for this couple. One factor complicating the interpretation of the results for the aquo redox couples is the lack of information concerning the coordination numbers of many of the ions of interest. Thus one possible explanation for the vanadium results is that the reduction of V(III) to V(II) is accompanied by an increase in the number of bound water molecules (including those held by hydrogen bonding). Such a change is sterically reasonable in view of the large ionic radius of V^{2+} (~0.8 Å[27]) and would result in an additional contribution to ΔG_λ^* and a smaller value of $\Delta S_{rc}°$, as is observed. Similarly, Cr(II) is highly Jahn–Teller distorted and the water molecules in the axial positions of the hydrated ion are very weakly held. As a consequence, the reduction of Cr(III) to Cr(II) will be accompanied by a decrease in the number of bound water molecules and this could in part be responsible for the large values of both ΔG_λ^* and $\Delta S_{rc}°$. A more detailed discussion of these effects must await the results of EXAFS studies which are currently in progress.[29] Fortunately calculations of the electronic coupling matrix elements indicate that corrections for nonadiabaticity are not large for the aquo redox couples considered.

The data in Table II and Figure 1 reveal that a dependence of ΔG_λ^* upon $\Delta S_{rc}°$ is also obtained for nonaquo redox couples. Thus both ΔG_λ^* and $\Delta S_{rc}°$ are markedly larger for $Co(en)_3^{3+/2+}$ than for $Ru(en)_3^{3+/2+}$; similar differences are also seen between $Co(bpy)_3^{3+/2+}$ and $Ru(bpy)_3^{3+/2+}$. It is likely that the larger values of $\Delta S_{rc}°$ for the cobalt couples are related to their larger $\Delta \bar{a}$ values;[30,31] the latter also account for the larger values of ΔG_{in}^* and hence of ΔG_λ^* for these systems.[32] Since the cobalt(III) complexes are low-spin $^1A_1$ while the cobalt(II) complexes are high-spin $^4T_1$, $\Delta S_{rc}°$ for the cobalt couples contains a small entropy contribution (3 cal deg^{-1} mol^{-1}) arising from the spin multiplicity change accompanying the electron transfer. A similar contribution is not present in the ruthenium systems since the ruthenium(III) and ruthenium(II) complexes are all low spin, and consequently no spin multiplicity change accompanies the electron transfer. Another consequence of the spin multiplicity change in the cobalt system is nonadiabaticity (that is, κ, the probability of electron transfer within the activated complex, is <1; nonadiabaticity increases the apparent value of ΔG_λ^* since ΔG_λ^* includes a term $-RT \ln \kappa$). It has been estimated[32] that κ for the $Co(NH_3)_6^{3+/2+}$ exchange reaction is $\sim 10^{-4}$. If a similar factor applies to the $Co(en)_3^{3+,2+}$ exchange reaction, ΔG_λ^* for the ethylenediamine couple should be decreased by about 5 kcal mol^{-1}. Although this correction is appreciable (and reduces the scatter in Figure 1), substantial differences between the cobalt and ruthenium systems remain even after corrections for spin multiplicity.

The differences in $\Delta S_{rc}°$ for $Fe(OH_2)_6^{3+/2+}$, $Ru(OH_2)_6^{3+/2+}$, and $Ru(NH_3)_6^{3+/2+}$ have recently been used to provide an estimate of $\Delta \bar{a} \approx 0.1$ Å for $Ru(OH_2)_6^{3+/2+}$.[5] The accuracy of this estimate depends upon the extent to which $\Delta S_{rc}°$ for the aquo couples differs from similar ammine couples due to the hydrogen-bonding ability of the aquo ligands.[2] Taking $\Delta \bar{a}$ for the $Fe(OH_2)_6^{3+/2+}$ couple as 0.14 Å, the empirical entropy correlation of Powell and Latimer[6a] predicts that $\Delta S_{rc}°$ should only be ca. 10 cal deg^{-1} mol^{-1} lower for an analogous aquo couple for which $\Delta \bar{a} = 0$. However, $\Delta S_{rc}°$ for the $Ru(NH_3)_6^{2+,3+}$ couple ($\Delta \bar{a} = 0.04$ Å[32]) is 25 cal deg^{-1} mol^{-1} smaller than for $Fe(OH_2)_6^{3+/2+}$ (Table II). Most likely, therefore, hydrogen-bonding effects do contribute to $\Delta S_{rc}°$ for the aquo couples.

