$(Ph_3PAu)_3V(CO)_5$ are essentially identical in band number, position, and relative intensities in a variety of solvents (ν_{CO} of **1** in THF 1958 (vs), 1890 (w), 1834 (s); in CH_2Cl_2 1954 (vs), 1879 (sh), 1825 (s) cm^{-1}) including CH_2Cl_2, THF, CH_3CN, and HMPA-CH_2Cl_2 (50:50 v/v; (1) is insoluble in neat HMPA). Nujol mull spectra of crystalline **1** are very similar to solution spectra except the two bands at lower energy are split due to solid-state effects (ν_{CO} in Nujol 1959 (s), 1889 (m), 1876 (sh), 1828 (s), 1810 (s) cm^{-1}). As was mentioned earlier, the solution spectra of **1** resemble those of $V(CO)_5L^-$ species (e.g., ν_{CO} of $[Et_4N][V(CO)_5Ph_3P]$ in THF 1965 (s), 1858 (m), 1823 (vs).[38,39] It is evident from a comparison of these spectra that the $(Ph_3PAu)_3$ ligand is a strong donor group to vanadium. By contrast, all of the ν_{CO} values for $(Ph_3Sn)_2V(CO)_5^-$ in a variety of solvents are above 1860 cm^{-1}.[1] An analysis of the ν_{CO} values for $Ph_3PAuMn(CO)_5$ indicates that an individual Ph_3PAu unit acts as a fairly good π acceptor and a strong σ donor to manganese.[40]

Treatment of $(Ph_3PAu)_3V(CO)_5$ with 4 equiv of Ph_3P in THF or 10 equiv of $[Et_4N]Br$ in CH_2Cl_2 (all at room temperature) also gave no reaction after ca. 24 h. On the basis of the crystal structure of **1** which shows the presence of Au-Au bonds as well as Au-V bonds, it is not surprising that individual Ph_3PAu units cannot be readily displaced as they can in mono((triphenylphosphine)gold) complexes. Structures of bis- and other tris((triphenylphosphine)gold) derivatives of metal carbonyls (e.g., $(Ph_3PAu)_2M(CO)_4$ (M = Fe,[8] Ru,[9] Os[10]) and $(Ph_3PAu)_3M(CO)_4$ (M = Mn, Re))[11] have not been determined. It seems possible in view of our results that gold-gold interactions may also be present, especially in the seven-coordinate $(Ph_3PAu)_3M(CO)_4$ complexes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE 79-12159) for support of this research. We also thank the NSF for partial support of our Enraf-Nonius X-ray diffraction and structure solving equipment (Grant CHE 77-28505). I am pleased to acknowledge Dr. Michael C. Palazzotto for his preliminary work on this system. I am also grateful to Professor Lou Pignolet and Mr. Mike McGuiggan for their invaluable assistance in the X-ray work.

Supplementary Material Available: Tables of root-mean-square amplitudes of thermal vibration (Å) and final thermal parameters and structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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[41] **Note Added in Proof**: The molecular structure of $[(Ph_3PAu)_3Mn(CO)_4]$ has been determined and shows gold-gold interactions to be present (Ellis, J.; Warnock G., to be submitted). Also, a recent communication on the molecular structure of $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$ shows this species to be a tetranuclear gold cluster and a derivative of $(Ph_3PAu)_4$ (De Martin, F.; Monassero, M.; Naldini, L.; Ruggeri, R.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1981**, 222).

Evidence for the Localized Fe(III)/Fe(II) Oxidation State Configuration as an Intrinsic Property of $[Fe_2S_2(SR)_4]^{3-}$ Clusters

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Abstract: Spectroscopic properties of the mixed-valence 2-Fe prosthetic group $[Fe_2S_2(S\text{-}Cys)_4]$ (**1**) of reduced ferredoxin proteins (Fd_{red}) have demonstrated the localized Fe(II) + Fe(III) (class II) oxidation state configuration. The lifetime of this configuration is $\gtrsim 10^{-7}$ s from spectra at 4.2-250 K and presumably at least $\sim 10^{-3}$ s at 300 K from ^1H NMR spectra. Reduction of the centrosymmetric Fd_{ox} analogue $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ $S_{2\text{-}o\text{-}x}yl$ = *o*-xylene-α,α'-dithiolate) in solution by electrochemical or chemical means affords several products. One of these exhibits a nearly featureless UV/visible spectrum, a near-infrared absorption band at 1750 nm, a virtually axial EPR spectrum with $g = 2.01$ and 1.94 observable to at least 80 K, and a Mössbauer spectrum in zero field at 4.2-180 K containing features fully consistent with tetrahedral $Fe^{II}S_4$ ($\delta = 0.60$, $\Delta E_Q = 3.06$ mm/s) and $Fe^{III}S_4$ sites ($\delta = 0.19$, $\Delta E_Q = 0.54$ mm/s). These properties are very similar to those of Fd_{red} proteins and allow identification of this reduction product as $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ (**3**), a synthetic analogue of the reduced protein group **1**. Inasmuch as **2** lacks any features which would tend to localize the electron added upon reduction, it is concluded that class II mixed-valence behavior is an intrinsic property of any $[Fe_2S_2(SR)_4]^{3-}$ species and probably of any species containing the planar bridged $[2Fe\text{-}2S]^{1+}$ core unit. Thus the localized electronic configuration of all Fd_{red} proteins thus far examined, which has been detected by one or more spectroscopic techniques capable of sensing lifetimes in the domain of relatively fast electron-transfer processes, is not necessarily a consequence of protein structure. The analogue **3** has as yet been obtained only in solution. The identity of the other reaction product(s) has not been ascertained but appears to be a species containing high-spin $Fe^{III}S_4$ sites.

Four types of iron-sulfur prosthetic groups, containing one to four Fe atoms, have been established in proteins. Among these the tetrahedral 1-Fe group $[Fe(S\text{-}Cys)_4]$ present in conventional rubredoxins (Rd) is structurally[2] and electronically[3] the simplest, and the 3-Fe group, having a cyclic [3Fe-3S] core of as yet incompletely defined properties, is the newest to be discovered.[4,5] The remaining two types, $[Fe_4S_4(S\text{-}Cys)_4]$[6] and $[Fe_2S_2(S\text{-}Cys)_4]$

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[1] (a) Harvard University. (b) Francis Bitter National Magnet Laboratory.

