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Stability Constants of Nickel Aminocarboxylate, Ammine, and Polyamine Mixed-Ligand Complexes

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The stability constants, K_{NiLX}, for the reaction NiL + X $\rightleftarrows$ NiLX are determined for a series of ten complexes where X is a unidentate or bidentate ligand and L is a multidentate ligand. The log K_{NiLX} values (25.0°, 0.50 μ) are: 1.35, $[Ni(edta)(NH_3)]^{2-}$; 2.00, $[Ni(heedta)(NH_3)]^{-}$; 2.54, $[Ni(nta)(NH_3)]^{-}$; 0.83, $[Ni(tetren)(NH_3)]^{2+}$; 2.00, $[Ni(edda)(NH_3)]$; 2.17, $[Ni(nta)(ox)]^{3-}$; 7.20, $[Ni(nta)(en)]^{-}$; 4.89, $[Ni(nta)(gly)]^{2-}$; 4.59, $[Ni(dien)(ox)]$ at 1.0 μ; 5.13, $[Ni(dien)(gly)]^{+}$. The variation in the stability constants could be explained only by a consideration of a number of factors including ion–ion and ion–dipole interactions, chelate ring formation, the type of coordinate bond being formed, and the influence of groups already coordinated. An empirical equation is obtained which relates the contribution of each of these factors to the free energy of formation of the mixed complex.

Introduction

Mixed-ligand complexes of metal ions have been recognized since Werner's time. In the past 18 years following studies by Schwarzenbach[3] and Froneaus[4] many stability constants for various mixed-ligand complexes have been reported. Nevertheless, the total amount of stability constant data concerning complexes which have two different ligands (other than the solvent) bound to one metal ion is small compared to the vast literature on stability constants.[5]

A number of investigators have observed the formation of ternary complexes from two binary complexes to be more favorable than a statistical distribution of the ligands. Polarization,[6,7] charge neutralization with decreased solvation,[8] and asymmetry of ligand field[9] have been used to explain the phenomena. Conditions necessary for mixed-complex formation have been suggested[10] and ternary constants have been correlated with binary constants[11,12] and with redox potentials.[13,14] In some of this work the change in free energy of coordinate bonds as a result of mixed-complex formation has been considered.[8,11,13]

The present work is a study of mixed complexes of nickel(II) with only amine, carboxylate, and water as the coordinate groups. The ligands were chosen in order to determine the effect of charge, the effect of the number and types of groups bound to the metal before and after mixed-complex formation, and the effect of chelation. Hence this work treats a restricted system but considers more parameters which might influence the stability constants than has been the case in previous studies of mixed complexes. These parameters are evaluated in terms of their contribution to the free energy of formation of the mixed complex.

The ligands used and their abbreviations are given in Table I.

Experimental Section

Reagents.—Nickel perchlorate was prepared from nickel carbonate and perchloric acid and recrystallized from water. All nickel solutions were standardized by edta titration using murexide indicator.

Ammonia and dien were purified by distillation. tetren was prepared and recrystallized as $[H_5(tetren)(SO_4)_{2.5}]\cdot 2.5H_2O$. Crystalline glycine hydrochloride was recrystallized from acetone–water. Nitrilotriacetic acid was purified by dissolving the solid in hot basic solution and adding HCl until crystals started to form. The acid was recrystallized from water. The sodium salt of heedta was prepared and recrystallized from water–ethanol. N,N′-Ethylenediaminediacetic acid was boiled in basic solution to remove the cyclic imide form.[15] After cooling, perchloric acid was added to give pH 5–7, and then 2-propanol was added until crystals started to form. It was recrystallized several times by the same procedure. Care was taken to use fresh solutions of edda because cyclization of the free ligand occurs slowly in solution even at pH 10.

Solutions of the other ligands were prepared from reagent grade chemicals without further purification.

The stock solutions of ammonia, dien, en, and gly were standardized by acid or base titration. The stock solutions of edda, heedta, nta, and tetren were standardized by a spectrophotometric mole ratio method with a standard copper solution.

Crystalline $[Ni(dien)Cl_2]$ was prepared by adding liquid dien to a slight excess of nickel chloride dissolved in 95% ethanol. Acetone was added until a precipitate appeared. The salt was recrystallized from a hot aqueous ethanol solution. *Anal.* Calcd for $[Ni(dien)Cl_2]$: C, 20.64; H, 5.63; N, 18.05; Cl, 30.46. Found: C, 20.63; H, 5.35; N, 17.89; Cl, 30.70.

