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Spectral, Electrochemical, and Electrocatalytic Properties of 1,10-Phenanthroline-5,6-dione Complexes of Transition Metals

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The synthesis and the spectral and the electrochemical characterization of 1,10-phenanthroline-5,6-dione (phen-dione) complexes of Ru, Fe, Os, Co, and Cu are presented. The visible spectra of these complexes are analogous to those of phenanthroline complexes except that there is a blue shift in the wavelength of maximum absorption. The electrochemical response of these complexes is characterized by metal-localized oxidations that are shifted positive from those of the analogous phenanthroline complexes. Both effects are consistent with the stronger π acidity of the phen-dione as compared to phenanthroline. The quinone-based redox properties of the phen-dione ligand are retained after coordination to a metal ion so that in nonaqueous solvents, the complexes exhibit two additional reduction waves. In aqueous solvent, only one additional pH-dependent wave is observed. In a number of cases, the complexes adsorb very strongly to give rise to electrodes modified with an electrochemically active layer of the complex. Some of the complexes exhibit electrocatalytic activity toward NADH oxidation both in solution and as immobilized films on electrodes.

Introduction

The development of electrocatalytic[1] systems depends in part on the development of systems that can undergo multiple electron transfers as well as being amenable to the fine tuning of redox potentials through synthetic variations or other means. This is dictated in part by the need to have systems whose redox levels can be shifted so as to achieve a good match with those of the desired rection and also by the need to transfer more than one electron so as to circumvent the formation of high-energy intermediates.

These aspects have been explored in a number of applications. Meyer[2] very recently made an extensive exposition of how to control reactivity by suitably modifying the coordination environment around a metal ion as well as how to achieve multiple electron transfers by coupling redox processes associated with dimers or higher order clusters. He also pointed to the importance of structural aspects in achieving desired elecrocatalytic effects.

The same types of effects have been explored in the use of macrocycles to acheive catalytic effects in reactions such as the reduction of O_2. An elegant example of this is the work of Anson, Collman, and co-workers[3] where the interplay among structure, ability to transfer more than one electron, and electrocatalytic acitivty was clearly demonstrated in a family of cofacial porphyrins.

We recently began a study of the control and modulation of electrochemical reactivity through the introduction of additional redox centers into a metal complex as well as through the control of redox potentials by changes in pH. The focus is on complexes of 1,10-phenanthroline-5,6-dione (phen-dione)[4] because this ligand has the ability to form stable complexes with a wide variety of metal ions and carries an *o*-quinone moiety with pH-dependent electroactivity. Metal complexes of this ligand potentially allow for the variation and control of redox properties over a wide range as well as the fine tuning of potentials through pH changes.

We present here work related to the synthesis, spectroscopic and electrochemical characterization, and electrocatalytic activity of phen-dione complexes of transition metals.

Experimental Section

Reagents. Tetra-*n*-butylammonium perchlorate (TBAP) (G. F. Smith) was recrystallized three times from ethyl acetate and dried in vacuo at 90 °C for 72 h, and phen-dione was obtained from G. F. Smith Co. All other ligands were obtained frm Aldrich Chemical Co. and were used as received. Acetonitrile and dimethyl sulfoxide (Me_2SO) (Burdick and Jackson, distilled in glass) were dried over 4-Å molecular sieves. Water was purified by passing through a Hydro Systems purification train. NADH was obtained from Sigma Chemicals and was used as received. All other reagents were of at least reagent grade quality and were used without further purification.

Synthesis. [Fe(phen-dione)$_3$](PF$_6$)$_2$·2H$_2$O (1). The preparation used 3.2 molar equiv of phen-dione in ethanol added to 1 equiv of ferrous ammonium sulfate dissolved in water. The formation of the complex was apparent by the immediate formation of a reddish solution. The mixture was allowed to stir at room temperature for 30 min, and the complex was precipitated as a red solid by the addition of saturated aqueous NH_4PF_6. The complex was collected, washed with water, and dried with ether. Because this material, as well as the other complexes, adsorbed very strongly on alumina and silica gel, recrystallization from acetonitrile/ether was used for purification. The complex was dried in vacuo for 24 h and stored in a desiccator. Anal. Calcd: C, 42.67; H, 2.17; N, 8.30. Found: C, 42.49; H, 2.29; N, 8.79.

