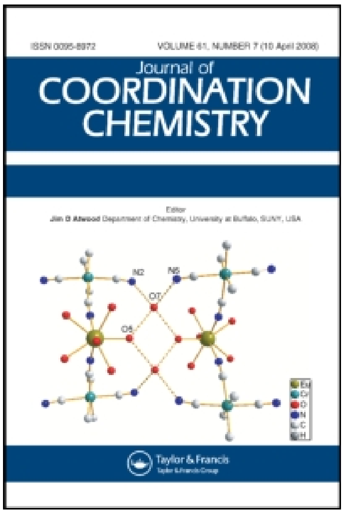

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Quinone-functionalized Transition Metal Complexes for Multi-electron Transfer. The Electrochemistry of a Bis -Naphthoquinone-Functionalized Schiff Base Ni(II) complex

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QUINONE-FUNCTIONALIZED TRANSITION METAL COMPLEXES FOR MULTI-ELECTRON TRANSFER. THE ELECTROCHEMISTRY OF A *BIS*-NAPHTHOQUINONE-FUNCTIONALIZED SCHIFF BASE Ni(II) COMPLEX

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$Ni(II)NQ_2en$, a Ni(II) complex with two naphthoquinone groups incorporated into a Schiff-base ligand, undergoes two reversible reductions in which the naphthoquinone (NQ) groups are each reduced by one electron to naphthsemiquinone radical anions (SQ):

$$\mathrm{Ni(II)NQ_2en} + \mathrm{e^-} \xrightarrow{E_1^0} [\mathrm{Ni(II)(SQ, NQ)en}]^-$$

$$[\mathrm{Ni(II)(SQ, NQ)en}]^- + \mathrm{e^-} \xrightarrow{E_2^0} [\mathrm{Ni(II)SQ_2en}]^{2-}$$

Analysis of the cyclic and differential pulse voltammetry waves shows that $E_2^0 - E_1^0 = -36\,\mathrm{mV}$, a ΔE^0 that corresponds to two *noninteracting* redox centers.

Keywords: Schiff base; Electrochemistry; Quinone

INTRODUCTION

The importance of multi-electron transfer in small molecule catalysis and the need to develop metal complexes that can support multi-electron transfer has been emphasized

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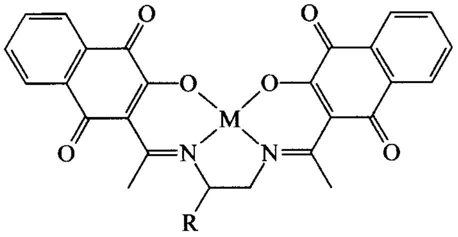
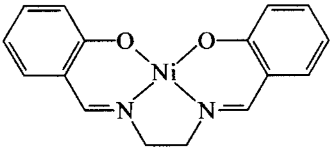
in several recent review articles [1–4]. Several strategies have been employed in developing catalysts that can support multi-electron transfer. Anson and coworkers have studied a series of transition metal porphyrins with redox-active Ru(II) ions bound at four peripheral sites on the macrocycle. The peripheral metal ions can transfer electrons to substrate molecules bound at the central metal ion. The four-electron reduction of O_2 to $2H_2O$ with these catalysts has been reported [5], although it now seems that the peripheral metal ions do not participate in the redox process directly but rather modify the electronic structure of the porphyrin such that the four-electron pathway is favored over the two-electron process [5]. Collman and coworkers have developed a number of covalently-linked cofacial porphyrin complexes, many of which function as four-electron catalysts for O_2 reduction, as well [1,6].

Our approach to this problem has been to synthesize coordination compounds in which redox-active quinone groups are incorporated into the organic ligand [7]. In protic solvents each quinone group can function as a two-electron couple [8], thus giving the ligand redox-activity in addition to any metal-centered redox-activity.

