equal, be less favorable for $Fe_{aq}{}^{3+/2+}$ self-exchange since $Fe_{aq}{}^{3+}$ is a considerably less strong oxidant than $Co_{aq}{}^{3+}$.[26] However, this could easily be offset by the manifold other factors that control the relative rates of competing inner- and outer-sphere pathways.[49] In any case, on this basis water bridging is more likely for $Fe_{aq}{}^{3+/2+}$ self-exchange than for the other aquo complexes considered here;[50] aside from $Ru_{aq}{}^{3+/2+}$, which is constrained to follow outer-sphere pathways, all the other couples considered here are ca. 1 V less strongly oxidizing than $Fe_{aq}{}^{3+/2+}$. Such pathways are clearly unavailable for cross-reactions involving substitutionally inert coreactants such as those in Table II, so that the $Fe_{aq}{}^{3+/2+}$ reactivity within these environments should reflect that for a "normal" outer-sphere pathway. Water- or hydroxo-bridged pathways are also unlikely within electrochemical redox environments, especially at mercury electrodes in view of the weak interaction between water molecules and this surface.[51]

Regardless of the detailed reasons for the anomalous behavior of $Fe_{aq}{}^{3+/2+}$ self-exchange it can be concluded that this couple is in some respects a nonideal choice for the detailed comparisons between experimental rate parameters and the predictions of contemporary theory.[1] Nevertheless, the required structural information is becoming available for a number of other redox couples,[30] enabling such comparisons to be made not only for self-exchange reactions[30] but also for a variety of cross-reactions and electrochemical processes.[43]

Acknowledgment. We are grateful to Dr. A. Ludi for communicating his results on ruthenium aquo crystal structures in advance of publication. This work is supported by the Air Force Office of Scientific Research.

Registry No. Ru, 7440-18-8; V, 7440-62-2; Fe, 7439-89-6; Eu, 7440-53-1; Cr, 7440-47-3.

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(49) Footnote 54 of ref 26.

(50) It was asserted[49] that the $Co_{aq}{}^{3+}$–$Fe_{aq}{}^{2+}$ reaction follows an outer-sphere pathway on the basis of the agreement with the rates of other cross-reactions involving $Co_{aq}{}^{3+}$ and outer-sphere reductants calculated by using eq 2 and the measured value of $k^{h}{}_{ex,Fe}$. However, using the present estimate of $k^{h}{}_{ex}$ for outer-sphere $Fe_{aq}{}^{3+/2+}$ self-exchange instead yields a $Co_{aq}{}^{3+}$–$Fe_{aq}{}^{2+}$ reaction rate ca. 10^5-fold larger than predicted from eq 2, indicative of a water-bridged pathway for this reaction as well.

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Activation Volume as Evidence for a Dissociative-Interchange Mechanism of Nickel(II) Ion Complexation with Isoquinoline in Water, *N*,*N*-Dimethylformamide, Acetonitrile, Methanol, and Ethanol

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Activation volumes for the complexation of nickel(II) ion with isoquinoline in various solvents were determined by a high-pressure stopped-flow technique. Values of activation volume for formation and dissociation of the (isoquinoline)nickel(II) complex are respectively 7.4 ± 1.3 and 8.9 ± 0.8 $cm^3\ mol^{-1}$ in water, 9.3 ± 0.3 and 12.2 ± 0.3 $cm^3\ mol^{-1}$ in *N*,*N*-dimethylformamide, 12.8 ± 0.6 and 9.9 ± 0.5 $cm^3\ mol^{-1}$ in methanol, and 12.6 ± 0.5 and 15.7 ± 1.1 $cm^3\ mol^{-1}$ in ethanol. The activation volume of the complex formation in acetonitrile is 9.4 ± 0.1 $cm^3\ mol^{-1}$. All the positive values of the activation volume strongly indicate that the ligand substitution reactions on nickel(II) ion proceed via a dissociative-interchange mechanism in these solvents.

