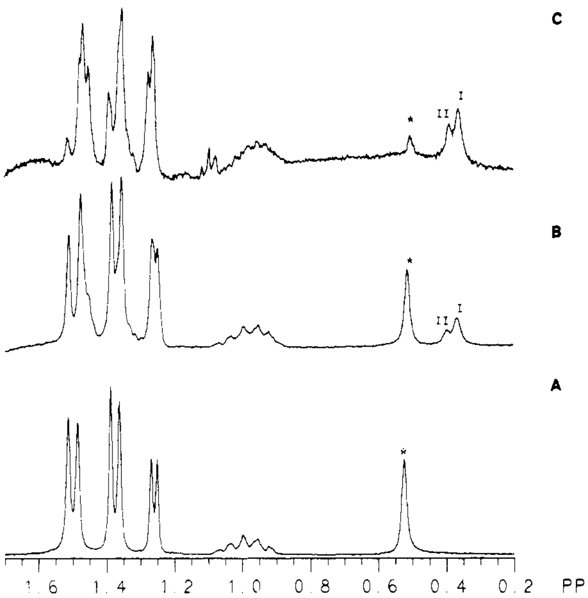

Figure 3. ^1H NMR spectra in D_2O of the upfield methyl region: (A) B_{12a}, 5 mM, pD 4.9 (designated with an asterisk); (B) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (4:1) [note that new species are present (signals I and II)], pD 4.9, after 8 days at room temperature; (C) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (12:1), pD 5, after 7 days at room temperature.

signals which are essentially identical to those of I (Table I). With time, II became more evident as observed with the $[Co(trpn)(H_2O)_2]^{3+}$ reactions. Because it is a secondary product formed after long time periods, we have not characterized II. However, some points are worthy of note. The H2 and C20H$_3$ signals are substantially shifted for both I and II into regions found with other amine ligands. Thus, we believe II is similar to I in having an axially coordinated trpn. The result for H2 rules out displacement of the coordinated 5,6-dimethylbenzimidazole for both I and II since a substantial downfield shift (below 9 ppm) would be expected.[12]

We also monitored the ^1H NMR spectra during the reaction of cyanocobalamin and $[Co(trpn)(H_2O)_2]^{3+}$. However, although $[Co(trpn)(H_2O)_2]^{3+}$ decomposed, releasing protonated trpn, even though the pD was kept at ~7, no ^1H NMR signals of either I or II were observed, even after long periods of time. This result is consistent with the axial ligation by trpn of B_{12a} since CN^- is a poorer leaving group than H_2O.

In conclusion, $[Co(trpn)(H_2O)_2]^{3+}$ is relatively unstable and tends to decompose readily under a broad range of conditions.[13] These conditions include those used previously.[3-6,13] The only new cobalamin products involve B_{12a}; the primary product formed is a simple trpn-B_{12} adduct formed by displacement of the axial aqua ligand. A secondary product, difficult to characterize because of its slow formation, probably also contains an axial coordinated trpn on the basis of the similarity in ^1H NMR shifts to the initial major product, but further studies would be necessary to characterize this minor product. However, when CNB_{12} is treated with $[Co(trpn)(H_2O)_2]^{3+}$, no evidence of the formation of I and II is found. The $[Co(trpn)(H_2O)_2]^{3+}$ complex, despite its promise as an agent to promote phosphodiester hydrolysis,[3,5] did not promote the hydrolysis of the phosphodiester group of either CNB_{12} or B_{12a}. Coordination of $[Co(trpn)(H_2O)_2]^{3+}$ to the phosphodiester group clearly does not occur, and furthermore, there is no hydrolysis of the amide groups.

Acknowledgment. A. M. Calafat is grateful to the Government of Spain for a postdoctoral Fulbright fellowship. This study was supported by NIH Grants GM 29225 and GM 29222. We thank Dr. M. Banaszczyk for helpful suggestions.

Registry No. CNB_{12}, 68-19-9; B_{12a}, 13422-52-1; trpn, 4963-47-7; $[Co(trpn)(H_2O)_2]^{3+}$, 96914-54-4; $[Co(trpn)(CO_3)]^+$, 118841-57-9.

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(13) The deligation reaction was noted briefly previously (Chin, J.; Kim, J. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 523-525), but it was not reported to occur in studies of phosphate ester hydrolysis.[3,4,6] We find decomposition occurs in the absence of B_{12} substrate. There appears to be less than 0.01 equiv of Co^{2+} present initially in our complex even after storage at ambient temperature for over 6 months as judged by the Zincon method (Rush, R. M.; Yoe, J. H. *Anal. Chem.* **1954**, *26*, 1345-1347). No detectable Co^{2+} was present in B_{12a}. The addition of 0.1 equiv of Co^{2+} had no effect on the deligation rate. The deligation appears to begin immediately after solutions are prepared, and thus any estimate of the Co^{2+} content should be high.

