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# Redox Chemistry of Bis(2,9-dimethyl-4,7-bis(sulfonatophenyl)-1,10-phenanthrolinato)copper(II/I). Reactions with Nickel Oxime Imine Complexes

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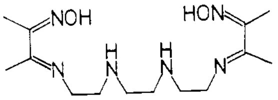
The copper(II) complex $Cu(dpsmp)_2OH_2^{2-}$ where $dpsmp^{2-}$ is a diphenylsulfonated derivative of 2,9-dimethyl-1,10-phenanthroline is five-coordinate and can be hydrolyzed with $pK_{ac} = 8.3$. Reduction of the complex by $Fe(CN)_6^{4-}$ and $Ni^{II}L$, a nickel(II) bis(oxime imine) complex, is described by a common mechanism involving a tetrahedral copper(II) intermediate $Cu(dpsmp)_2^{2-}$, which has the same geometry as the copper(I) product. Rates of Cu–$OH_2$ and Cu–OH bond cleavage are >334 and 26 $s^{-1}$, respectively, at 25.0 °C and in 0.10 M perchlorate media. Oxidation of the copper(I) complex $Cu(dpsmp)_2^{3-}$ by $Ni^{III}L^+$, a nickel(III) bis(oxime imine) complex, has also been examined, and the second-order rate constants are used to determine a self-exchange rate for $Cu(dpsmp)_2OH_2^{2-}/Cu(dpsmp)_2^{3-}$ of $5 \times 10^6$ $M^{-1}$ $s^{-1}$.

## Introduction



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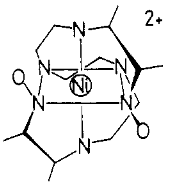

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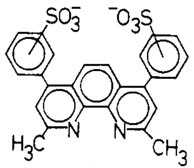
The sexidentate bis(oxime imine) ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $H_2L$ (**1**), allows stabilization[1] of a formally tetravalent nickel complex $Ni^{IV}L^{2+}$ (**2**). Reductions of this complex by the ascorbate ion,[2] $Co(phen)_3^{2+}$,[3] and $Co(edta)^{2-}$ [4] to give the corresponding nickel(II) complex have been reported and in all cases proceed by consecutive one-electron transfers with formation of nickel(III) intermediates. Reduction potentials for the nickel(IV/III/II) system are pH dependent.[3,5] Cyclic voltammetry results indicate a single two-electron nickel(IV/II) process at low pH, while at higher pH a nickel(III) intermediate can be detected. The reduction potentials (vs. NHE) of the nickel(IV) and nickel(III) complexes[3] are given in eq 1 and 2.

$$Ni^{IV}L^{2+} + e^- \rightleftharpoons Ni^{III}L^+ \qquad E° = 0.65\ V \tag{1}$$

$$Ni^{III}L^+ + e^- \rightleftharpoons Ni^{II}L \qquad E° = 0.42\ V \tag{2}$$

In an effort to establish the reactivity patterns of the nickel complexes, it seems pertinent to choose a one-electron reductant with a potential intermediate between those of nickel(IV) and nickel(III). The copper complex $Cu^{II}(dpsmp)_2OH_2^{2-}$ where $dpsmp^{2-}$ in 2,9-dimethyl-4,7-bis(sulfonatophenyl)-1,10-phenanthroline (**3**) has a potential of 0.62 V,[6,7] and the copper(I) complex should react only with $Ni^{IV}L^{2+}$ at higher pH. However, over the pH range 2.8–7.2, quantitative reduction of both nickel(IV) and nickel(III) was observed with only a fourfold excess of copper(I) over nickel(III). Clearly, a fuller investigation of this reduction is warranted.



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Previous kinetic studies involving the $Cu^{II/I}(dpsmp)_2^{2-/3-}$ reagent include oxidation by copper(III) peptide complexes[6] and reduction by $Fe(CN)_6^{4-}$,[7] a number of other iron(II) complexes,[8] and hydroquinone.[9] These studies have elucidated some of the complexities involved in copper–phenanthroline redox chemistry.[10,11]

In this paper we present results of kinetic studies of the reduction of $Ni^{IV}L^{2+}$ by $Cu^I(dpsmp)_2^{3-}$ and the oxidation of $Ni^{II}L$ by $Cu^{II}(dpsmp)_2OH_2^{2-}$, reinvestigation of the oxidation of $Fe(CN)_6^{4-}$ by $Cu^{II}(dpsmp)_2OH_2^{2-}$, and cyclic voltammetry investigations of the $Cu^{II/I}(dpsmp)_2^{2-/3-}$ couple.

## Experimental Section

**Materials.** Preparation of $Ni^{II}LH_2^{2+}$, $Ni^{III}L^+$, and $Ni^{IV}L^{2+}$ salts involved procedures outlined previously.[1,3] Solutions of $Cu^{II}(dpsmp)_2OH_2^{2-}$ were prepared by addition of sufficient excess (>2 $\times 10^{-4}$ M) of $dpsmp^{2-}$ ligand (Sigma) to a solution of $Cu(ClO_4)_2$ standardized iodometrically, to ensure 99% formation of the bis complex. Formation constants are likely[6] to be similar to those of the 2,9-dimethyl-1,10-phenantholine (dmp) complex where[12] $K_1 = 10^{6.1}$ $M^{-1}$ and $K_2 = 10^{5.6}$ $M^{-1}$. Solutions of $Cu^I(dpsmp)_2^{3-}$ were prepared by the addition of 2.2:1 $dpsmp^{2-}$ (disodium salt) to a solution of $Cu(ClO_4)_2$, which was then reduced with use of less than the stoichiometric amount of ascorbic acid. The solutions were standardized spectrophotometrically by using a Beckman 5270 spectrophotometer ($\epsilon_{483}$ 12 250 $M^{-1}$ $cm^{-1}$).[13] Potassium hexacyanoferrate(II), $K_4Fe(CN)_6$ (BDH, AnalaR), was used without further purification. Background electrolytes, $NaClO_4$ and $NaNO_3$, and borate, phosphate, and acetate buffers (all BDH, AnalaR), MES, HEPES, and Tris (Sigma), were used without further purification.