Introduction

Activation volumes for solvent exchange on metal ions including transition metals and typical elements in various solvents have been extensively measured by a high-pressure NMR method,[1,2] while for complex formation there are not as many data of activation volumes.[3] Caldin and Greenwood have recently reported volumes of activation for the complexation of nickel(II) ion in nonaqueous solvents by using a high-pressure laser-flash temperature-jump technique.[3c]

We have studied the mechanism of iron(III) ion complexation on the basis of activation volume obtained by a high-pressure stopped-flow apparatus.[4,5] The sign of activation volume for complexation will reflect the character of a metal ion. Thus the high-pressure stopped-flow technique is a powerful and reliable tool for the mechanistic investigation of complex formation. We present a high-pressure study on the complex formation of nickel(II) ion with isoquinoline in various solvents. This paper will provide a unified aspect of the mechanism of nickel(II) ion complexation.

Experimental Section

Solvents. Nonaqueous solvents purchased from Wakojunyaku (Osaka, Japan) were purified just before use. Distilled water was redistilled in the presence of alkaline potassium permanganate. Reagent grade acetonitrile was fractionally distilled twice from a packed column at high reflux ratio over diphosphorus pentoxide (2 g/dm^3) and calcium hydride (4 g/dm^3). The reflux was performed for 1 h prior to each distillation. Reagent grade methanol was dried over 3A molecular sieves for a few days and then twice distilled.

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Table I. Rate Constants and Activation Volumes for the Formation and Dissociation Reaction of the (Isoquinoline)nickel(II) Complex at 25 °C[a]

solvent[b]	$k_f^0/m^{-1}\ s^{-1}$ [c]	$\Delta V_f^{\ddagger}$/ cm³ mol⁻¹	k_d^0/s^{-1}	$\Delta V_d^{\ddagger}$/ cm³ mol⁻¹	K/m^{-1} [e]	ΔV°/ cm³ mol⁻¹ [f]	$\Delta V_{ex}^{\ddagger}$/ cm³ mol⁻¹ [g]	V°/ cm³ mol⁻¹ [i]	DN[j]
H_2O	$(2.03 \pm 0.13) \times 10^3$ 2.07×10^3 [d]	7.4 ± 1.3	30.9 ± 1.1 29.6[d]	8.9 ± 0.8	65.7 68.9	−1.5 ± 2.1	7.2 ± 0.2	18.1	18.0
DMF	$(2.04 \pm 0.03) \times 10^3$ 2.42×10^3 [d]	9.3 ± 0.3	21.6 ± 0.2 19.5[d]	12.2 ± 0.3	94.4 124	−2.9 ± 0.6	9.1 ± 0.3	77.4	26.6
CH_3CN	$(7.09 \pm 0.03) \times 10^2$ 1.24×10^3 [d]	9.4 ± 0.1					9.6 ± 0.3 7.3 ± 0.3[h]	52.8	14.1
CH_3OH	$(7.99 \pm 0.25) \times 10$ 9.65×10 [d]	12.8 ± 0.6	1.17 ± 0.03 1.94[d]	9.9 ± 0.5	68.0 49.7	2.9 ± 1.1	11.4 ± 0.6	40.7	19.0
C_2H_5OH	$(6.08 \pm 0.13) \times 10^3$ 6.08×10^3 [k]	12.6 ± 0.5 13.4[k]	12.0 ± 0.7 13.0[k]	15.7 ± 1.1 12.2[k]	507 468[k]	−3.1 ± 1.2 1.1 ± 0.1[k]		58.7	20.0

