

nitride phases relative to bromide carbide is unusual. We hypothesize that the distortions in the bromide and iodide represent a means of avoiding a substantial matrix effect¹⁹ and achieving short, strong Sc-C bonds that are about 0.03 Å less than the average in Sc₇Cl₁₂B and Sc₇Cl₁₂N.

A number of M₇X₁₂(Z) compounds have been prepared over the years. In addition to the scandium chlorides Sc₇Cl₁₂(B, N), several lanthanide iodides R₇I₁₂ have been obtained (R = La-Pr, Gd, Tb, Er, Lu), and three (La, Tb, Er) have been structurally refined in space group R $\bar{3}$.^{15,20} None of the lanthanide compounds was recognized as containing an interstitial atom but all gave typical problems associated with a missed interstitial in the form of residual electron density in the center of the clusters, sometimes quite large. Elongated ellipsoids ($B_{33}/B_{11} = 6.5-9$) for the isolated metal atom were again found for the lanthanum and gadolinium examples (but just the opposite for erbium), and the crystals also showed evidence of twinning or disorder. Polydomain twins have also been seen for Sm₇I₁₂.²¹

The above iodides may be less distorted and insufficiently acentric to be refined. We have been unable to refine the data for Sc₇Cl₁₂(B, N)⁹ in space group R $\bar{3}$, which gave the correlation problems encountered when a pseudocentric structure is refined by least squares. On the other hand, these structures gave rea-

sonable residuals when refined centrically and only moderate elongation of the Sc(1) thermal ellipsoids ($B_{33}/B_{11} = 3.7, 7.5$) so that a regular deviation from centricity, if any, is probably small. The analogue without an isolated cation, Zr₆I₁₂C,⁶ shows none of these problems.

Some of the twinning and disorder problems with the above lanthanide M₇I₁₂ phases may originate with the preparation method as all were obtained from melts. There is also the possibility that the twinning results during the descent from a high-symmetry supergroup, a disordered cubic structure in I23, for example. The fact that all of the Sc₇X₁₂Z phases we have studied were grown by vapor-phase transport may be important in obtaining better crystals with fewer problems. Of course, different and unknown interstitials may also be responsible in the former cases.

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Registry No. Sc₇I₁₂C, 103437-35-0; Sc₇Br₁₂C, 103368-85-0; Sc₇I₁₂B, 103368-86-1.

Supplementary Material Available: Tables of anisotropic thermal parameters, angles, and the EHMO parameters used (3 pages). Ordering information is given on any current masthead page.

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Photoelectrochemistry of Dianionic Maleonitriledithiolate Complexes of Nickel and Platinum in Ion-Exchange Films on Transparent Tin Oxide Electrodes

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The water-insoluble compounds of the dianionic bis(maleonitriledithiolate) complexes of Ni and Pt were ion-exchanged into films of quaternized poly(vinylpyridine) that had been deposited onto transparent tin oxide electrodes. The electrochemistry of these films in contact with aqueous electrolyte is analogous to that of the anions in acetonitrile solution. On irradiation with visible light, photocurrents are observed that are larger than the currents for the corresponding complexes in acetonitrile solution. The Pt complex, after irradiation, catalyzes the cathodic solvent wave. Recrystallization of the oxidized monoanionic complex occurs in the film so that its behavior is not stable in time. The rates of processes and currents in the film tend to be sensitive to anions from the supporting electrolyte.

Introduction

The square-planar complexes of the formula M(mnt)₂ⁿ⁻ where M is Ni, Pd, Pt, or Cu, mnt is the maleonitriledithiolate ligand, (CN)₂C₂S₂²⁻, and *n* ranges from 0 to 3, are of interest for photoelectrochemistry for several reasons. First, they exhibit absorption with charge-transfer character in the visible spectral region. Second, they have several available oxidation states in an interesting potential range. Third, their structures are very similar in the various oxidation states, which should favor rapid, facile electron transfers with minimal inner-sphere reorganization barriers. We have reported some solution photoelectrochemistry of these complexes.¹ The study was limited by two factors. One is that the complexes are insoluble in water so that the homogeneous photoelectrochemistry was limited to organic solvents. (We used acetonitrile.) The other is that the lifetime of states found to be active following excitation in the visible region appeared to be rather short.

