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Effects of Phenoxide Ligation on Iron–Sulfur Clusters. 2. Preparation and Properties of [Fe2S2(OAr)4]2- Ions

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The phenoxide-ligated dinuclear iron–sulfur clusters [Fe2S2(OAr)4]2- (I, Ar = phenyl; II, Ar = p-tolyl; III, Ar = p-C6H4Cl) have been synthesized by two methods: (i) reaction of FeCl3, NaOAr, and Li2S in acetonitrile; (ii) reaction of [Fe2S2Cl4]2- with NaOAr in acetonitrile. The preparation, reactivity, and electronic properties of these compounds are described. Isotropically shifted resonances due to the phenoxide protons are observed in the 1H NMR spectra of I–III; the direction and magnitude of these shifts are consistent with significant delocalization of spin into the π system of the phenyl rings. At any temperature, the magnitude of the isotropic shifts is approximately twice that observed for the corresponding arenethiolate analogues. The magnitude of the isotropic shifts increases with increasing temperature, consistent with intramolecular antiferromagnetic coupling. The room-temperature magnetic moment per iron, μ_{eff}/Fe, of ~1.6 μ_B is consistent with NMR results. Zero-field Mössbauer spectra of the solid Et4N+ salt of I show a single quadrupole doublet with parameters $\delta = 0.37$ mm/s, $\Delta E_q = 0.32$ mm/s, and $\Gamma = 0.26$ mm/s. Electrochemical data indicate that substitution of thiophenolate terminal ligands by phenolates results in a negative shift of approximately 200 mV of the first and second reduction potentials of the [Fe2S2]2+ core. The phenoxide-ligated dimers react with electrophiles such as PhCOCl and PhSH and are smoothly converted to [Fe2S2Cl4]2- and [Fe2S2(SPh)4]2-, respectively. The biological implications for tyrosyl coordination to 2 Fe-2 S centers are discussed.

Introduction

As a result of continuing investigation in the field of iron–sulfur biochemistry, several iron–sulfur centers with unusual structural and spectroscopic properties have recently been identified. Examples include the P clusters of nitrogenase[1,2] (presumed to be unusual 4 Fe–4 S clusters), the 3 Fe center of inactive aconitase,[3] and several systems with 2 Fe–2 S sites.[4] Among the possible means by which a protein could alter the properties of iron–sulfur centers are terminal coordination of the cluster by noncysteine ligands, addition of a fifth ligand, and protein-imposed distortions of the clusters from their normal geometries.

The Rieske iron–sulfur protein from *Thermus thermophilus* has recently been purified and characterized and shows strong evidence for non-cysteine coordination to 2 Fe–2 S clusters.[4a] Analytical results indicate the presence of approximately four iron atoms and four acid-labile sulfides per molecule; the amino acid composition has been determined and shows only four cysteines per molecule. Mössbauer spectra of the oxidized protein exhibit two quadrupole doublets with isomer shifts (δ) and quadrupole splittings (ΔE_q): $\delta(1) = 0.32$ mm/s, $\Delta E_q(1) = 0.91$ mm/s; $\delta(2) = 0.24$ mm/s, $\Delta E_q(2) = 0.52$ mm/s. Careful analysis of the Mössbauer spectra of the oxidized and reduced protein demonstrates unambiguously that the protein possesses two 2 Fe–2 S centers. Supporting evidence includes the observation that two electrons are required to obtain fully reduced protein and that double integration of the EPR signal observed upon reduction shows one spin per two iron atoms. This EPR signal is unusual in that it has $g_{av} = 1.85$; typical reduced plant ferredoxins containing 2 Fe–2 S centers exhibit $g_{av} = 1.94$ EPR signals. Each 2 Fe–2 S center must, therefore, be coordinated by two non-cysteine terminal ligands. Other unusual properties include a 400–600-mV shift in redox potential to higher potential compared to typical plant ferredoxins and the somewhat unusual optical absorption spectrum of the pink, oxidized protein, with bands at 325, 458, and 560 (sh) nm. Also of note is the strong similarity of the physical properties of the Rieske protein to those of the NADH-dependent, iron–sulfur containing dioxygenases.

Milk xanthine oxidase contains, in addition to Mo and flavin groups, two 2 Fe–2 S centers.[4b,5] In the reduced enzyme, these two sites exhibit different EPR spectra; one center has $g_{av} = 1.95$, typical of reduced 2 Fe ferredoxins, and the other shows a very broad signal with $g_{av} = 2.01$. This unusual EPR signal has not been explained despite extensive investigation of the enzyme.

Finally, a brief report[4c] suggests that the reaction of a metal-free pigment isolated from an Ascidian and containing no cysteine residues with ferrous sulfate results in the formation of a 2 Fe–2 S center.

To date, no synthetic [Fe2S2]2+ cluster with oxygen terminal ligands has been reported. In order to determine the effect of oxygen ligation on these clusters, we have prepared and characterized the first such series of complexes. We report herein the preparation, properties, and reactivity of the [Fe2S2(OAr)4]2- ions.

Experimental Section

Materials and Methods. All operations were carried out under an atmosphere of pure, dry dinitrogen. Dinitrogen was purified by passage over hot BASF R-3-11 catalyst and supported phosphorus pentoxide (Aquasorb). Solvents and reagents were either distilled under an inert atmosphere or thoroughly degassed by repeated evacuation and flushing with pure dinitrogen prior to use.

