the Fe2S3Fe3S2 and Fe2'S3'Fe3'S2' rhombi. This distortion is reflected in the nonequal Fe...Fe distances in the Fe<sub>3</sub>S<sub>3</sub> cyclohexane chairs: The Fe2...Fe3 distance at 3.732 (4) Å is considerably smaller than either Fe1...Fe3 or Fe1...Fe2 at 3.857 (4) and 3.824 (4) Å, respectively (see Table IV). A distortion of this kind is not observed in either the Br or the Cl analogues.

Apart from this slight compression in I, the origin of which is difficult to ascertain, the structural parameters of the [Fe<sub>6</sub>S<sub>6</sub>]<sup>3+</sup> core ligated by three different terminal ligands (ArO<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>)

**Table V.** Structural Comparison of Compounds Containing the  $[\text{Fe}_6\text{S}_6]^{3+}$  and  $[\text{Fe}_4\text{S}_4]^{2+}$  Cores

dist, Å or angle, deg	$[\text{Et}_4\text{N}]_3^- [\text{Fe}_6\text{S}_6(\text{OC}_6\text{H}_4\text{Me})_6]$	$[\text{Et}_4\text{N}]_3^- [\text{Fe}_6\text{S}_6\text{Br}_6]$	$[\text{Et}_4\text{N}]_3^- [\text{Fe}_6\text{S}_6\text{Cl}_6]^a$
$\overline{\text{Fe}-\text{Fe}}$	2.753 (5)	2.749 (4)	2.765 (3)
$\overline{\text{Fe}\cdots\text{Fe}}$	3.804 (37)	3.812 (20)	3.790 (8)
$\overline{\text{Fe}-\text{S}}$	2.276 (5)	2.274 (4)	2.276 (3)
$\overline{\text{Fe}-\text{X}}$	1.880 (11)	2.366 (9)	2.223 (2)
$\overline{\text{S}\cdots\text{S}^b}$	3.634 (6)	3.626 (5)	3.618 (5)
$\overline{\text{S}\cdots\text{S}^c}$	3.770 (40)	3.740 (21)	3.801 (9)
$\overline{\text{Fe}-\text{S}-\text{Fe}^b}$	74.6 (2)	74.3 (1)	74.7 (2)
$\overline{\text{Fe}-\text{S}-\text{Fe}^c}$	113.8 (2)	114.2 (9)	113.2 (2)
$\overline{\text{S}-\text{Fe}-\text{S}^b}$	105.4 (2)	105.7 (2)	105.1 (2)
$\overline{\text{S}-\text{Fe}-\text{S}^c}$	113.8 (3)	111.9 (5)	113.7 (3)
$\overline{\text{X}-\text{Fe}-\text{S}}$	111.0 (10)	111.5 (5)	111.0 (10)
$\overline{\text{Fe}-\text{Fe}-\text{Fe}^c}$	60.0 (1)	60.0 (5)	60.0 (2)
$\overline{\text{Fe}-\text{Fe}-\text{Fe}^d}$	87.1 (1)	87.7 (6)	86.5 (3)

<sup>a</sup> Reference 22b. <sup>b</sup> Values within the  $\text{Fe}_2\text{S}_2$  rhombic units. <sup>c</sup> Values within the  $\text{Fe}_3\text{S}_3$  "cyclohexane" units. <sup>d</sup> Angles within the two adjacent  $\text{Fe}_2\text{S}_2$  units.

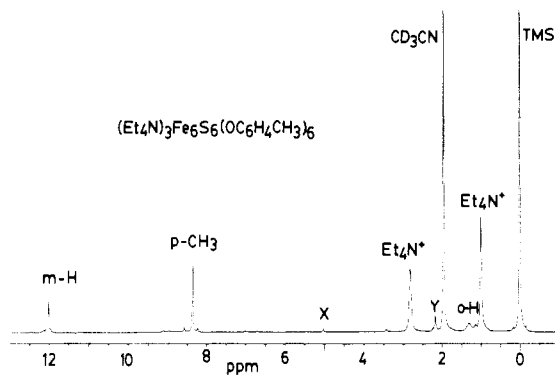
remain remarkably invariant (Tables IV, V). As in the chloro analogue, two types of Fe-Fe distances and Fe-S-Fe angles are present in I and II. The  $\text{Fe}_3\text{S}_3$  hexagonal moieties contain long Fe-Fe distances of 3.80 (4) and 3.81 (2) Å (in I and II) and unusually large Fe-S-Fe angles of 113.8 and 114.2°, respectively. These values resemble those reported for the  $[\text{Fe}_3\text{S}_3]$  structural unit found in *A. vinelandii* Ferredoxin I<sup>18</sup> (Fe-Fe = ~4.0 (1) Å; Fe-S-Fe = ~118°). The latter possesses a nearly planar, cyclic conformation.

