Effects of Coordination to Transition Metals on the Hydration and Electroactivity of the Chelating Ligand 1,10-Phenanthroline-5,6-dione

Yabin Lei, Chunnian Shi, and Fred C. Anson*

Arthur Amos Noyes Laboratories,[†] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received December 8, 1995[⊗]

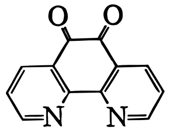
The intrinsically electroactive ligand in the title was coordinated to Co^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{+}, and the resulting hydration of the carbonyl groups of a portion of the coordinated ligand eliminated its electroactivity. The extent of hydration of the coordinated ligand was evaluated by means of rotating disk voltammetry. Estimates were obtained for the equilibrium constants governing the hydration reaction. The hydration induced by coordination of the ligand to the metal cations varied in parallel with the magnitude of the first association constant for the metal−ligand coordination.

The coordination chemistry and electrochemistry of the chelating ligand 1,10-phenanthroline-5,6-dione (pdon) have been examined in several studies.[1−7] (The structures of pdon and its reduced counterpart, pdol, are given in Figure 1.) Most recently, the effect of protonation of the basic nitrogen sites of the molecule on its electrochemical activity was described.[8] Protonation of pdon induces the partial hydration of the carbonyl groups to produce a nonelectroactive *gem*-diol.[8] The present study was carried out to determine if the hydration of the pdon ligand is also induced by its coordination to metal cations. The results showed that, in complexes formed between pdon and Co^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{+} in solution, the ligand is extensively hydrated and the extent of the hydration depends upon the stability of the pdon−metal complexes. In the complex formed between Cu^{+} and pdon adsorbed on graphite electrodes, the ligand is also very extensively hydrated.

Experimental Section

Materials. 1,10-Phenanthroline-5,6-dione (pdon) was prepared and purified by following the procedures of Yamada et al.[9] Other chemicals were commercial reagent grade products and were used as received. Solutions were prepared from laboratory-deionized water that was treated further by passage through a purification train (Milli-Q Plus).

Apparatus and Procedures. Conventional electrochemical instrumentation and two-compartment cells were employed. Edge-plane pyrolytic graphite working electrodes (0.32 cm^2) from Union Carbide were mounted on stainless steel shafts with heat-shrinkable tubing. To minimize the spontaneous adsorption of the ligand and its complexes on the graphite surface, electrodes were polished to a mirror finish using 0.05 μm alumina on a polishing wheel followed by sonication in pure water for 15 min. before each experiment. Uv−vis spectra were recorded with a HP8452 spectrophotometer (Hewlett Packard). Experiments were conducted at the ambient laboratory temperature, 22 ± 2 °C.


1,10-phenanthroline-5,6-dione (pdon)

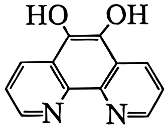

1,10-phenanthroline-5,6-diol (pdol)

Figure 1. Structures of the oxidized (pdon) and reduced (pdol) ligands employed in this study.

Results and Discussion

Voltammetry of pdon and $[Co(pdon)_3]^{2+}$ at a Rotating Disk Electrode. The electroreduction of pdon to pdol in aqueous media at pH values where the ligands are not protonated causes the very slightly soluble pdol to precipitate at the electrode surface, which makes the voltammetric response irreversible,[3] and can produce distortions in cyclic and rotating disk voltammograms.[8] The solubility of pdol is much greater in the presence of metal cations with which it forms complexes,[2,3,8] but even in solutions containing only pdon, it was possible to obtain current−potential curves for its reduction at rotating glassy carbon disk electrodes that exhibited initial plateau currents corresponding to a diffusion-convection-controlled process. For example, shown in Figure 2A is a set of current−potential curves for the reduction of pdon both in the absence and in the presence of Co^{2+}. In the absence of Co^{2+}, the cathodic plateau current is flat only in its initial portion but Levich plots[10] of this current vs the electrode (rotation rate)$^{1/2}$ were approximately linear (open squares in Figure 2B) with a slope corresponding to the two-electron reduction of pdon, which has a diffusion coefficient of 6.3×10^{-6} cm^2 s^{-1}.[8]

The addition of small quantities (relative to the pdon) of Co^{2+} to the solution of pdon produced two effects: The cathodic plateau current for the reduction of pdon diminished and an anodic wave appeared near 0.5 V where the $[Co(pdon)_3]^{2+}$ complex is oxidized to $[Co(pdon)_3]^{3+}$ (curves 2 and 3 in Figure