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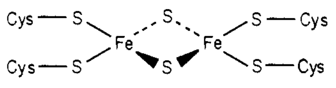
(1), possessing the cubane-type [4Fe–4S] and the binuclear



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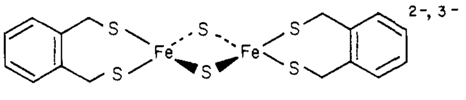


2 (2−)
3 (3−)

[2Fe–2S] core units, respectively, have been the subjects of numerous biological and physicochemical investigations. Structure **1**, originally deduced from spectroscopic and magnetic properties[7] and fully supported by property coincidences with structurally defined synthetic analogous such as [bis(μ-sulfido)-bis(*o*-xylene-α,α′-dithiolato)ferrate(III)]$^{2-}$[8-11] ($[\mathrm{Fe_2S_2(S_2\text{-}}o\mathrm{\text{-}xyl)_2}]^{2-}$, **2**), has recently been confirmed by X-ray crystallography of *Spirulina platensis* oxidized ferredoxin[12,13] ($\mathrm{Fd_{ox}}$).

Proteins containing group **1** exhibit in vitro the two oxidation levels indicated in series 1, below which are placed isoelectronic

$$\mathrm{Fd_{ox}([2Fe{-}2S]^{2+}) \rightleftharpoons Fd_{red}([2Fe{-}2S]^{1+})} \qquad (1)$$

$$\begin{array}{ccccc} [\mathrm{Fe_2S_2(SR)_4}]^{2-} & \rightleftharpoons & [\mathrm{Fe_2S_2(SR)_4}]^{3-} & \rightleftharpoons & [\mathrm{Fe_2S_2(SR)_4}]^{4-} \\ \mathrm{2Fe(III)} & & \mathrm{Fe(III) + Fe(II)} & & \mathrm{2Fe(II)} \end{array}$$

analogues and formal Fe oxidation states. The protein oxidation level corresponding to the analogue tetraanion has not been detected. Group **1** in $\mathrm{Fd_{ox}}$ proteins consists of two essentially equivalent high-spin Fe(III) ions which are antiferromagnetically coupled to give a spin-singlet ground state. The electronic similarities between $\mathrm{Fd_{ox}}$ and the analogues $[\mathrm{Fe_2S_2(SR)_4}]^{2-}$, as manifested in absorption and Mössbauer spectra and in J values of magnetic exchange interactions, are documented elsewhere.[8-11] Protein reduction affords $\mathrm{Fd_{red}}$, in which the two Fe atoms remain antiferromagnetically coupled ($-J \approx 100$ cm^{-1}[14]), leading to a doublet ground state and consequent EPR spectrum.[15] A highly significant feature of this oxidation level is the presence of spectroscopically distinct metal sites having the properties of high-spin tetrahedral Fe(III) and Fe(II). Thus group **1** in $\mathrm{Fd_{red}}$ is a class II[16] mixed-valence species. This electronic arrangement has been convincingly demonstrated by low-temperature Mössbauer spectroscopy[14b,17-22] and by detection of the near-infrared ligand field transition of tetrahedral Fe(II) in spinach and adrenal $\mathrm{Fd_{red}}$.[23] Additionally, ^{1}H NMR spectra are reasonably interpretable in terms of individual Fe(II) and Fe(III) sites.[14b,24]

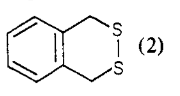
Inasmuch as over a dozen different proteins from diverse sources were examined in the preceding investigations, it is entirely probable that class II mixed-valence behavior is a general property of all $\mathrm{Fd_{red}}$ proteins containing group **1**. In contrast, the collective properties of protein $[\mathrm{Fe_4S_4(S\text{–}Cys)_4}]$ groups with core oxidation levels $[\mathrm{4Fe{-}4S}]^{3+,2+,1+}$ and of the analogues $[\mathrm{Fe_4S_4(SR)_4}]^{2-,3-}$ are inconsistent with localized valence states although all are mixed-valence (Fe(III)/Fe(II)) species. This situation is most apparent from Mössbauer spectra in which isomer shift differences between Fe sites (where resolvable) in proteins[25,26] and analogues[27,28] are far less than those of reduced group **1** (vide infra). Mössbauer data are indicative of partial delocalization in the mixed-valence $[\mathrm{3Fe{-}3S}]^{2+}$ oxidation level of 3-Fe groups.[5] A significant question that arises is whether the localized valence states of reduced group **1** are an *intrinsic* property of the group or are stabilized vs. a delocalized (class III-A[16]) configuration by protein structural and environmental factors. This question is addressed here by examination of certain spectroscopic properties of the reduced analogue $[\mathrm{Fe_2S_2(S_2\text{-}}o\mathrm{\text{-}xyl)_2}]^{3-}$ (**3**). This species has been detected electrochemically[8,9] but has not been otherwise investigated previously.

Experimental Section

Preparation of Compounds. For chemical reduction and/or Mössbauer spectra in solution salts of $[\mathrm{Fe_2S_2(S_2\text{-}}o\mathrm{\text{-}xyl)_2}]^{2-}$ and bis(*o*-xylene-α,α′-dithiolato)ferrate(II) ($[\mathrm{Fe(S_2\text{-}}o\mathrm{\text{-}xyl)_2}]^{2-}$) which are more soluble than those previously prepared[8,9,11,29] were desired. n-$\mathrm{Bu_4N^+}$ salts proved adequate in this respect; the following procedures were conducted under a purified dinitrogen atmosphere using degassed solvents.