The Fe-S bond lengths and Fe-S-Fe angles in the planar rhombic  $\text{Fe}_2\text{S}_2$  units of the  $[\text{Fe}_6\text{S}_6]^{3+}$  cores in both structures are nearly identical. The corresponding values are 2.271 (5) and 2.270 (4) Å and 74.6 (2) and 74.3 (1)° for I and II, respectively. Although statistically insignificant, there exists a consistent Fe-S bond length differentiation in the structures of the  $[\text{Fe}_6\text{S}_6]^{3+}$  cores in I, II, and  $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{3-}$ . The Fe-S bonds parallel to the idealized  $S_6$  axis are consistently longer than the Fe-S bonds in the  $\text{Fe}_3\text{S}_3$  chairs by an average of 0.012 Å.

As suggested previously,<sup>22b</sup> the  $\text{Fe}_6\text{S}_6$  cores in I and II can be considered as structural derivatives of the  $\text{M}_8\text{S}_6$  cubic units that exist in the naturally occurring pentlandite minerals. Such units have been structurally identified in the extended lattices of  $\text{Co}_9\text{S}_8$ ,<sup>29</sup>  $(\text{Ni},\text{Fe})_9\text{S}_8$ <sup>30</sup> and  $(\text{Fe},\text{Ni})_8\text{AgS}_8$ .<sup>31</sup> The  $\text{Co}_9\text{S}_8$  and  $\text{Fe}_9\text{S}_8$  cores also have been found in the structures of the isolated  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ <sup>32</sup> and  $[\text{Fe}_8\text{S}_6\text{I}_8]^{3-}$ <sup>33</sup> clusters.

The removal of any two metal atoms that lie on the same body diagonal of the  $\text{M}_8$  cube in the  $\text{M}_8\text{S}_6$  cage results in a structure geometrically identical with that of the  $\text{Fe}_6\text{S}_6$  cores in I and II.

**<sup>1</sup>H NMR Spectroscopy and Solution Magnetic Studies.** The <sup>1</sup>H nuclear magnetic resonance (NMR) spectra of the  $[\text{Fe}_6\text{S}_6\text{L}_6]^{3-}$  prismanes (L = aryloxy and arylthiolate) were measured in deuterated acetonitrile solution. At room temperature the phenyl ring proton resonances show isotropic shifts similar in pattern to those of  $[\text{Fe}_4\text{S}_4(\text{XAr})_4]^{2-}$  (X = O,<sup>10</sup> S<sup>34</sup>) and  $[\text{Fe}_2\text{S}_2(\text{XAr})_4]^{2-}$  (X = O,<sup>8,27</sup> S<sup>35</sup>) but significantly greater in magnitude. Isotropic shifts of the  $\text{ArO}^-$  and  $\text{ArS}^-$  prismane trianions at ambient temperature and those of the corresponding cubane analogues are compiled in Table VI. A representative spectrum of  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_6]$  is shown in Figure 4. The pattern of alternating



**Figure 4.** <sup>1</sup>H FT NMR spectra (360 MHz) of  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(\text{OC}_6\text{H}_4\text{-}p\text{-Me})_6]$  in  $\text{CD}_3\text{CN}$ . Signal assignments are indicated; X represents the  $p\text{-CH}_3$  signal of  $[\text{Fe}_4\text{S}_4(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)_4]^{2-}$ , and Y signifies unidentified impurity.

signs of the isotropic shifts of the phenyl ring proton resonances is typical for  $\text{ArX-M}$  (X = S, O, Se) paramagnetic complexes. It has been attributed previously to a dominant Fermi delocalization mechanism with negligible pseudocontact contributions.