There is reason to believe that mounting of these chromophores in a polymer film on an electrode can mitigate both problems. The film may be utilized in contact with an aqueous electrolyte, and in this context, the insolubility of the complexes in water may be advantageous in preventing leaching. Also, a complex localized

on a binding site in a film may acquire a longer lifetime by way of reduction of vibrational degrees of freedom, and as well, it may be possible to organize reaction partners in the film so as to utilize short-lived states more effectively. To test these concepts, we have prepared films from poly(vinylpyridine) that has been quaternized by reaction with benzyl chloride to produce a cationic polyelectrolyte. These films can incorporate the dianionic mnt complexes from acetonitrile solution to occupy up to 30% of the ion-exchange capacity of the film. We report some electrochemistry and photoelectrochemistry of such films doped with Ni(mnt)₂²⁻ and Pt(mnt)₂²⁻. The films are mounted on transparent tin oxide electrodes so that the films may be efficiently irradiated.

Experimental Section

Materials. The complexes were prepared and characterized as described in ref 1. Electrode materials are also described in ref 1. Poly(4-vinylpyridine-10%-*co*-styrene) was obtained from Aldrich Chemical Co. Dichlorodimethylsilane was purchased from Petrach Systems, Inc.

Poly(4-vinylpyridine-10%-*co*-styrene) (PVP) was quaternized with benzyl chloride from Fisher. A 2.5-g sample of PVP estimated to contain approximately 0.02 mol of vinylpyridine units was dissolved in 150 mL of spectrograde methanol in a three-neck flask fitted with a condenser and a gas bubbler. The solution was deaerated with N₂, and 12 mL (0.1 mol) of reagent grade benzyl chloride was added to the solution, which was heated to 60 °C. The pressure in the flask was then lowered and the temperature reduced to 55 °C. The sample was maintained at this

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Table I. Composition of SnO₂-Modified Electrodes Used in Photoelectrochemistry

electrode	modified electrode	concn of complex, mol cm ⁻³ × 10 ³	concn of complex, mol cm ⁻² × 10 ⁷	concn of polymer, ^a mol cm ⁻² × 10 ⁶	thickness (l), μm	(QPVP)/(M(mnt) ₂ ²⁻)	% QPVP sites neutralized by M(mnt) ₂ ²⁻
a	SnO ₂ -QPVP-Ni(mnt) ₂ ²⁻	0.884	2.83	3.23	3.2	11.41	17.51
b	SnO ₂ -QPVP-Ni(mnt) ₂ ²⁻	1.480	4.90	3.33	3.3	6.78	29.50
c	SnO ₂ -QPVP-Pt(mnt) ₂ ²⁻	1.410	4.50	3.19	3.2	7.08	28.24
d	SnO ₂ -QPVP-Pt(mnt) ₂ ²⁻	1.360	4.49	3.28	3.3	7.30	27.41
e	SnO ₂ -QPVP-Pt(mnt) ₂ ²⁻	2.490	7.72	3.22	3.1	4.16	48.02
f	SnO ₂ -QPVP-Pt(mnt) ₂ ²⁻	2.460	7.86	3.17	3.2	4.03	49.54

^a Expressed as moles of cationic sites.

condition for 60 h. Purification was accomplished by dissolution in methanol and reprecipitation with dry ether.

The degree of quaternization was determined by titration of the chloride counterions using AgNO₃ and the dichlorofluorescence end point. Assuming a *M_n* value of 232 for the quaternized vinylpyridine repeat unit and 10% styrene in the sample, the analyses indicated ≥99% quaternization.

Modified-Electrode Preparation. Pt foil and SnO₂-coated glass (NESA) disks from the O. H. Johns Co. were the substrates used. (Their resistance was less than 50 Ω.) A film of quaternized PVP (QPVP) could be formed on acid-cleaned Pt by dipping the metal two or three times into a 2.5% methanol solution of the polymer and then allowing solvent to evaporate at 35–40 °C in a closed vessel containing an atmosphere nearly saturated with methanol. This produced a smooth film.

