

vails. Lacking clear evidence to the contrary, we adhere to the view that the compressed form of $[\text{Fe}_4\text{S}_4]^{2+}$ cores in identical-ligand environments is the most stable arrangement, but one whose degree of distortion is subject to extrinsic effects of the environment. The different extents of compression of $[\text{Fe}_4\text{S}_4(\text{S}-t\text{-Bu})_4]^{2-}$ in two lattices provide a clear case in point. In three Fd_{ox} proteins the cores, bonded to four necessarily inequivalent cysteine residues, also have the compressed tetragonal structure.^{29,30} No structure of a Fd_{red} protein is available.

The proposition that the elongated tetragonal form of the $[\text{Fe}_4\text{S}_4]^+$ core is the intrinsically stable structure is based on the near-congruence of spectroscopic and magnetic properties of reduced clusters in solution with those of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$, which are nearly identical in the solid and solution states.^{8,9,11} Some eight $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ clusters exhibit this behavior. These include the $\text{R} = p\text{-C}_6\text{H}_4\text{Br}$ and CH_2Ph species, which have nontetragonal structures in the solid state. Solution structures are considered to be less perturbed than those in

the solid state and thus to correspond to the most stable configuration. Other $\text{R} =$ alkyl clusters, not being previously accessible, were not examined. If the proposal in reaction 5 is to be more generally upheld, the $\text{R} = \text{Et}$ and $t\text{-Bu}$ clusters, upon passing from the crystalline to the solution phase, must execute a compressed \rightarrow elongated tetragonal structural change. This process involves inversion in length of the 4 short + 8 long Fe-S bond sets and is comparable to the structural change in reaction 5 itself. The comparative properties of reduced clusters with $\text{R} =$ alkyl, as related to the occurrence of reaction 5, are under investigation.

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Registry No. A, 91294-56-3; B, 91294-59-6; $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SEt})_4]$, 91294-58-5; $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SMe})_4]$, 91294-61-0; $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$, 63182-82-1; $(\text{Me}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SEt})_{10}]$, 88271-63-0.

Supplementary Material Available: Crystallographic data for $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{S}-t\text{-Bu})_4]\cdot\text{MeCN}$ and $(\text{Me}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SEt})_4]$: listings of atom coordinates, anisotropic thermal parameters, and calculated hydrogen atom positions and temperature factors, tables of $10|F_o|$ and $10|F_c|$, and stereoviews of the clusters (42 pages). Ordering information is given on any current masthead page.

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Enhanced Reactivity of Nickel(II) Complexes Involving Multidentate Ligands in Their Complexation

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The formation rates of the 1:1 and 1:2 nickel(II) oxalato (ox^{2-}), glycinate (gly^-), and ethylenediamine (en) complexes with 1,10-phenanthroline have been studied spectrophotometrically by a stopped-flow technique. The rate law is expressed as $d[\text{Ni}(\text{phen})^{2+}]/dt = k_{\text{Ni}}[\text{Ni}^{2+}][\text{phen}] + k_{\text{NiA}}[\text{NiA}][\text{phen}] + k_{\text{NiA}_2}[\text{NiA}_2][\text{phen}]$, where phen refers to unprotonated 1,10-phenanthroline and A to a bidentate ligand. The enhanced reactivity of NiA as compared to that of Ni^{2+} ($k_{\text{Ni}} = (4.2 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{Ni}(\text{ox})} = (1.8 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{Ni}(\text{gly})} = (1.9 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{Ni}(\text{en})} = (1.6 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, all at 25 °C and $I = 1.00 \text{ M}$) is attributable to the labilizing effect of the bound ligand A on the rate of loss of coordinated water molecules at NiA. The labilizing effect of the coordinated aliphatic multidentate ligand is quantitatively accounted for in terms of the electron-donating ability of the coordinated ligand.