(n-Bu$_4$N)$_2$[Fe$_2$S$_2$(S$_2$-o-xyl)$_2$]. Because of its relatively high solubility, this compound could not be conveniently prepared by a recent improved synthesis of $[\mathrm{Fe_2S_2(SR)_4}]^{2-}$ complexes,[11] which relies on precipitation of the anion as a sparingly soluble salt from the reaction mixture. The following method is based on reaction 2. To a cold (~0 °C) solution

$$2[\mathrm{Fe(S_2\text{-}}o\mathrm{\text{-}xyl)_2}]^{2-} + 2\mathrm{S} \rightarrow [\mathrm{Fe_2S_2(S_2\text{-}}o\mathrm{\text{-}xyl)_2}]^{2-} + (\mathrm{S_2\text{-}}o\mathrm{\text{-}xyl})^{2-} +$$



(2)

of 3.21 g (15 mmol) of $\mathrm{Na_2(S_2\text{-}}o\mathrm{\text{-}xyl)}$ (from 0.69 g of sodium and 2.55 g of o-xyl(SH)$_2$[9]) in 40 mL of methanol was added with stirring a solution of 3.42 g (5.0 mmol) of $(n\text{-}\mathrm{Bu_4N})_2(\mathrm{FeCl_4})$ in 30 mL of methanol. The light brown solution was warmed to room temperature and stirred for 30 min, and the solvent was removed in vacuo. To the pale brown mixture formed after addition of 50 mL of acetonitrile was added 0.16 g (5.0 mmol) of elemental sulfur under rapid stirring, which was continued for 2 h. The solid materials, resulting from addition of 60 mL of anhydrous ether to the reaction mixture reduced to 10 mL in vacuo, were collected by filtration and were treated with 50 mL of warm (~50 °C) acetonitrile. The deep greenish brown filtrate from this mixture was

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Table I. Mössbauer Parameters at 4.2 K

compd[a]	Fe ox state	δ,[b,h] mm/s	ΔE_Q,[c] mm/s	ref
$(Et_4N)[Fe(S_2$-*o*-xyl$)_2]$	3+	0.13	0.57	29, *f*
$Na(Ph_4As)[Fe(S_2$-*o*-xyl$)_2]$	2+	0.61	3.34	29, *f*
$(n\text{-}Bu_4N)_2[Fe(S_2$-*o*-xyl$)_2]$ (soln)[d]	2+	0.56	2.75	*g*
$(Et_4N)_2[Fe_2S_2(S_2$-*o*-xyl$)_2]$	3+	0.17	0.36	8
$(n\text{-}Bu_4N)_2[Fe_2S_2(S_2$-*o*-xyl$)_2]$ (soln)[d]	3+	0.19	0.57	*g*
$(n\text{-}Bu_4N)_3[Fe_2S_2(S_2$-*o*-xyl$)_2]$ (soln)[d]	3+	0.19 (D2)	0.54	*g*
	2+	0.60 (D1)	3.06	
		0.17 (M1)[i]	0.31[j]	
		0.21 (M2)[i]	0.59[j]	
spinach Fd_{ox}	3+	0.15	0.65	17
spinach Fd_{red}[e]	3+	0.17	0.64	17
	2+	0.44	2.63	
adrenal Fd_{ox}	3+	0.15	0.61	17
adrenal Fd_{red}[e]	3+	0.17	0.68	17
	2+	0.46	2.77	
$(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$	2.5+	0.34	1.26	27b
$(Et_4N)_3[Fe_4S_4(SCH_2Ph)_4]$	2.25+	0.60	0.93, 1.41	28a

[a] Analogue complexes measured in solid state unless otherwise noted. [b,c] For present or past measurements in this laboratory: (*b*) ±0.03, (*c*) ±0.05 mm/s. [d] 7:3 v/v acetonitrile/HMPA. [e] ~250 K. [f] Frankel, R. B.; Papaefthymiou, G. C.; Lane, R. W.; Holm, R. H. *J. Phys.* (*Orsay, France*) 1976, *37*, C6-165. [g] This work. [h] All isomer shifts are referenced to, or have been corrected to refer to, Fe metal at 4.2 K. [i] Reaction byproduct (see text). [j] Assuming $\eta = 0$ and $V_{zz} \parallel H_{hf}$ in the magnetic hyperfine spectra.

concentrated in vacuo to 10 mL and 60 mL of anhydrous ether was added. Crystallization started almost immediately; cooling to −20 °C afforded 1.7 g (68%) of pure product as red-black crystals. Anal. Calcd for $C_{48}H_{88}Fe_2N_2S_6$: C, 57.69; H, 8.87; Fe, 11.18; N, 2.80; S, 19.25. Found: C, 57.13; H, 8.56; Fe, 11.32; N, 3.03; S, 19.74. For ^{57}Fe-enriched Mössbauer samples Fe_2O_3 (95 atom % ^{57}Fe) was dissolved in concentrated HCl, the solution was diluted with an equal volume of water and was treated under anaerobic conditions with electrolytic grade Fe powder (unenriched). After filtration $FeCl_2\cdot 2H_2O$ was isolated by evaporation of the solution. This material was converted to $(n\text{-}Bu_4N)_2(FeCl_4)$ and above preparation was followed. The samples of $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{2-}$ so prepared contained ~45 atom % ^{57}Fe, as judged from relative intensities of Mössbauer spectra of unenriched and enriched samples in acetonitrile solutions at 4.2 K.

$(n\text{-}Bu_4N)_2[Fe(S_2$-*o*-xyl$)_2]$. This compound was prepared by the procedure for the Et_4N^+ salt[29] except that methanol was used as the reaction solvent. The crude product was precipitated from the reaction solution with ether and was recrystallized from acetonitrile/ether. The compound was not analyzed; its spectral properties are the same as those of the Et_4N^+ salt.[29]

For use in the reactions and measurements next described hexamethylphosphoramide (HMPA) was distilled from sodium, and acetonitrile was refluxed over and distilled from alkaline permanganate, potassium bisulfate, and calcium hydride in succession.

Solutions of $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{3-}$. To a solution of 0.25 g (0.25 mmol) of $(n\text{-}Bu_4N)_2[Fe_2S_2(S_2$-*o*-xyl$)_2]$ in 4 mL of acetonitrile was slowly added with stirring the desired volume of 0.2 M sodium acenaphthylenide solution in HMPA. The initial greenish brown color changed to brownish black. $(n\text{-}Bu_4N)(BPh_4)$ (0.14 g, 0.25 mmol) was added to prevent possible precipitation of a sodium-containing salt of the trianion. After 30–40-min reaction time the resultant solutions were used for spectroscopic measurements. The amount of reducing agent was varied to prevent interference from $C_{12}H_8^{-}\cdot$ signals (EPR spectra) and to investigate the formation of a Fe-containing reaction byproduct. For UV/visible spectral examination $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{3-}$ was generated in an optically transparent thin-layer electrode (OTTLE) cell described elsewhere.[30]

Physical Measurements. All measurements were performed under strictly anaerobic conditions. Absorption spectra were recorded on a Cary Model 17 or 219 spectrophotometer. EPR spectra were obtained at X-band frequencies using a Varian E-109 spectrometer equipped with a Helitran Model LTD-3-110 temperature controller. Electrochemical measurements were performed with standard Princeton Applied Research instrumentation using a glassy carbon or Pt working electrode; all potentials were obtained at ~25 °C vs. a saturated calomel electrode as reference. Mössbauer spectra were obtained at 4.2–180 K with a constant acceleration spectrometer calibrated with Fe metal and equipped with a Janis Varitemp cryostat. The ^{57}Co in Rh source was maintained at room temperature. Spectra of polycrystalline solids and of solutions, prepared for measurement as described elsewhere,[28] were analyzed by a least-squares fitting program. The isomer shifts in Table I measured in this work are corrected for the second-order Doppler shift of Fe metal and thus refer to Fe metal at 4.2 K.