Acetonitrile was purified by the following three-step procedure: Reagent grade acetonitrile was refluxed for several hours over and distilled from calcium hydride. The distillate was stirred for 12 h with 5 g/L each of anhydrous sodium carbonate and potassium permanganate, followed by distillation at room temperature using a dry ice/2-propanol cold trap. Final distillation from phosphorus pentoxide produced acetonitrile of acceptable purity for synthesis as well as for electrochemistry and other physical measurements. Tetrahydrofuran and diethyl ether were purified by distillation from

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sodium/benzophenone ketyl or lithium aluminum hydride. *N*-methylpyrrolidinone (NMP) was distilled from calcium hydride and then from barium oxide. Benzoyl chloride was distilled from barium oxide at room temperature on a liquid-nitrogen trap. PhOH, *p*-tolOH, and *p*-ClC$_6$H$_4$OH were either sublimed twice or sublimed followed by vacuum distillation. Anhydrous sodium phenolates were prepared in one of two ways: by reaction of the appropriate phenol with sodium methoxide in anhydrous MeOH, followed by removal of the solvent in vacuo, addition of MeCN, and repeated evaporation to dryness; by reaction with metallic sodium in THF, followed by filtration and evaporation to dryness. Thiols, lithium sulfide, and all other reagents were of commercial reagent grade and were used without further purification. (Et$_4$N)$_2$[Fe$_2$S$_2$Cl$_4$][6] was prepared as described.

Preparations. (R$_4$N)$_2$[Fe$_2$S$_2$(OAr)$_4$] (Ar = Ph, *p*-tol, *p*-C$_6$H$_4$Cl). These complexes were prepared by either of two methods. Typical examples of each are described in detail below.

Method 1: By Direct Synthesis. To 1.3 g (8.1 mmol) of FeCl$_3$ dissolved in 50 mL of MeCN was added a solution of 2.2 g (8.1 mmol) of Bu$_4$NCl dissolved in 25 mL of MeCN. The solution changed color at this point from orange-brown to light yellow. This solution was then added to a slurry of 3.75 g (32.3 mmol) of NaOPh in 50 mL of MeCN. The color of the supernatant solution changed immediately from light yellow to bright red. The reaction mixture was stirred for 30 min, and the precipitate was removed by filtration. The filtrate was treated with 0.37 g (8.1 mmol) of Li$_2$S, and the mixture was stirred for 18 h, during which time a slow color change to a much more intense red occurred. The reaction mixture was then filtered and evaporated in vacuo to a volume of 20 mL. Addition of 80 mL of Et$_2$O and cooling to –20 °C for 8 h caused separation of the product as dark red microcrystals, which were collected by filtration, washed with Et$_2$O, and vacuum dried. Recrystallization was accomplished by addition of 50 mL of Et$_2$O to the crude product, followed by addition with stirring of several 1-mL aliquots of MeCN until all of the material was dissolved. Filtration and slow cooling to –20 °C caused separation of large dark red prisms. Volume reduction of the mother liquors, addition of 1 volume of Et$_2$O, and slow cooling to –20 °C afforded a second crop (10%). Typical yields are 40–50% after one recrystallization.

The purity of the compounds after one recrystallization was estimated at 98% by proton NMR spectra. The extraordinary sensitivity of these materials to air and moisture made obtaining satisfactory and reproducible elemental analyses extremely difficult; analytical results given below are typical.

Method 2: From (R$_4$N)$_2$[Fe$_2$S$_2$Cl$_4$]. A solution containing 1 g (1.73 mmol) of (Et$_4$N)$_2$[Fe$_2$S$_2$Cl$_4$] dissolved in 40 mL of MeCN was added with stirring to a slurry of 0.84 g (7.26 mmol) of anhydrous NaOPh in 10 mL of MeCN. An immediate color change from purple to deep red occurred. The reaction mixture was stirred for 0.5 h and filtered, and the filtrate was concentrated to half its volume. Slow addition of one volume of Et$_2$O to initiate crystallization, followed by cooling to –20 °C for 18 h, caused complete separation of the microcrystalline product, which was collected by filtration, washed twice with Et$_2$O, and vacuum dried. The crude product was recrystallized by dissolution in 25 mL of MeCN, slow addition of 20 mL of Et$_2$O, and slow cooling to –20 °C. Concentration of the mother liquors and slow cooling to –20 °C afforded a second crop, total yield 61%.

(Bu$_4$N)$_2$[Fe$_2$S$_2$(OPh)$_4$]. This compound was prepared as described above by method 1. Anal. Calcd for C$_{56}$H$_{92}$N$_2$O$_4$S$_2$Fe$_2$: C, 65.09; H, 8.98; N, 2.71; S, 6.22; Fe, 10.81. Found: C, 64.36; H, 8.71; N, 2.69; S, 6.30; Fe, 11.31. Mp: 182 °C dec.

(Et$_4$N)$_2$[Fe$_2$S$_2$(OPh)$_4$]. This compound was prepared as described above by method 2. Anal. Calcd for C$_{40}$H$_{60}$N$_2$O$_4$S$_2$Fe$_2$: C, 59.40; H, 7.48; N, 3.46. Found: C, 59.68; H, 7.57; N, 3.79.

(Me$_4$N)$_2$[Fe$_2$S$_2$(O-*p*-tol)$_4$]. This product was prepared by method 1. Anal. Calcd for C$_{36}$H$_{52}$N$_2$O$_4$S$_2$Fe$_2$: C, 57.45; H, 6.97, N, 3.72; S, 8.52; Fe, 14.84. Found: C, 57.64; H, 6.67; N, 3.80; S, 8.12; Fe, 14.98. Mp: >225 °C.

