lattice.[12] The $d_{yz}$ orbitals from neighboring nickel atoms, which are unobstructed by the ligands, should interact significantly. Since $\nu_4$ is associated with the electronic transition from the $d_{yz}$ orbital, the molecular perturbation (along with the proximity of $\nu_4$ to charge transfer) can be used to explain its intensity.[29] The other three spin-allowed bands steal intensity princi-

pally by a vibronic mechanism with only a small amount of intermolecular coupling involved, hence their temperature dependence. The enhanced absorptivity of the bands in the solution spectrum as compared to the crystal spectrum quite possibly indicates a distortion from centrosymmetry in solution.

**Fine-Structure Analysis.**—For a molecular complex, $Ni(dtp)_2$ is unusual in the impressive resolution of vibronic fine structure displayed by its crystal spectrum. The first three bands contain as many as six distinct progressions containing up to ten members each. The analysis of this vibronic structure will be published in part II of this series.

(29) It has been suggested by one reviewer that the agreement between the polarization of $\nu_4$ and the selection rule prediction for the $^1B_{2g} \leftarrow {}^1A_g$ transition may in fact be fortuitous and that the band might be an allowed charge-transfer transition with a small matrix element. Although we have given reasons for its assignment to a d–d transition, the charge-transfer possibility cannot be conclusively ruled out.

# The Kinetics of Substitution Reactions of Poly(ethylenamine)nickel(II) Complexes

BY WILLIAM S. MELVIN,[1a] DAVID P. RABLEN,[1b] AND GILBERT GORDON*

The rates of the ligand-substitution reactions of a series of nickel(II) complexes in aqueous solution have been measured by using the stopped-flow technique. The effects which nonlabile ligands have on subsequent substitution processes were examined. The complexes used in the study include hexaaquonickel(II), mono(ethylenediamine)nickel(II), mono(diethylenetriamine)nickel(II), and bis(ethylenediamine)nickel(II). The substituting ligands used were 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine. In that the actual rate of water exchange on each specific nickel(II) complex is reported in the literature, a direct comparison between ligand-substitution rates and water-exchange rates could be made. These experiments provide a test of the generally accepted mechanism for complex formation.

## Introduction

Interest in the relationship between substitution rates and water-exchange rates on transition metal ions has been widespread.[2] For the substitution of monodentate ligands on the aquated nickel(II) ion, a direct relationship apparently exists between these two processes.[3] In the absence of specific information to the contrary, this observation has been applied[4-6] to account for the increased reactivities which were observed when nonlabile ligands were coordinated to nickel(II). Although the extension of this simple relationship is appealing, it has been shown that a marked increase in the ligand-substitution rate[7] is not necessarily accompanied by a significant change in the water-exchange rate[8] in the metal ion complex.

The need for more specific experiments to examine the relationship between ligand-substitution rates and water-exchange rates is apparent and is the basis of the experiments reported here.

The nickel(II) complexes used to examine the effects which nonlabile ligands have on subsequent substitu-

tion processes are hexaaquonickel(II), mono(ethylenediamine)nickel(II), mono(diethylenetriamine)nickel(II), and bis(ethylenediamine)nickel(II). These complexes were chosen in that they allow direct rate comparisons without imposing severe changes on the basic nature of the complex. Since the number of coordinated water molecules on the nickel(II) complex can be varied systematically by changing the coordinated polyethylenamine and since the actual rate of water exchange on each nickel(II) complex is known,[9,10] direct comparisons between the ligand-substitution rates and water-exchange rates can be made. The specific ligands used to investigate these substitution reactions are 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine. These neutral heterocyclic molecules were used in an attempt to minimize rate differences due to electrostatic effects and to allow a direct examination of the effects of bidentate and tridentate chelation on the water-substitution reaction for a homologous series of nickel(II) complexes.

## Experimental Section

**Reagents.**—Reagents of the highest quality available were used. The white crystals of phenanthroline (phen) and bipyridine (bipy) were used without further purification. Terpyridine (terpy) was purified prior to use by sublimation.[7] Reagent grade $NiCl_2 \cdot 6H_2O$ was used to prepare stock solutions of nickel(II) which were standardized[11] either by direct titration with EDTA or by gravimetric methods with dimethylglyoxime.

(1) (a) Abstracted in part from the Ph.D. thesis of W. S. Melvin, submitted to the University of Iowa, Aug 1971. (b) Visiting scientist.

(2) (a) R. G. Wilkins and M. Eigen, *Advan. Chem. Ser.*, **49**, 55 (1965); (b) D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970), and references therein.

(3) R. H. Holyer, C. D. Hubbard, S. F. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

(4) D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1008 (1967).

(5) J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, **92**, 1875 (1970).

(6) G. G. Hammes and J. I. Steinfeld, *ibid.*, **84**, 4639 (1962).

(7) R. H. Holyer, C. D. Hubbard, S. F. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

(8) D. Rablen and G. Gordon, *ibid.*, **8**, 395 (1969).

(9) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).

(10) D. Rablen and J. P. Hunt, private communication, 1970.

(11) A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1961, pp 435, 479.

Ethylenediamine (en) and diethylenetriamine (dien) were purified by double distillation.[12] Stock solutions of ethylenediamine were standardized by acid titration after dilution with distilled water.[13] Green crystalline mono(diethylenetriamine)nickel(II) chloride was prepared according to the method given by Jackobs and Margerum.[12] The blue crystalline mono(diethylenetriamine)nickel(II) chloride hydrate complex was formed on exposure to the atmosphere.[14] Elemental analysis gave the following results for the blue complex. *Anal.* Calcd: Ni, 23.4; C, 19.2; H, 6.0; N, 16.8. Found: Ni, 23.2; C, 19.4; H, 5.6; N, 17.1.