From mechanistic considerations on the formation constants of metal complexes,^{1,2} it has been shown that, taking into account the statistical factor arising from the number of water molecules available for exchange, the water-exchange rate constant at MA ($k_{\text{MA}}^{-\text{H}_2\text{O}}$) is expressed as

$$\log(k_{\text{MA}}^{-\text{H}_2\text{O}}/\text{no. of H}_2\text{O in MA}) = \log(k_{\text{M}}^{-\text{H}_2\text{O}}/\text{no. of H}_2\text{O in M}) + \gamma E(\text{A}) \quad (1)$$

where $E(\text{A})$ refers to the electron-donor constant of the coordinated ligand A and γ is a constant characteristic of the metal ion M. By the use of the $E(\text{A})$ value as given by Edwards,³ the bound-ligand effect in the complexation kinetics of monodentate ligand complexes of chromium(III),⁴ cobalt(II),⁴ iron(III),⁴ nickel(II),⁴⁻⁶ oxovanadium(IV),⁴ zinc(II),⁷

and gallium(III)⁸ has been shown to be quantitatively described by eq 1.

For the complexation kinetics involving multidentate ligand complexes, rate constants for the substitution of water molecules in the first coordination sphere of MA, especially of NiA, have been determined for many systems,⁹ and it has been observed that a bound ligand exerts a significant influence on the reactivity of nickel(II). For A = aliphatic amine, the increasing lability of the water molecules at NiA with increasing number of nitrogen atoms bound to nickel(II) has been noted.^{10,11}

To understand how the bound-ligand effect of nickel(II) complexes can be correlated with the electron-donating ability

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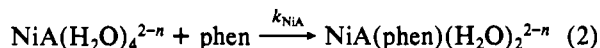
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of a coordinated multidentate ligand A, we have studied the complexation reaction kinetics given by eq 2, where A is a



bidentate ligand such as oxalate (ox^{2-}), glycinate (gly^-), or ethylenediamine (en) and phen refers to unprotonated 1,10-phenanthroline.

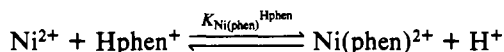
Experimental Section

Materials. Nickel oxide (99.999%) was dissolved in perchloric acid to prepare nickel perchlorate solution. The concentration of nickel was determined by an EDTA titration with Cu-EDTA-TAR as an indicator.¹² Reagent grade glycine and ethylenediamine were purified by recrystallization from distilled water and distillation under reduced pressure, respectively. Sodium oxalate of primary-standard quality (Wako-junyaku) was used without further purification. The solutions of these three bidentate ligands were prepared by weighing the well-dried reagent. 3-Morpholinopropanesulfonic acid (MOPS) was used to adjust the hydrogen ion concentration. Solutions of 1,10-phenanthroline and sodium perchlorate were prepared as described elsewhere.⁷

Measurements. All experiments were carried out in a room thermostated at $25 \pm 0.5^\circ\text{C}$. Temperature of the reaction solution was controlled to within $\pm 0.1^\circ\text{C}$. Ionic strength was maintained at 1.00 M ($M = \text{mol dm}^{-3}$) with sodium perchlorate. Equilibrium measurements were made with a highly sensitive spectrophotometer (Type SM 401, Union Giken, Osaka, Japan). Reaction rates of complex formation were followed by a stopped-flow spectrophotometer (Union Giken RA 401), equipped with a data processor (Union Giken RA 450). The reactions between the nickel(II) complexes employed and 1,10-phenanthroline yield complexes that possess spectral characteristics very similar to those of the mono(1,10-phenanthroline)nickel(II) complex. The changes in absorbance at 270 nm, a wavelength of maximum absorption of the 1:1 Ni(II)-phenanthroline complex, were accumulated to obtain high S/N curves. Hydrogen ion concentration was determined by an Orion 701A IONALYZER with a calomel electrode filled with saturated sodium chloride as an internal solution. A 1.00×10^{-2} M perchloric acid solution containing 0.99 M sodium perchlorate was employed as a standard of hydrogen ion concentration ($-\log [\text{H}^+] = 2.00$).

