9 in 75% yield. Addition of a second equivalent of vinyl acetylide gave in 61% yield (95% based on unconsumed starting material) a 45:55 mixture of trans and cis alcohols, which were separately reduced (100%) to alcohols **10**. When treated with KH in THF at room temperature,[26] both *trans*- and *cis*-**10** gave a mixture of two *E*/*Z* isomers of the 15-membered tetraeneone **11** (61% and 40%, respectively). Catalytic hydrogenation of this mixture gave a 97% yield of muscone (**12**).

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Observation of a Reversible Adsorbed Redox Couple Using Surface-Enhanced Raman Scattering: Pentaammine(pyridine)osmium(III)/(II) at Silver Electrodes

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We report surface-enhanced Raman scattering (SERS) for pentaamminepyridineosmium(III) and -(II) adsorbed on a silver electrode. This appears to be the first employment of SERS for following electron transfer with a simple adsorbed redox couple. We have been examining SERS of structurally simple adsorbates under electrochemically characterized conditions.[1-3] One objective is to relate SERS measurements to electrochemical phenomena; despite the recent proliferation of SERS studies,[4] few investigations of this type have been reported. Pentaammineosmium compounds[5] are particularly suitable for the present work since they are substitutionally inert in both III and II oxidation states and have formal potentials compatible with the potential range (ca. 0 to −1.0 V vs. the saturated calomel electrode, SCE) available at silver electrodes. Adsorbed redox couples having nitrogen heterocycle bridging groups constitute direct heterogeneous analogues of the much studied intramolecular redox systems in homogeneous solution.

Conventional conditions for the optimal appearance of SERS were employed,[3,4a] involving roughening the silver electrode by means of oxidation–reduction cycles using 0.1 M NaCl or NaBr supporting electrolytes, also containing 0.1–1.0 mM [$Os(NH_3)_5py]Cl_3 \cdot H_2O$[5] (py = pyridine) and 0.1 M HCl.[6] Raman excitation employed either 647- or 514-nm laser irradiation. All potentials quoted are vs. the SCE; other experimental details are given elsewhere.[3,7]

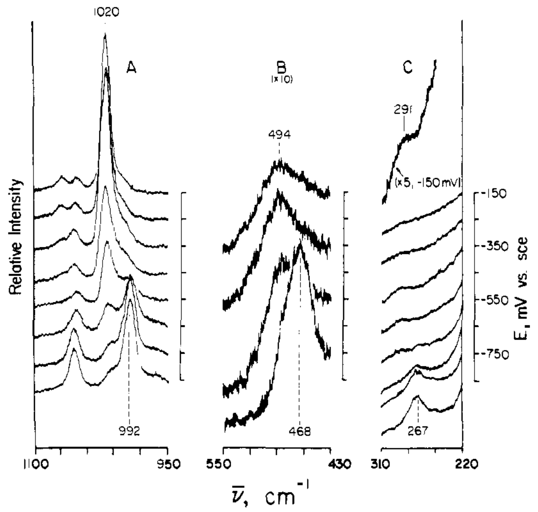

Figure 1. Potential-dependent SERS of $Os(NH_3)_5py$ III/II at roughened silver; 514.5-nm excitation, 100-mW incident power, scan speed 1 cm^{-1} s^{-1}, time constant 1 s, resolution 4 cm^{-1}. Solution contained 0.1 mM $Os(NH_3)_5py^{3+}$ in 0.1 M NaBr and 0.1 M HCl (291-cm^{-1} peak seen more clearly in ×5 top spectrum in C).