In the  $p\text{-CH}_3\text{C}_6\text{H}_4\text{O}$  prismane the ortho proton resonance is shifted to high fields (relative to the case of the diamagnetic phenol) while the meta and  $p\text{-CH}_3$  proton signals are shifted to low fields. The ortho signal as in the corresponding cubanes is identified by its relative broadness due to relaxation effects induced by its proximity to the paramagnetic center. The  $o\text{-H}$ ,  $m\text{-H}$ , and  $p\text{-CH}_3$  signals occur at 1.28, 12.00, and 8.32 ppm, respectively, and correspond to isotropic shifts of 5.52, -5.20, and -6.07 ppm. The analogous  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]^{3-}$  compound shows  $o\text{-H}$ ,  $m\text{-H}$ , and  $p\text{-CH}_3$  resonances at 3.62, 9.58, and 6.43 ppm, respectively, that correspond to smaller isotropic shifts of 3.45, -2.51, and -4.13 ppm. The low-field shift of the  $p\text{-CH}_3$  resonance is consistent with the assumption that  $\pi$  spin density at that position leads to a direct contact interaction with methyl protons through hyperconjugation.<sup>34</sup> As in the analogous  $[\text{Fe}_4\text{S}_4(p\text{-CH}_3\text{C}_6\text{H}_4\text{X})_4]^{2-}$  complexes the significantly larger isotropic shifts observed for the  $\text{ArO}^-$  vs. the  $\text{ArS}^-$  ligands suggest a more efficient spin propagation through the Fe-O-C bonds, which in turn implies a relatively more covalent Fe-O bond.

The magnitudes of the isotropic shifts in the  $[\text{Fe}_6\text{S}_6]^{3+}$  clusters are roughly twice as large as those of the corresponding  $[\text{Fe}_4\text{S}_4]^{2+}$  clusters and consistent with the greater magnetic moments of the former. The magnetic susceptibilities of the  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_6]^{3-}$  and  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]^{3-}$  complexes were measured in the solid state by a Faraday balance at ~298 K, and the calculated magnetic moments ( $\mu_{\text{eff}}^{\text{cor}}/\text{Fe}$ ) were 2.74 and 2.23  $\mu_B$ , respectively. The magnetic moments ( $\mu_{\text{eff}}^{\text{cor}}/\text{Fe}$ ) of the corresponding cubane clusters were found to be ~1.25 and ~1.1  $\mu_B$ , respectively.<sup>6,10</sup>

The temperature dependence of the isotropic shifts of the  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{X})_6]^{3-}$  (X = O, S) clusters were studied in the -40 to +60 °C temperature range in  $\text{CD}_3\text{CN}$  solution. In the NMR spectrum of  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]^{3-}$  the signals due to the prismane cluster diminished in intensity as the temperature increased above 5 °C, and they disappeared completely above 40 °C with concomitant increase in the intensities of the  $o\text{-H}$ ,  $m\text{-H}$ , and  $p\text{-CH}_3$  proton signals of the appearing  $[\text{Fe}_4\text{S}_4(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_4]^{2-}$  cluster. In the NMR study of the  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_6]^{3-}$  cluster, the thermal conversion to the corresponding  $[\text{Fe}_4\text{S}_4(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_4]^{2-}$  complex was much slower. After solutions of I were warmed to 80 °C for ca. 1/2 h, the prismane  $\rightarrow$  cubane conversion was ~40%. The transformation to the cubane homologues does not hinder the observation of the prismane isotropic shift behavior. Representative plots of the  $o$ -,  $m$ -, and  $p\text{-CH}_3$  proton isotropic shifts ( $\Delta H/H_0$ )<sub>iso</sub> vs.  $T$  for both clusters are linear and have been deposited. Although the ground state of these complexes is paramagnetic, the slight increase in the isotropic shifts with increasing temperature and magnetic susceptibility results within the temperature range studied here

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Table VI. Isotropic Shifts (ppm)<sup>a</sup>

	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	<i>m</i> -CH <sub>3</sub>	<i>p</i> -CH <sub>2</sub>	<i>p</i> -CH <sub>3</sub>
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ] <sup>b</sup>	5.52	-5.20				-6.07
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ]	v broad	-5.25			-4.60	-0.13
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S) <sub>6</sub> ] <sup>c</sup>	3.45	-2.51				-4.13
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S) <sub>6</sub> ] <sup>e</sup>	3.35, 3.51	-2.50	4.16	<i>f</i>		
[Et <sub>4</sub> N] <sub>2</sub> [Fe <sub>4</sub> S <sub>4</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>4</sub> ] <sup>c</sup>	2.33	-2.23				-2.77
[Et <sub>4</sub> N] <sub>2</sub> [Fe <sub>4</sub> S <sub>4</sub> (OPh) <sub>4</sub> ] <sup>c</sup>	2.31	-2.23	+2.86			
[Me <sub>4</sub> N] <sub>2</sub> [Fe <sub>4</sub> S <sub>4</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S) <sub>4</sub> ] <sup>d</sup>	1.28	-0.91				-1.63
[Me <sub>4</sub> N] <sub>2</sub> [Fe <sub>4</sub> S <sub>4</sub> ( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S) <sub>4</sub> ] <sup>d</sup>	1.02, 1.42	-1.07	1.89	0.42		