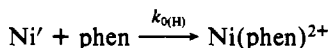
Results

Complexation Equilibrium of Nickel(II) with 1,10-Phenanthroline. Nickel(II) ion forms a 1:1 complex with 1,10-phenanthroline in acidic solution where the concentration of nickel ion is in excess over that of the ligand. Spectral change with isosbestic points at 273, 288, and 298 nm is attributable to the equilibrium



The equilibrium constant for this reaction was determined from the plot of the absorbance change at 280 nm vs. $-\log [\text{H}^+]$ to be $K_{\text{Ni}(\text{phen})}^{\text{Hphen}} = 10^{3.34 \pm 0.03}$ at 25°C and $I = 1.00$ M. With the K_{Hphen} value previously determined,⁷ we have $K_{\text{Ni}(\text{phen})}^{\text{phen}} = [\text{Ni}(\text{phen})^{2+}][\text{Ni}^{2+}]^{-1}[\text{phen}]^{-1} = 10^{8.65 \pm 0.05} \text{M}^{-1}$, as compared with $10^{8.67}$ at 25°C and $I = 0.1$ M¹³ and $10^{8.65}$ at 25°C and $I = 0.5$ M.¹⁴

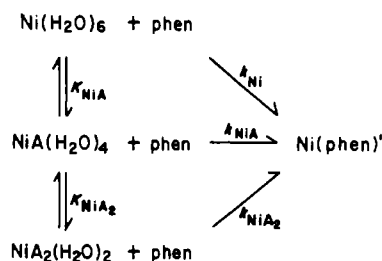
Reaction of Nickel(II) Ion with 1,10-Phenanthroline. All reactions were first order in nickel(II) ion, which was always held in sufficient excess to ensure pseudo-first-order kinetics and complete formation of the 1:1 complex. The unprotonated form of the ligand prevails under the experimental conditions. Then the reaction is expressed as



and the kinetic equation for this reaction is described as

$$d[\text{Ni}(\text{phen})^{2+}]/dt = k_{0(\text{H})}[\text{Ni}'][\text{phen}]$$

Scheme I



where $[\text{Ni}']$ denotes the total concentration of nickel(II) not combined with phen and $k_{0(\text{H})}$ is the conditional rate constant involving the concentration of hydrogen ion.

The conditional rate constant remains constant over the $-\log [\text{H}^+]$ range of 6–8, and $[\text{MOPS}]$ up to 10^{-3} M gives no kinetic effect. Since no hydrolysis of nickel ion should be taken into account under the present experimental condition, the kinetic equation is expressed by

$$d[\text{Ni}(\text{phen})^{2+}]/dt = k_{\text{Ni}}[\text{Ni}^{2+}][\text{phen}]$$

and the rate constant k_{Ni} was determined to be $(4.2 \pm 0.2) \times 10^3 \text{M}^{-1} \text{s}^{-1}$ at 25°C and $I = 1.00$ M, as compared with $3.9 \times 10^3 \text{M}^{-1} \text{s}^{-1}$ at 25°C ,¹⁵ $4.2 \times 10^3 \text{M}^{-1} \text{s}^{-1}$ at 25°C and $I = 0.05$ M,¹⁶ and $3.5 \times 10^3 \text{M}^{-1} \text{s}^{-1}$ at 25°C and $I = 0.3$ M.¹⁷