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Toward a Functional Model of Hydrogenase: Electrocatalytic Reduction of Protons to Dihydrogen by a Nickel Macrocyclic Complex

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and Robert H. Crabtree

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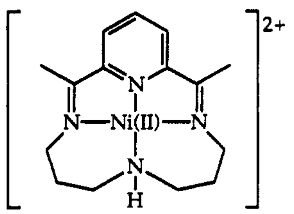
Functional modeling is an area of interest in bioinorganic chemistry. We have recently begun to screen a variety of Ni complexes for catalytic activity in reactions relevant to the nickel-containing metalloenzymes. For example, hydrogenases catalyze the reactions shown in eqs 1 and 2, and Ni has been

$$2H^+ + 2e^- \rightleftharpoons H_2 \tag{1}$$

$$D_2 + H_2O \rightleftharpoons HD + HOD \tag{2}$$

proposed to be the site for H_2 binding and oxidation.[1-4] We have already reported that certain Ni complexes catalyze eq 2,[5] and we now find that under electrochemical conditions, complex **1** catalyzes the physiologically important reaction shown in eq 2.



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Complex **1** is known to undergo two successive one-electron reductions.[6] In DMF solution the first couple corresponds to reduction of the ligand at -0.68 V (vs Ag/AgCl) to form a $[Ni^{II}L^{\bullet-}]^+$ species, which has been isolated and characterized by EPR spectroscopy. The second electron is delivered to the metal center at -1.25 V, to form a $[Ni^{I}L^{\bullet-}]^0$ complex. We have found that the application of an electrochemical potential of -1.1 V (pH 2.0, carbon electrode, Ag/AgCl reference) to aqueous solutions of **1** leads to visible bubbling of H_2, which is not observed in the absence of the catalyst. The potential is considerably lower than that required for the formation of the $[Ni^{I}L^{\bullet-}]^0$ complex, and the onset of catalysis results from the initial ligand-based reduction to form the $[Ni^{II}L^{\bullet-}]^+$ complex. The electrocatalytic reduction of protons to H_2 by Ni(I) has previously been observed.[7,8]

Experimental Section

Materials. Dimethylformamide (Burdick and Jackson) was used as received. Tetra-*n*-butylammonium perchlorate was purchased from

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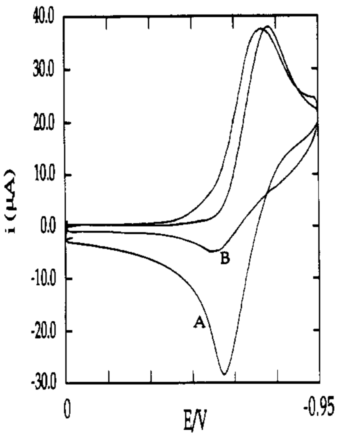

Figure 1. Cyclic voltammogram of (A) a 5 mM solution of **1** in 0.1 M TBAP/DMF with a glassy-carbon working electrode at 500 mV/s and (B) solution a upon addition of 0.4 equiv (2 mM) of HPF_6.

Johnson Matthey and recrystallized from ethanol/water. All other reagents were obtained from Aldrich Chemical Co. Compound **1** was prepared by literature methods.[9]

Electrochemical Measurements. Cyclic voltammetric (CV) and square-wave voltammetric (SWV) experiments were conducted on a Princeton Applied Research (PAR) Model 273 potentiostat. A single-compartment cell was fitted with a 3.0-mm-diameter glassy carbon disk as the working electrode, a nichrome wire as the auxiliary electrode, and a saturated calomel reference electrode (SCE). Ten-milliliter portions of 0.1 M TBAP/DMF or pH 2 phosphate buffer solutions of **1** were purged with N_2 for 10 min.

Controlled-potential electrolysis experiments were conducted in a gastight H-cell, with a medium glass frit separating the two compartments. The reference electrode (Ag/AgCl) with a ground-glass joint and Vycor frit was fitted to the main compartment, which was also connected to a 100-mL gas buret. Reticulated vitreous carbon (80 pores/cm^3) was used as the working electrode; a nichrome wire counter electrode was placed in the auxiliary compartment. In a typical experiment, a 5 mM solution of **1** in pH 2 phosphate buffer was purged with N_2 for 20 min. While the solution was stirred, potential of −1.1 V was applied until the current dropped to the background level and displacement of mineral oil in the buret ceased. Analysis of the resulting solutions by UV–vis spectroscopy showed that minimal diffusion between compartments occurred.

Analysis. Molecular hydrogen was characterized on a Varian Model 920 GC with a 2 ft × $^1/_4$ in. molecular sieve column at 65 °C with He carrier gas. During long-term experiments, H_2 evolution was quantified by manometry. Background runs were performed in the absence of catalyst, where only negligible H_2 production occurred. The total charge passed during catalytic runs was corrected for background current.

