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Photoelectrochemical Properties of a Metal Maleonitriledithiolate in an Ion-Containing Polymer Blend

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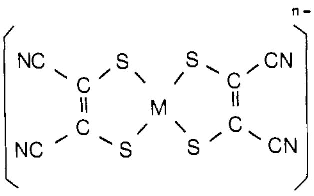
Metal maleonitriledithiolates (mnt) have been incorporated in polymer films composed of a quaternary ammonium ion containing polymer blended with PVP. These films also incorporate $Fe(CN)_6^{3-/4-}$ by ion exchange. Cyclic voltammetry indicates quasi-reversible behavior for the iron couple, but no reaction for the $M(mnt)_2^{2-}$ (M = Ni,Pt) species when the films are studied in the dark on transparent SnO_2 electrodes. The mnt complexes are apparently immobilized. Chronoamperometry indicated effective diffusion coefficients for the Fe species near 10^{-7} cm^2 s^{-1}. On irradiation in the main visible bands of the mnt complexes, photocurrent is observed that can be interpreted as photooxidation of the mnt complex with electron transfer to SnO_2 followed by rereduction with $Fe(CN)_6^{4-}$. $Fe(CN)_6^{4-}$ is regenerated at the dark counterelectrode. The transport of charge from the mnt complex to SnO_2 may be mediated by the π system of the polymer's pendant groups in the polymer blend.

Introduction

Ionomers and conductive organic polymers are prime candidates for chemically modified electrodes.[1,2] Dye-sensitized chemically modified electrodes may be useful in photogalvanic, photovoltaic, sensor, or electronic device applications. They also provide methods for evaluating photocatalyst systems.

Polymer films supporting dyes present three interesting possible mechanisms of conduction: (1) electronic conduction along the polymer; (2) ionic migration in the film; and (3) hopping conduction by redox electron exchange between dye and other electroactive molecules in the film. Dye incorporation may be accomplished via three routes: first, direct covalent bonding of the dye to the polymer backbone; second, a metal–ligand bond from a ligand on the polymer to a metal center in the dye; third, strong electrostatic interactions between charged sites of the polymer and an ionic dye.

The dianions of maleonitriledithiolate (mnt) form stable four-coordinate complexes with transition metals including nickel and platinum as represented by structure **1**. These square-planar anionic complexes are strongly colored and photoelectrochemically active.[3,4] The present paper presents the electrochemical and photoelectrochemical properties of $M(mnt)_2^{2-}$ (M = Ni, Pt) incorporated into an polymer film supported on an optically transparent electrode. The present polymer film is one known to retain anions of high charge against ion exchange with bulk solution electrolyte.[5] The results reflect an extension of the study of photoelectrochemistry in quaternized poly(vinylpyridine) films.[4] In the present case, much more stable performance is achieved.



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Experimental Section

Materials. $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ were synthesized according to the modified method reported by Persaud and Langford.[3] All solvents were reagent grade and used as received unless otherwise specified. Water was distilled in glass. $K_3Fe(CN)_6$ (potassium ferricyanide), $K_4Fe(CN)_6$ (potassium ferrocyanide), and potassium chloride were reagent grade and used as received. A 2.00×10^{-3} M solution of both ferri- and ferrocyanide in 1.00 M aqueous KCl was used as the redox couple solution (pH 6–7). The background electrolyte was 1.00 M aqueous KCl.