Results

Two types of synthetic analogues of the Fd_{ox} site **1** have been prepared by a variety of reactions[8,9,11,31-34] and fully characterized.[8-11,34] Those containing monofunctional thiolate ligands, $[Fe_2S_2(SR)_4]^{2-}$, are electrochemically reducible to $[Fe_2S_2(SR)_4]^{3-}$. However, the occurrence of the rapid sequential dimer → tetramer conversion reaction (3),[34] which is irreversible, precludes their use

$$2[Fe_2S_2(SR)_4]^{3-} \rightarrow [Fe_4S_4(SR)_4]^{2-} + 4RS^- \qquad (3)$$

as precursors for chemical or electrochemical generation of trianions in bulk concentrations. Limited electrochemical results,[8,9] augmented in this study, for the chelate complex $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{2-}$ (**2**) have revealed an initial one-electron reduction which more closely approaches chemical reversibility. While chemical and electrochemical reductions of this complex are not without complications, the collective spectroscopic evidence considered below suffices to demonstrate the formation of $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{3-}$ (**3**). For purposes of this study $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{2-}$ has the requisite property of rigorous equivalence of Fe(III) sites, as revealed in the centrosymmetric structure **2** found in the crystalline Et_4N^+ salt.[9]

Redox Properties. The existence of the analogue electron-transfer series (1) is demonstrated by the presence of two redox processes in the cyclic voltammograms of $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{2-}$ shown in Figure 1. These results are in agreement with those reported earlier,[8] and the present voltammograms are better resolved owing to the higher solubility of the n-Bu_4N^+ salt of the dianion. In the two steps observed in DMF solution $i_{p,c} \simeq i_{p,a}$. When the first step is scanned separately by using a switching potential of −1.7 V, the cathodic and anodic peak currents are equal. This behavior is illustrated in the 7:3 v/v acetonitrile/HMPA solvent medium employed in chemical generation of $[Fe_2S_2(S_2$-*o*-xyl$)_2]^{3-}$ (vide infra). Peak potential separations for both steps exceed the value of 59 mV for one-electron reversible charge transfer. Examination at scan rates of 0.05–10 V/s confirmed that, except for $i_{p,c} \simeq i_{p,a}$ in the 2−/3− step, the two processes depart from the usual criteria for reversible charge transfer.[35] In particular, $|E_{p,c} - E_{p,a}|$ increases as the scan rate

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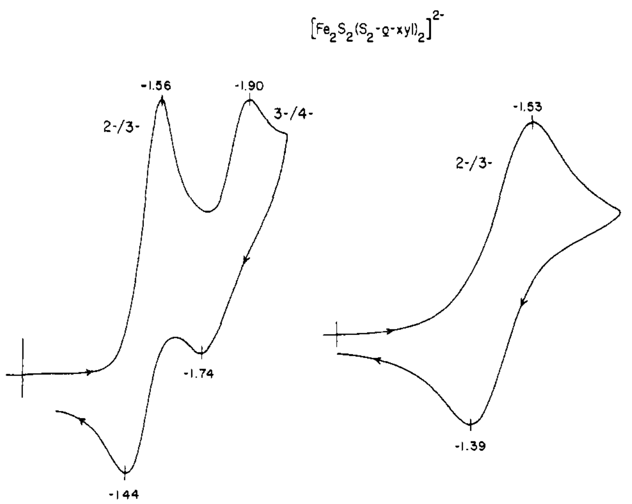


Figure 1. Cyclic voltammograms of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ in different solvents: left, in DMF at 100 mV/s showing reduction to 3– and 4– species; right, in 7:3 v/v acetonitrile/HMPA showing reduction to the 3– species. The second reduction is not well developed in this solvent.

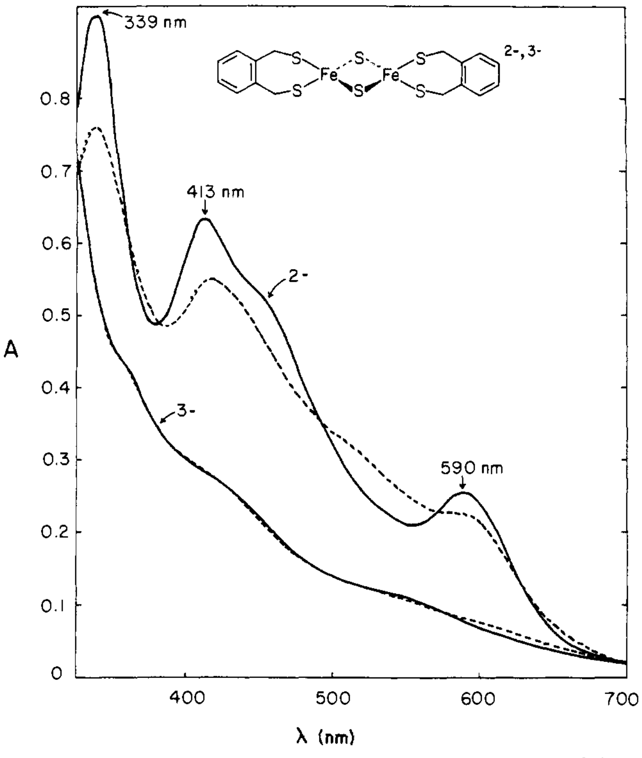


Figure 2. UV/visible absorption spectra of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-,3-}$ in acetonitrile containing 0.1 M (n-Bu_4N)ClO_4 recorded in an OTTLE cell: initial dianion solution followed by reduction at –1.7 V for 15 min (—); reoxidation of trianion solution at –0.6 V for 15 min followed by a repeat of the reduction step (---).

increases. These results indicate that reactions are subject to diffusion and/or charge-transfer kinetic effects and are electrochemically quasi-reversible but approach or achieve chemical reversibility on the time scale of cyclic voltammetry. Of the two processes the 2–/3– step is clearly the more reversible chemically in this sense. From the peak potentials obtained in DMF solution at 100 mV/s $E_{1/2}(2-/3-) = -1.50$ V and $E_{1/2}(3-/4-) = -1.82$ V. Thus for the disproportion reaction $2(3-) \rightleftarrows (2-) + (4-)$ $K_{dis} = 10^{-5.41}$, indicating that fully reduced solutions of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ contain concentrations of dianion and tetraanion too slight to be detected by the spectroscopic techniques employed here.