We report here on the electrochemistry of two similar Ni(II) complexes with *bis*-naphthoquinone-functionalized ligands that have the basic framework of the well-known salen ligand [9] (we identify the salen ligand as H_2sal_2en and its Ni(II) complex as Ni(II)sal_2en in order to be consistent with the nomenclature used to identify our quinone-functionalized ligands and their Ni(II) complexes). Fig. 1 shows the structures of the ligands and Ni(II) complexes; Ni(II)sal_2en is shown to emphasize its structural similarity to the two quinone-functionalized complexes. In pyridine the



H_2NQ_2en; M = 2H, R = –H
$H_2NQ_2(\pm)$-1,2-pn; M = 2H, R = $-CH_3$
Ni(II)NQ_2en; M = Ni(II), R = –H
Ni(II)$NQ_2(\pm)$-1,2-pn; M = Ni(II), R = $-CH_3$



Ni(II)sal_2en

FIGURE 1 Structures of the quinone-functionalized ligands and Ni(II) complexes used in this study. Ni(II)sal_2en is shown for comparison.

two naphthoquinone groups of Ni(II)NQ_2en undergo reversible one-electron reductions to semiquinone radical anions at potentials that are separated by −36 mV, i.e., $E_2^0 - E_1^0 = -36\,\mathrm{mV}$. In this case the naphthoquinone groups constitute *noninteracting* redox centers [10,11].

Several inorganic [12–17] and organic [18,19] systems have been reported that contain multiple redox centers that function more or less independently. The noninteraction of the naphthoquinone groups in Ni(II)NQ_2en is especially interesting since it indicates that redox-active ligands with multiple redox centers can be designed so that redox processes at one center do not strongly perturb neighbouring centers. Redox processes that result in anti-cooperative behavior and make subsequent electron transfer more difficult would obviously limit the ability of these systems to catalyze multi-electron redox reactions of small molecules.

EXPERIMENTAL

Synthesis

1-naphthylacetate was prepared by the method of Stoughton [20]. *2-acetyl-1-naphthol* was prepared from 1-naphthylacetate by the method of Chu *et al.* [21], *2-acetyl-4-amino-1-naphthol·HCl* was prepared from 2-acetyl-1-naphthol by the methods of Fieser and Fieser [22] and Spruit [23]. *2-acetyl-3-hydroxy-1,4-naphthalenedione* was prepared from 2-acetyl-4-amino-1-naphthol·HCl by the method of Spruit [23].

H_2NQ_2en 0.14 g (2.3 mmol) of ethylenediamine in 5 mL of dry methanol was added dropwise to a stirred suspension of 1.0 g (4.6 mmol) of 2-acetyl-3-hydroxy-1,4-naphthoquinone in 10 mL of dry methanol. When the addition was complete the resulting mixture was refluxed for 20 min and then cooled to room temperature. The yellow microcrystalline product was vacuum filtered and washed with 5 mL of diethyl ether. Yield: 0.92 g (86%). m.p. = 260–270°C (dec.). ^{1}H NMR (300 MHz, d_6 DMSO) δ 2.86 (s, 6H), 4.01 (s, 4H), 7.72 (m, 4H), 8.14 (m, 4H).

H_2NQ_2(±)-1,2-pn This ligand was prepared in an identical manner to H_2NQ_2en except that 0.17 g (2.3 mmol) of (±)-1,2-propanediamine was used in place of ethylenediamine. Yield: 1.1 g (73%). m.p. = 230–245°C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (d, 3H, $J = 6.6$ Hz), 2.77 (s, 3H), 2.82 (s, 3H), 3.86 (m, 2H), 4.45 (m, 1H), 7.70 (m, 4H), 8.12 (m, 4H), 14.27 (s, 2H).

Ni(II)NQ_2en 0.50 g H_2NQ_2en (1.1 mmol) and 0.27 g of Ni(II) acetate $4H_2O$ (1.1 mmol) were stirred for 20 min in 8 mL of DMF heated to 50°C. The mixture was vacuum filtered while still warm and washed several times with diethyl ether. The red microcrystalline product was dried under vacuum at 76°C for 12 h. Yield: 0.46 g (81%). m.p. = 350–360°C (dec.). Analysis calcd. for $C_{26}H_{18}N_2NiO_6$ (FW = 513.13): C, 60.86%; H, 3.54; N, 5.46; Ni, 11.44; O, 18.71, found: C, 60.44; H, 3.20; N, 5.48. MS (FAB) *m/z* 513 (MH^+). HRMS (FAB) calcd. for $C_{26}H_{19}N_6NiO_6$ (MH^+): 513.0596, found: 513.0577. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (s, 6H), 3.41 (s, 4H), 7.70 (m, 4H), 8.11 (m, 4H).

Ni(II)NQ_2(±)-1,2-pn This complex was prepared in an identical manner to Ni(II)NQ_2en except that 0.52 g (1.1 mmol) of H_2NQ_2(±)-1,2-pn was used as the ligand. The red microcrystalline product was dried under vacuum at 76°C for 12 h.