Stock solutions of NaNi(nta) and $Ni(tetren)SO_4$ were prepared by adding excess nickel to the ligand and then precipitating the excess as nickel hydroxide. The $Ni(tetren)^{2+}$ solution was converted to the perchlorate form by adding a stoichiometric amount of $Ba(OH)_2$ followed by perchloric acid. Other nickel complexes were freshly prepared from stoichiometric mixtures of stock solutions.

A number of salts were used for ionic strength control to avoid

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TABLE I

LIGANDS USED IN MIXED COMPLEXES

edta	$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$	Ethylenediaminetetraacetate ion
heedta	$(HOCH_2CH_2)(OOCCH_2)NCH_2CH_2N(CH_2COO)_2^{3-}$	Hydroxyethylethylenediaminetriacetate ion
edda	$(OOCCH_2)NHCH_2CH_2NH(CH_2COO)^{2-}$	Ethylenediaminediacetate ion
nta	$N(CH_2COO)_3^{3-}$	Nitrilotriacetate ion
gly	$H_2NCH_2COO^-$	Glycinate ion
ox	$OOC\text{–}COO^{2-}$	Oxalate ion
en	$H_2NCH_2CH_2NH_2$	Ethylenediamine
dien	$H_2NCH_2CH_2NHCH_2CH_2NH_2$	Diethylenetriamine
trien	$(H_2NCH_2CH_2NHCH_2\text{–})_2$	Triethylenetetramine
tetren	$(H_2NCH_2CH_2NHCH_2CH_2)_2NH$	Tetraethylenepentamine

precipitation or because different ligand salts were available. None of the anions used forms nickel complexes.

Measurements.—Absorbance values were obtained with a Cary 14 spectrophotometer using 10-cm cells and 0–0.5 or 0–1.0 slidewires. Each system was checked for equilibrium by repeating spectral scans over an interval of 1 day or more. Stationary absorbance measurements were made at the desired wavelengths. For each system calculations were made from data at two or more wavelengths. There was no variation of the constants with the wavelength.

A Beckman Research pH meter (Model 101900) was used for pH measurements calibrated with NBS standard buffers. The protonation constant for ammonia was measured at 0.50 *M* ionic strength. This gave a mixed concentration–activity constant where the activity of H^+ was defined operationally. However, this constant and subsequent pH measurements were used to calculate the concentration of NH_3 so that the stability constants for the ammine mixed complexes used only concentration units. In the case of the en and gly mixed complexes the literature values for the protonation constants at 0.5 μ were used.[5,16–18] The value of $-\log [H^+]$ was estimated by subtracting 0.1 unit from the measured pH relative to NBS buffers.[19,20] All solutions were maintained at 25.0°.

Protonation Constant of Ammonia.—The protonation constant of ammonia at an ionic strength of 0.50 μ ($NH_4Cl + KCl$) was determined spectrophotometrically by a procedure similar to that described by Ang.[21] Thymol blue (thymol sulfonephthalein) was the indicator (HZ) used. The pertinent equations are

$$K_{HZ} = \frac{[HZ]}{(H^+)[Z^-]},\ K_{NH_4} = \frac{[NH_4^+]}{[NH_3](H^+)}$$

$$\log K_{HZ} = pH + \log [(A - A_Z)/(A_{HZ} - A)]$$

$$\log K_{NH_4} = \log K_{HZ} - \log [(A - A_Z)/(A_{HZ} - A)] + \log [[NH_4^+]/[NH_3]]$$

where *A* is the observed absorbance of the solution at 596 mμ. A_{HZ} and A_Z are the absorbances for pure HZ and Z^-, respectively. The molar absorptivity of Z^- was 39,000 while that of HZ was negligible.

Solutions for the determination of $\log K_{HZ}$ of thymol blue were 2.3×10^{-5} *M* in thymol blue, 0.50 *M* in KCl, and 0.011–0.025 *M* in borax. The pH meter was standardized at pH 9.177 with a freshly prepared 0.010 *M* borax solution. The $\log K_{HZ}$ value was 8.76 ± 0.01.

Solutions in which the ammonium chloride to ammonia ratio varied from 9 to 1.8 were prepared for the determination of $\log K_{NH_4}$. The thymol blue concentration was 2.4×10^{-5} *M* and the ionic strength was adjusted to 0.50 *M* by the addition of KCl. The $\log K_{NH_4}$ was 9.43 ± 0.02.

Methods of Calculation. Computer Method.—The stability constants of the mixed-ligand complexes were determined by an iterative computer method and by a linear graphical method whenever possible. The computer program proposed by Conrow, *et al.*,[22] for the determination of formation constants from spectrophotometric data was used with slight modifications to convert from FORTRAN I to FORTRAN IV and to include the protonation constants of the second coordinating ligand. An IBM 7094 computer was used.

