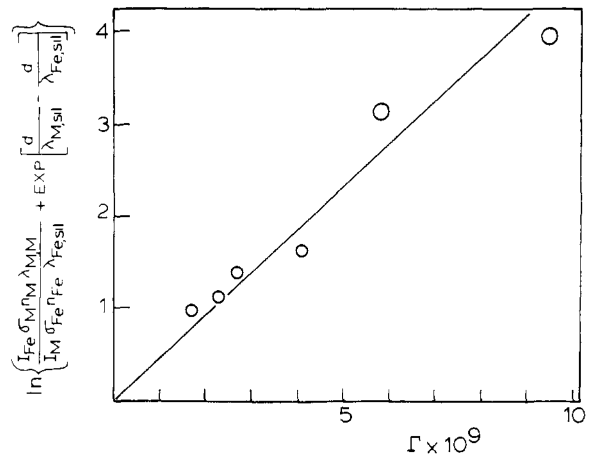

Figure 5. Plot of Fe $2p_{3/2}$ and $M_{5/2+7/2}$ relative XPES intensities in rearranged eq 2 vs. electrochemically measured coverage Γ, using parameters $\lambda_{M,M} = 14.3$ Å, $\lambda_{Fe,sil} = 13.9$ Å, $\lambda_{M,sil} = 37$ Å, $n_M = 6.3 \times 10^{22}$ atom/cm^3, and $n_{Fe} = 3.45 \times 10^{21}$ atoms/cm^3.

a situation that the prerequisites for charge transfer are stringent and require both facile counterion mobility and a reasonably open structure. The dependence of the electrochemical behavior on the counterion in a comparison of perchlorate and tetraphenylborate[3] and the variability of electrochemical reversibility from preparation to preparation are consistent with this view.

Secondly, the correspondence of an electrochemically measured quantity of ferrocene with a XPES-measured quantity of iron, Figure 5, indicates that to at least a first approximation all of the iron present is ferrocene iron and that all of the ferrocene iron is electroactive in the electrochemical experiment. This assertion has, of course, limitations with respect to the accuracy of the data fit represented in Figure 5, plus the uncertainties associated with its assumption that the ferrocene-silane film has a uniform thickness. XPES relations which assume simple forms of nonuniformity (such as metal-exposing pores), when compared to eq 1 and 2, show I_M/I_M^0 and I_{Fe}/I_M to be decreasingly responsive to film thickness at larger pore areas and at larger thicknesses. Model calculations indicate that effects of pores of area 10% of the total (causing ca. 30% error in d) could be accommodated within the data scatter. More extreme porosity would appear to be ruled out.

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Spectra of the H_2 Phthalocyanine in Low-Temperature Matrices

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Abstract: Laser emission and excitation spectra of H_2 phthalocyanine in solid Ar and Ne matrices were examined. The spectra display a sharp vibronic structure, both in excitation and emission. Polarization studies confirm the presence of two overlapping transitions in the red. It is suggested that a strong vibronic coupling is responsible for the appearance of several perpendicularly polarized bands below the Q_y origin.

I. Introduction

Porphyrin-type molecules are an extremely important class of compounds with a a key role in photosynthesis, oxygen transport, and other biologically important reactions. Their properties are therefore of great interest and over the years they were frequently studied by a variety of spectroscopic tools. Only in the last 5 years more than 200 publications dealt with the subject of phthalocyanine alone. The spectra of porphyrins were extensively studied in a variety of organic solvents. In particular, works by Gorokhovskii, Personov, and others in Spolskii matrices provided extensive information.[1-7]

The electronic spectroscopy of porphyrins is characterized

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by two strong transitions in the visible. The lower energy state located in the red spectral region is doubly degenerate in the symmetrically substituted metal porphyrins. The degeneracy is split in the less symmetric free base porphyrins, and the resulting two closely spaced bands are generally denoted Q_x and Q_y. A second, higher energy transition in the blue region is referred to as Soret bands, and its two components are denoted B_x and B_y.