(Et$_4$N)$_2$[Fe$_2$S$_2$(O-*p*-C$_6$H$_4$Cl)$_4$]. This compound was prepared by method 1. Anal. Calcd for C$_{40}$H$_{56}$N$_2$O$_4$Cl$_4$S$_2$Fe$_2$: C, 50.76; H, 5.96; N, 2.96; S, 6.78; Fe, 11.80. Found: C, 51.55; H, 6.09; N, 3.05; S, 7.99; Fe, 11.75. Mp: 138–140 °C dec.

(Et$_4$N)$_2$[Fe$_2$S$_2$Cl$_4$]. This previously reported compound was prepared by a modification of method 1 above for the preparation of (R$_4$N)$_2$[Fe$_2$S$_2$(OAr)$_4$] salts. A solution of 4 g (12.2 mmol) of (Et$_4$N)[FeCl$_4$] in 100 mL of MeCN was treated with 0.56 g (12.2 mmol) of Li$_2$S and stirred for 18 h. Subsequent workup of the reaction mixture proceeded as described in method 1; yield 51%. The optical spectrum of the material (MeCN) was identical with that reported.[6]
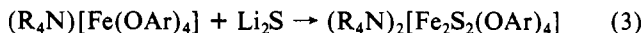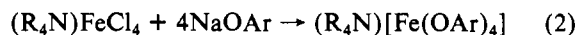
Ligand Substitution Reactions. [Fe$_2$S$_2$(OPh)$_4$]$^{2-}$ with PhSH. To 5.0 mL of a 7.88 mM solution of (Bu$_4$N)$_2$[Fe$_2$S$_2$(OPh)$_4$] in MeCN was added 166 μL of 0.95 M PhSH in MeCN. The resulting solution changed color from red to maroon rapidly and was stirred for 15 min. An optical spectrum of the solution was consistent with 98% formation of [Fe$_2$S$_2$(SPh)$_4$]$^{2-}$.

[Fe$_2$S$_2$(OPh)$_4$]$^{2-}$ with PhCOCl. To 5.0 mL of 7.88 mM (Bu$_4$N)$_2$[Fe$_2$S$_2$(OPh)$_4$] in MeCN was added 0.7 mL of 0.89 M PhCOCl in MeCN; the resulting solution was stirred for 12 h. A gradual color change from red to purple took place. An optical spectrum of the solution indicated 95% formation of [Fe$_2$S$_2$Cl$_4$]$^{2-}$.

Physical Measurements. All samples were handled under anaerobic conditions. Optical spectra were obtained on either a Cary 219 or a Cary 17 spectrophotometer. Proton NMR spectra were obtained on a Bruker WM-250 Fourier transform spectrometer equipped with a variable-temperature unit. Room-temperature magnetic susceptibility measurements were performed on an Alpha Faraday balance using Hg[Co(SCN)$_4$] as calibrant. Electrochemical measurements were performed on a PAR 174A polarographic analyzer equipped with an HP 4030A X-Y recorder. Either dc polarography at a dropping mercury electrode or cyclic voltammetry at Pt-flag or glassy-carbon electrodes were performed. All solutions contained either 50 mM Et$_4$N(ClO$_4$) or 50 mM Bu$_4$N(ClO$_4$) as supporting electrolyte. Potentials were measured vs. the saturated calomel electrode, and a Pt wire was employed as the counterelectrode. Mössbauer spectra were measured by Dr. T. Kent and Professor E. Münck at the Grey Freshwater Biology Institute, University of Minnesota, Navarre, MN. The Mössbauer spectrometer was of the constant-acceleration type and has been described elsewhere.[7] Isomer shifts are reported vs. metallic Fe foil at room temperature. Melting points were obtained in sealed capillaries in vacuo and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

Synthesis. The phenolate dimer complexes [Fe$_2$S$_2$(OAr)$_4$]$^{2-}$ (I, Ar = Ph; II, Ar = *p*-tol; III, Ar = *p*-C$_6$H$_4$Cl) can be synthesized by either of two methods. One method involves a direct "spontaneous self-assembly" reaction from simple starting materials, and the second, a ligand-exchange reaction of a preformed Fe$_2$S$_2$ cluster. Addition of 1 equiv of tetraalkylammonium chloride to an acetonitrile solution of FeCl$_3$ affords a pale yellow solution, presumably due to formation of FeCl$_4^-$ (reaction 1). Addition of the appropriate anhydrous

$$R_4NCl + FeCl_3 \rightarrow (R_4N)FeCl_4 \qquad (1)$$

$$(R_4N)FeCl_4 + 4NaOAr \rightarrow (R_4N)[Fe(OAr)_4] \qquad (2)$$

$$(R_4N)[Fe(OAr)_4] + Li_2S \rightarrow (R_4N)_2[Fe_2S_2(OAr)_4] \qquad (3)$$

sodium phenolate (reaction 2) causes a color change to bright red corresponding to formation of [Fe(OAr)$_4$]$^-$ (verified by optical spectra).[8] Addition of Li$_2$S results in formation of [Fe$_2$S$_2$(OAr)$_4$]$^{2-}$ (reaction 3), isolated as its tetraalkylammonium salt in moderate (~50%) yield after recrystallization. These materials are stable in the solid state and in solution in the absence of oxygen and water; they are extremely soluble in polar aprotic solvents, which makes purification and isolation in high yields difficult.