Yield: 0.40 g (69%). m.p. = 295–305°C (dec.). Analysis calcd. for $C_{27}H_{20}N_2NiO_6 \cdot H_2O$ (FW = 527.16): C, 59.49%; H, 4.07; N, 5.14; Ni, 10.77; O, 20.54, found: C, 59.48; H, 3.60; N, 5.16. MS (FAB) m/z 527 (MH^+). HRMS (FAB) calcd for $C_{27}H_{22}N_6NiO_6$ (MH^+): 527.0753, found: 527.0577. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (d, 3H, $J = 6.6$ Hz), 2.51 (s, 3H), 2.52 (s, 3H), 3.09 (d, 1H, $J = 12.6$ Hz), 3.42, (dd, 1H, $J = 13.8$, 5.4 Hz), 3.78 (m, 1H), 7.68 (m, 4H), 8.08 (m, 4H).

Physical Measurements

Nuclear magnetic resonance spectra were recorded in either $CDCl_3$ or DMSO-d_6 on a 300 MHz Bruker Avance spectrometer equipped with a broadband probe.

Mass spectra (FAB) were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program National Center for Research Resources, National Institute of Health.

Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Electrochemical Solvents and Electrolytes

Pyridine (Mallinckrodt) was dried over Linde 4 Å molecular sieves and twice distilled from BaO.

$[N(C_4H_9)_4][PF_6]$ ($TBAPF_6$) (Aldrich) and $[N(C_4H_9)_4][ClO_4]$ (TBAP) (Pfaltz and Bauer) were used without further purification.

Electrochemical Measurements

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronocoulometry (CC) were performed using a Bioanalytical Systems CV-50 W Voltammetric Analyzer. Nonaqueous electrochemical measurements were made using a Pt disk working electrode ($A = 0.02\,\mathrm{cm}^2$) and a Ag/0.01 M $AgPF_6$ (MeCN/0.1 M $TBAPF_6$) reference electrode. Either TBAP or $TBAPF_6$ was used as the supporting electrolyte. Due to the high resistance of pyridine/0.13 M $TBAPF_6$ solutions, all measurements were made with instrument-determined iR compensation. ΔE_p values (CV) and $W_{1/2}$ (peak width at half height) values (DPV) are reported for measurements made using 100% iR compensation. Ferrocene was used as an internal standard and found to behave reversibly under these conditions ($E^\circ = +0.15$ V *vs.* Ag/0.01 M $AgPF_6$(MeCN), $\Delta E_p = 57$ mV, $i_c/i_a = 1$). Background scans were recorded and subtracted from both CV and CC results. All measurements were made after purging the system of oxygen with prepurified nitrogen that had been passed through a drying column and a CO_2-scavenging column.

Buffers for the pH dependent electrochemistry were made using potassium hydrogenphthalate, potassium acetate or potassium hydrogenphosphate, depending on the pH required. The pH of the buffers was adjusted by the addition of either NaOH or HCl. Ni(II)NQ_2en was adsorbed from a 10^{-5} M CH_2Cl_2 solution onto a pyrolytic graphite working electrode ($A = 0.093\,\mathrm{cm}^2$) by immersion for 30 s followed by a 30 s rinse in distilled water. Aqueous electrochemical potentials are referenced to a Ag/AgCl(saturated KCl) reference electrode.

RESULTS

Cyclic voltammetry of Ni(II)NQ$_2$en in pyridine/0.1 M TBAPF$_6$ is shown in Fig. 2. A *quasi*-reversible wave is seen $+0.537$ V *vs.* Ag/0.01 M AgPF$_6$ (MeCN) ($\Delta E_p = 90$ mV, $i_a/i_c = 1.0$). A second wave is seen at -1.305 V with $\Delta E_p = 57$ mV. This wave meets the usual requirements of electrochemical reversibility: (1) the maximum anodic and cathodic currents are proportional to the square root of scan rate ($i_p \propto \nu^{1/2}$) up to $\nu = 400$ mV/s and (2) the maximum anodic and cathodic currents are identical ($i_{p,c}/i_{p,a} = 1$). It has, however, a maximum cathodic current, $i_{p,c}$, that is 1.9 times greater than $i_{p,a}$ for the couple at $+0.537$ V. An irreversible reduction is seen at $E_{p,c} = -1.985$ V. Using differential pulse voltammetry, peaks were observed at $+0.550$ V ($W_{1/2} = 110$ mV), -1.300 V ($W_{1/2} = 90$ mV) and -1.980 V ($W_{1/2} = 120$ mV).