[Os(phen)$_2$(phen-dione)](PF$_6$)$_2$·2H$_2$O (2). [Os(phen)$_2$Cl$_2$] in thoroughly deareated ethylene glycol was refluxed for 3 h in the presence of a 3-fold excess of phen-dione. The reaction mixture was allowed to cool, and an equal volume (ca. 20 mL) of water was added. The complex was precipitated as a dark green solid by adding aqueous saturated NH_4PF_6. The complex was collected, washed with water, and dried with ether. It was purified by recrystallization from acetonitrile/ether, dried in vacuo for 24 h, and stored in a desiccator. Anal. Calcd: C, 39.77; H, 2.39; N, 7.73. Found: C, 39.82; H, 2.24, N, 7.74.

[Os(bpy)$_2$(phen-dione)](PF$_6$)$_2$·2H$_2$O (3). This complex was synthesized by the procedure described for **2** above except that [Os(bpy)$_2$Cl$_2$] was used in place of [Os(phen)$_2$Cl$_2$].

[Ru(phen-dione)$_2$Cl$_2$] (4). This material was synthesized following the procedure of Meyer et al.[5] for the synthesis of [Ru(bpy)$_2$Cl$_2$] except that the phen-dione was used in place of 2,2′-bipyridine.

[Ru(phen-dione)$_3$](PF$_6$)$_2$·2H$_2$O (5). [Ru(phen-dione)$_2$Cl$_2$] was heated at reflux under N_2 in thoroughly deaerated 50/50 ethanol/water with 1.2 equiv of phen-dione for 3 h. When the reaction mixture had cooled, the complex was precipitated as a dark brown solid and purified by using the procedure described for **1** above.

[Ru(phen-dione)$_2$(bpy)](PF$_6$)$_2$·2H$_2$O (6). [Ru(phen-dione)$_2$Cl$_2$] was heated at reflux under N_2 in thorougly deaerated 50/50 ethanol/water with 1.2 equiv of 2,2′-bipyridine for a period of 3 h. After the reaction mixture was allowed to cool, the complex was precipitated (brown solid) and purified by using the procedure described for **1** above. Anal. Calcd: C, 40.66; H, 2.39; N, 8.37. Found: C, 40.81; H, 2.42; N, 9.13.

[Ru(bpy)$_2$(phen-dione)](PF$_6$)$_2$·2H$_2$O (7). [Ru(bpy)$_2$Cl$_2$]·2H$_2$O was reacted at reflux under N_2 with 1.2 molar equiv of phen-dione in thoroughly deareated 50/50 ethanol/water for a period of 3 h. After the reaction mixture was allowed to cool, the complex was precipitated (greenish brown solid) and purified as described for **1** above.

[Co(phen-dione)$_3$](PF$_6$)$_2$·3H$_2$O (8). Ethanol solutions of $CoCl_2·6H_2O$ and phen-dione in a 1/3.3 ratio were mixed and allowed to stir for 30 min. Precipitation (as a tan solid) and purification of the complex followed the procedure described for **1** above. Anal. Calcd: C, 41.80; H,

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(1) (a) Saveant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323. (b) Franklin, A. D., Ed. "Electrocatalysis on Non-Metallic Surfaces"; U.S. Government Printing Office: Washington, DC, 1976; NBS Spec. Publ. (U.S.) No. 455. (c) Breiter, M. W., Ed. "Electrocatalysis"; The Electrochemical Society: Princeton, NJ, 1974.

(2) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C.

(3) (a) Collman, J. P.; Marrocco, M.; Denisevich, P.; Koval, C.; Anson, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 117. (b) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027.

(4) The abbreviations used are 2,2′-bipyridine = bpy and phenanthroline = phen.

(5) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

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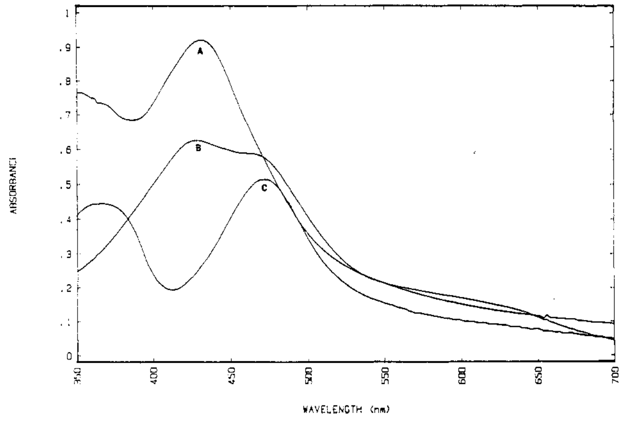

Figure 1. Visible absorption spectra in acetonitrile for 4.8 × 10^{-5} M solutions: (A) $[Ru(bpy)(phen\text{-}dione)_2]^{2+}$; (B) $[Os(phen)_2(phen\text{-}dione)]^{2+}$; (C) $[Fe(phen\text{-}dione)_3]^{2+}$.

