The Kinetic Behavior of Planar Nickel(II) Complexes. I.
Reaction with Ethylenediaminetetraacetic Acid[1]

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The kinetics of the reaction of EDTA with some planar, diamagnetic complexes of the type $[Ni(AO)_2-H]^+$ and $[Ni(C-alkylen)_2]^{+2}$ have been investigated spectrophotometrically in the pH range 6–12. The rates of ligand exchange were found to obey the expression: rate $= k[complex]_T + k'[EDTA]_T[complex]_T$ at constant pH and ionic strength. The N-alkylAO complexes and those of EnAO were approximately 200 times more stable kinetically than the parent complex. Steric hindrance accounts for the former slow rate while increased thermodynamic stability of the hydrogen bond accounts for the latter. The pH dependence of the rates is discussed in relation to the charge on the complex, which is related to the hydrogen-bond equilibrium constants, and with respect to association with $EDTA^{-2}$ in the 5 and 6 coördination positions. Catalysis by other chelating ligands has been shown and an explanation discussed involving a five-coördinate activated state.

Introduction

Kinetic studies of substitution reactions of nickel(II) complexes have been concerned primarily with the octahedral paramagnetic state.[2-4] The studies in the d^8 systems, which involve the square planar state, have used platinum(II), while palladium(II) and nickel(II) seldom have been studied. The Pt(II) complex reactions often are inconvenient for study due to extreme slowness and small spectral changes. It has been well established[5] that the substitution of planar Pt(II) complexes generally follows a two-term rate law

$$\text{rate} = k[\text{complex}] + k'[\text{complex}][\text{reactant ligand}]$$

The acid dissociation and ligand exchange studies of $[Ni(C\text{-substituted ethylenediamine})_2]^{+2}$ by Wilkins[6] provided information about the nature of planar complex reactions and the rates of formation and dissociation of a planar Ni(II) α-amineoxime[7] have extended this field. An extension of this work to other planar-forming ligands and to more complex reacting molecules was begun to provide a more precise knowledge of the operative mechanisms.

The ligands chosen for study were aliphatic α-amineoximes[8a] which in neutral solution form planar complexes with nickel(II) according to the equation

$$Ni^{+2} (aq) + 2AO \longrightarrow [Ni(AO)_2\text{-H}]^{+ \text{8b}} + H^+(aq)$$

with the structural formula shown below. EDTA was chosen as the primary reactant because of its hexadentate nature, the large formation constant of its complex with Ni(II) ($pK_1 = 18.5$), and the large spectral difference when compared to planar complex. Reported in this paper are the results of kinetic studies on the reaction of several α-amineoxime nickel(II) complexes with aqueous EDTA.
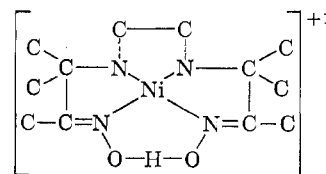
$[Ni(AO)_2\text{-H}]^+$, with dashed bridge, $[Ni(EnAO)\text{-H}]^+$

Experimental

Preparation of Compounds.—The nickel(II) complexes were prepared by methods described in the literature.[9] The compounds were characterized by analysis for either Ni or C, H, and N and by comparison of the absorption spectra with those reported for the known compounds. $[Ni(MeEnAO)\text{-H}]ClO_4$[10] and $[Ni(PnAO)\text{-H}]ClO_4$ are new and were prepared by the same method used for $[Ni(EnAO)\text{-H}]ClO_4$ using 1,2- and 1,3-propylenediamine, respectively.

Na_2EDTA was purified by solution in NaOH followed by slow precipitation with HCl. The middle third of this precipitation was collected, recrystallized, and dried. Solutions were standardized against Cu(s) and new standard solutions prepared weekly.

Rates of Reaction.—The reactions were initiated by injection of small amounts of concentrated complex ion solution to a thermostated, buffered EDTA solution. The rate of ligand exchange was followed by measurements of optical density as a function of time at the absorption maximum of the planar complex. In this region (380–420 mμ) the EDTA complexes of Ni(II) have nearly zero absorption. In most cases $[EDTA]_T$ was in at least 100-fold excess and acted as its own buffer. Ionic strength was controlled with A.R. grade KCl, KNO_3, or $NaClO_4$. Measurements were made with a Beckman Model DU spectrophotometer equipped with a cell compartment maintained at

(1) A preliminary report of this work was presented at the Sixth International Conference on Coördination Chemistry, Wayne State University, Detroit, Michigan, August, 1961.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, New York, N. Y., 1958, p. 111.

(3) A. K. Shamsuddin Ahmed and R. G. Wilkins, *Proc. Chem. Soc.*, 399 (1959); *J. Chem. Soc.*, 3700 (1959); 2091 (1960).

(4) D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Am. Chem. Soc.*, **83**, 1791 (1961).

(5) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Wilkins, and R. G. Pearson, "Chemistry of the Co-ordinate Compounds," Pergamon Press, New York, N. Y., 1958, p. 207; H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

(6) R. G. Wilkins, *J. Chem. Soc.*, 4521 (1957).

(7) R. K. Murmann, *J. Am. Chem. Soc.*, **84**, 1349 (1962).

(8) (a) (AO) = 2-amino-2-methyl-3-butanoneoxime, (N-alkylAO) = 2-alkylamino-2-methyl-3-butanoneoxime, (EnAO) = 2,2'-ethylenediaminobis(methylbutanone) dioxime, (MeEnAO) = 2,2'-(1,2-propylenediamino)-bis-2(methylbutanone) dioxime, (PnAO) = 2,2'-(1,3-propylenediamino)-bis-2(methylbutanone) dioxime, (TetraMeen) = 2,3-dimethyl,2,3-diaminobutane, (HMTETA) = 2,2'-ethylenediaminobis-(2methyl-3-butylamine); (b) the symbolism for the complexes has been described previously, see ref. 9 for amineoximes and ref. 6 for diamines.

(9) R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 521 (1957), **80**, 4174 (1958).

(10) The -H designation describes the loss of a hydrogen ion from an oxime group in the formation of a nearly symmetrical hydrogen bond.

constant temperature ($\pm 0.05°$) by circulating thermostated water.

The rates of disappearance of the planar complex were determined by plotting log $D_T - D/D_0 - D_\infty$ vs. time. In all cases (except where noted) straight lines were obtained for at least three half-times. The product of the slopes of these curves and -2.303 gave the pseudo-first-order rate constant k. Duplicate values of k agreed with a precision of $1-2\%$ except when $t_{1/2}$ was less than 2 min.

The pH of solutions was determined at constant temperature with a Beckman Model GS pH meter standardized before each measurement. The pH change during reaction was negligible and is believed to be accurate to ± 0.02.