<sup>a</sup> ( $\Delta H/H_0$ )<sub>iso</sub> = ( $\Delta H/H_0$ )<sub>diam</sub> - ( $\Delta H/H_0$ )<sub>obsd</sub>. <sup>b</sup> Measured in CD<sub>3</sub>CN solution at 293 K. Shifts vs. diamagnetic references: *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH 6.80, 2.25 (CH<sub>3</sub>); *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SH 7.07, 2.30 (CH<sub>3</sub>); *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH 6.80, 1.15 (CH<sub>3</sub>), 2.52 (CH<sub>2</sub>); *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SH 7.05, 2.23 (CH<sub>3</sub>). <sup>c</sup> From ref 10. <sup>d</sup> From ref 34a. <sup>e</sup> At -20 °C. <sup>f</sup> Obscured by [Et<sub>4</sub>N]<sup>+</sup>.

Table VII. Cyclic Voltammetric Data for the [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>2-/3-</sup> Clusters<sup>a</sup>

cluster (in CH <sub>2</sub> Cl <sub>2</sub> ) <sup>b</sup>	2-/3- couple			3-/4- couple		
	<i>E</i> <sub>1/2</sub> , V	$\Delta E$ , mV	<i>i</i> <sub>pc</sub> / <i>i</i> <sub>pa</sub>	<i>E</i> <sub>1/2</sub> , V	$\Delta E$ , mV	<i>i</i> <sub>pa</sub> / <i>i</i> <sub>pc</sub>
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> Cl <sub>6</sub> ]	+0.24	116	1.0	-0.70	139	
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> Br <sub>6</sub> ]	+0.27	128	1.0	-0.70		
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ]	-0.19	184	0.96			
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>6</sub> ]	-0.20	150	1.0	-1.16	196	0.97
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S) <sub>6</sub> ]	-0.17	163	0.98			
[Et <sub>4</sub> N] <sub>3</sub> [Fe <sub>6</sub> S <sub>6</sub> (SCH <sub>2</sub> Ph) <sub>6</sub> ] <sup>c</sup>	-0.24	173	1.0	-1.17	230	0.95

<sup>a</sup> For all measurements the scan rate was 200 mV/s. <sup>b</sup> Normally, the [Et<sub>4</sub>N]<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>] clusters are not soluble in this solvent. In the presence of excess [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub> as supporting electrolyte however they readily go into solution. <sup>c</sup> Generated in situ by adding the appropriate amount of thiol to a solution of [Fe<sub>6</sub>S<sub>6</sub>(OC<sub>6</sub>H<sub>4</sub>R)<sub>6</sub>]<sup>3-</sup>.

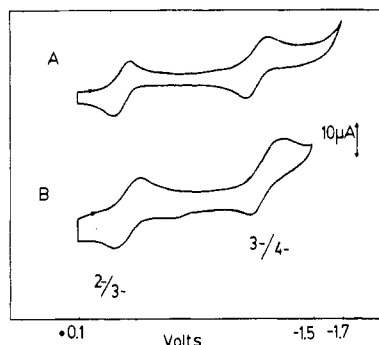


Figure 5. Cyclic voltammograms of [Fe<sub>6</sub>S<sub>6</sub>(OC<sub>6</sub>H<sub>4</sub>-*p*-Et)<sub>6</sub>]<sup>3-</sup> (A) and [Fe<sub>6</sub>S<sub>6</sub>(SCH<sub>2</sub>Ph)<sub>6</sub>]<sup>3-</sup> (B) generated in situ from A by addition of an appropriate amount of PhCH<sub>2</sub>SH in CH<sub>2</sub>Cl<sub>2</sub> solution (scan rate 200 mV/s; potentials vs. SCE; supporting electrolyte 0.1 M [Bu<sub>4</sub>N]ClO<sub>4</sub>).

indicate that the antiferromagnetic contribution to the magnetic properties is the dominant one.

