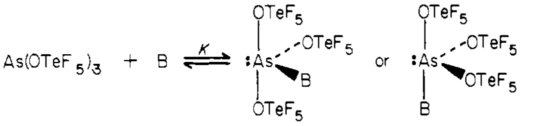
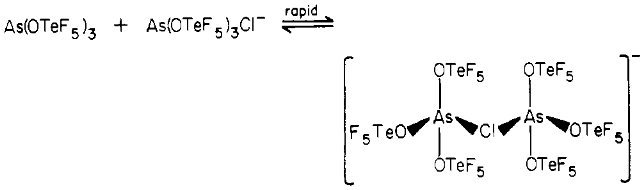
typical of $OTeF_5$ derivatives[14,15] and is in reasonable agreement with the data reported for this compound.[16]

The Lewis acidity of AsF_3 is limited to isolable adducts formed with alkali metal fluorides.[17] The AsF_4^- anion (local C_{2v} symmetry) has been structurally characterized in KAs_2F_7.[18] Using ^{19}F NMR spectroscopy, we have found that $As(OTeF_5)_3$ forms adducts with Lewis bases such as CH_3CN, Cl^-, and $OTeF_5^-$:[19–21]



The equilibrium constant, K, is large for B = Cl^- and $OTeF_5^-$ and is ~0.07 M^{-1} for B = CH_3CN. The equilibrium shown above is slowly maintained on the ^{19}F NMR time scale for B = CH_3CN and $OTeF_5^-$, as evidenced by sharp (line widths ~15 Hz) AB_4 resonances due to free $As(OTeF_5)_3$ and free (excess) $OTeF_5^-$, respectively, in these experiments. The AB_4 resonances due to $As(OTeF_5)_3(CH_3CN)$ and $As(OTeF_5)_4^-$, on the other hand, are considerably broader, most probably because of intramolecular exchange (pseudorotation of the axial and equatorial $OTeF_5$ groups in these adducts) that is insufficiently rapid to yield fast-exchange limit spectra.[22] Similarly, the AB_4 spectrum of $As(OTeF_5)_3Cl^-$ (see Figure 1 (bottom)) is also broad (line widths ~45 Hz at 22 °C) and broadens further as the temperature is lowered. However, a mixture of $As(OTeF_5)_3$ and $As(OTeF_5)_3Cl^-$ (~50:50) exhibits a sharp ^{19}F NMR spectrum (line width ~15 Hz):[23] the $OTeF_5$ groups of the two species are rapidly interconverting. While it is possible that the equilibrium shown above is faster for B = Cl^- than for B = CH_3CN and $OTeF_5^-$, we suggest the following exchange mechanism, which has no parallel for $As(OTeF_5)_3(CH_3CN)$ or $As(OTeF_5)_4^-$ because the $OTeF_5$ group has never been observed to bridge two elements:[5–7]



This type of intermolecular halogen exchange is not unexpected and has been suggested for species such as TeF_4,[24] SeF_4,[24] and $As_2F_3(SO_3F)_3$[25] and for BF_3/SF_4[26] and AsF_3/SbF_5[17] mixtures.

We have also found that the compounds $As(OTeF_5)_3$ and AsF_3 exhibit parallel chemical behavior *in addition to* their Lewis acidity: both can function as π-acids with low-valent transition metals. In the series of compounds $CpMn(CO)_3$, $CpMn(CO)_2(PF_3)$, and $CpMn(CO)_2(AsF_3)$, it was shown that AsF_3 is a stronger π-acid than PF_3.[27] Addition of $As(OTeF_5)_3$ or PF_3 to $W(CO)_5(THF)$ in THF solvent produces new infrared spectra with the concomitant disappearance of the $W(CO)_5(THF)$ spectrum (cm^{-1}):[28] $W(CO)_5(As(OTeF_5)_3)$ 2107 (A_1, w), 2004 (A_1, m), 1975 (E, s); $W(CO)_5(PF_3)$ 2101 (A_1, w), ~2005 (A_1, sh), 1975 (E, s). While detailed infrared studies of σ-donor vs. π-acceptor properties of ligands L are not complete for $W(CO)_5L$, our data clearly show that the π-acidity of $As(OTeF_5)_3$ and PF_3 are at least approximately equal.

