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Complexes of Quinone-Functionalized Chelating Ligands for Multiple Electron/Proton Transfer Reduction Reactions

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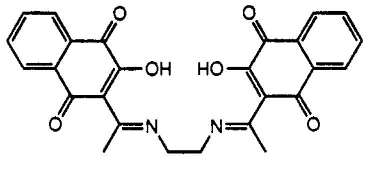
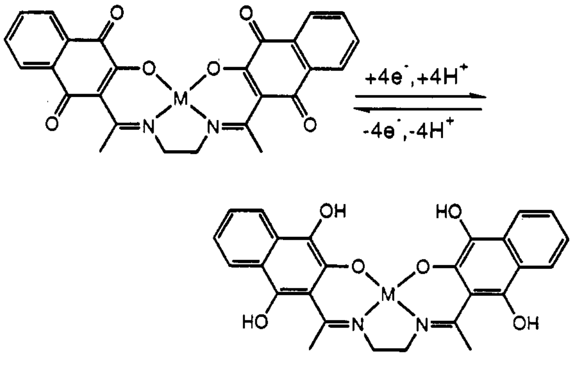
Small-molecule reduction processes often require rapid multiple electron/proton transfer steps to avoid formation of thermodynamically stable intermediates.[1] In biological systems metalloenzymes efficiently catalyze the reduction of dioxygen and dinitrogen in steps that provide four electrons in rapid succession.[2,3] Air fuel cell development[4] and interests in efficient ammonia production[5] have stimulated research on synthetic systems that may ideally operate with the rate and efficiency of the metalloenzymes. Multiple electron/proton transfer steps in both biological and synthetic reduction systems require the concerted activity of coupled redox centers that operate at electrochemical potentials capable of effecting reduction with minimum overpotential. Multidentate chelating and macrocyclic ligands, including porphyrins, have been used in the design of mono- and dimetallic systems that utilize the redox activity of cooperatively coupled metal centers.[6] Biological systems often take advantage of the combined redox activity of a single metal operating in concert with electroactive quinoid cofactors.[7] Synthetic systems designed on the basis of this principle are under investigation. We now describe preliminary results on the synthesis and characterization of a quinone-functionalized chelating ligand with complexes of Ni and Cu.



NQ$_2$en (I)

The ligand system chosen for investigation is based on the familiar SALEN ligand, but prepared with naphthoquinone substituents (I). Complexes will not involve direct metal–quinone bonding, although the quinone functional groups may be electronically coupled with the metal through the π system of the ligand. In the fully reduced bis(dihydroxynaphthalene) form, the ligand itself is capable of providing four electrons and four protons to a metal-bound substrate (eq 1). Redox-active Schiff base ligands of this type have the advantage of being relatively easy to synthesize, and the planarity of the metal complexes makes them good candidates for surface absorption for electrocatalytic purposes.



(1)

Synthesis of the (NQ)$_2$en ligand was carried out by Schiff base condensation of 2-hydroxy-3-acetyl-1,4-naphthoquinone with ethylenediamine, and complexes of Cu and Ni were prepared from the acetate complexes of the metal ions.[8] The Cu(II)

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(8) **H$_2$((NQ)$_2$en)** was prepared by the condensation of 2-hydroxy-3-acetyl-1,4-naphthoquinone (2.0 g, 9.2 mmol) with ethylenediamine (0.27 g, 4.5 mmol) in methanol (60 mL) solution. The solution was refluxed for 1 h, and the yellow microcrystalline product was collected and dried under vacuum. **Cu((NQ)$_2$en)(H$_2$O)** was formed by stirring H$_2$(NQ)$_2$en (0.5 g, 1.1 mmol) with Cu(OAc)$_2$·H$_2$O (0.22 g, 1.1 mmol) in warm DMF for 1 h. The brown microcrystalline product was collected, washed with diethyl ether, and dried under vacuum. Crystals suitable for structural