2.32; N, 8.13. Found: C, 41.52; H, 2.50; N, 8.06.

$[Cu(phen\text{-}dione)_2](PF_6)_2{\cdot}2H_2O$ (9). A solution of $CuCl_2{\cdot}2H_2O$ in ethanol was mixed with an ethanol solution containing 2 molar equiv of phen-dione. Upon mixing, the solution turned green, indicative of complex formation. After the mixture was allowed to stir for 30 min, the complex was precipitated (green solid) and purified as for **1** above. Elemental Anal. Calcd C, 43.31; H, 2.41; N, 8.42. Found: C, 43.61; H, 2.26; N, 9.34.

$[Co(phen)_3](PF_6)_2$, $[Cu(phen)_2](PF_6)$, and $[Cu(bpy)_2](PF_6)$ were synthesized by following published procedures.[6,7]

Optical and Infrared Spectroscopy. Electronic absorption spectra in acetonitrile solvent were obtained on a Hewlett-Packard Model 7451 spectrophotometer and infrared spectra were obtained on a Perkin-Elmer Model 137 spectrometer using KBr pellets.

Electrochemistry. Cyclic voltammetric experiments were performed on either a Princeton Applied Research Model 173 potentiostat, Model 179 digital coulometer and Model 175 universial programmer or a locally built potentiostat and signal generator combinaion. Data were recorded on a Hewlett-Packard Model 7045-B or Soltec Model VP-6423S X-Y recorder. Experiments in acetonitrile used 0.1 M TBAP as supporting electrolyte. Electrochemistry in aqueous media was performed in acetate, phthalate, phosphate, and borate buffers, depending on the desired pH. The ionic strength of the buffers was adjusted to 1.0 M by the addition of NaCl. A three-electrode system consisting of a platinum-disk or pyrolitic graphite working electrode, a platinum-wire counter electrode and a sodium-saturated calomel (SSCE) reference electrode was used in conjunction with a standard three-compartment electrochemical cell fitted with medium-porosity fritted glass disks.

All potentials are referenced to the sodium-saturated calomel electrode without consideration of the liquid junction potential.

An acidity scale in 50/50 and 75/25 (vol/vol) water Me_2SO mixtures was established by following the procedure of Evans and coworkers.[8]

Results and Discussion

Spectral Characteristics. Electronic absorption and infrared spectroscopic measurements were carried out in order to ascertain the effect of the phen-dione ligand on the spectral properties of the complexes. Representative visible spectra are shown in Figure 1, and the spectral data are collected in Table I. The visible spectra are similar to those of the corresponding phen or bpy complexes except that there is a blue shift in the maximum wavelength of absorption. For example the tris(phenanthrolinedione) complex of iron has a maximum absorption at 472 nm as compared to the tris(phenanthroline) complex, whose wavelength of maximum absorption is 508 nm. A similar effect is observed for the osmium and ruthenium complexes. In the case of ruthenium, we prepared the entire series $[Ru(bpy)_{3-x}(phen\text{-}dione)_x]^{2+}$ (where x goes from 0 to 3). As expected, the energy of the transition increases with increasing number of phen-dione ligands and, in fact, a plot of $1/\lambda_{max}$ vs. the number of coordinated phen-dione ligands is linear (r = 0.99), indicating the additivity of this effect. This effect essentially reflects the enhanced π acidity of the phen-dione ligand relative to that of phenanthroline.

Table I. Spectroscopic Data for phen-dione Complexes

complex	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	ν_{IR}(C=O), cm^{-1}
$[Os(bpy)_2(phen\text{-}dione)]^{2+}$	248	50.6	1690
	290	80.7	
	368	12.4	
	458	15.9	
	656	3.6	
$[Os(phen)_2(phen\text{-}dione)]^{2+}$	266	72.3	1688
	430	13.0	
	460	12.3	
	594	2.4	
$[Co(phen\text{-}dione)_3]^{2+}$	254	92.8	1692
	300	21.3	
	312	20.9	
$[Cu(phen\text{-}dione)_2]^{2+}$	734	0.16	1698
$[Ru(phen\text{-}dione)_3]^{2+}$	252	51.3	1650, 1700
	270	4.9	
	368	13.4	
	428	10.3	
$[Ru(bpy)(phen\text{-}dione)_2]^{2+}$	248	86.9	1667, 1633
	286	72.7	
	352	15.9	
	432	19.2	
$[Ru(bpy)_2(phen\text{-}dione)]^{2+}$	246	40.3	1690
	288	68.1	
	442	13.9	
$[Fe(phen\text{-}dione)_3]^{2+}$	252	76.1	1683
	300	23.8	
	312	26.9	
	368	7.7	
	472	9.5	
phen-dione	256	40.2	1675
	292	4.5	
	370	0.52	

The UV spectrum is dominated by ligand localized π to π^* transitions (see Table I).