Reaction of Nickel(II) Complexes with 1,10-Phenanthroline. Under conditions where only the $\text{NiA}(\text{H}_2\text{O})_4$ and $\text{NiA}_2(\text{H}_2\text{O})_2$ are responsible for the reaction of the nickel(II) complex, the reaction can be considered to proceed as in Scheme I (charges are omitted for simplicity), where $\text{Ni}(\text{phen})'$, refers to a mono(1,10-phenanthroline)nickel(II) complex involving a mixed-ligand complex such as $\text{NiA}(\text{phen})$ or $\text{NiA}_2(\text{phen})$. Since the total concentration of a bidentate ligand A is much higher than that of phen (see Table SI, supplementary material), NiA and NiA_2 are certainly in equilibrium with aquanickel during the reaction. When the coordination of one phen is quantitative, the kinetic equation for this reaction scheme is described as

$$d[\text{Ni}(\text{phen})']/dt = k_{0(\text{A})}[\text{Ni}'][\text{phen}] = \frac{k_{\text{Ni}}[\text{Ni}][\text{phen}] + k_{\text{NiA}}[\text{NiA}][\text{phen}] + k_{\text{NiA}_2}[\text{NiA}_2][\text{phen}]}{1 + K_{\text{NiA}}[\text{A}] + K_{\text{NiA}_2}[\text{A}]}$$

where $k_{0(\text{A})}$ is the conditional rate constant involving the concentration of a bidentate ligand A. The conditional rate constant $k_{0(\text{A})}$ was determined from the pseudo-first-order plot and summarized in Table SI (supplementary material).

The conditional rate constant $k_{0(\text{A})}$ can be written as

$$k_{0(\text{A})} = \frac{k_{\text{Ni}} + k_{\text{NiA}}K_{\text{NiA}}[\text{A}] + k_{\text{NiA}_2}K_{\text{NiA}}K_{\text{NiA}_2}[\text{A}]^2}{1 + K_{\text{NiA}}[\text{A}] + K_{\text{NiA}_2}[\text{A}]^2}$$

where $[\text{A}]$ refers to the concentration of the unprotonated and uncomplexed species of a bidentate ligand. For the system involving glycine and ethylenediamine, from the protonation and formation constants reported at 25°C and $I = 1.0$ M,^{18,19} the rate constants were determined from the least-squares procedure to be $k_{\text{Ni}(\text{gly})} = (1.9 \pm 0.2) \times 10^4 \text{M}^{-1} \text{s}^{-1}$, $k_{\text{Ni}(\text{gly})} = (4.2 \pm 0.4) \times 10^4 \text{M}^{-1} \text{s}^{-1}$, $k_{\text{Ni}(\text{en})} = (1.6 \pm 0.2) \times 10^4 \text{M}^{-1} \text{s}^{-1}$, and $k_{\text{Ni}(\text{en})_2} = (2.4 \pm 0.4) \times 10^4 \text{M}^{-1} \text{s}^{-1}$ at 25°C and $I = 1.00$ M. For the oxalate system, both the rate and the formation constants were determined also by the least-squares procedure to be $K_{\text{Ni}(\text{ox})} = 10^{3.74} \text{M}^{-1}$, $K_{\text{Ni}(\text{ox})_2} = 10^{2.69} \text{M}^{-1}$, $k_{\text{Ni}(\text{ox})}$

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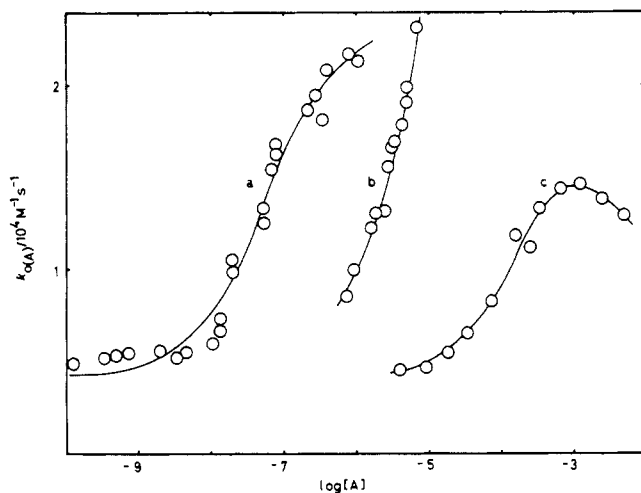


Figure 1. Plot of $k_{0(A)}$ vs. $\log [A]$. Bidentate ligand employed: (a) ethylenediamine; (b) glycine; (c) oxalate. Conditions: $C_{Ni} = 9.11 \times 10^{-5}$ M, $C_{phen} = 5.17 \times 10^{-6}$ M, $C_{MOPS} = 1.01 \times 10^{-3}$ M, 25 °C, $I = 1.00$ M.