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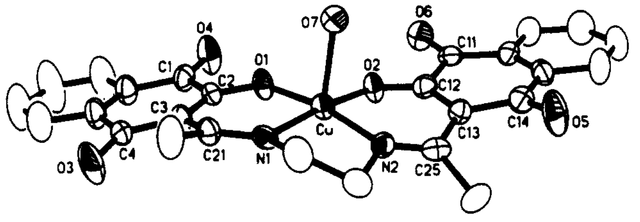


Figure 1. The $Cu((NQ)_2en)(H_2O)$ complex molecule.

complex, obtained in crystalline form as the aquo complex, $Cu((NQ)_2en)(H_2O)$, has been characterized crystallographically; a view of the molecule is shown in Figure 1.[9] Donor atoms of the tetradentate $(NQ)_2en$ ligand occupy basal sites of a square pyramid, with a slight twist between NQ rings.

Electrochemical characterization of the free $(NQ)_2en$ ligand and of $Cu((NQ)_2en)$ and $Ni((NQ)_2en)$ shows the strongly reductive character of the fully reduced bis(naphthalenediolate) ligand.[10] Cyclic and differential pulse voltammograms recorded on $(NQ)_2en$ show two closely spaced reductions at potentials of −0.903 and −1.065 V (vs NHE) as the quinone functionalities are reduced to the dianionic bis(naphthosemiquinone) form of the ligand. Further reductions take place at more negative potentials to give the bis(naphthalenediolate) tetraanion. The first reduction appears at −1.565 V; the second is outside the experimental potential range. Electrochemical experiments on $Ni((NQ)_2en)$ were carried out in dichloromethane, further limiting the negative potential range, but the observed NQ/SQ reductions (eq 2) were

$$Ni((NQ)_2en) \overset{e^-}{\rightleftarrows} Ni((NQ)(SQ)en)^- \overset{e^-}{\rightleftarrows} Ni((SQ)_2en)^{2-} \qquad (2)$$

found to occur at potentials that were quite similar to those of the free ligand. In noncoordinating solvents $Ni((NQ)_2en)$ is square planar and diamagnetic.[8] However, in pyridine the complex becomes six-coordinate and paramagnetic, with paramagnetically shifted proton resonances in the ^1H NMR spectrum. The metal of $Ni((NQ)_2en)$ is electrochemically inactive, while studies on Cu(SALEN) and on copper complexes prepared with SALEN-derived ligands show that the Cu(I)/Cu(II) couple typically occurs at potentials near the first reductions of $(NQ)_2en$.[11] Electrochemical characterization of $Cu((NQ)_2en)$ (Figure 2) shows reductions at −0.860, −1.065, and −1.580 V, with cyclic and differential pulse voltammograms that are nearly identical to those of the free ligand. This similarity strongly suggests that the reductions are ligand based. Metal ion reduction may occur for the bis(naphthalenediolate) (II) species, but at an extremely negative potential. Protonation of II to give the neutral bis(naphthalenediol) complex, $Cu(H_4(ND)_2en)$, would deactivate the ligand in much the same way that protonated catechol is inactive while the catecholate dianion is strongly reductive. The metal of $Cu(H_4(ND)_2en)$ may undergo reduction at a potential that is more similar to that of Cu(SALEN). The combined electrochemical activity of the ligand and metal of both $Cu((NQ)_2en)$ and $Cu(H_4(ND)_2en)$ illustrate the pH-selective chemical activity that is to be expected for complexes prepared with quinone-functionalized ligands.