[a] Errors are standard deviations. [b] In water $I = 0.10$ M (Ni^{2+}, Na^+, ClO_4^-) and pH 6.6–7.5, and in the other solvents $I = 0.10$ M (Na^+, ClO_4^-). [c] Rate constant at atmospheric pressure in the case of CH_3CN. [d] Rate constant at atmospheric pressure in $M^{-1}\ s^{-1}$ quoted from ref 6. [e] Calculated from k_f/k_d. [f] Derived from the relationship $\Delta V^{\circ} = \Delta V_f^{\ddagger} - \Delta V_d^{\ddagger}$. [g] Activation volume for solvent exchange obtained by a high-pressure NMR method.[2,16] [h] Obtained by Swaddle et al.[2] [i] Molar volume of solvent at 25 °C. [j] Gutmann donor number taken from ref 17. [k] The ΔV° value was determined to be 1.1 cm³ mol⁻¹ by measuring dilatometrically the reaction volume for the reaction of Ni(II) ion with isoquinoline in ethanol (Sengoku, K.; Funahashi, S.; Tanaka, M., unpublished results). The ΔV° ($= \Delta V_f^{\ddagger} - \Delta V_d^{\ddagger}$) value was thus kept at 1.1 in the nonlinear least-squares fitting.

Chemical grade ethanol was distilled once prior to the treatment with 3A molecular sieves. Then the dried ethanol was distilled twice.

Reagent grade *N,N*-dimethylformamide (DMF) was purified by the following procedure. After being dried over 3A molecular sieves for 1 day, DMF was decanted onto potassium hydroxide and stirred vigorously for 12 h. Then it was decanted onto P_2O_5 and stirred for 2 days. The treated DMF was distilled over P_2O_5 under reduced pressure at ca. 28 °C with nitrogen bleed. This procedure was repeated two more times.

Reagents. Nickel(II) perchlorate hexahydrate was prepared according to the following procedure. Five grams of nickel(II) oxide (99.998%, Mitsuwakagakuyakuhin, Osaka, Japan) was added to 50 cm³ of solution containing 13.5 cm³ of 60% perchloric acid (super special grade, Wakojunyaku). The mixture was heated for complete reaction. After the unreacted NiO was filtered, the filtrate was concentrated by evaporation and then the hexahydrate was crystallized.

For the work in methanol and ethanol as solvents, we used nickel(II) perchlorate monohydrate obtained by heating the hexahydrate at 90 ± 5 °C in vacuo.[6] For studies in acetonitrile the pale purple crystalline $Ni(CH_3CN)_6(ClO_4)_2$ prepared according to the literature[7] was employed. For DMF the $Ni(DMF)_6^{2+}$ ion was prepared in DMF from the hexahydrate by the dehydration with 3A molecular sieves. The concentration of nickel(II) solutions was determined by a replacement titration with the Cu–TAR–EDTA system.[8] For the hexakis(solvento)nickel(II) perchlorates, the concentration determined by weighing was in very good agreement with that by the titration.

Isoquinoline (isoq, Wakojunyaku) was distilled in the presence of potassium hydroxide under reduced pressure and stored in a refrigerator. The isoquinoline solutions were prepared by dissolving weighed portions. Sodium perchlorate hydrate was prepared as described previously[9] and was converted to the anhydrous salt by drying at about 60 °C in vacuo. 2-(*N*-Morpholino)ethanesulfonic acid (MES, Dotite, Kumamoto, Japan) was recrystallized from aqueous ethanol three times and dried under vacuum.[10]

Measurements. The temperature of the reaction solution was controlled to within ±0.1 °C by a thermoelectric circulating bath. Solvents and solutions were prepared fresh and used within 24 h after preparation. All solutions were 0.1 M (M ≡ mol dm⁻³) in $NaClO_4$ except for aqueous solutions, in which the ionic strength was adjusted to 0.1 M by both sodium perchlorate and nickel(II) perchlorate. Solutions of nickel(II) perchlorate and isoquinoline were prepared at 25 °C in molar concentration scale. The molar concentrations were converted to the pressure-independent molal (mol kg⁻¹ ≡ *m*) scale. In all kinetic experiments, increase in absorbance at 325 nm due to the formation of the 1:1 complex ($(Ni(isoq))^{2+}$) was followed spectrophotometrically as a function of reaction time by a high-pressure stopped-flow apparatus (Type FIT-3).[11] Nickel(II) perchlorate was used in large excess over isoquinoline ($[Ni(ClO_4)_2] = (4 \times 10^{-3})$–$(2 \times 10^{-2})$ M, [isoq] $\simeq 2 \times 10^{-4}$ M). First-order plots were linear for at least 3 half-lives. In the case of water as solvent, MES was used to maintain constant pH. It was confirmed that the variation of the pH of buffered solution from 6.6 to 7.5 did not affect the rate at atmospheric pressure. Thus the pH variation with change in pressure does not affect the rate.[12]

