tively. The differentiation of eq. 3 by pH gives $dE/d(\mathrm{pH}) = -0.058n$ 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, $[\mathrm{Fe\text{-}C_8(H^+)}]^{2-}$ and $[\mathrm{Fe\text{-}C_8}]^{2-}$, 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 $[\mathrm{Fe\text{-}C_8(H^+)}]^{2-}$.

Similar electrochemical behaviors have been observed for the aqueous micellar solutions of $[\mathrm{Fe\text{-}C_4}]^{2-}$ and $[\mathrm{Fe\text{-}C_{12}}]^{2-}$. 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 $[\mathrm{Fe_4S_4(SCH_2CH(CH_3)_2)_4}]^{2-}$ (pK = 3.9)[12] in *N*-methylpyrrolidinone–H_2O (6:4 v/v) and $[\mathrm{Fe_4S_4(SCH_2CH_2CO_2)_4}]^{6-}$ (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_4S_4 core and/or the cysteine ligand.[15]

Registry No. $[\mathrm{Fe\text{-}C_4}]^{2-}$, 72276-57-4; $[\mathrm{Fe\text{-}C_8}]^{2-}$, 88510-43-4; $[\mathrm{Fe\text{-}C_{12}}]^{2-}$, 88510-44-5; $[n\text{-}\mathrm{Bu_4N}]_2[\mathrm{Fe\text{-}C_4}]$, 88510-45-6; $[n\text{-}\mathrm{Bu_4N}]_2[\mathrm{Fe\text{-}C_8}]$, 88510-46-7; $[n\text{-}\mathrm{Bu_4N}]_2[\mathrm{Fe\text{-}C_{12}}]$, 88510-47-8.

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(11) The present $[\mathrm{Fe\text{-}C_8}]^{2-}$ 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_4S_4 clusters containing alkylthiolate ligands in water.[12,13]

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Synthesis of CF_3NBr_2 and CF_3NBrCl. 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 $CF_3CF_2NBr_2$ and $CF_3CF{=}NBr$ 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_3NBr_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

			products[a]	
N-Cl (amt[a])	Br_2/MF[a]	t[b]	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_3NClBr (0.6)	10/10 (CsF)	12		0.5[c]
CF_3NClBr (0.5)	10/20 (CsF)	12		0.1[c]
CF_3NCl_2 (1.0)	10/10 (CsF)	42	0.2	0.3[c]
CF_3NCl_2 (1.0)	10/20 (CsF)	40	0.3	0.1[c]
CF_3NCl_2 (0.9)	10/10 (KF)	40	0.4	trace[c]
CF_3NCl_2 (1.0)	10/10 (NaF)	40	0.5	c
CF_3NCl_2 (1.0)	10/10 (LiF)	40	0.2	c
CF_3NCl_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_3NCl_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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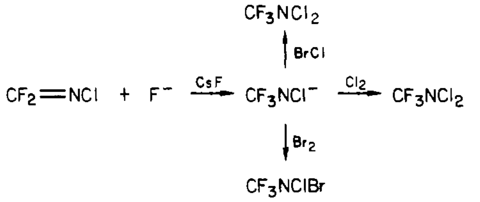
Caution! While we have experienced no explosions during the handling of small quantities of these materials, many structurally similar *N*-halo compounds are known to be powerful explosives. Due caution must be exercised while conducting experiments such as those described here. In a typical reaction, $CF_2{=}NCl$, Br_2, and CsF were allowed to react in a 100-mL glass reactor containing a Teflon-coated magnetic stirring bar at 22 °C in the absence of light. The mixture was stirred for an appropriate time, and the products were then separated by pumpng through a series of cold traps. Essentially pure CF_3NClBr and CF_3NBr_2 were then obtained by brief treatment with excess C_2H_4 at 22 °C to remove unreacted Br_2, followed by reseparation. The reactions are summarized in Table I.

The formation of CF_3NBrCl can be explained by oxidation of the intermediate anion CF_3NCl^- by Br_2, in the same way that CF_3NCl_2 is formed from Cl_2 and $CF_2{=}NCl$ (eq 1) and CF_3NBrF from Br_2 and $CF_2{=}NF$ (eq 2).[5] In the above examples, there is no reaction in the absence of CsF.


(1)

$$\begin{tikzcd}
 & CF_3NCl_2 & \\
CF_2{=}NCl + F^- \arrow[r, "CsF"] & CF_3NCl^- \arrow[u, "BrCl"] \arrow[r, "Cl_2"] \arrow[d, "Br_2"] & CF_3NCl_2 \\
 & CF_3NClBr &
\end{tikzcd} \qquad (1)$$

$$CF_2{=}NF + F^- \xrightarrow{CsF} CF_3NF^- \xrightarrow{Br_2} CF_3NFBr \qquad (2)$$

The formation of CF_3NBr_2 in the reaction of CF_3NCl^- with Br_2 requires a substitution of Cl by Br in CF_3NBrCl. We have found that this substitution can be readily accomplished in both CF_3NBrCl and CF_3NCl_2 by reaction with Br_2 in the presence of CsF.

