# Catechol-Pendant Terpyridine Complexes: Electrodeposition Studies and Electrocatalysis of NADH Oxidation

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The synthesis, spectroscopic characterization, and electrochemical characterization, including the electrodeposition onto glassy carbon (GC) and platinum (Pt) electrodes, of electroactive films of the homoleptic catechol-pendant terpyridine complexes $[M(L^2)_2]^{2+}$ (where M = Co, Cr, Fe, Ni, Ru, and Os, and $L^2$ = 4′-(3,4-dihydroxyphenyl)-2,2′:6′,2″-terpyridine) are described. The potential dependence of the deposition was probed through electrochemical quartz crystal microbalance (EQCM) studies. Multilayer equivalent films were found to deposit at potentials less than that of the catechol oxidation process. Whereas the heteroleptic ruthenium(II) complex $[Ru(tpy)(L^2)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) did not deposit onto electrode surfaces, the corresponding osmium(II) heteroleptic complex $[Os(tpy)(L^2)]^{2+}$ deposited onto Pt and GC electrodes, suggesting that the metal center can play an important role in the deposition process. The heteroleptic cobalt(II) complex $[Co(v\text{-}tpy)(L^2)]^{2+}$ (v-tpy = 4′-vinyl-2,2′:6′,2″-terpyridine) was found to deposit onto Pt or GC electrodes through either a catechol-based deposition or a v-tpy-based electropolymerization, depending on the potential range over which a homogeneous solution of the complex was cycled. The electrochemical response of $[Co(L^2)_2]^{2+}$-modified GC electrodes in aqueous solution was robust and pH-dependent over the pH range 1−11, suggesting that the catechol moieties retain their pH-dependent redox activity upon immobilization. The application of these complexes, in solution and as electrodeposited films, to the electrocatalytic oxidation of NADH was also probed. $[Co(L^2)_2]^{2+}$ in solution plus $[Co(L^2)_2]^{2+}$- and $[Co(v\text{-}tpy)(L^2)]^{2+}$-modified GC electrodes were found to catalyze the oxidation of NADH in pH 7 phosphate buffer solution.

## Introduction

Film formation, by electropolymerization, of various substituted phenanthrolines and polypyridines has been previously reported.[1,2] Meyer and coworkers[2] have reported on the oxidative electropolymerization of metal complexes of 5-amino-1,10-phenanthroline and related the surface coverage of the resulting films to the redox potential of the metal centers. They have characterized the electrochemical and photophysical properties of such films and have employed them in electrocatalytic applications.

The catechol-pendant terpyridine ligand 4′-(3,4-dihydroxyphenyl)-2,2′:6′,2″-terpyridine ($L^2$) was first synthesized by Ward et al.[3] and was used to prepare multinuclear oligomers via deprotonation of the catechol group and subsequent binding of metal ions. We became interested in this ligand and its metal complexes for their application in such processes as the electrocatalytic oxidation of NADH. Investigations of the redox reactivity of $\beta$-nicotinamide adenine dinucleotide (NADH) and its oxidized form ($NAD^+$) are important, in part, because over 300 dehydrogenases use these compounds as cofactors. Materials that can catalyze such redox processes and, additionally, that may be attached to electrode surfaces are of particular interest because of their potential utility in a wide range of sensor applications. The major difficulty arises as a result of the high overpotential that is typically encountered for NADH oxidation at bare electrode surfaces.[4,5] Although the reversible potential for NADH oxidation is estimated to be −0.32 V vs NHE,[6] there is typically a very high overpotential which can be as large as 1.0 V.[7]

It is generally accepted that *o*-quinones can be quite active in the electrocatalytic oxidation of NADH, and as a result, numerous derivatives incorporating such a group have been employed.[8] In previous work we have demonstrated that electrodeposited films of 3,4-dihydroxybenzaldehyde[9−12] as well as transition-metal complexes of 1,10-phenanthroline-5,6-dione[13] (both of which contain catechol/*o*-quinone groups) are very active in the electrocatalytic oxidation of NADH. In fact, we have previously developed aldehyde and alcohol biosensors by

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coupling the enzymatic activities of aldehyde and alcohol dehydrogenases with the electrocatalytic activity (toward NADH oxidation) of films derived from these materials. Hilt et al.[14] have also reported the use of transition-metal complexes of 1,-10-phenanthroline-5,6-dione for the efficient regeneration of $NAD(P)^+$ in enzymatic synthesis.

Herein we report on the synthesis and characterization of transition-metal complexes of the ligand 4′-(3,4-dihydroxyphenyl)-2,2′:6′,2′′-terpyridine ($L^2$). These materials undergo electrodeposition, and the influence of the applied potential on the deposition was probed through electrochemical quartz crystal microbalance (EQCM) studies. These electrodeposited films also exhibit electrocatalytic activity toward the oxidation of NADH.

## Experimental Section

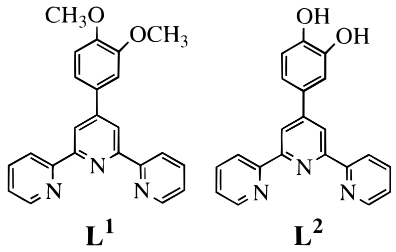
**Materials.** All reactions were carried out under an atmosphere of dry dinitrogen, unless otherwise stated, using standard Schlenk and cannula techniques. Solvents (analytical grade) were used without further purification. Acetonitrile (Burdick and Jackson, distilled in glass) for electrochemical experiments was dried over 4 Å molecular sieves. Tetra-*n*-butylammonium perchlorate (TBAP) (GFS Chemicals) was recrystallized three times from ethyl acetate and dried under vacuum for 96 h. Phosphate buffer solutions of pH 3, 5, 7, and 11 were prepared, and $H_2SO_4$ was used for the preparation of pH 1 solutions. 4′-(3,4-Dimethoxyphenyl)-2,2′:6′,2′′-terpyridine ($L^1$), $[Ru(L^1)_2]^{2+}$, and $[Ru(tpy)(L^1)]^{2+}$ were prepared according to the procedure of Ward et al.[3] $Ru(tpy)Cl_3$,[15] $Os(tpy)Cl_3$,[16] and 4′-vinyl-terpyridine[17] were prepared according to literature methods. Silica gel for column chromatography was purchased from ICN. All other reagents were purchased from Aldrich and used as received.

