

The results of the present structure determination support the idea that the M-N-O angle in complexes of the type $\text{MX}(\text{NO})\text{L}_2$ may be sensitive to changes of M, X, L and the coordination geometry of the complex. Further studies of these compounds are in progress.

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Thermodynamics of Ion Association. XXII. Nickel Complexes of Glycine, Diglycine, Triglycine, and Glycyl- γ -aminobutyric Acid¹

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Calorimetric studies have been made at 25° of the formation of nickel complexes of diglycine, triglycine, and glycyl- γ -aminobutyric acid and of subsequent proton dissociation from the triglycinate species at higher pH. The data have been combined with potentiometric measurements to provide ΔG , ΔH , and ΔS data for each of the equilibria. Values of the thermodynamic data strongly support a common structure for all the mono complexes at lower pH in which the nickel ion is bound to the terminal NH_2 and the oxygen of the peptide group.

There is considerable interest in the elucidation of the structures of metal peptide complex species in aqueous solution in view of their importance as model systems in biological studies. The results of a recent calorimetric study² of copper di-, tri-, and tetraglycine complexes indicated a common structure for each CuL^+ species where L^- represents the polyglycine anion. In these complexes, the copper ion is probably bound to the terminal amine nitrogen and the oxygen atom of the first peptide group in a five-membered chelate ring structure. Under progressively more alkaline conditions, stepwise ionization of the peptide hydrogen atoms takes place and metal coordination is transferred from the oxygen to the nitrogen atom of the peptide group in the formation of multichelated structures. Pasternack and his coworkers have recently studied the reactions of copper(II) with both glycyglycine and glycylysarcosine using temperature-jump techniques.³ The kinetic results are consistent with the proposed bidentate nitrogen and oxygen binding at lower pH. The proton ionization from the glycyglycine complex at higher pH is much slower and takes place with a considerably larger activation energy than that for the formation of CuL^+ reflecting the proposed structural rearrangement.

The coordination changes which take place in the presence of copper ions appear to be quite well characterized, but in the case of the corresponding nickel complexes, the situation is much less clear. In the pH range 4.5–6, stability constants for complexes between the nickel ion and the polyglycine anions, NiL^+ , were first reported by Evans and Monk⁴ and by Li and Chen.⁵ In one case,⁴ it was suggested that the metal-

ligand bonding involves neither the terminal amino nor the carboxylate groups. Li and Chen, however, proposed a metal-peptide chelate structure in which the nickel ion is attached to the terminal amino group and the immediately adjacent peptide group.⁵ The kinetics of formation of the nickel-glycylsarcosine complex was studied, using a temperature-jump method by Kustin and Pasternack.⁶ By comparing the kinetic data with those of the corresponding cobalt(II) complexes it was suggested that the coordination of the charged carboxylate group was not important in the formation of the nickel complexes. The rate constant for the glycylysarcosine complex was close to the values for the tri- and tetraglycine species⁷ indicating the nonparticipation of the carboxylate group in the oligoglycine ligands as well. The results of a recent nmr investigation, on the other hand, have been interpreted in terms of the binding of the charged carboxylate group to the nickel ion under neutral and slightly acidic conditions.⁸

The magnitude of the enthalpy changes accompanying ion association reactions in solution can yield information concerning the nature of the ligand atom bound to the metal ion,⁹ but hitherto, no direct calorimetric studies have been made of the nickel-polyglycine systems. In the present work, potentiometric and calorimetric investigations have been made of the formation of nickel complexes with glycine, diglycine, triglycine, and glycyl- γ -aminobutyric acid and also the proton dissociations from the nickel-polyglycine species.

Experimental Section

Glycine was obtained from Baker and Adamson and the diglycine and glycyl- γ -aminobutyric acid were obtained from Nutritional Biochemical Corp. and used without further purification. The source of triglycine and the method of purification

(1) Supported by National Science Foundation Grant GP 9231.