A maximum of 25 reiterations was used in the computer program to find the best fit of the equilibrium constant and molar absorptivity of the complex. The reliability of the calculated constant was tested by applying a pseudo-*F* test to the sum of the squares of the difference between calculated and observed absorbances at the equilibrium value and at a value equal to ±10% of the equilibrium constant. The constant was included in the average of the computer results only if the ratio of the sum of squares at ±10% *K* to the sum of squares at *K* was more than the standard *F* value at the 95% confidence level.

Graphical Method.—The stability constant and molar absorptivity of the complex also were calculated by a slope–intercept graphical method. The stability constant can be calculated from a graphical plot of eq 1 if the following conditions are valid: the parent complex is completely formed; only a 1:1 mixed-ligand complex is formed between NiL and X; $[NiLX] << ML_T + X_T$; and $[NiLX]^2 << ML_TX_T$.

$$\frac{(NiL_T + X_T)\Delta A}{X_T} = \frac{-[1 + (H^+)K_{HA}]\Delta A}{K_{NiLX}X_T} + bNiL_T\Delta\epsilon \quad (1)$$

where NiLX is the mixed-ligand complex, NiL is the parent complex, NiL_T is the sum of [NiL] and [NiLX], X_T is the sum of [X], [HX], and [NiLX], A_0 is the absorbance of NiL_T, ΔA is the change in the absorbance $(A - A_0)$, $\Delta\epsilon$ is the difference in molar absorptivity between ϵ_{NiLX} and ϵ_{NiL}, K_{NiLX} is equal to $[NiLX]/[NiL][X]$, K_{HX} is equal to $[HX]/(H^+)[X]$, and *b* is the cell path.

The stability constant and the molar absorptivity of the mixed-ligand complex were calculated from the slope and intercept, respectively, of a plot of $(NiL_T + X_T)\Delta A/X_T$ *vs.* $[1 + (H^+)K_{HA}] \cdot \Delta A/X_T$. The slope and intercept were determined by least squares.

Results

The stability constants were determined spectrophotometrically under conditions such that there was negligible dissociation of the parent complex, NiL, and negligible interference from protonated or hydroxide species of NiL.

Three to six sets of solutions were prepared for each system with four to nine solutions for each set. Most sets of solution were measured at two or more wavelengths so that six to ten sets of data were available to calculate the constant. The concentration of the second coordinating ligand, X, within a given set was

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TABLE II

SUMMARY OF STABILITY CONSTANTS AND CONDITIONS USED

K_{NiLX}	Conditions[a]					
	$10^3[NiL]$, *M*	$[X]$, *M*	pH	No. of sets of solutions	Ionic strength, *M* (salt used)	Log K_{NiLX}[b]
$\frac{[Ni(edta)(NH_3)^{2-}]}{[Ni(edta)^{2-}][NH_3]}$	0.95–7.6	0.006–2.6	9.2–10.2	4	0.50 (KCl)	1.35 ± 0.05[c]
	2.0	0.1–0.4	9.97	1	1.00 ($NaClO_4$)	1.39 ± 0.01[d]
$\frac{[Ni(heedta)(NH_3)^-]}{[Ni(heedta)^-][NH_3]}$	1.9–9.5	0.008–0.27	8.6–10.0	6	0.50 (KCl)	2.00 ± 0.07
$\frac{[Ni(nta)(NH_3)^-]}{[Ni(nta)^-][NH_3]}$	9.7–13.6	0.06–0.66	7.5–8.2	4	0.50 ($NaClO_4$)	2.54 ± 0.04
$\frac{[Ni(tetren)(NH_3)^{2+}]}{[Ni(tetren)^{2+}][NH_3]}$	9.1–18.8	0.07–0.71	9.3–10.2	4	0.50 ($NaClO_4$)	0.83 ± 0.05[e]
$\frac{[Ni(edda)(NH_3)]}{[Ni(edda)][NH_3]}$	10.4–12.5	0.13–0.51	7.3–8.0	4	0.50 ($NaClO_4$)	2.00 ± 0.06
$\frac{[Ni(nta)(ox)^{3-}]}{[Ni(nta)^-][ox^{2-}]}$	9.85	0.008–0.1	6.7–8.2	4	0.50 (KNO_3)	2.17 ± 0.04
$\frac{[Ni(nta)(en)^-]}{[Ni(nta)^-][en]}$	9.85–19.7	0.009–0.15	6.0	3	0.50 ($NaClO_4$)	7.20 ± 0.06
$\frac{[Ni(nta)(gly)^{2-}]}{[Ni(nta)^-][gly^-]}$	9.85–19.7	0.01–0.15	6.3–7.0	4	0.50 (NaCl)	4.89 ± 0.04
$\frac{[Ni(dien)gly)^+]}{[Ni(dien)^{2+}][gly^-]}$	5.0–6.5	0.002–0.017	6.7–7.0	3	0.50 (NaCl)	5.13 ± 0.09
$\frac{[Ni(dien)(ox)]}{[Ni(dien)^{2+}][ox^{2-}]}$	$[NiCl_2] = 0.003$ $[dien] = 0.0015–0.014$	0.015	5.65	3	1.00 (KCl)	4.59 ± 0.05