Despite the complexities, there appears to be a consistent correlation between ΔG_λ^* and $\Delta S_{rc}°$ for the outer-sphere exchange reactions considered here. The apparent simplicity of this correlation is somewhat deceiving since a number of factors contribute to $\Delta S_{rc}°$ that may not always affect ΔG_λ^* in a similar way. Nevertheless, on the basis of the present survey the correlation seems well worth pursuing further, both as a means of estimating $\Delta \bar{a}$ and hence ΔG_{in}^* and as a means of gaining further clues as to the nature of the solvent rearrangement process required for the electron transfer.[33]

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Registry No. $Cr(OH_2)_6^{3+}$, 14873-01-9; $Cr(OH_2)_6^{2+}$, 20574-26-9; $V(OH_2)_6^{3+}$, 21374-21-0; $V(OH_2)_6^{2+}$, 15696-18-1; $Fe(OH_2)_6^{3+}$, 15377-81-8; $Fe(OH_2)_6^{2+}$, 15365-81-8; $Ru(OH_2)_6^{3+}$, 30251-72-0; $Ru(OH_2)_6^{2+}$, 30251-71-9; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(en)_3^{3+}$, 21393-87-3; $Ru(en)_3^{2+}$, 21393-86-2; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(en)_3^{3+}$, 14878-41-2; $Co(en)_3^{2+}$, 23523-25-3; $Co(sep)^{3+}$, 72496-77-6; $Co(sep)^{2+}$, 63218-22-4; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(bpy)_3^{2+}$, 15878-95-2; $Ru(NH_3)_2(bpy)_2^{3+}$, 55266-15-4; $Ru(NH_3)_2(bpy)_2^{2+}$, 56993-98-7; $Ru(NH_3)_4(bpy)^{3+}$, 69799-61-7; $Ru(NH_3)_4(bpy)^{2+}$, 54194-87-5; $Ru(NH_3)_5(py)^{3+}$, 33291-25-7; $Ru(NH_3)_5(py)^{2+}$, 21360-09-8.

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(30) A value of $\Delta \bar{a} = 0.17$ Å has been determined for the $Co(sep)^{3+/2+}$ couple.[22] Although $\Delta \bar{a}$ is apparently unavailable for $Co(en)_3^{3+/2+}$, the closely related $Co(NH_3)_6^{3+/2+}$ exhibits the similar value $\Delta \bar{a} = 0.18$ Å.[31]

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(33) On the basis of the data in Figure 1, we predict that $\Delta S_{rc}°$ will be less than 25 cal deg^{-1} mol^{-1} if $k_{ex} > 10^3$ M^{-1} s^{-1}; similarly, if $\Delta S_{rc}° > 25$ cal deg^{-1} mol^{-1}, then k_{ex} will be less than 10^3 M^{-1} s^{-1} ($\mu = 0.1$–1.0 M; 25 °C).

On the Study of a Mixed-Valence Hemin Dimer

Sir:

Hematins such as μ-oxo-bis[(tetraphenylporphinato)iron(III)] [$(TPPFe)_2O$] are antiferromagnetically coupled oxo-bridged dimers containing high-spin iron(III).[1] The similar, but not isoelectronic, nitrido-bridged dimer $(TPPFe)_2N$ is a mixed-valence iron(III,IV) system which behaves as a simple one electron per dimer paramagnet.[1-4] Interest in these systems has been stimulated by the electron-transfer role of hemes in the biological electron-transport chain.[1]

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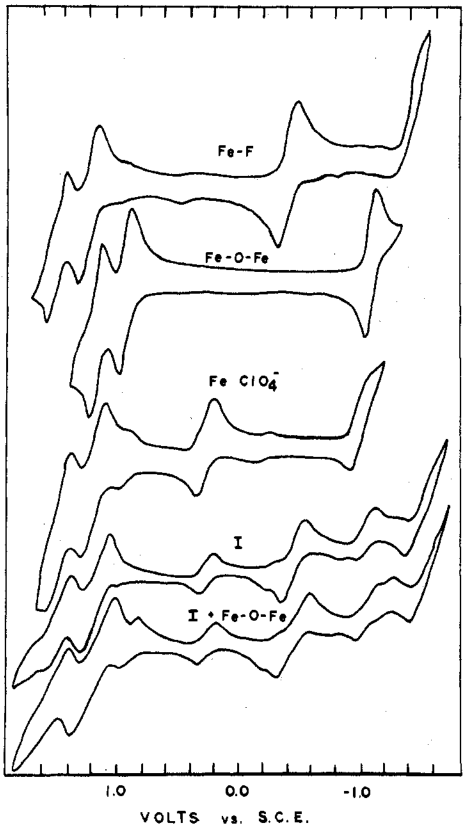