**Electrochemical Studies.** The cyclic voltammetry (Figure 5) of the [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-</sup> clusters (L = Br<sup>-</sup>, *p*-EtC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, *p*-MeC<sub>6</sub>H<sub>4</sub>S<sup>-</sup>) was studied in CH<sub>2</sub>Cl<sub>2</sub> solution. The electrochemical behavior of [Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>]<sup>3-</sup> has been reported previously.<sup>22b</sup>

All of the [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-</sup> clusters exhibit well-defined oxidation waves that are attributed to the [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-/2-</sup> couple and are reversible by the *i*<sub>pc</sub>/*i*<sub>pa</sub> ratio criterion. The 3-/2- redox couples occur at +0.24, +0.27, -0.17, and -0.19 V for L = Cl<sup>-</sup>, Br<sup>-</sup>, ArS<sup>-</sup>, and ArO<sup>-</sup>, respectively (Table VII). This trend is identical with the one observed for the homologous [Fe<sub>4</sub>S<sub>4</sub>L<sub>4</sub>]<sup>2-</sup> "cubane" clusters and demonstrates effectively the pronounced effect of the terminal ligands on the electron affinity of the [Fe<sub>6</sub>S<sub>6</sub>]<sup>4+</sup> cores. The oxidized species can be isolated (for L = Cl<sup>-</sup>, Br<sup>-</sup>), and the dianionic prismanes have been characterized.<sup>23</sup> The [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>2-</sup> derivatives are obtained by [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> oxidation of the corresponding trianions and display a characteristic violet color in solution. The limited stability of these solutions, at ambient temperatures, however precludes the isolation of the [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>2-</sup> clusters. In coordinating solvents such as CH<sub>3</sub>CN or DMF only irreversible waves are observed for the [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-</sup> clusters.

The potentials of the 3-/4- redox couples for the [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-</sup> clusters are approximately 450 mV more negative than those of the 2-/3- couples (Table VII). The waves corresponding to the 3-/4- redox couple are quasi-reversible for L = Cl<sup>-</sup> or Br<sup>-</sup> and

show *i*<sub>pa</sub>/*i*<sub>pc</sub> ratios of ~0.80. These ratios approach unity when L = ArO<sup>-</sup> or ArS<sup>-</sup> and suggest that at least on the voltammetric time scale the tetraanions are accessible with the proper terminal ligands.

The ability of the [Fe<sub>6</sub>S<sub>6</sub>(XAr)<sub>6</sub>]<sup>3-</sup> (X = O, S) clusters to shuttle reversibly between *three* different oxidation levels is rare among Fe/S clusters. Such an electrochemical behavior was reported recently for the [Fe<sub>4</sub>S<sub>4</sub>(SAR)<sub>4</sub>]<sup>-</sup> clusters<sup>9</sup> (Ar = (*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; 2,3,5,6-Me<sub>4</sub>C<sub>6</sub>H). The latter reversibly can be reduced to the 2- and 3- levels.

A multielectron irreversible oxidation is observed for all [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-</sup> clusters at potentials centered around +0.6 V. The products of this oxidative degradation of the [Fe<sub>6</sub>S<sub>6</sub>] cores have not been characterized as yet. A similar, multielectron, oxidative degradation of the [Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]<sup>2-</sup> cluster results in the formation of the [Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>]<sup>2-</sup> prismane.<sup>23</sup>

### Summary and Conclusions

The [Fe<sub>6</sub>S<sub>6</sub>L<sub>6</sub>]<sup>3-</sup> and the [Fe<sub>4</sub>S<sub>4</sub>L<sub>4</sub>]<sup>2-</sup> clusters belong to the homologous series [Fe<sub>2</sub>S<sub>2</sub>L<sub>2</sub>]<sub>*n*</sub><sup>*n*-</sup>. The relative thermodynamic stabilities (*n* = 2 vs. *n* = 3) of these labile clusters depend to a great extent on the nature of the terminal ligands, L, attached to the iron atoms. Our studies thus far indicate that for L = ArS<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup> the prismane homologues (*n* = 3) are metastable and thermally and readily convert to the cubanes (*n* = 2). By contrast, the aryloxy prismane clusters (L = ArO<sup>-</sup>, *n* = 3) show stability comparable to that of the analogous cubanes. The relative instability of the *n* = 3 vs. the *n* = 2 oligomers follows the order ArS<sup>-</sup> > X<sup>-</sup> > ArO<sup>-</sup>.