**Cyclic Voltammetry.** Cyclic volammetric behavior of the $Cu(dpsmp)_2OH_2^{2-}$ complex was examined under argon at 25.0 °C in

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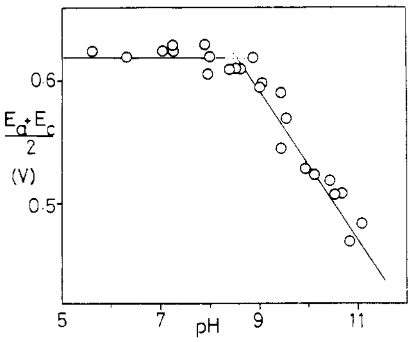


**Figure 1.** Plot of $(E_a + E_c)/2$ against pH for cyclic voltammetry experiments on $Cu(dpsmp)_2^{2-/3-}$ at 25.0 °C and in 0.10 M $NaClO_4$.

$1.0 \times 10^{-2}$ M borate or HEPES buffer and in 0.10 M $NaClO_4$ with $[Cu^{2+}]_T = 1.0 \times 10^{-4}$ M and $[dpsmp^{2-}]_T = 1.0 \times 10^{-3}$ M unless otherwise noted. A three-electrode system consisting of a carbon-paste working electrode, a platinum-wire auxiliary electrode, and a Ag/AgCl reference electrode was used. Voltammograms were generated with use of either a Bioanalytical Systems Inc. CV-1 instrument or a Princeton Applied Research Corp. 173 potentiostat in conjunction with a 175 universal programmer and 176 current to voltage converter and were recorded on a Tektronix 5111 storage oscilloscope fitted with two 5A21N differential amplifiers or a J. J. Lloyd Ltd. P151 X-Y recorder. All potentials are quoted vs. NHE (normal hydrogen electrode).

**Kinetic Studies.** Kinetic measurements were made in $1.0 \times 10^{-2}$ M buffer and in 0.10 M $NaClO_4$ or $NaNO_3$ solution at 25.0 °C unless otherwise noted. A number of the reagents in solution showed sensitivity to oxygen, and in these cases bubbling argon gas for a minimum of 15 min prevented significant deterioration.

The pH of solutions was determined immediately after reaction by using an EIL 7055 pH meter. A saturated-calomel (NaCl) reference electrode was used and hydrogen ion concentrations were evaluated by the relationship $-\log [H^+] = pH - 0.02$ correcting for both hydrogen ion activity and liquid-junction potential.

Reactions were monitored at the absorption maximum of $Ni^{IV}L^{2+}$ at 500 nm or at the maximum of $Cu(dpsmp)_2^{2-}$ at 483 nm by using an Applied Photophysics stopped-flow spectrophotometer. Pseudo-first-order conditions with an excess of oxidant or reductant were used as indicated for appropriate experiments, and in general good first-order traces were obtained. In some of the $Cu^{II}(dpsmp)_2OH_2^{2-}$ reductions, a slow second phase accounting for no more than 5% reaction was detected. This was not examined in detail but is dependent on the free $[dpsmp^{2-}]$ concentration.

Observed rate constants were evaluated by least-squares analysis of appropriate plots using a PET 2001 microcomputer. Normally three rate determinations were made for each kinetic experiment. Linear regression techniques with appropriate weighting were employed for data analysis.

## Results and Discussion

**Cyclic Voltammetry.** Voltammograms run on solutions of $Cu^{II}(dpsmp)_2OH_2^{2-}$ show a single couple with peak-to-peak separation $(E_a - E_c)$ approaching 60 mV at scan rates 10–20 mV $s^{-1}$. The reduction potential of $Cu^{II}(dpsmp)_2OH_2^{2-}$, eq 3, is found to be 617 ± 4 mV over the pH range 5–8 in good agreement with earlier determinations.[6,7] However, above pH 8, the potential is pH dependent (Figure 1).

$$Cu^{II}(dpsmp)_2OH_2^{2-} + e^- \rightleftharpoons Cu^I(dpsmp)_2^{3-} + H_2O \quad (3)$$

At pH 8.0 in the pH-independent potential region, the voltammetric response is quasi-reversible.[14] While the midpoint potential $(E_a + E_c/2)$ remains constant with increasing scan rate, $\nu$ (Figure 2), the peak-to-peak separation $(E_a - E_c)$, increases from around 60 mV at low scan rates to 220 mV at 10 V $s^{-1}$. Both anodic, $i_{pa}$, and cathodic, $i_{pc}$, peak currents are well-defined over the whole range of scan rates examined, and the ratio $i_{pa}/i_{pc}$ is unity and invariant with $\nu$. The peak current shows a linear dependence on $\nu^{1/2}$.

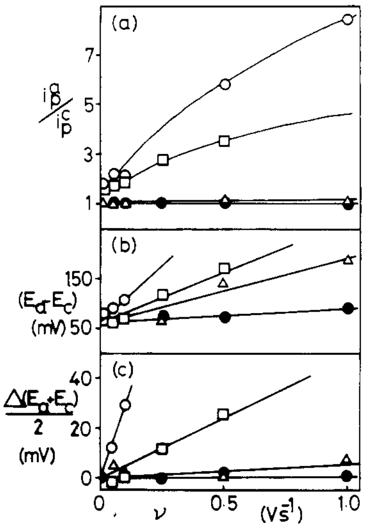


**Figure 2.** Plots of (a) the peak current ratio, (b) the peak-to-peak separation, and (c) the shift in peak position for cyclic voltammetry experiments as a function of scan rate (25.0 °C; in $1.0 \times 10^{-2}$ M borate buffer and 0.10 M $NaClO_4$): pH 8.00 (●), 8.98 (△), 9.90 (□), 10.70 (○).