Absorption Spectra. Shown in Figure 2 are UV/visible spectra resulting from two cycles of oxidation–reduction carried out in an OTTLE cell. As discussed elsewhere[8,9] the spectrum of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$, the initial species in the redox sequence, closely resembles that of oxidized group **1**. Reduction of the dianion in acetonitrile at a potential (–1.7 V) less cathodic than $E_{1/2}(3-/4-)$ affords a nearly featureless spectrum whose intensity is ca. 50% diminished relative to the oxidized complex. Oxidation at –0.6 V results in a spectrum showing the basic features of the dianion but with ca. 15% reduction in intensity of the 413-nm peak and increased absorption near 500 nm. Rereduction of this solution gave a spectrum essentially coincident with that from the first reduction. Repetitions of the redox cycle gave similar results, with 15–20% reduction of intensity near 413 nm. These results show that each cycle is not strictly reversible over the time period (15 min) required to achieve a constant spectrum upon electrolysis. However, the spectra of the reduced species and their intensity differences with the initial dianion spectrum are quite typical of Fd_{red} spectra and their intensities compared to Fd_{ox} spectra (e.g., parsely $Fd_{red,ox}$[36]) at 350–700 nm.

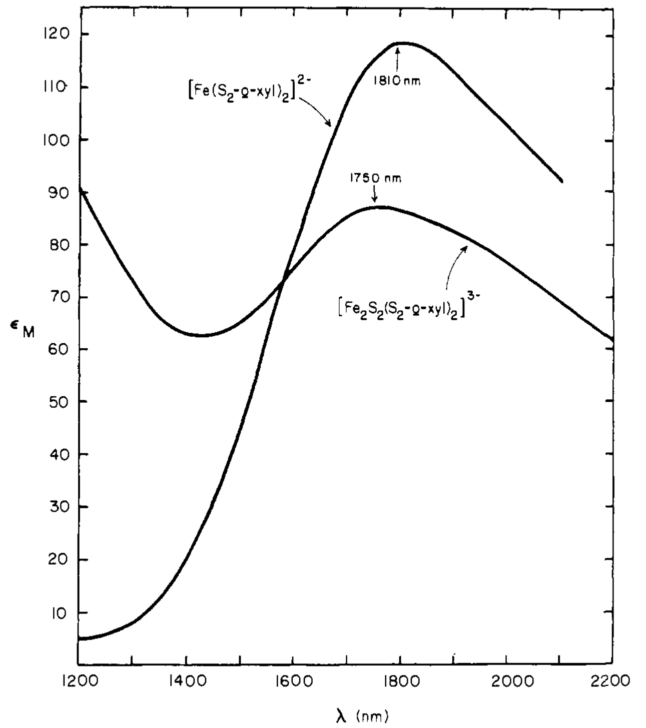
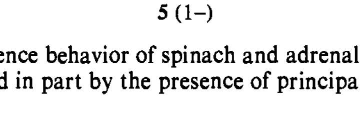


Figure 3. Near-infrared absorption spectra of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ in DMF and $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ in 7:3 v/v acetonitrile/HMPA (generated by reduction of the dianion with 1.15 equiv of $Na^+C_{12}H_8^-$). The spectrum of the latter solution was recorded ca. 30 min after addition of reductant.

Additional evidence for identification of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ as a product of reduction follows from the near-infrared absorption spectra presented in Figure 3. Reduction of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ with a small excess (1.15 equiv) of sodium acenaphthylenide results in the appearance of a band at 1750 nm ($\epsilon_M = 86$). In this medium $C_{12}H_8^-$· ($E_{1/2}(0/1-) = -1.68$ V) can cause reduction to the trianion ($E_{1/2}(2-/3-) = -1.46$ V, Figure 1) but not the tetraanion. The band arises from the $^5E \rightarrow {}^5T_2$ ligand field transition of tetrahedral Fe(II), as shown by the appearance of a corresponding feature at 1810 nm ($\epsilon_M = 121$) in the spectrum of the tetrahedral Rd_{red} analogue $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ [29] (**4**) in DMF solution.[37] The class II mixed-valence behavior of spinach and adrenal Fd_{red} has been demonstrated in part by the presence of principal near-infrared



4 (2–)
5 (1–)

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[36] Mayhew, S. G.; Petering, D.; Palmer, G.; Foust, G. P. *J. Biol. Chem.* **1969**, *244*, 2830.

[37] In acetonitrile solution $\lambda_{max} = 1800$ nm ($\epsilon_M = 123$).[29]

