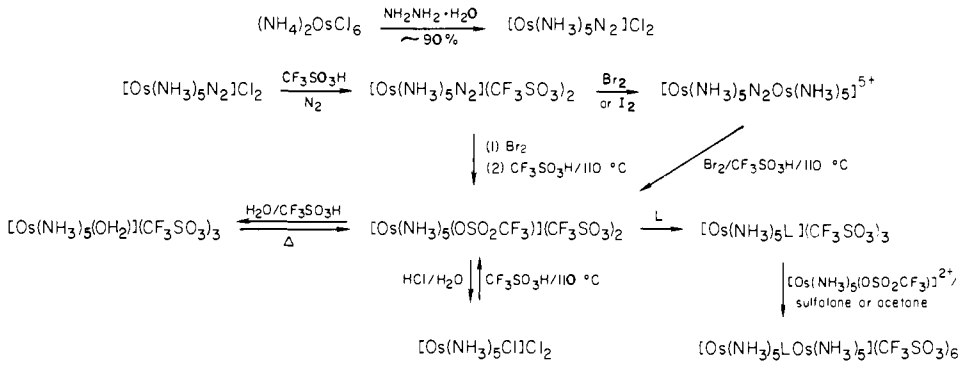
Scheme I



However, addition of CF_3SO_3H to the more basic solvents (H_2O, pyridine, pyrazine) is necessary to suppress base-catalyzed disproportionation reactions, which ultimately lead to multiple substitution and/or oligimerization.[9,13,14] In poorly coordinating solvents such as sulfolane, acetone, or triethyl phosphate, other ligands may be substituted, leading to preparations in moderate to excellent yields. This approach has also been applied successfully to the synthesis of binuclear decaammine complexes.[1,2] The overall chemistry is summarized in Scheme I, and spectral and electrochemical properties of selected complexes prepared by the above methods are presented in Table I.[15] Although most of these complexes have been reported previously,[14,16] the above methods represent the simplest and highest yield preparative routes. It is also worth noting that the intensities of some of the electronic absorption bands of the N-heterocyclic complexes as measured by us are greater than those reported elsewhere.[16] Near-IR spectral properties for several Os(III) complexes have been reported,[14,16] and their absence in analogous d^6 Os(II) complexes supports their assignment as intra t_{2g} transitions split by spin–orbital coupling and/or the symmetry requirement of the ligand field in the pentaammine complexes. The presence of such bands serves as a useful diagnostic tool for the Os(III) oxidation state. In general, a medium-intensity ($\epsilon \sim 10^2$ M^{-1} cm^{-1}) narrow transition occurs at ~2100 nm, along with other weaker transitions for the complexes containing π-acceptor ligands. For those where π-bonding is weak (e.g., $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ and $[Os(NH_3)_5(OH_2)]^{3+}$), only weak ($\epsilon \lesssim 10$ M^{-1} cm^{-1}) transitions have been observed.[17]

An interesting aspect of the redox chemistry is the range of potentials at which the osmium complexes with π-acceptor ligands are reversibly reduced.[16] In particular, the $[Os(NH_3)_5(CH_3CN)]^{3+/2+}$ couple (E_f = –0.25 vs. NHE) occurs at a potential that should make it a useful, fast, outer-sphere, and weakly colored redox reagent. Further, the redox potentials of the N-heterocyclic complexes makes them ideal candidates for the study of surface-enhanced Raman spectroscopy at silver electrodes, where very strong signals are observed. Some of these signals are sensitive to the electrode potential around E_f for the Os(III)/Os(II) couple.[18]

In summary, the ready synthesis of the relatively air-stable $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ complex has provided a convenient and high-yielding entry into the pentaammineosmium and decaamminediosmium series of complexes. This greatly facilitates assessing the impact of π-donor effects on osmium relative to analogous ruthenium complexes and provides ready access to other significant comparisons including mixed-valence interactions,[1,2] redox chemistry,[2,16] reactions of coordinated ligands, and substitution and linkage isomerization processes.