---

[†] Contribution No. 9165.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Eckert, T. S.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 4431.
(2) Eckert, T. S.; Bruice, T. C.; Gainor, J. A.; Weinreb, S. M. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2553.
(3) Hilt, G.; Steckhan, E. *J. Chem. Soc., Chem. Commun.* **1993**, 1706.
(4) Itoh, S.; Fukishima, H.; Komatsu, M.; Ohshiro, Y. *Chem. Lett.* **1992**, 1583.
(5) Gillard, R. D.; Hill, R. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1217.
(6) (a) Evans, D. H.; Griffith, D. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *134*, 301. (b) *Ibid.* **1982**, *136*, 149.
(7) Goss, C.; Abruña, H. D. *Inorg. Chem.* **1985**, *24*, 4263.
(8) Lei, Y.; Anson, F. C. *J. Am. Chem. Soc.* **1995**, *117*, 9849.
(9) Yamada, M.; Tanaka, Y.; Yoshimoto, Y.; Kuroda, S.; Shimao, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006.
(10) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962; pp 345−57.

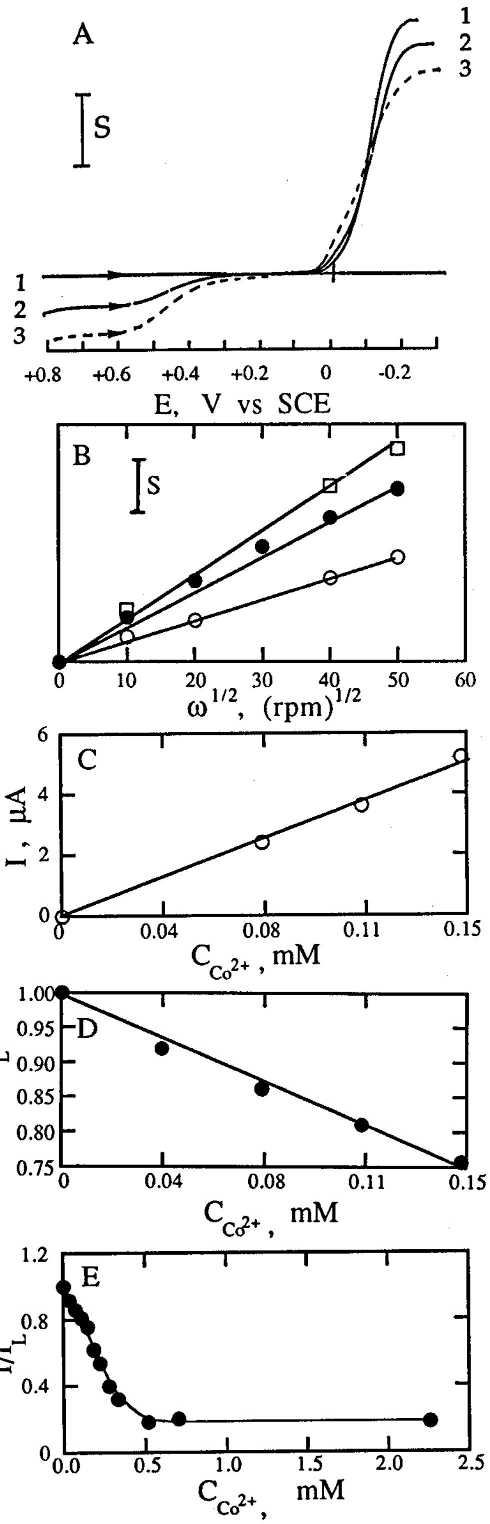
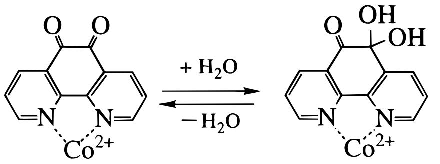


Figure 2. (A) Current−potential curves for the reduction of 1 mM pdon and the oxidation of $[Co(pdon)_3]^{2+}$ at a rotating glassy carbon disk electrode. Total concentrations of Co(II): (1) 0, (2) 0.074, (3) 0.148 mM. Supporting electrolyte: 0.05 M acetate buffer at pH 5. Electrode rotation rate = 1600 rpm. $S = 20$ and 100 μA for the anodic and cathodic currents, respectively. (B) Levich plots for the reduction of 1 mM pdon in the absence of Co^{2+} (□) and in the presence of 0.074 mM Co^{2+} (●), $S = 100$ μA; Levich plot for the oxidation of $[Co(pdon)_3]^{2+}$ (○), $S = 5$ μA. (C) Anodic plateau currents for the oxidation of $[Co(pdon)_3]^{2+}$ as a function of the concentration of Co(II). The total concentration of pdon was 1 mM, and the electrode rotation rate was 100 rpm. (D) Cathodic plateau currents for the reduction of pdon relative to its value in the absence of Co(II) as a function of the concentration of Co(II). The currents were measured at a rotation rate of 2500 rpm. (E) Extension of (D) to higher concentrations of Co(II).