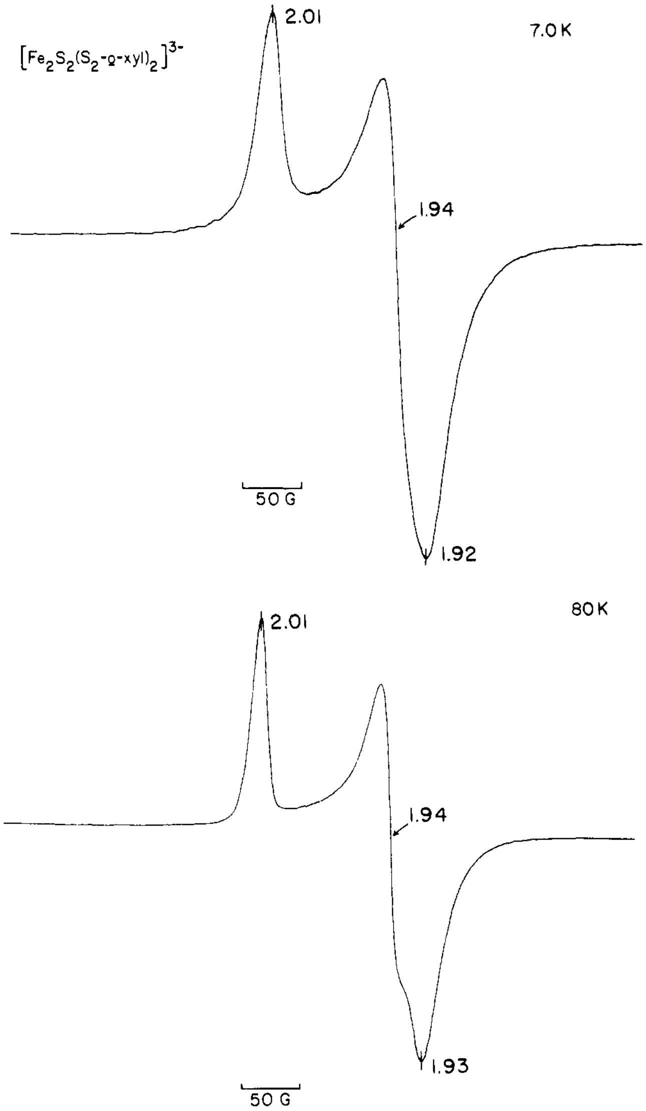

Figure 4. X-band EPR spectra of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ in 7:3 v/v acetonitrile/HMPA formed by treatment of a 32 mM solution of the dianion with 0.9 equiv of $Na^+C_{12}H_8^-$. Spectrometer settings: microwave power, 60 mW; modulation amplitude, 0.8 G; modulation frequency, 100 kHz. Top: 7.0 K, receiver gain 3.2 × 10^2. Bottom: 80 K, receiver gain, 6.3 × 10^2. The spectra were recorded ca. 45 min after addition of reductant.

bands at ~6000 cm^{-1} (1670 nm), also assigned to transitions of $^5E \rightarrow {}^5T_2$ parentage.[23] The apparent lower extinction coefficient of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ vs. $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ in the near-infrared region and the lack of spectral reversibility in the spectroelectrochemical experiments suggest that the trianion is not the only reaction product, a matter confirmed by Mössbauer spectroscopy (vide infra).

EPR Spectra. Spectra of the reaction product of $(n\text{-}Bu_4N)_2[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]$ with a slight deficiency (0.9 equiv) of sodium acenaphtylenide in 7:3 v/v acetonitrile/HMPA, determined at 7.0 and 80 K, are shown in Figure 4. The spectrum at 7.0 K is nearly axial whereas that at 80 K is just resolvably rhombic. These spectra are very similar to those of adrenal[15,38] (g = 2.02, 1.93) and a number of bacterial[15,39] Fd_{red} proteins whose spectra are axial or nearly so. Algal and higher plant Fd_{red} proteins (e.g., spinach Fd_{red}, g = 2.05, 1.96, and 1.89[15,38]) generally give well-resolved rhombic spectra. When protein structure is unfolded in

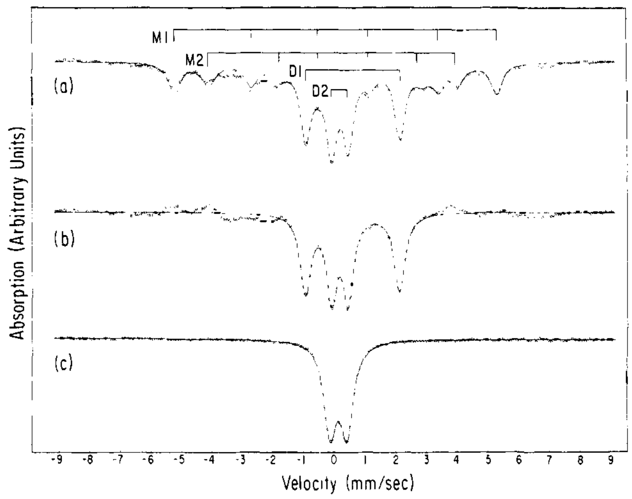

Figure 5. Mössbauer spectra at 4.2 K: (a) from the reaction of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ with 1.3 equiv of $Na^+C_{12}H_8^-$ in 7:3 v/v acetonitrile/HMPA after 4.5 h reaction time; subspectra D1, D2, M1, and M2 are described in the text; (b) spectrum (a) after subtraction of M1 and M2; (c) $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ in 7:3 v/v acetonitrile/HMPA.

4:1 v/v Me_2SO/H_2O, the resonances of such proteins tend to sharpen and spectral anisotropy is reduced.[40,41] In general, spectroscopic properties of unfolded proteins as compared to proteins in their native conformations more closely approach corresponding analogue properties.[42] The spectral features of Figure 4 were also observed when more dilute solutions of the dianion were reacted with 0.9–1.3 equiv of reductant. In all cases spectra were observable to at least 80 K but with some attenuation in intensity. The spectra do not saturate under the temperature and microwave power conditions affording intensity reduction or elimination of $[Fe_4S_4(SR)_4]^{3-}$ signals.[28] A similar behavior exists for reduced 2-Fe vs. 4-Fe protein sites.[15,40,43] These results allow definte assignment of the spectra in Figure 4 to $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$. However, other reaction products were formed as evidenced by much weaker signals at $g \approx 2.03$ and 2.06 and a strong signal at $g \approx 4.3$ typical of rhombic high-spin Fe(III). The intensities of these signals increased somewhat as the amount of reductant was increased. The former two signals appeared only when >1 equiv of reductant was used. Observation of these signals at 80 K indicates that they do not arise from a $[Fe_4S_4(SR)_4]^{3-}$ species.

Mössbauer Spectra. The spectrum resulting from the reduction of $(n\text{-}Bu_4N)_2[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]$ with excess sodium acenaphthylenide (1.3 equiv) in 7:3 v/v acetonitrile/HMPA (4.5-h reaction time at room temperature) is shown in Figure 5a. This spectrum can be decomposed into four subspectra: two quadrupole doublets, D1 and D2, and two spectra with magnetic hyperfine structure, M1 and M2. As the temperature is increased in the interval 20–80 K the outer lines of M1 and M2 simultaneously decrease with concomitant increase in intensity near the D2 feature. Above 80 K and to 180 K, the highest temperature of measurement, the spectrum consists of D1 and a broadened doublet centered at D2 whose intensity is enhanced compared to lower temperatures. With use of the clearly resolved outer four lines of both M1 and M2 at 4.2 K, the isomer shifts (δ), quadrupole splittings (ΔE_Q), and magnetic hyperfine fields were calculated for these subspectra, which were then subtracted from spectrum (a). The resultant spectrum, consisting essentially of D1 and D2 and representing

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about 50% of the original intensity, is shown in Figure 5b together with the computer fit. Spectral parameters are collected in Table I.