The reactivity of a given metal complex is strongly dependent on the electronic and steric properties of its array of ligands. Frequently the two types of effects are inseparable, but it is well recognized that steric properties can be as important or more important than electronic properties in some cases.[29] Despite all of the elegant work that has been done with bulky trialkyl- and triarylphosphines and trialkyl and triaryl phosphites, the very recent synthesis of $Fe(CO)_4[P(OC(CF_3)_2CN)_3]$[30] is the only other literature report of a metal complex with a bulky *π-acid* phosphine or arsine. We are continuing to study the σ- and π-acidity of $As(OTeF_5)_3$ and $P(OTeF_5)_3$.

Acknowledgment is made to the Research Corp. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We thank Professor K. Seppelt for helpful comments concerning the synthesis of $HOTeF_5$, Professors D. E. Leyden and J. R. Norton for the use of their IR spectrometers, and C. E. Bronniman for recording the ^{19}F NMR spectra, which were obtained in the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE-8208821.

Registry No. $As(OTeF_5)_3(CH_3CN)$, 88548-68-9; $As(OTeF_5)_4^-$, 88548-69-0; $As(OTeF_5)_3Cl^-$, 88548-70-3; $W(CO)_5(As(OTcF_5)_3)$, 88548-71-4; $W(CO)_5(THF)$, 36477-75-5; $W(CO)_5(PF_3)$, 18461-47-7; $As(OTeF_5)_3$, 50652-21-6.

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Redox Behavior of Fe_4S_4 Clusters Surrounded by Hydrophobic Groups, $[Fe_4S_4(SC_6H_4R\text{-}p)_4]^{2-}$ (R = n-C_4H_9, n-C_8H_{17}, and n-$C_{12}H_{25}$), in Aqueous Micellar Solutions

Sir:

Iron–sulfur proteins such as 4-Fe ferredoxins function as electron carriers in metabolism, and the active sites are known to be embedded in a hydrophobic environment of proteins.[1]

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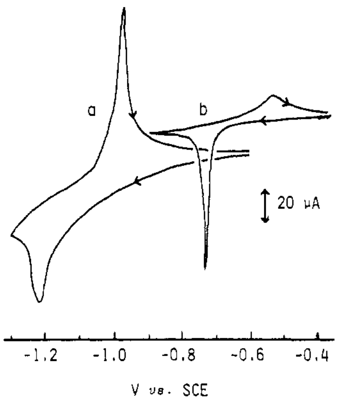

Figure 1. Cyclic voltammograms of $[Fe\text{-}C_8]^{2-}$ in Me_2SO (a) and in an aqueous micellar solution (pH 7.30) (b) at a scanning rate of 0.2 V s^{-1}.

Another characteristic feature of the iron–sulfur proteins may involve hydrogen bonding between the NH group of peptide chains and the sulfur atom of the Fe_4S_4 core and/or the cysteine ligands.[2] On the other hand, most of the synthetic $[Fe_4S_4X_4]^{2-}$ clusters (X = S-*t*-Bu, SPh, Cl, etc.) are hardly soluble in water and only a few water-soluble Fe_4S_4 clusters surrounded by hydrophilic substituents have been prepared. The redox potentials of these synthetic clusters in organic solvents (for the water-insoluble clusters) are fairly negative compared with those of 4-Fe ferredoxins in water. This may correspond to the fact that destruction of the tertiary structure of peptide chains of ferredoxins upon a change of media from H_2O to Me_2SO–H_2O (8:2 v/v) results in a shift of redox potentials to more negative.[3] Although the difference between the redox potentials of water-soluble synthetic clusters and 4-Fe ferredoxins in water is not so much (<80 mV) in some cases,[3] the former are still more negative than the latter. This communication reports the electrochemical study on some synthetic Fe_4S_4 clusters surrounded by hydrophobic substituents in aqueous micellar solutions to understand the extrinsic effects on the redox potential of the Fe_4S_4 clusters.