(2) (a) A. P. Brunetti, M. C. Lim, and G. H. Nancollas, *J. Amer. Chem. Soc.*, **90**, 5120 (1968); (b) G. H. Nancollas and D. J. Poulton, *Inorg. Chem.*, **8**, 680 (1969).

(3) R. F. Pasternack, M. Angwin, and E. Gibbs, *J. Amer. Chem. Soc.*, **92**, 5878 (1970).

(4) W. P. Evans and C. B. Monk, *Trans. Faraday Soc.*, **51**, 1244 (1955).

(5) N. C. Li and M. C. M. Chen, *J. Amer. Chem. Soc.*, **80**, 5678 (1958).

(6) K. Kustin and R. F. Pasternack, *J. Phys. Chem.*, **73**, 1 (1969).

(7) G. Davies, K. Kustin, and R. F. Pasternack, *Inorg. Chem.*, **8**, 1535 (1969).

(8) M. K. Kim and A. E. Martell, *J. Amer. Chem. Soc.*, **91**, 872 (1969).

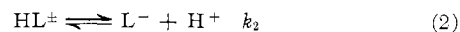
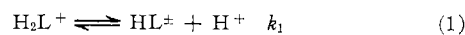
(9) G. Degischer and G. H. Nancollas, *J. Chem. Soc. A*, 1125 (1970).

have been described previously.^{2a} Nickel nitrate solution was prepared by dissolving the solid salt obtained from Fisher Scientific, in doubly distilled water which had been boiled and cooled under nitrogen. The concentration of nickel was determined by titrating samples against standard EDTA solution¹⁰ and also by passing samples through a Dowex 50 cation-exchange column and titrating the displaced acid with standard sodium hydroxide. The results from the two methods agreed to within 0.1%. Potassium nitrate solution was also standardized by the ion-exchange method.

Potentiometric Experiments.—Emf measurements were made using the apparatus and methods described previously.^{2a} Titrations were performed by adding sodium hydroxide to a solution containing a metal to ligand molar ratio of 1:2 for glycine, diglycine, and glycyl- γ -aminobutyric acid. In the case of triglycine, both 1:1 and 1:2 molar ratios were used. In determining the protonation constants of the ligands, similar titrations were performed in the absence of nickel ion. The ionic strength was maintained at 0.1 *M* by the addition of potassium nitrate solution. This mixture was titrated calorimetrically with nitric acid.

Results and Discussion

Successive proton dissociations of the ligand molecules can be expressed in terms of equilibria 1 and 2



in which L^- represents the anionic form of the ligands $\text{G}^- = \text{glycine}$, $\text{GG}^- = \text{diglycine}$, $\text{GGG}^- = \text{triglycine}$, and $\text{G-}\gamma\text{-A}^- = \text{glycyl-}\gamma\text{-aminobutyric acid}$. k_1 and k_2 were determined potentiometrically by titrating the neutral ligands with nitric acid and sodium hydroxide, respectively. The method of evaluating k_1 and k_2 from the experimental data has already been described.^{2a} Values of k_1 and k_2 for glycine and glycyl- γ -aminobutyric acid obtained in a similar manner are given in Table I; each value corresponds to the mean

TABLE I
PROTON DISSOCIATION CONSTANTS AT 25°

Glycine				Glycyl- γ -aminobutyric acid			
Ref	<i>I</i> , <i>M</i>	<i>p</i> <i>k</i> ₁	<i>p</i> <i>k</i> ₂	Ref	<i>I</i> , <i>M</i>	<i>p</i> <i>k</i> ₁	<i>p</i> <i>k</i> ₂
This work	0.1	2.39 ± 0.02	9.56 ± 0.01	This work	0.1	4.22 ± 0.02	8.12 ± 0.01
11	→0	2.39	9.77				
12,13	0.1	2.35	9.60				

of at least 21 experimental points. Some literature^{11–13} values for glycine are also presented for comparison in Table I and it is seen that the agreement with the present work is good.