Somewhat surprisingly for molecules of this size, many porphyrins can be vaporized without decomposition. At the temperatures needed for their vaporization, enormous numbers of vibrational and rotational levels are populated, and the gas-phase electronic spectra appear continuous.[8-10] Very recently Levy and co-workers have succeeded in seeding supersonic jets with phthalocyanine molecules,[11] and observed excitation spectra of the "cold" molecules, showing sharp vibronic structure. An alternate approach is provided by the matrix isolation technique. The porphyrin spectra in weakly interacting rare-gas solids should not be significantly perturbed and could permit convenient studies of the vibrationally and rotationally cold porphyrin molecules. Pioneering matrix work was carried out by Bajema et al.,[12] who studied phthalocyanine both as a free base and with zinc ligand in several low-temperature matrices. They observed two relatively broad and structured absorption bands in the red, which they assigned to the electronic origins of the expected[13] Q_x and Q_y states. One of the potential limitations of the usefulness of matrix isolation spectroscopy is the various mechanisms of homogeneous or inhomogeneous line broadening. If the lines are broad and vibronic structure is not resolved, little information can in general be obtained. If inhomogeneous broadening dominates the line shapes, one can circumvent this problem by selective site excitation, and still obtain a sharp vibronic structure. In the present work we use laser excitation to reexamine the matrix spectra of free base phthalocyanine and its N-deuterated counterpart. We show that under conditions of narrow band width excitation sharp vibronic structure can indeed be obtained.

II. Experimental Section

Techniques similar to those reported by Bajema et al.[12] were used to prepare the phthalocyanine-containing matrices. The phthalocyanine was vaporized at ~600 K. The vapor was mixed with the matrix gas and passed through a second furnace heated to ~750 K. The gas mixture was then deposited on a sapphire substrate cooled to 4.2 K by liquid He. Total sample quantities of 4-5 mmol were deposited over a period of 3-4 h and their concentration was estimated to be near to 1:1000.

The phthalocyanine was obtained from Eastman Kodak and used without purification. A deuterated sample was prepared by finely grinding the solid, suspending it in D_2O, and boiling the mixture for several hours under reflux.

The fluorescence spectra were excited using a home-built dye laser pumped by a Molectron UV 300 N_2 laser. The sample reemission was resolved in a SPEX 1401 B double monochromator and digitized in a Biomation 610 B waveform recorder. The time window containing the laser pulse was then digitally integrated, averaged, and stored in the memory of a minicomputer controlling the experiment.

III. Results

Our absorption spectra in Ar matrix are, except for a somewhat simpler appearance, similar to those reported by Bajema et al.[12] They consist of two strong and relatively sharp (fwhm ≈ 20 cm^{-1}) bands located at 14 770 and 15 774 cm^{-1}, respectively. Each of the bands is accompanied by a weaker satellite shifted some 70 cm^{-1} further red. The relative intensities of the two components depend on the deposition conditions and history of the sample, with annealing increasing the relative intensity of the lower energy component. In the deuterated sample the 14 770-cm^{-1} band remains unchanged in position and shape, but the higher energy absorption shifts distinctly to lower energies and appears at 15 736 cm^{-1}. We have investigated in less detail spectra in Ne matrix, where the absorption bands are considerably broader (fwhm ≈ 100 cm^{-1}) and shifted to higher energies.