2A). The reported equilibrium constants for the complexation of Co^{2+} by pdon[2] are sufficiently large that all of the Co^{2+} is present as $[Co(pdon)_3]^{2+}$ under the conditions employed in Figure 2A. The anodic plateau currents yielded a linear Levich plot (open circles in Figure 2B), but the cathodic plateau currents did not (solid circles in Figure 2B).

The anodic plateau current increased with the concentration of Co(II) as shown in Figure 2C. At the same time, the cathodic plateau current for the combined reduction of coordinated and uncoordinated pdon decreased (even though the total quantity of pdon present did not change) (Figure 2D). The decrease is presumed to reflect the hydration of the carbonyl groups of the pdon molecules that are coordinated to the Co(II) cations because the *gem*-diol resulting from the hydration (reaction 1) is not electroreducible.[8]



(1)

At the highest electrode rotation rate used in Figure 2B (2500 rpm), very little of the hydrated form of the ligand is converted to the unhydrated form during the time required for it to cross the diffusion-convection (Levich) layer at the rotating disk electrode.[10] This conclusion follows from the observation that the current at 1600 rpm lies very close to the straight line drawn from the origin through the point at 2500 rpm in Figure 2B. Thus, the hydration−dehydration equilibrium can be regarded as approximately "frozen" at a rotation rate of 2500 rpm. At lower rotation rates, the positive deviations of the measured currents from the straight line reflect the changes in the extent of hydration of the coordinated ligand that occur as the complex crosses the Levich layer at the electrode surface. Thus, the magnitude of the plateau current measured at 2500 rpm provides a measure of the equilibrium concentration of unhydrated pdon (both coordinated and uncoordinated) present in the solution.[8] The plateau current for the reduction of pdon decreased by 25% when the initially 1 mM solution of pdon also contained 0.15 mM Co^{2+} (Figure 2D). If all of the pdon coordinated to the Co(II) in the $[Co(pdon)_3]^{2+}$ complex were hydrated, the cathodic plateau current would have decreased by 45%. Thus, it appears that only a fraction of the coordinated pdon becomes hydrated. This fraction can be estimated from the plateau currents at the rotating disk electrode.

The cathodic plateau current in the presence of Co^{2+} will be given by eq 2, where I is the measured plateau current, I_L is the

$$\frac{I}{I_L} = 1 - \frac{3C_{Co}K_H^{Co}}{C_{pdon}^0(1 + K_H^{Co})} \tag{2}$$

Levich current for the reduction of pdon in the absence of Co^{2+}, C_{Co} is the concentration of Co(II) in the solution, C_{pdon}^0 is the initial concentration of (unhydrated) pdon present in the solution (the diffusion coefficients of coordinated and uncoordinated pdon are assumed to be equal), and K_H^M is the equilibrium constant governing the hydration of pdon coordinated to metal M, defined as

$$K_H^M = \frac{[\text{pdon-}H_2O]_c}{[\text{pdon}]_c} \tag{3}$$

where $[\text{pdon-}H_2O]_c$ and $[\text{pdon}]_c$ are the concentrations of coordinated pdon that are hydrated and unhydrated, respectively.

$K_H^{Co}/(1 + K_H^{Co})$ is the fraction of the coordinated pdon that is hydrated and therefore nonelectroactive, and $3C_{Co}$ is the total concentration of coordinated pdon under conditions where the only complex formed is Co(pdon)$_3^{2+}$. According to eq 2, the slope of the line in Figure 2D is $3K_H^{Co}/(C^0_{pdon}(1 + K_H^{Co}))$, from which one calculates K_H^{Co} =1.2. This value of K_H^{Co} corresponds to the hydration of 54% of the pdon in the tris complex with Co^{2+}; i.e., the formula of the complex is [Co(pdon)$_{1.36}$(pdon-H$_2$O)$_{1.64}$]$^{2+}$. As the ratio of Co^{2+} to pdon is increased to values where the tris complex is no longer the primary form of complex present, plots such as the one in Figure 2D become nonlinear and I/I_L eventually diminishes to a value that is independent of further additions of Co^{2+} (Figure 2E). This behavior indicates that K_H^{Co} becomes greater as the number of pdon ligands coordinated to each Co^{2+} cation decreases, as would be expected if the hydration-inducing action of the Co^{2+} cations increased when it was not shared with other coordinated pdon ligands. (Calculations using the reported equilibrium constants for the coordination of pdon to Co^{2+}[2] show that about 80% of the coordinated pdon was present in its hydrated form at the highest concentration of Co^{2+} employed in Figure 2E.)