Solutions containing equilibrated mixtures of aquo and the mono-, bis-, and tris(ethylenediamine) complexes of nickel(II) were prepared from standardized solutions of nickel(II) chloride, hydrochloric acid, and ethylenediamine. The required amounts of sodium chloride were added to maintain a total chloride ion concentration of 0.10 $M$. Occasionally, the amount of hydrochloric acid required in the preparation of the equilibrated mixtures resulted in total chloride ion concentrations greater than 0.10 $M$. In these cases, no additional sodium chloride was added. The pH of each solution was measured by using a Radiometer Model 26 pH meter calibrated with standard buffers. The concentrations of all of the nickel(II) species in solution were calculated using a computer program described by Perrin and Sayce.[15] The equilibrium distributions of the various species were calculated on the basis of the observed pH values, the acid dissociation constants of mono- and diprotonated ethylenediamine species, enH$^+$ and enH$_2{}^{2+}$, and the nickel(II)-ethylenediamine complex formation constants of Holmes and Williams.[16]

**Kinetic Experiments.**—The reactions between the various poly(ethylenamine)nickel(II) species and the substituting ligands yield complexes which possess spectral characteristics very similar to the mono(aromatic amine)nickel(II) complexes previously reported.[3,7] The formation reactions of the phenanthroline, bipyridine, and terpyridine complexes reported here were monitored at 369.5, 305.0, and 331.0 nm, respectively. The total chloride ion concentration was maintained at 0.10 $M$ whenever possible. A Durrum stopped-flow spectrophotometer was used to study the rate of the formation reactions. The temperature was controlled to ±0.20° by means of a Forma temperature bath. The reactions were followed under pseudo-first-order conditions with a large excess of the nickel(II) complex under consideration. The high concentration of the nickel(II) ($\geq 10^{-3}$ $M$ complex) and $\sim 10^{-5}$ $M$ aromatic ligand ensured the formation of the appropriate mono(aromatic amine)-ethylenaminenickel(II) complex. All of the pseudo-first-order rate constants were evaluated by means of a nonlinear least-squares computer program.[17] All reactions gave excellent first-order plots for 2–3 half-lives. The second-order rate constants for Ni(H$_2$O)$_6{}^{2+}$ and Ni(dien)$^{2+}$ were computed from the average pseudo-first-order rate constants from replicate runs. Fresh solutions of Ni(dien)$^{2+}$ were prepared immediately preceding each kinetic experiment. The data treatment for the calculation of the second-order rate constants for Ni(en)$^{2+}$ and Ni(en)$_2{}^{2+}$ was simplified considerably by the spectral similarities of the mono(aromatic amine) complexes of Ni(H$_2$O)$_6{}^{2+}$, Ni-(en)$^{2+}$, and Ni(en)$_2{}^{2+}$. Differences in the molar extinction coefficients of the reaction products with a particular heterocyclic amine were not observed. Under these conditions the overall rate of formation of the reaction products is given by

$$d[NiL]/dt = k_{obsd}[L]$$

where

$$k_{obsd} = k_0[Ni(H_2O)_6{}^{2+}] + k_1[Ni(en)^{2+}] + k_2[Ni(en)_2{}^{2+}] \quad (1)$$

and L denotes the incoming aromatic ligand. The species Ni(en)$_3{}^{2+}$ was assumed[18] not to contribute to the overall rate

(12) N. E. Jackobs and D. W. Margerum, *Inorg. Chem.*, **6**, 2038 (1967).

(13) F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **74**, 5243 (1952).

(14) N. F. Curtis and H. K. L. Powell, *J. Chem. Soc. A*, **12**, 3069 (1968).

(15) D. D. Perrin and J. G. Sayce, *Talanta*, **14**, 833 (1967).

(16) F. Holmes and D. R. Williams, *J. Chem. Soc. A*, 1256, 1702 (1967).

(17) For a detailed description of the original program, see Los Alamos publication LA-2367 + addenda. A 360/65 Fortran IV version of this program and its various subroutines are described in detail by E. Grimley, Ph.D. Thesis, University of Iowa, 1970.

(18) At pH 6.0 ± 0.2, the amount of Ni(en)$_3{}^{2+}$ in the equilibrated mixture was always less than 6% of the total nickel(II) species in solution. Experiments described in a later section show that at these low concentrations, the dissociation of the tris species does not contribute significantly to the overall rate of reaction.

of reaction. A simultaneous calculation for the second-order rate constants of Ni(en)$^{2+}$ and Ni(en)$_2{}^{2+}$ was made by means of eq 1 with the nonlinear least-squares computer program.[17] The observed pseudo-first-order rate constants, the calculated concentrations of the nickel(II) species, and the independently determined second-order rate constants for the Ni(H$_2$O)$_6{}^{2+}$ reactions were supplied as independent variables. The parameters to be fitted were the second-order rate constants, $k_1$ and $k_2$.

## Results

**Hexaaquonickel(II) Kinetics.**—The substitution reactions of Ni(H$_2$O)$_6{}^{2+}$ with phenanthroline, bipyridine, and terpyridine have been reported previously.[3,7] Since the rates of these substitution reactions under somewhat different experimental conditions were required for the data analysis reported here, these reactions were reinvestigated. These results are shown in Table I.