Results and Discussion

Protonation in Nonaqueous Solution. The cyclic voltammogram of **1** in DMF solution is shown in Figure 1A. The wave at −0.68 V corresponds to the $[Ni^{II}L]^{2+}/[Ni^{II}L^{\bullet -}]^{+}$ couple. Addition of HPF_6 to these solutions leads to a decrease in anodic current for the $[Ni^{II}L]^{2+}/[Ni^{II}L^{\bullet -}]^{+}$ couple, as shown in Figure 1B. We studied this effect from 0.1–1 equiv of H^+; the voltammogram shown in Figure 1B was recorded in the presence of 0.4 equiv (2 mM) of H^+. As expected, ~40% of the oxidative wave is lost under these conditions. The decrease in i_a continues monotonically with increasing concentrations of H^+.

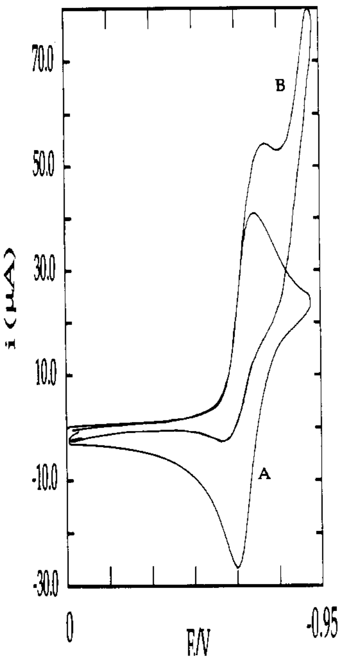

Figure 2. Cyclic voltammogram of (A) a 5 mM solution of **1** in 0.1 M TBAP/DMF with a glassy-carbon working electrode at 500 mV/s and (B) solution a upon addition of excess CF_3CH_2I.

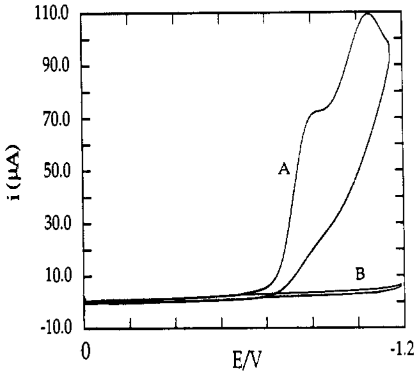

Figure 3. Cyclic voltammogram of a pH 2 phosphate buffer solution at 500 mV/s with (A) 7.5 mM **1** and (B) no catalyst added.

Notably, there is no increase in i_c with added H^+. Hydrogenation of L in **1** has been observed,[10] but this is a $2e^-/2H^+$ process. If addition of H^+ was inducing ligand hydrogenation, then an increase in i_c with $[H^+]$ would be observed. In fact, it is difficult to envision a reaction of the ligand that could be restricted to $1e^-$ after the addition of a proton. The scan-rate and $[H^+]$ dependences are consistent with an EC mechanism, where protonation of the complex follows the reversible, one-electron, ligand-reduction step.[11] As expected for an E_rC_i mechanism, there is a positive shift in the cathodic peak potential upon addition of $[H^+]$ that is evident in Figure 1B. It therefore appears that reduction of the ligand activates the metal center toward H^+.

As a working hypothesis, we envisage a mechanism in which the reduced metal is protonated to give a hydride. This is plausible because there is no other basic site but the metal in the complex, and no case of hydrogen production via transition metal catalysis has been reported in which metal hydrides were not involved. If this is true, the $[Ni^{II}L^{\bullet -}]^{+}$ species should also be reactive toward other electrophiles.

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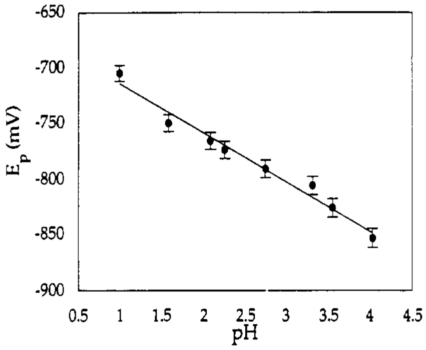

Figure 4. Plot of E_p vs pH for 0.1 M phosphate buffer solutions of **1** (5 mM). A least-squares fit gives the solid line with a slope of 45 mV/pH unit.