Reaction of $[\text{Ni}(\text{MeAO})_2\text{-H}]^+$ with $[\text{Ni}(\text{AO})_2\text{-H}]^+$.—Equimolar amounts of the two complexes were dissolved in water and held at $25.3°$; final pH 7.88. At suitable time intervals a portion was removed and allowed to react with an EDTA solution ($0.025\ M$) at a pH of 9.48. This reaction was followed spectrophotometrically at 419 mμ. Figure 1 shows some of these curves which may be separated into three components: $[\text{Ni}(\text{AO})_2\text{-H}]^+$, $[\text{Ni}(\text{AO})(\text{MeAO})\text{-H}]^+$, and $[\text{Ni}(\text{MeAO})_2\text{-H}]^+$. The extinction coefficients of the starting complexes at 419 mμ are 143 and 133 (AO, MeAO, respectively) and that of the mixed complex is estimated to be 138 (later found to be 139 $\pm$ 1). With a knowledge of the molar absorbancies and the $t_{1/2}$ for $[\text{Ni}(\text{AO})\text{-H}]^+$ and $[\text{Ni}(\text{MeAO})_2\text{-H}]^+$ the concentration of each species was graphically determined. At equilibrium the amount of the starting complexes was less than 2% and an accurate determination of the $t_{1/2}$ for $[\text{Ni}(\text{AO})(\text{MeAO})\text{-H}]^+$ was possible.

The acid dissociation constant for $[\text{Ni}(\text{AO})_2(\text{H}_2\text{O})_2]^{+2}$ is known[9] but that of $[\text{Ni}(\text{AO})_2\text{-H}]^+$ has not been determined. The constant was determined by measuring the increase in absorption of solutions containing known amounts of complex as a function of the pH. A graph of log I_0/I vs. pH showed a sharp transition which was due to the loss of one H^+ and from which K_1 was obtained. At $25.3°$ and $\mu = 0.10$ pK_a for $[\text{Ni}(\text{AO})_2\text{-H}]^+$ is 10.8.

Results

$$\text{H}^+(\text{aq}) + [\text{Ni}(\text{AO})_2\text{-H}]^{+\ 11} + \text{EDTA}^{-4} \rightarrow [\text{Ni}(\text{EDTA})]^{-2} + 2\text{AO}.$$—Preliminary experiments showed the rate of reaction to be dependent on $[\text{Ni}(\text{AO})_2\text{-H}^+]_T$,[11] $[\text{EDTA}]_T$, and ionic strength but essentially unaffected by the presence of products ($\text{Ni}(\text{EDTA})^{-2}$ and AO). In most of the measurements it was satisfactory to use EDTA as its own buffer since the reaction does not liberate large quantities of acid and the displaced ligands counteract this through their basic character.

EDTA Dependence.—In the presence of a large excess of $[\text{EDTA}]_T$ the dissociation of $[\text{Ni}(\text{AO})_2\text{-H}^+]$, $[\text{Ni}(\text{N-alkylAO})_2\text{-H}]^+$, $[\text{Ni}(\text{EnAO})\text{-H}]^+$, and $[\text{Ni}(\text{TetraMeen})_2]^{+2}$ followed first order kinetics over at least five half-lives. In Fig. 2 is shown the pseudo-first-order rate constant as a function of $[\text{EDTA}]_T$ for several of these complexes at a constant pH of 9.50. The complexes of AO and TetraMeen react a great deal faster than the others studied (note the change in ordinate) and have a high EDTA dependency. With the complexes of N-alkylAO and that of TetraMeen, the reaction is carried by two paths corresponding to the expression: rate $= k[\text{complex}]_T + k'[\text{complex}]_T \cdot [\text{EDTA}]_T$. The rate for $[\text{Ni}(\text{AO})_2\text{-H}]^+$ and $[\text{Ni}(\text{En-}$

Fig. 1.—First order graph of the reaction of planar Ni(II) complexes with EDTA, pH 9.48, $T = 25.3°$, $[\text{EDTA}]_T = 0.025\,M$: A, $[\text{Ni}(\text{MeAO})_2\text{-H}]^+$; B, $[\text{Ni}(\text{AO})_2\text{-H}]^+$; C, 1–1 ratio of A and B initially; D, 1–1 ratio of A and B after 200 min. at $25.3°$ and pH 7.88; E, $[\text{Ni}(\text{AO})(\text{MeAO})]^+$.

Fig. 2.—Pseudo-first-order rate constants for the reaction of planar Ni(II) complexes with EDTA, $25.3°$, pH 9.50, $\mu = 0.3$: TetraMeen and AO, $k \times 10^2$.

$\text{AO})\text{-H}]^+$ has only a single term, rate $= k'[\text{complex}]_T \cdot [\text{EDTA}]_T$. For the AO complex, due to the high value of k', an EDTA independent term, equal in magnitude to that of the N-alkylAO complexes, would not be observable. With $[\text{Ni}(\text{EnAO})\text{-H}]^+$ a slight curvature is noted and probably is due to ionic strength changes. The ionic strength cannot be controlled precisely because of complicated equilibria involved with the reactants.

Hydrogen Ion Dependence.—The large hydrogen ion dependence of the rate is given in Fig. 3. With $[\text{Ni}(i\text{-PrAO})_2]^{+2}$ a first-order dependence on $[\text{H}^+]$ is