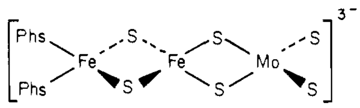
Spectrum a is interpreted in terms of at least two Fe–S species formed in the reduction of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$. The desired reaction product, $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$, having a spin-doublet ground state, is clearly not associated with magnetic subspectra M1 and M2. Detection of the latter was facilitated by the use of dianion samples enriched by ~45 atom % in ^{57}Fe. These samples do not show M1 and M2 prior to reduction (Figure 5c). We have been unable to suppress the formation of species giving rise to these subspectra by variations in reductant quantity (0.5–2.0 equiv) or reaction time (45 min to 4.5 h) in 7:3 v/v acetonitrile/HMPA or pure HMPA as solvents. In all instances M1 and M2 were present in 4.2 K spectra but with slightly different intensities relative to D1 and D2. Identification of the species responsible for M1 and M2 has not been pursued.[44] From the data in Table I it is evident that such species are not of the type $[Fe_4S_4(SR)_4]^{2-}$, resulting from reaction 3 or its reduction product, $[Fe_4S_4(SR)_4]^{3-}$.

Spectrum b is composed of doublets D1 and D2 with relative intensities 1:1. Comparison of the parameters of D1 and $[Fe_2\text{-}o\text{-xyl})_2]^{2-}$ and of D2 with those of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ and the Rd_{ox} analogue $[Fe(S_2\text{-}o\text{-xyl})_2]^{1-}$ (**5**), all of which are given in Table I, demonstrate that D1 and D2 are associated with Fe(II) and Fe(III), respectively. That D2 does not arise from unreduced dianion (Figure 5c) was shown by the appearance of an electronic spectrum, essentially identical with that in Figure 2 after electrochemical reduction, when the dianion was treated with 1.0 equiv of sodium acenaphthylenide in 7:3 v/v acetonitrile/HMPA. From these results D1 and D2 are clearly attributable to $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$. Parameters of the trianion spectrum are in reasonable agreement with those of two typical Fd_{red} proteins given in Table I. The value of $\delta(Fe(II)) - \delta(Fe(III)) = 0.41$ mm/s for the trianion is somewhat larger than protein values (0.25–0.34 mm/s[14b,17-21]) at 4.2–200 K.

Discussion

Taken together, the electrochemical results and the UV/visible and near-infrared absorption, EPR, and Mössbauer spectra clearly identify $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$ as one reduction product of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$. The identical Fe(III) sites of the dianion in the crystalline state[9] are preserved in solution on the basis of a single methylene proton resonance[10] (although broadened by paramagnetic relaxation effects) and one quadrupole doublet in the Mössbauer spectrum (Figure 5c). Thus there is no evidence of any structural or electronic feature of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ which would tend to localize the electron added upon reduction. That $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$ has the same electronic ground state as the reduced group **1** in proteins is evident from their closely similar EPR spectra and the observations of both trianion and Fd_{red} spectra at temperatures as high as ~80 K. The presence of the tetrahedral Fe(II) near-infrared ligand field band (Figure 3) and, more decisively, the separate Fe(II) and Fe(III) quadrupole doublets in the Mössbauer spectrum (Figure 5b) demonstrate that $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$ is a class II mixed-valence species. The well-resolved doublets persist to at least 180 K, revealing the integrity of the localized valence states to at least this temperature for a time which is long compared to the lifetime of the 14.4 KeV first excited state of ^{57}Fe, viz., 1.4×10^{-7} s. By our criteria[42] $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$ is an analogue of reduced group **1** in proteins.

Whereas discrete binuclear Fe(II, II) and, especially, Fe(III, III) synthetic complexes are not uncommon, those of the Fe(II, III) type are rare. To our knowledge the only other species approaching this description and containing a bridged Fe_2S_2 fragment is $[MoFe_2S_6(SPh)_2]^{3-}$, of proposed structure **6**.[45] In this complex, which has a spin-doublet ground state, electron distribution over the two Fe atoms must be unsymmetrical and is observed in the (small) isomer shift difference of 0.12 mm/s at 4.2 K. Because of its composition and spectroscopic properties,[45] this species does not meet criteria for a protein site synthetic analogue. Among other discrete Fe(II, III) complexes the trinuclear species $[Fe_3O(OAc)_6(H_2O)_3]$ exhibits in its Mössbauer spectra localized valence states below ~200 K but a single averaged quadrupole doublet at 298 K.[46] The behavior at higher temperatures, where the intersite electron-transfer rate is comparable to or much faster than the ^{57}Fe excited state relaxation rate, has not been found for any Fd_{red} protein containing group **1** at temperatures up to ~250 K.



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The Fe sites of group **1** in Fd_{ox} proteins must be inequivalent in principle because of the lack of symmetry of the protein structure. There is some indication that site inequivalence is detectable in the absorption[47] and Mössbauer[17,21,22] spectra of several proteins at low temperature. This inequivalence appears most definite in *Halobacterium* Fd_{ox}[21] and the oxidized terminal benzene dioxygenase protein of *P. putida*.[22] It might be conjectured that such inequivalence, possibly accentuated by some unequal protein perturbation of the two sites upon the event of reduction, is responsible for the localized nature of reduced group **1**. These factors cannot of course be dismissed, particularly in the absence of high resolution Fd_{ox} and Fd_{red} structures. However, they are unnecessary if one accepts the reasonable assumption that the Fe site environments of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-,3-}$ in the solution media used here are not more differentially perturbed than in $Fd_{ox,red}$ proteins themselves. From the properties of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$ we conclude that *class II mixed-valence behavior is an intrinsic property of any* $[Fe_2S_2(SR)_4]^{3-}$ *species* and probably of any species containing the planar $[2Fe\text{-}2S]^{1+}$ core unit. This conclusion addresses only the point that the localized electronic configuration is not an exigency of protein structure and is detectable by spectroscopic technique(s) which sense lifetimes in the rate domain of relatively fast electron-transfer processes. From Mössbauer spectra the localized nature of reduced group **1** is also emphasized by comparison with the very small ($\lesssim 0.1$ mm/s) differences among apparent δ values for individual or pairs of Fe sites in mixed-valence $[Fe_4S_4(S\text{-}Cys)_4]$ protein clusters.[25,26] For protein group **1** the $\geq 10^{-7}$ s lifetimes of the Fe(II, III) sites at $T \lesssim 250$ K from Mössbauer spectroscopy can presumably be increased to at least $\sim 10^{-3}$ s at ~300 K on the basis of ^1H NMR spectra.[14b,24]