[a] At 25.0°. [b] Error limits are standard deviations except where noted. Two or more wavelengths were used for most sets and all data were used which met the test criteria. [c] Constants calculated at three wavelengths: 380, 545, and 580 mμ. [d] Two wavelengths: 380 and 980 mμ. Error limit is range. [e] One wavelength: 540 mμ.

varied to give a range of at least 20–80% mixed-complex formation. The pH and NiL concentration were constant for each set but were varied between sets of solutions.

Table II summarizes the conditions used and gives the average stability constant with the standard deviation for all of the sets of data which met the criteria of the graphical method and the reliability test of the computer method. Complete information including spectra, individual absorbance values, molar absorptivities, graphical plots, the computer program, and evaluation of the data are given in ref 1. Absorbance measurements were the limiting source of precision for all systems except $[Ni(nta)(en)]^-$, and in this case the precision was limited by the pH measurement.

With $[Ni(nta)(ox)]^{3-}$ the calculations were done only by the computer method because the oxalate concentrations were not large enough to meet the conditions for the graphical method.

The pH range in which $[Ni(nta)(en)]^-$ could be studied was very limited owing to interference from the disproportionation reaction to give $Ni(nta)_2^{4-}$ and $Ni(en)_2^{2+}$. The same was true for $[Ni(dien)(gly)]^+$.

The $[Ni(nta)(gly)]^{2-}$ complex was studied below pH 7 to meet the requirements for the graphical plot.

The stability constant for the addition of oxalate ion to $Ni(dien)^{2+}$ was too large to measure by direct spectrophotometric techniques. Therefore the reaction system in eq 2 was used. The successive stability constants of the nickel oxalate complexes[11] used in the calculations are log $K_1 = 4.10$, log $K_2 = 3.05$, and log $K_3 = 1.36$. The protonation constants of dien are log $K_1 = 10.06$, log $K_2 = 9.36$, and log $K_3 = 4.86$.[23,24] Absorbance and pH measurements were made within 2 hr after solution preparation. After 12 hr or more nickel oxalate frequently precipitated.

$$Ni(ox)_2^{2-} + H_2dien^{2+} \rightleftarrows Ni(dien)(ox) + ox^{2-} + 2H^+ \quad (2)$$

The stability constant for each datum point was calculated assuming a $[Ni(dien)(ox)]$ complex. All three nickel oxalate species and the mixed-ligand complex were taken into consideration for the absorbance and equilibrium constant calculations. A special reiterative program was written for the computations.

The stability constant of the dien complex of Ni(ox) was log $K = 11.44 \pm 0.05$. The value of the oxalate complex of $Ni(dien)^{2+}$ used in the present comparison was calculated from the combined formation constants of the dien mixed complex, Ni(ox), and $Ni(dien)^{2+}$ and found to be log $K = 4.59 \pm 0.05$. The error limits do not consider the accuracy of the other constants used in its calculation and this constant is the least certain of the ten mixed complexes.

Discussion

Stability constants log $K = 2.26$ at 380 mμ and log $K = 2.56$ at 980 mμ have previously been reported for $[Ni(edta)(NH_3)]^{2-}$ by Bhat and Krishnamurthy.[25]

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Neither value agrees with the value we measured. We repeated our measurements using the same conditions as those reported by Bhat and Krishnamurthy and found log K = 1.39 at 1.00 μ ($NaClO_4$) and 25.0° for both 380 and 980 mμ. It appears that their constant was in error because they assumed complete formation of the mixed complex under conditions in which this was not valid. The value reported in the present work agrees with the value found by temperature-jump relaxation,[26] log K = 1.36, and with the estimated value of log K = 1.3 by Jørgensen.[27]

Israeli reported log K = 4.4 for the glycine complex of Ni(nta)$^-$, at 0.5 M $NaNO_3$. The temperature was not given.[28]

Curtis[29] has reported spectrophotometric evidence for a $[\{Ni(dien)\}_2ox]^{2+}$ complex in aqueous solution, although he did not determine its stability constant. The concentration conditions of the present work did not favor the formation of a hemioxalate complex and our data could not be resolved in terms of such a complex. Our data did fit the assumption of a 1:1 complex.