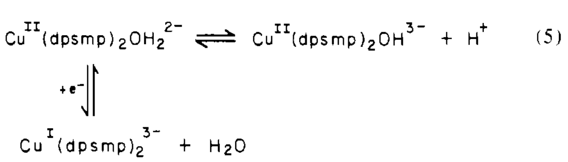
The conditions used ($[Cu^{2+}]_T = 1.0 \times 10^{-4}$ M, $[dpsmp^{2-}] = 1.0 \times 10^{-3}$ M) are sufficient to ensure complete formation of the bis complex, eq 4. When the $[dpsmp^{2-}]$ concentration

$$Cu^{II}dpsmp(OH_2)_n + dpsmp^{2-} \rightleftharpoons Cu^{II}(dpsmp)_2OH_2^{2-} \quad (4)$$

is decreased at pH 7.5, well above the protonation constants of the ligand (2.65, 5.80),[13] no variation in the midpoint potential was detected above $5 \times 10^{-5}$ M excess ligand concentration with $[Cu^{2+}]_T = 1.0 \times 10^{-5}$ M. With a ligand excess of $5 \times 10^{-6}$ M, the reduction potential was 575 mV. Since the copper(I) complexes of similar 2,9-dimethylated phenanthroline ligands are considerably more stable than the copper(II) complexes,[12] any dependence on $[dpsmp^{2-}]$ should be due to dissociation of the latter species, eq 4. This allows a value for $K_2$ for the complex of $10^{4.9}$ $M^{-1}$ to be estimated.

Above pH 8.5, the midpoint potential at low scan rates decreases linearly with increasing pH. The pH dependence has a slope of −57 ± 9 mV per pH unit and equals the pH-independent value of 617 mV at pH 8.3. In this region where the potential is pH dependent, significant changes in the voltammetric response take place and the reaction is best described as a CE mechanism with reduction of the copper(II) complex coupled to a deprotonation process. Anodic shifts in midpoint potential and increases in peak-to-peak separation are noted with increasing scan rate and take place at progressively lower scan rates as the pH is increased. Though the anodic current increases linearly with $\nu^{1/2}$, the cathodic current does not such that $i_{pa}/i_{pc}$ increases with increasing scan rate and pH (Figure 2). For example, at pH 10.7 and a scan rate of 10 V $s^{-1}$, the couple appears irreversible.

A pH dependence of this type is most readily explained by deprotonation of the oxidized complex $Cu^{II}(dpsmp)_2^{2-}$ (eq 5)



$$\begin{array}{ccc} Cu^{II}(dpsmp)_2OH_2^{2-} & \rightleftharpoons & Cu^{II}(dpsmp)_2OH^{3-} + H^+ \quad (5) \\ {\scriptstyle +e^-}\Big\updownarrow & & \\ Cu^I(dpsmp)_2^{3-} + H_2O & & \end{array}$$

with a $pK_{ac}$ around 8.3. Since no evidence for a comparable $Cu^I(dpsmp)_2^{3-}$ deprotonation was detected up to pH 11.5, it seems probable that the $pK_{ac}$ refers to a ligand directly bound to the metal center and is most likely the proposed,[7] coordinated water molecule.

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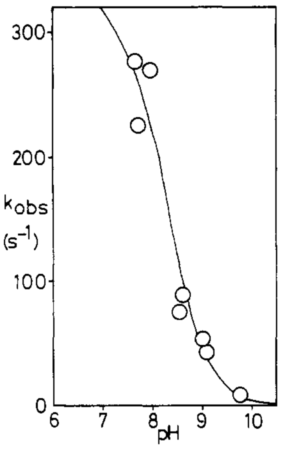

**Figure 3.** Plot of $k_{obsd}$ against pH for the reduction of $Cu(dpsmp)_2OH_2^{2-}$ by $Fe(CN)_6^{4-}$ ($[Fe(CN)_6^{4-}] = 1.0 \times 10^{-3}$ M; 25.0 °C; in 0.10 M $NaClO_4$).

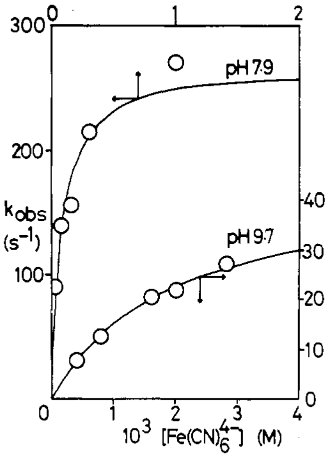

**Figure 4.** Plots of $k_{obsd}$ against $[Fe(CN)_6^{4-}]$ at pH 7.9 and 9.7 (25.0 °C; in 0.10 M $NaClO_4$).

The cyclic voltammetry results thus provide evidence for a copper(II) complex that is subject to hydrolysis. The data are not inconsistent with a change in geometry with release of coordinated solvent on reduction to copper(I). McMillin and co-workers[15] have provided structural evidence for such a change in coordination using similarly sterically constrained bipyridyl ligands.

However, hydrolysis, which markedly affects redox characterstics with $pK_{ac}$ 8.3, contradicts an earlier report[7] on the reduction of $Cu(dpsmp)_2OH_2^{2-}$ by $Fe(CN)_6^{4-}$ where no pH dependence was noted over the range 7.5–9.0. This reaction was reexamined.

**Reduction of $Cu(dpsmp)_2OH_2^{2-}$ by $Fe(CN)_6^{4-}$.** Under conditions of excess $[Fe(CN)_6^{4-}]$, the initial reduction of $Cu(dpsmp)_2OH_2^{2-}$ is first order in $[Cu(dpsmp)_2OH_2^{2-}]$ and the pseudo-first order-rate constant, $k_{obsd}$, with $[Fe(CN)_6^{4-}] = 1.0 \times 10^{-3}$ M is shown in Figure 3 as a function of pH. Clearly the reaction is pH dependent. The data are presented in Table I.