Scheme I

$$\mathrm{Ni}^{2+} + \mathrm{isoq} \overset{K_{os}}{\rightleftharpoons} \mathrm{Ni}^{2+}\cdots\mathrm{isoq} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{Ni(isoq)}^{2+}$$

I II

Results

The reaction of Ni^{2+} with isoquinoline in various solvents is expressed by eq 1. The reaction is first order with respect

$$\mathrm{Ni}^{2+} + \mathrm{isoq} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{Ni(isoq)}^{2+} \tag{1}$$

to isoquinoline. The pseudo-first-order rate constant k_0 dependent on the concentration of Ni^{2+} is given by eq 2,[13] where

$$k_0 = k_f[\mathrm{Ni}^{2+}] + k_d \tag{2}$$

k_f is a second-order rate constant for the formation of the (isoquinoline)nickel(II) complex and k_d is a first-order rate constant for the dissociation of the complex. The apparatus FIT-3 guaranteed excellent reproducibility of rate constants in all solvents studied (see Table SI[14]). Numerical data of rate constants are tabulated in Table SI.[14] Data in DMF are plotted according to eq 2, and the result is depicted in Figure 1, which shows a good linearity at any pressure. Plots of logarithmic values of the slope (k_f) and the intercept (k_d) of the straight lines are linearly related to pressure (Figure 2), showing no pressure dependence of activation volumes ($\Delta V^{\ddagger}$) for both formation and dissociation reactions. Therefore we can rewrite eq 2 as eq 3, where k_f^0 and k_d^0 refer to rate con-

$$k_0 = k_f^0 \exp(-\Delta V_f^{\ddagger} R^{-1} T^{-1} P)[\mathrm{Ni}^{2+}] + k_d^0 \exp(-\Delta V_d^{\ddagger} R^{-1} T^{-1} P) \tag{3}$$

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(14) Supplementary material.

Table II. Rate Constants and Activation Volumes for Complexation of Ni(II) Ion[a]

solvent	ligand	k_f(25 °C)/M^{-1} s^{-1}	$\Delta V_f^{\ddagger}$/cm^3 mol^{-1}	method[b]	ref
H_2O	isoq	$(2.03 \pm 0.13) \times 10^3$[c]	7.4 ± 1.3	SF	this work
	NH_3	$(6.5 \pm 0.2) \times 10^3$ (30 °C)	6.0 ± 0.3	TJ	3a
	glycinate	2.1×10^4	10 ± 1	TJ	3b
	murexide	1.0×10^4	12.2 ± 1.5	TJ	18
	imidazole	7×10^3 (28 °C)	11.0 ± 1.6	TJ	19
	PADA[d]	$(1.17 \pm 0.03) \times 10^3$	8.2 ± 2.1	LF	3c
			7.7 ± 0.3	TJ	3a
	malonate	$(3.08 \pm 0.15) \times 10^5$	16.0 ± 2.1[e]	PJ	20
DMF	isoq	$(2.04 \pm 0.03) \times 10^3$[c]	9.3 ± 0.3	SF	this work
	PADA	$(1.32 \pm 0.09) \times 10^3$	11.5 ± 1.5	LF	3c
CH_3CN	isoq	$(7.09 \pm 0.03) \times 10^2$[c]	9.4 ± 0.1	SF	this work
CH_3OH	isoq	$(7.99 \pm 0.25) \times 10$[c]	12.8 ± 0.6	SF	this work
C_2H_5OH	isoq	$(6.08 \pm 0.13) \times 10^3$[c]	12.6 ± 0.5	SF	this work
Me_2SO[f]	PADA	$(5.8 \pm 0.3) \times 10^3$ (50 °C)	11.3 ± 1.0	LF	3c