$= (1.8 \pm 0.2) \times 10^4$ M $^{-1}$ s $^{-1}$, and $k_{Ni(ox)_2} = (1.1 \pm 0.4) \times 10^4$ M $^{-1}$ s $^{-1}$ at 25 °C and $I = 1.00$ M. Plots of $k_{0(A)}$ vs. $\log [A]$ are shown in Figure 1. The lines are the theoretical curves calculated with the values obtained.

Discussion

It is now generally accepted that the complex formation of nickel ion with 1,10-phenanthroline in aqueous solution occurs by the I_d mechanism,²⁰ and the overall formation rate constant k_{Ni} is given by $k_{Ni} = K_{os(Ni,phen)}k_{Ni}^{-H_2O}$, where $K_{os(Ni,phen)}$ is the formation constant of the outer-sphere complex, which can be estimated from the Fuoss equation. For the complexation reaction described by eq 2, $k_{NiA}^{-H_2O}$ can be correlated with the overall formation rate constant k_{NiA} as $k_{NiA} = K_{os(NiA,phen)}k_{NiA}^{-H_2O}$, providing the I_d mechanism is operative for all cases.²¹

With the water-exchange rate constants thus calculated, the bound-ligand effect of the 1:1 bidentate ligand complex NiA on the water-exchange rate can be estimated by the difference between $\log (k_{NiA}^{-H_2O}/4)$ and $\log (k_{Ni}^{-H_2O}/6)$, which is shown in Table I under the heading of $R(A)$. The positive values of $R(A)$ indicate that coordinated bidentate ligands do have the expected labilizing effect on the water-exchange rate at NiA. If this labilizing effect is attributable to the electron donation from the ligand coordinated to the nickel center, it is expected that eq 1 can also be applicable to the bidentate system. From these $R(A)$ values and the γ value of 0.48²² for nickel(II), the expected $E(A)$ can be estimated as shown in Table I.

Unfortunately no $E(A)$ value for multidentate ligands has yet been established. However the expected value of $E(A)$ is significantly different from that of the calculated, assuming the following additivity for the $E(A)$ value of the bidentate ligands: $E^\circ(ox^{2-}) = 2E(OAc^-) = 1.92$, $E^\circ(gly^-) = E(NH_3) + E(OAc^-) = 2.80$, and $E^\circ(en) = 2E(NH_3) = 3.68$. A comparison of the expected values of $E(A)$ and $E^\circ(A)$ for a given ligand reveals that for $A = ox^{2-}$, the value of $E(ox^{2-})$ is slightly lower than that of $E^\circ(ox^{2-})$ and that for $A = gly^-$