Table I. Pseudo-First-Order Rate Constants for the Reduction of $Cu(dpsmp)_2OH_2^{2-}$ by $Fe(CN)_6^{4-}$ at 25.0 °C and in 0.10 M $NaClO_4$[a]

| pH | $10^4[Fe(CN)_6^{4-}]$, M | $k_{obsd}$, $s^{-1}$ |
|---|---|---|
| 7.09[b] | 2.00 | 268 ± 5 |
| 7.64[b] | 10.0 | 276 ± 15 |
| 7.68[c] | 10.0 | 225 ± 4 |
| 7.77[b] | 4.00 | 305 ± 5 |
| 7.93[c] | 0.15 | 55 ± 5 |
| 7.93[c] | 3.00 | 215 ± 7 |
| 7.94[c] | 1.50 | 156 ± 6 |
| 7.95[c] | 0.30 | 90 ± 10 |
| 7.97[c] | 0.75 | 139 ± 4 |
| 7.97[b] | 10.0 | 271 ± 9 |
| 8.24[c] | 4.00 | 51 ± 1 |
| 8.51[c] | 10.0 | 74 ± 7 |
| 8.62[b] | 10.0 | 88 ± 3 |
| 9.01[c] | 10.0 | 53 ± 2 |
| 9.10[c] | 10.0 | 42 ± 1 |
| 9.40[c] | 8.00 | 20.5 ± 0.5 |
| 9.42[d] | 4.00 | 17.3 ± 0.1 |
| 9.45[d] | 16.0 | 43.2 ± 0.5 |
| 9.47[d] | 12.0 | 41.1 ± 4.4 |
| 9.69[c] | 20.0 | 21.9 ± 0.2 |
| 9.72[c] | 16.0 | 20.6 ± 0.3 |
| 9.74[c] | 4.00 | 7.7 ± 0.2 |
| 9.74[c] | 8.00 | 12.7 ± 0.4 |
| 9.76[c] | 10.0 | 9.2 ± 0.2 |
| 9.77[c] | 28.0 | 27.4 ± 2.3 |

[a] $[Cu(II)] = (0.5–10) \times 10^{-5}$ M. [b] Tris buffer ($1.0 \times 10^{-2}$ M). [c] Borate buffer ($1.0 \times 10^{-2}$ M). [d] Borate buffer ($5.0 \times 10^{-3}$ M).

At pH 9.7, a plot of $k_{obsd}$ against $[Fe(CN)_6^{4-}]$ (Figure 4) shows a nonlinear dependence changing from first to zero order in $[Fe(CN)_6^{4-}]$ and can be analyzed according to expression 6, with $a = 44 \pm 3$ $s^{-1}$ and $b = (1.9 \pm 0.2) \times 10^{-3}$ M. At pH

$$k_{obsd} = \frac{a[Fe(CN)_6^{4-}]}{b + [Fe(CN)_6^{4-}]} \tag{6}$$

7.9, similar behavior is observed with $a = 267 \pm 37$ $s^{-1}$ and $b = (7.5 \pm 2.9) \times 10^{-5}$ M, showing that both parameters are pH dependent. The pH dependence can be described by the expression (7), which is of the same form as (6). Best fit

$$k_{obsd} = \frac{\dfrac{k_{1a}[H^+] + k_{1b}K_{ac}}{[H^+] + K_{ac}}[Fe(CN)_6^{4-}]}{k_{-1a}/k_2 + k_{-1b}/k_2[OH^-] + [Fe(CN)_6^{4-}]} \tag{7}$$

parameters $k_{1a} = 334 \pm 40$ $s^{-1}$, $k_{1b} = 26 \pm 5$, $k_{-1a}/k_2 = (4.4 \pm 6) \times 10^{-7}$ M, $k_{-1b}/k_2 = 70 \pm 20$, and $K_{ac} = (5.4 \pm 2.1) \times 10^{-9}$ M yield the calculated curve in Figure 3. This rate law is derived from a mechanism (eq 8–11) in which a rear-

$$Cu(dpsmp)_2OH_2^{2+} \rightleftharpoons Cu(dpsmp)_2OH^{3-} + H^+ \quad K_{ac} \tag{8}$$

$$Cu(dpsmp)_2OH_2^{2-} \rightleftharpoons Cu(dpsmp)_2^{2-} + H_2O \quad k_{1a}, k_{-1a} \tag{9}$$

$$Cu(dpsmp)_2OH^{3-} \rightleftharpoons Cu(dpsmp)_2^{2-} + OH^- \quad k_{1b}, k_{-1b} \tag{10}$$

$$Cu(dpsmp)_2^{2-} + Fe(CN)_6^{4-} \rightarrow Cu(dpsmp)_2^{3-} + Fe(CN)_6^{3-} \quad k_2 \tag{11}$$

rangement of the complex $Cu(dpsmp)_2OH_2^{2-}$ is rate determining at high $[Fe(CN)_6^{4-}]$ concentrations and as such is in agreement with previous work.[7] However, an unreactive hydrolyzed $Cu(dpsmp)_2OH^{3-}$ must now be included. It is important to point out that the parameter $k_{-1a}/k_2$ is essentially indeterminate from the present data since rates measured at lower pH values show pronounced limiting first-order behavior, $k_{1a}$.

The values of $k_{1a}$ and $k_{1b}$, 334 and 26 $s^{-1}$, respectively, are consistent with the expected strengths of Cu–$OH_2$ and Cu–OH bonds. Perhaps it should be mentioned that the value of $k_{1a}$, 334 $s^{-1}$, approaches the upper limit of first-order rate constants accurately measurable by the stopped-flow technique[16] and might be considered a lower limit for this parameter. This may explain why no limiting kinetic behavior is detected[9] in the reduction of $Cu(dpsmp)_2OH_2^{2-}$ by hydroquionone at pH 6. Water exchange at $Cu(H_2O)_6^{2+}$ is a rapid process with a

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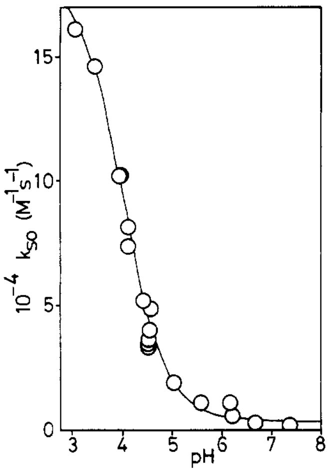

**Figure 5.** Plot of $k_{so}$ against pH for the oxidation of $Cu(dpsmp)_2^{3-}$ by nickel(III) (25.0 °C; in 0.10 M $NaNO_3$).

rate in excess of $10^9\ s^{-1}$ as a result of Jahn-Teller distortions and rapid inversion of the axes.[17] Considerably lower rates are to be expected if this inversion is prevented by complexation, and it is noteworthy that water exchange in the copper(II) complex with 2,2′,2″-triaminotriethylamine, which has a trigonal-bipyramidal structure, is only $2 \times 10^5\ s^{-1}$.[18]

Attack by $OH^-$ on the proposed four-coordinate $Cu(dpsmp)_2^{2-}$ is $2 \times 10^8$ times more rapid than attack by $H_2O$ and reflects the differing properties of these reagents as nucleophiles. Electron transfer may proceed by an inner-sphere mechanism in which there is a cyanide bridge from iron(II) to the copper center since the rate of electron transfer, $k_2$, is intermediate between the substitution rates for $OH^-$ and $H_2O$, but no definite conclusions can be drawn.