**Apparatus.** NMR spectra were obtained in the designated solvents on a Varian 200 (200 MHz) or Varian 400 (400 MHz) spectrometer. Mass spectra were recorded at the Mass Spectrometry Laboratory, University of Illinois, Urbana, IL. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. Electronic spectra were recorded on a Hewlett−Packard 8451A diode array spectrophotometer. Electrochemical experiments were carried out with a BAS CV-27 potentiostat. Three-compartment electrochemical cells (separated by medium-porosity sintered glass disks) and with the provision for gas addition were employed. All joints were standard-taper so that all compartments could be hermetically sealed with Teflon adapters. Platinum disk (geometric area = 0.008 $cm^2$) or glassy carbon (GC) electrodes (geometric area = 0.20 $cm^2$) were used as working electrodes. The electrodes were polished prior to use with 1 $\mu$m diamond paste (Buehler) and rinsed thoroughly with water and acetone. A large area platinum wire coil was used as a counter electrode. All potentials are referenced to a saturated Ag/AgCl electrode without regard for the liquid junction potential. EQCM instrumentation has been described previously.[18]

## Results and Discussion

**Synthesis and Characterization of the Complexes.** Initially, we were interested in the potential ability of the catechol-pendant bis(terpyridyl)cobalt(II) complex $[Co(L^2)_2]^{2+}$ to electrocatalyze the oxidation of NADH. However, once we synthesized this complex and found that it deposited on both Pt and GC electrodes (vide-infra), we became interested in determining whether other transition-metal complexes of this ligand behaved similarly. Scheme 1 illustrates the 4′-substituted terpyridine ligands $L^1$ and $L^2$. The homoleptic complexes $[M(L^1)_2]^{2+}$ (M = Co, Fe, Ni) were prepared in high yield by heating the ligand with the appropriate metal chloride in methanol at reflux. The ruthenium(II) complex of $L^1$ was prepared following the procedure of Ward,[3] while the osmium(II) complex was prepared from $OsCl_3$ and $L^1$ in ethylene glycol at reflux. The catechol pendant ligand $L^2$ and its homoleptic and heteroleptic complexes were prepared via deprotection of the methyl ether groups of $L^1$ or the appropriate metal complex of $L^1$ in concentrated hydrobromic acid at reflux. Alternately, these complexes may be prepared by demethylation using $BBr_3$ in $CH_2Cl_2$ as reported by Ward.[3] The complex $[Cr(L^2)_2]^{2+}$ was prepared by the room-temperature coordination of $L^2$ to $CrCl_2$ in deoxygenated aqueous methanol. The complexes $[Co(L^2)_2]Cl_2$ and $[Co(L^2)_2]Br_2$ were similarly prepared from $CoCl_2$ and $L^2$ in methanol containing either LiCl or LiBr, respectively. The heteroleptic cobalt(II) complex $[Co(v\text{-}tpy)(L^2)]^{2+}$ was prepared from $Co(L^2)Cl_2$ (which was obtained by heating $[Co(L^2)_2]Cl_2$ at 100 °C in vacuo according to the procedure of Hogg and Wilkins[19]) and v-tpy in methanol at reflux (Scheme 2).

Scheme 1



The complexes were all characterized by FAB mass spectrometry, elemental analysis, and electronic spectroscopy. The $^1H$ NMR of the diamagnetic complexes exhibited the expected number of signals associated with the terpyridyl ligands and the catechol or dimethoxyphenyl pendant groups. The complexes all showed intense absorptions in the UV spectral region assigned to $\pi \rightarrow \pi^*$ transitions. As expected, an intense broad absorption, which is ascribed to metal-to-ligand charge-transfer (MLCT) transitions was observed in the visible region of the spectra for the Fe(II), Ru(II), and Os(II) complexes. The cobalt(II) complexes also showed a number of charge-transfer bands which were more intense than the bands reported for $[Co(tpy)_2]^{2+}$,[19] but similar to the analogous complexes of the isomeric ligands 4′-(2,5-dimethoxyphenyl)-2,2′:6′,2′′-terpyridine ($L^3$) and 4′-(2,5-dihydroxyphenyl)-2,2′:6′,2′′-terpyridine ($L^4$).[20] Detailed descriptions of synthetic procedures as well as full analytical and spectroscopic data are given in the Supporting Information.