(11) The equation is written for the AO complex but applies for all of the α-amineoxime complexes studied as well as those of the di- and tetramines. The subscript T is meant to signify the total concentration of all forms of the complex or of EDTA.
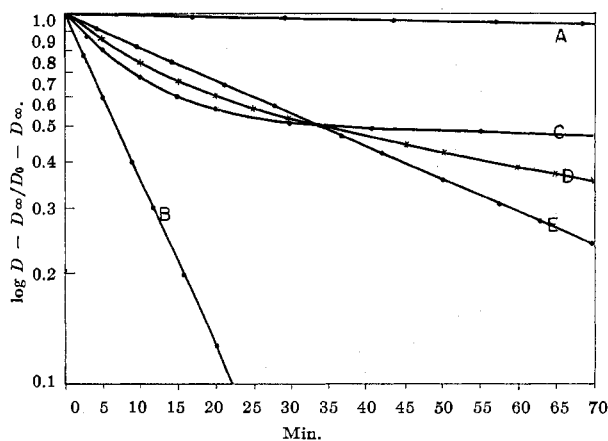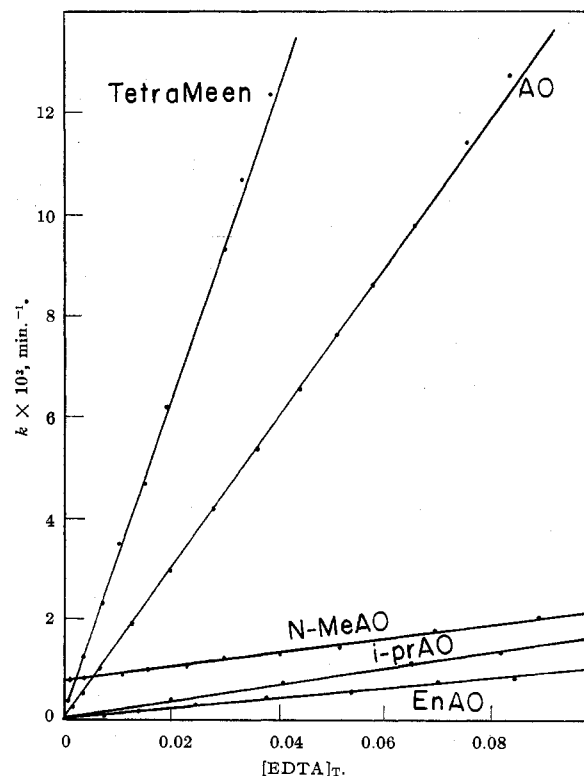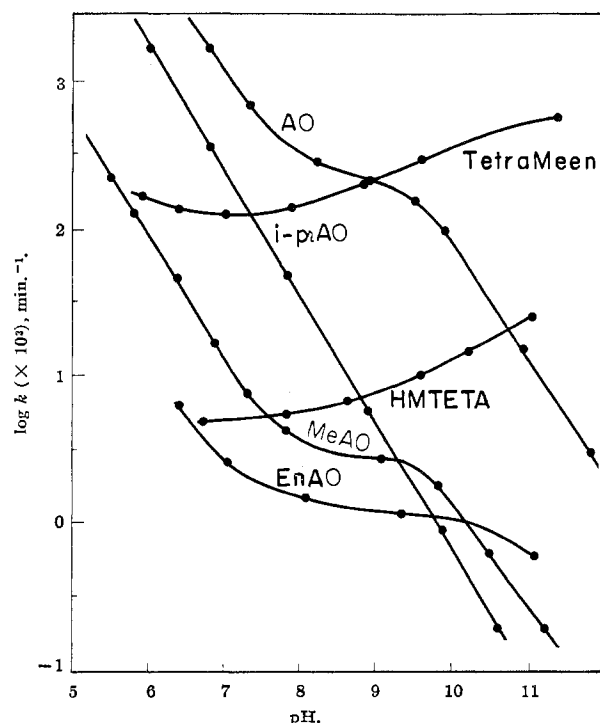
Fig. 3.—Pseudo-first-order rate constant for the reaction of various planar Ni(II) complexes with EDTA: [EDTA]$_T$ = 0.10M, T = 25.3°.
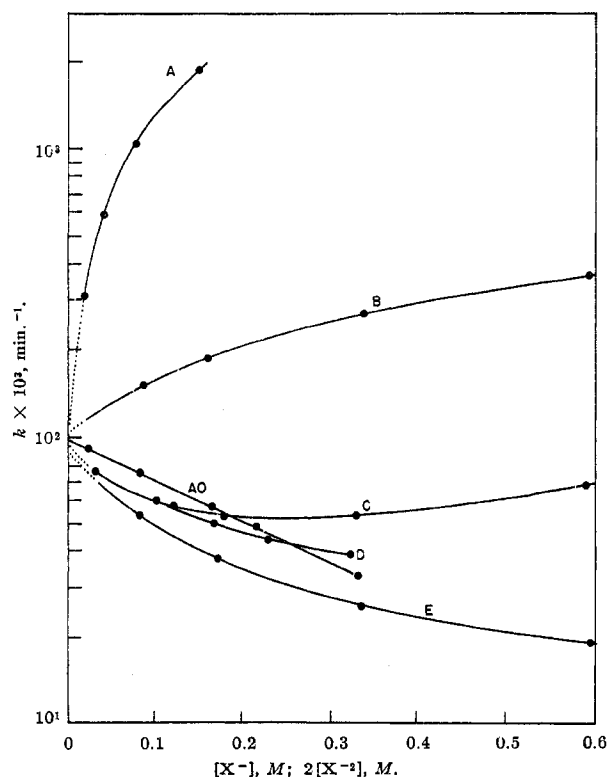

Fig. 4.—Pseudo-first-order rate constant for [Ni(AO)$_2$-H]$^+$ *vs.* negative ion concentration, [EDTA]$_T$ = 0.016M, pH = 9.00, T = 25.3°: A, glycine^{-1}; B, oxalate^{-2}; C, malonate^{-2}; D, OAc$^-$, NO$_3^-$; E, adipate^{-2}.

noted in the pH range 6–11, while all of the other α-amineoxime complexes show first order behavior in the pH regions 5–7 and 10–12 with a middle region of nearly zero slope. N-n-Alkyl substitution causes a large

(200 X) rate decrease and is essentially independent of alkyl chain length, while the tetradentate ligand, EnAO, also gives slow reactions having a longer pH independent region displaced to a more alkaline region. The complex of TetraMeen reacts slightly faster in both acid and base than in neutral media in the pH region 6–11.

The same rate values were obtained at different wave lengths (± 10 mμ of A_{max} of the complex). Conductometric measurements with complexes of AO and MeAO showed identical rates with those obtained colorimetrically.

Amineoxime Dependence.—The reaction is essentially independent of the free ligand as shown in Table I. The slight trend is due to changes in ionic strength, which was not constant. The last two experiments show a small ligand effect at higher AO concentrations but interpretation is difficult because of the accompanying salt effect.

TABLE I

Pseudo-First-Order Rate Constants

[Ni(AO)$_2$-H]$^+$, [EDTA]$_T$ = 0.100 M, pH 9.00 $\pm$ 0.02, 25.3°, 419 mμ

[KCl]	[AO] free	10^3k, min.$^{-1}$
0.200	0.000	186.0
.195	.005	190.0
.190	.010	192.0
.180	.020	195.0
.00	.00	88.0^a
.10	.10	69.8^a
.20	.20	52.1^a

^{a} [EDTA]$_T$ = 0.016 M.

Specific Ion effects are shown in Fig. 4 for negative ions with [Ni(AO)$_2$-H]$^+$. Similar curves are obtained with the MeAO complexes. The rate decreases with increasing ionic strength at constant pH and [EDTA]$_T$. Although the concentrations were too high for a precise theoretical description, this is the general form for a reaction involving ions of unlike charge.[12] The reaction is unaffected by changes in positive ions (Na$^+$, Li$^+$, K$^+$, and Ni^{+2}). Negative ions which are capable of spanning two coördinating positions show abnormal behavior. Figure 4 shows the effect of bidentate ligands. Similar curves are obtained for the compounds of AO and N-alkylAO. A rough correlation exists between the formation constant for the association of Ni(II) with the bidentate ligand and the catalysis of the rate with EDTA (Table II). A chelate ring greater than six gives no catalytic activity, while adipic acid anion lowers the rate compared to simple negative ions. It is significant that the latter occurs only with [Ni(AO)$_2$-H]$^+$.

Pyridine or NH$_3$ have a small effect, as shown by Table III.

The different behavior of [Ni(EnAO)-H]$^+$ compared to [Ni(AO)$_2$-H]$^+$ complexes is shown by a comparison of Fig. 4 with the ethylenediamine dependence of the

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 139.

TABLE II[13]
FORMATION CONSTANTS WITH NICKEL(II)

Ligand	log K_1 (25°)
Ethylenediamine	7.6
Glycinate^{-1}	5.8
Oxalate^{-2}	5.3
Malonate^{-2}	4.0
Adipate^{-2}	2.0
Acetate^{-1}	0.7

TABLE III
PSEUDO-FIRST-ORDER RATE CONSTANTS
[Ni(AO)$_2$-H]$^+$, 25.3°, [EDTA]$_T$ = 0.016 M, pH 9.00

[NH$_3$]$_T$	10^3k, min.$^{-1}$	[pyridine]$_T$	10^3k, min.$^{-1}$
0.04	100.0	0.04	96.2
.08	92.5	.08	95.0
.12	81.5	.16	103.0

rate of reaction with EDTA (Fig. 5). The presence of the free chelating ligands such as ethylenediamine, oxalate^{-2}, etc., has no abnormal effect on the rate of reaction of EDTA with [Ni(EnAO)-H]$^+$, in sharp contrast to the catalytic effect on the bidentate amine-oxime complex.