The electrochemistry of the related complex Ni(II)NQ$_2$(±)-1,2-pn is similar to that of Ni(II)NQ$_2$en. Waves are seen at $+0.565$ V ($\Delta E_p = 90$ mV) and at -1.255 V ($\Delta E_p = 88$ mV). The latter is reversible up to $\nu = 400$ mV/s. The maximum cathodic current for the wave at -1.255 V is now only 1.45 times greater than $i_{p,a}$ for the $+0.565$ V process. An irreversible reduction is seen at $E_{p,c} = -1.960$ V.

Chronocoulometry, shown in Fig. 3, was used to study two waves at $+0.537$ V and -1.305 V observed for Ni(II)NQ$_2$en. The starting potential was 0 V in both cases and the potential was stepped 100 mV beyond $E_{p,a}$ and $E_{p,c}$, respectively. The slopes of the Q *vs.* $t^{1/2}$ plots for these two couples are 3.54×10^{-7} C/ms$^{1/2}$ and 7.28×10^{-7} C/ms$^{1/2}$, respectively. The ratio of the slopes is 2.1/1.0. The ratio of the slopes of the Q *vs.* $t^{1/2}$ plots for the similar waves observed for Ni(II)NQ$_2$(±)1,2-pn is 2.0/1.0.

Cyclic voltammetry in aqueous buffer with Ni(II)NQ$_2$en adsorbed onto a pyrolytic carbon working electrode is shown in Fig. 4. Both ΔE_p and the peak widths at

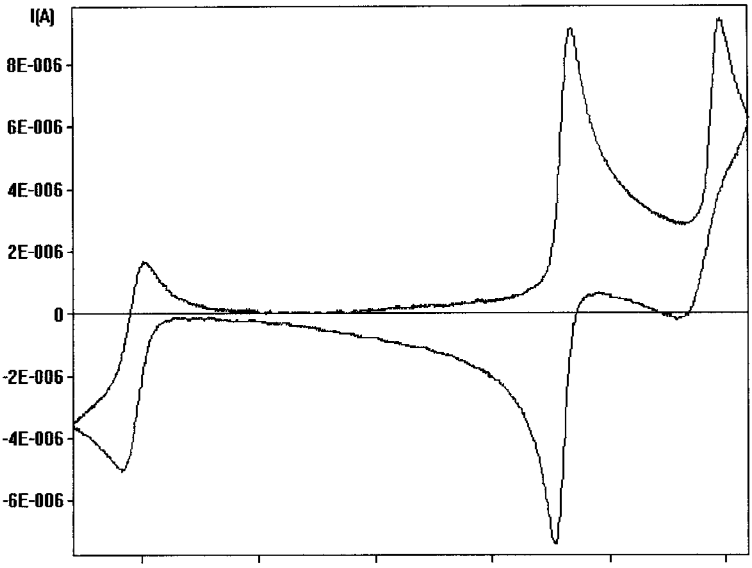


FIGURE 2 Cyclic voltammetry of 1.0×10^{-3} M Ni(II)NQ$_2$en in pyridine/0.13 M TBAPF$_6$. Working electrode: Pt disk. Reference electrode: Ag/0.01 M AgPF$_6$ (MeCN). $\nu = 100$ mV/s.