### TABLE I
KINETIC DATA[a] FOR THE SUBSTITUTION REACTION BETWEEN HEXAAQUONICKEL(II) AND 1,10-PHENANTHROLINE, 2,2'-BIPYRIDINE, AND 2,2',2''-TERPYRIDINE AT 25°

| [Ni(H$_2$O)$_6{}^{2+}$], m$M$ | $k_{obsd}$, sec$^{-1}$ | $10^{-3}k_0$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| Nickel(II)–Phenanthroline Reaction | | |
| 2.52 | 7.48 | 2.96 ± 0.12 |
| 5.18 | 15.2 | 2.94 ± 0.08 |
| 10.20 | 4.28 | 0.42 ± 0.02[b] |
| Nickel(II)–Bipyridine Reaction | | |
| 2.50 | 4.03 | 1.61 ± 0.01 |
| 5.11 | 8.25 | 1.61 ± 0.01 |
| Nickel(II)–Terpyridine Reaction | | |
| 2.52 | 4.01 | 1.59 ± 0.02 |
| 5.18 | 7.49 | 1.45 ± 0.03 |

[a] Rates measured at nearly neutral pH with 0.10 $M$ chloride ion. Wilkins[2a,7] reported the following second-order rate constants at 25°: phenanthroline, 3.2 × 10$^3$ $M^{-1}$ sec$^{-1}$; bipyridine, (1.4–1.6) × 10$^3$ $M^{-1}$ sec$^{-1}$; terpyridine, 1.4 × 10$^3$ $M^{-1}$ sec$^{-1}$. The uncertainties represent deviations from the average for replicate experiments. [b] Temperature 0.2°; Wilkins[7] reported values for the second-order rate constant between 4.6 and 5.1 × 10$^2$ $M^{-1}$ sec$^{-1}$.

**Mono(diethylenetriamine)nickel(II) Kinetics.**—The substitution reactions of Ni(dien)$^{2+}$ were also measured in aqueous solution in the presence of 0.10 $M$ chloride ion. The substitution rates were not noticeably affected by hydrogen ion in the pH range 6.8–8.4. The results of these experiments are given in Table II.

**Mono- and Bis(ethylenediamine)nickel(II) Kinetics.** —A prerequisite to a detailed study on the substitution reactions of Ni(en)$^{2+}$ and Ni(en)$_2{}^{2+}$ is a reasonably good characterization of the various nickel(II) complexes in solution. The acid dissociation constants for ethylenediamine and the complex formation constants for the various nickel(II) complexes have been reported.[13,16] The reported values from two independent investigations are listed in Table III. These values appear to be in reasonable agreement with the exception of the value for the Ni(en)$_3{}^{2+}$ complex formation constant. The reported values differ in the two determinations by almost an order of magnitude. Necessarily, the calculated equilibrium concentrations of the various species in solution are a direct function of the particular set of equilibrium constants employed in the calculation. Thus, the second-order substitu-

TABLE II

KINETIC DATA[a] FOR THE SUBSTITUTION REACTION
BETWEEN MONO(DIETHYLENETRIAMINE)NICKEL(II)
AND 1,10-PHENANTHROLINE, 2,2'-BIPYRIDINE,
AND 2,2',2''-TERPYRIDINE

| [Ni(dien)$^{2+}$], m$M$ | $k_{obsd}$, sec$^{-1}$ | Temp, °C | $10^{-3}k_f$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| Mono(diethylenetriamine)nickel(II)–Phenanthroline | | | |
| 0.868 | 20.6 | 25 | 23.7 ± 1.1 |
| 1.01 | 24.8 | 25 | 24.6 ± 1.7 |
| 2.00 | 45.4 | 25 | 22.7 ± 2.9 |
| 2.56 | 50.0 | 25 | 19.5 ± 0.4 |
| 3.02 | 73.4 | 25 | 24.3 ± 2.0 |
| 4.06 | 99.9 | 25 | 24.6 ± 1.7 |
| 5.82 | 109 | 25 | 18.7 ± 1.6 |
| | | Av | 22.6 ± 1.98 |
| 4.29 | 25.1 | 4 | 5.86 ± 0.09 |
| 3.53 | 28.5 | 9 | 8.08 ± 0.27 |
| 2.89 | 33.5 | 14 | 1.16 ± 0.05 |
| 3.06 | 53.9 | 19 | 1.76 ± 0.04 |
| $\Delta H^{\ddagger} = 10.3 ± 0.5$ kcal/mol; $\Delta S^{\ddagger} = -3.8 ± 1.9$ eu | | | |
| Mono(diethylenetriamine)nickel(II)–Bipyridine | | | |
| 0.623 | 7.03 | 25 | 11.3 ± 0.1 |
| 0.653 | 6.58 | 25 | 10.1 ± 0.3 |
| 0.938 | 10.5 | 25 | 11.2 ± 0.1 |
| 0.975 | 10.7 | 25 | 11.0 ± 0.1 |
| 1.05 | 11.6 | 25 | 11.0 ± 0.1 |
| 1.62 | 17.7 | 25 | 10.9 ± 0.2 |
| 1.63 | 18.6 | 25 | 11.4 ± 0.1 |
| 3.00 | 34.4 | 25 | 11.5 ± 0.1 |
| 4.15 | 46.7 | 25 | 11.2 ± 0.1 |
| 5.01 | 57.4 | 25 | 11.5 ± 0.1 |
| | | Av | 11.1 ± 0.3 |
| 4.33 | 11.8 | 4.5 | 2.73 ± 0.04 |
| 4.33 | 14.4 | 8.5 | 3.32 ± 0.03 |
| 4.33 | 20.8 | 14 | 4.80 ± 0.07 |
| 3.18 | 22.1 | 18 | 6.95 ± 0.03 |
| $\Delta H^{\ddagger} = 11.0 ± 0.6$ kcal/mol; $\Delta S^{\ddagger} = -3.3 ± 2.2$ eu | | | |
| Mono(diethylenetriamine)nickel(II)–Terpyridine | | | |
| 0.715 | 5.91 | 25 | 8.26 ± 0.02 |
| 1.07 | 8.44 | 25 | 7.89 ± 0.06 |
| 1.80 | 14.4$_5$ | 25 | 8.03 ± 0.01 |
| 2.21 | 15.6 | 25 | 7.06 ± 0.01 |
| 4.05 | 31.5 | 25 | 7.78 ± 0.04 |
| 4.97 | 38.7 | 25 | 7.79 ± 0.01 |
| 6.16 | 44.5 | 25 | 7.23 ± 0.19 |
| | | Av | 7.72 ± 0.33 |
| 5.22 | 9.34 | 5 | 1.79 ± 0.01 |
| 5.22 | 15.1 | 12 | 2.89 ± 0.04 |
| 2.25 | 12.6$_5$ | 20.1$_5$ | 5.62 ± 0.01 |
| $\Delta H^{\ddagger} = 11.7 ± 0.4$ kcal/mol; $\Delta S^{\ddagger} = -1.6 ± 1.3$ eu | | | |