**Electrochemical Studies.** The cyclic voltammetric responses of the complexes were recorded in acetonitrile solution, and their metal- and ligand-centered formal potentials are presented in Table 1. The behavior of the homoleptic and heteroleptic Ru(II) complexes of $L^1$ and $L^2$ are in agreement with the values reported by Ward et al.[3] Briefly, for $L^1$ complexes of ruthenium, there was a second chemically irreversible oxidation wave at potentials more positive than that of the Ru(II/III) oxidation, which was assigned to the oxidation of the dimethoxyphenyl group. As a point of comparison, they noted that 1,2-dimethoxy-

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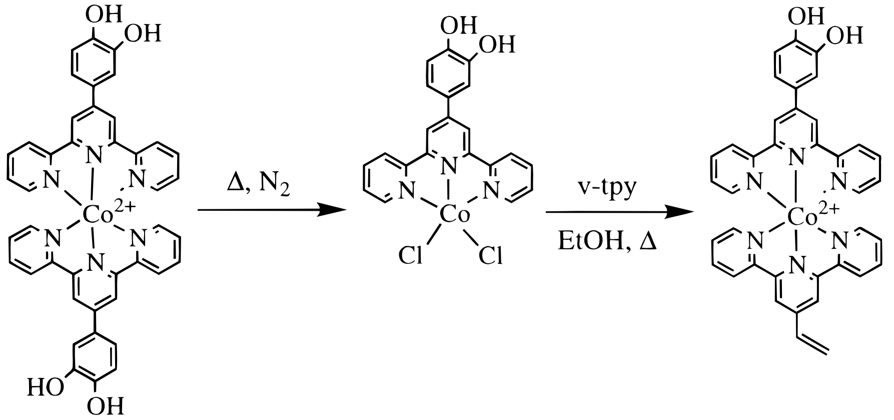
**Scheme 2**



$[Co(L^2)_2]^{2+}$ $Co(L^2)Cl_2$ $[Co(v\text{-}tpy)(L^2)]^{2+}$

**Table 1.** Electrochemical Data for the Complexes[a] (V vs Ag/AgCl)

| complex | M(II/III) | $E^b$ | tpy/tpy$^-$ | tpy$^-$/tpy$^{2-}$ |
|---|---|---|---|---|
| $[Co(L^1)_2]^{2+}$ | 0.28 | 1.65 | −0.74[c] | −1.54 |
| $[Co(L^2)_2]^{2+}$ | 0.28 | 1.52 | −0.80[c] | −1.54 |
| $[Co(v\text{-}tpy)(L^2)]^{2+}$ | 0.28 | 1.39 | −0.72[c] | |
| $[Cr(L^2)_2]^{2+}$ | −0.15 | 1.45 | −0.97 | −0.50[c] |
| $[Fe(L^1)_2]^{2+}$ | 1.10 | 1.62 | −1.20 | −1.31 |
| $[Fe(L^2)_2]^{2+}$ | 1.21 | 1.05 | −1.22 | |
| $[Ni(L^1)_2]^{2+}$ | 1.78 | 1.66 | −1.14 | −1.31 |
| $[Ni(L^2)_2]^{2+}$ | 1.78 | 1.38 | −1.16 | |
| $[Ru(L^1)_2]^{2+}$ | 1.28 | 1.66 | −1.16 | −1.36 |
| $[Ru(L^2)_2]^{2+}$ | 1.41 | 1.20 | −1.33 | −1.60 |
| $[Ru(tpy)(L^1)]^{2+}$ | 1.32 | 1.67 | −1.20 | −1.45 |
| $[Ru(tpy)(L^2)]^{2+}$ | 1.42 | 1.22 | −1.20 | −1.47 |
| $[Os(L^1)_2]^{2+}$ | 0.93 | 1.62 | −1.14 | −1.31 |
| $[Os(L^2)_2]^{2+}$ | 0.98 | 1.05 | −1.28 | −1.52 |
| $[Os(tpy)(L^1)]^{2+}$ | 0.93 | 1.60 | −1.17 | −1.44 |
| $[Os(tpy)(L^2)]^{2+}$ | 0.95 | 1.15 | −1.14 | |

[a] Recorded in $CH_3CN$, 0.1 M TBAP. [b] For $[M(L^1)_2]^{2+}$ $E^{o\prime}$; for $[M(L^2)_2]^{2+}$ $E_{pa}$ catechol oxidation. [c] M(II/I) couple.

benzene affords soluble oligomers or polymers bound to the surface via coupling of a radical cation, and they used Osteryoung Square Wave voltammetry to show that this oxidation led to an electrochemically active product. The cyclic voltammograms for the complexes $[M(L^1)_2]^{2+}$ (M = Co, Fe, Ni, Os) showed both metal- and terpyridine-centered processes similar to those exhibited by the corresponding $[M(tpy)_2]^{2+}$ complexes. In addition, there was a redox process at ca. +1.6 V, which is ascribed to the two superimposed quasireversible one-electron oxidations of the dimethoxyphenyl groups to the radical cation as typically observed for aryl ethers.[21]

The electrochemical behavior of the complexes of $L^2$ was complicated by their deposition onto the electrode surface at negative potentials. In this section, we will discuss only the response observed on the initial anodic scan. At positive potentials, the cyclic voltammograms exhibited an irreversible wave between +1.0 and +1.4 V which is ascribed to the irreversible oxidation of the catechol group. Comparison of the potentials for the M(II/III) processes for the $[M(L)_2]^{2+}$ (M = Fe, Ru, or Os and L = $L^1$ or $L^2$) complexes shows a positive shift of ca. 100 mV for the catechol-pendant ($L^2$) complexes that is attributable to an increase in the ligand's $\pi$ acidity, since the catechol-pendant groups are oxidized prior to the M(II/III) couple in the complexes of $L^2$. In contrast, for the complexes of Ni and Co there was virtually no difference in the formal potentials of the $L^1$ and $L^2$ complexes. In the case of Ni(II) we ascribe this to the fact that the oxidation processes associated with the ligands occur prior to the metal-localized oxidation. Conversely, in the case of Co(II), the metal-localized process precedes the ligand-localized redox reactions for both $L^1$ and $L^2$. All of these effects demonstrate the degree to which formal potentials of metal-centered redox processes can be modulated by deliberate changes in the pendant substituent of the terpyridine ligand.