Figure 1. Cyclic voltammograms observed for several (tetraphenylporphinato)iron complexes, from top to bottom: (1) (tetraphenylporphinato)iron(III) fluoride, (2) μ-oxo-bis[(tetraphenylporphinato)iron(III)], (3) the ion pair consisting of (tetraphenylporphinato)iron(III) and the perchlorate ion, (4) the product (I) of the reaction between μ-oxo-bis[(tetraphenylporphinato)iron(III)] and HBF_4 as prepared by the method of Wollman and Hendrickson, and (5) compound I and an equal weight of added μ-oxo-bis[(tetraphenylporphinato)iron(III)]. All the voltammograms were observed with 1 mM solutions in CH_2Cl_2 with 100 mM Bu_4NClO_4 as a supporting electrolyte. A commercial aqueous SCE reference electrode, a Pt-button working electrode, and a Pt-wire auxiliary electrode with Bioanalytical Systems electronics were used for the current vs. voltage measurements.

Electrochemical studies[4-6] of $(TPPFe^{III})_2O$ in CH_2Cl_2 revealed a reversible one electron oxidation at $E_{1/2} = 0.84$ V (vs. SCE). The electrochemical product, presumably $[(TPPFe^{III,IV})_2O]^+$, is stable for hours in CH_2Cl_2, decays to $(TPPFe^{III})_2O$, and was isolated as a solid perchlorate salt.[5,6] No magnetic or Mössbauer measurements have been carried out on the solid product.

Wollman and Hendrickson[7] treated $(TPPFe^{III})_2O$ with HBF_4 in air. The $CHCl_3$ solution was evaporated to dryness, and the solid product, which was presumed to be the result of air oxidation, was formulated as $[(TPPFe^{III,IV})_2O]BF_4$. The magnetic susceptibility of the solid product was studied as a function of temperature, and the results were interpreted by using a μ-oxo-bridged mixed-valence model. Our examination of the product of that reaction by cyclic voltammetry quite clearly shows that there are no oxo-bridged species present and thus their product can not be formulated as a mixed-valence dimer. The actual product is a mixture of hemin fluoride and hemin fluoroborate, both of which contain only iron(III).

A typical hemin halide such as TPPFeCl is an $S = {}^5/_2$ paramagnet but TPPFeF is unusual. Earlier work[8] showed that TPPFeF exists in two solid phases: a normal paramagnetic phase and an antiferromagnet phase. Both solids dissolve to form monomeric TPPFeF in CH_2Cl_2 solution. A fluoroborate salt was also shown to be $[(TPPFe)_2F]BF_4$, an antiferromagnetic solid.[8] In CH_2Cl_2 solution that salt dissociates as $[(TPPFe)_2F]BF_4 \rightarrow TPPFeF + [TPPFe]^+ + BF_4^-$. The earlier work[8] also noted that attempted preparations of $TPPFeBF_4$ always resulted in a product which also contained TPPFeF in various amounts.

Electrochemical studies of TPPFeCl in CH_2Cl_2 have been carried out and interpreted,[9] and the results found for TPPFeF are similar[10] and are presented in Figure 1. In CH_2Cl_2 (0.1 M Bu_4NClO_4), $TPPFe^{III}F$ undergoes oxidation to $[TPPFe^{IV}]^{2+}$ at 1.16 V and to a cation radical, $[TPPFe^{IV}]^{3+}$ at 1.44 V. Reduction of $TPPFe^{III}F$ to $[TPPFe^{II}]$ occurs at −0.48 V, and an anion radical is produced at −1.5 V. Cyclic voltammograms of $(TPPFe^{III})_2O$ have also been interpreted,[4-6] and one is included in Figure 1. In CH_2Cl_2, $(TPPFe^{III})_2O$ is oxidized to $[(TPPFe^{III,IV})_2O]^+$ at 0.84 V with further oxidations at 1.12 and 1.50 V. Reduction to an anion radical occurs at −1.12 V. The entire voltammogram is unchanged by the addition of a stoichiometric amount of Bu_4NBF_4.