[a] pH range 6.8–8.4; 0.10 $M$ chloride ion; the uncertainties represent deviations from the average for replicate experiments except for the activation parameters where the uncertainties represent standard deviations calculated directly by the nonlinear least-squares computer program.

tion rates[19] of Ni(en)$^{2+}$ and Ni(en)$_2^{2+}$ will be a direct function of the calculated equilibrium concentrations of the various nickel(II) species. The following total analytical concentration ranges were used: $0.003 < $[Ni$^{2+}$]$_{total} < 0.22$ $M$, $0.05 < $[en]$_{total} < 1.3$ $M$, and $0.09 < $[H$^+$]$ < 1.2$ $M$. The resulting species concentration ranges as calculated from the data of Holmes and Williams[16] are $1.0 \times 10^{-6} < $[Ni$^{2+}$]$ < 7.6 \times 10^{-3}$ $M$, $1.3 \times 10^{-6} < $[Ni(en)$^{2+}$]$ < 1.0 \times 10^{-3}$ $M$, $3.0 \times 10^{-5} < $[Ni(en)$_2^{2+}$]$ < 6.2 \times 10^{-3}$ $M$, $7.0 \times 10^{-6} < $[Ni(en)$_3^{2+}$]$ < 1.0 \times 10^{-1}$ $M$, and $6.0 < $pH$ < 8.5$.

Because nickel(II) is a labile species, the dissocia-

(19) Because of the apparent discrepancy in the value of $K_3$, the substitution rates were calculated using both sets of equilibrium constants and are reported in detail in ref 1a. It should be noted that the substitution rates calculated on the basis of Holmes and Williams' protonation and complex formation constants are internally more consistent than those obtained with the data of Basolo and Murmann (*vide infra*).

TABLE III

EQUILIBRIUM CONSTANTS FOR THE
NICKEL(II)–ETHYLENEDIAMINE SYSTEM AT 25°

| | Basolo and Murmann[13] | Holmes and Williams[16] |
|---|---|---|
| p$K_1^a$ | 10.18 | 9.90 |
| p$K_2^a$ | 7.47 | 7.32 |
| Log $K_1$ | 7.60 ± 0.03 | 7.49 ± 0.02 |
| Log $K_2$ | 6.48 ± 0.03 | 6.45 ± 0.02 |
| Log $K_3$ | 5.03 ± 0.03 | 4.11 ± 0.03 |
| Ionic strength | 0.5 $M$ (NO$_3^-$) | 0.3 $M$ (ClO$_4^-$) |

[a] Acid dissociation constants for ethylenediamine.

tion rates of the individual nickel(II)–ethylenediamine complexes are of particular importance to the studies reported here. These rates have been reported[20] and indicate that the amount of dissociation which occurs for either Ni(en)$^{2+}$ or Ni(en)$_2^{2+}$ during a typical stopped-flow experiment is negligible. However, this is not the case[20c,21] with Ni(en)$_3^{2+}$. Table IV lists the

TABLE IV

A COMPARISON OF THE OBSERVED[a] AND CALCULATED
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE
Ni(en)$^{2+}$– AND Ni(en)$_2^{2+}$–PHENANTHROLINE OR
–BIPYRIDINE REACTIONS AT pH 6

| Phenanthroline reaction | | | Bipyridine reaction | | |
|---|---|---|---|---|---|
| Starting concn ratio Ni(en)$^{2+}$/ Ni(en)$_2^{2+}$ | $k_{obsd}$, sec$^{-1}$ | $k_{calcd}$, sec$^{-1}$ | Starting concn ratio Ni(en)$^{2+}$/ Ni(en)$_2^{2+}$ | $k_{obsd}$, sec$^{-1}$ | $k_{calcd}$, sec$^{-1}$ |
| 15.5 | 14.8 ± 0.4 | 13.8 | 15.5 | 8.31 ± 0.1 | 9.21 |
| 1.80 | 28.8 ± 0.5 | 27.2 | 2.13 | 14.1 ± 0.2 | 13.8 |
| 1.19 | 32.2 ± 1.7 | 32.7 | 1.80 | 17.4 ± 0.1 | 17.8 |
| 15.9 | 29.6 ± 2.4 | 31.3 | 1.76 | 29.5 ± 0.7 | 29.8 |
| 4.45 | 10.4 ± 0.5 | 10.7 | 1.80 | 43.1 ± 0.9 | 44.8 |
| 2.31 | 40.0 ± 1.1 | 39.7 | 1.19 | 22.0 ± 0.8 | 22.3 |
| 0.065 | 12.5 ± 0.5 | 12.6 | 15.9 | 19.2 ± 0.2 | 17.2 |
| 0.215 | 19.6 ± 0.3 | 19.4 | 4.45 | 6.83 ± 0.1 | 6.15 |
| 0.080 | 18.9 ± 1.6 | 19.5 | 2.31 | 25.1 ± 0.5 | 25.0 |
| | | | 0.065 | 11.9 ± 0.2 | 10.9 |
| | | | 0.215 | 15.9 ± 0.1 | 15.8 |
| | | | 0.080 | 17.2 ± 0.2 | 16.7 |