**Electrodeposition of Complexes of $L^2$. EQCM Studies of $[Co(L^2)_2]^{2+}$.** The electrodeposition of the homoleptic cobalt(II) complex was studied in most detail, using voltammetric and EQCM methods, and will be discussed first. Since details of the EQCM technique have been described previously in a number of reviews,[22] only a brief description is given here. A decrease or increase in the frequency of a quartz crystal resonator usually indicates mass loading onto or unloading off of the quartz crystal, respectively. However, since changes in frequency are caused not only by changes in mass but also by changes in solution properties, such as viscosity and density, and film properties, such as viscoelasticity, roughness, thickness, and solvophilicity of the film in contact with the quartz crystal resonator, the main factor that causes frequency changes during the deposition of the $[M(L^2)_2]^{2+}$ complexes onto the quartz crystal resonator needs to be established. In doing so, admittance measurements of the quartz-crystal resonator are particularly informative.[23]

Figure 1 shows the typical current (CV) (Figure 1A) and frequency (Figure 1B) responses as a function of applied potential for an acetonitrile solution containing $[Co(L^2)_2]^{2+}$. The waves, which on the initial voltammetric scan were centered at +0.2 and −0.8 V, correspond to metal-localized Co(II/III) and Co(II/I) processes, respectively. The increase in current with continuous potential scanning indicates the accumulation of an electroactive film on the electrode surface. The overall decrease in frequency upon continuous potential scanning also demonstrates that deposition of the $[Co(L^2)_2]^{2+}$ complex is taking place on the electrode surface. On the first scan, the frequency decreased during the cathodic sweep from ca. −0.4 V and continued to decrease gradually even after scan reversal (at −1.20 V) until the potential of the Co(II/III) process was

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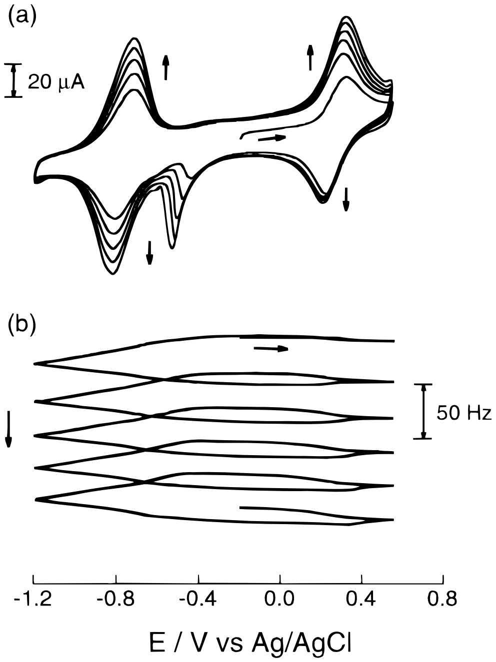

**Figure 1.** Current (A) and frequency (B) responses as a function of applied potential between +0.5 and −1.2 V at 100 mV $s^{-1}$ for a Pt electrode in contact with a 0.10 M TBAP/AN solution containing 0.1 mM $[Co(L^2)_2](PF_6)_2$.

reached. If the potential was cycled positive of that of the Co(II/III) oxidation process, the frequency increased dramatically, indicating that the film was rapidly stripped from the electrode surface at potentials above +0.7 V. At more negative potentials, the frequency also increased if the first ligand-centered reduction peak at ca. −1.7 V was cycled through, suggesting that the film was also stripped at these potentials.

As mentioned previously, there could also be changes in solvation and film morphology, such as rigidity, which may also give rise to frequency changes. Impedance measurements during film deposition at −0.2 V showed that the resistance increased linearly by 4 Ω over a 5 min period, indicating a continual change in the film's morphology and/or roughness. This suggests that frequency changes must be interpreted with care since they do not arise solely as a result of mass changes in the deposition of $[Co(L^2)_2]^{2+}$ films.

Also of interest is the charge-trapping peak that appears at ca. −0.5 V. This potential corresponds to the onset of a gradual decrease in the frequency, which probably represents the initiation of deposition of the complex onto the electrode surface. When the potential was cycled through the Co(II/III) process, the frequency increased slightly and continued to increase until the charge-trapping peak was reached. We have addressed the EQCM response for charge-trapping peaks in electropolymerized films of transition-metal complexes of vinyl-terpyridine previously.[18]

It should also be noted that a film began to deposit as soon as a potential within the above-mentioned range was applied to the electrode. For example, if a potential of 0 V (which is within the above-mentioned range) was applied to the QCM electrode, the frequency gradually decreased (ca. 20 Hz). Upon cycling the potential to +1.5 V the frequency increased by about 20 Hz, suggesting that the deposited film was stripped. If the potential was then continuously cycled between −0.2 and +1.5 V, only small frequency changes were observed (ca. 2−4 Hz).

We have previously reported[24] that upon continued potential scanning for the electropolymerization of $[Co(v\text{-}tpy)_2]^{2+}$, two new waves appeared at ca. −0.03 and −1.10 V vs SSCE, in addition to those of the Co(II/III), Co(II/I), and ligand-based reduction processes. These new waves were ascribed to the generation of $[Co(N,N',N''\text{-}v\text{-}tpy)(N,N'\text{-}v\text{-}tpy)(AN)]^{2+}$ (AN = acetonitrile) within the electropolymerized film, in which there is partial displacement of the terpyridine ligand(s) and coordination by an acetonitrile molecule(s). Similar waves were not observed for electrodeposited films of $[Co(L^2)_2]^{2+}$. This may reflect differences in the steric effects that the polymerization of the pendant vinyl moiety of the v-tpy ligand, to form a polymer backbone, places on the cobalt complex as compared with the $[Co(L^2)_2]^{2+}$ deposition, which does not appear to place the same steric limitations on the metal center.