Electrochemical studies of an "ionic" hemin $[TPPFe^{III}]ClO_4$ have also been carried out,[11,12] and Figure 1 presents similar results. $[TPPFe^{III}]ClO_4$ (prepared by the treatment of TPPFeCl with $AgClO_4$) undergoes a reduction to $[TPPFe^{II}]^-$ at 0.24 V (with some slight anion dependence) and a second reduction to $[TPPFe^{I}]$ at −1.02 V. The reduction at −1.02 V has also been observed when $[TPPFe^{II}]$ was electrochemically produced from TPPFeCl.[9]

The product (I) of the reaction of $(TPPFe^{III})_2O$ and HBF_4 as carried out by Wollman and Hendrickson[7] was isolated and shown to reasonably reproduce the reported electronic spectrum ($\lambda_{max} = 418$ nm in CH_2Cl_2) and Mössbauer parameters ($\delta = 0.40 \pm 0.05$ mm/s (relative Fe), $\Delta = 1.51 \pm 0.05$ mm/s, $\Gamma = 0.332$ and 0.322 mm/s at 80 K).

Product I was examined electrochemically in CH_2Cl_2, and the results are shown in Figure 1. The effect of addition of $(TPPFe^{III})_2O$ to the same solution is also shown. It is quite clear that both the reduction at −1.12 V and the oxidation at 0.84 V (to produce $[(TPPFe^{III,IV})_2O]^+$) which are characteristic of $(TPPFe)_2O$ are absent and only become apparent upon the addition of $(TPPFe^{III})_2O$. Clearly the treatment of $(TPPFe)_2O$ with HBF_4 does not produce $[(TPPFe^{III,IV})_2O]^+$. Comparison of the cyclic voltammograms indicates that $(TPPFe)_2O$ and HBF_4 produce a mixture of TPPFeF and $TPPFeBF_4$, as observed earlier.[8] The complexity revealed in the magnetic measurements by Wollman and Hendrickson is due to the presence of a mixture of two compounds, one of which is antiferromagnetic,[8] and not because of the presence of any mixed-valence species.

The disruption of the oxo-bridge in $(TPPFe)_2O$ upon treatment with HBF_4 is consistent with the proven lability of the bridge toward weak acids[13] and the failure to observe any infrared Fe–O–Fe stretch in the product.

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Registry No. $(TPPFe^{III})_2O$, 12582-61-5; HBF_4, 16872-11-0; TPPFeF, 55428-47-2; $[(TPPFe)_2F]BF_4$, 61037-51-2; $TPPFeClO_4$, 59370-87-5.

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X-ray Photoelectron Spectra of Copper Complexes Considered as Models for Metalloproteins Containing Copper–Sulfur Bonds[1]

Sir:

Recent studies on the X-ray photoelectron spectra (XPS) of metal complexes of the sulfur-containing amino acids cysteine and penicillamine[2,3] have demonstrated that a *negative* chemical shift is characteristic of the binding of the thiol (RSH) group in these ligands to a metal ion. However, one group of metal–thiol (M–SR) complexes which exhibit some unusual XPS properties are the copper complexes of cysteine (I), penicillamine (II), α-mercaptopropionylglycine (III), and N-mercaptoacetylglycyl-L-histidine (IV).[4–8] As a result of XPS investigations on these species, Weser and co-workers[4–6,8] proposed that they contained Cu(I) sites bound to sulfur radicals, i.e., $Cu^{I}(SR)$.

The purpose of the present communication is both to offer an alternative interpretation of the XPS of these copper complexes and to point out errors in previous analyses of these results.[4–8]

The abbreviations cyst, pen, MPG, and MAGH will be used for the appropriate anionic forms of the complexed ligands I, II, III, and IV, respectively. The copper–cysteine complex was described[4] as being of 1:1 stoichiometry, $[Cu(cyst)]_n$, while the two penicillamine complexes which were studied[4–6] comprised the structurally characterized[9] complex $Tl_5[Cu_{14}(pen)_{12}Cl]$ and a violet product of poorly defined stoichiometry. The complexes of ligands III and IV, $Na[Cu(MPG)]\cdot 2H_2O$ and $Na_2[Cu(MAGH)]\cdot 2H_2O$,[7,8] are believed to contain $[NO_2S]$[10] and $[N_3S]$[7] donor sets, respectively; in the case of $Na[Cu(MPG)\cdot 2H_2O$, one of the oxygens arises from a coordinated water molecule.