[a] The uncertainties correspond to average deviations for replicate runs.

observed and calculated pseudo-first-order rate constants at pH 6.0 ± 0.2 for Ni(en)$^{2+}$ and Ni(en)$_2^{2+}$ for the substitution reaction with phenanthroline and bipyridine. At this pH, the solutions contain less than 6% Ni(en)$_3^{2+}$. The results of the fitting of the data in Table IV to eq 1 with individual weights of $1/k_{obsd}^2$ are given in Table V. Weights of $1/k_{obsd}^2$ were used to minimize the per cent error in that each pseudo-first-order rate constant was known to about the same relative precision.

At pH values greater than 6, the concentration of Ni(en)$_3^{2+}$ becomes significant when compared to the concentrations of Ni(en)$^{2+}$ and Ni(en)$_2^{2+}$. Some typical data which illustrate the effect of the dissociation of Ni(en)$_3^{2+}$ to form Ni(en)$_2^{2+}$ on the overall reaction rate are given in Table VI . It should be noted that as the fraction of total nickel(II) species present

(20) The value of $k_d$ for Ni(en)$^{2+}$ is 0.145 sec$^{-1}$ in 0.2 $M$ acid and is approximately $7 \times 10^{-8}$ sec$^{-1}$ in neutral solution; $k_d$ for Ni(en)$_2^{2+}$ is 5.2 sec$^{-1}$ in 0.2 $M$ acid: (a) A. K. S. Ahmed and R. G. Wilkins, *Proc. Chem. Soc., London*, 399 (1959); (b) *J. Chem. Soc.*, 2901 (1960); (c) J. P. Jones and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 470 (1970).

(21) The rate of dissociation of Ni(en)$_3^{2+}$ in 0.2 $M$ acid is 87 sec$^{-1}$ while in the pH 6–9 region the rate has been estimated (see ref 20c) to be 32–83 sec$^{-1}$. Thus, dissociation of the tris species does occur during the time of the stopped-flow experiment even in the neutral pH range.

TABLE V
MONO- AND BIS(ETHYLENEDIAMINE)NICKEL(II)
SECOND-ORDER SUBSTITUTION RATE CONSTANTS[a]
AT pH 6 AND 25°

| Complex | $(k_1$ or $k_2) \times 10^{-3}$, $M^{-1}$ sec$^{-1}$ | |
|---|---|---|
| | Phenanthroline | Bipyridine |
| Ni(en)$^{2+}$ ($k_1$) | 9.46 ± 0.28 | 5.08 ± 0.24 |
| Ni(en)$_2{}^{2+}$ ($k_2$) | 9.39 ± 0.29 | 8.20 ± 0.32 |

[a] Uncertainties correspond to standard deviations. Essentially the same results[1a] were obtained using the equilibrium data of Basolo and Murmann;[13] for example, the rate constants for Ni(en)$^{2+}$ and Ni(en)$_2{}^{2+}$ using phen were calculated to be $(10.7 \pm 0.3) \times 10^3$ and $(9.97 \pm 0.38) \times 10^3$ $M^{-1}$ sec$^{-1}$, respectively; for bipy, respective rates of $(6.23 \pm 0.24) \times 10^3$ and $(9.31 \pm 0.54) \times 10^3$ $M^{-1}$ sec$^{-1}$ were obtained.

TABLE VI
CALCULATED SECOND-ORDER RATE CONSTANTS FOR THE
BIS(ETHYLENEDIAMINE)NICKEL(II)–LIGAND REACTION
AT pH VALUES GREATER THAN 6 AT 25° ASSUMING
THAT THE TRIS SPECIES DOES NOT CONTRIBUTE TO THE RATE

| pH | $k_{obsd}$, sec$^{-1}$ | $10^{-3}k_2$, $M^{-1}$ sec$^{-1}$ | % bis | % tris |
|---|---|---|---|---|
| | | Phenanthroline | | |
| 6.56 | 23.0 ± 0.2 | 10.7 | 74 | 25 |
| 6.85 | 26.2 ± 0.9 | 8.6 | 75 | 25 |
| 7.54 | 21.8 ± 0.3 | 9.8 | 74 | 26 |
| 7.00 | 58.5 ± 3.6 | 14.1 | 26 | 74 |
| | | Bipyridine | | |
| 6.87 | 20.4 ± 0.1 | 8.2 | 83 | 15 |
| 6.53 | 21.1 ± 0.2 | 9.5 | 74 | 25 |
| 6.90 | 24.0 ± 0.3 | 8.9 | 74 | 25 |
| 7.55 | 17.4 ± 0.1 | 7.9 | 74 | 26 |
| 6.58 | 34.2 ± 0.1 | 11.1 | 58 | 41 |
| 6.99 | 40.8 ± 0.3 | 14.0 | 25 | 75 |
| 7.51 | 33.7 ± 0.1 | 19.0 | 3.3 | 96.7 |

as Ni(en)$_3{}^{2+}$ increases, the observed second-order substitution rates also increase.[22]

