A strong absorption peak at 1220 cm^{-1} was attributed to F–H–F bond deformation, similar to the peak at 1233 cm^{-1} in the KHF_2 spectrum of Jones and Penneman.[5] The infrared spectrum of KH_2F_3 reported by Azman, *et al.*,[6] had a series of peaks at 1020, 1050, and 1082 cm^{-1} which they attributed to F–H–F bending. A peak at 1825 cm^{-1} was attributed to H–F stretching, similar to the peak at 1770 cm^{-1} in the spectrum of Azman.[6] Jones and Penneman[5] had observed a peak at 1820 cm^{-1} in solutions of KHF_2 in concentrated aqueous HF and attributed the peak to $H_2F_3^-$ ions. The salt is soluble in water, methanol, ethanol, acetonitrile, and DMF. It is slightly soluble in acetone, pyridine, benzene, carbon tetrachloride, carbon disulfide, and dichloromethane. It is insoluble in cyclohexane and chloroform.

It is not hygroscopic. The assay of a sample, as determined by titration with standard base, changed from 100.5 to 98.75% after standing in air for 36 hr. An infrared curve of a sample left standing in air for 48 hr had no peak which could be attributed to the presence of water.

The voltammetry of a 0.5 *M* solution of the salt in acetonitrile was investigated using a rotating platinum electrode (Sargent Model S-30420) and a saturated calomel reference electrode. The platinum electrode was rotated with a synchronous motor (Sargent Model S-76485) at 600 rpm. The voltammogram was obtained with a Sargent Model XV polarograph, without ir-drop compensation. A useful anodic working range of 0–2.4 V *vs.* sce was observed. This is similar to the range available in solutions of perchlorates in acetonitrile.[7]

The usefulness of the salt for electrolytic fluorination has been demonstrated. Controlled-potential electrolysis of 9,10-diphenylanthracene at 1.65 V *vs.* sce in a 0.4 *M* solution of the salt in acetonitrile produced 9,10-difluoro-9,10-dihydro-9,10-diphenylanthracene[8] in 43% yield.

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Kinetics and Mechanism of the Formation of Nickel(II) and Cobalt(II) Complexes of Glycine and Di-, Tri-, and Tetraglycine in Neutral to Acid Solution[1a]

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Previously, the temperature-jump[2,3] and stopped-flow[4] techniques have been used to determine complexation rate constants for glycine and some oligoglycines with nickel(II) and cobalt(II) ions. The temperature-jump studies are dependent, in part, on independent determinations of the stability constants for these systems. Recent studies have led to a better understanding of[5] and to new stability constants for[6] many of these systems. The stopped-flow technique, on the other hand, is less sensitive to equilibrium data but has been restricted to studies on the formation of the nickel(II) mono complexes, only. In neither case were activation studies carried out.

As a result, we have decided to reexamine the kinetics of nickel(II) and cobalt(II) peptide complexation, including activation studies for the formation of the mono complex of nickel(II). The studies have been carried out at pH's below the narrow region which gives rise to the yellow, diamagnetic complex for nickel;[5,6] therefore, this investigation refers to the so-called octahedral complexes of both metal ions.[7]

Treatment of Data

Relaxation Spectra.—The observed relaxation processes have been assigned to reactions of the type

$$\mathrm{MY}_{n-1}{}^{(3-n)+} + \mathrm{Y}^- \underset{k_{-n}}{\overset{k_n}{\rightleftharpoons}} \mathrm{MY}_n{}^{(2-n)+} \qquad (1)$$

In eq 1 $n = 1, 2,$ or 3; the symbol M is Ni or Co; the symbol Y^- represents the anionic form of the ligand, with all peptide nitrogen hydrogens (only glycine is not a peptide) attached. For the sake of convenience a further symbolism will be employed; namely, Y^- is G^- for glycine, HG_2^- for diglycine, $H_2G_3^-$ for triglycine, and $H_3G_4^-$ for tetraglycine. Hydrogens appearing in the G symbolism are bound to a peptide nitrogen.