Hydrolysis of the copper(II) complex occurs with a $pK_{ac}$ of 8.27 in reasonable agreement with the cyclic voltammetry results. It is perhaps unfortunate that previous electron-transfer studies with $Cu(dpsmp)_2OH_2^{2-}$ have been carried out[7,8] at pH 8, in the steepest part of the pH dependence curve. Small differences in pH between studies might provide an explanation for different limiting rate behavior.[8]

**Oxidation of $Cu(dpsmp)_2^{3-}$ by $Ni^{IV}L^{2+}$.** Under conditions of excess $[Cu(dpsmp)_2^{3-}]$ concentration, absorbance measurements show that reduction of $Ni^{IV}L^{2+}$ by $Cu(dpsmp)_2^{3-}$ proceeds quantitatively to give $Ni^{II}L$ or its protonated forms over the pH range 3.0–7.3. However, when the stopped-flow technique is used, only one reaction is observed that, corresponding to half the expected absorbance change, is attributed to nickel(III) reduction.[3] The reaction shows a first-order dependence on both $[Ni^{III}L^+]$ and $[Cu(dpsmp)_2^{3-}]$ (Table II), and the second-order rate constant shows the strong pH dependence (Figure 5) typical[3,4] of reactions of $Ni^{III}L^+$.

The pH behavior was analyzed with use of expression 12

$$k_{so} = \frac{k_{3a}[H^+] + k_{3b}K_{aIII}}{[H^+] + K_{aIII}} \qquad (12)$$

where $k_{3a} = (1.83 \pm 0.76) \times 10^5\ M^{-1}\ s^{-1}$, $k_{3b} = (3.8 \pm 2.2) \times 10^3\ M^{-1}\ s^{-1}$, and $K_{aIII} = (1.05 \pm 0.14) \times 10^{-4}\ M^{-1}$. A mechanism consistent with this rate law, eq 13–15, involves

$$Ni^{III}LH^{2+} \rightleftharpoons Ni^{III}L^+ + H^+ \quad K_{aIII} \qquad (13)$$

$$Ni^{III}LH^{2+} + Cu(dpsmp)_2^{3-} \rightarrow \quad k_{3a} \qquad (14)$$

$$Ni^{III}L^+ + Cu(dpsmp)_2^{3-} \rightarrow \quad k_{3b} \qquad (15)$$

protonation of the nickel(III) complex with $pK_{aIII}$ 3.98, which is in excellent agreement with previous determinations.[2–4] The protonated complex, $Ni^{III}LH^{2+}$, is more reactive than $Ni^{III}L^+$ reflecting the difference in redox potentials between the two complexes.[3] This is similar to the behavior observed with $Co(phen)_3^{2+}$ [3] and the ascorbate ion[2] as reductants.

Table II. Pseudo-First-Order Rate Constants for Reduction of Nickel(III) by $Cu(dpsmp)_2^{3-}$ at 25.0 °C and in 0.10 M $NaNO_3$[a]

| pH | $10^5 \times [Cu(dpsmp)_2^{3-}]$, M | $10^5 \times [Cu(dpsmp)_2OH_2^{2-}]$, M | $10^1 k_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| 3.02[b] | 1.23 | 2.27 | 19.8 ± 0.9 |
| 3.43[c] | 3.22 | 1.78 | 47.0 ± 0.2 |
| 3.92[c] | 3.22 | 1.78 | 33.0 ± 0.2 |
| 3.94[b] | 2.37 | 1.13 | 24.1 ± 1.9 |
| 4.10[b] | 2.65 | 2.85 | 19.5 ± 0.6 |
| 4.10[b] | 2.65 | 0.85 | 21.6 ± 1.8 |
| 4.18[c] | 3.22 | 1.78 | 25.6 ± 0.6 |
| 4.40[b] | 3.52 | 0.88 | 18.3 ± 2.0 |
| 4.53[d] | 2.28 | 1.44 | 8.2 ± 0.2 |
| 4.53[d] | 4.56 | 2.88 | 18.1 ± 0.4 |
| 4.53[d] | 11.40 | 7.20 | 37.2 ± 0.4 |
| 4.53[d] | 22.80 | 14.40 | 78.8 ± 1.7 |
| 4.56[b] | 2.63 | 0.87 | 12.8 ± 0.2 |
| 5.03[c] | 3.22 | 1.72 | 5.98 ± 0.14 |
| 5.59[e] | 3.52 | 0.88 | 3.80 ± 0.29 |
| 6.05[e] | 9.85 | 4.17 | 2.37 ± 0.12 |
| 6.05[e] | 6.40 | 2.71 | 1.37 ± 0.22 |
| 6.05[e] | 3.49 | 1.48 | 0.80 ± 0.04 |
| 6.05[e] | 2.46 | 1.04 | 0.75 ± 0.06 |
| 6.20[f] | 3.22 | 1.78 | 3.61 ± 0.09 |
| 6.68[e] | 3.52 | 0.88 | 0.82 ± 0.08 |
| 7.36[e] | 3.52 | 0.88 | 0.46 ± 0.06 |
| 6.21[g] | 7.30 | 1.73 | 4.08 ± 0.16 |

[a] $[Ni(III)] = (1.5\text{–}8.4) \times 10^{-6}$ M. [b] Acetate buffer ($2.5 \times 10^{-2}$ M). [c] Acetate buffer ($1.0 \times 10^{-2}$ M). [d] Acetate buffer ($1.5 \times 10^{-2}$ M). [e] Phosphate buffer ($2.5 \times 10^{-2}$ M). [f] Phosphate buffer ($1.0 \times 10^{-2}$ M). [g] Phosphate buffer ($1.5 \times 10^{-2}$ M).