No significant hydrogen ion dependence for the Ni(en)$_2{}^{2+}$ substitution rate with either phenanthroline or bipyridine was observed.[1a]

Thus, the data shown in Table VI are strongly suggestive that dissociation of Ni(en)$_3{}^{2+}$ occurs during the course of the stopped-flow experiment. If this is the case, dissociation will lead to an increase in the actual Ni(en)$_2{}^{2+}$ concentration and to an enhanced rate of reaction. This hypothesis was tested by repressing the dissociation reaction given by

$$Ni(en)_3{}^{2+} = Ni(en)_2{}^{2+} + en \tag{2}$$
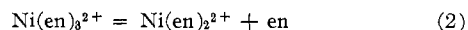
Thus, an almost constant ethylenediamine concentration was maintained during the experiment.[23] The results of four experiments designed to determine the effect of constant ethylenediamine concentration on the Ni(en)$_2{}^{2+}$ substitution rate are given in Table VII. These data indicate that in the presence of relatively constant ethylenediamine concentration, the observed second-order rate constants are consistent[24] with the

(22) At high concentrations of Ni(en)$_3{}^{2+}$ the small concentrations of Ni(H$_2$O)$_6{}^{2+}$ and Ni(en)$^{2+}$ have a negligible effect on the overall rate of reaction. Thus, the second-order rate constants were calculated directly by dividing the observed pseudo-first-order rate constants by the calculated concentration of Ni(en)$_2{}^{2+}$ at the instant of dilution in the stopped-flow experiment.

(23) When equal amounts of free ethylenediamine are present in both mixing syringes for the stopped-flow experiment, the resulting concentration of ethylenediamine remains constant while the concentration of the remaining species in solution are diluted by half.

(24) In this context, it should be noted that we have used the equilibrium constants reported by Holmes and Williams,[16] since the corresponding values reported by Basolo and Murmann[13] result in calculated second-order rate constants which vary monotonously with increasing concentrations of Ni(en)$_3{}^{2+}$. These rate constants vary in the range $(14-25) \times 10^3$ $M^{-1}$ sec$^{-1}$ in contrast to the values reported in Table VII.

TABLE VII
THE EFFECT OF ADDED ETHYLENEDIAMINE ON THE
BIS(ETHYLENEDIAMINE)NICKEL(II)–BIPYRIDINE
SUBSTITUTION RATE AT CONSTANT ETHYLENEDIAMINE
CONCENTRATION FOR EACH EXPERIMENT

| [Ni(en)$^{2+}$], m$M$ | [Ni(en)$_2{}^{2+}$], m$M$ | [Ni(en)$_3{}^{2+}$], m$M$ | $k_{obsd}$, sec$^{-1}$ | $10^{-3}k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|
| 0.030 | 2.21 | 0.756 | 19.1 ± 0.2 | 8.6 |
| 0.029 | 2.21 | 0.766 | 17.6 ± 0.2 | 8.0 |
| 0.066 | 4.15 | 11.8 | 38.9 ± 0.1 | 9.4 |
| . . . | 1.77 | 52.3 | 12.8 ± 0.1 | 7.2 |

Ni(en)$_2{}^{2+}$–bipyridine substitution rate which was obtained at pH 6 in the absence of appreciable concentrations of Ni(en)$_3{}^{2+}$. Thus, we conclude that dissociation of Ni(en)$_3{}^{2+}$ cannot be neglected in experiments with high tris species concentration and variable ethylenediamine concentration.

The temperature dependence of the Ni(en)$^{2+}$ and Ni(en)$_2{}^{2+}$ reactions was not studied in detail. The errors in the thermodynamic quantities for the formation of the various complexes combined with additional errors resulting from the substitution reactions would rule out meaningful interpretations. By using the calculated second-order rate constants obtained[25] at 0.2° in conjunction with those at 25°, estimates of the activation parameters for the Ni(en)$^{2+}$ and Ni(en)$_2{}^{2+}$ reactions with phenanthroline and bipyridine were made. The enthalpy values were similar to those obtained in the water-exchange measurements.[9,10] The entropy values for Ni(en)$_2{}^{2+}$ were appreciably smaller than those reported for the water-exchange measurements.

## Discussion

The results of the substitution studies reported here show that the coordination of ethylenediamine or diethylenetriamine to nickel(II) substantially increases the rates of substitution of aromatic ligands relative to Ni(H$_2$O)$_6{}^{2+}$. These rates and the reported ammonia-substitution rates[4] related to this study are summarized in Table VIII, which also shows the mag-

TABLE VIII
SUMMARY OF SECOND-ORDER SUBSTITUTION RATE
CONSTANTS AT 25°, ($k_{ML} \times 10^{-3}$, $M^{-1}$ sec$^{-1}$)

| Substituting ligand | Ni(H$_2$O)$_6{}^{2+}$ | Ni(en)$^{2+}$ | Ni(dien)$^{2+}$ | Ni(en)$_2{}^{2+}$ |
|---|---|---|---|---|
| phen | 2.9$_5$ | 9.5 | 22.$_6$ | 9.3 |
| bipy | 1.6$_1$ | 5.0 | 11 | 8.4 |
| terpy | 1.5$_2$ | . . . | 7.7 | . . . |
| NH$_3$[a] | 2.8 | 12 | 43 | . . . |
| | Water-Exchange Rates | | | |
| H$_2$O[b] | 0.44 | 4.4$_0$ | 18[c] | 54.4 |