Reaction of a slight excess of the appropriate anhydrous sodium phenolate with [Fe$_2$S$_2$Cl$_4$]$^{2-}$ in acetonitrile at ambient temperatures effects full substitution of the terminal chloride ligands with phenolate ligands (reaction 4). This method takes

$$[Fe_2S_2Cl_4]^{2-} + 4NaOAr \rightarrow [Fe_2S_2(OAr)_4]^{2-} + 4NaCl \qquad (4)$$
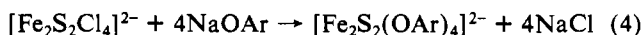
advantage of the insolubility of NaCl in acetonitrile to drive

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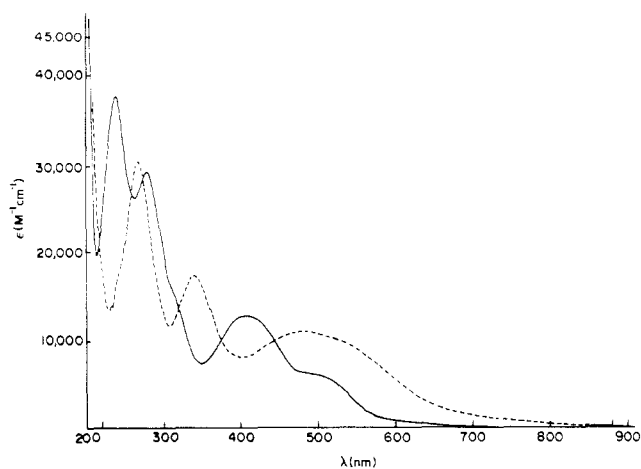(8) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1982**, *104*, 5255.

Figure 1. Electronic absorption spectra of the $[Fe_2S_2(OPh)_4]^{2-}$ (—) and $[Fe_2S_2(SPh)_4]^{2-}$ (- - -) ions in acetonitrile solution at 22 °C.

complex	electronic spectral features^a	$(\Delta H/H)_{iso}$,^{b} ppm
$[Fe_2S_2(OPh)_4]^{2-}$	240 (38.7)	c (o-H)
	280 (29.6)	−3.84 (m-H)
	405 (12.9)	4.87 (p-H)
	~500 (sh, 6.1)	
$[Fe_2S_2(O-p-tol)_4]^{2-}$	245 (38.5)	4.34 (o-H)
	284 (29.5)	−3.94 (m-H)
	418 (13.7)	−4.60 (p-CH$_3$)
	~500 (sh, 8.0)	
$[Fe_2S_2(O-p-C_6H_4Cl)_4]^{2-}$	248 (36.6)	c (o-H)
	282 (23.1)	−3.63 (m-H)
	410 (11.0)	
	~500 (sh, 5.0)	

^{a} Measured in MeCN at ~22 °C. λ_{max}, nm (ϵ, 10^3 M^{-1} cm^{-1}). ^{b} Measured in MeCN-d_3 solution at 22 °C. Shifts vs. diamagnetic references: PhOH, −7.02; p-tolOH, −6.85, −2.21 (p-CH$_3$); p-ClC$_6$H$_4$OH, −6.87. ^{c} Obscured.

the reaction to completion and is analogous to the corresponding method used to prepare $[Fe_4S_4(OAr)_4]^{2-}$ salts. Phenolate dimer salts prepared by this method are of comparable purity and obtained in yields comparable to or greater than those found for the first method of preparation. The first method of preparation is in general the most convenient as it is a "one-pot" synthesis, which avoids the necessity of preparing the air-sensitive precursor, $[Fe_2S_2Cl_4]^{2-}$.

A new preparation of $[Fe_2S_2Cl_4]^{2-}$ can be realized by a modification of the first method described above. One equivalent of anhydrous Li$_2$S is allowed to react with [FeCl$_4$]$^-$, affording $[Fe_2S_2Cl_4]^{2-}$, which is isolated as its tetraalkylammonium salt in 50% yield after recrystallization. This represents a twofold improvement in the total yield of this complex over the traditional synthetic route: reaction of $[Fe_2S_2(SR)_4]^{2-}$ (50% starting from FeCl$_3$) and acyl chlorides to give $[Fe_2S_2Cl_4]^{2-}$ (50%; total of 25% from FeCl$_3$). Holm and co-workers[9] have recently reported a convenient synthesis of this complex from FeCl$_3$ using (Me$_3$Si)$_2$S.

Electronic Absorption Spectra. The optical spectra of I and $[Fe_2S_2(SPh)_4]^{2-}$ are shown in Figure 1. Comparative spectral data for I–III are given in Table I.

The spectra presented in Figure 1 clearly show a qualitative similarity. Both have strong absorption maxima in the 400–500-nm range, each with an additional unresolved feature at lower energy. Corresponding bands at 405 nm (OPh) and 490 nm (SPh) are tentatively assigned to terminal ligand-to-metal charge-transfer transitions. The large blue shift (~70–80 nm) observed on oxygen substituion is as expected on the basis of simple electronegativity arguments and on results obtained for the phenolate tetramer dianions[2] but is approximately twice as large as the corresponding blue shifts for the tetramers (~40 nm). There are two differences between the phenolate dimers and tetramers that may cause this difference. First, the formal iron oxidation state is higher in the dimer (Fe^{3+}) vs. the tetramer (Fe$^{2.5+}$); second, the dimer has two coordinated phenolates vs. one for the tetramer. Corresponding terminal ligand-to-metal charge-transfer bands for the phenolate tetramer (410 nm) and dimer (405 nm) are at approximately the same energy, which suggests that phenoxide is capable of decreasing the effective change on iron, presumably through a relatively covalent Fe–O bond. The difference in the blue shifts obtained upon phenolate substitution of thiophenolate for the tetramers (~40 nm) vs. the dimers (~85 nm) is consistent with the observation[10] that complexation of Fe^{3+} by successive phenolate groups produces a blue shift in the

visible absorption maximum by approximately 50 nm per phenolate group. Interaction of the iron atoms with an increasing number of p π electrons would be expected to raise the energy of the metal orbitals. This effect seems to be approximately additive for the phenoxide dimers.