Random Copolymer. Styrene (Aldrich) and chloromethylstyrene (Polysciences) were distilled under reduced pressure prior to use. Triethylamine (Aldrich), triethanolamine (Aldrich), and azoisobutyronitrile (AIBN, Chemical Dynamics Corp.) were used as received. The random ternary copolymer was prepared according to the procedure described by Montgomery and Anson.[5] First, a random binary copolymer was prepared from a benzene solution containing 2.4 M chloromethylstyrene, 0.60 M styrene, and 0.06 M AIBN as free radical initiator. The solution was thoroughly degassed with prepurified nitrogen. The polymerization was carried out at 60 °C for 24 h. The styrene–chloromethylstyrene copolymer was precipitated with *n*-hexane. The second part of the preparation involved converting the chloromethylstyrene moiety of the copolymer to quaternary amine groups by using the Menschutken reaction.[6] A 10-fold molar excess of triethylamine was added to a solution of the binary copolymer in benzene, and the solution was refluxed for 1 h. This was followed by addition of a 10-fold molar excess of triethanolamine, after which refluxing was continued for 1 h. Concentrated HCl was added to the resulting ternary copolymer to neutralize the unreacted amines. The solution was then dialyzed against water for 3 days. After the dialysis, THF was added to improve the solubility of the copolymer. The resulting ion-containing polymer was reprecipitated by using cold 2-propanol to yield a pale yellow powder.

Polymer Blend. Poly(vinylpyridine-10%-*co*-styrene) (PVP) (Aldrich) was used as received. A 2% (w/v) solution of PVP was prepared in Spectrograde methanol (Anachemia). A similar 2% solution of the ion-containing copolymer was prepared. Polymer blends were prepared by mixing 2:1 (v/v) quantities of the ionic polymer and the PVP solutons with vigorous stirring.

Electrode Modification. The $M(mnt)_2^{2-}$ complexes were incorporated into the polymer blend by mixing different volumes (typically 2–8 mL) of a 1×10^{-3} M solution of the metal complex in methanol to the previously prepared polymer blend solution. The resulting solution was then stirred and heated gently until the final volume was reduced to that of the original polymer blend solution, thereby preparing polymer solutions containing varying degrees of loading of the metal complex.

Plates of SnO_2-coated "Nesa" glass (supplied by the O. H. Johns Glass Co.) were used to prepare optically transparent electrodes (OTE's) in a Teflon flow cell previously described (7). The OTE's were pretreated by soaking them in absolute ethanol for 2 days, rinsed with acetone, and then dried in air for 15 min. Aliquots (0.5–1.0 mL) of the deep red polymer solution (I) were solvent cast on leveled OTE's with a syringe. Aliquots of the polymer blend without the mnt complex were cast on OTE's in a

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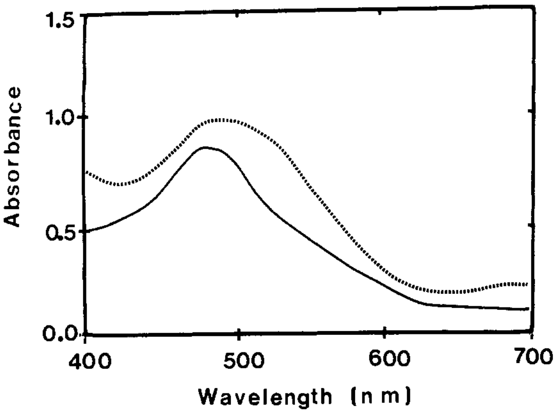

Figure 1. Visible absorption of the polymer film loaded with $Ni(mnt)_2^{2-}$ (- -), and $Ni(mnt)_2^{2-}$ in methanol (—).

similar fashion (II). Slow evaporation was ensured by covering the electrodes with an inverted crystallization dish.

Electrochemical Measurements. Once the solvent had evaporated, the red transparent films coated on the conductive glass were placed in the Teflon flow cell[7] equipped with a platinum wire counter electrode and an Ag/AgCl (saturated KCl) reference electrode. The latter electrode was separated from the electrolyte by a glass frit. Electrolyte and redox solutions were pumped through silicone tubing to the cell by a locally constructed peristaltic pump. The solutions were circulated from a closed reservoir to the flow cell at a rate of 1.6 mL/min. The $Fe(CN)_6^{3-/4-}$ redox couple was incorporated via ion exchange with the chloride counterions of the copolymer moiety. Cyclic voltammetric measurements and single-step chronoamperometric measurements were made by using a Metrohm E-506 potentiostat coupled with a Methrohm E-612 scanner. Solutions were deoxygenated with prepurified nitrogen prior to electrochemical measurements.