[a] Reference 4. [b] $k_e \times 10^{-5}$, sec$^{-1}$; see ref 9 and 10 for details. [c] Rablen and Hunt[10] reported two rates of exchange of water for Ni(dien)$^{2+}$. The rate constant used here corresponds to that for the fastest rate of exchange.

nitude of the change in the rate of water exchange as a function of the number of aliphatic amines coordinated to the metal ion. The water-exchange rates at 25° have been shown[9] to increase regularly with a corresponding increase in the number of aliphatic amine nitrogens coordinated to nickel(II). Although

(25) The protonation and complex formation constants reported by Basolo and Murmann[13] at 0° were used to calculate the equilibrium distributions since Holmes and Williams[16] reported only 25° values.

the actual water-exchange rates on the poly(ethylenamine)nickel(II) complexes increase regularly, it is apparent that these increases are not reflected as dramatically in the rates of ligand substitution.

The substitution reactions of the poly(ethylenamine)nickel(II) complexes may be considered to occur through a series of elementary steps.[3] For example, in the overall reaction

$$(dien)Ni(H_2O)_3{}^{2+} + phen \xrightarrow{k_{ML}} (dien)Ni(H_2O)(phen)^{2+} + H_2O$$
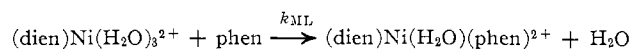
the first step is presumed to occur rapidly and corresponds to an outer-sphere association between (dien)-$Ni(H_2O)_3{}^{2+}$ and phenanthroline. The formation of the chelated product may be envisioned as proceeding through a reactive intermediate in which phenanthroline behaves as a monodentate ligand. With the assumption that the rate of formation of the chelated product is primarily determined by the initial loss of a coordinated water molecule[6] and that the equilibrium constant for the outer-sphere association process is small, this mechanism can be expressed[2] in its limiting form as

$$k_{ML} = k_e K_{os} \tag{3}$$

where $k_{ML}$ is the observed second-order rate constant for complex formation, $k_e$ is the first-order water-exchange rate for the specific metal ion complex, and $K_{os}$ is the equilibrium constant for the outer-sphere association process.

Under these implicit assumptions and by utilizing the ligand-substitution rates measured here and the independently measured water-exchange rates,[9,10] a direct calculation of the outer-sphere association constant can be made. To compare the outer-sphere association constants for all the nickel(II) complexes, a statistical correction should be applied to the formation[4,6] rates. This statistical correction accounts for the possibility that a ligand in the outer-sphere is in a position to react[26] with a probability equal to that of $Ni(H_2O)_6{}^{2+}$. Table IX lists the outer-sphere as-

TABLE IX

CALCULATED OUTER-SPHERE ASSOCIATION CONSTANTS ($K_{os}$, $M^{-1}$)[a]

| Ligand | $Ni(H_2O)_6{}^{2+}$ | $Ni(en)^{2+}$ | $Ni(dien)^{2+}$ | $Ni(en)_2{}^{2+}$ |
|---|---|---|---|---|
| phen | 0.06$_5$ | 0.03$_2$ | 0.02$_5$ | 0.005 |
| bipy | 0.03$_6$ | 0.01$_7$ | 0.01$_2$ | 0.004$_6$ |
| terpy | 0.03$_5$ | ... | 0.009 | ... |
| NH$_3$ | 0.06$_4$ | 0.04$_1$ | 0.04$_8$ | ... |

[a] Average value 0.03 ± 0.02 $M^{-1}$.

sociation constants calculated from eq 4 where $n$ represents the number of sites occupied by nonlabile coordinated ligands on the nickel(II) complex.

$$6k_{ML}/(6 - n) = k_e K_{os} \tag{4}$$

An important comparison lies in the $K_{os}$ values calculated from the independently measured rate data and the theoretically calculated values from the Debye[27,28] or Fuoss[29,30] equations. For $Ni(H_2O)_6{}^{2+}$ a value between 3.5 and 5 Å has been used[6] as a reasonable estimate for the distance of closest approach.

These distances result in a value of about 0.07–0.2 for the calculated outer-sphere association constant for reactions between nickel(II) and various neutral ligands.

The average outer-sphere association constant from the data reported here and listed in Table IX is 0.03 ± 0.02 $M^{-1}$. This difference should not be taken as an indication that a change in mechanism has occurred but only as a reflection of the tenuous assumptions[18,19,21,24] and approximations applied. The results obtained here are, in fact, in reasonable agreement with the Eigen-type interchange mechanism.[31] The most significant conclusion is that *the actual rate of water exchange on a metal ion complex cannot be inferred from its rate of ligand substitution.* Clearly, the generalities of the accepted mechanism by which substitution reactions occur appear to apply rather well for the substitution of monodentate ligands. This simple mechanism should not be taken too literally and must be applied with a limited degree of caution.[32–35] In many cases, there is a reasonable correlation between the rate of ligand substitution and the rate of water exchange. The two rates do not appear to be related exactly by a calculated outer-sphere association constant and related statistical factors. Therefore, the actual rate of water exchange may differ significantly from that estimated from ligand-exchange studies.