Experiments directed toward isolation of crystalline salts of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{3-}$ are in progress. The availability of such materials will facilitate structure determination and a further examination of electronic properties, including magnetically perturbed Mössbauer spectra and the Fe(II) → Fe(III) intervalence transition. The latter has not been located in solution samples

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[44] The following information is pertinent to the identification of the species: (i) the relative intensities of M1 and M2 are ~1:1; (ii) values of δ, ΔE_Q, and magnetic hyperfine fields (M1, 327 ± 5 kOe; M2, 251 ± 5 kOe) are consistent with high-spin Fe(III)–S_4 sites, despite the reducing conditions under which the sites are produced; (iii) M1 and M2 have very similar temperature dependencies, with both collapsing into doublets above 80 K whose parameters are close to those of D2. From these results a reasonable hypothesis is that M1 and M2 arise from one molecular species having two inequivalent sites whose paramagnetic relaxation times at 4.2 K are long compared to the ^{57}Fe Larmor precession time but decrease at higher temperatures. The sites are apparently related to that in high-spin tetrahedral $[Fe(S_2\text{-}o\text{-xyl})_2]^{1-}$ (**5**) whose spectral parameters (Table I) and hyperfine field (380 kOe) are similar to, but certainly not identical with, those of M1 and M2. The $g \approx 4.3$ resonance is consistent with a $S = {}^5/_2$ species having a rhombic zero field splitting.

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and will be of use in estimating barriers to intramolecular electron transfer. Spectra in applied magnetic fields have been obtained but have proven less than optimal for purposes of interpretation owing to the presence of impurity subspectra M1 and M2. Considerations, as to cause of the localized valence nature of $[Fe_2S_2(SR)_4]^{3-}$ will be presented upon completion of these studies.

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Chemisorption of Halogen on Copper and Silver Clusters

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Rochester, New York 14650. *Received February 23, 1981*

Abstract: We report He I photoemission spectra for chemisorption of halogen on Ag and Cu clusters of different sizes. The spectral shape shows a strong size dependence for Cl/Ag, but little size dependence is noted for Cl/Cu. This effect is explained in terms of the orbital interactions between p orbitals of the halogen and d orbitals of the metal cluster. The predominant effect of cluster size on Cl-chemisorbed spectra persists up to a mean particle size of 30–40 atoms. Computations by extended Hückel procedures reproduce the experimental trends and allow assignment of the bonding and antibonding peaks in the experimental spectrum. Small silver clusters are more reactive than bulk films or single crystals for the decomposition of $CHCl_3$, leading to Cl overlayer formation.

The ultraviolet photoemission spectra (UPS) using He I and He II have been reported for a number of metal clusters.[1-6] These studies have shown that the measured density of states (DOS) depends markedly on the size of the cluster. These UPS results agree with a similar effect found for transition metals by using ESCA spectroscopy.[7,8] Many photoemission studies have now indicated that transition- or noble-metal clusters containing 100–150 atoms or more are required for bulklike spectra. Since this measurement primarily reflects the density of states of the cluster, it is of some interest to learn how the chemical properties of the metal cluster change with size.

Chemisorption is a tool whereby the chemical interaction of an adsorbate with a metal cluster can be measured. Grunze[3] studied the chemisorption of CO molecules on Pd particles of various sizes and found that the molecular orbitals of CO shift closer to the Fermi energy (E_F) of the metal as particle size increases. This facilitates interaction with d states of Pd closer to E_F. This shift in CO molecular orbitals was attributed to either an increasing relaxation energy of CO or a Pd work function change, but the two possible causes could not be separated.

We previously observed that the orbital spectrum of a chemisorbed species depends upon the size of the metal cluster support.[9] This was shown for I_2 chemisorbed on silver clusters. The UPS He I spectrum of the chemisorbed I shows two peaks whose intensity ratio is dependent upon the size of the silver cluster. This effect was interpreted in terms of the ability of the silver cluster to transfer electrons to the halogen. Larger clusters generally have smaller ionization potentials,[10] and thus electron transfer should be easier from the large clusters. This trend of decrease in ionization potential vs. increase in cluster size is reported in the ab initio calculations of Bauschlicher et al.[11] for Be clusters and Melius et al.[12] for Ni clusters. It has been found in experimental measurements for Na clusters by Herrmann et al.[13]

The present work extends our investigation to other adsorbates (Cl) and to other metal clusters (Cu). This study was prompted by the significant degree of interaction of halogen p orbitals with metal d orbitals that we observed in prior studies. The p orbitals of halogen are positioned below the d band of Cu and predominantly above the d band of Ag, as deduced from photoemission studies on these ordered surfaces.[14,15] Thus, it is of interest to learn how these interactions are modified by cluster size for the two extreme cases.

Experimental Section

The clusters were prepared inside the spectrometer by evaporation from thermally heated tungsten sources using high-purity wires. The substrate was carbon prepared by prior evaporation onto mica by using the technique and equipment described by Hamilton et al.[16] Upon introduction into the spectrometer, the carbon film was ion-etched with Xe to remove traces of O_2 or S. These samples remained clean for a few days before use as substrates for the evaporated metal.

The metal coverage was monitored by Auger spectroscopy[17] and with a quartz crystal oscillator. These data were calibrated by using neutron activation analysis to ensure proper determination of the amount of material deposited. The change in frequency of the quartz oscillator was proportional to the film thickness. These evaporated metal deposits on amorphous carbon have been characterized by electron microscopy.[16] The size distribution of the particle diameters was determined as a function of metal coverage so that a mean particle size can be associated with each deposit. The shape of the particles was shown to be hemispherical with a small flattening. Thus, the mean number of atoms in a cluster could be determined for a given metal coverage. In the following discussions we associate a mean size with particular spectra based upon this analysis although it must be remembered that an actual particle

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