The SnO₂ disks were subjected to more extensive pretreatment. After being refluxed in concentrated H₂SO₄, disks were washed with distilled water and absolute ethanol and then dried under vacuum. To improve mechanical adherence of polymer films, the SnO₂ disks were refluxed in 5% dichlorodimethylsilane in toluene under a N₂ atmosphere for 3 h after which they were washed with dry toluene and dried under vacuum. The silanization was necessary to avoid peeling of films containing M(mnt)₂²⁻. The film of silane is not measurable with a profilometer and is probably a "monolayer". It is not "bonded" to the polymer since Me₂SO, DMF, and methanol can dissolve off films. After silanization, PVP films could be formed by dropping solution onto the disk and allowing for evaporation on a rotating stage.

Ion exchange of M(mnt)₂²⁻ ions into the films was either by direct exchange of the chloride form with a 4 × 10⁻³ M complex solution in refluxing acetonitrile or by exchange for perchlorate after chloride forms were soaked for 5 min in 0.1 M NaClO₄ in CH₃OH. Most films were used in the chloride form. The extent of ion exchange was estimated by dissolution of the films after washing and measurement of visible absorption in solution using a Perkin-Elmer 522 or Cary 2290 spectrophotometer.

Thickness of polymer films on SnO₂ was measured as mechanical surface profile using a Talysurf Taylor-Gibson step profilometer. The ion exchange of M(mnt)₂²⁻ complexes did not measurably change film thickness. The amount of QPVP was measured gravimetrically. The M(mnt)₂²⁻ exchange was estimated spectrophotometrically. The film was dissolved in a measured volume of Me₂SO and the solution spectrum recorded in the visible region. Alternatively, the complex was displaced into CH₃CN by ion exchanges with 1.0 M NaClO₄. The profilometer was not useful for films on Pt. Thickness was, instead, estimated by establishing a correlation with the number of ion-exchange sites vs. thickness of films on SnO₂. Quantities of QPVP could also be confirmed by measurement of absorbance at 256 nm in a methanol solution. As will be seen below, electrodes used in photoelectrochemistry develop a history. Thus, various experiments were performed with fresh electrodes at the start of each series. This accounts for a number of distinct electrodes of similar type being reported below.

Electrochemical Technique. Potentials were controlled by a PAR 363 potentiostat in conjunction with a locally fabricated triangular function generator and X-Y recorder. Solution (homogeneous) measurements in the dark were made at a Pt electrode (0.5 cm²) in a conventional polarographic cell or at SnO₂ in a Teflon cell of the type used in photoelectrochemical experiments. Reference electrodes were either Ag/AgCl (saturated KCl) separated by a glass frit or Ag/Ag⁺ (0.1 M AgNO₃) in CH₃CN. This second was found to be at +0.27 V vs. the first. The counterelectrode was Pt in all cases.

Photoelectrochemical Technique. The SnO₂ electrodes had a "window" from 360 to 600 nm. They were mounted over silicone "O" rings to make electrical contact with a brass ring. (The films were removed in this contact zone.) The disks were bolted down to a Teflon cell permitting an optical and electrode area of 0.78 cm². The cell and leads were enclosed in a Faraday cage. (Solutions in CH₃CN were prepared in a closed system where CH₃CN was pumped into a reservoir

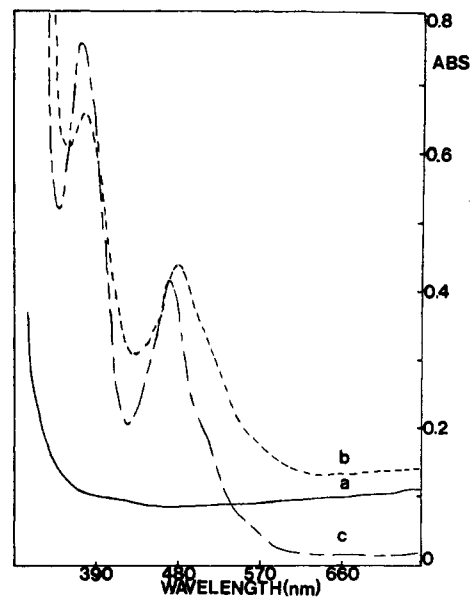


Figure 1. Absorption spectra of (a) the polymer film, (b) the film loaded with Ni(mnt)₂²⁻, and (c) Ni(mnt)₂²⁻ in CH₃CN.

where solutions were prepared. Solutions were then pumped through the electrochemical cell at 4.5 mL/min.)