SERS spectra were recorded over the frequency range 140–3500 cm^{-1} in 100-mV potential increments from −150 to −850 mV. A summary of some representative vibrational bands is given in Table I; typical spectra as a function of potential are shown in Figure 1.[8] Assignments are based on comparisons with spectra for structurally similar pyridine and ammine complexes[9] and from selective deuteration of the pyridine or ammonia ligands.[3] Aside from the appearance of the halide surface modes at 235 and 180 cm^{-1} for chloride and bromide electrolytes, respectively, the spectral frequencies were essentially identical in both media. (This supports the assignment of the 291- and 267-cm^{-1} vibrations to osmium–pyridine stretching rather than to surface-ligand modes.) At potentials positive of -500 mV, the SERS vibrational frequencies for adsorbed $Os^{III}(NH_3)_5py$ are closely similar to those seen for the bulk Raman and infrared spectra (Table I). However, notable spectral changes occurred as the potential was made more negative. In particular, the intensities of the Os–py stretching (291 cm^{-1}), $Os–NH_3$ stretching (494 cm^{-1}), and symmetric ring breathing (1020 cm^{-1}) modes decreased sharply between −500 and −700 mV, being replaced by corresponding peaks having frequencies 20–30 cm^{-1} lower. These changes could be entirely reversed by returning the potential to less negative values. In contrast, adsorbed pyridine shows little change ($\lesssim 2$ cm^{-1}) in SERS vibrational frequencies and only mild intensity changes over this potential region[10] (Table I).

These spectral changes are consistent with a one-electron reduction of the adsorbed Os(III) complex to the corresponding Os(II) species. Metal–ligand stretching modes commonly exhibit such a dependence upon oxidation state.[9] Of the various pyridine vibrations, the symmetric ring breathing mode is known to be sensitive to the coordinating environment, exhibiting decreasing frequencies as the electron density on the pyridine ring increases.[11] This latter effect is expected to be especially important for $Os^{II}(NH_3)_5py$ on account of the high degree of π-bonding.[5,12]

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Table I. Summary of Representative Vibrational Frequencies (cm^{-1}) Observed for $Os^{III}(NH_3)_5py$, $Os^{II}(NH_3)_5py$, and Pyridine at Silver Electrodes and in Bulk Media[a]

$Os(NH_3)_5py$						
IR[b] Os(III)	IR[b] Os(II)	Raman[c] Os(III)	SERS[d] −150 mV	SERS[d] −750 mV	pyridine SERS[g]	assignment[h]
			291 w	267 m		Os-py stretch
		501 w	494 w	468 m		Os-NH_3 stretch
		654 w	653 m	648 s	625 w,[e] 623[f]	in-plane ring deformation
1022 m	990 m	1020 s	1020 vs	992 s	1007 vs,[e] 1007[f]	sym ring breathing
1055 w	1055 w		1050 m	1053 s	1035 s,[e] 1035[f]	trigonal ring breathing

[a] vs = very strong, s = strong, m = medium, w = weak. [b] Infrared data obtained by using $Os(NH_3)_5py{\cdot}I_3$ and $Os(NH_3)_5py{\cdot}I_2$ in CsI pellets. [c] Normal Raman data obtained by using $Os(NH_3)_5py{\cdot}Cl_3$ in KBr pellets. [d] Surface-enhanced Raman vibrational modes for electrochemically roughened silver electrode in 0.1 M NaBr + 0.1 M HCl + 0.1 mM $Os(NH_3)_5py^{3+}$ at indicated potentials vs. SCE. [e] From this work, for 10 mM pyridine in 0.1 M NaBr. [f] From ref 10, for 50 mM pyridine in 0.1 M KCl. [g] Frequencies were potential independent (±2 cm^{-1}) from −150 to −750 mV. [h] See text for details.

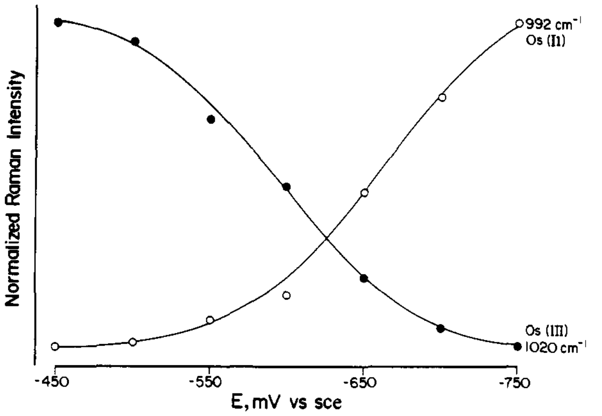

Figure 2. Normalized intensity of the symmetric ring breathing mode as a function of electrode potential. Osmium oxidation states are indicated. Data are as in Figure 1.