That the reduction of nickel(III) by $Cu(dpsmp)_2^{3-}$ is thermodynamically favorable under the experimental conditions used is only partially understandable in terms of the change in the redox potential of the reductant due to hydrolysis of $Cu(dpsmp)_2OH_2^{2-}$ (eq 16). A further contributing factor

$$Cu^{II}(dpsmp)_2OH_2^{2-} \rightleftharpoons Cu^{II}dpsmp + dpsmp^{2+} \qquad (16)$$

is ligand dissociation from the copper(II) product to give $Cu^{II}(dpsmp)$, which is a poorer oxidant. This is conveniently brought about since the small $[dpsmp^{2-}]$ excess required to fully form $Cu(dpsmp)_2^{3-}$ is insufficient to ensure complete formation of the corresponding copper(II) complex.

**Reduction of $Cu(dpsmp)_2OH_2^{2-}$ by $Ni^{II}LH^+$.** Increasing the free $[dpsmp^{2-}]$ concentration allows complete formation of the copper(II) complex, which with a large excess of nickel(II) enables oxidation of the nickel(II) complex to nickel(III) to be examined.

The reaction exhibits a first-order dependence on both reactants with first-order rates well below the limiting rates observed with $Fe(CN)_6^{4-}$ (Table III). The second-order rate constant shows a complex dependence on pH (Figure 6) requiring a minimum of two protic equilibria.

There are three protonations associated with the reactive species in solution with literature $pK_a$ values of 5.90 for (17),

$$Ni^{II}LH_2^{2+} \rightleftharpoons Ni^{II}LH^+ + H^+ \quad K_{aII} \qquad (17)$$

$$Ni^{III}LH^+ \rightleftharpoons Ni^{II}L + H^+ \quad K_{aI} \qquad (18)$$

$$Cu(dpsmp)_2OH_2^{2-} \rightleftharpoons Cu(dpsmp)_2OH^{3-} + H^+ \quad K_{ac} \qquad (19)$$

7.80 for (18) in 0.1 M KCl media,[5] and 8.3 for (19) from the

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[17] Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; ACS Monogr. No. 174, p 1.

[18] Rablen, D. P.; Dodgen, H. W.; Hunt, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1771.

**Table III.** Pseudo-First-Order Rate Constants for the Oxidation of Nickel(II) by $Cu(dpsmp)_2OH_2^{2-}$ at 25.0 °C and in 0.10 M $NaClO_4$ [a]

| pH | $10^4 \times$ [Ni(II)], M | $k_{obsd}$, $s^{-1}$ | pH | $10^4 \times$ [Ni(II)], M | $k_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|---|
| 3.88[b] | 1.0 | 0.068 ± 0.003 | 7.04[d] | 0.1[f] | 0.52 ± 0.04 |
| 4.92[c] | 1.0 | 0.83 ± 0.04 | 7.04[d] | 0.2[f] | 0.75 ± 0.04 |
| 4.95[b] | 1.0 | 0.78 ± 0.02 | 7.04[d] | 0.4[f] | 3.80 ± 0.06 |
| 5.19[c] | 1.0 | 1.29 ± 0.04 | 7.04[d] | 0.8[f] | 6.21 ± 0.22 |
| 5.55[c] | 1.0 | 1.75 ± 0.03 | 7.04[d] | 1.0[f] | 7.75 ± 0.25 |
| 5.72[b] | 1.0 | 1.41 ± 0.01 | 7.11[e] | 1.0 | 6.64 ± 0.49 |
| 5.94[b] | 1.0 | 3.24 ± 0.05 | 7.28[e] | 1.0 | 4.53 ± 0.93 |
| 6.16[b] | 1.0 | 5.81 ± 0.13 | 7.32[g] | 1.0 | 5.05 ± 0.12 |
| 6.43[c] | 1.0 | 5.80 ± 0.02 | 7.51[g] | 1.0 | 2.63 ± 0.02 |
| 6.53[c] | 1.0 | 8.02 ± 0.30 | 7.70[e] | 1.0 | 1.79 ± 0.09 |
| 6.72[b] | 5.0 | 33.1 ± 2.5 | 7.92[e] | 1.0 | 1.26 ± 0.03 |
| 6.74[d] | 1.0 | 6.9 ± 0.6 | 8.01[g] | 1.0 | 1.20 ± 0.04 |
| 6.74[d] | 2.0 | 11.83 ± 0.02 | 8.26[g] | 1.0 | 0.90 ± 0.04 |
| 6.74[d] | 4.0 | 23.5 ± 0.2 | 8.41[g] | 1.0 | 0.56 ± 0.04 |
| 6.74[d] | 8.0 | 51.5 ± 7.6 | 8.79[e] | 1.0 | 0.120 ± 0.003 |
| 6.92[c] | 1.0 | 8.91 ± 0.35 | 8.95[g] | 1.0 | 0.188 ± 0.016 |
| 6.92[e] | 1.0 | 5.52 ± 0.21 | 9.58[g] | 1.0 | 0.045 ± 0.001 |
| 7.00[b] | 1.0 | 8.42 ± 0.40 | | | |

[a] [Cu(II)] = (1–2) × $10^{-5}$ M. [b] MES buffer (1.0 × $10^{-2}$ M). [c] MES buffer (5.0 × $10^{-3}$ M). [d] HEPES buffer (1.0 × $10^{-2}$ M). [e] Tris buffer (1.0 × $10^{-2}$ M). [f] [$Cu(dpsmp)_2OH_2^{2-}$]; [Ni(II)] = (1–2) × $10^{-6}$ M. [g] Tris buffer (5.0 × $10^{-3}$ M).