Irradiation was either from a Coherent 6-W Ar ion laser at 514 nm or from a 200-W tungsten lamp filtered by 6 cm of water and a 420 nm cutoff filter.

Results

1. Characterization. The composition of six representative electrodes used for photoelectro and electrochemistry are summarized in Table I. Electrochemical parameters of a set of similar electrodes on both Pt and SnO₂ are summarized in Table II. The two groups are parallel but not the same because of "history" effects. Comparison with ref 1 will show that the cyclic voltammetry (CV) peaks of the 2-/1- anion quasi-reversible couple are present. As well, incorporation of the 2- complex into the ion-exchange film has little effect on the absorption spectra. A representative example is shown in Figure 1, where the spectra of Ni(mnt)₂²⁻ in various environments are compared. Even the minor differences indicated between ion-exchange film and solution may not be due to genuine changes in the spectrum but may be base line effects produced by the light scattering in the film. These results suggest that the anions are incorporated without significant modification of structure or reactivity.

2. Electrochemistry. The first electrochemical reference point is the behavior of the polymer support film without an mnt complex. Since the chloride forms of the polyelectrolyte show significant water solubility, this reference could only be established using films with perchlorate counterions produced by exchanging anions in a 0.10 M solution in acetonitrile. Figure 2 shows a voltammogram of a film on tin oxide in the voltage range between +0.71 and -1.22 V. The polymer is reduced near -1.0 V, and this process is only partially reversible. A "window" for study extends to about -0.8 V. It is observed, however, that the presence of an mnt complex in the film renders the polymer peak quasi-reversible.

Table II. Dark Electrochemical Parameters and Composition of Modified Electrodes on Pt and SnO₂^a

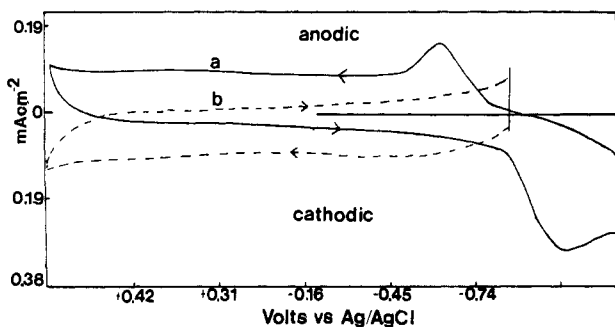
(A) Parameters ($i_{pc}/i_{pa} = 1$)							
no.	scan rate, mV/s	E_{pc} , V	E_{pa} , V	E_p , mV	i_{pc} , A/cm ²	i_{pa} , A/cm ²	D_{app} , cm ² s ⁻¹ × 10 ¹²
1	30	0.170	0.350	180	320	120	12.00
	100	0.166	0.370	208	615	264	
2	30	0.190	0.350	150	71	52	2.20
	100	0.200	0.370	160	124	92	
3	30	0.140	0.350	210	112	112	8.08
	100	0.120	0.370	249	195	195	
4	30	0.120	0.400	280	121	78	6.41
	100	0.080	0.430	350	195	134	
5	30	0.230	0.360	120	7	7	1.03
	100	0.200	0.380	150	18	15	
6	30	0.210	0.380	170	137	69	2.41
	100	0.180	0.410	230	214	132	
7	30	0.089	0.430	298	117	117	2.41
	100	0.061	0.390	373	181	181	

(B) Composition							
no.	modified electrode	concn of complex, mol cm ⁻³ × 10 ³	concn of complex, mol cm ⁻² × 10 ⁷	concn of polymer, ^c mol cm ⁻² × 10 ⁶	thickness (<i>l</i>), μm	(QPVP)/(M(mnt) ₂ ²⁻)	% QPVP sites neutralized by M(mnt) ₂ ²⁻
1	Pt-QPVP-Ni(mnt) ₂ ²⁻	1.39	4.18	2.68	3.0	6.40	31.14
2	Pt-QPVP-Pt(mnt) ₂ ²⁻	0.96	2.88	2.66	3.0	9.20	21.62
3	SnO ₂ -QPVP-Ni(mnt) ₂ ²⁻	0.87	1.92	2.36	2.2	12.30	16.24
4	SnO ₂ -QPVP-Pt(mnt) ₂ ²⁻	1.24	2.24	1.66	1.8	7.40	26.88
5	Pt-QPVP-Pt(mnt) ₂ ²⁻	0.62	2.48	3.25	4.0	12.50	15.27
6	SnO ₂ -QPVP-Ni(mnt) ₂ ²⁻	1.23	2.46	1.73	2.0	7.03	28.43
7	SnO ₂ -QPVP-Ni(mnt) ₂ ²⁻	0.94	1.88	2.25	2.0	12.00	16.67