Photoelectrochemistry. The modified electrode was illuminated from the SnO_2 side of the flow cell with either an Ar ion laser (Spectra-Physics) or a 300-W tungsten–halogen lamp filtered by a 5.5-cm water filter and a 400-nm cutoff filter to remove IR and UV radiation, respectively. The electrode area exposed for these measurements was 2.0 cm^2. Short circuit photocurrent measurements were recorded using a Keithley (Model 177) multimeter in conjunction with a strip chart recorder.

Results

a. Spectra. The visible absorption spectra of the modified SnO_2 electrodes differ slightly from the absorption spectra of a methanolic solution of $Ni(mnt)_2^{2-}$. The band assigned[3] as metal to ligand ($xy \rightarrow L\pi^*$) charge transfer is red shifted by 16 nm from 472 to 488 nm (Figure 1). Similarly, the band of the Pt complex is red shifted from 472 to 484 nm. The present result is in contrast to observation for a quarternized-PVP (QPVP) film where the shift was smaller.[4] As noted below, the mnt complex is mobile in the QPVP film but not in the present film. The present film does not have the benzylpyridinium group of QPVP but does have the blended PVP, which is absent from the QPVP film. The relative intensity of the band may be used to approximate roughly the amount of dye incorporated in the film. Accurate quantitation must account for the scatter arising from the polymer film and SnO_2 OTE.

b. Dark Electrochemistry. Steady-state cyclic voltammograms of the polymer blend films without the metal complexes I in 1.0 M KCl indicate a well-defined irreversible reaction of the pyridinium ion to pyridine radicals at a $E_{1/2} = -0.60$ V. The quaternized random ternary copolymer portion of the blend is inactive over the electrochemical window in aqueous solution.

Polymer-modified electrodes containing the nickel or platinum complex II exhibit similar electrochemical behavior (Figure 2a). The characteristic rapid one-electron transfers between $M(mnt)_2^{2-}$ and $M(mnt)_2^{-}$, which are normally seen in the solution electrochemistry of the complexes, are absent; at most a minimal signal attributable to the layer in direct contact with the SnO_2 is seen. This can be attributed to strong electrostatic interactions with the cationic polymer sites. The complex is immobile, and only complexes immediately adjacent to the electrode can react. This result is in sharp contrast to the readily observable electrochemistry of $M(mnt)_2^{2-/-}$ in QPVP films.[4]

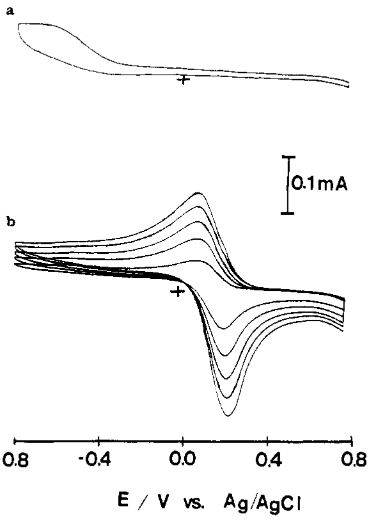

Figure 2. Cyclic voltammograms of a polymer film, 22 μm, loaded with $Ni(mnt)_2^{2-}$ in contact with 1 M KCl (a) and in contact with 2×10^{-3} M $Fe(CN)_6^{3-/4-}$ (b). Scan rates vary from 10 to 50 mV/s in 10 mV/s steps. Anodic currents are downward.