[a] Errors quoted are given by the original authors. [b] Abbreviations: SF, stopped-flow; TJ, temperature-jump; LF, laser-flash TJ; PJ, pressure-jump. [c] In m^{-1} s^{-1}. [d] Pyridine-2-azodimethylaniline. [e] According to ref 20, $\Delta V_f^{*\ddagger}$ was estimated to be 8.7 ± 2.1 cm^3 mol^{-1}. [f] Dimethyl sulfoxide.

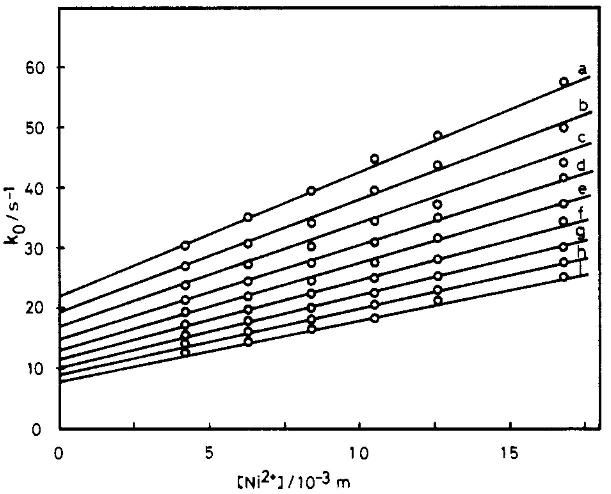

Figure 1. Nickel(II) ion concentration dependence of k_0 in DMF at different pressures and at 25 °C: (a) 1 kg cm^{-2}; (b) 250 kg cm^{-2}; (c) 500 kg cm^{-2}; (d) 750 kg cm^{-2}; (e) 1000 kg cm^{-2}; (f) 1250 kg cm^{-2}; (g) 1500 kg cm^{-2}; (h) 1750 kg cm^{-2}; (i) 2000 kg cm^{-2}.

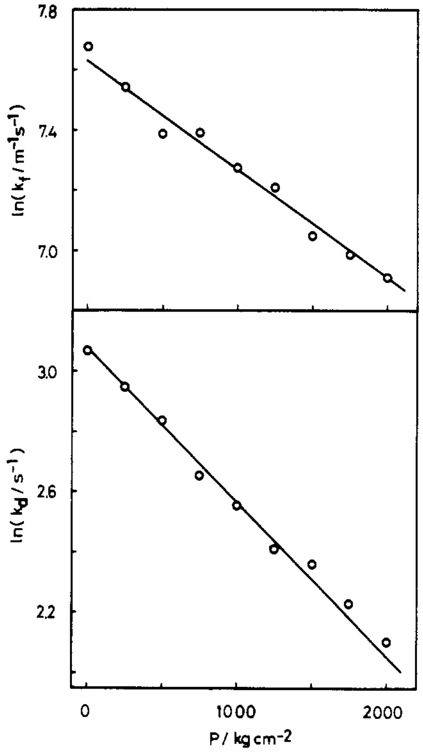

Figure 2. Pressure dependence of k_f and k_d in DMF at 25 °C.

stants at zero pressure. The most probable values of k_f^0, k_d^0, ΔV_f^*, and ΔV_d^* were obtained by applying nonlinear least-squares fitting (SALS)[15] to eq 3. In water, methanol, and ethanol first-order rate constants are also given by eq 2. Under the present experimental conditions, the dissociation reaction in acetonitrile is negligible, since the plot of k_0 vs. $[Ni^{2+}]$ lies along a straight line starting from the origin: $k_0 = k_f[Ni^{2+}]$. Since a plot of ln k_f vs. pressure was also linear, it is possible to calculate the activation volume from the slope by a linear least-squares fitting. The obtained values of rate constants and activation volumes for the formation and dissociation of the (isoquinoline)nickel(II) complex are listed in Table I together with related data.