In the infrared region of the spectrum the bands associated with the carbonyl stretch are the most relevant. By comparison of the spectra of the metal complexes with those of phen-dione and phenanthroline, it was determined that the bands centered at about 1700 and 1300 cm^{-1} (Table I) are carbonyl stretches on the phen-dione ligand. In general, the carbonyl stretches are relatively insensitive to changes in the metal center, a reflection of the fact that the effect of the metal center and its coordination environment on the carbonyl stretch is a secondary effect.

Electrochemical Characterization. Cyclic voltammetry (CV) was used to examine the electrochemical behavior of these complexes. To better understand the observed behavior, we begin by describing the electrochemical behavior of phen-dione and then preceed to discuss the electrochemical behavior of the complexes.

The phen-dione ligand is electrochemically active due to the presence of the o-quinone moiety. (It should be mentioned that phenanthroline itself is also electroactive, but at much more negative potentials than those used in this work.) As with quinones in general, the electrochemical behavior is strongly dependent on whether an aprotic solvent such as acetonitrile or an aqueous solvent is employed. In acetonitrile the free ligand shows two reversible one-electron-reduction waves (Figure 2A). The formal potentials for the processes are −0.45 and −1.25 V, and they represent the formation of the ion radical and dianion of the ligand. In aqueous solvent the process is the two-electron, two-proton reduction of the quinone to the hydroquinone so that only a single, pH-dependent electrochemical wave is observed (Figure 2B). We observe a shift of about 63 mV/pH unit, close to the expected value of 59 mV/pH unit for the two-electron two-proton process. It should be mentioned, however, that at pH higher than about 5, the reduction process is chemically irreversible, so that only a reduction wave (i.e. no oxidation counterpart) is observed (Figure

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(6) Schilt, A. A. "Analytical Applications of 1,10-Phenanthroline and Related Compounds"; Pergamon Press: Oxford, 1969; Int. Ser. of Monogr. Anal. Chem. Vol. 32.

(7) McWhinnie, W. R.; Miller, J. D. *Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(8) Evans, D. H.; Griffith, D. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *134*, 301.

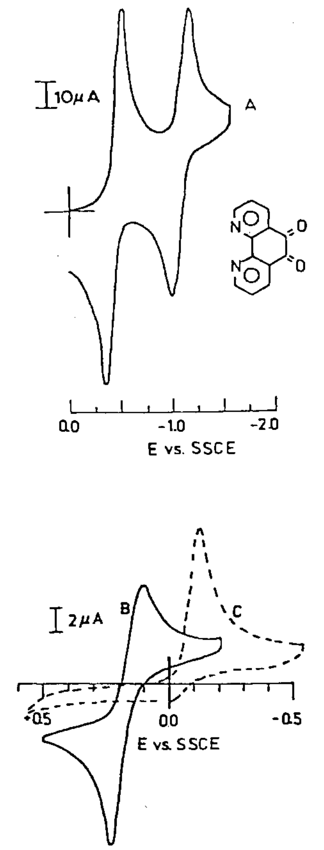

Figure 2. (A) Cyclic voltammogram for a 1.2 mM solution of phen-dione in acetonitrile containing 0.1 M TBAP at a pyrolitic graphite electrode (0.07 cm^2) at a sweep rate of 0.2 V/s. (B, C) Cyclic voltammograms on a platinum electrode (0.03 cm^2) at 0.2 V/s for 1.1 mM phen-dione in aqueous solutions of pH 2.85 (acetate buffer) (curve B) and pH 6.8 phosphate buffer (curve C).

2C). Evans and co-workers[8,9] have studied the pH dependence of the reduction of this ligand, and they observed reversible voltammograms at pH values up to 9.2 in a 50/50 mixture of Me_2SO/H_2O as solvent. They do report, however, that at pH greater than 9 phen-dione gives rise to 4,5-diazafluorenone. We believe the same process is involved here, except that the absence of Me_2SO in our case makes it occur at lower pH values.

This is supported by cyclic voltammetric experiments of the ligand as a function of pH in 50/50 and 75/25 water/Me_2SO mixtures. In 50/50 water/Me_2SO we obtained results in accordance with those reported by Evans and co-workers.[8] In 75/25 water/Me_2SO, the reduction process became chemically irreversible at a pH of about 7.2, indicating a decreased stability of the reduction product. Thus, we believe that the processes observed by Evans and ourselves are the same except that they take place at a lower pH as the water/Me_2SO ratio increases.