Table I. Apparent Diffusion Coefficients of $Fe(CN)_6^{3-/4-}$ in Polymer Blend Films

electrode	thickness, μm	diffusion coeff, cm^2/s × 10^7
1	10	6.0
2	11	1.0
3	16	0.42
4	20	0.67

As the redox couple is circulated through the cell, the cationic polymer blend incorporates a substantial amount of $Fe(CN)_6^{3-/4-}$ by ion exchange with the initial chloride counterions. Voltammetry is shown in Figure 2b. The separation between the anodic and cathodic hexacyanoferrate peaks, E_p, is virtually the same for films I and II and has a value of 150–170 mV at a scan rate of 100 mV/s. The scan rate dependence of a modified electrode in contact with the redox couple is also shown in Figure 2b. The peak separation increases as the film thickness is increased. Thick films (20 μm or greater) exhibit peak separations in the range 200–250 mV under the same conditions.

The rate of charge transport across the polymer blend film by the redox couple in the film (in the dark) is determined by the apparent diffusion coefficient, D_{app}.[8] Chronoamperometric measurements were performed on both polymer films I and II. The contents of the flow cell's reservoir were changed from a solution containing the redox couple to a solution containing only the background electrolyte. The background electrolyte was pumped through the tubing and the flow cell until the $Fe(CN)_6^{3-/4-}$ was completely flushed from the solution phase of the system, leaving only the redox couple species and the dye in the film. Chronoamperometric measurements were conducted by stepping the potential of a nonflowing system from +0.6 to −0.6 V. Under the conditions of the experiment, semiinfinite linear diffusion may be assumed and Cottrell plots can be used to evaluate D_{app} if all other parameters are known. The concentration of the incorporated redox couple was calculated by chronocoulometry. Film thicknesses were measured with a micrometer. The apparent diffusion coefficients of $Fe(CN)_6^{3-/4-}$ in the films were evaluated and are listed in Table I. The values are somewhat smaller in these thick films than values reported for thin films of this polymer

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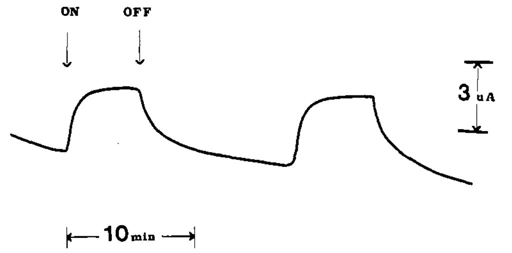


Figure 3. Typical short-circuit photocurrent profile of a modified electrode loaded with Ni(mnt)$_2^{2-}$ in contact with 2 × 10^{-3} M Fe(CN)$_6^{3-/4-}$ illuminated with white light filtered to remove IR and UV light.

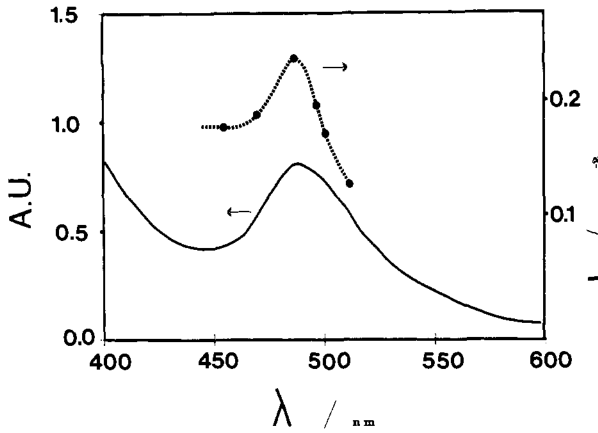


Figure 4. Absorption spectra of polymer-modified electrode loaded with Ni(mnt)$_2^{2-}$ (—) and short-circuit photocurrents of a polymer-modified electrode with Ni(mnt)$_2^{2-}$ in contact with 2 × 10^{-3} M Fe(CN)$_6^{3-/4-}$ in 1 M KCl when illuminated with an argon ion laser in the single-line mode at 100-mW (-●---●-).

blend on carbon.[5] The apparent diffusion coefficient of Fe(CN)$_6^{3-/4-}$ in the films does not follow a film-thickness dependence. The selected values in Table I are representative of the D_{app} in these films and depend on electrode preparation.