The interpretation just given for the results shown in Figure 2D,E depends upon the observation that little or no conversion of hydrated to unhydrated pdon occurs during the time required for the Co(II)−pdon complexes to cross the Levich layer[10] at the rotating disk electrode. At a rotation rate of 2500 rpm, this time is ca. 40 ms. The reduced ligand, pdol (Figure 1), surely forms a more stable complex with Co^{2+} than does pdon (hydrated or not).[1,2] However, the experimental results indicate either that ligand exchange between the coordinated and hydrated pdon and pdol generated in the Levich layer at the electrode surface requires more than 40 ms or that any hydrated pdon ligand displaced from the complex with Co(II) by pdol does not reach its equilibrium dehydrated state within 40 ms. The establishment of the equilibrium between hydrated and unhydrated forms of protonated pdon was demonstrated in our previous study to require a few seconds,[8] and it would not be surprising if the same time scale applied to the dehydration of pdon, whose hydration was induced by its coordination to Co^{2+} instead of H$^+$.

Behavior of the [Fe(pdon)$_3$]$^{2+}$ Complex. Current−potential curves for the reduction of pdon in the presence and absence of Fe^{2+} are shown in Figure 3A. Although no equilibrium constants have been reported for the complexation of Fe^{2+} by pdon, the linear increase in absorbance with the concentration of Fe^{2+} at the band maximum of 484 nm (Figure 3B) matched that expected for the formation of the tris complex, [Fe(pdon)$_3$]$^{2+}$, on the basis of previous measurements with an isolated salt of this complex.[7] It is noteworthy that two closely-spaced waves appear in the current−potential curves obtained with mixtures of pdon and its tris complex with Fe^{2+} (curves 2−4 in Figure 3A). The reduction of the portion of the pdon that is coordinated to Fe^{2+} but remains unhydrated occurs at a more positive potential than that where the uncoordinated pdon is reduced because of the stronger association of Fe^{2+} with the reduced form of the ligand, pdol. This stronger binding would not result in double waves if the rate of exchange among bound and unbound ligands were rapid, so the appearance of the double waves is good evidence that the ligand exchange reactions are slow. The analogous Fe^{2+} complexes with 9,10-phenanthroline also exhibit sluggish rates of ligand exchange.[11] The absence of a double-reduction wave for pdon in the presence of Co^{2+} (Figure 2A) implies that the difference in the affinities of pdon and pdol for Co^{2+} is smaller than is true in the case of Fe^{2+}.