With the above information in mind, the electrochemical behavior of this family of complexes can be addressed, and by consideration of the individual components of the complexes, the voltammetric response can be qualitatively predicted. The presence of metal centers such as Fe, Ru, and Os suggests that a metal-localized oxidation should be expected. In aprotic solvents the phen-dione should contribute two reduction waves, and each bipyridine or phenanthroline ligand will contribute an additional reduction wave (at more negative potentials than the phen-dione-based processes). In aqueous media a single, pH-dependent, phen-dione-based redox wave should be observed along with a pH-independent metal-localized oxidation. In aqueous media the bpy- and phen-localized reductions are beyond hydrogen evolution and thus are not observed.

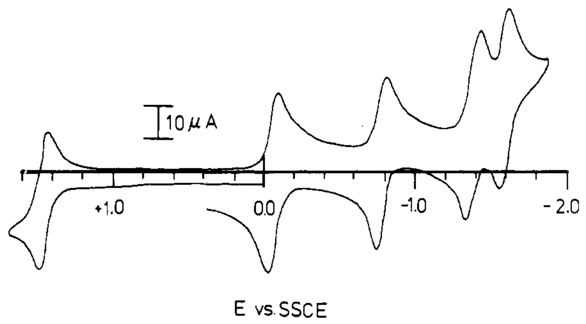

Figure 3. Cyclic voltammogram at 0.2 V/s for 1.5 mM $[Ru(bpy)_2(phen\text{-}dione)]^{2+}$ in acetonitrile containing 0.1 M TBAP at a platinum electrode (0.03 cm^2).

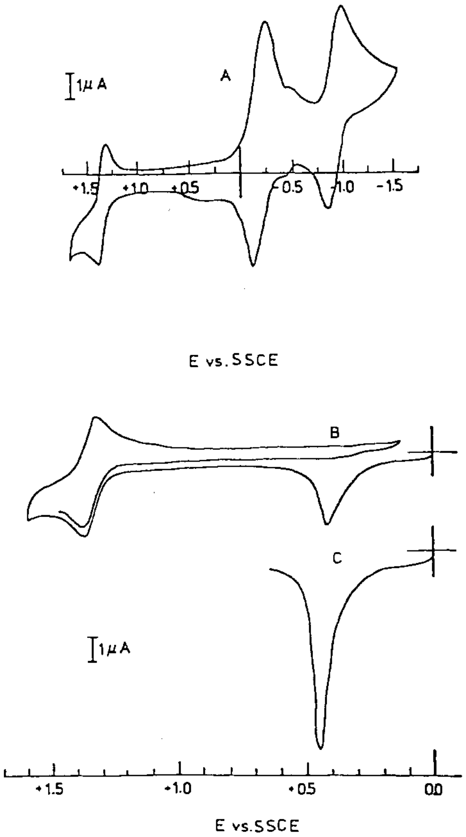

Figure 4. (A) Cyclic voltammogram at a platinum electrode (0.03 cm^2) at 0.2 V/s for 0.5 mM $[Fe(phen\text{-}dione)_3]^{2+}$ in acetonitrile containing 0.1 M TBAP. (B, C) Cyclic voltammograms for $[Fe(phen\text{-}dione)_3]^{2+}$ in acetonitrile depicting the adsorption of the complex upon standing at 0.0 V for 10 s (curve B) and 30 s (curve C).

Our experiments support the above predictions. Figure 3 shows a cyclic voltammogram of $[Ru(bpy)_2(phen\text{-}dione)]^{2+}$ in acetonitrile/0.1 M TBAP. The complex exhibits five one-electron reversible waves, which can be ascribed to the following processes: the wave centered at $E^{\circ\prime} = 1.35$ V is associated with the metal-localized $Ru^{II/III}$ oxidation, analogous to that of other bpy and phen complexes of ruthenium. The potential of this wave is shifted positive relative to that of the analogous phen compound, again consistent with the higher π acidity of the ligand. The reduction waves at −1.39 and −1.59 V are associated with bipyridine-localized reductions. This leaves two redox processes at −0.065 and −0.77 V that we ascribe to the reduction of the coordinated phen-dione ligand. The potentials are shifted positive relative to that of the free ligand due to the coordination to the ruthenium center. In aqueous solvent (Figure 6A) the complex exhibits a single, pH-dependent phen-dione-based wave, which shifts by approximately 56 mV/pH unit.