^aSubscripts: p = peak; c = cathode; a = anode; app = apparent. ^bApparent diffusion coefficient obtained from i vs. $t^{-1/2}$ plot upon polarization beyond the anodic wave potential. ^cExpressed as moles of cationic sites.

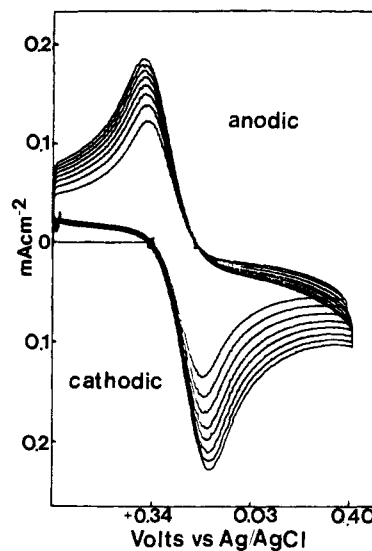
Table III. Relation between Percent of Ion-Exchange Sites Occupied by mnt Complex and Ratio of Cathodic to Anodic Peak Currents

% charge neutralized by M(mnt) ₂ ²⁻	i_{pc}/i_{pa}
16.5	1.0
21.0	1.3
26.5	1.6
28.4	1.9
30.5	2.6

**Figure 2.** Cyclic voltammograms for the quaternized polymer films in contact with water (a) and with 0.1 M KCl (b).

A representative cyclic voltammogram from an electrode loaded with the Ni complex is shown in Figure 3. In all cases, plots of peak current against square root of scan rate were linear. As well, the plot of current vs. square root of time after a potential step to a potential positive of the anodic peak was linear.

In Table II, closer inspection reveals that, despite the presence of the wave for the 2-/1- couple at potentials close to those found in solution, the peak currents and charges passed are not identical in all cases. In Table III, the ratio of cathodic to anionic peak currents is shown as a function of loading of ion-exchange sites with the dianionic complex. It is apparent that high loading is associated with departure of the current ratio from unity. Table IV shows the effects of anion changes in the series fluoride, chloride, bromide on the reversibility of the CV's. (There was little effect of changes of cation (i.e. Li⁺, Na⁺, K⁺) in the supporting electrolyte.)

**Figure 3.** Cyclic voltammograms of Ni(mnt)₂²⁻ in the film in contact with 0.1 M KCl (electrode 3). Scan rates vary from 30 to 100 mV/s in successive steps of 10 mV/s.**Table IV.** Effect of Electrolyte on Peak Potentials of SnO₂-QPVP-Ni(mnt)₂²⁻

electrode character ^d	electrolyte	E_{pc} , ^a V	E_{pa} , ^b V	ΔE_p , ^c mV
similar to 7	0.1 M NaBr	0.074	0.453	379
	0.1 M NaCl	0.099	0.483	384
	0.1 M NaF	0.130	0.532	402
similar to 6	0.1 M NaBr	0.054	0.440	100
	0.1 M NaCl	0.073	0.470	397
	0.1 M NaF	0.054	0.640	586

^a E_{pc} = cathodic peak potential. ^b E_{pa} = anodic peak potential. ^c ΔE_p = peak separation in mV. ^dSee Table II, part B.