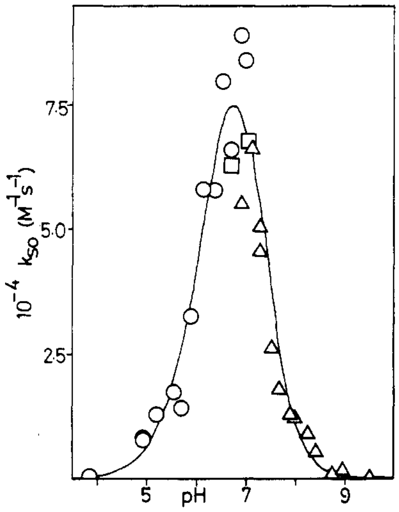

**Figure 6.** Plot of $k_{so}$ against pH for the reduction of $Cu(dpsmp)_2OH_2^{2-}$ by nickel(II) (25.0 °C; in 0.10 M $NaClO_4$). Buffers: ○, MES; □, HEPES; △, Tris.

present study. The limiting second-order rate at low pH can be assigned to reaction 20 and an increase in rate with in-

$$Ni^{II}LH_2^{2+} + Cu(dpsmp)_2OH_2^{2-} \rightarrow \qquad (20)$$

creasing pH is consistent with the greater ease of oxidation of successively deprotonated nickel(II) species, $Ni^{II}LH^+$ and $Ni^{II}L$, reactions 21 and 22. However, the abrupt rate decrease found at higher pH can only partly be described by a single deprotonation constant, $K_{ac}$. The apparent p$K_a$ value, around 7.5, is also much lower than p$K_{ac}$ derived from other sources.

$$Ni^{II}LH^+ + Cu(dpsmp)_2OH_2^{2+} \rightarrow \quad k_{-3a} \qquad (21)$$

$$Ni^{II}L + Cu(dpsmp)_2OH_2^{2+} \rightarrow \quad k_{-3b} \qquad (22)$$

Two alternative explanations were considered: (a) that $k_{-3a}$ is the dominant pathway and that the abrupt decrease in rate is due to deprotonations 18 and 19 with $k_{-3b} << k_{-3a}$ (this violates the principle of microscopic reversibility since thermodynamic considerations and the rates $k_{3a}$ and $k_{3b}$ predict $k_{-3b} > k_{-3a}$) and (b) that, in addition to deprotonation ($K_{ac}$), this pathway is subject to [$OH^-$] inhibition (no strong buffer dependencies were found ruling out a general base mechanism).

**Table IV.** Rate and Equilibrium Constants Derived in This Study

| | | $Fe(CN)_6^{4-}$ | Ni(III) | Ni(II) |
|---|---|---|---|---|
| p$K_{ac}$ | 8.3[a] | 8.27 | | (8.0)[b] |
| p$K_{aI}$ | 7.33[c] | | | 7.20 |
| p$K_{aII}$ | 6.47[c] | | | 6.25 |
| p$K_{aIII}$ | 4.05[c] | | 3.98 | |
| $k_{1a}$ | | ≥334 | | |
| $k_{1b}$ | | 26 | | |
| $k_{3a}$ | | | 1.83 × $10^5$ | |
| $k_{3b}$ | | | 3.8 × $10^3$ | |
| $k_{1a}k_2/k_{-1a}$ | | 8.4 × $10^8$ | | |
| $k_{1b}k_2/k_{-1b}$ | | 3.7 × $10^{-1}$ | | |
| $k_{1a}k_4/k_{-1a}$ | | | | (5.6 ± 1.2) × $10^3$ |
| $k_{1a}k_5/k_{-1a}$ | | | (8.4 × $10^4$)[b,d] | ((2.6 ± 0.8) × $10^4$)[b] |
| $k_{1a}k_6/k_{-1a}$ | | | (8.7 × $10^6$)[b,d] | (8.1 ± 2.1) × $10^6$ |
| $k_{1b}k_6/k_{-1b}$ | | | | (1.2 ± 0.5) × $10^{-3}$ |
| $k_{-1b}/k_{-1a}$ | | (2 × $10^8$)[b] | | (3 ± 4) × $10^8$ |

[a] From cyclic voltammetry. [b] Results in parentheses are approximate. [c] Reference 3. [d] Calculated from potentials in ref 3.

Hydroxide ion inhibition results in the mechanism of reaction of $Cu(dpsmp)_2OH_2^{2-}$ proposed for $Fe(CN)_6^{4-}$ if the reductant, unlike $Fe(CN)_6^{4-}$, does not complete effectively with $OH^-$ for the four-coordinate intermediate $Cu(dpsmp)_2^{2-}$.

Under conditions where no rate saturation is detected, the expression for the second-order rate constant is (23), which

$$k_{so} = \{k_{1a}k_4[H^+]^3 + k_{1a}k_5K_{aII}[H^+]^2 + k_{1a}k_6K_{aII}K_{aI}[H^+] + k_{1b}k_6K_{ac}K_{aII}K_{aI}\}/\{(k_{-1a} + k_{-1b}[OH^-]) \times ([H^+] + K_{ac})(K_{aI}K_{aII} + [H^+]K_{aII} + [H^+]^2)\} \qquad (23)$$

is derived from the mechanism (24)–(26). This rate law omits

$$Ni^{II}LH_2^{2+} + Cu(dpsmp)_2^{2-} \rightarrow \quad k_4 \qquad (24)$$

$$Ni^{II}LH^+ + Cu(dpsmp)_2^{2-} \rightarrow \quad k_5 \qquad (25)$$

$$Ni^{II}L + Cu(dpsmp)_2^{2-} \rightarrow \quad k_6 \qquad (26)$$

pathways where the protonated nickel(II) complexes compete with hydroxide ion, which can be justified on the basis of the known reactivity patterns of these complexes compared to $Ni^{II}L$. A total of eight unknowns are required for solution of the rate expression, and a nonlinear analysis procedure was employed. Although a convergent fit was found with all eight parameters, it did not give chemically reasonable values for the acidity constants; particularly, the copper acidity constant p$K_{ac}$, known to be in the region pH 8, is masked by the [$OH^-$] inhibition and cannot be determined accurately. The fit was found to be insensitive to p$K_{ac}$ in the region of 7.8–8.2, consequently this parameter was fixed at 8.0, and the best fit parameters for the other constants are shown in Table IV. These yield the calculated curve shown in Figure 6.

The acidity constants for the nickel(II) complexes, p$K_{aII}$ = 6.25 and p$K_{aI}$ = 7.20, are in reasonable agreement with the previously reported values,[5] bearing in mind changes in the reaction medium.[19] It is also possible to compare the kinetically derived equilibrium constant for reactions 21 and 22, 0.14 and 2.1 × $10^3$, respectively, with values 0.5 and 2.5 × $10^3$ derived from the reduction potentials. Again, agreement is excellent. Further, the ratio $k_{1a}/k_{1b}$ in the present study is 23, in good agreement, and within experimental error of the value of 13 obtained in the $Fe(CN)_6^{4-}$ reaction. The ratio $k_{-1b}/k_{-1a}$ is (3 ± 4) × $10^8$ $M^{-1}$ in this study compared with

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(19) p$K_{aI}$ and p$K_{aII}$ Values of 7.33 and 6.47, respectively, can be obtained from cyclic voltammetry results in ref 3 in 0.1 M $NaNO_3$ and at 25.0 °C.