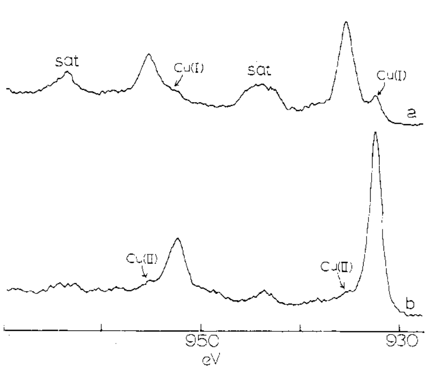

Figure 1. Cu 2p binding energy spectra of (a) $Cu(en)_2(SCN)_2$ and (b) $[Cu(py)_2(SCN)_2]_n$. Spectra were recorded on a Hewlett-Packard Model 5950A ESCA spectrometer using Al $K\alpha_{1,2}$ radiation (1486.6 eV). An electron "floodgun", to reduce surface charging effects to a minimum, and an X-ray-beam power of 1000 W were used in recording both spectra. Times for the data accumulation are as follows: (a) 23 min; (b) 4.5 min.

The features common to the XPS of the five copper complexes are (1) evidence that the copper is present as Cu(I) rather than Cu(II) and (2) S 2p binding energies in the range 163.0–163.9 eV.[4–8] The XPS evidence in favor of Cu(I) is, with one exception, clear-cut since not only are the Cu 2p binding energies of Cu(I) complexes significantly lower than those of their Cu(II) analogues but satellite structure associated with the primary Cu 2p photolines is observed with Cu(II) species but is absent in the XPS of Cu(I).[11–13] The one exception to this observation concerns some conflicting data[7,8] for the complex $Na_2[Cu(MAGH)]\cdot 2H_2O$. While the two sources[7,8] agree as to the values of the Cu $2p_{3/2}$ (932.1 eV) and S 2p (163.0 eV) binding energies, Younes, Pilz, and Weser[8] reported no Cu(II) satellite while Sugiura[7] observed such a feature (albeit weak) at 943.5 eV.[14] The presence of Cu(II) satellite structure requires that a primary Cu $2p_{3/2}$ photoline due to Cu(II) be present; this peak must therefore be contained within the broad high-energy tail[14] of the much more intense Cu(I) Cu $2p_{3/2}$ peak which is centered at 932.1 eV.

The almost exclusive detection of Cu(I) in the XPS measurements is somewhat surprising in view of the knowledge that certain of these complexes possess bulk properties which are characteristic of Cu(II), for example, the ESR Cu hyperfine structure associated with the paramagnetic complex $Na[Cu(MPG)]\cdot 2H_2O$[10] and the crystal structure of $Tl_5[Cu_{14}(pen)_{12}Cl]$ which reveals eight Cu(I) and six Cu(II) sites.[9] Nonetheless, Weser and co-workers[4–6,8] excluded the possibility that X-ray-induced reduction from Cu(II) to Cu(I) had occurred within the spectrometer. This conclusion was based principally upon the following three observations: (1) The XPS of the complex $Cu(en)_2(SCN)_2$, which contains Cu–S bonds, was purported to show[8] that this complex is not subject to photoreduction under the same experimental conditions as those used in recording the XPS of the other copper complexes. (2) Treatment of the violet copper–penicillamine complex with 3% H_2O_2 produces a material whose XPS now shows the presence of Cu(II) and oxidized sulfur (S 2p = 169.2 eV).[4,5] (3) If in the preparation of the violet copper–penicillamine complex a threefold excess of Cu(II) is used in the reaction, then the XPS of the resultant brown-green reaction mixture shows the presence of large quantities of Cu(II) in addition to Cu(I).[5,15]

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(1) Part 27 of the series "X-Ray Photoelectron Spectra of Inorganic Molecules". Part 26: Brisdon, B. J.; Mialki, W. S.; Walton, R. A., accepted for publication in *J. Organomet. Chem.*

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