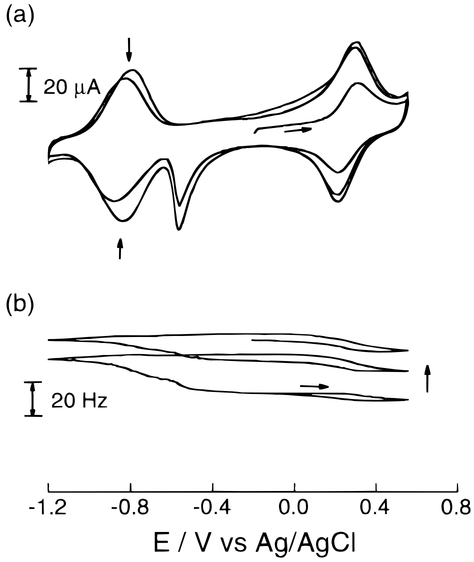

**Figure 2.** Current (A) and frequency (B) responses as a function of applied potential between +0.5 and −1.2 V at 100 mV $s^{-1}$ for a $[Co(L^2)_2]^{2+}$-modified Pt electrode in contact with a fresh 0.10 M TBAP/AN solution.

The deposited films are not particularly robust under potential cycling in acetonitrile solution. When a $[Co(L^2)_2]^{2+}$-modified electrode was placed in fresh acetonitrile solution and the potential cycled over the same range as for the deposition, the increase in frequency and the decrease in current indicated that the film was rapidly lost as shown in Figure 2. In contrast, when this experiment was repeated in methylene chloride solution, after an initial sharp drop in the peak currents for the redox processes (possibly due to the removal of weakly bound material) they stabilized and remained virtually constant over numerous cycles. This difference in the stability of the deposited films might arise from differences in the solubility of the complexes in these two solvents, with the solubility being much higher in acetonitrile than in methylene chloride.

**Electrodeposition of $[M(L^2)_2]^{2+}$ (M = Cr, Fe, Ni, Ru, or Os).** The homoleptic complexes, $[M(L^2)_2]^{2+}$ (M = Co, Cr, Fe, Ru, Os, or Ni) could be deposited onto both Pt and GC electrodes by cycling the potential over values that were negative of the catechol oxidation process. Deposition was arrested when the potential was swept to values beyond the oxidation of the catechol-pendant group (for all homoleptic metal complexes). Similarly, the deposition was also stopped in the case of the Co(II), Cr(II), and Ni(II) complexes of $L^2$ when the potential was scanned over a range (negative values) that resulted in the generation of the neutral complex. Thus, in general, the

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electrodeposition of these complexes was limited to a potential window that was negative of the catechol oxidation but positive of the generation of the neutral complex: $E^{o\prime}_{[M(L^2)_2]^{1+/0}} < E_{dep} < E^{o\prime}_{Cat}$. As was the case for the Co(II) complex of $L^2$ described earlier, electrodeposited films of these materials were not stable under cycling in acetonitrile in the absence of the complex in solution. In general, such potential cycling resulted in the loss of the deposited material from the electrode surface.

**Heteroleptic Complexes.** To probe the mechanism of deposition, the voltammetric behavior of the heteroleptic Ru(II) complex $[Ru(tpy)(L^2)]^{2+}$ was studied. As reported by Ward,[3] in an anodic scan, the complex exhibits the catechol oxidation and the Ru(II/III) redox process at +1.12 and +1.36 V, respectively. In a cathodic scan, there are two ligand-centered reductions at −1.26 and −1.53 V. Repetitive cycling over various potential ranges did not result in an increase in the peak current, indicating that under these conditions there was no deposition of the complex. In contrast, the homoleptic Ru(II) complex $[Ru(L^2)_2]^{2+}$ exhibited responses characteristic of deposition over similar potential ranges. Given these results, we postulated that only homoleptic complexes of $L^2$ are able to deposit and that interactions of the two catechol moieties might be responsible, at least in part, for the deposition process perhaps in a way akin to the electro-oxidative generation of poly-phenylene oxide.

As a further test, we prepared the heteroleptic Os(II) complex $[Os(tpy)(L^2)]^{2+}$. Surprisingly, this complex was found to deposit onto both Pt and GC electrode surfaces over essentially the same potential range as the analogous homoleptic Os(II) complex, $[Os(L^2)_2]^{2+}$. These results would suggest that the metal center can play a significant role in the deposition of the complex. The deposition behavior for the heteroleptic complexes may be associated with some interaction of the M(II/III) and the catechol oxidation process. On this point, we note that the Ru(II/III) couple is observed at a potential (+1.41 V) positive of the catechol oxidation (+1.20 V), while the Os(II/III) couple is observed at a potential (+0.98 V) that is negative of the catechol oxidation (+1.05 V). Thus, it would appear that the presence of the ligand in the catechol form plays an important role, perhaps via hydrogen bonding, in the electrodeposition process. The differences in the propensity for deposition between the Ru(II) and Os(II) homoleptic complexes could be a reflection of the fact that the ligand is present in the quinone form in the former and catechol in the latter and thus the hydrogen bonding interactions would be correspondingly different, being larger for the Os(II) complex.