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Registry No. I, 83781-30-0; $[Os(NH_3)_5N_2]Cl_2$, 20611-50-1; $[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$, 83781-31-1; $[Os(NH_3)_5(CH_3CN)](CF_3SO_3)_3$, 83781-33-3; $[Os(NH_3)_5(pz)](CF_3SO_3)_3$, 83781-35-5; $[Os(NH_3)_5(pzMe)](BF_4)_4$, 83781-37-7; $[Os(NH_3)_5(py)]^{3+}$, 83781-38-8; $[Os(NH_3)_5(pyd)]^{3+}$, 70252-41-4; $[Os(NH_3)_5(pyr)]^{3+}$, 83781-39-9; $[Os(NH_3)_5(pzH)]^{4+}$, 83781-40-2.

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(14) Buhr, J. D. Ph.D. Thesis, Stanford University, Stanford CA, 1978.

(15) $[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$ has $\nu(OH_2)$ at 3400–3500 cm^{-1}. Anal. Calcd for $C_3H_{17}F_9N_5O_{10}S_3Os$: C, 4.87; H, 2.31; N, 9.46. Found: C, 4.96; H, 2.39; N, 8.95. $[Os(NH_3)_5(CH_3CN)](CF_3SO_3)_3$ has $\nu(C{\equiv}N)$ at 2295 (w) cm^{-1}. Anal. Calcd for $C_5H_{18}F_9N_6O_9S_3Os$: C, 7.86; H, 2.38; N, 11.0. Found: C, 7.8; H, 2.5; N, 10.7. $[Os(NH_3)_5pyrazine](CF_3SO_3)_3{\cdot}H_2O$: Anal. Calcd for $C_7H_{21}F_9N_7O_{10}S_3Os$: C, 10.26; H, 2.58; N, 11.95. Found: C, 10.4; H, 2.6; N, 12.0. $[Os(NH_3)_5(methylpyrazinium)](BF_4)_4$: Anal. Calcd for $C_5H_{22}B_4F_{16}N_7Os$: C, 8.37; H, 3.09; N, 13.66. Found: C, 8.4; H, 3.1; N, 13.5. All microanalyses were performed by the Stanford University microanalyst. With some complexes, it is necessary to use the Kirsten–Dumas method in order to obtain satisfactory analytical figures (Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161–6164).

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Electron Transfer across Polypeptides. 4. Intramolecular Electron Transfer from Ruthenium(II) to Iron(III) in Histidine-33 Modified Horse Heart Cytochrome *c*

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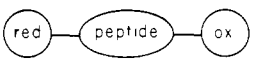
We have demonstrated that intramolecular rates of electron transfer can be significantly altered when different peptide units separate the same donor and acceptor metal ions as shown schematically in I.[1-5] In an attempt to extend this work to



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†Center for Fast Kinetics Research, University of Texas, Austin, TX 78712

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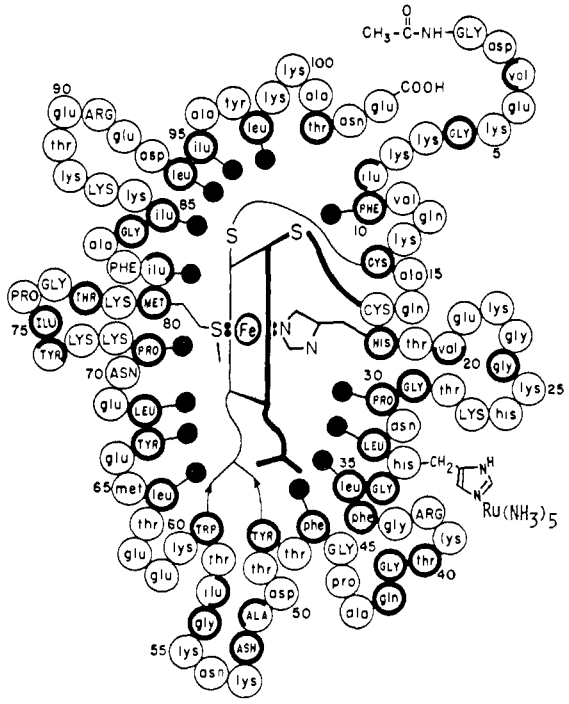