(2 ± 4) × $10^8$ in the $Fe(CN)_6^{4-}$ case, again showing good agreement although this is somewhat fortuitous since accurate determination of $k_{-1a}$ in the latter instance is not possible. The rate data for all the reactions are summarized in Table IV. With the complexity of the rate expressions in mind, overall agreement between the two systems examined is remarkable. The two studies complement each other, allowing evaluation of the different parameters, relating to the copper equilibria. That the different kinetic behavior can be described by the same mechanism lends considerable credence to the concept of a reactive intermediate in the reaction.

**General Remarks.** Previously, the Marcus relationship (27)

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (27)$$

has been used to evaluate the self-exchange rate constant for the copper(II/I) redox couple.[6,9] However, the evidence in this paper points to involvement of a tetrahedral $Cu(dpsmp)_2^{2-}$ intermediate in the reduction of $Cu(dpsmp)_2OH_2^{2-}$. Marcus type relationships are applicable to reactions where preequilibria are involved provided the transition state for the copper complex is independent of its reaction partner. Equation 28 is modified to (29) where $P^*$ is the preequilibration constant.[20,21] It has been argued from crystallographic studies on related compounds[15] that this constant $P^*$ should be small.

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (28)$$

$$\log f = [\log (K_{12}/P^*)]/[4 \log (K_{11}K_{22}/P^*Z^2)] \qquad (29)$$

When reduction of the tetrahedral intermediate is diffusion controlled, $k_{diff}$, the second-order rate constant for $Cu(dpsmp)_2OH_2^{2-}$ reduction, is $P^*k_{diff}$. The fastest reduction involves $Fe(CN)_6^{4-}$, and if diffusion control is assumed in this case, the calculated diffusion-controlled rate constant, $k_{diff}$, of 2 × $10^{10}$ $M^{-1}$ $s^{-1}$ gives a lower limit around $10^{-2}$ $M^{-1}$ for $P^*$. However, in this case the second-order rate constant is unreliable, and this uncertainty in $P^*$ prevents meaningful application of eq 29.

Marcus type behavior should be observed if the reactions of $Cu(dpsmp)_2^{2-/3-}$ are predominantly outer sphere in nature. Second-order rate constants for reactions of $Cu(dpsmp)_2OH_2^{2-}$ and $Cu(dpsmp)_2^{3-}$ with various reductants and oxidants are presented in Table V together with electrostatics corrected Marcus calculations.[22] The self-exchange rate data for the nickel complexes are based on the best available estimates, but the chemistry is complicated by inner-sphere processes. Nevertheless, apart from a few instances where the rate data are unreliable, the evaluated self-exchange rate constants lie in a narrow range from 8 × $10^5$ to 1.8 × $10^7$ $M^{-1}$ $s^{-1}$ with a mean of 4.9 × $10^6$ $M^{-1}$ $s^{-1}$. This strongly suggests that reactions of the tetrahedral $Cu(dpsmp)_2^{2-/3-}$ complex are predominantly outer sphere in nature. The reaction of $Fe(CN)_6^{4-}$ is a notable exception, and though the second-order rate constant is somewhat unreliable, it would appear that this complex reacts by an inner-sphere pathway, possibly involving cyanide bridges.

**Table V.** Calculations for the Electrostatics-Corrected Self-Exchange Rate for $Cu(dpsmp)_2OH_2^{2-}/Cu(dpsmp)_2^{3-}$ at 25 °C and in 0.10 M Salt Solution

| | $\Delta G^{\circ a}$ | $\Delta G_{12}^{\ddagger}$ | $\Delta G_{11}^{\ddagger}$ | $\Delta G_{22}^{\ddagger b}$ | $k_{22}$ |
|---|---|---|---|---|---|
| | Reactions with $Cu(dpsmp)_2OH_2^{2-}$ | | | | |
| $Ni^{II}L$ | −4.61 | 5.58 | 10.76 | 5.25 | 1.4 × $10^7$ |
| $Ni^{II}LH^+$ | +0.46 | 8.99 | 10.53 | 8.37 | 7.3 × $10^4$ |
| $HQ^{-\,c}$ | −3.00 | 3.89 | 4.5 | 5.97 | 4.2 × $10^6$ |
| | Reactions with $Cu(dpsmp)_2^{3-}$ | | | | |
| $IrCl_6^{2-\,d}$ | −6.27 | 3.44 | 7.69 | 5.60 | 7.8 × $10^6$ |
| $Ni^{III}L^+$ | +4.61 | 10.12 | 10.76 | 5.11 | 1.8 × $10^7$ |
| $Ni^{III}LH^{2+}$ | −0.46 | 7.82 | 10.53 | 6.95 | 8.0 × $10^5$ |

[a] Units kcal $mol^{-1}$. [b] Work functions calculated with radii of 11.5 Å for $Cu(dpsmp)_2^{2-/3-}$, 6 Å for $Ni^{II}L^{+/0}$ and $Ni^{II}LH^{2+/+}$, and 3.5 Å for $IrCl_6^{3-}$. [c] Reference 9, 0.2 M ionic strength. [d] Reference 6.

These data are the first to be presented where a reaction of a copper–phenanthroline derivative has been studied in both oxidative and reductive directions. Previous indications that a structural barrier to electron transfer might reduce the self-exchange efficiency of the copper(II) species compared with copper(I) are invalid, and alternative explanations for the discrepancies in the literature must be sought. The self-exchange rate in this case is relatively high indicating that the structural barrier is low and consistent with the modest value for $P^*$.

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**Registry No.** $Cu(dpsmp)_2OH_2^{2-}$, 88376-65-2; $Cu(dpsmp)_2^{3-}$, 88376-66-3; $Fe(CN)_6^{4-}$, 13408-63-4; $Ni^{II}L$, 59980-38-0; $Ni^{III}L^+$, 59980-37-9.

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