We were also interested in determining whether the activity of the catechol groups toward NADH catalysis was affected by the deposition process. Hence, we prepared the heteroleptic cobalt(II) complex $[Co(v\text{-}tpy)(L^2)]^{2+}$, which, in principle, could be deposited via electropolymerization of the vinylterpyridine ligand as well as through the same type(s) of process(es) that gave rise to electrodeposition of the $L^2$ complexes. The operative mode of deposition could be controlled by the range over which the potential was swept. In the case of films generated via electropolymerization of the vinylterpyridine group, one would anticipate that the catechol moiety would remain undisturbed since it was not involved in the electropolymerization process. Thus, the expectation would be that such a film, if formed, would retain its electrocatalytic activity toward the oxidation of NADH. On the other hand, if the potential was swept over a range where the $L^2$ complexes undergo deposition, one would expect that the same type of film as the $[Co(L^2)_2]^{2+}$ would be generated in terms of stability and behavior. Initially, the cyclic voltammetric response of $[Co(v\text{-}tpy)(L^2)]^{2+}$ in acetonitrile solution at a GC electrode over the potential range of −1.0 to +0.5 V (values typical of those for the deposition of the $L^2$ complexes) was obtained. After the initial cycle, the peaks for the Co(II/III) redox couple shifted negatively and decreased in current before slowly increasing with additional cycling. This might arise from a blocking effect of the electrode surface at the early stages of deposition, so that the contribution from diffusion is decreased, resulting in a decrease in the current. The current response is a combination of the responses due to film formation and diffusion (recall that the complex is also present in solution) and their interplay could give rise to the observed behavior. The Co(II/I) couple appeared to be less sensitive to such an effect and exhibited an increase in peak current (albeit small at the early stages of deposition) due to film formation and possibly the increasing effect of self-exchange.[24,25] When such a modified electrode (Pt or GC) was placed in a fresh acetonitrile solution and the potential cycled, the film was rapidly stripped from the electrode surface. This behavior suggests that the film was deposited through a catechol type deposition process, which is consistent with the potential range over which the deposition was carried out.

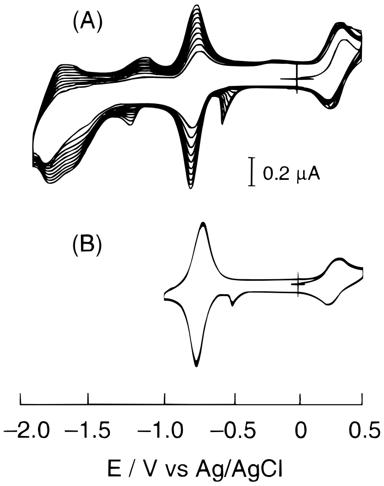

**Figure 3.** (A) Cyclic voltammetric response between −1.9 and +0.5 V at 100 mV s$^{-1}$ of 0.3 mM $[Co(v\text{-}tpy)(L^2)](PF_6)_2$ at a Pt electrode in 0.10 M TBAP/AN solution. (B) Cyclic voltammetric response for 20 cycles between −1.0 and +0.5 V at 100 mV s$^{-1}$ for a $[Co(v\text{-}tpy)(L^2)]^{2+}$-modified Pt electrode in contact with a fresh 0.10 M TBAP/AN solution ($\Gamma = 1.0 \times 10^{-10}$ mol cm$^{-2}$).

Figure 3A shows the deposition of $[Co(v\text{-}tpy)(L^2)]^{2+}$ onto a Pt electrode surface when the potential was cycled to more negative potentials over the range of −1.9 to +0.5 V, where electropolymerization of the vinylterpyridine group takes place. In this case, rapid film formation was readily apparent. Concomitant with film growth was the appearance of a cathodic charge-trapping peak at −0.6 V, in addition to a new couple at −1.2 V. This couple is most likely associated with the formation of a cobalt(II) complex with acetonitrile coordinated to the metal center (i.e., $[Co(L^2)(N,N'\text{-}v\text{-}tpy)(AN)]^{2+}$) as previously reported for $[Co(v\text{-}tpy)_2]^{2+}$.[24] When such a modified electrode (Pt or GC) was placed in a fresh acetonitrile solution and the potential cycled, the film showed a very stable response (Figure 3B), which is, again, consistent with deposition via electropolymerization of the vinylterpyridine. Film deposition onto the electrode surface was additionally confirmed by EQCM measurements and by comparison with the reported behavior of numerous other $[M(v\text{-}tpy)_2]^{2+}$ complexes including [Co(v-

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(25) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685.

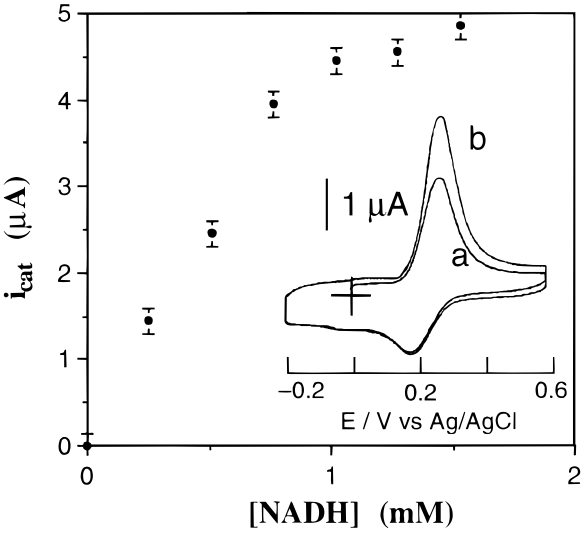

**Figure 4.** Plot of the catalytic current versus the concentration of NADH in pH 7 phosphate buffer solution containing 0.5 mM [Co($L^2$)$_2$]Br$_2$. Inset: cyclic voltammograms showing 0.5 mM [Co($L^2$)$_2$]Br$_2$ in pH 7 phosphate buffer at a GC electrode before (a) and after (b) the addition of 25 μL of a 25.5 mM solution of NADH (final NADH concentration 0.3 mM). Scan rate: 20 mV s$^{-1}$.