The electrochemistry of the other complexes under study was qualitatively similar to that described above, and the results are

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(9) Evans, D. H.; Griffith, D. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *136*, 149.

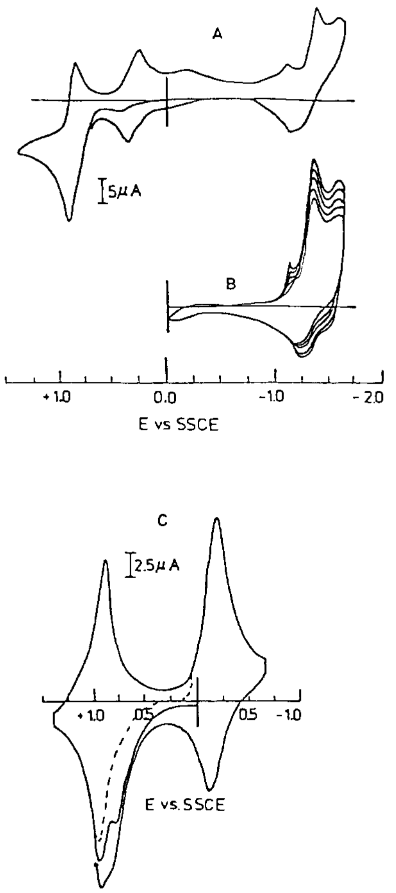

Figure 5. (A) Cyclic voltammogram at a platinum electrode (0.03 cm^2) at 0.2 V/s for 1.5 mM $[Os(phen)_2(phen\text{-}dione)]^{2+}$ in acetonitrile solution containing 0.1 M TBAP. (B) Consecutive sweeps depicting the surface deposition of the complex. (C) Cyclic voltammogram at 0.5 V/s in acetonitrile containing 0.1 M TBAP for a platinum electrode (0.03 cm^2) modified with a thin film of $[Os(phen)_2(phen\text{-}dione)]^{2+}$.

Table II. Electrochemical Data for Phenanthroline-5,6-dione Complexes of Transition Metals

complex	formal potentials^a				
	metal	phen-dione		bpy or phen	
phen-dione		−0.445	−1.251		
$[Co(phen\text{-}dione)_3]^{2+}$	+0.65	−0.112	−0.425		
$[Cu(phen\text{-}dione)_2]^{2+}$	+0.42^b	+0.98^b	−0.385		
$[Fe(phen\text{-}dione)_3]^{2+}$	+1.36	−0.175	−0.92		
$[Ru(phen\text{-}dione)_3]^{2+}$	+1.40	−0.13	−0.86		
$[Ru(bpy)(phen\text{-}dione)_2]^{2+}$	+1.43	−0.16	−0.89	−1.52	
$[Ru(bpy)_2(phen\text{-}dione)]^{2+}$	+1.35	−0.065	−0.77	−1.39	−1.59
$[Os(bpy)_2(phen\text{-}dione)]^{2+}$	+1.01	−0.067	−0.655	−1.32	−1.54
$[Os(phen)_2(phen\text{-}dione)]^{2+}$	+0.93	+0.38^b	−0.175	−1.31	−1.53

^{a} In acetonitrile with 0.1 M TBAP, potentials in volts referenced to SSCE. ^{b} E_p anodic.

summarized in Table II. There were, however, some observations that merit further description. Unlike the tris(bipyridine) complexes of iron and ruthenium, which show separate reduction waves for each of the ligands, cyclic voltammograms of the tris(phenanthrolinedione) complexes indicate that all the phen-dione ligands are electroactive at the same potential (e.g. Figure 4A for $[Fe(phen\text{-}dione)_3]^{2+}$). Thus, only two reduction waves are observed, and the height of these is considerably larger (ca. 3 ×) than that for the metal-localized oxidation.

In acetonitrile solution, $[Fe(phen\text{-}dione)_3]^{2+}$, $[Ru(bpy)(phen\text{-}dione)_2]^{2+}$, $[Os(phen)_2(phen\text{-}dione)]^{2+}$, and $[Co(phen\text{-}dione)_3]^{2+}$ all adsorbed strongly on the electrode surface to form electroactive layers. For the iron and ruthenium compounds adsorption took place at potentials negative of +0.40 and +0.60 V, respectively. If the potential was scanned in the positive direction after the electrode was potentiostated in the previously mentioned region, a sharp desorption peak was observed at about 0.45 V for the iron complex (Figure 4B,C) and at about 0.70 V for the ruthenium complex.