The tetrabutylammonium salts of $[Fe_4S_4(SC_6H_4R\text{-}p)_4]^{2-}$ (R = n-C_4H_9, n-C_8H_{17}, and n-$C_{12}H_{25}$; abbreviated as $[Fe\text{-}C_4]^{2-}$, $[Fe\text{-}C_8]^{2-}$, and $[Fe\text{-}C_{12}]^{2-}$, respectively)[4] were synthesized by the reaction of $FeCl_3$, MeONa, NaSH, and the appropriate *p*-alkylbenzenethiol obtained according to the literature[5] in MeOH, followed by treatment with n-Bu_4NBr in a manner similar to that for $[n\text{-}Bu_4N]_2[Fe_4S_4(SC_6H_5)_4]$.[6] An aqueous micellar solution of $[Fe\text{-}C_4]^{2-}$, $[Fe\text{-}C_8]^{2-}$, or $[Fe\text{-}C_{12}]^{2-}$ was prepared by the addition of an Me_2SO (1 cm^3) solution of the cluster (5.8 μmol) to a $C_6H_4(COOH)(COOK)$–NaOH (pH 4–6), KH_2PO_4–Na_2HPO_4 (pH 6–8), H_3BO_4–KCl–NaOH (pH 8–10), or Na_2HPO_4–NaOH (pH >10) buffer solution (0.5 mol dm^{-3}, 25 cm^3) containing Triton X-100 ((6.3–24) × 10^{-3} cm^3).

Figure 1 shows the cyclic voltammograms of $[Fe\text{-}C_8]^{2-}$ in Me_2SO and in an aqueous micellar solution at pH 7.3 on an Hg working electrode at 20 °C, with Et_4NBr and KH_2PO_4–Na_2HPO_4 as supporting electrolytes, respectively. The appearance of a sharp anode peak (trace a in Figure 1) and a sharp cathode peak (trace b in Figure 1) may be due to the weak adsorption of $[Fe\text{-}C_8]^{3-}$ in Me_2SO and $[Fe\text{-}C_8]^{2-}$ in the micellar solution on an Hg electrode, respectively. The enhancement of these peak currents may arise from an electron transfer involving the adsorbed clusters at nearly the same potential as the normal electron transfer.[7] The redox potentials of the process (2–/3–) are −1.10 V in Me_2SO and −0.64 V (vs. SCE) in the micellar solution;[8] the latter value is compared to those of 4-Fe ferredoxins (−0.280 to −0.429 V vs. SHE[9]) and 8-Fe ferredoxins (−0.405 to −0.490 V vs. SHE), determined by various equilibrium techniques.[3]

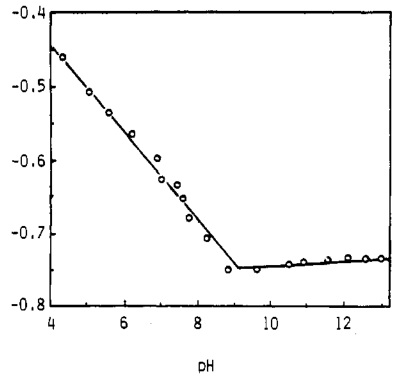

Figure 2. Plot of the redox potential (V vs. SCE) of $[Fe\text{-}C_8]^{2-}$ vs. pH at 20 °C.

Table I. Electrochemical Parameters for the Clusters in Aqueous Micellar Solutions at 20 °C

cluster	E^a	$dE/d(pH)^b$	pK^b
$[Fe\text{-}C_4]^{2-/3-}$	−0.624	−0.052	9.44
$[Fe\text{-}C_8]^{2-/3-}$	−0.625	−0.059	9.07
$[Fe\text{-}C_{12}]^{2-/3-}$	−0.646	−0.063	8.64

[a] V vs. SCE at pH 7.00. [b] Estimated errors are ±5%.

Although the redox potentials of the cluster in micellar solutions remained unchanged on the addition of various amounts of Triton X-100, they shifted to more positive with an increase in the proton concentration. A plot of the redox potential against pH (4–12) in micellar solutions is shown in Figure 2, which reveals that there is a linear relation with a slope of −0.059 V/pH unit in the range pH 4–9.[10] In the pH values higher than 9, however, the redox potential is almost independent of pH, and two straight lines connecting the potential–pH plots intersect each other at pH 9.07. The change of the redox potentials of $[Fe\text{-}C_8]^{2-}$ with pH may be explained by the participation of protons in the redox reaction. If one assumes that n protons interact with $[Fe\text{-}C_8]^{2-}$ with an equilibrium constant K in micellar solutions (eq 1), the Nernst

$$[Fe\text{-}C_8(H^+{}_n)]^{2-} \overset{K}{\rightleftharpoons} [Fe\text{-}C_8]^{2-} + nH^+ \qquad (1)$$