To determine the enthalpy of proton dissociation ΔH_A and ΔH_B corresponding to equilibria 1 and 2, respectively, the ligand solutions were titrated with nitric acid. For equilibrium 2, the ligand solution contained initially a suitable amount of sodium hydroxide while for equilibrium 1, no alkali was added prior to titrations. The experimental procedure and method of calculation have been reported for the di- and triglycine systems^{2a} the results for glycine and glycyl- γ -aminobutyric acid are given in Table II. The calorimetric results of Anderson, Greenhalgh, and Izatt¹¹ for glycine, given in parentheses in Table II, refer to $I = 0$.

In solutions containing nickel ions with metal to

(10) G. Schwarzenbach, "Complexometric Titrations," H. Irving, Translator, Interscience, New York, N. Y., 1957.

(11) K. P. Anderson, W. O. Greenhalgh, and R. M. Izatt, *Inorg. Chem.*, **5**, 2106 (1966).

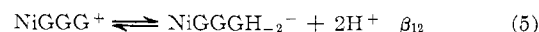
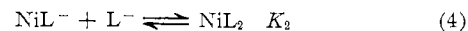
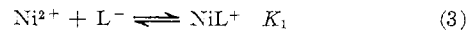
(12) E. J. King, *J. Amer. Chem. Soc.*, **67**, 2178 (1945).

(13) E. J. King, *ibid.*, **73**, 155 (1951).

TABLE II
THERMODYNAMIC FUNCTIONS FOR PROTON DISSOCIATION AT 25°

Equilibrium	ΔG , kcal mol ⁻¹	ΔH , kcal mol ⁻¹	ΔS , cal deg ⁻¹ mol ⁻¹
Glycine			
1	3.23	1.10	-7.2
2	13.04	10.20 (10.76)	-9.5 (-8.6)
Glycyl- γ -aminobutyric Acid			
1	5.76	0	-19.3
2	11.07	10.1	-3.2

ligand molar ratios less than 1:2 reactions 3–5 with



equilibrium constants K_1 , K_2 , and β_{12} , respectively, must be taken into account. Equilibrium 5 applies to the nickel-triglycine system at pH values greater than 8, NiGGH_{-2}^- referring to the deprotonated species. K_1 and K_2 for all the systems were determined potentiometrically by titrating a mixture of nickel nitrate with the respective ligands in 1:2 molar ratio with standard sodium hydroxide. The ionic strength of the solution was maintained at 0.10 ± 0.002 *M* by adding potassium nitrate solution.

Values of K_1 and K_2 were calculated by using expressions for mass balance and electroneutrality and the derived eq 6 involving the average ligand number \bar{n} .¹⁴

$$\frac{\bar{n}}{(1-\bar{n})[\text{L}]} = \frac{\bar{n}-2}{1-\bar{n}} [\text{L}]K_1K_2 + K_1 \quad (6)$$

The K_1 and K_2 values, obtained from the linear plots of $\bar{n}/(1-\bar{n})[\text{L}]$ against $(\bar{n}-2)[\text{L}]/(1-\bar{n})$, were refined by choosing a set of K_2 values in the neighborhood of the value indicated graphically and calculating K_1 values for each titration point. The value of K_2 corresponding to the lowest standard deviation in K_1 was determined and typical sets of data for diglycine and glycyl- γ -aminobutyric acid are summarized in Table III.

TABLE III
ASSOCIATION CONSTANTS FOR NICKEL COMPLEX FORMATION WITH GLYCYLGLYCINE (GG) AND GLYCYL- γ -AMINOBUTYRIC ACID (G- γ -A)