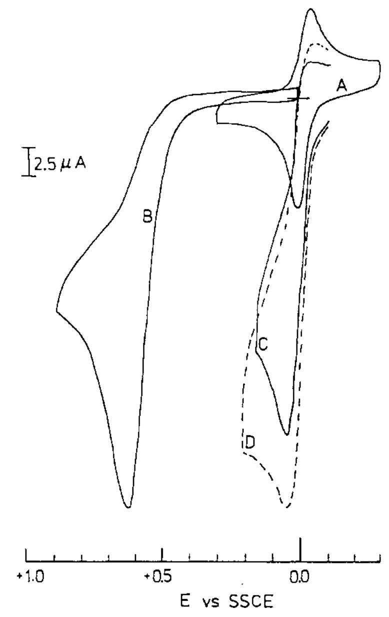

Figure 6. Solution electrocatalysis of NADH oxidation at a pyrolytic graphite electrode (0.07 cm^2): (A) cyclic voltammogram at 10 mV/s for 1.2 mM $[Ru(bpy)_2(phen\text{-}dione)]^{2+}$ in aqueous phosphate buffer (pH 6.8); (B) cyclic voltammograms at 10 mV/s for the direct oxidation of 5 mM NADH in aqueous phosphate buffer (pH 6.8). Conditions for curves C and D are the same as for curve A except for the presence of NADH at 4 and 5 mM concentrations, respectively.

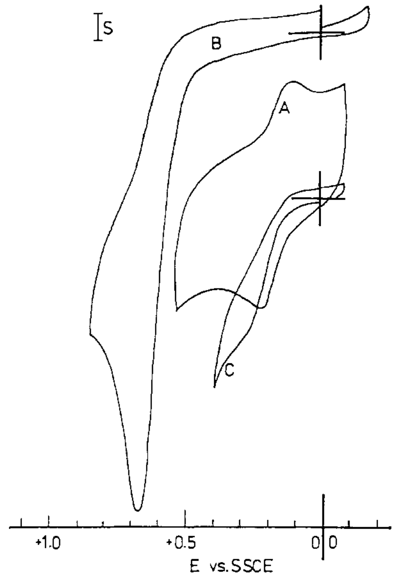

Figure 7. Surface electrocatalysis of NADH oxidation: (A) cyclic voltammogram at 0.2 V/s in aqueous phthalate buffer (pH 4.1) for a Pt electrode (0.1 cm^2) modified with a film of $[Os(phen)_2(phen\text{-}dione)]^{2+}$, s = 5 μA; (B) cyclic voltammogram at 0.2 V/s for the oxidation of 2.3 mM NADH at the naked platinum electrode; s = 5 μA; (C) same as for curve A but in the presence of 2.3 mM NADH, s = 25 μA.

For $[Os(phen)_2(phen\text{-}dione)]^{2+}$ (Figure 5A) it was found that when the potential between 0.0 and −1.80 V (Figure 5B) was scanned, the complex forms an electrochemically active film on the surface of the electrode, as the increasing current on successive sweeps suggests (Figure 5B). The film deposit retains the electrochemical reactivity of the complex in both acetonitrile (Figure 5C) and in water (Figure 7A). As predicted earlier, in aqueous solution the complex shows two waves, one which is independent of pH and is associated with the metal-localized oxidation and a second, pH-dependent wave associated with the phen-dione ligand (Figures 5 and 7). A film of this material was electrodeposited on a transparent electrode (tin oxide on glass), and the visible spectrum of the film was essentially identical with that of the complex in acetonitrile solution, indicating that there were no major changes in the coordination environment around the metal. At this point, we do not know the nature of the reaction(s) leading to the electrodeposition of this complex.

$[Co(phen\text{-}dione)_3]^{2+}$ adsorbed from both acetonitrile and aqueous solution to again give an electroactive layer on the surface of the electrode. The adsorbed material exhibited the expected pH dependence (59 mV/pH unit) in aqueous solvents.

The electrochemical behavior of $[Cu(phen\text{-}dione)_2)]^+$ was quite complex. It seems that upon oxidation at about +0.60 V, the complex decomposes (analogous to phenanthroline and bipyridine complexes of copper) to yield the free ligand and copper ions. This was confirmed by the fact that waves could be observed at potentials that were virtually identical with those of the free ligand itself, and furthermore when the potential well in the negative region was scanned, the plating of copper was apparent. For this reason the behavior of this material was not pursued further.