Table I. Bound-Ligand Effect of NiA Complexes and the Effective $E(A)$ Values

A ^a	incoming ligand ^a	$R(A)$	expected $E(A)$	effective $E(A)$
ox ²⁻	phen	0.82 ^b	1.70	1.70
gly ⁻	phen	0.84 ^b	1.79 ± 0.04	1.86
	NH ₃	0.88 ^c		
en	phen	0.76 ^b	1.63 ± 0.25	2.58
	NH ₃	0.81 ^{c,d}		
	H ₂ O	1.00 ^e		
	phen	0.69 ^f		
	bpy	0.67 ^f		
ida ²⁻	pada	0.99 ^g	2.06	1.88
dien	NH ₃	1.48 ^{c,d}	2.92 ± 0.60	3.31
	pada	1.84 ^g		
	phen	1.18 ^f		
	bpy	1.13 ^f		
	terpy	1.01 ^f		
	H ₂ O	1.44 ^h		
	pada	1.76 ⁱ		
nta ³⁻	NH ₃	0.76 ^{c,d}	1.98 ± 0.29	1.91
	pada	0.98 ^g		
	pada	1.11 ⁱ		
edda ²⁻	pada	1.14 ⁱ	2.37	2.62
trien	pada	1.75 ^g	3.81 ± 0.15	4.05
	H ₂ O	1.82 ^h		
	pada	1.93 ⁱ		
tren	pada	1.61 ^g	4.25 ± 0.91	4.05
	H ₂ O	2.48 ^j		
tetren	H ₂ O	2.56 ^k	5.32	4.79

^a Ligand abbreviations: ida²⁻, iminodiacetate; dien, diethylenetriamine; nta³⁻, nitrilotriacetate; trien, triethylenetetramine; tren, 2,2',2''-triiminotriethylamine; tetren, tetraethylenepentamine; bpy, 2,2'-bipyridine; terpy, 2,2',2''-terpyridine; pada, pyridine-2-azo-*p*-dimethylaniline. ^b This work. ^c Reference 10. ^d Jones, J. P.; Billo, E. J.; Margerum, D. W. *J. Am. Chem. Soc.* 1970, 92, 1875–80. ^e Desai, A. G.; Dodgen, H. W.; Hunt, J. P. *Ibid.* 1969, 91, 5001–4. ^f Reference 23. ^g Reference 11. ^h D. P. Rablen, quoted in: Hunt, J. P. *Coord. Chem. Rev.* 1971, 7, 1–10. ⁱ Grant, M. W.; Wilson, C. J. *J. Chem. Soc., Faraday Trans. 1* 1976, 1362–7. ^j Rablen, D. P.; Dodgen, H. W.; Hunt, J. P. *J. Am. Chem. Soc.* 1972, 94, 1771–2. ^k Rablen, D. P.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* 1976, 15, 931–3.

and on the negative value of $\Delta E(A) = (E(A) - E^\circ(A))$ increases with the number of nitrogen donors in A. The other interesting feature of $\Delta E(A)$ is that $\Delta E(gly^-)$ is very close to $\Delta E(ida^{2-})/2$ and $\Delta E(nta^{3-})/3$.

These results lead us to conclude that the value of the effective $E(A)$ for a multidentate ligand is characteristic of the nature of the donor atoms involved in A and depends on the number of bidentate segment. Then this effective $E(A)$ should be given by the summation of $E(X)$ of each donor atom X involved in A corrected for the effect of vicinal functions. For example, the effective $E(A)$ for edda²⁻ (ethylenediamine-*N,N'*-diacetate) is described as

$$\begin{aligned} \text{effective } E(\text{edda}^{2-}) &= 2(E(NH_3) + \Delta E_{NN} + \Delta E_{NO}) + \\ &\quad 2(E(OAc^-) + \Delta E_{ON}) \\ &= E^\circ(\text{edda}^{2-}) + (\Delta E_{NN} + \Delta E_{NN}) + \\ &\quad 2(\Delta E_{NO} + \Delta E_{ON}) \end{aligned}$$

where ΔE_{XN} and ΔE_{XO} represent the vicinal effect of $-CH_2CH_2NH_2$ and $-CH_2CO_2^-$ on the electron-donating ability of the donor atom X involved in A and the effect of vicinal functions ($\Delta E_{NN} + \Delta E_{NN}$) and ($\Delta E_{NO} + \Delta E_{ON}$) are characteristic of ethylenediamine and glycine segments, respectively. From the $R(A)$ values listed in Table I, ΔE parameters are determined: $2\Delta E_{OO} = -0.22$, $\Delta E_{NO} + \Delta E_{ON} = -0.94$, and $2\Delta E_{NN} = -1.10$. These ΔE values enable us to express the effective $E(A)$ as a function of the number of amino (n_N) and acetate (n_O) groups involved in A: $E(A)$ for polyamines = $(E(NH_3))n_N + 2\Delta E_{NN}(n_N - 1) = 1.10 + 0.74n_N$; $E(A)$ for dicarboxylate = $2E(OAc^-) + 2\Delta E_{OO} = 1.70$; $E(A)$ for ami-