The hexacyanoferrate redox couple remains in the polymer film at a concentration for some time after the electrode is placed in contact with the background electrolyte. Cyclic voltammograms of polymer films that were soaked in 10–50 mM Fe(CN)$_6^{3/4-}$ are similar to those shown in Figure 2b. Continuous CV scanning over a period of 4 h reveals a gradual leaching of the Fe(CN)$_6^{3-/4-}$ into the background electrolyte solution. The leaching of the redox couple from the polymer reaches a limit of 45–50% of its initial concentration in the film. In contrast, the water-insoluble M(mnt) complexes do not appear to leach from the polymer film. Polymer modified electrodes containing the Pt(mnt)$_2^{2-}$ or the Ni(mnt)$_2^{2-}$ complexes were soaked in 1 M KCl for 2 days without any leaching of the complexes to the solution.

The polymer film swells to accommodate more electrolyte. The high retention values and diffusion coefficients of the Fe(CN)$_6^{3-/4-}$ in the composite film have been linked to the internal morphology of the films. The polymer film appears to segregate into hydrophilic and hydrophobic domains.[9]

c. Photoelectrochemistry. Photoelectrochemical measurements using visible light from the projector were conducted after the dark current had stabilized to a minimum (0.1–0.2 μA; ca. 1–3 h). When the polymer-modified electrode (I) was illuminated from the SnO$_2$ side, small anodic photocurrents (2–5 μA) were recorded. A typical photocurrent profile is shown in Figure 3. The relatively slow response of the cell could be attributed to several factors including slow diffusion of ions in the film, slow charge transport via redox reactions in the film or at interfaces, and a reduced mobility due to the trapping of charge carriers moving across the polymer. The following analysis will point toward a partial distinction among these factors.

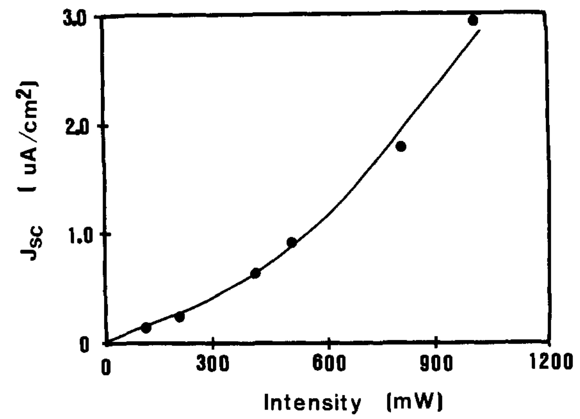
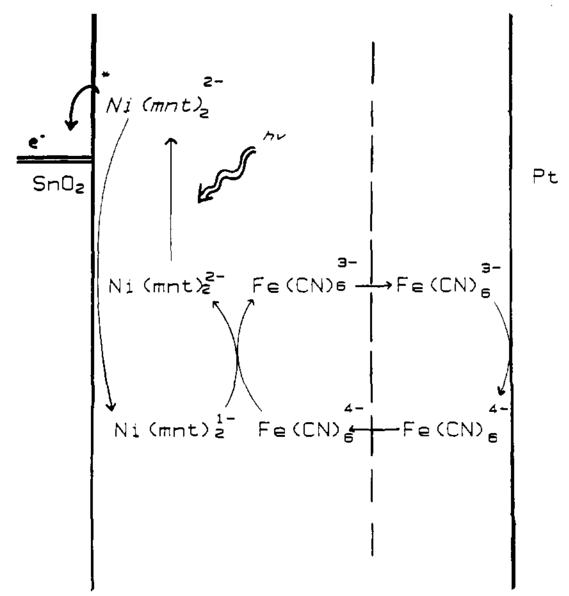


Figure 5. Short-circuit photocurrents of a polymer-modified electrode with Ni(mnt)$_2^{2-}$ in contact with 2 × 10^{-3} M Fe(CN)$_6^{3-/4-}$ in 1 M KCl as a function of illumination intensity at 488 nm using an argon ion laser in the single-line mode.