pH	GG ^a			G- γ -A ^b			
	10 ⁴ [GG ⁻], <i>M</i>	10 ³ [Ni-GG], <i>M</i>	10 ⁻⁴ <i>K</i> ₁ , <i>M</i> ⁻¹	pH	10 ⁴ [G- γ -A ⁻], <i>M</i>	10 ³ [Ni-G- γ -A], <i>M</i>	10 ⁻⁴ <i>K</i> ₁ , <i>M</i> ⁻¹
5.601	0.242	1.303	1.258	6.410	0.803	1.716	1.278
5.734	0.316	1.567	1.248	6.529	0.988	1.819	1.263
5.851	0.398	1.816	1.246	6.575	1.069	1.853	1.261
5.958	0.488	2.047	1.245	6.621	1.157	1.880	1.253
6.059	0.590	2.259	1.242	6.667	1.249	1.904	1.251
6.155	0.703	2.449	1.240	6.714	1.950	1.921	1.241
6.248	0.830	2.616	1.236	6.758	1.449	1.937	1.246
6.336	0.967	2.764	1.243	6.804	1.562	1.945	1.239
5.426	1.127	2.882	1.236	6.849	1.675	1.953	1.244
6.513	1.304	2.978	1.234	6.895	1.798	1.954	1.244
6.601	1.508	3.045	1.224	6.942	1.935	1.947	1.236
6.687	1.727	3.094	1.229	6.988	2.071	1.941	1.242
6.775	1.982	3.113	1.223	7.106	2.466	1.902	1.243
6.861	2.254	3.118	1.235	7.228	2.922	1.844	1.261
				7.357	3.485	1.756	1.254
				7.490	4.121	1.661	1.299

^a Total ligand concentration 1.116×10^{-2} *M*; total nickel concentration 5.710×10^{-3} *M*. ^b Total ligand concentration 8.072×10^{-3} *M*; total nickel concentration 3.807×10^{-3} *M*.

(14) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N. Y., 1961.

Values for the equilibrium constants and their standard deviations are given in Table IV together with values obtained by other workers.

TABLE IV
ASSOCIATION CONSTANTS IN KNO₃ MEDIA

Reactions	Log K	I, M	Ref
1. Ni + G ⇌ NiG	5.79	0.1 (KNO ₃)	a
	5.73	0.1 (KCl)	b
2. NiG + G ⇌ NiG ₂	4.78	0.1 (KNO ₃)	a
	4.76	0.1 (KCl)	b
3. Ni + GG ⇌ NiGG	4.11	0.1 (KNO ₃)	a
	4.17	0.14	
	3.34	0.1 (KNO ₃)	c
	3.93	0.16 (KNO ₃)	d
4. NiGG + GG ⇌ NiGG ₂	4.18	0.15 (KNO ₃)	e
	3.21	0.1 (KNO ₃)	a
	4.07	0.1 (KNO ₃)	c
5. Ni + G-γ-A ⇌ NiG-γ-A	3.25	0.15 (KNO ₃)	e
	4.11	0.1 (KNO ₃)	a
6. NiG-γ-A + G-γ-A ⇌ Ni(G-γ-A) ₂	3.38	0.1 (KNO ₃)	a
7. Ni + GGG ⇌ NiGGG	3.69	0.1 (KNO ₃)	a
	3.72	0.15 (KNO ₃)	e
	3.70	0.16 (KNO ₃)	d
8. NiGGG + GGG ⇌ Ni(GGG) ₂	3.04	0.1 (KNO ₃)	a
	2.90	0.16 (KNO ₃)	d

^a This work. ^b H. Irving, R. J. P. Williams, D. J. Ferrett, and A. E. Williams, *J. Chem. Soc.*, 3494 (1954). ^c M. K. Kim and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 5138 (1967). ^d R. B. Martin, M. Chamberlin, and J. T. Edsall, *ibid.*, **82**, 495 (1960). ^e Reference 4.