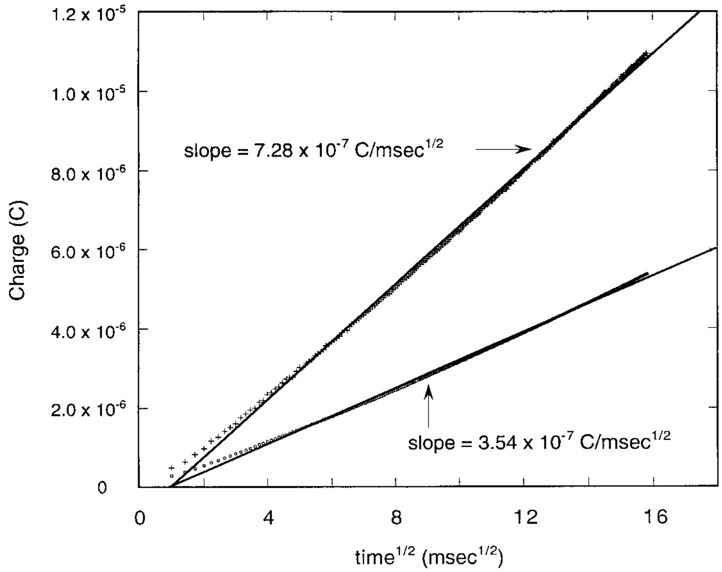


FIGURE 3 Chronocoulometry of 1.0×10^{-3} M Ni(II)NQ$_2$en in pyridine/0.13 M TBAPF$_6$. The upper curve corresponds to the -1.305 V couple and the lower to the $+0.537$ V couple. Working electrode: Pt disk. Reference electrode: Ag/0.01 M AgPF$_6$ (MeCN).

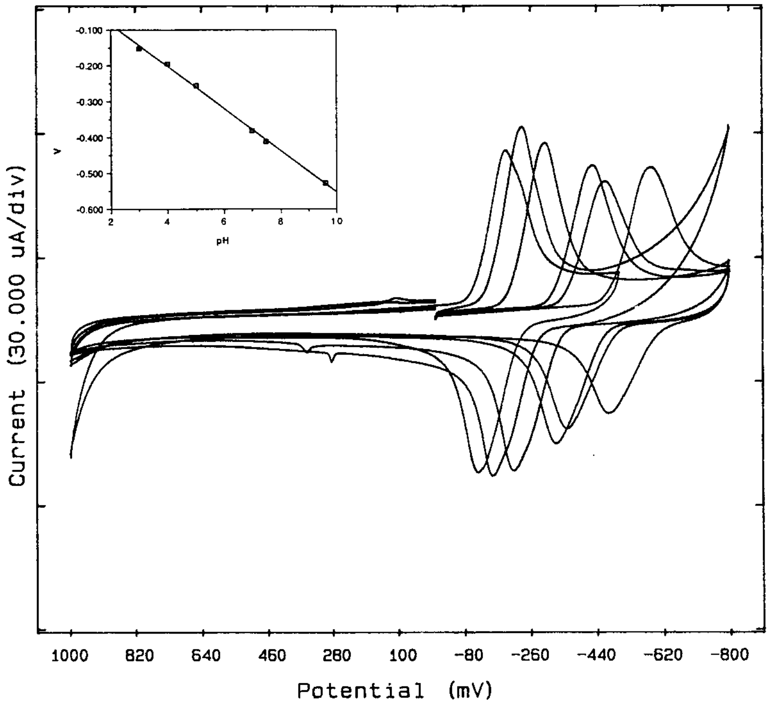


FIGURE 4 Cyclic voltammetry of Ni(II)NQ$_2$en adsorbed onto a pyrolytic graphite working electrode (coverage $= 1.4 \times 10^{-9}$ mol/cm^2). $E_{1/2}$ shifts to more negative potentials with increasing pH. Reference electrode: Ag/AgCl(satturated aqueous KCl). $\nu = 100$ mV/s. Inset: $E_{1/2}$ *vs.* pH, slope $= -59$ mV/pH.

half-height show a slight pH dependence, with ΔE_p increasing from 70 mV at pH 3.0 to 110 mV at pH 9.6 and $W_{1/2}$ increasing from 110 mV to 145 mV over the same range.

DISCUSSION

The aqueous electrochemistry of adsorbed Ni(II)NQ$_2$en can be attributed to the naphthoquinone/naphthalenediol couple. The -59 mV/pH unit shift in $E_{1/2}$ is predicted by the Nernst equation for the $4e^-/4H^+$ process

$$\mathrm{Ni(II)NQ_2en} + 4e^- + 4H^+ \rightarrow \mathrm{Ni(II)(H_2ND)_2en} \quad (\mathrm{H_2ND} = \text{naphthalenediol}).$$

This has been observed for quinones covalently bound to electrode surfaces, as well [24]. The observed ΔE_p and $W_{1/2}$, however, are much greater than the values predicted for redox-active species adsorbed on the working electrode surface of 0 mV and 90.6/n mV, respectively [25]. Integration of the currents, assuming a four-electron process, indicates a coverage of 1.39×10^{-9} mol/cm^2, a value that corresponds to multilayer coverage [26]. This possibly restricts access of the solution to the adsorbed complex and results in protonation of the reduced species that is slower than diffusion controlled, causing ΔE_p and $W_{1/2}$ to increase. Slight anti-cooperativity in the reduction of the two naphthoquinones, i.e., the second quinone might be more difficult to reduce, could also produce larger ΔE_p and $W_{1/2}$ values.