Figure 1. Heme packing diagram of ruthenium-modified cytochrome *c* (His-33) derivative (adapted from ref 15). Heavy and light circles indicate side chains that are inside and outside of the interior of the molecule, respectively. Black dots mark residues whose side chains pack against the heme.

proteins, we have examined the reaction of $[(NH_3)_5Ru(OH_2)]^{2+}$ with horse heart cytochrome *c*. We have selected the $[(NH_3)_5Ru^{II}(OH_2)]$ ion as an inorganic redox reagent for the modification of cytochrome *c* because of its kinetic inertness and its selectivity of binding to nitrogen and sulfur ligands.[6] Because of the kinetic inertness of both the ruthenium(II) and -(III) states, NMR and other physical techniques can be used to characterize the point of attachment of the ruthenium center.[7]

The reaction of cytochrome *c* with high concentrations of $[(NH_3)_5Ru(OH_2)]^{2+}$ at pH 7 resulted in the formation of a covalently bound ruthenium–cytochrome *c* derivative[7] with 1 ± 0.1 ruthenium atoms per heme. Cytochrome *c* has three amino acid side chains to which ruthenium(II) can bind with high affinity at pH 7: His-33, His-26, and Met-65. (His-18 and Met-80 are ligated to the Fe(II)–heme and are not available for binding.) NMR and peptide mapping[7] experiments showed that the ruthenium is bound to the His-33 site (Figure 1). UV–visible and circular dichroism spectra showed no detectable difference between this ruthenium derivative and the native cytochrome *c*.[7] The ruthenium derivative was also active in the biological electron-transfer assay with cytochrome *c* oxidase.[7] In this communication we report our results on the intramolecular electron-transfer properties of this Ru(III)–cyt *c*(III) derivative.

The reduction potential for cytochrome *c* at 25 °C is 0.26 V vs. NHE[8] (pH 7). The reduction potential of $[(NH_3)_5RuHis]^{2+}$[9] is +0.07 V vs. NHE (pH 7).[4] The ruthenium-modified cytochrome shows two reduction waves corresponding to the above ruthenium and heme components. Upon reduction of the ruthenium–cytochrome *c* derivative with 1 equiv of electrons, the Ru(III)–cyt *c*(II) is expected to be the thermodynamically stable product. Any Ru(II)–cyt *c*(III) produced should undergo intramolecular electron transfer to give the Ru(III)–cyt *c*(II).

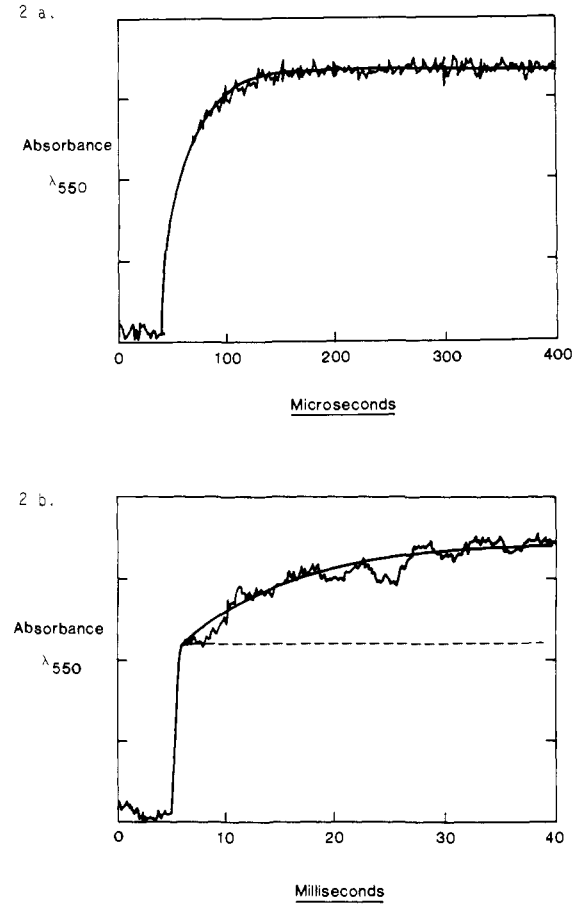

Figure 2. Absorbance vs. time plot (pulse radiolysis) for the reduction of (a) ferricytochrome *c* by $CO_2^{\cdot-}$, (b) ruthenium-modified cytochrome *c* (His-33) by $CO_2^{\cdot-}$. Dashed line indicates end of fast reaction (formation of precursor complex) and start of slow reaction (intramolecular electron transfer).