Some of the same ammine mixed complexes were studied in temperature-jump relaxation kinetic work[26] and gave similar stability constants. The relaxation data gave log values of 1.40 for $[Ni(tetren)(NH_3)]^{2+}$ at 0.40 μ, 2.2 for $[Ni(nta)(NH_3)]^-$ at 0.25 μ, 1.54 for $[Ni(heedta)(NH_3)]^-$ at 0.25 μ, and 1.36 for $[Ni(edta)(NH_3)]^{2-}$ at 0.40 μ. Considering the differences in ionic strength, the agreement is satisfactory except for the tetren complex, but the tetren system gave the poorest fit in the relaxation study.

It is interesting to note that in some cases the stability constants of the mixed complexes are not much different from the formation constants of the complexes formed from the nickel aquo species. This is seen in the case of $[Ni(nta)(en)]^-$, log K = 7.20, compared to $Ni(en)^{2+}$, log K = 7.60;[16] $[Ni(dien)(gly)]^+$, log K = 5.13, compared to $Ni(gly)^+$, log K = 5.77;[5] and [Ni(dien)(ox)], log K = 4.59, compared to Ni(ox), log K = 4.10.[11] The latter example is especially interesting because the stability constant of oxalate with $Ni(dien)^{2+}$ is greater than that of oxalate with aquonickel. In some cases the stability constant of the mixed complex is much lower than that of the simple nickel complex. This is particularly true for $[Ni(nta)(ox)]^{3-}$, log K = 2.17, compared to Ni(ox), log K = 4.10, and $[Ni(tetren)(NH_3)]^{2+}$, log K = 0.84, compared to $Ni(NH_3)^{2+}$, log K = 2.80.[5]

Factors Affecting Values of the Stability Constants

The variation of the stability constants in Table II cannot be explained without consideration of a number of factors. It is desirable to evaluate the relative importance of electrostatic effects, chelation, and the number and types of groups bound. It was assumed that each of these effects could be treated independently and that the free energy change in mixed-complex formation could be treated as the sum of free energy changes associated with each. Equation 3 gives the

$$\Delta G_{\mathrm{NiLX}} = (b\Delta G_{\mathrm{LN}} + a\Delta G_{\mathrm{LC}}) + (d\Delta G_{\mathrm{Ch}} + Z_1Z_2\Delta G_{\mathrm{Z}} + Z_1\Delta G_{\mathrm{DZ}} + n\Delta G_{\mathrm{XN}} + c\Delta G_{\mathrm{XC}}) \quad (3)$$

effects which were considered. The first two terms refer to the effect which groups coordinated to the nickel have on the second ligand; $b\Delta G_{\mathrm{LN}}$ is for b bound nitrogens and $a\Delta G_{\mathrm{LC}}$ for a bound carboxylate groups. The remaining terms are for the interaction of the second ligand, X, with the complex NiL. The term $d\Delta G_{\mathrm{Ch}}$ is for d chelate rings formed by X. The ion–ion electrostatic term is $Z_1Z_2\Delta G_{\mathrm{Z}}$ where Z_1 and Z_2 are the charges of NiL and X, respectively. The ion–dipole term is $Z_1\Delta G_{\mathrm{DZ}}$. The last two terms, $n\Delta G_{\mathrm{XN}}$ and $c\Delta G_{\mathrm{XC}}$, refer to the free energy changes resulting from n amine bonds and c carboxylate bonds replacing coordinated water.

Equation 3 was fitted by computer to the values of the stability constants in Table II by means of a weighted linear regression analysis program (WRAP).[30] A value was assigned to ΔG_{Ch} (−3.82 kcal) from Schwarzenbach's calculation of the chelate effect for nickel(II).[31] The formation constant for $Ni(NH_3)^{2+}$, log K = 2.85,[5,32] was included and weighted heavily. This value appears in the terms ΔG_{DZ} and ΔG_{XN}. The point 0,0 was weighted heavily to ensure no intercept value would be obtained. The values determined for ΔG_{i} are: 0.55 kcal for ΔG_{LN}, −0.58 kcal for ΔG_{LC}, 1.03 kcal for ΔG_{Z}, −0.61 kcal for ΔG_{DZ}, −2.68 kcal for ΔG_{XN}, and 0 for ΔG_{XC}.

In all complexes the ligand X is assumed to displace only coordinated H_2O molecules and not segments of L. There are several reasons to believe that edta and heedta have five or fewer groups coordinated to nickel and that the complexes have one or more waters coordinated.[33–36] The fact that one carboxylate group is not coordinated in $Ni(edta)^{2-}$ led to the use of separate terms for coordinated carboxylates (ΔG_{LC}) and for electrostatic effects (ΔG_{Z} and ΔG_{DZ}).