Electrocatalysis of NADH Oxidation. It is well documented that the direct oxidation of NADH (dihydronicotinamide adenine dinucleotide) at a platinum electrode surface suffers from a very large overpotential. Reported values for its oxidation on Pt electrodes range from about +0.7 to +0.9 V (vs. NHE)[10] whereas the reported reversible formal potential is about −0.32 V.[11] The oxidation of NADH and its electrocatalysis is also of interest from the standpoint of analytical applications for its determination in serum samples. Kuwana and co-workers[12,13] as well as Miller and co-workers[14] have investigated the electrocatalytic oxidation of NADH in homogeneous solution as well as by modified electrodes. They find that the process can be carried out by quinone groups and that, within this group, the *o*-quinones show the highest activity. Since the complexes under study carry such an *o*-quinone moiety, we decided to determine if these materials would be active toward the electrocatalytic oxidation of NADH.

We first explored the catalysis in homogeneous solution and chose to use the $[Ru(bpy)_2(phen\text{-}dione)]^{2+}$ complex since its electrochemical response was well characterized and it did not suffer from complications of adsorption. Figure 6A shows a cyclic voltammogram on a pyrolitic graphite electrode for a solution of $[Ru(bpy)_2(phen\text{-}dione)]^{2+}$ (1.7 mM) in aqueous phosphate buffer at pH 6.8, and one can see a well-developed wave associated with the quinone moiety of the phen-dione ligand. Figure 6B shows the voltammetric response for a solution containing NADH at a concentration of 5 mM. Parts C and D of Figure 6 show the electrochemical response for the ruthenium complex in the presence of 4 and 5 mM concentrations of NADH, respectively. (In curve D the concentration of NADH equals that of curve B.) It is immediately apparent that there is a very strong catalytic effect by the metal complex since the current at potentials in the vicinity of $E^{\circ\prime}$ for the complex increases dramatically, indicating that the compound is being turned over by the oxidation of NADH. There is very little cathodic current on the reverse sweep because only a small amount of the complex is present in the oxidized form. The current increase when the concentration of NADH is increased implies that the overall process is controlled by the diffusion of NAdH to the electrode surface. Identical peak currents for curves B and D support this.

Since the electrocatalytic activity of the material was clear, we explored the same reaction but at an electrode modified with a film of one of the complexes. $[Os(phen)_2(phen\text{-}dione)]^{2+}$ was chosen for this application because we had demonstrated that we could deposit thin films of this material on the surface of an electrode from acetonitrile solution.

Figure 7 shows the results obtained. Curve A is a cyclic voltammogram in aqueous phthalate buffer (pH 4.1) for a 0.1 cm^2 platinum electrode modified with a thin layer of the osmium complex. There is a wave present at about +0.15 V that we associate with the coordinated phen-dione ligand. Curve B represents the oxidation of 2.3 mM NADH at the naked electrode. Curve C shows the electrochemical response of the modified electrode in contact with the solution containing 2.3 mM NADH. The shape of the wave has now changed substantially as there is no discernible cathodic current. Furthermore the peak current is much larger than that for the case where there was no NADH present; the current scale for the voltammogram in the absence of NADH is 5 μA whereas the one for the modified electrode in the presence of NADH was obtained at 25 μA. Clearly, there is a dramatic catalytic effect by the immobilized complex. It should be mentioned, however, that the electroactivity decayed with time due to the desorption of the complex from the surface.

In conclusion, we have shown that one can modulate the electrochemical reactivity of transition-metal complexes by incorporating additional redox states localized on the ligands. Some of the materials were shown to be electrocatalytic toward the oxidation of NADH both in solution and on an electrode surface. The synthetic methodology is basically an extension of that for phenanthroline and bipyridine complexes, so a broad range of mixed-ligand and even mixed-metal complexes can be prepared. These results clearly point to the fact that these materials have potentially very interesting electrocatalytic applications both in solution and as immobilized layers.

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[10] (a) Moiroux, J.; Elving, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 6533. (b) Dryhurst, G. "Electrochemistry of Biological Molecules"; Academic Press: New York, 1977. (c) Blaedel, W. J.; Jenkins, R. A. *Anal. Chem.* **1975**, *47*, 1337. (d) Leduc, P.; Thevenot, D. *Bioelectrochem. Bioenerg.* **1974**, *1*, 96. (e) Leduc, P.; Thevenot, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 543. (f) Jaegefeld, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *110*, 295.

[11] (a) Clarke, W. M. *J. Appl. Phys.* **1938**, *9*, 97. (b) Rodkey, L. *J. Biol. Chem.* **1955**, *213*, 777.

[12] Jaegfeldt, H.; Kuwana, T.; Johansson, G. *J. Am. Chem. Soc.* **1983**, *105*, 1805.

[13] Ueda, C.; Tse, D. C.-S.; Kuwana, T. *Anal. Chem.* **1982**, *54*, 850.

[14] Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5728.