3. Photoelectrochemistry. Six electrodes carrying M(mnt)₂²⁻ will be discussed; their loading and polymer concentrations were summarized in Table I. Steady-state current voltage curves under

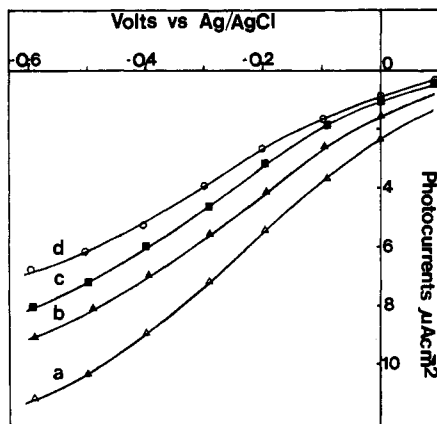


Figure 4. "Steady-state" photocurrent voltammograms for films carrying $\text{Ni}(\text{mnt})_2^{2-}$ in contact with 0.1 M KCl. From bottom (a) to top (d) the curves represent successive scans.

illuminations are presented in the voltage range 0.0 to -0.6 V, where $\text{SnO}_2\text{-QPVP}$ is inactive. Electrodes a and b carry the Ni complexes the photocurrent potential curves (shown in Figure 4 for electrode a) are of similar form to those reported earlier for the Ni complexes in solution.¹ Cathodic photocurrents are observed with the suggestion of a pseudopolarographic wave near -0.3 V.

There are two major differences from behavior of complexes in homogeneous CH_3CN solution. First, the observed cathodic photocurrent is several microamperes compared to *maxima* of a few nanoamperes in homogeneous solution. The film molar concentrations are larger than solution concentrations. This may be in part responsible for this increase. But complexes cannot diffuse nearly as freely in the films, so the reasons for increases must be sought in a factor beyond concentration effects. Second, the electrodes are not stable. On initiation of illuminations, photocurrent grows over a short but perceptible period before reaching an approximate stationary state. Also, as Figure 4 shows, the photocurrents decay on repetition of the experiment. The behavior of electrode b was similar to that of a except that changes on successive scans were smaller at the higher loading and that the maximum currents did not increase proportionately to concentration increase. CV's recorded after use of electrodes for steady-state photoelectrochemical voltammograms show that the $\text{Ni}^{2+}/\text{Ni}^+$ couple has become less reversible (peak broadening). It is worth noting that changes in the CV after photoelectrochemical runs were more significant for the anodic peaks.

The first point to be made about electrodes carrying $\text{Pt}(\text{mnt})_2^{2-}$ is the time dependence of the photocurrents. There are four stages of an experiment: (1) On initiation of illumination a photocurrent is observed promptly. (2) As illumination continues, this current rises slowly. (3) When the light is turned off, the current drops promptly to a value that is above the initial base line. (4) It then completes the return to base line in a slower (several seconds) decay. It is not possible to speak of a well-defined steady-state current, and the values of photocurrent vary by more than 20% as one repeats measurements on one electrode. In Figure 5, representative behavior of electrode c is shown. The figure shows the second "scan" of the photocurrent potential curve. The curve marked c represents the total photocurrent as read after 2 min of illumination. Curve a shows that part which appears promptly (photocurrent observable immediately after the light is turned on), and curve b shows the part that grows in over 2 min.

A dark voltammogram recorded after a photoelectrochemical scan shows a reduction of peak height and some peak broadening similar to that described above for $\text{Ni}(\text{mnt})_2^{2-}$. But, in addition, after photoelectrochemical runs, solvent reduction appears to have moved to less cathodic potentials and is preceded by a shoulder.

The spectrum of this Pt complex in the film also changes after photolysis. The main visible band at 472 nm decreases, a small peak appears at 445–450 nm, and a near-IR band at 855 nm appears. Electrode d was treated similarly to electrode c except

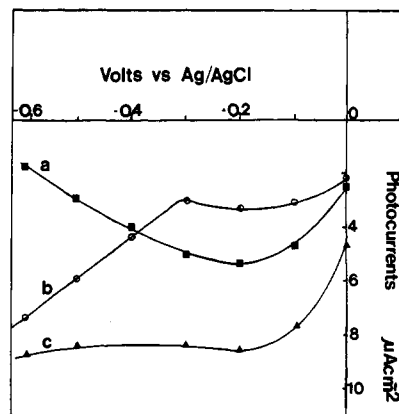


Figure 5. "Steady-state" photocurrent voltammograms for films carrying $\text{Pt}(\text{mnt})_2^{2-}$ in contact with 0.1 M KCl: (a) prompt photocurrent; (b) slow photocurrent; (c) total photocurrent. Scans begin from 0 V (see text).