Neither triglycine nor tetraglycine forms tris complexes.[5] Although glycine and diglycine form three complexes, experimental conditions were chosen so that not more than two reactions were appreciably coupled in any given experiment. Therefore, the general treatment of Hammes and Steinfeld could be applied.[2]

A complication in these studies is the dissociation of peptide hydrogens. In the G symbolism, an example would be

$$\mathrm{Ni(H_2G_3)^+} \rightleftharpoons \mathrm{Ni(G_3)^-} + 2\mathrm{H}^+ \qquad (2)$$

This process did not interfere with the analysis for two reasons. First, the reactions have been observed to be slow,[8] lying outside the time range of the temperature-jump technique. Second, to ensure (a) that the reactions will indeed be slow and (b) that species such as $Ni(G_3)^-$ will be in the minority, the pH was kept

[1] (a) The authors gratefully acknowledge partial support of PHS Research Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service, and of the Petroleum Research Fund for Grant 2982B (R. F. P.). (b) Department of Chemistry, Ithaca College, Ithaca, N. Y. 14850.

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[7] For detailed kinetic data, order Document No. NAPS-00359 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Remit $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

[8] R. G. Wilkins, private correspondence.

in the range 7–8. Reaction pathways *via* hydrolytic species of the type MOH^+ and/or other protonated forms of the ligand, especially the neutral form HY, have been tested. Within the limits of experimental error these reactions, which would lead to $[H^+]$-dependent terms, were not required to fit the data, nor did their inclusion improve the fit of the data. Therefore, reactions involving these species can be assumed to be insignificant under the conditions of this investigation.

Activation Analysis.—Studies of the kinetics of nickel complexation were feasible at temperatures other than 25°. (Attempts at a like treatment of cobalt(II) reactions were unsuccessful, owing to the smaller magnitude of the effects.) It proved possible to obtain values for k_1, despite the lack of equilibrium data.

Consider the first (uncoupled) reaction of (1). The reciprocal of the relaxation time is

$$1/\tau = k_1\{([\mathrm{Ni}^{2+}]/(1 + \alpha)) + [\mathrm{Y}^-]\} + k_{-1} \qquad (3)$$

where α is a term arising from the presence of rapid steps (in this case, acid–base reactions) always in equilibrium with (1).[2] Solutions could be prepared (at pH 7) so that the condition $[\mathrm{Ni}^{2+}]_0 \gg [\mathrm{Y}^-]_0$ (where the subscript zero refers to total stoichiometric concentration) allowed the approximation $[\mathrm{Ni}^{2+}]_0 \approx [\mathrm{Ni}^{2+}] \gg [\mathrm{Y}^-]$. The simplified form of eq 3, namely

$$1/\tau \cong k_1([\mathrm{Ni}^{2+}]_0/(1 + \alpha)) + k_{-1} \qquad (4)$$

was used to plot $1/\tau$ *vs.* $[\mathrm{Ni}^{2+}]_0/(1 + \alpha)$, yielding straight lines of slope k_1 and intercept k_{-1}.

While this procedure frequently leads to an imprecise determination of k_{-1}, it proves useful for obtaining k_1. As a check on the validity of this method, the ratio of rate constants was used to formulate the equilibrium quotient at the different temperatures employed; *viz.*, $K_1^{\mathrm{Ni}} = k_1/k_{-1}$. The values of nickel-complex stability quotients for similar ligands vary by a factor of about 2 with a rise in temperature from 25 to 40°.[9] Equilibrium quotients consistent with known values and with this trend were obtained by the use of (4).

Results and Discussion

The rate constants given in Table I were obtained by (1) reanalyzing previous temperature-jump results with the best available equilibrium data,[7] (2) carrying out additional relaxation experiments at 25°, and (3) performing new relaxation experiments over a temperature range from 25 to 57°. Within experimental error a plot of log k *vs.* $1/T$ for all three peptides describes a single straight line. Therefore, in terms of activation, the kinetic data fit the single Arrhenius equation

$$k_1 = 2.0 \times 10^{13} \exp[(-13{,}800 \pm 1400)/RT] \qquad (5)$$

for reaction of nickel(II) with di-, tri-, and tetraglycine.