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(21) The absence of any marked incoming-ligand specificity (compare $R(A)$ values in Table I for a given ligand) is consistent with the I_d mechanism for the complexation reaction as given in eq 2, in which solvent exchange at NiA is the rate-determining step. The data employed to calculate $R(A)$ values in Table I are restricted to those obtained by NMR methods and by complexation kinetics with a neutral incoming ligand.

(22) The original γ value of 0.40⁴ was recalculated to be 0.48, excluding the data for $A = 2NH_3$ and $3NH_3$.

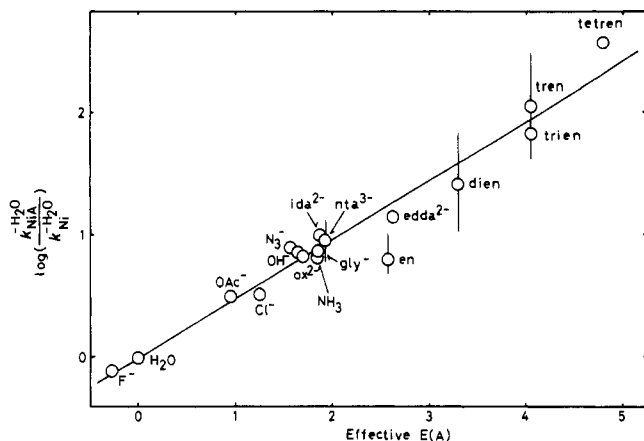


Figure 2. Plot of $\log(k_{\text{NiA}}^{-\text{H}_2\text{O}}/\text{no. of H}_2\text{O in NiA}) - \log(k_{\text{Ni}}^{-\text{H}_2\text{O}}/6)$ vs. effective $E(A)$.

nopolyacetate = $E(\text{NH}_3) + (E(\text{OAc}^-))n_{\text{O}} + (\Delta E_{\text{NO}} + \Delta E_{\text{ON}})n_{\text{O}}$; $E(A)$ for ethylenediaminepolyacetate = $2E(\text{NH}_3) + 2\Delta E_{\text{NN}} + (E(\text{OAc}^-))n_{\text{O}} + (\Delta E_{\text{NO}} + \Delta E_{\text{ON}})n_{\text{O}} = 2.58 + 0.02n_{\text{O}}$. Thus calculated effective $E(A)$ values are listed in Table I.

The plot of $\log(k_{\text{NiA}}^{-\text{H}_2\text{O}}/\text{no. of H}_2\text{O in NiA}) - \log(k_{\text{Ni}}^{-\text{H}_2\text{O}}/6)$ vs. effective $E(A)$ is given in Figure 2 together

with the data for monodentate ligands. Figure 2 indicates that, taking into account the difference in experimental conditions to determine the value of k_{NiA} , the bound-ligand effect of NiA on the water-exchange rate is reasonably well described by eq 1.

The bound-ligand effect of the 1:2 complex NiA_2 on the water-exchange rate can also be estimated by the difference between $\log(k_{\text{NiA}_2}^{-\text{H}_2\text{O}}/2)$ and $\log(k_{\text{Ni}}^{-\text{H}_2\text{O}}/6)$. The values of $R(A_2)$ thus calculated are 0.90, 1.48, and 1.24 for oxalate, glycinate, and ethylenediamine complexes, respectively. The values of $R(A_2)$ for the latter two complexes are close to the corresponding values of $2R(A)$. The two water molecules in these two bis complexes are thought to be in a cis configuration. Previously the two water molecules on $\text{Ni}(\text{en})_2^{2+}$ have been assigned a cis configuration in aqueous solution.²³ The value of $R(A_2)$ for bis(oxalato)nickelate is definitely lower than $2R(A)$. This may suggest a possibility of the trans isomer being involved in the reaction of this complex.