equation for the redox potential (E) of $[Fe\text{-}C_8(H^+{}_n)]^{2-/3-}$ (eq 2) can be written as eq 3 where $E^{\circ\prime}$ and F are the formal

$$[Fe\text{-}C_8(H^+{}_n)]^{2-} + e^- \rightleftharpoons [Fe\text{-}C_8(H^+{}_n)]^{3-} \qquad (2)$$

$$E = E^{\circ\prime} + \frac{RT}{F}\ln\frac{[Fe\text{-}C_8(H^+{}_n)]^{2-}}{[Fe\text{-}C_8]^{3-}} - \frac{2.303RT}{F}(n(\mathrm{pH}) - \mathrm{p}K) \qquad (3)$$

potential of an electrode and the Faraday constant, respec-

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(8) The redox potential was approximated as an average of the cathode and anode peak potentials, since the average was essentially constant (±10 mV) irrespective of the sweep rate from 30 to 500 mV/s.

(9) $E_{SHE} = E_{SCE} + 0.242$ V at 25 °C.

(10) A plot of the cathode peak potential at sweep rate 200 mV/s vs. pH also gives a linear relation with a slope of −0.059 V/pH unit in the range pH 4–9.

tively. The differentiation of eq. 3 by pH gives dE/d(pH) = −0.058n as a theoretical value for the slope of the E vs. pH plot at 20 °C. The theoretical value thus obtained is in good agreement with the experimental value, −0.059 V/pH unit when $n = 1$. The protonated and deprotonated species, [Fe-C$_8$(H$^+$)]$^{2-}$ and [Fe-C$_8$]$^{2-}$, may, therefore, exist as an equilibrium mixture (eq. 1 with $n = 1$) in micellar solutions at pH lower than 9,[11] whereas the equilibrium of eq. 1 lies much farther to the right at pH higher than 9, where the redox potential remains essentially constant. The intersection of the two straight lines obtained from the redox potential vs. pH plot (Figure 2) gives the pK value for the proton dissociation of [Fe-C$_8$(H$^+$)]$^{2-}$.

Similar electrochemical behaviors have been observed for the aqueous micellar solutions of [Fe-C$_4$]$^{2-}$ and [Fe-C$_{12}$]$^{2-}$. The electrochemical parameters for the three clusters are listed in Table I, which indicates that the pK values estimated from the plots of the redox potential vs. pH decrease with lengthening the alkyl chain of the thiolate ligands. The pK values obtained in the present micellar solutions are larger than those of [$Fe_4S_4(SCH_2CH(CH_3)_2)_4$]$^{2-}$ (pK = 3.9)[12] in N-methylpyrrolidinone–H$_2$O (6:4 v/v) and [$Fe_4S_4(SCH_2CH_2CO_2)_4$]$^{6-}$ (pK = 7.4)[13] in water, which were obtained from the plots of the absorbance of electronic spectra vs. pH. It should be noted that the redox potentials of the present clusters are markedly influenced by the concentration of hydrogen ions in contrast to the situation for *Clostridium acidi-urici* and *Clostridium pasteurianum* ferredoxins, whose redox potentials have been reported not to vary so much with the change of pH (0.011–0.016 V/pH unit between pH 6.5 and 8.2).[14] Such a large dependence of the redox potential on pH in the present study may reflect the lability of protons coordinated to the present clusters. This is also in striking contrast to the case for high-potential iron proteins, in which stable hydrogen bondings are formed between the NH group of peptide chains and the sulfur atom of the Fe$_4$S$_4$ core and/or the cysteine ligand.[15]

Registry No. [Fe-C$_4$]$^{2-}$, 72276-57-4; [Fe-C$_8$]$^{2-}$, 88510-43-4; [Fe-C$_{12}$]$^{2-}$, 88510-44-5; [n-Bu$_4$N]$_2$[Fe-C$_4$], 88510-45-6; [n-Bu$_4$N]$_2$[Fe-C$_8$], 88510-46-7; [n-Bu$_4$N]$_2$[Fe-C$_{12}$], 88510-47-8.