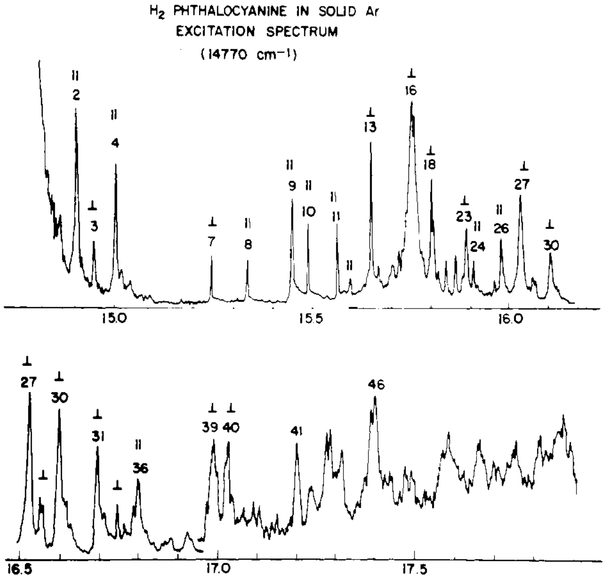

Figure 1. H_2 phthalocyanine excitation spectrum in solid Ar. The intensity of the 0-0 emission at 14 770 cm^{-1} was monitored. Bands are numbered for easy correlation with Table I. The prevailing polarization is shown for some of the bands.

Emission spectra with excitation in the blue in the Soret band are again in fair agreement with the previous work and mainly the strong 0-0 band at 14 770 cm^{-1} is seen. This band has a width of about 20 cm^{-1} and, like the absorption bands, it has a weaker lower frequency satellite near 14 700 cm^{-1}, whose relative intensity depends somewhat on the experimental conditions. The sharper and simpler appearance of our spectra as compared with those of ref 10 is probably due to the lower 4.2 K deposition temperatures employed in the present work.

Figure 1 shows an excitation spectrum of the 14 770-cm^{-1} emission in solid Ar, observed with monochromator slits adjusted for ≈1 cm^{-1} band-pass. The broad band corresponding to the 15 755-cm^{-1} absorption band occurs strongly in the spectrum. In addition, a large number of other bands are observed. The bands at the lower energy end of the spectrum are less than 2 cm^{-1} wide, and this width is undoubtedly experimental. With increasing energy the width of the vibronic bands gradually increases and most bands above 16 000 cm^{-1} have widths in excess of 6-10 cm^{-1}. Finally, above about 17 500 cm^{-1} most of the structure disappears and the remaining absorption is practically continuous. The excitation spectrum of the lower energy component at 14 700 cm^{-1} is in all respects analogous to the spectrum of Figure 1, except for a uniform 70-cm^{-1} shift of all the bands. Phthalocyanine is apparently trapped in solid Ar in two distinct sites, or rather the inhomogeneous distribution shows two maxima ~70 cm^{-1} apart. The sharp bands in the excitation spectrum clearly represent the vibronic structure of phthalocyanine in the two excited electronic states expected in this energy range.

The study of fluorescence polarization can provide very useful information about nonrotating matrix isolated molecules,[14,15] in particular in the case of several overlapping electronic transitions. We find that the phthalocyanine fluorescence is indeed strongly polarized and, furthermore, that the polarization ratio $p = I_{\parallel}/I_{\perp}$ changes depending on which of the vibronic bands is excited. Table I summarizes the exci-

Table I. H_2 Phthalocyanine Excitation Spectrum (cm^{-1})

no.	$\bar{\nu}$	I	$\Delta\nu$	P	no.	$\bar{\nu}$	I	$\Delta\nu$	P
1	14 770	vs	0	2.5	24	15 911	m	1141	2.2
2	14 902	s	132	2.4	25	15 964	w		
3	14 948	m	178	0.8	26	15 982	m		1.5
4	15 001	s	231	2.1	27	16 030	m	1260	0.8
5		w			28	16 059	w	1289	
6		w			29	16 067	w	1297	
7	15 245	m	475	0.7	30	16 105	s	1335	0.8
8	15 337	m	567	2.3	31	16 203	m	1433	0.8
9	15 450	s	680	2.2	32	16 221	w	1451	
10	15 491	m	721	2.1	33	16 254	m	1484	0.8
11	15 565	m	795	2.2	34	16 271	w	1501	
12	15 597	w	827	1.5	35	16 299	m	1529	
13	15 650	s	880	0.6	36	16 307	m	1537	2.2
14	15 669	w	899		37	16 389	w	1619	0.8
15	15 721	w	951		38	16 431	w	1661	
16	15 754	vs	985	0.7	39	16 494	m	1724	
17	15 760	s	990	0.7	40	16 531	m	1761	
18	15 804	s	1034	0.7	41	16 706	m	1936	
19	15 809	m	1039	0.7	42	16 782	w	2012	
20	15 821	w	1051		43	16 792	m	2022	
21	15 841	m	1071	0.9	44	16 821	w	2051	
22	15 865	m	1095		45	16 895	m	2125	
23	15 893	s	1113	0.8	46	16 905	m	2135	