tpy)$_2$]$^{2+}$ and [Co(v-tpy)(tpy)]$^{2+}$.[17,24,26,27] This type of response is characteristic of electrodes modified with [M(v-tpy)$_2$]$^{2+}$ complexes and suggests that if the potential is cycled over the range −1.9 to +0.5 V, the deposition is mainly associated with electropolymerization involving the vinyl group. Thus, the potential range −1.9 to +0.5 V was used to prepare films of [Co(v-tpy)($L^2$)]$^{2+}$ for the assessment of electrocatalytic activity in the oxidation of NADH.

**Electrocatalysis of NADH Oxidation. Aqueous Electrochemistry of [Co($L^2$)$_2$]Br$_2$.** As mentioned earlier, one of the objectives of the present work was to ascertain if transition-metal complexes of the catechol-pendant terpyridine ligand were electrocatalytically active in the oxidation of NADH, since *o*-quinones (which are related by a simple redox reaction to catechols) are known to catalyze such a reaction. As a representative complex we chose the [Co($L^2$)$_2$]$^{2+}$ complex, and initial studies were carried out in homogeneous solution.

In pH 7 phosphate buffer, [Co($L^2$)$_2$]Br$_2$ exhibits a well-defined wave at a formal potential of +0.28 V at a GC electrode (scan a in Figure 4 inset). The shape of the voltammogram also suggests that there might be some adsorption of the complex onto the GC electrode. Upon the addition of 25 μL of a 25.5 mM solution of NADH[28] (final NADH concentration was 0.3 mM) to [Co($L^2$)$_2$]Br$_2$ in pH 7 phosphate buffer solution there was an enhancement in the anodic current of a freshly polished GC electrode (scan b in Figure 4 inset), indicative of an electrocatalytic effect. The magnitude of the catalytic current (defined as the difference in current in the presence and absence of NADH) was dependent on the concentration of NADH. As shown in the main panel of Figure 4, the catalytic current was proportional to the concentration of NADH for values of up to 1 mM. However, for higher NADH concentrations, the response leveled off, suggesting a saturation response, as is often observed. It should be mentioned that in pH 7 phosphate buffer solution, the free ligand ($L^2$) did not exhibit any redox response up to +1.0 V. Moreover, the addition of NADH to such a solution did not alter the response.

**[Co($L^2$)$_2$]$^{2+}$-Modified GC Electrodes.** After having established that catechol-pendant terpyridine complexes were catalytically active in aqueous solution toward the oxidation of NADH, we then set out to determine if such activity was retained for electrodes modified with electrodeposited films of these materials. As an initial step, the electrochemical response of a [Co($L^2$)$_2$]$^{2+}$-modified GC electrode in aqueous solution was investigated. First, [Co($L^2$)$_2$]$^{2+}$ was deposited onto a GC electrode by cycling the potential five times over the range of +0.5 to −1.2 V in an acetonitrile solution. The electrode was rinsed with acetone and water and then placed in a buffer solution that had been degassed with nitrogen for at least 10 min. Solutions of pH 1, 3, 5, 7, and 11 were studied. The [Co($L^2$)$_2$]$^{2+}$-modified GC electrode was found to be electroactive at all pH values studied. At pH 1 and 11, only a single redox process was observed. At pH 3, 5, and 7, three redox processes were observed in the aqueous solutions: two redox couples at ca. +0.2 and +0.5 V were observed, plus an irreversible oxidation at ca. +0.95 V (which was only observed on the initial potential cycle). When the potential was cycled only over the first two redox processes, the anodic peak current of the second process decreased slightly with continued scanning, while the response for the first process remained virtually unchanged. The first process, whose potential ($E^{o\prime} = +0.18$ V) was essentially independent of pH, is ascribed to the Co(II/III) couple. The second process, which was pH-dependent and much better defined at lower pH values, is ascribed to the catechol oxidation. A plot of peak potential versus pH for this process was linear and had a slope of −58 mV/pH unit, which is very close to the anticipated Nernstian value of −59 mV/pH unit (see Supporting Information).

The ability of a [Co($L^2$)$_2$]$^{2+}$-modified GC electrode to catalyze the oxidation of NADH was then tested. A [Co($L^2$)$_2$]$^{2+}$ film was prepared using the method described above and placed in an aqueous pH 7 phosphate buffer solution. Scan a in Figure 5a shows the initial potential cycle for this [Co($L^2$)$_2$]$^{2+}$-modified electrode whose surface coverage was $3.8 \times 10^{-11}$ mol cm$^{-2}$. Following the addition of NADH, there was a dramatic increase in the peak current for the anodic process (scan b in Figure 5a), consistent with a very strong electrocatalytic effect.

We also tested the electrocatalytic activity of electrodes modified with [Co(v-tpy)($L^2$)]$^{2+}$ generated via reductive electropolymerization as described above. The voltammetric response of a [Co(v-tpy)($L^2$)]$^{2+}$-modified GC electrode (surface coverage of $2.0 \times 10^{-11}$ mol cm$^{-2}$) in a pH 7 phosphate buffer solution was similar to that of a [Co($L^2$)$_2$]$^{2+}$-modified GC electrode. As seen in scan a of Figure 5b, there was a wave centered at about +0.33 V which is ascribed to the catechol/*o*-quinone redox couple. Upon the addition of NADH, there was a dramatic enhancement of the anodic current (scan b in Figure 5b), with virtually no current on the cathodic sweep in a manner virtually identical to that exhibited by GC electrodes modified with [Co($L^2$)$_2$]$^{2+}$. This demonstrates that complexes with only one $L^2$ ligand retain their electrocatalytic activity toward NADH and that electrodeposition of [Co($L^2$)$_2$]$^{2+}$ does not render the catechol groups electrocatalytically inactive.