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(11) The present [Fe-C$_8$]$^{2-}$ cluster in micellar solutions has undergone no hydrolysis reaction under anaerobic conditions, as confirmed from no change of the visible spectra for 10 h. This is in contrast to the case for Fe$_4$S$_4$ clusters containing alkylthiolate ligands in water.[12,13]

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Synthesis of CF$_3$NBr$_2$ and CF$_3$NBrCl. Novel Metal Fluoride Promoted Conversion of N-Cl Bonds to N-Br Bonds

Sir:

The synthesis of fluorinated compounds containing the N,N-dichloro group is readily accomplished by the addition of ClF to a variety of carbon–nitrogen multiple bonds.[1] For example, the following reactions proceed in high yield:[2–4]

$$\mathrm{ClCN + 2ClF \rightarrow ClCF_2NCl_2}$$

$$\mathrm{R_fCN + 2ClF \rightarrow R_fCF_2NCl_2}$$

$$\mathrm{CF_2{=}NCl + ClF \rightarrow CF_3NCl_2}$$

We have recently shown that the cesium fluoride promoted chlorination of C–N multiple bonds with Cl$_2$ is also an effective method for the synthesis of the same compounds.[5]

$$\mathrm{R_fCN + 2Cl_2 + 2CsF \rightarrow RCF_2NCl_2 + 2CsCl}$$

$$\mathrm{CF_2{=}NCl + Cl_2 + CsF \rightarrow CF_3CF_2NCl_2 + CsCl}$$

In related work, HgF$_2$ has also been shown to be effective in these transformations, where the HgF$_2$/Cl$_2$ mixture behaves as an in situ source of ClF.[6]

$$\mathrm{ClCN + 2Cl_2 + HgF_2 \xrightarrow{HgF_2} CF_3NCl_2/ClCF_2NCl_2\ (3{:}1) + HgCl_2}$$

$$\mathrm{CF_3CN + 2Cl_2 + HgF_2 \rightarrow CF_3CF_2NCl_2 + HgCl_2}$$

The latter reaction could also be extended to Br$_2$ to yield both CF$_3$CF$_2$NBr$_2$ and CF$_3$CF=NBr and represented the first example of a thermally stable NBr$_2$ derivative. Cesium fluoride is also effective in promoting the reaction of Br$_2$ with C–N multiple bonds, but in the case of nitriles the reaction stops at the imine.[5,7]

$$\mathrm{CF_2{=}NF + 2Br_2 + CsF \rightarrow CF_3NBrF + CsBr_3}$$

$$\mathrm{CF_3CN + 2Br_2 + CsF \rightarrow CF_3CF{=}NBr + CsBr_3}$$

We were interested in preparing the first example of a stable compound containing an –NClBr function, and we investigated the CsF-promoted reaction of Br$_2$ with CF$_2$=NCl.[8] The reaction worked well, but to our surprise, CF$_3$NBr$_2$ was also formed.

$$\mathrm{CF_2{=}NCl \xrightarrow{Br_2/CsF} CF_3NBrCl + CF_3NBr_2}$$

Table I. Metal Fluoride Promoted Reactions of N-Cl with Br$_2$

N-Cl (amt[a])	Br$_2$/MF[a]	t[b]	products[a] CF$_3$-NBrCl	 CF$_3$-NBr$_2$
CF$_2$=NCl (2.0)	1.7/8.5 (CsF)	11	0.4	0.6[c]
CF$_2$=NCl (2.0)	4.0/9.2 (CsF)	11	0.9	0.6[d]
CF$_2$=NCl (2.0)	2.0/20 (CsF)	12	0.8	*d*
CF$_3$NClBr (0.6)	10/10 (CsF)	12		0.5[c]
CF$_3$NClBr (0.5)	10/20 (CsF)	12		0.1[c]
CF$_3$NCl$_2$ (1.0)	10/10 (CsF)	42	0.2	0.3[c]
CF$_3$NCl$_2$ (1.0)	10/20 (CsF)	40	0.3	0.1[c]
CF$_3$NCl$_2$ (0.9)	10/10 (KF)	40	0.4	trace[c]
CF$_3$NCl$_2$ (1.0)	10/10 (NaF)	40	0.5	*c*
CF$_3$NCl$_2$ (1.0)	10/10 (LiF)	40	0.2	*c*
CF$_3$NCl$_2$ (1.0)	10/10 (CaF$_2$)	40		*c*

[a] Amounts in millimoles. [b] Time in hours in the absence of light at 22 °C. [c] Starting NCl recovered. [d] Some CF$_3$NCl$_2$ formed.

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(8) As far as we could determine, there are no reported examples of the isolation of –NBrCl derivatives.

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