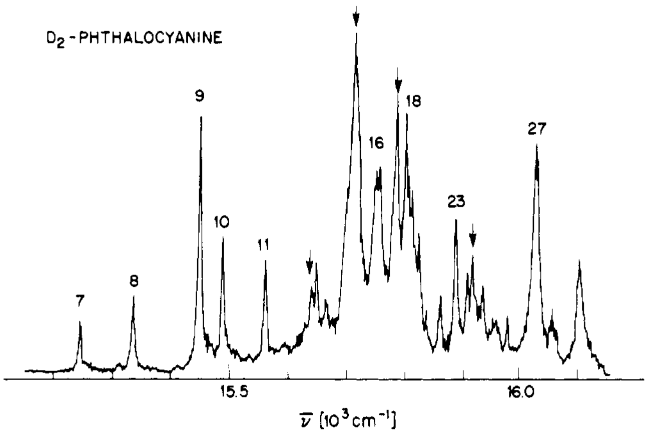

Figure 2. Part of the excitation spectrum of the partially deuterated sample of phthalocyanine. The arrows indicate the shifted bands.

Table II. H_2 Phthalocyanine Emission Bands (cm^{-1})

no.	$\bar{\nu}$	$\Delta\nu$	no.	$\bar{\nu}$	$\Delta\nu$
1	14 770	0	6	13 628	1142
2	14 199	571	7	13 585	1185
3	14 085	685	8	13 420	1350
4	14 042	728	9	13 224	1546
5	13 971	799			

tation spectrum results for the major 14 770-cm^{-1} "site". For each band we give the wavenumber, $\Delta\nu$, from the 14 770-cm^{-1} origin and the polarization ratio P. Figure 2 shows the effect of deuterium substitution on the excitation spectrum. Most of the bands appear unchanged. The strong band at 15 755 cm^{-1} is now weak, however, and a new strong band of similar shape appeared at 15 716 cm^{-1}. This 36-cm^{-1} red shift is in agreement with the observed shift in the absorption spectrum. Also several other bands in this region display small shifts.

The appearance of the emission spectra does not depend on which of the sharp excitation maxima is excited and the emission is clearly vibrationally relaxed. Figure 2 shows the spectrum obtained with excitation in the vibronic band at 15 245 cm^{-1}. The vibrationless band at 14 770 cm^{-1} dominates the spectrum. Unlike in the spectra with excitation in the higher energy Soret band in the blue, the emission is now sharp with fwhm < 2 cm^{-1}. In the more sensitive trace where the gain was increased by a factor of 16, several weaker vibronic bands appear at lower energies. These clearly represent the vibrational structure of the phthalocyanine ground electronic state. The assignment of all these bands to phthalocyanine is confirmed by their excitation spectra, which are identical with that of the 14 770-cm^{-1} 0-0 band. The observed emission bands are listed in Table II.

We have studied in less detail the excitation spectra in neon. Like the absorption spectrum, the emission with blue excitation is also broad. When the fluorescence is monitored with narrow bandwidth detection, a sharp excitation spectrum is again observed, and gives upper state frequencies identical with those obtained from the solid Ar spectra. With a shift of the monochromator wavelength within the broad 0-0 fluorescent band, all the bands in the excitation spectrum shift also by the same margin. Apparently, in solid neon the inhomogeneous site distribution is unstructured and extends over more than 150 cm^{-1}.