The ArS<sup>-</sup> prismanes are obtained by Cl<sup>-</sup>-exchange reactions from the [Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>]<sup>3-</sup> cluster or by protonation of the ArO<sup>-</sup> ligands in the [Fe<sub>6</sub>S<sub>6</sub>(OAr)<sub>6</sub>]<sup>3-</sup> clusters by aryl thiols. They are exceedingly unstable and rapidly transform to the corresponding cubanes. These observations are relevant in the interpretation of Fe/S core extrusion experiments that employ aryl thiols. The possibility that the latter reactions can extrude metastable cores other than Fe<sub>4</sub>S<sub>4</sub> or Fe<sub>2</sub>S<sub>2</sub> is a very real one. Furthermore, the rapid transformation of these metastable cores to the more stable Fe<sub>4</sub>S<sub>4</sub> homologues may well lead to erroneous conclusions regarding such Fe/S centers that may reside *inside* certain "unorthodox" Fe/S proteins. The existence of the Fe<sub>6</sub>S<sub>6</sub> core in synthetic Fe/S clusters and the surprising stability of these cores in a non-sulfur terminal-ligand environment suggest that Fe/S clusters of hitherto unknown nature may be stabilized in certain metalloproteins. Such clusters may be anchored to the protein entirely by non-sulfur terminal



ligands (i.e. tyrosine or histidine imidazole). The presence of non-sulfur terminal ligands already has been suggested for the Rieske protein from *T. thermophilus*, where two of the coordination sites on the  $\text{Fe}_2\text{S}_2$  centers are thought to be occupied by the nitrogen atoms of two histidine imidazole residues.<sup>16</sup> The possible involvement of non-sulfur terminal ligands on the iron atoms of the Fe/Mo/S aggregate in nitrogenase has been suggested by the small number of cysteinyl residues in the Fe-Mo protein of nitrogenase<sup>36</sup> and by recent Fe EXAFS studies. In the latter, performed on the Fe-Mo cofactor of nitrogenase, each of the iron atoms shows (on the average) approximately one light atom (O or N) at a distance of 1.81 (7) Å.<sup>37</sup>

The availability of a preformed hexanuclear Fe/S cluster in the form of the  $\text{Fe}_6\text{S}_6$  prismanes presents a unique opportunity for the assembly of heterometallic Fe/Mo/S clusters of possible structural relevance to the Fe/Mo/S center of nitrogenase. The assembly of such clusters is possible by virtue of the stereochemical position of the sulfur atoms in the  $\text{Fe}_6\text{S}_6$  hexagonal units of  $\text{Fe}_6\text{S}_6$  clusters. The latter can serve as tridentate ligands for coordinatively unsaturated  $\text{M}(\text{L})_n$  fragments. In our quest for at least a structural analogue for the active site in nitrogenase we have synthesized and characterized the  $[(\text{Fe}_6\text{S}_6\text{L}_6)(\text{M}(\text{CO})_3)_2]^{n-}$  oc-

tanuclear clusters ( $\text{L} = \text{ArO}^-$ ,  $\text{M} = \text{Mo}$ ,  $n = 3$ ;<sup>38</sup>  $\text{L} = \text{Cl}$ ,  $\text{M} = \text{Mo}$ ,  $n = 3, 4$ ;<sup>39</sup>  $\text{L} = \text{ArO}^-$ ,  $\text{M} = \text{W}$ ,  $n = 3$ <sup>40</sup>). The adduct-forming properties of the  $[\text{Fe}_6\text{S}_6\text{L}_6]^{n-}$  clusters and the characterization of the polymetallic products are presently under investigation in our laboratory.