Discussion

The reaction of nickel(II) ion with isoquinoline is expressed as Scheme I. Step I is the fast equilibrium formation of an outer-sphere complex from reactants. Step II is the equilibrium process between the outer-sphere complex and the final product. The second-order rate constant k_f for the formation reaction is written as $k_f = K_{os}k_f^*/(1 + K_{os}[Ni^{2+}])$ by equilibrium and rate constants defined in Scheme I. Since $1 >> K_{os}[Ni^{2+}]$ under the present experimental conditions, we have $k_f = K_{os}k_f^*$. Thus the activation volume for the formation equals the sum of partial molal volume changes in each step: $\Delta V_f^* = \Delta V_{os}^\circ + \Delta V_f^{**}$. Therefore, the reaction volume for the overall complexation is expressed by eq 4.

$$\Delta V^\circ = \Delta V_f^* - \Delta V_d^* = \Delta V_{os}^\circ + \Delta V_f^{**} - \Delta V_d^* \quad (4)$$

In Table I are tabulated activation volumes for solvent exchange (ΔV_{ex}^*), molar volumes of solvents (V°), and values of the Gutmann donor number (DN) together with rate constants obtained by Chattopadhyay and Kratochvil.[6] The rate constants k_f and k_d and equilibrium constant K ($=k_f/k_d$) are in reasonable agreement with the literature values.[6] We observe no parallel relationship between activation volumes (ΔV_f^* or ΔV_d^*) and V° of the solvent. This is also the case for solvent exchange, as stated by Merbach et al.[16] There

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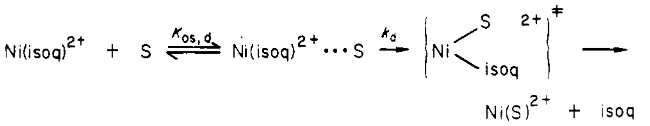
Inorg. Chem. **1983**, *22*, 2567–2572

is also no simple correlation between $\Delta V^{\ddagger}$ and DN.

In the present system, since isoquinoline has no formal charge, and if there is any, its dipole may be little, ΔV_{os}° would not exceed the uncertainty in the observed $\Delta V^{\ddagger}$. Consequently the observed activation volume $\Delta V_f^{\ddagger}$ should almost equal the $\Delta V_f^{*\ddagger}$. On the other hand, $\Delta V_{ex}^{\ddagger}$ measured by a high-pressure NMR technique involves no contribution of ΔV_{os}°. The positive $\Delta V_{ex}^{\ddagger}$ values considerably smaller than those of molar volumes of solvents strongly point to a dissociative interchange (I_d) mechanism.[16] Since $\Delta V_f^{\ddagger}$ is close to $\Delta V_{ex}^{\ddagger}$, as apparent from values in Table I, the mechanism for the complex formation should be similar to that for the solvent exchange on nickel(II) ion in different solvents.