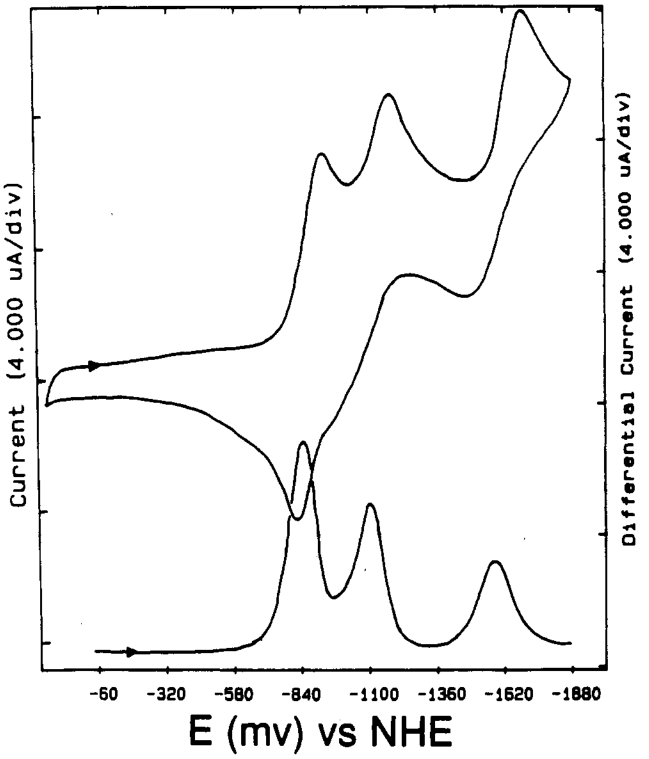
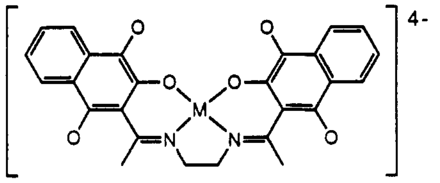


Figure 2. Cyclic and differential pulse voltammograms of $Cu((NQ)_2en)$, recorded in DMF solution, at a scan rate of 100 mV/s.



II

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Supplementary Material Available: Tables giving crystal data, atomic coordinates, bond lengths, bond angles, and thermal parameters for $Cu((NQ)_2en)(H_2O)$ (11 pages). Ordering information is given on any current masthead page.

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characterization were grown by slow evaporation of a 1:1 pyridine–cyclooctane solution. UV–vis (CH_2Cl_2): 570 nm (550 M^{-1} cm^{-1}), 477 (sh), 433 (5200), 345 (sh), 328 (54 000). EPR (powder at 77 K): $g_\parallel = 2.06$, $g_\perp = 2.21$. $Ni((NQ)_2en)$ was prepared using the procedure described above beginning with $Ni(OAc)_2{\cdot}4H_2O$. The complex was isolated as a red microcrystalline product. UV–vis (CH_2Cl_2): 510 nm (2700 M^{-1} cm^{-1}), 484 (2800), 370 (15 000), 307 (41 000). ^1H NMR ($CDCl_3$): δ 7.60–8.20 (m, 8H, Ar H), 3.4 (m, 4H, $-CH_2-$), 2.55 (m, 6H, $-CH_3$).

(9) Crystal data for $Cu((NQ)_2en)(H_2O)$: triclinic, $a = 7.856(2)$ Å, $b = 9.728(2)$ Å, $c = 16.033(3)$ Å, $\alpha = 98.62(2)°$, $\beta = 96.26(2)°$, $\gamma = 112.15(2)°$, $V = 1103.6(4)$ $Å^3$, space group $P\bar{1}$, $Z = 2$, $d_{calcd} = 1.613$ g cm^{-3}. Of the 2897 unique reflections measured, 1831 with $I > 3\sigma(I)$ were considered observed and included in the refinement. At convergence, $R = 0.057$ and $R_w = 0.059$.

(10) Cyclic and differential pulse voltammograms were obtained with a Cypress CYSY-1 computer controlled electroanalysis system. $(NQ)_2en$ and $Cu((NQ)_2en)$ were studied in DMF solution; voltammograms for $Ni((NQ)_2en)$ were obtained in CH_2Cl_2 due to the low solubility of the complex in DMF. Solutions were prepared with complex concentrations of 10^{-4} M and with 0.1 M concentrations of TBHP electrolyte. A platinum disk working electrode and a platinum wire counter electrode were used. A Ag/Ag^+ reference electrode was used, and the Fc/Fc^+ couple was used as an internal standard.

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