The energy of the major band in the phenolate dimers is shifted upon substitution of the p-H by CH$_3$ and Cl. The order of the shifts is in contrast to those observed for the thiophenolate analogues.[11] In the thiophenolate series, simple inductive effects account for the order Cl (483 nm) < H (490 nm) < CH$_3$ (502 nm). The electron-withdrawing p-Cl group causes a shift to higher energy while the electron-donating p-CH$_3$ group results in a shift to lower energy, as expected. The order of visible maxima for the phenolate dimers, as given in Table I, is p-H < p-Cl < p-CH$_3$. This does not follow the order observed for the thiolate dimers nor does it correlate with the phenol acidity (p-Cl > p-H > p-CH$_3$), indicating that other effects may be dominant. Since halide substituents in the para position are capable of participating in resonance structures that increase the negative charge at the donor atom, and since these effects are expected to be much greater for phenols than thiophenols (greater overlap of oxygen p orbitals with π system of ring), the observed order may be due in part to dominant electron-donating π effects overcoming the normal σ inductive electron-withdrawing effects, resulting in a net red shift for the p-Cl vs. the parent phenolate analogue. Resonance effects would be especially important for the deprotonated phenolate anion, which could form quinonoid type structures more easily. The trend found here for the phenolate dimers has also been observed by Ackermann and Hesse[10] in the absorption maxima due to ligand-to-metal charge transfer of 1:1 iron(III)–phenolate complexes in alcohol solution (p-H (580 nm) < p-Cl (585 nm) < p-CH$_3$ (610 nm)).

Magnetic Susceptibility. The magnetic susceptibility of the Et$_4$N$^+$ salt of I has been measured at room temperature by the Faraday method. The data were corrected for the diamagnetic contributions due to ligands and cations using Pascal's constants,[12] resulting in a value for μ_{eff}/Fe of 1.64 μ_B. This result is comparable to magnetic moments per iron obtained for $[Fe_2S_2(S_2-o-xyl)_2]^{2-}$[13] (1.43 μ_B) and $[Fe_2S_2Cl_4]^{2-}$ (1.38 μ_B) and suggests the presence of intramolecular antiferromagnetic spin coupling.

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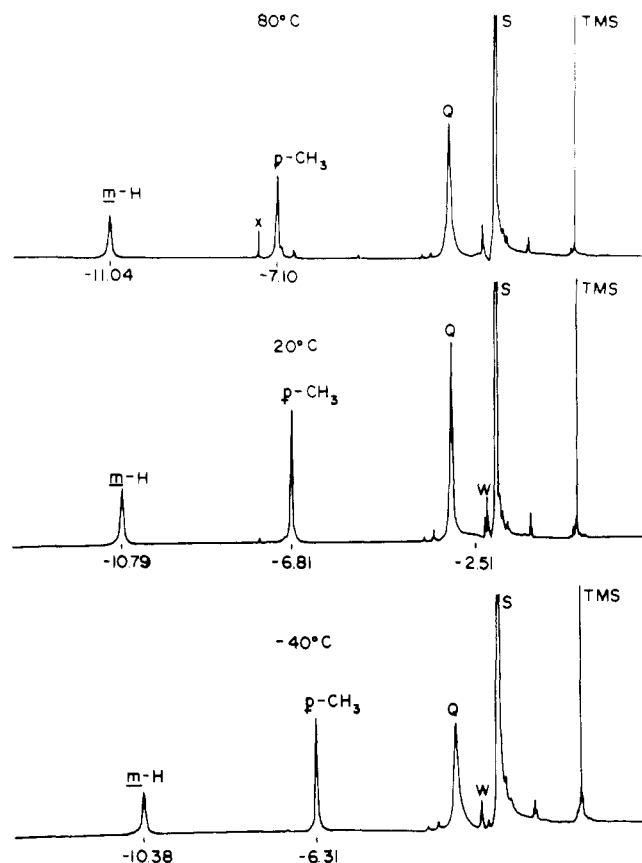(10) Ackermann, G.; Hesse, D. *Z. Anorg. Allg. Chem.* **1970**, *375*, 77.
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Figure 2. Proton magnetic resonance spectra (250 MHz) of $(Me_4N)_2[Fe_2S_2(O$-p-$tol)_4]$ in MeCN-d_3 solution at various temperatures. Peaks from protons of the cations are indicated by Q, solvent by S, water by W, and unidentified impurities by X. Chemical shifts are in ppm from internal Me_4Si.

Table II. Comparison of Relative Isotropic Shifts[a] for Various Metal–Sulfur Centers in CD_3CN Solutions

complex	ortho	para	complex	ortho	para
$[Fe_4S_4(SPh)_4]^{2-}$ [b]	1.34	1.96	$[Fe_2S_2(OPh)_4]^{2-}$ [f]	i	1.27
$[Fe_4S_4(OPh)_4]^{2-}$ [c]	1.04	1.29	$[MoFeS_4(SPh)_2]^{2-}$ [g]	1.25	1.49
$[Fe_4S_4(SPh)_4]^{3-}$ [d]	i	1.68	$[MoFeS_4(OPh)_2]^{2-}$ [h]	1.03	1.09
$[Fe_2S_2(SPh)_4]^{2-}$ [e]	1.09	1.81			

[a] Relative to meta shift (taken to be 1.00) at 22–25 °C. [b] Reference 15. [c] Reference 2. [d] Reference 16. [e] Reference 14. [f] This work. [g] Reference 17. [h] Reference 18. [i] Obscured.