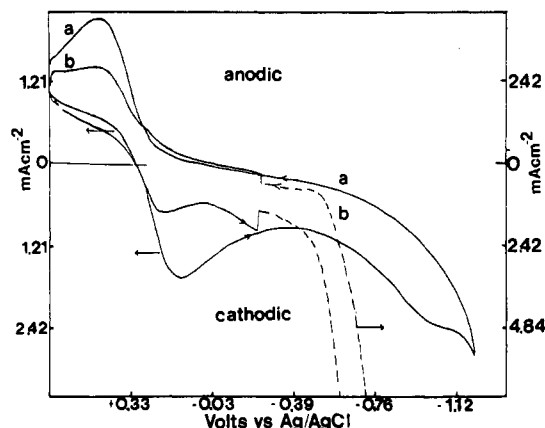


Figure 6. Cyclic voltammogram of $\text{Pt}(\text{mnt})_2^{2-}$ bearing electrode f in contact with 0.1 M KCl (a) before and (b) after irradiation for 10 h at -0.4 V.

that photoelectrochemical experiments were initiated at -0.6 V and stepped to 0.0 V in the anodic direction. Behavior was qualitatively similar to that seen with electrode c, but "final" (after two runs) photocurrents were somewhat smaller than those seen in the experiments with electrode c. Electron micrographs reveal that microcrystallites are forming on the surface of what was initially a smooth, featureless, film as a consequence of running photoelectrochemistry. The distribution of complex in the film changes significantly.

Electrodes e and f were used in experiments to determine the effects of irradiation from front and back (through the solutions and through the glass). Electrode e was used in back (through the glass) illumination and electrode f was used in front (through the solution) illumination. The significant result is that the *prompt* component of the photocurrent is initially larger when illumination is from the back (glass). Conversely, the slow photocurrents were a larger fraction of initial currents with illumination from the front (solution) side.

A final experiment involved prolonged irradiation of an electrode for 10 h polarized at -0.40 V. The electrolyte solution was circulated through the cell at 20 mL/min. The voltammograms before and after this prolonged irradiation are shown in Figure 6. After irradiation the wave for reduction in the polymer is not seen since bubbles vigorously evolve from the surface of the modified electrode at -0.50 V. The color was distinctly green, indicating the $\text{Pt}(\text{mnt})_2^{2-}$ complex in the film. The spectrum before the after irradiation is shown in Figure 7.

Discussion

The nickel complexes in the film show significantly increased photocurrents compared to homogeneous solution. Two possible reasons suggest themselves. The first is that excited-state lifetimes are extended by immobilization. There is precedent for this idea.^{2,3}

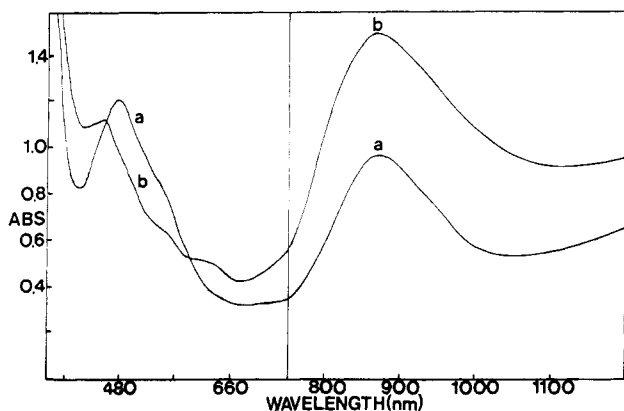


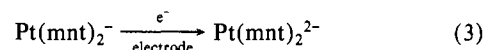
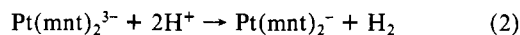
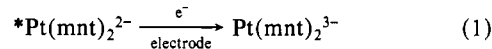
Figure 7. Absorption spectra of the electrode described in Figure 6 (a) before and (b) after irradiation.