Using pulse radiolysis, we have studied the $CO_2^{\cdot-}$ reduction of both the native ferricytochrome *c*(III) and its ruthenium derivative under similar conditions. The rate of the bimolecular reduction of cyt *c*(III) by $CO_2^{\cdot-}$ (eq 1) was measured. Figure 2a shows the

$$CO_2^{\cdot-} + \text{cyt } c(\text{III}) \xrightarrow{k} CO_2 + \text{cyt } c(\text{II}) \qquad (1)$$

absorbance vs. time trace for this reaction. The cyt *c*(III) was 1.85×10^{-5} M in a solution of 0.1 M $NaHCO_2$ containing 1 mmol phosphate buffer, pH 7.0. This solution was degassed with argon and saturated with N_2O prior to the pulse radiolysis experiment. The reaction was monitored at λ 550 nm, and the absorption spectrum of the product showed a band between 545 and 550 nm, corresponding to the formation of cyt *c*(II). The pulse radiolysis experiments were done with 100-ns pulses (~1 Krd) and 800-ns pulses (~13 Krd). Rate constant $k = 2.1 \times 10^9$ M^{-1} s^{-1} (22 °C) was calculated. A similar rate constant was observed by Simic et al.[10] under slightly different conditions.

The ruthenium-modified cyt *c* was treated under similar conditions (2.2×10^{-5} M Ru–cyt *c* in 0.1 M $NaHCO_2$ containing 2 mmol phosphate buffer degassed as above, pH 6.7, 22 °C) to generate the Ru(II)–cyt *c*(III) intermediate. The absorbance vs. time plot for this reaction is shown in Figure 2b. Two reactions are observed on the millisecond time scale. First a rapid reaction occurs, corresponding to the reduction of ruthenium–cytochrome *c* with $CO_2^{\cdot-}$ (eq 2). The reduction is expected to have a bimolecular rate constant analogous to that for the reduction of the

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$$CO_2^{\bullet} + \text{Ru(III)-cyt } c\text{(III)} \xrightarrow{k'} \text{Ru(II)-cyt } c\text{(III)} + CO_2$$
$$\text{or} \qquad \downarrow k_u \qquad (2)$$
$$CO_2^{\bullet} + \text{Ru(III)-cyt } c\text{(III)} \xrightarrow{k''} \text{Ru(III)-cyt } c\text{(II)} + CO_2$$

unmodified cyt c(III) (eq 1). After that, a slow increase in absorbance occurs with time (Figure 2b). The absorbance vs. time for this part of the trace fits first-order kinetics with a rate constant $k_u = 82 \pm 20\ s^{-1}$. This reaction corresponds to the intramolecular electron-transfer reaction shown in eq 3. The rate constant k_u

$$\text{Ru(II)–cyt } c\text{(III)} \xrightarrow{k_u} \text{Ru(III)–cyt } c\text{(II)} \qquad (3)$$

was found to be independent of dosage (at low dosage). At high dosage the proportion of the signal due to the slow reaction decreases,[14] as expected, if both the iron and ruthenium centers on the same molecule are reduced. The intermolecular electron-transfer reaction[11] involving two different cytochrome molecules is expected to be negligible at the concentrations used (ca. 2×10^{-5} M).