It is seen that the values compare very well with the literature values except in the case of nickel diglycine where values of K_1 and K_2 in ref 15 are in reverse order from the values obtained in this work and by others.^{4,16}

At the higher pH values reaction 5 must be taken into account in the case of nickel triglycine. Defining $\alpha = 1 + [H]/k_1 + [H]^2/k_1k_2$, $\beta = [H] + [Na] - [OH]$, and $\gamma = 1 - [H]^2/k_1k_2$, we derive the equation

$$[L]^2 + b[L] + c[L] + d = 0 \quad (7)$$

in which

$$b = \frac{2\alpha + (4T_{Ni} - T_L - \beta)K_2}{\alpha + \gamma}$$

$$c = \frac{(3\alpha - \gamma) + 2k_1(T_{Ni} - T_L)}{(\alpha + \gamma)k_1}$$

$$d = \frac{\beta - 3T_L}{(\alpha + \gamma)k_1}$$

where T_{Ni} is the total concentration of nickel ion, and T_L , the total concentration of triglycine. Equation 7 was solved by using a Newton-Raphson iterative procedure and calculated values of β_{12} are given in Table V; the mean value of $p\beta_{12}$ is 16.44 ± 0.01 .

Determinations of the enthalpy of reaction corresponding to equilibria 3-5 were carried out by titrating a mixture containing nickel ions, ligand, potassium nitrate, and sodium hydroxide with nitric acid. The advantages of this back-titration procedure have been discussed earlier.^{2a} The measured heat change, Q_{exptl} , corrected for the heat of dilution of the nitric acid into 0.1 M potassium nitrate is made up of terms associated with the formation of the various species represented by subscripts in the equation

$$Q_{\text{exptl}} = Q_{NiL} + Q_{NiL_2} + Q_{HL} + Q_{H_2L} + Q_{H_2O} \quad (8)$$

(15) M. K. Kim and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 5138 (1967).

(16) R. B. Martin, M. Chamberlin, and J. T. Edsall, *ibid.*, **82**, 495 (1960).

TABLE V
DISSOCIATION CONSTANTS OF NICKEL-TRIGLYCINE COMPLEXES^a

pH	10 ⁴ [L], M	10 ⁴ [ML], M	10 ⁴ [ML ₂], M	10 ³ [MLH- ₂], M	10 ¹⁷ β ₁₂
7.467	2.133	2.870	6.711	0.054	3.588
7.596	2.232	2.874	7.035	0.115	4.165
7.732	2.310	2.859	7.243	0.191	3.764
7.831	2.347	2.815	7.245	0.293	3.712
7.911	2.362	2.757	7.139	0.408	3.661
7.978	2.364	2.691	6.973	0.531	3.587
8.034	2.356	2.619	6.766	0.658	3.520
8.082	2.341	2.544	6.532	0.788	3.480
8.125	2.322	2.467	6.283	0.920	3.433
8.164	2.299	2.389	6.024	1.052	3.387
8.196	2.271	2.310	5.752	1.186	3.407
8.226	2.241	2.229	5.478	1.320	3.419
8.255	2.208	2.149	5.202	1.453	3.427
8.284	2.173	2.068	4.928	1.586	3.398
8.310	2.135	1.987	4.652	1.719	3.401
8.332	2.094	1.906	4.375	1.852	3.450
8.352	2.049	1.824	4.100	1.984	3.526
8.372	2.003	1.743	3.827	2.116	3.596
8.390	1.954	1.661	3.558	2.247	3.675
8.428	1.847	1.498	3.034	2.506	3.815
8.462	1.727	1.335	2.527	2.527	4.041
8.501	1.593	1.171	2.045	3.017	4.200

^a Initial conditions: total ligand concentration 5.303×10^{-3} M; total metal concentration 6.506×10^{-3} M.

from which eq 9 may be derived, where $\Delta[Ni]$ and

$$\frac{Q_{NiL} + Q_{NiL_2}}{\Delta[Ni]} = \frac{\Delta[NiL_2]}{\Delta[Ni]} \Delta H_{NiL_2} + \Delta H_{NiL} \quad (9)$$

$\Delta[NiL_2]$ represent the concentration changes of these species from point to point in the enthalpy titrations for which Q_{exptl} is measured. Individual Q values were calculated using the methods described previously.^{2a} Values of ΔH_{NiL} and ΔH_{NiL_2} were obtained by a least-squares procedure from the linear plots of $(Q_{NiL} + Q_{NiL_2})/\Delta[Ni]$ against $\Delta[NiL_2]/\Delta[Ni]$. Some typical plots are given in Figures 1 and 2 and values of the