Figure 6 shows the rate dependence on [EDTA]$_T$ when the oxalate ion is in excess. The rate is nearly independent of [EDTA]$_T$, which is unexpected since less than 1% reaction between oxalate ion and the complexes occurs at equilibrium in this concentration range.

The slight increase when TetraMeen is added is given in Fig. 7. It reaches a limiting value between the rate for [Ni(AO)$_2$-H]$^+$ and [Ni(TetraMeen)$_2$]$^{+2}$ under the same conditions.

Activation Energies.—Table IV gives a comparison of the Arrhenius parameters for several complexes under identical conditions.

TABLE IV
KINETIC DATA, $k = A \exp(-E_a/RT)$ FOR PSEUDO-FIRST-ORDER
REACTIONS WITH EDTA; pH 9.48, [EDTA]$_T$ = 0.025 M

Species	k, sec.$^{-1}$ (25.3°)	E_a (kcal. mole^{-1})	log A (sec.$^{-1}$)
[Ni(AO)$_2$-H]$^+$	1.58×10^{-3}	12.1 ± 0.2	17.5 ± 0.2
[Ni(MeAO)$_2$-H]$^+$	1.92×10^{-5}	14.5 ± .2	19.7 ± .2
[Ni(EnAO)-H]$^+$	1.25×10^{-5}	14.4 ± .2	19.4 ± .2

C-Methyl substitution on the ethylene bridge in the EnAO type complexes has a profound effect. Although complete details are not available, the studies given below show this effect.

[Ni(AO)$_2$-H]$^+$ + [Ni(MeAO)$_2$-H]$^+$ → 2[Ni(AO)-(MeAO)-H]$^+$.—The rate of this reaction is relatively

TABLE V
PSEUDO-FIRST-ORDER RATE CONSTANTS OF REACTION
44.5°, [EDTA]$_T$ = 0.025 M, pH 9.48

Species	k, min.$^{-1}$
[Ni(EnAO)-H]$^+$	3.14×10^{-3}
[Ni(MeEnAO)-H]$^+$	5.4×10^{-5}
[Ni(PnAO)-H]$^+$	6.9×10^{-5}

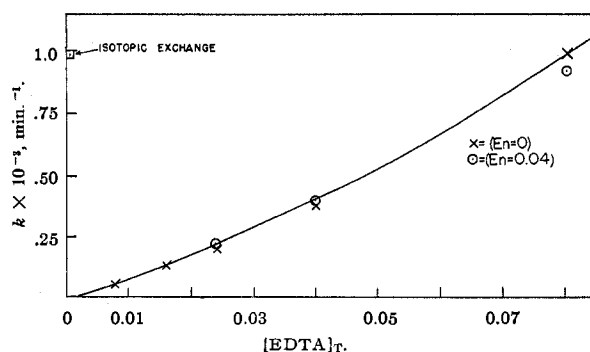(13) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Part 1, Metcalfe and Cooper, London, 1957.

Fig. 5.—Pseudo-first-order rate of [Ni(EnAO)-H]$^+$ reaction with EDTA, T = 25.3°, pH 9.00, μ = 0.30; ligand exchange, pH 9.00, T = 25.3°, ligand = 4 × 10^{-3}M.

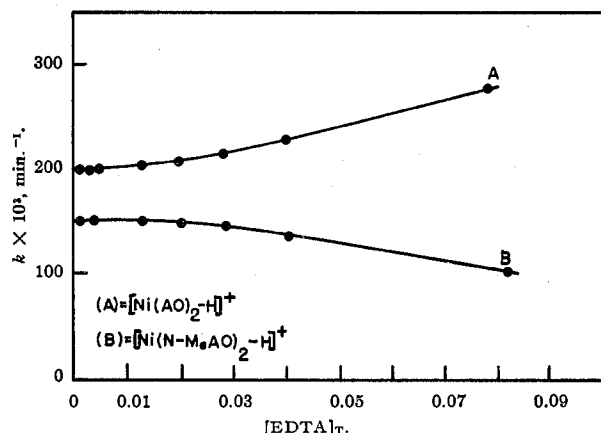

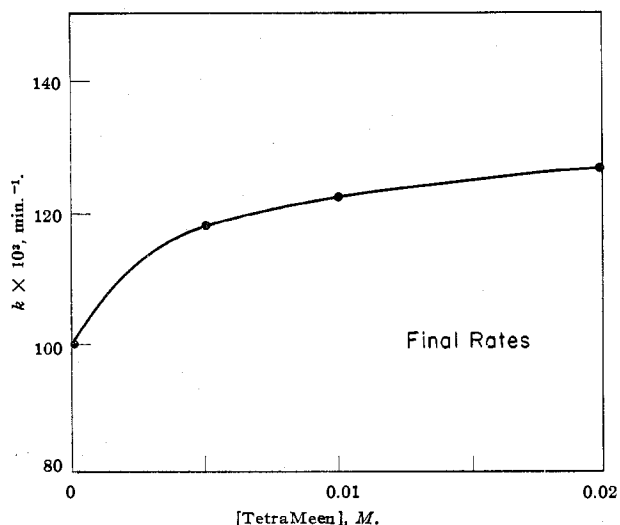Fig. 6.—Rate constant of reaction in the presence of oxalate ion: pH 9.00, T = 25.3°, oxalate ion = 0.04 M.

Fig. 7.—Pseudo-first-order rate constants for [Ni(AO)$_2$-H]$^+$ with EDTA: [EDTA]$_T$ = 0.016M, pH 9.00, T = 25.3°, μ = 0.30.

slow at pH 7.88 and goes nearly to completion. A lower estimate for K_{eq} is 2000. The reaction follows second order kinetics and assuming the following rate expression: rate = k[Ni(AO)$_2$-H]$^+$[Ni(MeAO)$_2$-H]$^+$ has a value of k of 14.6 l. mole^{-1} min.$^{-1}$ at 25.3° (pH 7.88).

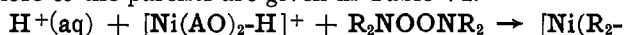The properties of the mixed complex compared with those of the parents are given in Table VI.

$$H^+(aq) + [Ni(AO)_2\text{-}H]^+ + R_2NOONR_2 \rightarrow [Ni(R_2\text{-}$$

Table VI
Molar Absorbances and Pseudo-First-Order Rate Constants
[EDTA]$_T$ = 0.025, pH = 9.48, 25.3°

	A_{max}, mμ	$t_{1/2}$, min.	10^3k, min.$^{-1}$
[Ni(AO)$_2$-H]$^+$	418.5	6.6 ± 0.2	105
[Ni(AO)(MeAO)-H]$^+$	422.0	34 ± 3	20.7
[Ni(MeAO)$_2$-H]$^+$	423.5	540 ± 10	1.28

NOONR$_2$)]$^{-2}$ + 2AO.—A comparison of EDTA with 1,2-bis-2-di-(carboxymethyl)-aminoethoxyethane ((HOOC–CH$_2$)$_2$–N–CH$_2$–CH$_2$–O–CH$_2$–)$_2$(R$_2$NOONR$_2$) was made to see if structural changes in this reactant are important. Although R$_2$NOONR$_2$ was carefully repurified and is believed to contain only one species, the reaction with planar complexes did not follow first-order kinetics. This was especially apparent at high pH values. The initial rates were about 2–3 times faster than with EDTA at the same concentration and pH and were also pH dependent. The difference in rates between [Ni(AO)$_2$-H]$^+$ and [Ni(MeOA)$_2$-H]$^+$ was about the same as that found with EDTA.