For cobalt the oligopeptide k_1 rate constants show little variation among themselves. To a first approximation, the value of this rate constant may be taken as $3 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ for di-, tri-, and tetraglycine with cobalt(II). Although all four glycines attack as mononegative anions, the glycine value is approximately 5 times the oligoglycine value. The difference between these two rate constants, plus the fact that increasing the ligand size produces no appreciable effect on the k_1 rate constant, indicates that the decrease in reactivity is not due to a simple electrostatic effect. The lack of a variation in k_{-1} for the three oligopeptides and the difference from the glycine k_{-1} for cobalt(II) indicate that the binding for the amino acid is different from that of the peptides and that for the peptides the same type of binding is involved. Further evidence for the invariance of bonding mode among the oligopeptides may be found from a consideration of the nickel results.

TABLE I

RATE CONSTANTS FOR COMPLEXATION OF Co(II) AND Ni(II) WITH GLYCINES AT $\mu = 0.10\ M$

	Temp, °C	n	k_n, M^{-1} sec^{-1}	k_{-n}, sec^{-1}
(a) Cobalt				
Glycine	25	1	1.5×10^6	3.4×10
		2	2.0×10^6	3.3×10^2
		3	0.8×10^6	3.3×10^3
Diglycine	25	1	2.0×10^5	2.0×10^2
		2	1.6×10^5	8.4×10^2
Triglycine	25	1	3.1×10^5	2.8×10^2
		2	1.0×10^5	4.0×10^2
Tetraglycine	25	1	2.6×10^5	2.6×10^2
		2	2.3×10^5	7.2×10^2
(b) Nickel				
Glycine	25	1	4.1×10^4	5.7×10^{-2}
		2	5.6×10^4	9.3×10^{-2}
		3	4.3×10^4	1.1×10
Diglycine	25	1	3.2×10^3	1.5
		2	9.2×10^3	7.3
		3	4.0×10^3	1.3×10
	35.5	1	4.0×10^3	. . .
	46	1	9.9×10^3	. . .
	56	1	1.4×10^4	. . .
Triglycine	25	1	1.7×10^3	3.0×10^{-1}
		2	5.5×10^3	4.4
	35.5	1	3.3×10^3	. . .
	46.5	1	9.9×10^3	. . .
	57	1	1.4×10^4	. . .
Tetraglycine	25	1	1.8×10^3	4.0×10^{-1}
		2	4.9×10^3	2.5
	31.5	1	2.2×10^3	. . .
	37.5	1	4.8×10^3	. . .
	46	1	7.1×10^3	. . .
	56	1	1.8×10^4	. . .

Once again, the k_1 values for the higher glycines are essentially the same ($k_1 \approx 2 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$) and the dissociation rate constants are also in reasonable agreement. Furthermore, the activation analysis shows that a single set of activation parameters suffices to describe all three peptides over a temperature range, indicating that, within this range, a single rate constant describes the complexation kinetics of each peptide. As it had been observed for cobalt, the nickel–glycine k_1 is appreciably larger than that of the peptides. In fact, the ratio of k_1 values here is on the order of 20, whereas for cobalt it is 5.

Little variation of the k_2 values is observed for the

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peptides with either nickel(II) or cobalt(II). As before, the k_2 for glycine is appreciably greater. Increasing the ligand size does not appreciably decrease k_2, indicating therefore that the larger glycine k_2 cannot be ascribed to less blocking of coordinating sites by the bound ligand.

Consequently, it may be concluded that glycine complexation of nickel and cobalt is normal and may be compared with other ligands[10] and with the H_2O^{17} nmr studies on these two ions.[11] Chelation by the simplest peptides of identical charge derived from glycine is a slower process. Special intramolecular processes required by the peptides to form the stable chelate species may be the source of this relative kinetic inefficiency.