Registry No. Nickel, 7440-02-0; 1,10-phenanthroline, 66-71-7.

Supplementary Material Available: A listing of conditional rate constants $k_{0(A)}$ (Table SI) (2 pages). Ordering information is given on any current masthead page.

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Stereochemical Nonrigidity in Six-Coordinate Group 6B Metal Carbonyl Derivatives via a Nondissociative Pathway

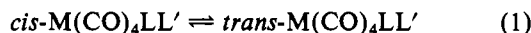
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The *cis*- $\text{M}(\text{CO})_4(^{13}\text{CO})\text{PR}_3 \rightleftharpoons \text{trans}-\text{M}(\text{CO})_4(^{13}\text{CO})\text{PR}_3$ ($\text{M} = \text{Cr}$, $\text{R} = \text{Et}$; $\text{M} = \text{W}$, $\text{R} = \text{OMe}$, Me , Et , *i*-Pr) isomerization reactions have been studied kinetically in cyclohexane-*d*₁₂ by ¹³C NMR spectroscopy. These isomerization reactions were shown to proceed via an *intramolecular* process, based on the lack of ¹³C incorporation into the $\text{M}(\text{CO})_5\text{PR}_3$ derivatives or formation of $\text{M}(\text{CO})_5(^{13}\text{CO})$ under reaction conditions of ligand rearrangement. The *cis* \rightleftharpoons *trans* CO scrambling process in the tungsten pentacarbonyl derivatives displays a dependence on the steric nature of the phosphorus ligand, with the rate decreasing $\text{PMe}_3 > \text{PEt}_3 > \text{P-}i\text{-Pr}_3$. The origin of this steric effect is seen in the activation parameters ($\Delta H = 9.2$ kcal mol⁻¹ and $\Delta S = -54.9$ eu), which are indicative of gross reorganization in the transition state with little metal-ligand bond weakening. On the other hand, activation parameters for carbon monoxide ligand isomerization in $\text{Cr}(\text{CO})_4(^{13}\text{CO})\text{PEt}_3$ ($\Delta H = 26.6$ kcal mol⁻¹ and $\Delta S = 1.80$ eu) are consistent with considerable metal-ligand bond breaking in the transition state with little reorganization taking place.

Introduction

There is increasing awareness that neutral, six-coordinate molecules of the general formula $\text{M}(\text{CO})_4\text{LL}'$ can undergo ligand rearrangements in their *intact* state (e.g., eq 1). In-



vestigations where definitive intramolecular isomerization mechanisms have been established in complexes containing monoligating groups include (a) $\text{M}(\text{CO})_4(\text{ER}_3)_2$ ($\text{M} = \text{Re}$, Ru , Os ; $\text{E} = \text{Si}$, Ge , Sn , Pb ; $\text{R} = \text{organic group}$, Cl),^{1,2} $\text{Cr}(\text{CO})_4[\text{C}(\text{OMe})\text{Me}]\text{PR}_3$ ($\text{R} = \text{Et}$, Cy),³ $\text{Mo}(\text{CO})_4[\text{PR}_3]_2$ ($\text{R} = \text{Me}$, Et , *n*-Bu),⁴⁻⁶ and $\text{PhMn}(\text{CO})_4\text{P}(\text{OPh})_3$.⁷ Presumably,

the pathway for these nondissociative, intramolecular rearrangement processes proceeds through either a trigonal-prismatic⁸⁻¹³ or bicapped-tetrahedron¹⁴ intermediate or transition state.

In the instances cited above there is a thermodynamic preference for either the *cis* or *trans* isomeric form depending

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