Scheme I



In the absence of Ni(mnt)$_2^{2-}$ or Pt(mnt)$_2^{2-}$ the polymer blend films supported on SnO$_2$ transparent electrodes exhibit virtually no short-circuit photocurrent response (100–150 nA).

The argon ion laser, in single-line mode, was used as an irradiation source in order to examine photocurrents as a function of wavelength in the vicinity of the main visible band of the complex. The power of each argon ion line was adjusted to 100 mW/cm^2 by using a Coherent Radiation power meter. The resulting photocurrents are superimposed on a visible spectrum in Figure 4. The absorption maximum appears at 488 nm, corresponding to one of the main lines of the argon ion laser. The action spectrum maps the peak. Photocurrent increases with increasing power (Figure 5) with a slight upward curvature.

Discussion

The initial facts that a mechanism for the photoeffects must satisfy are the observations that the photocurrent is anodic, that it has an action spectrum matching Ni(mnt)$_2^{2-}$, and that the M(mnt)$_2^{2-/-}$ is not electrochemically active in the dark while the Fe(CN)$_6^{3-/4-}$ couple is electroactive. These facts can be accommodated for the mechanism shown in Scheme I. The excited state of the reduced metal maleonitriledithiolate dye transfers an electron to the SnO$_2$ electrode yielding Ni(mnt)$_2^-$, which has an appropriate potential (0.37 V vs Ag/AgCl) to oxidize Fe(CN)$_6^{4-}$. Some excess Fe(CN)$_6^{3-}$ diffuses out of the film and the counter Pt electrode effects the reduction of Fe(III). No other reasonable sequence can account for the facts listed. A similar mechanism operates with the Pt complex.

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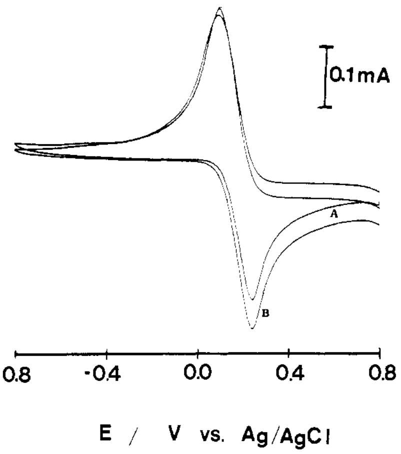

Figure 6. Cyclic voltammogram of a polymer-modified electrode with $Ni(mnt)_2^{2-}$ in contact with 2×10^{-3} M $Fe(CN)_6^{3-/4-}$ in 1.0 M KCl (A) in the dark, and (B) under visible light illumination. Scan rate = 5 mV/s. Anodic currents are downward.

The slow response of the system is associated with the diffusion coefficients approximately for the Fe couple obtained in the chronoamperometric experiments.

The fact that the nickel and platinum complexes are electroinactive in the composite film is quite surprising. This contrasts the results of the complex incorporated by ion exchange in the QPVP films.[4] The method of preparation in the latter case differs from the present preparation of the polymer film composites. The metal maleonitriledithiolate complexes appear to be bound by strong electrostatic interactions to the quaternized alkyl ammonium sites in the copolymer moiety of the polymer blend. Axial ligation of the complex to pyridine sites of the poly(vinylpyridine) moiety of the blend should not be discounted as possible binding sites for the strongly colored complexes. The photoresponse of the system is complex, and a mechanism of charge transport is not clear.