Proton Nuclear Magnetic Resonance. Proton magnetic resonance spectra have been measured for the series of phenoxide complexes I–III in acetonitrile solution at room temperature and as a function of temperature for I and II. In addition to resonances due to the cation and residual undeuterated solvent, isotropically shifted resonances due to the phenoxide protons are observed; the room-temperature shifts are given in Table I. Representative 250-MHz ^1H NMR spectra at various temperatures of II are shown in Figure 2.

At room temperature, the phenoxide protons of I appear at -10.86 ppm and approximately -2.15 ppm. At higher temperatures, a broad signal appears slightly upfield of the cation resonance at approximately -3.06 ppm and is assigned to the ortho proton. The partially obscured resonance at approximately -2.15 ppm, which moves downfield at lower temperatures, disappears upon substitution of the p-H for a CH_3 group and is replaced by a resonance at -6.81 ppm, whose intensity corresponds to three protons. The resonance at -2.15 ppm is therefore assigned to the p-H, and the remaining resonance at -10.86 ppm, to the m-H.

Several features of these spectra suggest that, as with the thiophenolate dimers,[14] dominant contact interactions are responsible for the observed isotropic shifts: (i) the alternation of the signs of the shifts as one proceeds around the aromatic ring; (ii) the lack of attenuation of the magnitude of the shifts with increasing distance from the metal center; (iii) the sign reversal upon replacement of the p-H by a CH_3 group. The magnitudes of the shifts relative to those of the meta protons are listed in Table II. The relative shifts for the para protons are slightly less than the corresponding values for $[Fe_2S_2$-

$(SPh)_4]^{2-}$ due to a somewhat larger increase in the meta vs. the para shifts, but the general trend para > ortho > meta is obeyed. Since the relative shifts should reflect relative spin densities[15] provided the shifts are contact in origin, the data support the conclusion that dipolar interactions are negligible in these systems.

The only significant difference between the NMR spectra of the phenolate dimers and the thiophenolate dimers is that the magnitude of the isotropic shifts is larger for phenolate than for the corresponding thiophenolate analogues. These shift increases are somewhat smaller than those for the Fe_4S_4 system, where the phenolate shifts are approximately twice as large as the corresponding thiophenolate shifts. These data again suggest increased delocalization of unpaired spin density upon replacement of thiophenolate ligands by phenolates.

The isotropic shifts of the phenyl protons of the phenoxide dimers are temperature dependent; the magnitude of the shifts increases with increasing temperature over the entire temperature range. This result provides further evidence for intramolecular antiferromagnetic coupling and parallels the magnetic behavior of $[Fe_2S_2(S_2$-o-$xyl)_2]^{2-}$ [13] and $[Fe_2S_2Cl_4]^{2-}$ [6], two structurally characterized dimers for which variable-temperature magnetic data are available.

^{57}Fe Mössbauer Spectra. The ^{57}Fe Mössbauer spectrum of a solid sample of the Et_4N^+ salt of I diluted with boron nitride was obtained at 4.2 K and zero field. It consists of a single quadrupole doublet with isomer shift $\delta = 0.37$ mm/s, quadrupole splitting $\Delta E_q = 0.32$ mm/s, and linewidth $\Gamma = 0.26$ mm/s. The isomer shift is relative to Fe metal at room temperature. The spectrum was also measured in a small (~ 600 G) applied magnetic field. The spectrum remained essentially unchanged, indicating the presence of a diamagnetic ground state ($S = 0$), which is consistent with the magnetic data suggesting antiferromagnetic coupling. These results are comparable to those obtained for the thiolate dimers, except for the magnitude of the isomer shift, δ. Mössbauer spectra of the complexes $[Fe_2S_2X_4]^{2-}$ [11] where X = SPh and $X_2 = S_2$-o-xyl have been obtained, but the isomer shifts were measured relative to Fe metal at 4.2 K. Holm and co-workers[19] have reported a correction factor of $+0.12$ mm/s in the isomer shift vs. Fe metal at 298 and 4.2 K for various reduced tetramers, and a difference of $+0.11$ mm/s was obtained[2] for the isomer shift of $[Fe_4S_4(SPh)_4]^{2-}$. With a correction of $+0.11$ mm/s, the thiolate parameters are as follows: $\delta = 0.28$ mm/s, $\Delta E_q = 0.36$ mm/s ($X_2 = S_2$-o-xyl);[11] $\delta = 0.28$ mm/s, $\Delta E_q = 0.32$ mm/s (X = SPh).[11] The increased isomer shift for the phenolate dimer is consistent with increased ferrous character of the iron. This suggests that phenolate is capable of donating significantly more electron density to iron than is thiophenolate, which may be due to a substantial degree of covalency in the Fe–O bonds. This increase in isomer shift for the phenolate vs. thiophenolate dimers is approximately twice that found for the corresponding tetramer system,[2] presumably due to the