Discussion

Previous work[7] has shown that an inverse relationship exists between the thermodynamic stability of planar nickel(II) complexes of substituted α-amineoximes and their rate of decomposition in acid. A list of the acid stability is i-PrAO < n-PrAO = n-BuAO < MeAO < AO < EnAO < MeEnAO = PnAO. With HMTETA, TetraMeen, and anilino-AO the acid dependence is markedly different, preventing a direct comparison. It has been postulated[7,14] that dissociation of the ligand from the complex plays a significant part in the mechanism of acid decomposition. Since the MeAO complex is much slower acting than that of AO it is apparent that the reaction with EDTA does not proceed by a simple dissociation and in fact a dissociative path can contribute only slightly to the over-all reaction.

The complex ion reactant consists of an equilibrium of several species. Their relative concentration with increasing pH increases in the order: [Ni(AO)$_2$(H$_2$O)$_2$]$^{+2}$, [Ni(AO)$_2$-H]$^+$, [Ni(AO)$_2$-H(OH)]^0. Only the first species is paramagnetic.[15] The structure of [Ni(AO)$_2$-H(OH)]^0 is unknown but it is probable that it contains one or more rather loosely bound waters or hydroxy groups in the *trans*-position and may be a negatively charged ion. The forms of EDTA present in the pH range 6–12 are primarily EDTA^{-2}, EDTA^{-3}, and EDTA^{-4}.

Spectrally determined rates measure the rate of loss of the diamagnetic yellow species and are insensitive to paramagnetic blue intermediate forms. Conductometric measurements, however, are sensitive to each ligand loss. Since the same rates were observed by both methods, the reactions subsequent to the magnetic

change are by comparison fast. The products are [Ni(EDTA)]$^{-2}$ and AO in their acid–base forms. The backward reaction is negligible due to a large K_F for the EDTA complex and is not observed in the concentration and pH ranges studied.

The EDTA dependence of the rate (Fig. 2) shows that two paths are operative with the Ni(II) complexes of MeAO, i-PrAO (k × 10^3 = 0.08 at EDTA = 0), and TetraMeen corresponding to the expression: rate = k[complex]$_T$ + k'[complex]$_T$[EDTA]$_T$, while for AO and EnAO, only an EDTA dependent path is present. The first path is due to dissociation or to displacement of one of the chelating molecules by water followed by the rapid entry of an EDTA ion as postulated by Wilkins.[14] This is substantiated by isotopic ligand exchange studies[16] which (after correction for a factor of two because two ligands are given off in the EDTA reaction) are identical with the EDTA reaction rates. Only the complexes of low thermodynamic stability show an EDTA independent term, which is expected if an inverse relationship between the dissociation rate and the formation constant exists. The rates of formation of many Ni(II) complexes are nearly independent of the ligand[17,18] and thus K_F often is inversely related to the dissociation rate constant. The dissociation rate constant of stable complexes would not be observed over the large EDTA dependent route.

The EDTA path is operative in all diamagnetic Ni(II) complexes studied and may proceed through either a direct displacement or through a CN = 5 activated state formed by ion pair association of an EDTA ion above the complex plane. The latter is preferred on the basis of the lack of catalytic effect by monodentate ligands as described later, although the former mechanism cannot be ruled out.

The rate dependence on pH is due to its modification of the complex hydrogen bond and not to the EDTA ion charge. Complexes containing only amine nitrogens (HMTETA and TetraMeen) show a small pH dependence for the EDTA reaction similar to that for the acid dissociation.[14] The acid region increase probably arises from protonation of the half-bonded intermediate preventing reformation while the slight basic region rate increase results from increased EDTA complex association due to increased EDTA ion charge.

[Ni(i-PrAO)$_2$-H]$^+$ shows a first order dependence on [H$^+$]. This compound is believed[9] to be in the *trans* configuration due to steric hindrance between alkyl groups. Although the acid–base dissociation constants of this complex are not known, titration data indicate

(14) R. G. Wilkins, *J. Chem. Soc.*, 4521 (1957); A. K. Shamsuddin Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959), 2895 (1960).

(15) R. K. Murmann, unpublished work.

(16) (a) D. L. Lewis and R. K. Murmann (to be published): (EDTA = 0), T = 25°, pH 7.7; for [Ni(MeAO)$_2$-H]$^+$, k_{exch} = 6.2 × 10^{-4} min.$^{-1}$, k_{EDTA} = 12.8 × 10^{-4} min.$^{-1}$. (b) R. G. Wilkins, ref. 6: (EDTA = 0), T = 25°, pH 7.7; for [Ni(TetraMeen)$_2$]$^{+2}$, k_{exch} = 8 × 10^{-3} min.$^{-1}$, k_{EDTA} = 17.0 × 10^{-3}.

(17) M. Eigen, "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1960, p. 373.

(18) A. K. Shamsuddin Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2905 (1960).
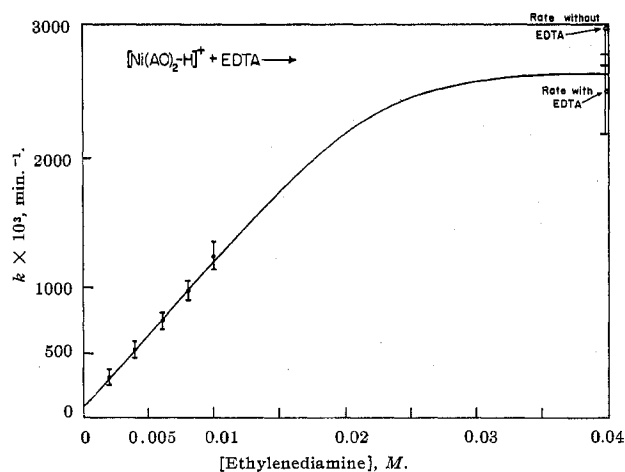
Fig. 8.—Ethylenediamine dependence of pseudo-first-order rate constant: pH 9.00, $T = 25.3°$, $[EDTA]_T = 0.016M$.

Fig. 9.—Upper curve: pH dependence of the pseudo-first-order rate constant for $[Ni(AO)_2-H]^+$ with EDTA; $[EDTA]_T = 0.10M$, $T = 25.3°$. Lower curves: log of concentration of EDTA species (based on 10) as a function of pH; O = log of concentration of $[Ni(AO)_2-H]^+$ as a function of pH.

that in this pH range the small concentration of the +2 charged complex would increase linearly with acidity, suggesting that the +2 charged complex is the reacting species.