Unfortunately, no luminescence evidence is available to decide the present case. The second possibility is that either neighboring complexes or, more probably, the π^* levels of the pyridine units of the backbone are available to act as electron-transfer partners with the excited state in the short time available before it decays. (An energy-transfer mechanism is less likely since excited-state lifetimes are so short in solution.^{1,4}) Whichever mechanism is responsible for the increase, the mobility of ionic species in the present films is not great and may limit efficiency. There is a requirement to transport anions in and out of the film as the charge on the complex changes, and the voltammograms of films are quite

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 (4) Persaud, L.; Sharma, D. K.; Langford, C. H. *Inorg. Chim. Acta* **1986**, *114*, L5.

sensitive to anions in the supporting electrolyte. We are now trying to extend work to ion-exchange polymer films in which ions are more mobile.

The Pt complexes behave similarly to those of Ni, with the quantitative difference that "recrystallization" on the film is more pronounced and the history of a film is more important. In addition, the development of the mixed-oxidation-state system produces an interesting heterogeneous electrocatalytic system for H_2 evolution at modest overpotentials. It is difficult to suggest just how the system may work. One possibility is



Two objections can be raised. First, the above cycle does not appear to need to wait for the "recrystallization" of the complex in the film into the solid particles "visible" to SEM, whereas the generation of H_2 is important only after some time of irradiation. Second, picosecond flash results reported recently⁴ indicate that the "triplet" excited state of $Pt(mnt)_2^{2-}$ is directly quenched by water in what is probably an electron-transfer step. Thus, the path is more complex. The steps shown in eq 1-3 may reflect, at best, a simplified monomolecular model for reactions occurring at the surface of mixed-oxidation-state microcrystalline particles. When solid $(R_4N)_2Pt(mnt)_2$ powders are dispersed in O_2 -free water and irradiated, they do undergo oxidation.

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Registry No. $Ni(mnt)_2^{2-}$, 14876-79-0; $Pt(mnt)_2^{2-}$, 15152-99-5; SnO_2 , 18282-10-5; KCl, 7447-40-7; NaBr, 7647-15-6; NaCl, 7647-14-5; NaF, 7681-49-4; Pt, 7440-06-4; 4-vinylpyridine-styrene copolymer compound with benzyl chloride, 103564-34-7.

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Semireduced Bridging Ligands Containing $-N=N-$ Multiple Bond Coordination Sites. ESR Study of Binuclear Group 6 Metal Carbonyl Complexes

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Centrosymmetric binuclear metal carbonyl complexes of anion radical ligands containing the azo group $-N=N-$ were studied by ESR. The ligands employed were 1,2,4,5-tetrazine (tz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), and azo-2,2'-bipyridine (abpy), and the following radical complexes were studied: $(\mu-(N^1, N^4)\text{-tz}^{\cdot-})[M(CO)_5]_2$ ($M = Mo, W$); $(\mu\text{-bptz}^{\cdot-})[M(CO)_4]_2$ and $(\mu\text{-abpy}^{\cdot-})[M(CO)_4]_2$ ($M = Cr, Mo, W$). The ESR spectra of abpy species are line rich and insufficiently resolved so that ENDOR spectroscopy was used in one case, viz., $(\mu\text{-abpy}^{\cdot-})[Mo(CO)_4]_2$. In contrast, the tetrazine complexes exhibit a rather simple ESR hyperfine structure because of spin localization at the four nitrogen centers in the tetrazine ring. The observed response of the hyperfine structure on metal coordination is well reproduced by HMO-McLachlan perturbation calculations of the spin distribution. Double coordination of equivalent metal fragments and spin localization at the tetrazine nitrogen centers create exceptionally favorable conditions to detect metal isotope coupling; a survey of these and several related anion radical complexes shows that the small metal isotope splittings are caused by σ/π spin polarization originating from the coordinating nitrogen π center.

Introduction

Compounds containing the azo group, $-N=N-$, such as azoalkanes, azoaromatics, or the cyclic conjugated 1,2,4,5-tetrazines are generally π -electron deficient;¹ they may be reduced at rather positive potentials² to form stable anion radicals³ or

dianions.^{2a,c} The nitrogen atoms in the azo linkage $-\bar{N}=\underline{N}-$ have unshared electron pairs available for coordination of electrophiles,

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