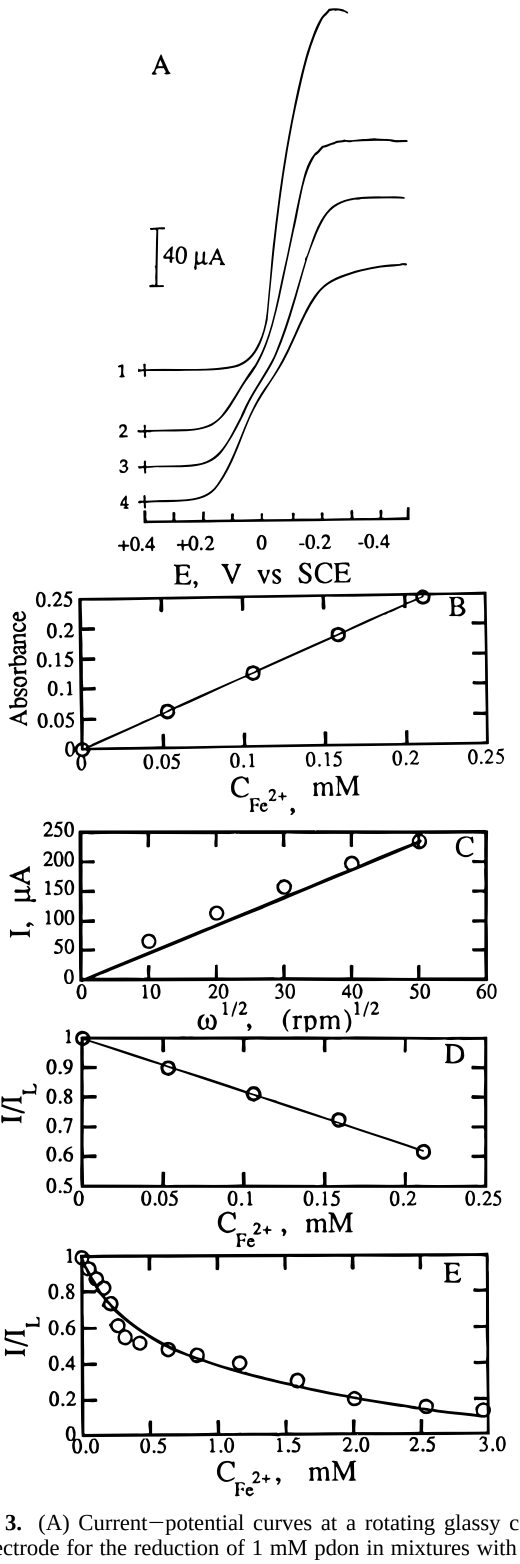


Figure 3. (A) Current−potential curves at a rotating glassy carbon disk electrode for the reduction of 1 mM pdon in mixtures with Fe^{2+}. [Fe(II)] = (1) 0, (2) 0.11, (3) 0.16, (4) 0.21 mM. Electrode rotation rate: 900 rpm. The position of zero current is shown by the + marks. Other conditions were as in Figure 2A. (B) Absorbance at 484 nm of a 1 mM solution of pdon to which Fe^{2+} was added. Optical path length: 1 mm. Supporting electrolyte was as in Figure 2A. (C) Levich plot of the plateau current for the reduction of 1 mM pdon in the presence of 0.16 mM Fe^{2+}. (D) Plateau currents for curves like those in (A) relative to the plateau current in the absence of Fe^{2+}. Currents were measured at a rotation rate of 1600 rpm. (E) Extension of (D) to higher concentrations of Fe^{2+}.

The plateau currents for the reduction of pdon in Figure 3A

---

[11] Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; Allyn & Bacon, Inc.: Boston, 1974; Chapter 8.

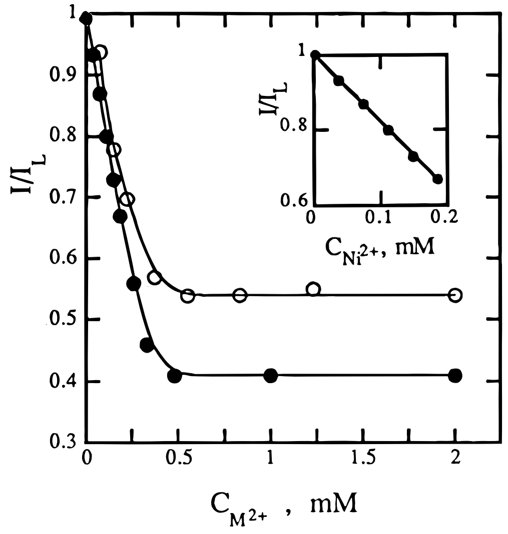


Figure 4. Plateau currents for the reduction of 1 mM pdon in the presence of Ni^{2+} (●) or Zn^{2+} (○) relative to the plateau current in the absence of either metal cation. Supporting electrolyte was as in Figure 2A. Currents were measured at a rotation rate of 2500 rpm. The insert shows the initial portion of the curve for Ni^{2+} on an expanded scale.

were measured as a function of the electrode rotation rate. As with the corresponding complex with Co^{2+}, the plateau current at 1600 rpm fell close to the straight line drawn from the origin through the point at 2500 rpm (Figure 3C), indicating that the hydration−dehydration equilibrium was essentially frozen at a rotation rate of 2500 rpm. The decrease in the plateau current as the quantity of Fe^{2+} added to the solution was increased is shown in Figure 3D. The decrease in the currents was somewhat greater that obtained with mixtures of Co^{2+} and pdon (Figure 2C), and the hydration constant calculated from eq 2 using the slope of the line in Figure 3D is $K_{\mathrm{H}}^{\mathrm{Fe}} = 1.7$, which corresponds to the hydration of 63% of the coordinated pdon ligands in the tris complex with Fe^{2+}.