The puzzle presented by the mechanism is how the electron is transported from the excited $Ni(mnt)_2^{2-}$ complex to the SnO_2 electrode. Two possibilities present themselves. One is energy migration from the point of excitation to the interface, with charge separation being limited to the interface. This seems unlikely. Earlier reports indicate short excited-state lifetimes for the complex,[3,10] and it is difficult to see how an exciton mechanism can be consistent with upward curvature of the current–intensity curve. The other possibility is that the excited state of $Ni(mnt)_2^{2-}$ transfers an electron to π^* levels of an aromatic ring of the polymer and that transfer to the electrode is an analogue of conductivity in polystyrene after electron injection.[11] This mechanism is energetically allowed on the basis of the energy of the lowest lying excited state of the complex and the reduction potential of aromatic groups. The ^1A_g ground state of the $Ni(mnt)_2^{2-}$ complex is located at −0.1 V versus NHE. The reduction potential of the pyridinium group lies at −0.45 V versus NHE. Excitation to the lowest excited state of the complex adds 3.06 eV of photon energy to the reduction power, making transfer to the pyridinium group thermodynamically feasible.

Further support for this mechanism comes from the wavelength dependence of photocurrents in a similar phthalocyanine film to be reported elsewhere.[12] In this mechanism, the slow response would be related to trap-controlled charge migration in this film. The magnitude of the photoresponse is dependent on the energetics of charge transfer, the lifetime of the excited state (in this case, the picosecond domain), and the polymer morphology. The highly disordered amorphous nature of this film can give rise to a large number of localized states.

Figure 6 shows a cyclic voltammogram of the electrode under illumination that foreshadows use of as a photoswitch or photodiode-like device. At potentials between 0.1 and 0.8 V vs Ag/AgCl, the dark currents are small and irradiation in the milliwatt per square centimeter range can turn on a current of several microamperes. The larger anodic photocurrents are in agreement with the proposed mechanism in Scheme I. Localized energy states in the polymer film at these potentials may be slightly altered to allow for greater conduction of charge through the polymer film.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) and Actions Structurantes for financial support.

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Nitrile Complexes of Pentaammineosmium(II) and -(III)

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Earlier work on nitrile complexes of $(NH_3)_5Os^{2+}$ and $(NH_3)_5Os^{3+}$ has been extended to include as ligands nitriles (RC≡N) that are stronger π acids. There is a progressive decrease in the C≡N stretching frequency for the Os(II) complexes along the series R = CH_3, CH_2=CH, C_6H_5, C_6F_5. The same order is observed for the Os(III) species, supporting the conclusion that back-bonding is significant also for Os(III). For the complexes of the nitriles with R = C_6H_5, C_6F_5, and $C_{14}H_9$ (9-anthracene), two absorption bands are observed in the visible region at energies below those attributable to the ligand itself, which are assigned to MLCT. For Os(III), at the present level of refinement, only when R = $C_{14}H_9$ do the UV–visible spectra reveal interesting features. There is a prominent peak at 453 nm, which we assign to MLCT. At still lower energies, a progression of peaks, with separations suggesting a vibrational component, is observed, which we tentatively ascribe to a ligand-centered singlet–triplet transition induced by the paramagnetic metal ion. When the complex of C_6H_5CN is prepared by the reaction of $(NH_3)_5Os^{II}$ with the ligand, two forms are observed. The minor component, in which the metal is bound to the ring in an η^2 mode, is thought to rearrange slowly to the major N-bound form, by an intramolecular mechanism.

Introduction

Nitriles have figured prominently[1] in the development of the chemistry of ruthenium ammines. In line with our current program of exploring the chemistry of the pentaammineosmium moiety, where complexes of Os(II) with π-acid ligands appeared to be of special interest, we undertook to prepare and characterize some (nitrile)pentaammineosmium complexes. Several, including that with the acetonitrile as the heteroligand, had already been characterized in our laboratories.[2] In view of the evidence

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(2) Work mainly by P. A. Lay, in preparation for publication.

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