For a reducing agent such as $CO_2^{\bullet}$, one would not expect significant discrimination between the two electronic isomers Ru(II)–cyt c(III) and Ru(III)–cyt c(II). However, we observed only 30–40% of the Ru(II)–cyt c(III) intermediate in this reduction. We are currently using different alcohol radicals such as pentaerythritol ($C(CH_2OH)_4$) in an effort to increase the concentration of the Ru(II)–cyt c(III) intermediate. Simic et al.[10] have shown that the pentaerythritol radical reduces cyt c with a rate constant $<10^6\ M^{-1}\ s^{-1}$. By use of different alcohols the amount of Ru(II)–cyt c(III) could be increased since such a bulky radical may show selectivity toward the surface-bound $[(NH_3)_5Ru^{III}]$ moiety over the less exposed heme group.

The results in this communication have extended our intramolecular electron-transfer measurements from model peptides[2,3] to proteins. The distance between the His-33 moiety and the heme can be estimated from the crystal structures[12] of the oxidized and reduced tuna cytochrome c to be 12–16 Å, depending on which imidazole nitrogen the ruthenium is bound to and the conformation of the His-33 side chain. This long-range electron transfer across polypeptides, although in itself not biologically relevant, demonstrates that given a driving force of ~0.1 eV, electron transfer within proteins can take place rapidly at long distances.

We are currently attempting the synthesis of a variety of ruthenium–cytochrome c derivatives with different substituted ruthenium complexes of the type $[L(NH_3)_4Ru^{III}]$[13] in order to observe intramolecular electrons transfer from the ruthenium to the iron (heme), as well as from the iron (heme) to the ruthenium in the protein. Experiments with such derivatives should help us to understand the effect of driving force on the rate of intramolecular electron transfer between a donor and acceptor held at long distances. Other experiments of this nature with redox reagents covalently bound to proteins at different distances will help us to understand the dependence of rate of electron transfer on distance for different intervening peptide residues.

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Registry No. $[(NH_3)_5Ru(OH_2)]^{2+}$, 21393-88-4; Ru, 7440-18-8; Fe, 7439-89-6; histidine, 71-00-1; cytochrome c, 9007-43-6.

(14) The fate of Ru(II)–cyt c(II) could not be determined under the experimental conditions used since slow changes (ca. <500 ms) could not be monitored because of the large S/N ratio of the xenon detector.

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Reaction between Cyanate Ion and Ethylene Coordinated to Platinum: A New Route to Carbamoyl Complexes

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Nucleophilic attack to coordinated olefins[1] and oxidative addition to central metal[2] are known to occur readily in platinum(II) complexes. We now show that an appropriate combination of these two processes leads to the formation of a chelating *N*-ethylenecarbamoyl group from ethylene and cyanate ion.

We recently isolated a stable olefin complex of platinum(II), $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ (tmen = *N,N,N',N'*-tetramethylethylenediamine),[3] the reactivity of which toward nucleophiles was greatly enhanced and resembled that of other cationic complexes of platinum-group metals such as iron,[4] ruthenium, and rhodium.[5]

The reaction of a suspension of $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)](ClO_4)$, in water at room temperature, with twice the stoichiometric amount of sodium cyanate afforded a white precipitate in 40% yield based on platinum, and neutralization of the resulting basic solution produced a further 30% yield of product. This compound dissolved in dichloromethane and could be isolated as colorless needles upon cooling.

The elemental analysis [$C_{10}H_{23}ClN_4O_3Pt$ (C, H, Cl, N)] and ^1H NMR [(CD_2Cl_2, $Si(CH_3)_4$) δ 2.99, 2.81, 2.79, and 2.75 (4 s, 4 × 3 H, CH_3N); 5.60 (br, $^3J_{Pt-H}$ = 66 Hz, HN)[6] and other unresolved resonances in the range 2.2–3.7 (m, 8 H, CH_2)] and IR spectra [(KBr pellets, cm^{-1}) 3540 and 3410 (ν_{OH}, water of crystallization), 3270 and 1630 (ν_{NH} and $\nu_{C=O}$, carbamoyl group),[7] 2210 and 1330 (ν_{asym} and ν_{sym}, isocyanate group), 350 (ν_{PtCl})] were in accord with the formula $[\overline{Pt(CH_2CH_2NHC{=}O)}Cl(NCO)$-

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