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Table III. Electrochemical Data for [Fe₂S₂(OAr)₄]²⁻

| complex | process | DCP^{a,b} | | | DPP^{a,b} | | CV^{a,c} |
		$E_{1/2}$, V	slope, mV	i_d/C, μA/mM	E, V	$W_{1/2}$, mV	E_{pc}, V
[Fe₂S₂(OPh)₄]²⁻	2-/3-	-1.35	-75	0.94	-1.39	250	-1.38
	3-/4-	-1.85	-93	1.14	-1.90	225	-1.95
[Fe₂S₂(O-p-tol)₄]²⁻	2-/3-	-1.38	-54	0.86	-1.42	180	-1.52
	3-/4-	-1.73	-43	0.94	-1.76	135	-1.94
[Fe₂S₂(O-p-C₆H₄Cl)₄]²⁻	2-/3-	-1.26	-52	1.54	-1.29	140	-1.41
	3-/4-	-1.65	-51	1.84	-1.69	125	-1.85

^{a} In NMP solution at 23 °C vs. SCE. All are average values of three scans. ^{b} 5 mV/s; 2 drops/s. ^{c} 100 mV/s.
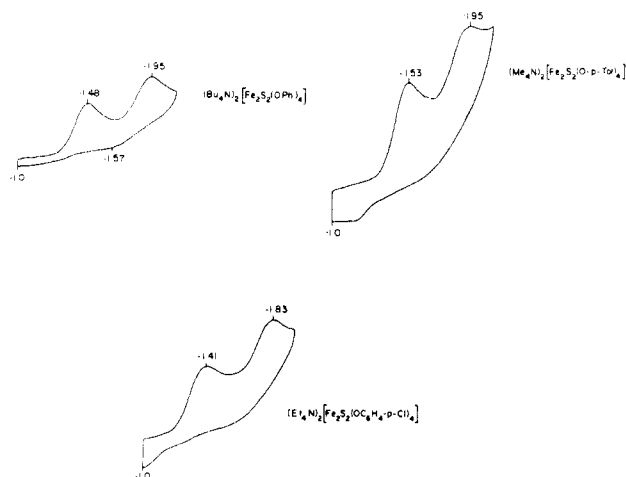
Figure 3. Cyclic voltammograms for (Bu₄N)₂[Fe₂S₂(OPh)₄], (Me₄N)₂[Fe₂S₂(O-p-tol)₄], and (Et₄N)₂[Fe₂S₂(O-p-C₆H₄Cl)₄] in NMP at a glassy-carbon electrode. Scan rates are 100 mV/s.

presence of two coordinated phenolates per iron vs. one per iron in the tetramer.

Electrochemistry. Electrochemical measurements on I–III have been performed by using three methods: dc polarography (DCP), differential-pulse polarography (DPP), and cyclic voltammetry (CV). Measurements were made on 1–2 mM solutions in NMP over the potential range +1.0 to -2.0 V. Each compound exhibits two well-defined cathodic processes corresponding to formation of the tri- and tetraanions. Typical cyclic voltammograms for each comound are presented in Figure 3; electrochemical data are listed in Table III.

Comparison of the data with corresponding data for the [Fe₂S₂(SAr)₄]²⁻ (Ar = Ph, p-tol, p-C₆H₄Cl)[11] complexes reveals several similarities. First, the thiophenolate analogues also show two cathodic processes over the same potential range. In dc polarography, the diffusion currents are in reasonable agreement with those obtained for the thiophenolate dimers and the phenolate and thiophenolate tetramers measured under similar conditions for a one-electron process. Slopes of log [i/(i_d - i)] vs. E are usually somewhat less than the theoretical value of 59 mV for a reversible one-electron reduction. Peak half-widths obtained by DPP are in adequate agreement with corresponding values obtained for phenolate tetramers for such a process. The slopes (DCP) and peak half-widths (DPP) obtained for I are unusually large compared to those of II and III, suggesting that the reduction process for this compound is less reversible by these criteria. These data show that, as for the thiolate dimers, the electron-transfer series [Fe₂S₂-(OAr)₄]²⁻,³⁻,⁴⁻ is realized and that the electron transfers are quasi-reversible by polarographic techniques.

In the CV experiments, two well-developed cathodic peaks with essentially no reverse (anodic) peaks are observed for each phenolate dimer. This result indicates that no 2-/3- or 3-/4- dimer process satisfies the diagnostic criteria for reversible charge transfer. This behavior is very similar to results ob-

tained for the [Fe₂S₂(SAr)₄]²⁻⁻¹¹ and [Fe₂S₂Cl₄]²⁻⁻⁶ complexes.

The reduction potentials for the phenolate dimers exhibit variation with substitution of the p-H by CH₃ and Cl. By any method used, the order observed is p-Cl < p-H < p-CH₃, with 20–100-mV negative shifts between members of the series. This trend is also observed for the corresponding arylthiolate dimers and can be explained by simple inductive effects of the electron-releasing CH₃ and electron-withdrawing Cl groups. It is, however, somewhat surprising considering the order observed for the shifts in the electronic absorption maxima.

The most important results obtained from the electrochemical data are that the same pattern of two one-electron reductions typical of all [Fe₂S₂L₄]²⁻ clusters[6,11] is observed and that the potentials of these reductions are approximately 200 mV more negative than those of the arylthiolate analogues. Simple electronegativity arguments would predict the phenolate dimers to be easier to reduce than the thiolate analogues, as the more electronegative oxygen atoms should decrease the electron density at the [Fe₂S₂]²⁺ core, as is observed for the [Fe₂S₂Cl₄]²⁻ ion. Again, phenoxide is apparently capable of transferring more electron density to the [Fe₂S₂]²⁺ core than is thiophenoxide. This is consistent with the Mössbauer and ¹H NMR results. Similar behavior has been observed for the [MoFeS₄X₂]²⁻⁻¹⁷,¹⁸ and the [Fe₄S₄X₄]²⁻⁻²,²⁰ systems, where X = SAr and OAr.