With all other AO complexes a first-order dependence on $[H^+]$ is noted in the acid and basic regions with a middle level section. The level portion is caused primarily by the acid–base character of the complex hydrogen bond and occurs at pH values consistent with the hydrogen bond strength. From infrared spectra and K_{eq} measurements[9] the acidity of $[Ni(AO)_2-H]^+$ type ions increases in the order: EnAO, AO, MeAO, EtAO, i-PrAO; the midpoint of the level section of the pH dependency is at pH 9.4, 8.5, 8.4, 8.2, and 0, respectively. The interpretation is complicated by the high and low acidity mechanism but the close correlation suggests that the hydrogen bond stability results in a pH region of nearly constant rate. This is further suggested by the fact that the pH range is longer with the stronger hydrogen-bonded complexes. Figure 9 shows a comparison between the rates for $[Ni(AO)_2-H]^+$, the relative concentrations of EDTA species, and the relative amount of complex in the $[Ni(AO)_2-H]^+$ form. The latter were calculated from the measured K_{eq} while for EDTA they were obtained from the literature.[13] There is little correlation between the EDTA charge and the rate, and considering the near acid independence of the di- and tetramine complexes these features probably are due to the acid–base forms of the complex. The rapid (almost first order in $[H^+]$) drop in rate upon increasing the pH (6.0–7.5) probably is due to a decrease in the small concentration of $[Ni(AO)_2(H_2O)_2]^{+2}$, which dissociates rapidly. In the level portion (7.5–9.5), the reaction is carried primarily by $[Ni(AO)_2-H]^+$, whose dissociation would be expected to be slow because of the tetradentate nature of the hydrogen-bonded ligand. In the basic region, pH 9.5, the planar complex loses another H^+ and goes to $[Ni(AO)_2-H(OH)]^0$ (waters omitted). This is extremely stable to substitution because of its zero charge or because of occupancy of the fifth position by OH^-. Its formation lowers the concentration of
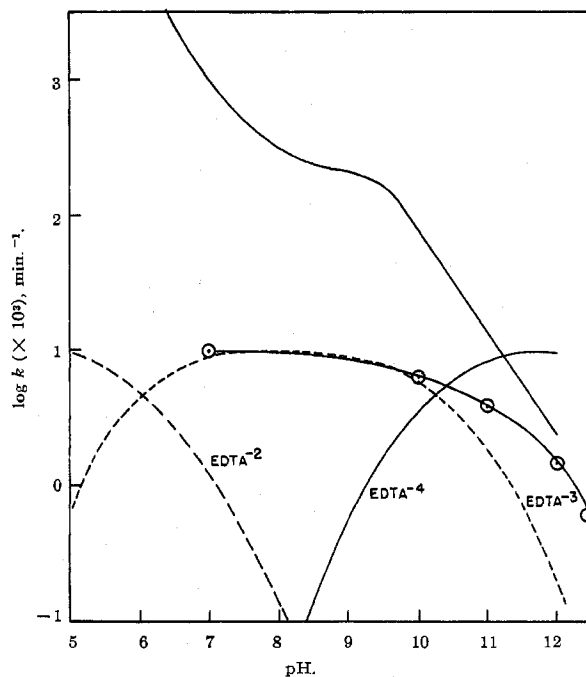
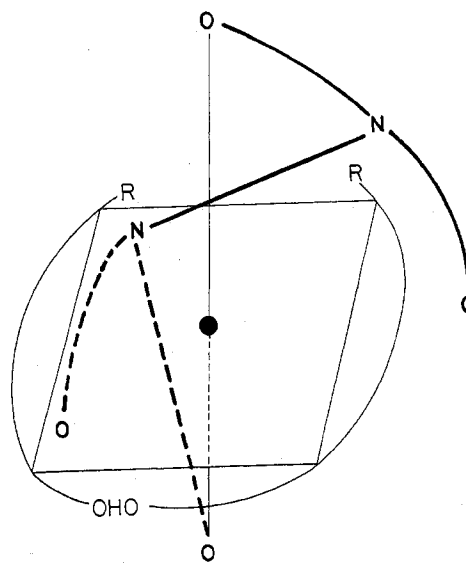

Figure 10.

$[Ni(AO)_2-H^+]$, resulting in a slower rate.

Isotopic ligand exchange[16a] shows a similar minimum in the rate in the region of maximum concentration of hydrogen-bonded complex. In this case the rate increase on the alkaline side is due to the increased free ligand since the rate of isotopic ligand exchange is ligand dependent.

$[Ni(MeAO)_2-H]^+$ is about 0.005 times as fast as $[Ni(AO)_2-H]^+$, although its thermodynamic stability is smaller. Increasing the alkyl size has very little effect. The decrease is in the EDTA dependent portion of the reaction and is due to steric factors involved in the association of EDTA with the complex. Since

NH₃ and pyridine have no effect, it is doubtful that a displacement mechanism is operative, in agreement with previous work on Pt(II) complexes.[2,5] A one-position attachment of EDTA in the activated state using a carboxyl oxygen would not offer any appreciable steric effect, while the use of its amine nitrogen would present a small interference with only the MeAO and EnAO complexes. If a one-ended ion pair were the effective activated state, then the EnAO complex should have a very large EDTA dependence, which is not found. A more satisfactory explanation for the extreme rapidity of the AO and TetraMeen complexes and their large EDTA dependence is found in an activated state having an EDTA ion spanning the *trans*-positions of the complex (Fig. 10). This model is sterically favorable and places the amine nitrogens and the carboxyl oxygens in the proper positions for attachment when either AO ligand dissociates. This association facilitates the ligand dissociation by lowering the ligand field stabilization energy of the structure. Because of charge repulsions, the bridge cannot form across the hydrogen bond nor can chelation sterically occur with MeAO because of the C–C bridge connecting the amine nitrogens in EnAO. The small EDTA effect with these ligands probably is due to facilitation of dissociation by one-ended association of EDTA or by prevention of re-formation of a chelate by a half-bonded ligand by EDTA reaction at one of the planar positions. There is some support for the chelated EDTA activated state in the effect of organic dibasic anions on the rate. The adipate ion is of just the correct length to span *trans*-positions and it is noted that with the AO complex (but not MeAO) the rate is a great deal slower than with shorter dibasic acid anions. This suggests that competition for these positions between the EDTA and adipate ions causes a slower reaction because only the former can complete the reaction.