The computer fit indicates that the primary factors determining the stability of the mixed complexes are chelation (ΔG_{Ch}), the presence of nitrogen donors in X (ΔG_{XN}), and the ion–ion electrostatic term (ΔG_{Z}). Aside from the electrostatic effect, the replacement of H_2O by a carboxylate group has no effect ($\Delta G_{\mathrm{XC}} = 0$). Other factors do make significant contributions, however. The ion–dipole (permanent and induced) is less than the ion–ion term but is still important. The bound nitrogens (ΔG_{LN} = +0.55 kcal) tend to reduce

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Table III

Comparison of Calculated[a] and Observed Values of ΔG_{NiLX} (kcal)

Complex	$b\Delta G_{\mathrm{LN}}$	$a\Delta G_{\mathrm{LC}}$	$d\Delta G_{\mathrm{Ch}}$	$Z_1Z_2\Delta G_Z$	$Z_1\Delta G_{\mathrm{DZ}}$	$n\Delta G_{\mathrm{XN}}$	ΔG_{NiLX} Calcd	Obsd
$[\mathrm{Ni(edta)(NH_3)}]^{2-}$	1.10	−1.74	0	0	1.22	−2.68	−2.10	−1.85
$[\mathrm{Ni(heedta)(NH_3)}]^{-}$	1.10	−1.74	0	0	0.61	−2.68	−2.71	−2.72
$[\mathrm{Ni(nta)(NH_3)}]^{-}$	0.55	−1.74	0	0	0.61	−2.68	−3.26	−3.44
$[\mathrm{Ni(tetren)(NH_3)}]^{2+}$	2.75	0	0	0	−1.22	−2.68	−1.15	−1.14
$[\mathrm{Ni(edda)(NH_3)}]$	1.10	−1.16	0	0	0	−2.68	−2.74	−2.72
$[\mathrm{Ni(nta)(ox)}]^{3-}$	0.55	−1.74	−3.82	2.06	0	0	−2.95	−2.95
$[\mathrm{Ni(nta)(en)}]^{-}$	0.55	−1.74	−3.82	0	0.61	−5.36	−9.76	−9.79
$[\mathrm{Ni(nta)(gly)}]^{2-}$	0.55	−1.74	−3.82	1.03	0	−2.68	−6.66	−6.65
$[\mathrm{Ni(dien)(gly)}]^{+}$	1.65	0	−3.82	−2.06	0	−2.68	−6.91	−6.98
$[\mathrm{Ni(dien)(ox)}]$	1.65	0	−3.82	−4.12	0	0	−6.29	−6.24

[a] Using $\Delta G_{\mathrm{LN}} = 0.55$, $\Delta G_{\mathrm{LC}} = -0.58$, $\Delta G_{\mathrm{Ch}} = -3.82$, $\Delta G_Z = 1.03$, $\Delta G_{\mathrm{DZ}} = 0.61$, and $\Delta G_{\mathrm{XN}} = -2.68$ kcal.

the coordinating strength of X. The effect of the bound carboxylate groups must be considered as a combination of ΔG_{LC}, ΔG_Z, and ΔG_{DZ}. Although ΔG_{LC} is −0.58 kcal, this is offset by the electrostatic terms so that carboxylate groups do not necessarily increase the coordinating strength of X.

Table III shows the fit of the calculated and observed values of ΔG_{NiLX}. The empirical equation gives an excellent fit for these ten complexes. The prediction of other stability constants can be used to test the validity of the equation. Table IV shows that the agreement is good except in the case of Ni(trien)(ox) where there may be a change in the coordination positions of trien. Some variations may be due to ionic strength differences.

Table IV

Comparison of Calculated and Observed ΔG_{NiLX} for Mixed-Ligand Complexes Reported in the Literature

Complex	ΔG_{NiLX}, kcal Calcd	Obsd	μ	Ref
$[\mathrm{Ni(en)(NH_3)}]^{2+}$	−2.80	−3.05	0.25	*a*
$[\mathrm{Ni(dien)(NH_3)}]^{2+}$	−2.25	−2.53	0.25	*a*
$[\mathrm{Ni(trien)(NH_3)}]^{2+}$	−1.70	−1.90	0.40	*a*
$[\mathrm{Ni(gly)(NH_3)}]^{+}$	−3.32	−3.20	0.25	*a*
$[\mathrm{Ni}(\alpha,\beta\text{-dpa})(\mathrm{NH_3})]^{+}$	−2.77	−2.56	0.25	*a*
$[\mathrm{Ni(trien)(ox)}]$	−5.74	−4.35	0.10	*b*
$[\mathrm{Ni(ox)(en)}]$	−10.34	−9.78	1.00	*c*

[a] See ref 26. [b] D. W. Margerum and W. Crouse, to be published. [c] See ref 11.