Indeed, an almost identical frequency shift in this mode is seen for the infrared spectra of the bulk Os(III) and Os(II) complexes (Table I).

Using rapid-scan cyclic voltammetry (50–100 V s^{-1}) and very dilute $Os(NH_3)_5py^{3+}$ concentrations (~50 μM),[13] the formal potential of the adsorbed Os(III)/(II) couple, E_f^a, was found to be −670 mV in 0.1 M HCl at roughened silver, (cf. the formal potential for the bulk couple, E_f^b = -655 mV). Moderate adsorption (~(3–4) × 10^{-11} mol cm^{-2}) was indicated by the charge underneath the almost symmetric cyclic voltammograms. Formal potentials, E_f^a, were also determined from the SERS intensity–potential data. Figure 2 shows the potential dependence of the normalized integrated intensities of the 1020- and 992-cm^{-1} SERS ring breathing modes in the vicinity of E_f^a. Assuming the intensities are proportional to the corresponding surface concentrations, a Nernstian treatment[3] gave values of E_f^a (−630 ± 10 mV), similar to those determined electrochemically.

The appearance of SERS signals for the present system is in itself noteworthy since coordinated pyridine is unable to bind to the surface via the nitrogen lone pair. Such surface coordination is often regarded as a preprequisite for the appearance of SERS for adsorbed pyridine.[4a] Adsorption of the coordinated pyridine is likely to occur edgewise via a C=C bond;[14] the alternative flat orientation will be sterically hindered by the presence of the coordinated pentaammineosmium. Direct metal–pyridine bonding is also consistent with the excellent mediating properties of coordinated pyridine for pentaamminecobalt(III) reduction at metal surfaces.[15] Nevertheless, the adsorbate–electrode interactions are presumably weak, as evidenced by the similarity of E_f^a and E_f^b, and the vibrational frequencies of $Os(NH_3)_5py$ III/II at the surface and in bulk media. SERS of osmium and ruthenium complexes containing coordinated pyrazine and 4,4′-bipyridine ligands that are able to bind to the surface via the exposed nitrogen, thereby yielding stronger adsorbate–surface interactions, will be described elsewhere.[3]

The present results illustrate the potential of SERS for monitoring heterogeneous electron-transfer processes and suggest that adsorbates bound to SERS-active sites are energetically similar to those observed by conventional electrochemistry.

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Registry No. $[Os(NH_3)_5py]Cl_3$, 70252-36-7; $Os^{II}(NH_3)_5py$, 70252-47-0; Ag, 7440-22-4.

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Circularly Polarized Fluorescence of Aromatic Poly(α-amino acids)

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This communication describes studies of circularly polarized fluorescence (CPF) of aromatic poly(α-amino acids) having 1- and 2-naphthyl and 9-anthryl groups on their side chains. The nature of monomer, excimer, and exciton fluorescence state is discussed on the basis of the dissymmetry of fluorescence.

Aromatic poly(α-amino acids) such as poly(L-1- and 2-naphthylalanines)[1,2] (poly(1- and 2-NapAla)) and poly(anthrylmethyl L-aspartate)[3] (poly[Asp(OCH_2-9-Ant)]) have been prepared with an expectation that they may work as a molecular conductor that can transport electrons across biological mem-

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† To whom correspondence should be addressed at the Research Center for Medical Polymers and Biomaterials.

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(2) Sisido, M.; Egusa, S.; Imanishi, Y. *J. Am. Chem. Soc.*, in press. Poly(2-NapAla) showed an exciton splitting in the CD spectrum at the ^1B_b band ($[\theta]_{234}$ = 6.0 × 10^5, $[\theta]_{219}$ = −2.3 × 10^5 deg cm^2 $dmol^{-1}$) in trimethyl phosphate.

(3) Poly[Asp(OCH_2-9-Ant)] was prepared from Asp(OCH_2-9-Ant) NCA. The polymer showed an exciton splitting at the ^1B_b band ($[\theta]_{265}$ = −1.9 × 10^5, $[\theta]_{235}$ = 2.8 × 10^5, deg cm^2 $dmol^{-1}$) in trimethyl phosphate.