The rates of substitution appear to follow a reactivity pattern similar to that which Margerum[4] noted for ammonia substitution, that is $Ni(H_2O)_6{}^{2+} <$ $Ni(en)^{2+} < Ni(dien)^{2+}$. In addition, the substitution rates show a small decrease in the order phenanthroline > bipyridine > terpyridine. Although this is the same reactivity order which Wilkins[3] found for a variety of first-row transition metal ions, this reactivity order does not appear to be generally applicable to all transition metal ion substitution reactions.[32]

It is interesting to note that phenanthroline appears to react nearly twice as rapidly as bipyridine in the reactions reported here with the exception of $Ni(en)_2{}^{2+}$. This difference in reactivity probably originates from the structural differences between phenanthroline and bipyridine and the use of the limiting form of the rate law shown in eq 3. This seems to suggest that molecules such as ammonia, pyridine, imidazole, and phenanthroline will substitute more readily than will flexible molecules such as bipyridine or terpyridine. In confirmation of this point, Hoffmann[36] reported evidence from relaxation studies for diminution of apparent second-order rate constants owing to the increasing effect of the bond-breaking step in the overall substitution process.

The statistically corrected substitution rates with phenanthroline reach a maximum value at $Ni(dien)^{2+}$ with $Ni(en)_2{}^{2+}$ reacting somewhat more slowly. When bipyridine is the substituting ligand, the statistically corrected rates are similar for $Ni(dien)^{2+}$ and $Ni(en)_2{}^{2+}$. These observations are not anticipated on the basis of the reported $^{17}O$ nmr water-exchange

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measurements.[9] The water-exchange measurements show a continuous increase in exchange rate as the number of nitrogen donor atoms increases on nickel(II) at 25°. This suggests that factors other than the water-exchange rate are influencing the substitution process. In this context it is interesting that $Ni(en)_2^{2+}$ apparently fails to discriminate between phenanthroline and bipyridine. Jones and Margerum[20c] in their investigation of the equilibrium between $Ni(en)_2^{2+}$ and $Ni(en)_3^{2+}$ reported the rate of first bond formation for the reaction between $Ni(en)_2^{2+}$ and en is $5.5 \times 10^6 \ M^{-1} \ sec^{-1}$. The overall rate constant including ring closure to give $Ni(en)_3^{2+}$ is $\sim 1.0 \times 10^6 \ M^{-1} \ sec^{-1}$. In this case a selectivity factor for chelate formation is more than $10^3$ times greater in the case of ethylenediamine over that of bipyridine. Thus the structure of the incoming ligand can be important.

On the basis of optical spectra considerations, the two water molecules on $Ni(en)_2^{2+}$ have been assigned[37,38] a cis configuration in aqueous solution. The presence of appreciable amounts of a trans isomer seems unlikely in that kinetically distinguishable water molecules were not observed in the $^{17}O$ nmr water-exchange measurement.[9] This tends to rule out cis-trans isomerization as a governing factor in differences for the $Ni(en)_2^{2+}$ species.

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# Thioxanthate Complexes. Carbon Disulfide Eliminations to Form Bridged Mercaptide Dimers of Nickel(II) and Palladium(II)

BY J. M. ANDREWS, D. COUCOUVANIS, AND J. P. FACKLER, JR.*

Alkyl thioxanthate complexes of nickel(II) undergo a spontaneous solution reaction to eliminate carbon disulfide and form a dimeric mercaptide-bridged complex. Using proton magnetic resonance spectroscopy (pmr) and visible spectroscopy, a kinetic study of this reaction was carried out. The reaction is found to be first order in thioxanthate complex, both in the disappearance of the starting material and in the formation of the mercaptide-bridged species, in chloroform and tetrahydrofuran. Pseudo-first-order kinetics was observed in carbon disulfide. The carbon disulfide dependence is attributed to an equilibrium between the thioxanthate complex and this solvent. The rate of the reaction at a given temperature increased as the alkyl group was varied from ethyl to *tert*-butyl to benzyl, and in the one case studied, the reaction was faster when the metal was nickel than when it was palladium. Rate constants for the reaction were of the order of $10^{-3}$ to $10^{-1} \ min^{-1}$ depending on solvent, temperature, alkyl group, and metal. Activation parameters were in the ranges $\Delta H^{\ddagger} = 22.0$–$23.8$ kcal/mol and $\Delta S^{\ddagger} = +3$ to $-7$ eu. Radioactive labeling of the mercaptide sulfur of the thioxanthate complex showed that it forms the bridge in the mercaptide-bridged dimeric complex. The syntheses of the thioxanthate-bridged mercaptide complexes of platinum(II), iron(III), and cobalt(III) also are reported in this paper.

## Introduction

Transition metal complexes of many monoanionic 1,1-dithiolates have been prepared and studied.[1,2] Of these probably the most poorly characterized are the complexes of alkyl trithiocarbonates (thioxanthates).[3,4] In 1961 Schaeffer[5] reported the preparation of some thioxanthate complexes; however, the chemical properties of these compounds were not discussed. Later, Ewald and Sinn[6] reported the isolation of several thioxanthate complexes of Ni(II), Cu(II), Co(III), and Fe(III). These authors found the complexes unstable, but the decomposition products were not characterized.

During the past 5 years, we have prepared several metal thioxanthates. With few exceptions these materials decompose when dissolved in organic solvents to produce mercaptide-bridged dimers, reaction 1. Several of these bridged mercaptide dimers have been characterized.[7-10] In view of the dearth of information about metal mercaptide complexes generally and the recognition that metal mercaptide species play important roles in biological systems,[11] we began a detailed study of the mechanism that leads to the formation of the mercaptide-bridged species from the thioxanthate. We chose nickel(II) and palladium(II) complexes for the study since dimerization rates are particularly suited to investigation by conventional techniques. A preliminary report of these results has appeared.[12]

$$2M(S_2CSR)_n \longrightarrow 2CS_2 + [M(SR)(S_2CSR)_{n-1}]_2 \quad (1)$$

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