When the ratio of Fe^{2+} to pdon was increased to values where fewer than three pdon ligands were coordinated to each Fe^{2+} cation, the plateau currents continued to decrease but in a nonlinear fashion as shown in Figure 3E. With a 3 mM solution of Fe^{2+}, where almost all of the pdon ligand may be assumed to be coordinated, the cathodic plateau current decreased to less than 20% of its value in the absence of Fe^{2+}. Thus, Fe^{2+}, like Co^{2+}, induces greater hydration of the coordinated pdon ligand as the number of ligands coordinated to the metal center decreases.

The electrochemical response from the $[Fe(pdon)_3]^{3+/2+}$ couple was not investigated because the potential where the couple appeared was too close to the anodic background in the pH 5 supporting electrolyte required to avoid protonation of pdon.

Complexes of pdon with Ni^{2+} and Zn^{2+}. Addition of Ni^{2+} or Zn^{2+} to solutions of pdon produced decreases in the plateau currents for the reduction of pdon that were similar to but somewhat smaller than those resulting from the addition of Co^{2+} or Fe^{2+}. The results are summarized in Figure 4. In the case of Ni^{2+}, the initial decrease in I/I_{L} was proportional to the quantity of Ni^{2+} added, and calculations using the reported complexation equilibrium constants[2] showed that the $[Ni(pdon)_3]^{2+}$ complex was the predominant form present. On this basis, the slope of the plot of I/I_{L} vs $C_{Ni^{2+}}$ in the inset to Figure 4 was used to calculate a value for $K_{\mathrm{H}}^{\mathrm{Ni}}$ of 1.6. The value of I/I_{L} became essentially constant at concentrations of Ni(II) above 0.5 mM (Figure 4) although calculations based on the reported equilibrium constants indicate that the distribution of complexes among $[Ni(pdon)_3]^{2+}$, $[Ni(pdon)_2]^{2+}$ and $[Ni(pdon)]^{2+}$ changes substantially between [Ni(II)] = 0.5 and 2 mM. The abrupt halt in the decrease in I/I_{L} for the Ni(II)−pdon system in Figure 4 occurs close to $C_{Ni^{2+}} = 0.33$ mM, which corresponds to the point where essentially all of the pdon is complexed to Ni^{2+}. This behavior suggests that a pdon ligand coordinated to Ni^{2+} is hydrated to about the same extent, whether or not additional pdon ligands are also coordinated to the Ni^{2+} center.

If this surmise is adopted, the level value of $I/I_{\mathrm{L}} = 0.41$ for Ni^{2+} in Figure 4 can be used to calculate a value of $K_{\mathrm{H}}^{\mathrm{Ni}}$ that should apply to pdon in all of its complexes with Ni^{2+}. The value obtained in this way is $K_{\mathrm{H}}^{\mathrm{Ni}} = 1.4$, which may be compared with the value obtained from the slope of the initial potion of the plot of I/I_{L} vs C_{Ni}, $K_{\mathrm{H}}^{\mathrm{Ni}} = 1.6$. The reasonable agreement between these two values supports the suggestion that a single value of $K_{\mathrm{H}}^{\mathrm{Ni}}$ can be applied to all Ni^{2+}−pdon complexes.

The reported equilibrium constants for the complexation of Zn^{2+} by pdon[2] are such that a mixture of tris, bis, and mono complexes is calculated to be present even during the early stages of a titration of pdon with Zn^{2+}. This property of the Zn^{2+}−pdon system prevented the estimation of a hydration constant from the initial slope of a plot of I/I_{L} vs C_{Zn}. However, the abrupt leveling off of the I/I_{L} values near a stoichiometric ratio of 3 pdon ligands per Zn^{2+} ion suggested that, as with the Ni^{2+}−pdon system , the extent of hydration of pdon coordinated to Zn^{2+} did not depend on the total number of pdon ligands coordinated to the metal. On this basis, the level value of $I/I_{\mathrm{L}} = 0.54$ for Zn^{2+} (Figure 4) was used to obtain an estimate for $K_{\mathrm{H}}^{\mathrm{Zn}}$ of 0.9.

Mixtures of pdon and Cu^{2+}. Additions of Cu^{2+} to solutions containing stoichiometric excesses of pdon at pH 5 produced large decreases in the plateau currents for the reduction of pdon. However, quantitative measurements were complicated because the known $[Cu(pdon)_2]^{2+}$ complex[7] is reduced to $[Cu(pdon)_2]^{+}$ at slightly less negative potentials than those where the ligand is reduced and the deposition of Cu metal on the electrode surface was frequently observed. For these reasons, no value of $K_{\mathrm{H}}^{\mathrm{Cu(I)}}$ was obtained although it appeared to be considerably larger than the hydration constants obtained for the other metal cations investigated.