Interpretation of the nonaqueous electrochemistry of Ni(II)NQ$_2$en is greatly aided by comparison with that of Ni(II)sal$_2$en [27,28]. Both complexes provide an identical N_2O_2 coordination environment about the Ni(II) metal ion. The H$_2$sal$_2$en ligand, however, shows no redox-activity in the potential range between +1.0 and −2.0 V (*vs.* 1 M NaCl calomel) and Ni(II)sal$_2$en shows metal-based redox activity only at the extremes of this potential range. Any redox processes observed for Ni(II)NQ$_2$en inside this range not obviously due to the metal ion may thus be attributed to the naphthoquinone ligand.

The *quasi*-reversible wave at +0.537 V can be assigned as the metal-based Ni(III)/Ni(II) couple. In DMF the Ni(III)/Ni(II) couple of Ni(II)sal$_2$en is observed at +0.895 V *vs.* 1 M NaCl calomel reference electrode. This corresponds to approximately +0.760 V *vs.* the Ag/0.01 M AgPF$_6$(MeCN) reference electrode used in the present study. The difference in E^0 values for the two complexes is probably due to the fact that the pyridine solvent employed in the present study coordinates to the metal center more strongly than DMF.

Since the free ligand H$_2$NQ$_2$en shows two irreversible waves at $E_p = -1.25$ V and -1.35 V in CH$_2$Cl$_2$/0.1 M TBAPF$_6$ and the Ni(II)/Ni(I) couple in Ni(II)sal$_2$en occurs at much more negative potentials the wave at −1.305 V is assigned as the (naphthoquinone)$_2$/(semiquinone radical anion)$_2$ couple. The quinone/semiquinone couple is observed in this potential region for other structurally similar naphthoquinones [8] as well.

Confirmation that this wave represents a two-electron process is provided in several ways. The maximum cathodic and anodic currents are 1.9 times greater than those observed for the one-electron Ni(III)/Ni(II) couple. The slope of the linear portion of the Q *vs.* $t^{1/2}$ plot obtained from chronocoulometry is proportional to the number of electrons transferred [29]. For Ni(II)NQ$_2$en the Ni(III)/Ni(II) couple at $+0.537$ V can serve as an internal one-electron standard. The slopes of the plots obtained for the two waves are in a ratio of 2.1/1.0.

When (±)-1,2-propanediamine replaces ethylenediamine the Ni(II)NQ$_2$ (±)-1,2-pn complex results. The methyl group of the diamine breaks up the approximate C_{2v} symmetry of the Ni(II) complex and places the two quinone groups in slightly different environments. In the cyclic voltammogram of Ni(II)NQ$_2$(±)-1,2-pn the nonequivalence of the two quinone groups is readily seen in the wave at -1.254 V in the increase in ΔE_p to 88 mV.

The irreversible wave at -1.985 V probably represents further ligand reduction since the Ni(II)/Ni(I) couple in Ni(II)sal$_2$en is reversible [27] and the free ligand shows an irreversible reduction at approximately the same potential. The maximum cathodic current is only slightly less than that of -1.305 V wave, suggesting that it also represents a two-electron process.

The theory of cyclic voltammetry and differential pulse voltammetry for two-electron processes has been discussed by several authors [30–32] and digital simulations of cyclic and differential pulse voltammetry for two-electron processes have also appeared in the literature [31–33]. When the second electron transfer is easier than the first by more than 180 mV the CV wave is characterized by $\Delta E_\mathrm{p} = 28.5$ mV and an i_p $2^{3/2}$ greater than the i_p for a one-electron process. If, on the other hand, the second electron transfer is more difficult than the first by more than 90 mV the CV shows two separate waves. For the case where $-90\,\mathrm{mV} \leq E_2^0 - E_1^0 \leq -180\,\mathrm{mV}$ the two waves are merged into a single wave with ΔE_p and i_p values determined by the precise value of $E_2^0 - E_1^0$.