Interestingly, values of $\Delta V_d^{\ddagger}$ are all positive and comparable to those of $\Delta V_f^{\ddagger}$ and $\Delta V_{ex}^{\ddagger}$. Assuming the same reaction process for dissociation as for formation



$$\mathrm{Ni(isoq)}^{2+} + \mathrm{S} \overset{K_{os,d}}{\rightleftharpoons} \mathrm{Ni(isoq)}^{2+}\cdots\mathrm{S} \xrightarrow{k_d} \left[\mathrm{Ni}\begin{matrix}\mathrm{S}\\ \mathrm{isoq}\end{matrix}\right]^{2+\ddagger} \longrightarrow \mathrm{Ni(S)}^{2+} + \mathrm{isoq}$$

we have $k_d = K_{os,d}k_d^*[S]/(1 + K_{os,d}[S])$. In the case of dissociation, the entering ligand is a solvent molecule (S) and the leaving ligand is isoquinoline. Since $1 < K_{os,d}[S]$, we have $k_d \simeq k_d^*$. Thus, the observed dissociation reaction corresponds to the reaction from an outer-sphere complex $(\mathrm{Ni(isoq)})^{2+}\cdots\mathrm{S}$ to the (solvento)nickel(II) ion. The transition state is the same as for the formation. The mechanism is a dissociative interchange also for the dissociation.

All available values of activation volume for the complexation of Ni(II) ion are compiled in Table II. The activation volume is similar for different entering ligands despite their different size. This would imply that the volume increase caused by the lengthening of the metal ion bond with a leaving solvent molecule is compensated to a similar extent for different entering ligands by the volume decrease due to penetration of a donor atom into the inner sphere.

We conclude that all the formation and dissociation of the 1:1 nickel(II) complex and the solvent exchange on nickel(II) ion in various solvents can be accommodated within the framework of a similar I_d mechanism.

Registry No. Ni, 7440-02-0; CH_3CN, 75-05-8; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; DMF, 68-12-2; isoq, 119-65-3.

Supplementary Material Available: Table SI listing numerical data of rate constants for complexation of Ni(II) ion with isoquinoline in DMF, CH_3CN, CH_3OH, C_2H_5OH, and H_2O under high pressure up to 2000 kg cm^{-2} and at 25 °C (4 pages). Ordering information is given on any current masthead page.

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Binuclear Metal Complexes. 1. Synthesis, Characterization, and Electrochemical Studies of Dicopper(II) Complexes with 4-Methyl-2,6-di(acyl/benzoyl)phenol

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Synthesis and characterization of the mono- and binuclear copper(II) complexes, $Cu(R,R')L_2\cdot H_2O$ and $Cu_2(R,R')L_2(ClO_4)_2\cdot 2H_2O$, have been made with the ligands 4-methyl-2,6-di(acyl/benzoyl)phenol, designated as (R,R')HL, where R and R′ stand for the substituents in the di(acyl/benzoyl) moiety. The following substituents have been used: R = R′ = H, Me, Pr, Ph; R = Ph, R′ = Me. Electrochemical studies of these compounds have been made in DMF with use of a HMDE. All of the five Cu^{II}–Cu^{II} complexes undergo two-electron reduction to Cu^{I}–Cu^{I} species at a single potential as evidenced from cyclic voltammetric and coulometric measurements. Among these, the electron-transfer processes in $Cu_2(Ph,Ph)L_2(ClO_4)_2\cdot 2H_2O$ and $Cu_2(Ph,Me)L_2(ClO_4)_2\cdot 2H_2O$ occur reversibly; others show quasi-reversible behavior. The $E_{1/2}$ values are about −0.05 V vs. SCE. The electrochemically reduced Cu^{I}–Cu^{I} species show an absorption band at 470 nm. The mononuclear copper(II) complexes undergo quasi-reversible reduction with $E_{1/2} \simeq -0.43$ V.

Introduction

The structure–function relationship in copper proteins is a subject of considerable importance. Hemocyanin, tyrosinase, lacasse, ceruloplasmin, and ascorbic acid oxidase are copper proteins that contain a strongly coupled binuclear copper active site but perform different biological functions.[1-9] The dicopper units, referred to as type 3 coppers, are characterized inter alia by large antiferromagnetic coupling constants and relatively high positive two-electron redox potentials.

In the last few years, model studies with reference to the type 3 coppers have addressed ligand environment, redox behavior, magnetic exchange interactions, and reactivity of the metal centers.[10-20] In the context of redox behavior of

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