IV. Discussion

1. Mechanisms of Line Broadening and Selective Site Excitation. In a small molecule electronic transition often leads to pronounced change in some particular bond length or angle, and as a result of the Franck-Condon principle one then observes a long progression in the associated vibrational mode. The electronic transition in phthalocyanine involves the extensive delocalized Π system. The electron density is distributed over the entire molecule and the changes resulting from the electronic transition are more subtle. The Franck-Condon principle will under these conditions place the bulk of the intensity into the vibrationless 0-0 band with only a weak occurrence of transitions involving vibrational excitation. Accordingly, the origin band dominates the spectrum both in our work and in that of ref 12. Since the electron density is distributed over the extensive Π system, one would also not expect dramatic changes in the guest-host interaction potentials and might predict appearance of sharp zero phonon lines in the electronic transition. The rather substantial inhomogeneous broadening, however, results in overlapping of individual vi-

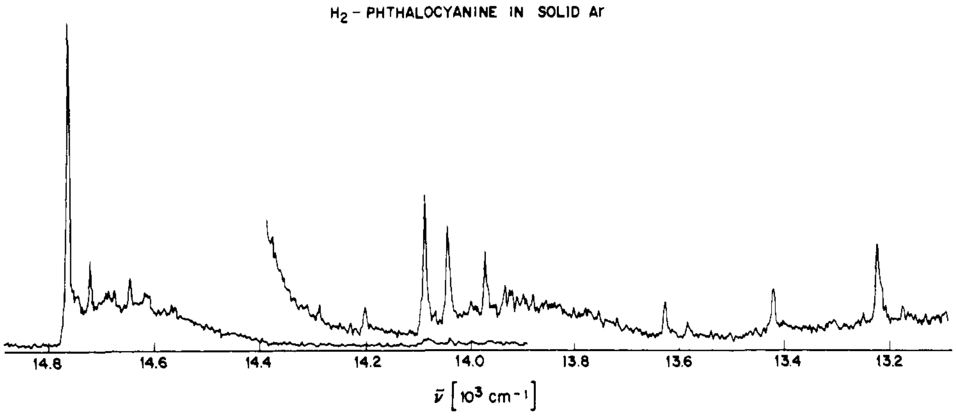

Figure 3. H_2 phthalocyanine emission spectrum in solid Ar at 4.2 K.

brational bands and obliterates the excited vibronic structure in the absorption spectrum. In the laser excitation spectrum, on the other hand, the inhomogeneous broadening is removed by selecting only a narrow range out of the inhomogeneously broadened structure. Furthermore, the high power available in tunable dye lasers will easily saturate the Franck-Condon allowed 0-0 transition, and lead to the relatively prominent appearance of the weaker vibronic bands in the excitation spectrum.

Of interest is the origin of the broadening of the bands at the high-energy end of the excitation spectrum. Most of the inhomogeneous broadening was removed by the narrow bandwidth detection, and the symmetric appearance of those bands which are not distorted due to overlapping suggests that the broadening is also not due to phonon sidebands. Spectral lines can also be broadened according to the uncertainty principle, due to dephasing or relaxation processes, and this is probably the major broadening mechanism in the present case. For the lowest vibrational levels the density of vibronic states is relatively low, and the relaxation is too slow to show observable broadening with our relatively low resolution (1 cm^{-1}). Higher in the vibrational manifold the density of states increases drastically and so do the vibrational relaxation rates. This is similar to the situation near the dissociation limit of diatomic molecules where, as the vibrational spacing decreases, one sees increasing line widths owing to fast relaxation processes.[15,16] It is interesting to note that the line widths do not appear to be a monotonic function of vibrational energy, which may suggest a more subtle dependence of the relaxation rate on the vibrational level.

2. Vibrational Structure in the Phthalocyanine Spectra. Since both the emission and excitation spectra show a sharp vibronic structure, one could obtain extensive information about the vibrational structure of phthalocyanine both in the ground and excited electronic state. Complete vibrational assignment in a molecule with ~350 vibrational degrees of freedom is clearly not feasible. A useful tool in vibrational assignment is isotopic substitution, and we have therefore examined the deuterated compound, whose partial excitation spectrum is shown in Figure 3. Our deuteration method will only exchange the two central hydrogens and accordingly most bands appear unshifted. Several frequencies (denoted by arrows in Figure 3) do, however, exhibit distinct shifts, and must involve motion of the central hydrogens. Selective isotopic substitution of the phenyl ring hydrogens, as well as labeling with ^{15}N and ^{13}C, should, in view of the sharp vibrational structure observed, permit at least partial assignment of the vibrational frequencies in the upper electronic state.