Metal Ion-Induced Hydration of Adsorbed pdon. The pdon ligand is strongly adsorbed on the surface of graphite electrodes, and the adsorption persists when the coated electrode is transferred to supporting electrolyte solutions containing no pdon. In our previous study,[8] we concluded that the hydration of pdon in solution induced by protonation of the nitrogen sites did not occur when pdon was adsorbed on graphite. It was therefore of interest to determine if adsorbed pdon was susceptible to hydration induced by coordination of metal cations to the nitrogen sites. In the case of coordination of Cu(I) to adsorbed pdon, extensive hydration of the ligand, as judged by its diminished electroactivity, was readily demonstrated. In Figure 5A is shown a cyclic voltammogram for pdon irreversibly adsorbed on a pyrolytic graphite electrode in a pure acetate supporting electrolyte at pH 5, where no hydration of pdon occurs in solution.[8] When 10^{-5} M Cu^{2+} was added to the supporting electrolyte used in Figure 5A, there were drastic changes in the cyclic voltammetric response obtained during continuous cycling of the electrode potential, as shown in Figure 5B. The response that develops near 0.3 V can be assigned to the adsorbed Cu(II)/Cu(I)−pdon couple on the basis of previous results with an analogous adsorbed ligand.[12] The simultaneous shift in the position and the decrease in the magnitude of the peak currents for the pdon/pdol couple near 0 V that also occur,

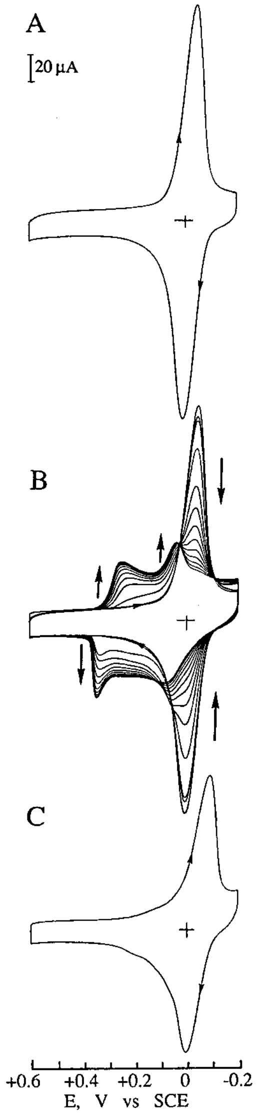


Figure 5. Cyclic voltammograms for pdon adsorbed on edge plane pyrolytic graphite electrodes before and after coordination of Cu^{2+} to the adsorbed ligand. Scan rate = 50 mV s^{-1}. (A) Voltammogram was recorded in pure supporting electrolyte: 0.1 M $NaClO_4$ + 0.05 M acetate buffer at pH 5.2. (B) Voltammograms were recorded after the electrode from (A) was transferred to supporting electrolyte solution that also contained 10^{-5} M Cu^{2+}. The potential was cycled until a new steady response was obtained, 6−8 min. (C) Voltammogram was recorded after the electrode from (B) was transferred to supporting electrolyte solution that also contained 10^{-4} M Na_2edta. The potential was cycled until a steady response was obtained, 2−3 min.

reflect the hydration of the adsorbed ligand induced by its coordination to Cu^{+}, which produces a decrease in the electroactivity of the ligand. The clear isosbestic point in the cathodic peaks indicates that the initially adsorbed pdon is being converted into a single new electroactive form. The pattern is consistent with the coordination of Cu^{2+} to the adsorbed pdon followed by reduction of the resulting complex to a Cu(I)−pdon complex near 0.3 V. The stronger binding by Cu(I) of the reduced ligand, pdol, than of pdon causes the ligand reduction peak to shift to more positive potentials, but the apparently extensive hydration of the pdon in the Cu(I)−pdon complex diminishes the magnitude of the shifted cathodic peak to a value that reflects the quantity of unhydrated pdon present in the Cu(I)−pdon complex. It is evident from the large decrease in the ligand reduction current that pdon in the adsorbed Cu(I)−pdon complex is extensively hydrated.