The determination of ΔE^0 for reversible two-electron redox processes is greatly aided using the working curves developed by Myers and Shain [34] for cyclic voltammetry, and by Richardson and Taube [31] for both cyclic and differential pulse voltammetries. Analysis of the two-electron couple at -1.305 V for Ni(II)NQ$_2$en indicates that $E_2^0 - E_1^0$ for this process is -36 mV, a value close to the -35.6 mV separation derived theoretically by Ammar and Savéant [10] and Flanagan *et al.* [11] for two *noninteracting* redox centers. In this case the difference between E_2^0 and E_1^0 arises through symmetry-dependent entropic effects [35]. Theory predicts that the maximum current observed for such a process using cyclic voltammetry should be twice that of a one-electron couple. That the maximum current of the -1.305 V wave is 1.9 times greater than that of the one-electron Ni(III)/Ni(II) couple is probably due to the fact that the latter couple occurs close to pyridine's anodic limit, making precise current measurements difficult. When the noninteracting naphthoquinones are no longer in identical environments, as with Ni(II)NQ$_2$(±)-1,2-pn, a different ΔE^0 value is observed. Analysis of the two-electron wave for this complex yields a value of $\Delta E_\mathrm{p} = 88$ mV and $\Delta E^0 = -62$ mV, indicative of slight anti-cooperativity. The nonaqueous electrochemistry of Ni(II)NQ$_2$en is summarized in Scheme 1.

A number of interesting metal complexes have been reported that undergo two-electron transfer with $E_1^0 \approx E_2^0$. In all of these cases the redox-activity is metal-based at either mononuclear [36,37], binuclear [12–15] or higher order polynuclear metal centers [16,17]. The two-electron redox process observed for Ni(II)NQ$_2$en, however, is localized on the organic ligand and is therefore best compared with the electrochemistry of the biquinone systems of Miller, Katz and coworkers. They found that quinone groups linked by either linear [38] or helical [39,40] aromatic spacers of various lengths underwent reduction in one-electron steps separated by at least 150 mV. This

$$[\mathrm{Ni(III)NQ_2en}]^{+} + \mathrm{e}^{-} \rightarrow \mathrm{Ni(II)NQ_2en}\ E^{0} = +0.537\,\mathrm{V}\ \mathit{vs.}\ \mathrm{Ag/AgPF_6}$$

$$\left.\begin{array}{l}\mathrm{Ni(II)NQ_2en} + \mathrm{e}^{-} \rightarrow [\mathrm{Ni(II)(SQ,NQ)en}]^{-}\ E^{0} = -1.287\ \mathrm{V}\\ [\mathrm{Ni(II)(SQ,NQ)en}]^{-} + \mathrm{e}^{-} \rightarrow [\mathrm{Ni(II)SQ_2en}]^{2-}\ E^{0} = -1.323\ V\end{array}\right\} E_2^0 - E_1^0$$

$$= -36\,\mathrm{mV}$$

$$[\mathrm{Ni(II)SQ_2en}]^{2-} + \mathrm{e}^{-} \rightarrow [\mathrm{Ni(II)(ND,SQ)en}]^{3-}\ E_{\mathrm{P,c}} \approx -1.95\,\mathrm{V}$$

$$[\mathrm{Ni(II)(ND,SQ)en}]^{3-} + \mathrm{e}^{-} \rightarrow [\mathrm{Ni(II)ND_2en}]^{4-} E_{\mathrm{p,c}} \approx -2.00\,\mathrm{V}$$

(NQ = naphthoquinone, SQ = naphthsemiquinone radical anion,
ND = naphthalenediol dianion)

SCHEME 1. Nonaqueous electrochemistry of $\mathrm{Ni(II)NQ_2en}$.

was attributed to electron delocalization over both quinone centers for the radical anion. Similar results have also been reported for linked *ortho*-quinones [41] and three benzoquinone centers linked by methylene groups [42].

The noninteraction of the naphthoquinone groups in $\mathrm{Ni(II)NO_2en}$ is somewhat surprising given the ~5.5 Å separation between NQ centers [7] but clearly indicates that the two naphthoquinone π systems are completely localized. This behavior is observed in both the presence and absence of protons.

CONCLUSION

The incorporation of quinones into organic ligands where they can serve as either electron reservoirs, for reduction reactions, or electron sinks, for oxidations, is an attractive way to give transition metal catalysts multi-electron redox capability. That several quinone centers can be incorporated into one ligand and observed to function independently is especially important. The versatility of the quinones for this application is further seen in the ease with which the quinone reduction potential can be shifted to values appropriate for the reaction being catalyzed by substitution with either electron donating groups, such as -OR or -$\mathrm{NR_2}$, or electron withdrawing groups, such as -$\mathrm{NO_2}$ [8,43].

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