Less information is obtained about the ground state of phthalocyanine. While in the excitation spectrum the weaker vibronic transitions can be relatively enhanced by increasing laser power and saturating the stronger bands, in emission the relative intensities are still controlled by the Franck-Condon principle. The bands terminating in vibrationally excited ground-state levels are weak, but several can be observed in the expanded trace in Figure 2.

Somewhat puzzling is the behavior of the strong perpendicular band at 15 753 cm^{-1}, denoted previously Q_y and assigned as an origin of a second electronic state. While the 14 770-cm^{-1} band shows within experimental error (±2 cm^{-1}) no shift upon deuteration, the 15 753-cm^{-1} band shifts 37 cm^{-1} to 15 716 cm^{-1}. A shift of this magnitude could of course easily occur, if there is a change in vibrational frequencies involving the hydrogen motion. The two quasi-degenerate electronic states Q_x and Q_y can, however, be expected to have similar vibrational structure, and yet no shift is observed in the position of the Q_x origin.

Of interest also are the polarization data; presence of both parallel and perpendicularly polarized bands confirms the presence of at least two electronic states. All the bands below the Q_y origin must be assigned to the Q_x vibrational levels, and one would expect them to have the same, parallel polarization. Yet, several fairly strong perpendicular bands appear below the accepted 15 753-cm^{-1} Q_y origin. Reassignment of the first perpendicularly polarized band at 14 948 cm^{-1} as the Q_y origin appears quite unlikely. It would be quite difficult to rationalize its relative weakness and, furthermore, it would leave no obvious assignment for the strong 15 753-cm^{-1} band.

It appears preferable to retain the 15 753-cm^{-1} assignment for the Q_y origin, in spite of the inherent difficulties. A very strong vibronic mixing with the Q_x levels, or with some higher lying state of the same symmetry, must then be invoked to explain the appearance of perpendicularly polarized, i.e., non-totally-symmetric Q_x vibrational levels. Similarly, strong mixing of this type with some Q_x vibrational levels involving motion of the central hydrogen atoms may be responsible for the observed shift of the Q_y origin upon deuterium substitution. In particular it may be noted that the very strong perpendicular band at 15 650 cm^{-1} in Figure 1 is very substantially reduced in intensity in the deuterated spectra (see Figure 3). It should therefore probably be assigned to the H_2 isotopic species. It is possible that this is due to the vibrational level responsible for the upward shift of the Q_y origin in the H_2 species. We have, however, not been able to identify its D_2 counterpart.

The present study clearly leaves many questions unanswered, and additional work would be useful. In particular, studies of related metal phthalocyanines, as well as of the corresponding tetrabenzo porphyrins, might provide additional clues. Also more detailed studies of samples with varying degrees of deuteration should permit a firm assignment of the individual bands to the H_2, HD, and D_2 phthalocyanine species.

Our preliminary work does, however, clearly demonstrate that the matrix emission and excitation spectra exhibit sharp vibronic structure, and together with photoselection studies can provide extensive information about porphyrin-type molecules.

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Polymeric Ligands as Anchoring Groups for the Attachment of Metal Complexes to Graphite Electrode Surfaces

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Abstract: Coatings of poly(4-vinylpyridine) (PVP) and polyacrylonitrile (PAN) have been applied to pyrolytic graphite electrodes by simple exposure of the electrodes to solutions of the polymers. The resulting coatings are very durable and extract metal complexes from solutions as dilute as 5×10^{-8} M. With higher concentrations, very large quantities of metal complexes can be bound to the polymer coatings and their electrochemical responses observed. The behavior of attached Ru(edta), Ru(NH$_3$)$_5$, and Cu(II) complexes is described. Ru^{II}(edta) undergoes ligand substitution reactions while bound to the PVP coating to form cross-links between pyridine sites in the polymer. Examples are given of polymeric coatings to which two different metal complexes are bound as well as electrodes on which both PVP and PAN coatings are present.