As expected from our hypothesis, this is indeed the case. Figure 2 shows the cyclic voltammogram of **1** in DMF in the presence and absence of CF_3CH_2I. Clearly, electrocatalytic reduction of the alkyl iodide occurs upon reaching the $[Ni^{II}L]^{2+}/[Ni^{II}L^{\bullet -}]^+$ couple. Again, one-electron reduction of the ligand bound to Ni(II) activates the metal center toward electrophiles. Reaction of an electrophile E^+ with $[Ni^{II}L^{\bullet -}]^+$ would be expected to give $[E\text{-}Ni^{III}L]^+$. Efforts to characterize intermediates in this system are underway, but have not so far been successful. Paramagnetic hydrides and alkyls are rather rare in part because characterization of these unstable species is difficult. In DMF, the $[Ni^{II}L^{\bullet -}]^+$ species initiates electrocatalysis with the more reactive electrophile, CF_3CH_2I, but not with the proton. Electrocatalytic reduction of H^+ is observed in aqueous solution, possibly because acid-base equilibrium is required.

Cyclic Voltammetry in Aqueous Solution. In aqueous solution at a glassy-carbon working electrode, catalytic currents resulting from H_2 evolution are observed for the reduction of **1** (Figure 3). The catalytic currents for both cathodic peaks are linearly dependent on the concentration of **1** with a zero intercept, suggesting a mechanism that is monomolecular in catalyst. Furthermore, the peak current varies linearly with $v^{1/2}$, ruling out electrode adsorption from the electrocatalytic mechanism.[11] Sauvage et al. have shown that electrode adsorption lowers the potential of electrocatalytic H^+ reduction by Ni(II/I) couples in aqueous solution.[8]

The shoulder at ~−0.9 V (Figure 3) can be further resolved using square-wave voltammetry.[12] The E_p for the square-wave voltammogram is pH-dependent, with a slope of 45 mV/pH unit (Figure 4). The value observed here is intermediate between what we would expect for a $1e^-/1H^+$ reduction, such as would be seen if the protonation gave a $Ni^{III}\text{-}H$ species, and a $1e^-/2H^+$ reduction, as would be observed if protonation gave the dihydrogen complex, $Ni^{III}\text{-}H_2$.[11] The intermediate value may result from the presence of two pathways or from the failure of square-wave voltammetry to resolve the appropriate potential. Nonetheless, our observations that the catalytic current is first order in **1** and that the peak potential becomes more negative with increasing pH are consistent with either of these pathways, but not one involving a dinuclear Ni complex.

Controlled-Potential Electrolysis. In order to produce macroscopic quantities of H_2, we moved to controlled-potential electrolysis of pH 2 solutions of **1** at a more negative potential. For example, 12 h of electrolysis at −1.1 V electrolysis resulted in the evolution of 14.2 mL of H_2, the identity of which was confirmed by gas chromatography. A control experiment in the absence of catalyst for 12 h produced only 0.3 mL of H_2. From coulometry, we calculate a total turnover number of 12.7 with a current efficiency for H_2 evolution of >95%.[13]

Mechanism and Biological Relevance. Our measurements in DMF suggest the storage of an electron in L, followed by an outer-sphere protonation step to form a 5-coordinate $Ni^{III}\text{-}H$ species. A $Ni^{III}\text{-}H$ species has been proposed as the active form in the redox cycle of hydrogenase.[14] In aqueous solution, this species reacts further to produce H_2. The mechanism shown in eqs 3-6 is a working hypothesis consistent with our observations.

$$[Ni^{II}L]^{2+} + e^- \rightleftharpoons [Ni^{II}L^{\bullet -}]^+ \quad (3)$$

$$[Ni^{II}L^{\bullet -}]^+ + H^+ \rightleftharpoons [H\text{-}Ni^{III}L]^{2+} \quad (4)$$

$$[H\text{-}Ni^{III}L]^{2+} + e^- + H^+ \rightleftharpoons [H_2\text{-}Ni^{II}L]^{2+} \quad (5)$$

$$[H_2\text{-}Ni^{II}L]^{2+} \rightleftharpoons [Ni^{II}L]^{2+} + H_2 \quad (6)$$

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Magnetochemistry of the Tetrahaloferrate(III) Ions. 3. Specific Heat of Bis[4-bromopyridinium tetrachloroferrate(III)]-4-Bromopyridinium Chloride

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Introduction

The crystal structure and magnetic susceptibilities of bis[4-bromopyridinium tetrachloroferrate(III)]-4-bromopyridinium chloride were recently reported.[2] This substance is a canted antiferromagnet, ordering at 2.34 K, and is one of a large series of related materials.[2-5]

The specific heat of a system is an important indicator of cooperative magnetic behavior.[6] Thus, the observation of a λ-anomaly indicates that a phase transition has taken place and identifies precisely the transition temperature, while broad maxima are generally indicative of the presence of substantial short-range order.

Though the existence of pairs of metal ions was apparent in the crystal structure of $2[4\text{-}Br(py)H][FeCl_4]\cdot[4\text{-}Br(py)H]Cl$, there was no noticeable contribution of short-range order to the susceptibility of the compound. We present here strong evidence,

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