In the presence of molecules or ions capable of chelate formation the rate of reaction with EDTA is remarkably catalyzed (Fig. 4). The initial reaction does not involve EDTA but is carried to completion by it and the observed rate is directly related to the chelating ability of the ligand. With strong chelating agents (ethylenediamine, glycine) the observed spectral changes do not follow first-order kinetics. The initial fast portion is the replacement of an AO type ligand by the substituting bidentate ligand to form a species of low absorption at 400 mμ, while the latter portion of the reaction is governed by the reaction of this complex with EDTA. With low concentrations of foreign ligands or using weaker coördination reagents, the reaction follows first-order kinetics because the equilibrium concentration of the fast reacting species is very small and is generated rapidly. Figure 6 shows that the reaction becomes zero order in [EDTA]$_T$ when oxalate ion is present, the slight oxalate ion effects being due to ionic strength changes in the solution (MeAO) and to a composite of ion pair slowing, and direct reaction with EDTA hastening, the reaction with AO. With oxalate ion the rate is first order in oxalate ion in the

range 0.04–0.32 M. Figure 8 shows that at constant [EDTA]$_T$ the rate is linearly related to the [ethylenediamine] but at high concentrations a limiting rate is reached. Figure 5 shows that a similar effect is not observed with [Ni(EnAO)-H]⁺, suggesting that the intermediate whether it has the foreign ligand attached in one or two positions also must be slow to react with EDTA. The probable reason for this type of catalysis is in the formation of an intermediate complex, which, due to low ligand field stabilization energy, goes to the octahedral paramagnetic state and reacts rapidly. To test this, a diamine of high chelating ability and known to form planar Ni(II) bis-complexes was used. Figure 7 shows, in agreement with this hypothesis, that the rate is only slightly affected by TetraMeen. Actually the final rate with excess TetraMeen is intermediate between that for [Ni(AO)₂-H]⁺ and [Ni(Tetra-Meen)₂]⁺², suggesting a rapid formation of [Ni(AO)(TetraMeen)]⁺², which is diamagnetic and reacts with EDTA at an intermediate rate. The difference between en and TetraMeen may be explained on the basis of the diamagnetic, planar character of the intermediate mixed ligand complex [Ni(AO)(TetraMeen)]⁺², as compared with the faster dissociating paramagnetic [Ni(AO)(en)(H₂O)₂]⁺². A schematic of this catalytic process is given below, where AA represents any bidentate chelating ligand. The equilibrium involving AA is rapid,

$$H^+ + [Ni(AO)_2\text{-}H]^+ + AA \underset{}{\overset{rapid}{\rightleftharpoons}} [Ni(AO)(AA)(H_2O)_2]^{+2} + AO$$

$$k_1 \downarrow EDTA \qquad\qquad k_2 \downarrow EDTA$$

$$products \qquad\qquad products + AA$$
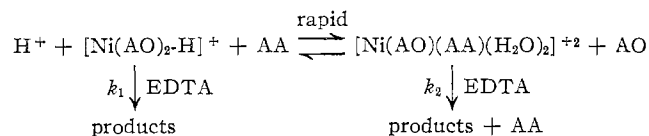
giving the mixed complex. If the mixed complex has a low ligand field stabilization energy and/or is paramagnetic, then $k_2 > k_1$. Little is known about the reason for the rapidity of the reaction between AA groups and diamagnetic complexes. However, the same effect is noted in isotopic exchange measurements and probably is related to displacement by AA following coördination at the fifth position.

The Arrhenius parameters are a composite of those for the individual routes but they provide some confirmation of the mechanisms proposed. E_a and log A for EnAO and MeAO complexes are about the same, which is expected since the route in both cases is primarily dissociation coupled with a one-ended EDTA associative path. With [Ni(AO)₂-H]⁺, E_a is considerably lower, due to the fact that the main portion of the reaction is carried through the chelated EDTA activated state which would have a lower activation energy. Log A decreases because of the decreased probability of having the associated ion pair. With isotopic ligand exchange reactions E_a is somewhat higher but again the AO complex has a lower value than that of MeAO.[16a] In this case the activated state for the AO complex always involves an AO coördinated at the fifth position, while, due to steric hindrance, free MeAO is seldom involved in the activated state.

Reactions of R₂NOONR₂ were expected to parallel those of EDTA. That the kinetics are complex may

mean that we were unable to prepare a pure sample of the amino acid or, more probably, that the intermediate reactions are slow and the concentration of intermediates builds up. However, the features with EDTA are, for the most part, shown by R_2NOONR_2, making it probable that they are rather general.

A single C-methyl substitution on the ethylenediamine ring of EnAO has a remarkable stabilizing effect (50 ×) on the complex and a change of equal magnitude is observed by inserting a methylene group in the ring (PnAO). This effect is not understood, but the kinetic stability may be related to an increase in K_F due to decreased ring strain. A tetradentate ligand forming four chelate rings (due to the hydrogen bond) may achieve stronger bonding by separating the coördinating atoms. This may be accomplished by addition of a methylene group or by C-methyl substitution. With these ligands even Cu(II) is kinetically slow. In 0.10 M HCl at 24.5°, first order kinetics are observed and $t_{1/2}$ = 3.0 min. With EDTA the reaction also is measurable and has characteristics similar to those of Ni(II) but with a larger EDTA dependent path.

The different stabilities of $[Ni(AO)_2\text{-}H]^+$ and $[Ni(MeAO)_2\text{-}H]^+$ made possible studies of the ligand exchange rate. The rate is about the same as the dissociative path for $[Ni(MeAO)_2\text{-}H]^+$ with EDTA and twice the isotopic ligand exchange rate at [ligand] = 0. The fact that isotopic ligand exchange of the AO complex is very fast coupled with the above similarity suggests that the slow step is the dissociation of $[Ni(MeAO)_2\text{-}H]^+$.

It has been postulated[9] that the low K_F (formation constant) value for $[Ni(R\text{-}AO)_2\text{-}H]^+$ is due to the steric repulsion of N-methyl groups due to the *cis*-geometry demanded by the hydrogen bond. The equilibrium constant for the reaction

$$[Ni(AO)_2\text{-}H]^+ + [Ni(MeAO)_2\text{-}H]^+ \underset{\longleftarrow}{\overset{K_{eq}}{\rightleftharpoons}}$$
$$2[Ni(AO)(MeAO)\text{-}H]^+$$
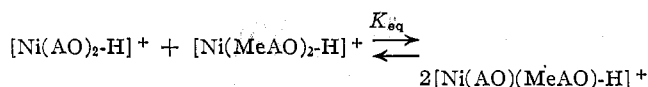
is large (2000), much greater than statistically expected, and is due to the relief of this steric hindrance. The formation constant of $[Ni(AO)(MeAO)\text{-}H]^+$, K_F^{ab} = $[Ni(AO)(MeAO)\text{-}H^+][H^+]/[Ni^{+2}][AO][MeAO]$, is related to the formation constant of $[Ni(AO)_2\text{-}H^+]$, K_F^a, and that of $[Ni(MeAO)_2\text{-}H]^+$, K_F^b, by the expression: log K_F^{ab} = $1/2$(log K_F^a + log K_F^b + log K_{eq}). If K_{eq} is estimated at 2000, log K_F^a = 6.1,[9] and log K_F^b is estimated to be 1.5 on the basis of the similarity of its titration curve with that of *n*-PrAO, whose stability constant has been given,[9] then log K_F^{ab} is 5.5. This is a great increase over the thermodynamic stability of the bis-MeAO complex.[9] The mixed complex should resemble the AO rather than the MeAO complex in kinetic stability on the basis of both thermodynamic stability and the lack of steric hindrance which is found to be the case (Table VI). Further evidence that the value for K_F^{ab} is of the right order of magnitude is

shown by the titration curve of Ni^{+2}, AO, and MeAO, in a 1-1-1 molar ratio. It closely resembles that of a solution containing Ni^{+2} and AO, in a 1-2 ratio.