$$CF_3NCl_2 \xrightarrow{CsF/Br_2} CF_3NBrCl \xrightarrow{CsF/Br_2} CF_3NBr_2$$

There is no reaction under the same conditions in the absence of CsF, and CsF alone is also unreactive. Similarly, BrCl does not form a significant amount of either CF_3NBrCl or CF_3NBr_2 in the presence of CsF, and it converts CF_3NBrCl back to CF_3NCl_2.[9] The active species in these reactions may be $CsF{\cdot}Br_2$, which may contain a significant concentration of the anion FBr_2^-.[10] Very active CsF readily absorbs bromine to form a bright yellow-orange solid with only a small equilibrium pressure of Br_2 at 22 °C.[11] The Br_2 is removed very slowly by pumping on the solid under dynamic vacuum at 22 °C, and even heating at 100 °C will not readily remove all the Br_2. Active KF also absorbs Br_2 but to a lesser degree.[11] Potassium fluoride with Br_2 is only effective in converting CF_3NCl_2 to CF_3NBrCl and not to CF_3NBr_2.

We expected that NaF and LiF would be ineffective in promoting the reaction of CF_3NCl_2 with Br_2. However, both result in reasonable yields of CF_3NClBr (see Table I). To ascertain whether the formation of CF_3NClBr was a surface reaction only and not due to the metal fluoride itself, we tried CaF_2 under the same conditions and it was unreactive. This result, combined with the fact that the formation of CF_3NBr_2 is only observed with CsF, would suggest that these reactions are fluoride promoted. However, additional studies with other fluorides and non-fluoride-containing solids will be required to establish this with certainty.

The novel compounds CF_3NBrCl and CF_3NBr_2 are pale yellow solids melting at −62.5 to −61.5 °C and −56.4 to −55.5 °C, respectively. They are thermally stable in the dark at 22 °C, but they readily decompose under the influence of Pyrex-filtered sunlight.

$$2CF_3NBrX \xrightarrow{h\nu} CF_3N{=}NCF_3 + 2BrX \quad (X = Cl, Br)$$

The compounds are readily identified by their MH^+ and M^+ molecular ions with the expected isotope ratios in the CI and EI mass spectra, by their ^{19}F NMR (internal $CFCl_3$) $\delta(CF_3NBrCl) = -72.3$ (s) and $\delta(CF_3NBr_2) = -70.5$ (s), $\delta(CF_3NCl_2) = -78$, and by their characteristic IR spectra. The latter are very similar to those of CF_3NCl_2 except in the 850–650-cm^{-1} region where each show two characteristic strong absorptions (cm^{-1}): CF_3NCl_2, 812 and 708; CF_3NBrCl, 787 and 688; CF_3NBr_2, 758 and 675.

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Registry No. $CF_2{=}NCl$, 28245-33-2; CF_3NClBr, 88453-17-2; CF_3NCl_2, 13880-73-4; CsF, 13400-13-0; KF, 7789-23-3; NaF, 7681-49-4; LiF, 7789-24-4; CF_3NBr_2, 88453-18-3; $CF_3N{=}NCF_3$, 372-63-4.

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[9] BrCl is a very powerful chlorination reagent (more reactive than Cl_2) in the CsF-catalyzed reactions of R_fCN and $R_fCF{=}NR_f$: Zheng, Y.; DesMarteau, D. D., to be submitted for publication.

[10] This polyhalogen anion does not appear to be known, and this may indicate that Br_2F^- is not the active species in the reactions with $-NClBr$ and $-NCl_2$. However, Br_2Cl^- is well characterized: Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *64*, 4853.

[11] Cesium fluoride (99.9%) was activated by fusing it in a Pt dish, followed by grinding in a ball mill to a very fine powder under very anhydrous conditions. Potassium fluoride was similarly activated.

Copper(I)–Dioxygen Reactivity. 2. Reaction of a Three-Coordinate Copper(I) Complex with O_2, with Evidence for a Binuclear Oxo–Copper(II) Species: Structural Characterization of a Parallel-Planar Dihydroxo-Bridged Dimer

Sir:

Investigations of the nature of the reactions of dioxygen with complexes of Cu(I) are relevant both in the bioinorganic chemistry of copper[1] and in oxidation and oxygenation catalysis by copper.[2] In enzymatic systems, hemocyanins are arthropodal and molluscan oxygen carriers containing copper ion active sites, where Cu(I) reacts reversibly with dioxygen.[1] The copper monooxygenases tyrosinase and dopamine β-hydroxylase mediate hydroxylation reactions of organic substrates utilizing O_2 as the oxygen source,[3] whereas the multicopper "blue" oxidases reduce dioxygen to water at copper centers. In synthetic systems, copper(II) complexes are known to carry out efficient oxidation reactions, facilitated by the rapid reoxidation of Cu(I) to Cu(II) in the catalytic cycle.[2a,4]

As part of our studies of new copper(I) coordination chemistry and dioxygen reactivity, we recently observed that

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