Table 1. Estimated Values of Equilibrium Constants for the Hydration of pdon Induced by Its Coordination to Cations

hydration-inducing cation[a]	$K_H^{M\ b,c}$	comments	$10^{-5}K$,[d] M^{-1}
Co^{2+}	1.2	applies to $Co(pdon)_3^{2+}$ complex	1.0
Fe^{2+}	1.7	applies to $Fe(pdon)_3^{2+}$ complex	*f*
Ni^{2+}	1.6	applies to mixtures of complexes	2.0
Zn^{2+}	0.9	applies to mixtures of complexes	0.32
$H^{+\ e}$	2.5	ref 8	$K_a^{-1} = 1.8 \times 10^2\ M^{-1\ g}$

[a] Supporting electrolyte: 0.05 M acetate buffer at pH 5.0 in which uncoordinated pdon is not hydrated. [b] $K_H^M \equiv [pdon\text{-}H_2O]_c/[pdon]_c$, where $[pdon\text{-}H_2O]_c$ and $[pdon]_c$ are the concentrations of the hydrated and nonhydrated forms, respectively, of the coordinated ligand. [c] The precision obtained in replicate measurements was ±20%. [d] $K_1 = M(pdon)^{2+}/([M^{2+}][pdon])$; from ref 2. [e] Supporting electrolyte: 0.1 M H_2SO_4. [f] No values reported. Reference 1.

Exposure of the coated electrode of Figure 5B to a 10^{-4} M solution of Na_2edta (edta = ethylenediaminetetraacetate) removed Cu^{2+} from the electrode surface and produced the cyclic voltammogram shown in Figure 5C. The area under the peaks for the reduction of pdon is significantly greater than that of the final curve in Figure 5B, as expected if removal of $Cu^{2+/+}$ from the adsorbed pdon restored it to its unhydrated state. The peak area in Figure 5C is smaller than that of the original voltammogram for the adsorbed pdon (Figure 5A) because some of the ligand is apparently desorbed from the surface during the complexation−decomplexation steps. However, the clear increase in the area of the peak for the pdon/pdol couple when the electrode of Figure 5B is stripped of copper cations shows that Cu(I) induces the hydration of pdon when it coordinates to the adsorbed ligand.

The voltammogram in Figure 5B obtained after the coordination reaction was complete contained almost no response at the potential where uncoordinated pdon is reduced. The peak current for the reduction of the coordinated pdon that remained unhydrated was about 25% as great as the peak current before the electrode was exposed to Cu^{2+}. These observations are consistent with a value for $K_H^{(Cu(I))ads}$ of about 3, but this value is only a rough estimate.

Interestingly, the rate of conversion of the hydrated, adsorbed Cu(I)−pdon complex to its unhydrated form is apparently quite low: When the final steady voltammogram in Figure 5B was recorded by scanning the electrode to more positive potentials from an initial potential of −0.2 V, where all nonhydrated pdon is reduced to pdol, there was no increase in the anodic peak current for the oxidation of coordinated pdol. If equilibrium between the hydrated and nonhydrated coordinated pdon were rapidly established, one would expect conversion of the hydrated into the nonhydrated form of the ligand as the latter was removed by electroreduction. The contrary result observed suggests that the hydration−dehydration reactions proceed much more slowly in the adsorbed state than in solution.

Experiments in which adsorbed pdon was coordinated to other metal cations (Fe^{2+}, Ni^{2+}, Co^{2+}) produced ambiguous results concerning the extent of hydration of the coordinated pdon ligand in the adsorbed complexes. It was not possible to distinguish between ligand desorption and ligand hydration as

---

(12) Zhang, J.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1993**, *348*, 81.

the cause of the diminished voltammetric peak areas that resulted in the presence of the metal cations.

Concluding Remarks

The values of the equilibrium constants estimated in this study for the hydration of pdon coordinated to four metal cations and the proton in solution are collected in Table 1. The constants could not be measured with high precision, but there appears to be a rough correlation between the extent of hydration and the affinity of the pdon ligand for the metal center as reflected in the reported equilibrium constants for the formation of the $[M(pdon)]^{2+}$ complexes given in the last column of Table 1. This trend probably reflects a correlation between the strength of the metal−pdon bond and the decrease in the electron density at the carbonyl groups that favors their hydration.[13] Despite the higher affinity of pdon for metal cations than for the proton, a larger value of K_H applies to protonated pdon; protonation is evidently particularly effective in withdrawing electron density from the carbonyl groups of the pdon ligand.

Acknowledgment. This work was supported by the National Science Foundation.

IC951569H

---

(13) March, J. *Advanced Organic Chemistry. Reaction Mechanisms and Structure*; Wiley: New York, 1992; pp 882−884.