Polymeric molecules have been advanced as potent modification agents in experiments with chemically modified electrodes.[1-4] Some of the first reports involved the coating of electrodes with electroinactive polymers,[1] but more recently electrodes coated with polymeric molecules containing electroactive groups have been described.[2-5] One of the most attractive aspects of polymeric coatings is the relative ease with which they can be applied—simple dip coating by immersion of the electrode in a solution of the polymer[1-5] often suffices to produce quantities of anchored ligand sites as great as or greater than result from more elaborate coating procedures.[3,6,7]

By attaching molecules such as polyvinylpyridine (PVP) or polyacrylonitrile (PAN) that contain many sites for metal coordination, electrode surfaces that accept a variety of metal ions can be prepared. In a recent communication[5] we described experiments in which large quantities of Ru(edta) and Ru(NH$_3$)$_5$ complexes were coordinatively attached to pyrolytic graphite electrodes coated with PVP or PAN. In the present report these studies have been expanded to include mixed coatings of two different polymeric ligands as well as electrode surfaces to which two different metal complexes are attached simultaneously. Among the special properties of the PVP coatings are an ability to extract metal ions from solutions as dilute as 5×10^{-8} M. When Ru(edta) complexes are attached to the PVP coating a rich surface coordination chemistry ensues that can be modified by control of the electrode potential.

Experimental Section

Materials. Pyrolytic graphite disks were cut from cylindrical stock (Union Carbide Corp., Parma, Ohio) with the basal planes of the graphite perpendicular to the axis of the cylinder. The disks were sealed to the ends of glass tubing by means of heat-shrinkable polyolefin tubing (Alpha Wire Co.). Electrical contact was made to the rear face of the disks using a few drops of mercury. The mounted disks were freshly cleaved before each set of experiments by cutting a thin section through the polyolefin sheath and the graphite disk with a scalpel. The exposed area of each disk was 0.17 cm^2.

Poly(4-vinylpyridine) (Borden Inc., Philadelphia, Pa.) was recrystallized twice from methanol-diethyl ether. The average molecular weight of the sample, determined viscometrically,[8] was 7.4×10^5 corresponding to about 7000 pyridine groups per molecule of polymer. Polyacrylonitrile was provided by Dr. S. Margel. Its molecular weight was not measured.

Aquoethylenediaminetetraacetatoruthenium(III) prepared from RuCl$_3$ as described by Mukaida et al.[9] was found to contain chloride. A chloride-free product was obtained by dissolving the initial yellow-green solid in water, reducing the volume to ca. 10 mL/g, and allowing the solution to stand overnight at room temperature. The resulting yellow precipitate was washed with water and methanol and dried under vacuum. Anal. Calcd for RuC$_{10}$H$_{15}$N$_2$O$_{10}$: C, 29.0; H, 3.72; N, 6.81. Found: C, 29.4; H, 3.70; N, 6.86.

Solutions of aquoethylenediaminetetraacetatoruthenium(II) were prepared by reducing solutions of the Ru(III) complex with amalgamated zinc or by controlled-potential electrolysis at a mercury pool electrode.

Solutions of aquopentaammineruthenium(II) were prepared by electrolytic reduction of chloropentaammineruthenium(II) at a mercury pool electrode.

Reagent grade chemicals were used without futher purification. Aqueous solutions were prepared from triply distilled water. The supporting electrolyte for most electrochemical measurements was 0.2 M CF$_3$COONa adjusted to the desired pH with CF$_3$COOH.

Apparatus and Procedures. Voltammograms were obtained with a PAR (Princeton Applied Research) Model 174 instrument and an *x-y* recorder (Houston Instruments). Conventional two-compartment

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