Preliminary success has been achieved in using MeEnAO and EDTA as quantitative selective analytical reagents for Ni(II) on the basis of the slow reaction, $t_{1/2}$ = 300,000 min. (room temperature), of EDTA with $[Ni(MeEnAO)\text{-}H]^+$. All other common ions except Pt(II) and Pd(II) react rapidly. A solution containing Ni(II) treated with excess MeEnAO followed by buffered EDTA solution when compared spectrally at 390 mμ with the same unknown solution treated identically except for MeEnAO gave directly the concentration of Ni(II). It is very rapid and insensitive to most other ions.

Summary

The reaction of planar nickel(II) complexes of α-amineoxime and C-substituted α-diamines with EDTA proceeds using the rate law: rate = $k[\text{complex}]_T$ + $k'[\text{complex}]_T[\text{EDTA}]_T$. This is the same expression found for platinum(II) complexes when reacting with a variety of reagents. The EDTA independent term probably describes the dissociation of the complex which is followed by the rapid entry of an EDTA molecule-ion. The EDTA dependent path is due to rapid association of EDTA at the fifth (and perhaps the sixth) position followed by the rate determining dissociation or replacement of the ligand.

Alkyl substitution on the amine nitrogen diminishes the EDTA dependent path due to steric hindrance. This is interpreted in terms of an activated state for the non-substituted complex containing EDTA bound at both *trans*-positions. The Arrhenius parameters are in agreement with these mechanisms.

From the hydrogen ion dependence and the rate changes with substitution on the complex ligand the reaction is only slightly affected by the charge of EDTA. The rate is strongly dependent on the charge of the nickel complex and $k_a \gg k_b > k_c$. This shows the
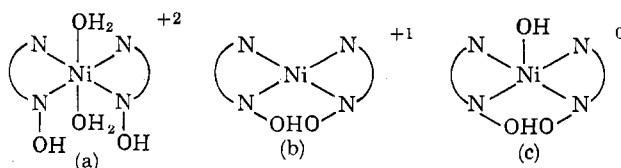
importance of the hydrogen bond and the association of OH^- in the fifth position in lowering the rate.

Chelating ligands (ethylenediamine, oxalate ion, etc.) catalyze the reaction with EDTA by rapidly replacing one amineoxime ligand, forming small amounts of the mixed ligand complex. This complex then reacts rapidly with EDTA if its crystal field stabilization energy is low compared to the original complex.

The kinetics of ligand exchange between $[Ni(AO)_2\text{-}H]^+$ and $[Ni(MeAO)_2\text{-}H]^+$ are governed by the rate of dissociation of the latter complex. The formation

constant for [Ni(AO)(MeAO)-H]$^+$ is large compared to [Ni(MeAO)$_2$-H]$^+$, showing that steric hindrance due to methyl group interaction is extremely important.

Steric hindrance to approach the 5 and 6 positions of planar Ni(II) complexes gives complexes of extreme stability to reaction with EDTA. This may be used to advantage in the analytical determination of Ni(II) in the presence of other transition ions.

Spectrochemical Studies of a Series of Amides as Ligands with Nickel(II) and Chromium(III)

By RUSSELL S. DRAGO, DEVON W. MEEK, MELVIN D. JOESTEN,[1] and LOUIS LaROCHE

The syntheses and spectra of some amide complexes of nickel(II) perchlorate and chromium(III) perchlorate are described. The ligand field parameters Dq and β are calculated for the octahedral complexes. Evidence is presented to support the presence of a steric effect in the interaction of some of these amides with the metal ions. The spectrochemical parameters Dq and β are compared with those reported for other ligands. These parameters also are compared with data which measure the donor properties of the amides toward phenol.

Introduction

Research[2] in the area of non-aqueous solvents has led us to believe that, instead of solvent autoionization, basicity and dielectric constant are the essential properties for understanding the behavior of solutes in many non-aqueous solvents. As a result, we have been concerned with the evaluation of the free energy of adduct formation between the acids iodine[3,4] and phenol[5] with several Lewis bases which may be employed as non-aqueous solvents. To gain information about the nature of the interaction of various solvents and Lewis bases with metal ions, we have evaluated the position of several of these ligands in the spectrochemical and nephelauxetic series.[6] We have described earlier[6] the spectral properties, Dq, and β values for cobalt(II), nickel(II), and chromium(III) complexes of dimethyl sulfoxide, tetramethylene sulfoxide, and pyridine N-oxide. In this article we report spectral data for the nickel and chromium complexes of a series of amides. The relative positions of these amides in the spectrochemical and nephelauxetic series have been determined. The Dq values are compared with enthalpy results for the interaction of the amides with phenol. The data can be rationalized from a consideration of inductive and steric effects.

Experimental

The metal amide complexes were prepared by the following procedure. The aquated metal perchlorate was dehydrated with a 40% excess of 2,2-dimethoxypropane[7] by stirring for 2 hr. at room temperature. The resulting solution then was treated with a sevenfold mole ratio of the amide. The volatile material then was removed by pumping at 1 mm. pressure until a viscous oil was obtained. The N,N-dimethylformamide (DMF) and N-methylformamide (NMF) complexes of nickel(II) and the acetamide and N,N-dimethylacetamide (DMA) complexes of chromium(III) were isolated as solids by extracting the respective oil with ether and ethanol. Oils of the other amide complexes did not solidify upon treatment with several solvents.

Anal. Calcd. for [Ni(NMF)$_6$](ClO$_4$)$_2$: C, 23.55; H, 4.91; N, 13.73. Found: C, 23.17; H, 5.27; N, 13.10.

Anal. Calcd. for [Ni(DMF)$_6$](ClO$_4$)$_2$: C, 31.05; H, 6.08; N, 12.07. Found: C, 30.97; H, 6.09; N, 11.76.

Anal. Calcd. for [Cr(acetamide)$_6$](ClO$_4$)$_3$: C, 20.45; H, 4.29; N, 11.92. Found: C, 21.63; H, 4.64; N, 12.09.

Anal. Calcd. for [Cr(DMA)$_6$](ClO$_4$)$_3$: C, 33.03; H, 6.23; N, 9.64. Found: C, 32.39; H, 6.43; N, 9.07.

Spectrophotometric Measurements.—Near-infrared and visible absorption spectra were obtained with a recording Cary spectrophotometer, Model 14M. The spectra of the solutions were measured in 1.0-cm. matched quartz cells with the solvent as the reference.

Solutions of the amide complexes were prepared by dissolving the oil or solid in the respective amide as a solvent. For solid amides, methylene chloride or nitromethane was used to dissolve the complex and excess amide was added to the solution. Spectral evidence is presented later to indicate that these conditions produce octahedral species in solution of the type [M(amide)$_6$]$^{+n}$. The solutions of the formamide and acetamide complexes exhibited distinctive light green and yellowish green solutions' respectively. The formamide derivatives, as a group, and acetamide form the light green solutions and have higher values of Dq than the other acetamide derivatives, which give yellowish green solutions. Typical spectra for the two series of ligands are illustrated in Fig. 1.

The O–H frequency shifts for the phenol–amide adducts were obtained by the method described previously.[8] Infrared spectra were obtained with a Beckman Model IR-7 spectrophotometer,

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