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**Registry No.** I, 94499-96-4; II, 94499-92-0;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(\text{O}-p\text{-C}_2\text{H}_3\text{C}_6\text{H}_4)_6]$ , 102538-68-1;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(\text{O}-2,4,6\text{-}(\text{CH}_3)_3\text{C}_6\text{H}_2)_6]$ , 102538-70-5;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(\text{OC}_6\text{H}_5)_6]$ , 102538-72-7;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$ , 91294-19-8;  $[\text{Et}_3\text{MeN}]_3[\text{Fe}_6\text{S}_6\text{Br}_6]$ , 102538-73-8;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]$ , 94499-98-6;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(m\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]$ , 102538-75-0;  $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{2-}$ , 93530-53-1;  $[\text{Fe}_6\text{S}_6\text{Br}_6]^{2-}$ , 93530-57-5;  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_6]^{2-}$ , 94499-99-7;  $[\text{Fe}_6\text{S}_6(p\text{-C}_2\text{H}_3\text{C}_6\text{H}_4\text{O})_6]^{2-}$ , 102538-78-3;  $[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})_6]^{2-}$ , 94500-00-2;  $[\text{Fe}_6\text{S}_6(\text{SCH}_2\text{Ph})_6]^{2-}$ , 102538-79-4;  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(\text{SCH}_2\text{Ph})_6]$ , 102538-77-2;  $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{4-}$ , 94500-01-3;  $[\text{Fe}_6\text{S}_6\text{Br}_6]^{4-}$ , 102538-80-7;  $[\text{Fe}_6\text{S}_6(p\text{-C}_2\text{H}_3\text{C}_6\text{H}_4\text{O})_6]^{4-}$ , 102538-81-8;  $[\text{Fe}_6\text{S}_6(\text{SCH}_2\text{Ph})_6]^{4-}$ , 102538-82-9.

**Supplementary Material Available:** Tables of positional and thermal parameters and bond distances and angles for the cations of I and II and figures showing the temperature dependence of the isotropically shifted phenyl ring proton resonances of  $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{S}_6(p\text{-CH}_3\text{C}_6\text{H}_4\text{X})]^{n-}$  ( $\text{X} = \text{S}, \text{O}$ ) (11 pages). Ordering information is given on any current masthead page.

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## Notes

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### Intramolecular Electron Transfer in the One-Electron Oxidation Product of (Tetraphenylporphinato)nickel(II), As Studied by Resonance Raman Spectroscopy

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There is much current interest in porphyrin radical cations because of their involvement in photoinduced electron transfer in natural and synthetic systems<sup>1</sup> and because of the occurrence of a  $\text{Fe}^{\text{IV}}$  porphyrin radical as an identifiable intermediate in peroxidase enzymes.<sup>2</sup> A point of considerable interest is the competition between electron removal from the porphyrin ring vs. the central metal ion of metalloporphyrins. It is known that iron(III) porphyrin radicals are stable when the axial ligands are chloride or perchlorate,<sup>3</sup> but oxidation to the iron(IV) porphyrin is favored when there is an oxo ligand, e.g. in compound II of horseradish peroxidase,<sup>4</sup> while removal of a second electron (compound I) is from the porphyrin ring.<sup>5</sup> The metal vs. porphyrin based oxidation products are in general valence tautomers rather than resonance forms, because the valence porphyrin orbitals,  $a_{1u}$  or  $a_{2u}$ , are of odd parity and are orthogonal to the even-parity valence d orbitals of the redox-active transition metals.

An early example of this valence tautomerism was discovered by Dolphin and co-workers,<sup>6</sup> who noted that oxidation of nickel tetraphenylporphine ( $\text{Ni}^{\text{II}}\text{TPP}$ ) gave a green solution, with an absorption spectrum characteristic of  $\text{TPP}^{+\cdot}$ . Freezing the solution to 77 K led to an orange product when the oxidation had been

carried out electrolytically in hexafluorophosphate electrolyte, although no spectral change was observed when bromine oxidation was used. The orange product was established to be a nickel(III) porphyrin via its anisotropic ESR spectrum ( $g_{\perp} = 2.286$ ,  $g_{\parallel} = 2.086$ ) as well as its optical spectrum. Apparently,  $\text{PF}_6^-$  stabilizes the  $\text{Ni}^{\text{III}}$  product at low temperature, whereas  $\text{Br}^-$  does not.

We have reexamined this system using resonance Raman (RR) spectroscopy, which provides a sensitive probe of the porphyrin structure via the porphyrin vibrational mode frequencies. The results are fully consistent with the interpretation from optical and ESR spectra. The green product shows large frequency shifts, associated with porphyrin cation radical formation, whereas the orange product shows essentially the same frequencies as  $\text{Ni}^{\text{II}}\text{TPP}$ , because electron removal from the  $\text{Ni}^{\text{II}}$   $d_{z^2}$  orbital has a negligible effect on porphyrin structure. Because of this sensitivity to the ligand structure, resonance Raman spectroscopy is expected to be a useful probe of valence tautomerism.

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