Ligand-Exchange Reactions. The phenoxide dimer complexes are extremely sensitve to water, acidic solvent impurities, and strongly donating oxygen solvents, as are the phenoxide tetramers. This behavior necessitates rigorous purification of solvents for use in recrystallization and solution studies.

The phenolate dimers react with electrophiles such as acyl halides. Treatment with 4 equiv of benzoyl chloride in acetonitrile results in rapid, quantitative conversion to the corresponding dimeric chloro complex (reaction 5), as demonstrated by optical spectra. This reactivity has also been documented for the thiophenolate[21] tetramers and proceeds, presumably, by the same mechanism.[6]

$$[Fe_2S_2(OAr)_4]^{2-} + 4PhCOCl \rightarrow [Fe_2S_2Cl_4]^{2-} + PhCO_2Ar \tag{5}$$
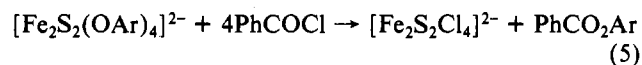
Reaction of the phenolate dimers with 4 equiv of thiophenol results in immediate formation of the thiophenolate derivative (reaction 6). This reactivity again is as expected in view of

$$[Fe_2S_2(OAr)_4]^{2-} + 4PhSH \rightarrow [Fe_2S_2(SPh)_4]^{2-} + 4ArOH \tag{6}$$
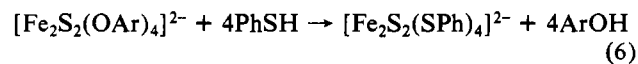
the lability of phenolate ligands and the greater acidity of

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thiophenol vs. phenol.[21] Previous investigations of the thiolate dimers show that they too undergo facile ligand-exchange processes. For example,[11] the $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ complex is smoothly converted to $[Fe_2S_2(SAr)_4]^{2-}$ by treatment with the appropriate thiophenol. In addition, analogous reactivity has been demonstrated for the phenolate tetramers. It is apparent that the phenolate dimers undergo facile ligand exchange with retention of the Fe_2S_2 core.

Conclusions

Phenolate-ligated binuclear Fe–S clusters can be prepared and isolated in crystalline form as their tetraalkylammonium salts. The optical spectra exhibit the expected blue shift upon oxygen substitution. Comparison with the thiophenolate analogues reveals that the magnetic properties remain virtually unchanged upon substitution of phenolate for thiophenolate, while the isotropically shifted phenyl protons in the ^1H NMR reflect a substantial increase in unpaired spin density in the aromatic ring. An increased isomer shift in the ^{57}Fe Mössbauer spectra and a substantial negative shift in the reduction potentials suggest that the phenolate ligands transfer more electron density to the $[Fe_2S_2]^{2+}$ core than do thiophenolates, consistent with the NMR results.

Comparison of corresponding physical properties of phenolate- and thiophenolate-ligated Fe_2S_2 centers with the analogous Fe_4S_4 centers shows a clear trend. The blue shifts in the optical absorption maxima, the isotropic NMR shifts of the phenyl protons, and the negative shifts of the reduction potentials upon substitution of thiophenolate by phenolate ligands are in each case approximately *twice* as large for the Fe_2S_2 complexes as for the Fe_4S_4 complexes. This is probably due to coordination of two phenolates to each iron in the dimers compared to one phenolate per iron in the tetramers.

Results obtained for Fe_2S_2 clusters with phenolate ligands suggest that substitution of a cysteinyl thiol ligand to an Fe_2S_2 core in a protein by a tyrosyl phenolate should have only a minor effect on cluster redox properties. This observation is entirely consistent with results obtained for the phenoxide tetramers and indicates that tyrosyl ligation could provide a labile coordination site with minimal change in cluster reduction potentials.

Comparison of the data obtained for the phenolate dimers with that of the oxidized Rieske protein shows several similarities. The ^{57}Fe Mössbauer isomer shift for the phenolate dimer (0.37 mm/s) is approximately the same as that for one of the iron atoms (0.32 mm/s) of the oxidized protein. The optical absorption spectrum of the oxidized protein has a broad band centered around 458 nm with unresolved features to higher and lower energy and should be dominated by terminal ligand-to-metal charge-transfer transitions in this region. The optical spectra of the phenolate dimers have a broad transition in this region with unresolved features to lower energy and seem to be consistent with the possibility of two tyrosines and two cysteines as terminal ligands. The sensitivity of the phenolate dimers to water precludes measurement of their redox potentials in mixed aqueous–organic media. It is therefore difficult to compare the phenolate dimer potentials directly with those of the Rieske protein. Johnson and Holm[22] have observed that coordination of the $[Fe_4S_4]^{2+}$ core by carboxylate ligands results in substantial positive shifts in cluster redox potentials. If the as yet unknown carboxylate-ligated Fe_2S_2 complexes show a similar shift in redox potentials vs. the thiolate analogues, the observed protein potentials may suggest coordination by glutamate or aspartate carboxylates to the iron atoms. Taken together, the data are not inconsistent with coordination of the Rieske center by one or two tyrosines, but carboxylate, mixed phenolate–carboxylate, or nitrogen ligation remains reasonable alternatives.

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