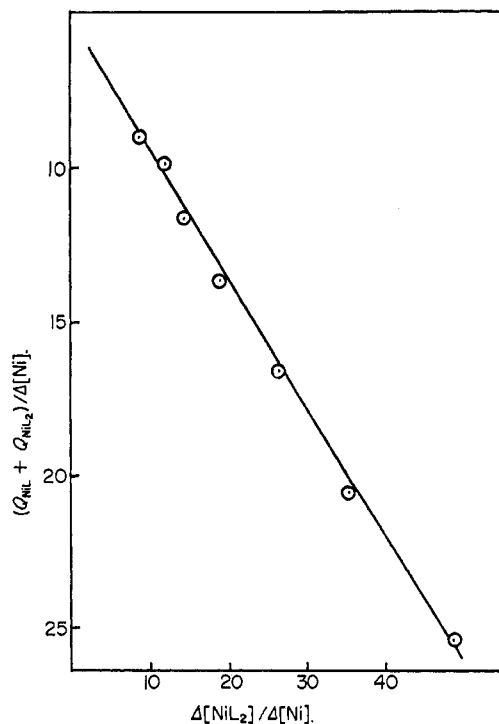


Figure 1.—Plot of $(Q_{NiL} + Q_{NiL_2})/\Delta[Ni]$ against $\Delta[NiL_2]/\Delta[Ni]$ for nickel-glycylglycine complex formation at 25°.

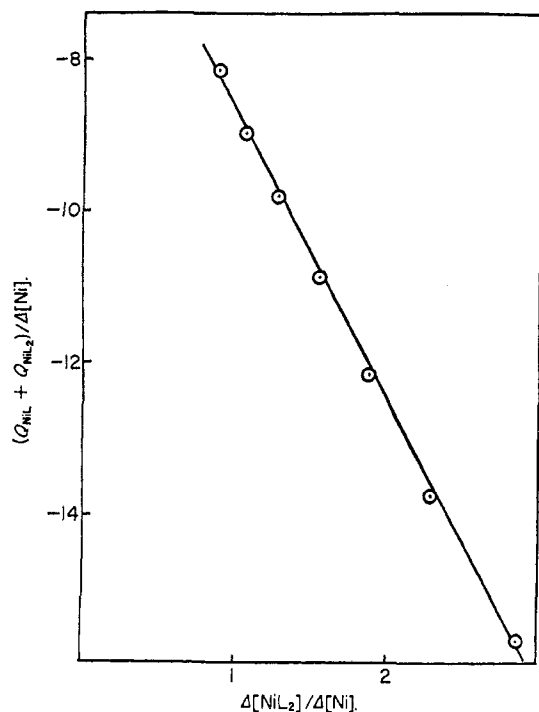


Figure 2.—Plot of $(Q_{\text{NiL}} + Q_{\text{NiL}_2})/\Delta[\text{Ni}]$ against $\Delta[\text{NiL}_2]/\Delta[\text{Ni}]$ for nickel-glycyl- γ -aminobutyric acid complex formation at 25°.