The predictions of eq 3 are excellent which might be expected by fitting seven variables. Actually, the assignment of the chelation effect and the heavy weighting of the $\mathrm{Ni(NH_3)^{2+}}$ stability constant permitted only four variables to be fitted without limitations. Attempts to fit the data with fewer variables were not successful and more variables gave no better fit. The empirical equation neglects many effects including statistical variations which are minor for these systems. The electrostatic terms treat the over-all charge of the complex as a point charge which is a gross approximation. No correction was made for the bonding of one group on the other when X is bidentate. Nor were multiple dipoles considered. There is a rationale for this because intraligand repulsion from induced dipoles also was neglected.

Equation 3 also predicts the free energy change ($\Delta G_f = \Delta G_{\mathrm{NiLX}}$) for many monodentate and bidentate complexes of nickel (see Table V). With more than two dentate groups in a ligand, a correction term was needed for the effect which groups have on each other. This was accomplished by assigning a value of $\Delta G_{\mathrm{Ch}} = -2.10$ kcal for the second, third, and fourth chelate rings. The reduced value for ΔG_{Ch} combines many effects but allows reasonable predictions as shown in Table V.

Table V

Comparison of Calculated and Observed ΔG_f[a] for Aminocarboxylate and Polyamine Complexes of Nickel

Complex	ΔG_f, kcal Calcd	Obsd[b]	Diff. kcal column 3 − 2
$\mathrm{Ni(NH_3)^{2+}}$	−3.90	−3.88	+0.02
$\mathrm{Ni(NH_3)_2^{2+}}$	−3.35	−3.05	+0.30
$\mathrm{Ni(NH_3)_3^{2+}}$	−2.80	−2.35	+0.45
$\mathrm{Ni(NH_3)_4^{2+}}$	−2.25	−1.62	+0.63
$\mathrm{Ni(en)^{2+}}$	−10.40	−10.34	+0.06
$\mathrm{Ni(en)_2^{2+}}$	−9.30	−8.84	+0.46
$\mathrm{Ni(en)_3^{2+}}$	−8.20	−6.80	+1.40
Ni(ox)	−7.94	−5.58	+2.36
$\mathrm{Ni(ox)_2^{2-}}$	−3.77	−4.15	−0.38
$\mathrm{Ni(ox)_3^{4-}}$	−2.02	−1.85	+0.17
$\mathrm{Ni(gly)^{+}}$	−8.56	−7.85	+0.71
$\mathrm{Ni(gly)_2}$	−7.56	−6.53	+1.03
$\mathrm{Ni(dien)^{2+}}$	−15.18	−14.45	+0.73
$\mathrm{Ni(trien)^{2+}}$	−19.96	−19.18	+0.78
$\mathrm{Ni(tetren)^{2+}}$	−24.74	−23.70	+1.04
Ni(edda)	−17.50	−18.36	−0.76
$\mathrm{Ni(edta)^{2-}}$	−23.72	−24.98	−1.26
$\mathrm{Ni(heedta)^{-}}$	−21.66	−23.12	−1.46
$\mathrm{Ni(nta)^{-}}$	−16.88	−15.68	+1.20
Ni(ida)	−12.72	−11.23	+1.49

[a] ΔG_f values are for stepwise formation of the complexes. [b] Stability constants are from ref 5.

Conclusions

This study has shown that several factors contribute significantly to the stability of mixed complexes. With ten nickel aminocarboxylate and polyamine complexes it was possible to separate these factors into a chelation term, an ion–ion or ion–dipole term, and terms for the number of amine and carboxylate groups bound to nickel. It is interesting that these factors can be combined to predict the stability constants of many other complexes. Although the correlation is empirical, large deviations from the predicted values would suggest the replacement of groups other than water or would suggest steric interference.

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Aromatization of an Aliphatic Amine Oxime Nickel(II) Complex by Molecular Oxygen

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In basic aqueous media, molecular oxygen as well as other oxidizing agents oxidize an aliphatic tetradentate α-amine oxime complex of nickel(II), [Ni(PnAO)-H]$^+$.[2] Four electrons are ultimately removed from the organic portion of the complex resulting in the diamine chelate ring becoming pseudo-aromatic in character. The product (in yields of 90% of theoretical) has the empirical formula [Ni(PnAO)-6H]^0, is planar, and is stable at room temperature to replacement reaction by neutral or basic cyanide solutions. Its structure in solution and in the solid state is deduced by infrared and proton nmr studies.