Comparison of the peak potential for the electrocatalytic oxidation of NADH by the three complexes studied ([Co($L^2$)$_2$]Br$_2$ in solution, plus [Co($L^2$)$_2$]$^{2+}$- and [Co(v-tpy)($L^2$)]$^{2+}$-modified GC electrodes) indicates that [Co($L^2$)$_2$]Br$_2$ has the most negativepotential followed by [Co(v-tpy)($L^2$)]$^{2+}$ and then

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(27) Arana, C.; Keshavarz, M.; Potts, K. T.; Abruña, H. D. *Inorg. Chim. Acta* **1994**, *225*, 285.

(28) The direct oxidation of NADH at a GC electrode in the absence of the complex took place at about +1.0 V.

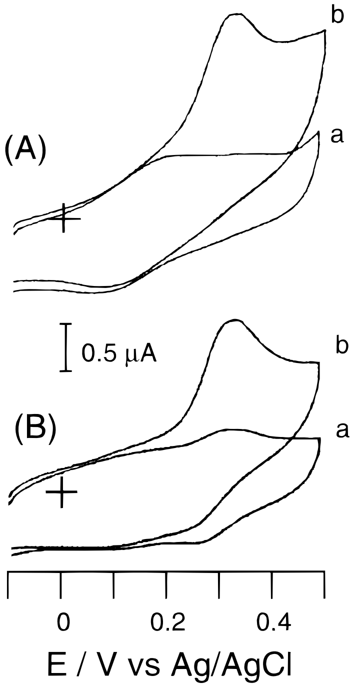

**Figure 5.** (A) A $[Co(L^2)_2]^{2+}$-modified electrode ($\Gamma = 3.8 \times 10^{-11}$ mol cm$^{-2}$) in pH 7 phosphate buffer solution before (a) and after (b) the addition of NADH (final NADH concentration 0.21 mM). (B) A $[Co(v\text{-}tpy)(L^2)]^{2+}$-modified electrode ($\Gamma = 2.0 \times 10^{-11}$ mol cm$^{-2}$) in pH 7 phosphate buffer solution before (a) and after (b) the addition of NADH (final NADH concentration 0.21 mM). Scan rate 10 mV s$^{-1}$.

$[Co(L^2)_2]^{2+}$. This suggests that $[Co(L^2)_2]Br_2$ in solution provides the largest electrocatalytic effect for the oxidation of NADH. Since $[Co(L^2)_2]Br_2$, in solution, and surface immobilized $[Co(L^2)_2]^{2+}$ have the identical electroactive species, it again suggests that the catechol groups are involved in the deposition process, making them somewhat less active in the oxidation of NADH relative to the complex in solution.

Finally, it should be mentioned that in a way analogous to the behavior in solution, an electrode modified with an adsorbed layer of $L^2$ did not exhibit any electrocatalytic activity toward NADH oxidation.[29]

## Conclusions

We have described the electrochemical, spectroscopic, and EQCM characteristics of transition-metal complexes of the ligand 4′-(3,4-dihydroxyphenyl)-2,2′:6′,2′′-terpyridine ($L^2$). We have demonstrated that the complexes $[M(L^2)_2]^{2+}$ (M = Co, Cr, Fe, Ru, Os, or Ni) deposit from acetonitrile solution onto Pt and GC electrodes at potentials negative of the catechol oxidation peak. The films are not strongly bound, since when $[M(L^2)_2]^{2+}$-modified electrodes were placed in fresh acetonitrile solution the films desorbed rapidly. The electrochemical response of $[Co(L^2)_2]^{2+}$-modified GC electrodes in aqueous solution was more robust than in nonaqueous solution, and the response of the catechol redox process was shown to be pH-dependent in solutions out of the range of pH 1−11. The heteroleptic ruthenium(II) complex, $[Ru(tpy)(L^2)]^{2+}$, did not deposit onto electrode surfaces, while the corresponding heteroleptic osmium(II) complex, $[Os(tpy)(L^2)]^{2+}$, did. This suggests that the metal center can play a strong role in the deposition process. $[Co(L^2)_2]^{2+}$, in solution, as well as $[Co(L^2)_2]^{2+}$-modified GC electrodes were found to catalyze the oxidation of NADH in pH 7 phosphate buffer solution. A film consisting of an electrodeposited layer of the complex $[Co(v\text{-}tpy)(L^2)]^{2+}$ was found to be more robust, as well as able to catalyze the oxidation of NADH in pH 7 phosphate buffer solution.

**Acknowledgment.** This work was supported by the Office of Naval Research and the National Science Foundation.

**Supporting Information Available:** Detailed descriptions of synthetic procedures, full analytical and spectroscopic data, cyclic voltammogram for a $[Co(L^2)_2]^{2+}$-modified GC electrode in pH 5 phosphate buffer solution, plot of $E^{o\prime}$ vs pH for a $[Co(L^2)_2]^{2+}$-modified GC electrode in different buffer solutions. Ordering and access information is given on any current masthead page.

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(29) The GC electrode was modified by casting 50 μL of 2 mM $L^2$ in acetonitrile.