TABLE VI
THERMODYNAMIC FUNCTION AT 25°

Reactions	ΔG , kcal mol ⁻¹	ΔH , kcal mol ⁻¹	ΔS , cal deg ⁻¹ mol ⁻¹
$\text{Ni} + \text{G} \rightleftharpoons \text{NiG}$	-7.88	-5.0	9.6
$\text{NiG} + \text{G} \rightleftharpoons \text{NiG}_2$	-6.49	-4.4	7.0
$\text{Ni} + \text{GG} \rightleftharpoons \text{NiGG}$	-5.61	-5.4	0.7
$\text{NiGG} + \text{GG} \rightleftharpoons \text{NiGG}_2$	-4.38	-4.2	0.6
$\text{Ni} + \text{G-}\gamma\text{-A} \rightleftharpoons \text{NiG-}\gamma\text{-A}$	-5.61	-4.6	3.4
$\text{NiG-}\gamma\text{-A} + \text{G-}\gamma\text{-A} \rightleftharpoons \text{Ni(G-}\gamma\text{-A)}_2$	-4.61	-4.2	1.7
$\text{Ni} + \text{GGG} \rightleftharpoons \text{NiGGG}$	-5.03	-5.0 ^a	0.6 ^a
$\text{NiGGG} + \text{GGG} \rightleftharpoons \text{NiGGG}_2$	-4.17	-4.2 ^a	-0.5 ^a
$\text{NiGGG} \rightleftharpoons \text{NiGGGH-}_2 + 2\text{H}^+$	22.5	19.7	-9.4

^a Estimated values (see text).

thermodynamic functions are given in Table VI. Because of the narrow pH range accessible to experimental study of the triglycine system before the interference of equilibrium 5, it was not possible to determine ΔH_{NiL} and ΔH_{NiL_2} by the method described above. The value of $\Delta H_{\text{NiLH-}_2}$ was determined by introducing a term $Q_{\text{NiLH-}_2}$ into eq 8 and solving for ionic species in a manner similar to that described above. Values of ΔH_{NiGGG} and $\Delta H_{\text{Ni(GGG)}_2}$ required for the calculation were assumed to be the same as the corresponding values for glycine, diglycine, and glycyl- γ -aminobutyric acid. The justification for this choice stems from the fact that for the copper complexes, the values of ΔH_{CuL} for glycine, diglycine, and triglycine were almost identical.^{2a} Moreover, the value of $\Delta H_{\text{NiLH-}_2}$ in the present work is not at all sensitive to the individual choices of ΔH_{NiGGG} and $\Delta H_{\text{Ni(GGG)}_2}$, since the concentrations of these species were very small.

It is seen in Table VI that free energies of formation of mono and bis nickel-glycine complexes are appreciably more negative than in the case with diglycine or glycyl- γ -aminobutyric acid. Moreover, these enhanced stabilities are the result of more favorable entropy

changes; the enthalpy change in each case is strikingly constant. This indicates that the ligands are bound in these complexes in bidentate structures similar to that for glycine itself with the nickel ion bonded to the terminal NH_2 group and the oxygen of the first peptide group. The results for glycyl- γ -aminobutyric acid lend particular weight to the validity of this conclusion. The enthalpy changes for the formation of its complexes are close to those for the corresponding diglycine complexes. Glycyl- γ -aminobutyric acid would not be expected to act as a tridentate ligand since such a complex would involve the formation of an unstable eight-membered ring structure. An alternative possibility for formulating the structure of the NiL^+ species would involve the nitrogen of the peptide group. In the case of the diglycine complex, the carboxylate group would be in a favorable position to coordinate with the nickel atom since the resulting structure would involve a stable five-membered ring. However, in the case of glycyl- γ -aminobutyric acid, the formation of such a complex would still involve an unstable seven-membered ring structure.

Potentiometric experiments at very high ligand to metal ratios led Martin, Chamberlin, and Edsall¹⁶ to suggest that dissociation of the peptide hydrogen atom occurs at $\text{pH} > 10$. Recently¹⁷ a solid-state X-ray structure determination of single crystals obtained from such solutions indicates that the coordination center in the complex involves the primary amine nitrogen, the deprotonated peptide nitrogen atom, and the carboxylate group. Unlike the corresponding copper system in which dissociation takes place in the monodiglycinate, CuL^+ , in the case of nickel, dissociation occurs only in the bis species, NiL_2 . In the present study, attempts to determine the enthalpy of proton dissociation were unsuccessful since, in the accessible ranges of ligand to nickel ratio, precipitation of nickel hydroxide took place before the proton dissociation could be studied. In the corresponding triglycinate complexes, the proton dissociation could be studied without interference from nickel hydroxide. It is interesting to note here again that the nickel-triglycine system is different from its copper analog. Whereas in the copper-triglycine system, the dissociation of the two peptide protons occurs in a stepwise manner with a pK difference of close to 2 units,^{2a} in the nickel system the dissociation appears to take place in a single step as is evidenced from the flat titration curve. Further, the onset of dissociation is accompanied by the appearance of an absorption band with a maximum at 430 $\text{m}\mu$, which increases in intensity with no shift in frequency as dissociation progresses. In contrast, for the copper system the absorption maximum undergoes a shift in frequency as titration progresses.¹⁵ The nmr results of Mathur and Martin¹⁸ also suggest that the dissociation of peptide protons occurs in one step in nickel triglycine.