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Iodine as a Reference Soft Acid in Nonaqueous Solvents

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It is well known that empirical sequences showing relative hardness or softness of Lewis acids or bases are often altered by changing from one reference reactant to another. Drago and Wayland[1] proposed a double-scale enthalpy equation (eq 1) allowing a quantitative

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

basis for rationalizing such variations by resolving the molar enthalpy for adduct formation into electrostatic and covalent contributions. (The quantities E and C refer to the electrostatic and covalent parameters, respectively, for a given acid (A) and base (B) forming a 1:1 addition compound in a poorly solvating medium.) Iodine was selected as the reference soft acid and was assigned equal values (unity) of E_A and C_A. Since the electronic spectrum of iodine shows sizable solvatochromic effects, the study reported herein was undertaken to examine the correspondence between the spectral energetics of I_2–B adducts and the Drago–Wayland enthalpy parameters. The comparison of the magnitude of this spectral shift to other solvent properties was surveyed, as well.

The relationship between the Mulliken charge-transfer model[2] and the double-scale enthalpy equation was developed by Drago and Wayland, and the major consequence of this is that both electrostatic and covalent terms contribute significantly to the ground-state energy for the complex, even though the energies of interaction for such acids and bases are small. For specific complexes with I_2, Mulliken assigned the blue shift of the 520-mμ band (gas phase) of iodine in complexing solvents to repulsive exchange interactions between the iodine and the donor, and, therefore, the strength of the charge-transfer interaction proportionately raises the energy of the iodine excited state. However, since the total wave function for the ground state for the donor–I_2 complex involves the weaker London and dipole–dipole forces as well as the larger exchange forces, the Mulliken treatment does not preclude small blue shifts in poorly complexing aprotic solvents. Voigt[3] has attributed the latter effect to contact-charge-transfer perturbations and has observed a degree of correlation to the ionization potential of the solvent. The magnitude of the blue shift relates in a regular manner to the solvent ionization potential only for those liquids containing the same donor atom, and no correspondence between these variables is found for solvents having different donor atoms. The same conclusion applies when the dielectric constant of the base is plotted against λ_{max} of iodine. (Graph is not included here.)

Examination of the frequency shift in terms of both E_B and C_B should assist in clarifying which exerts the larger influence in specific I_2–donor interactions. The data required for such correlations are summarized in Table I and include the basic solvents for which Drago–Wayland parameters have been determined. Iodine transition energies ($E_T = 2.859 \times 10^{-3}/\lambda_{max}$) were calculated from the absorption maxima reported by Voigt.[3] Although not included herein, plots of the change in transition energy $[\Delta E_T = (E_T)_{soln} - (E_T)_{vap}]$ as a function of E_B or $-\Delta H$ were completely scattered with no general trends being apparent.

The shift in the I_2 transition energy with C_B of the solvent is shown in Figure 1. For each of the curves, it is clear that the magnitude of the I_2 blue shift increases with the increasing covalent parameters of the donor. In contrast to the solvent ionization potential, the C_B *vs.* ΔE_T function places the donors largely into two major groups: aprotic solvents (curve A) and hydrogen-bonding solvents (curve B). However, one important aprotic base, pyridine, falls well away from the curve, in contrast to the reasonably close fit for the other nitrogen bases. In terms of Pearson's HSAB principle,[4] the aromatics and aprotic oxygen, sulfur, and nitrogen bases on curve A usually show predominantly soft characteristics, and the hydrogen-bonding oxygen and nitrogen bases of curve B are hard. For the latter, increased stabilization of the ground state through hydrogen bonding in I_2–B may be responsible for raising E_T to a higher value than that for the aprotic base having the same donor atom.

The Kosower Z value[5] for a coordinating solvent has been useful in the estimation of the solvation energy for inorganic species in nonaqueous media, and in a number

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