During a study of the kinetic and thermodynamic stability of complexes of the tetradentate ligand PnAO,[3] it was noted that alkaline solutions of its nickel(II) complex slowly changed color and deposited crystals of a new complex on exposure to a CO_2-free atmosphere. It was demonstrated that [Ni(PnAO)-H]$^+$ was oxidized by molecular oxygen in a nonreversible fashion. Since this was a novel reaction and one related to the unsolved problem of the oxidation of bis(dimethylglyoxamato)nickel(II) by molecular oxygen and other oxidizing agents, studies were carried out to ascertain the nature of the oxidized product.

The starting complex, [Ni(PnAO)-H]$^+$, is one of a series of closely related compounds whose molecular structure has been reasonably well established[4] and some of the work to be presented confirms it as I. The resulting oxidized complex will be shown to have the molecular structure given by II. This paper reports studies to determine the stoichiometry of the reaction shown in Figure 1, its generality, and the structure and reactivity of the product.

Experimental Section

PnAO.—The preparative method used for EnAO[4] was modified using 1,3-diaminopropane. To a 10% excess of 2-chloro-2-methyl-3-butanone oxime in 400 ml of 0° absolute methanol was added 0.45 mole of 1,3-diaminopropane. It was maintained at 0–5° for 2 hr and at room temperature for 2 hr; then it was refluxed for 15 hr. The solvent was removed under vacuum and the solid was extracted with water. A large excess of a saturated solution of Na_2CO_3 followed by several milliliters of 10 *M* NaOH was added until a pH of 10–11 was reached. The white crystalline solid was collected, washed with cold water, and recrystallized from boiling methanol; yield, recrystallized, 53% of theory; mp 180–181°. *Anal.* Calcd for $C_{13}H_{28}O_2N_4$: C, 57.32; H, 10.36; N, 20.57. Found: C, 57.38; H, 10.28; N, 20.49.

[Ni(PnAO)-H]ClO$_4$.—This was prepared by the addition of equivalent amounts of PnAO dissolved in dilute HCl and $NiCl_2 \cdot 6H_2O$ followed by sufficient NaOH solution to make the mixture permanently neutral. Addition of an excess of $NaClO_4$ solution gave small yellow crystals which were recrystallized twice from hot water; yield, 80% of theory. *Anal.* Calcd for $C_{13}H_{27}O_6N_4ClNi$: C, 36.35; H, 6.34; N, 13.04; Ni, 13.67. Found: C, 36.35; H, 6.35; N, 12.95; Ni, 13.69. ϵ_{max} (water): 426 mμ, 130; 269 mμ, 7.8×10^3; 254 mμ, 7.5×10^3.

[Ni(PnAO)-6H]^0.—Oxygen gas was bubbled through a mixture of 1.0 g of [Ni(PnAO)-H]Cl and 15 ml of 1 *M* NaOH. After about 1 week the nearly colorless solution was removed and the orange crystals were collected. Extraction with ether removed insoluble impurities and after removal of this solvent it was recrystallized by the slow addition of water to an alcohol solution. A more rapid method involves adding solid KIO_3 (4–5 moles/mole of complex) to the [Ni(PnAO)-H]$^+$Cl$^-$ dissolved in 2 *M* aqueous NaOH. Within a few minutes the orange product crystallizes and may be purified as above. Either method can give yields about 90% of theory. *Anal.* Calcd for $C_{13}H_{22}O_2N_4Ni$: C, 48.03; H, 6.82; N, 17.24; Ni, 18.06. Found: C, 48.00; H, 7.00; N, 17.05; Ni, 17.93. ϵ_{max}(ethanol): 486 mμ, 145; 385 mμ, 3.2×10^3; 336 mμ, 5.2×10^3; 256 mμ, 1.6×10^4.

All chemicals were of reagent grade, recrystallized where necessary. The water was distilled and deionized by a double-bed column. For visible–ultraviolet spectral measurements a Beckman DU instrument fitted with a constant-temperature (25.1 ± 0.05°) cell compartment was used. Infrared spectra were taken as Nujol mulls on a Perkin-Elmer Model 237B instrument. Proton nmr measurements were made on concentrated solutions in deuterated solvents at about 30° with a Varian A-60 nmr spectrometer. An internal standard, tetramethylsilane, was employed. Oxygen uptake measurements were made using a conventional Warburg apparatus at 25.10 ± 0.05°. Magnetic susceptibility measurements were made with a conventional Gouy apparatus at two field strengths at room temperature. The

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[1] Abstracted in part from the Ph.D. thesis of E. G. Vassian, University of Missouri, 1967.

[2] The designation [-H] is meant to imply the essentially complete ionization of an H$^+$ from the ligand of the complex.

[3] PnAO is an abbreviation for 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone) dioxime.

[4] R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 521 (1957); R. K. Murmann, *ibid.*, **80**, 4174 (1958).