The dissociation of peptide hydrogen from nickel triglycinate is accompanied by a change in color from pale green to very intense yellow. The yellow complex is diamagnetic whereas the original green complexes are paramagnetic. The change in color and magnetic behavior accompanying the dissociation process has been attributed to a change in coordination from octa-

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hedral for the green complex to planar for the yellow complex. Recently an X-ray structure determination of solid single crystals of nickel-tetraglycine complex shows that the nickel ion is coordinated to the four available nitrogen centers arranged in a plane while the carboxylate group remains free.¹⁷ This corresponds closely to the suggested structure for nickel triglycine with the carboxylate group in place of one of the nitrogens in the tetraglycine complex. An X-ray structure determination of nickel diethylenediaminomalonate, which shows a color change behavior similar to that of nickel triglycine, confirms that in this complex the nickel ion is again planar.¹⁸

Comparing the copper and nickel complexes of di- and triglycine reveals that the driving force in the dis-

(19) R. M. Lewis, private communication.

sociation of the peptide hydrogen from the complexes appears to be intimately related to the strength of the bond formed between the two metals with the ligands. Thus the copper complexes are formed with greater exothermic enthalpy changes than the nickel complexes, and correspondingly the dissociation of the peptide hydrogen from the copper complexes occurs at lower pH than the nickel analog. In the diglycine case the dissociation occurs only from the bis complex suggesting that the formation of a mono complex is insufficient to compensate energetically for the dissociation of a proton from the peptide group. It is also reasonable to assume that the resulting change of coordinating centers from oxygen to nitrogen favors the copper ion as compared with the nickel ion in view of the higher copper-amine bond energy.

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Spectral and Magnetic Behavior of Some Cobalt(II) and Nickel(II) Complexes Involving Coordination by the Halo Group

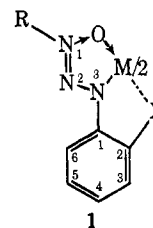
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Halo groups attached to benzene rings are capable of occupying coordination positions in some triazene 1-oxide complexes of the general structure 1. On the basis of comparisons of magnetic moments and electronic spectra of the various complexes with those of one cobalt(II) complex of definitely known structure it is concluded that all the cobalt(II) complexes except one ($X = I$) are pseudooctahedral both in the solid state and in the solution phase (benzene) in which the complexes are monomeric. The iodo complex is grossly planar in the crystalline state but becomes pseudooctahedral in the solution phase. All the pseudooctahedral complexes show splittings of the ν_1 crystal field band. The splittings (which follow the orders $F < Cl < Br < I$ and $OCH_3 < SCH_3$) are attributed to the low symmetry of the ligand field. In this class of complexes, the octahedral quartet state of cobalt(II) is more readily achieved than the octahedral triplet state of nickel(II). Among nickel(II) complexes, those having $X = OCH_3, OC_2H_5,$ and SCH_3 show magnetic moments and electronic spectra typical of a distorted octahedral geometry both in solid and in solution. On the other hand, nickel(II) complexes with $X =$ halogen are diamagnetic in the crystalline state but become partially paramagnetic in the solution phase. On the basis of spectral and magnetic data it is shown that planar ($S = 0$) \rightleftharpoons pseudooctahedral ($S = 1$) equilibria exist in these solutions. The pseudooctahedral form involves halogen coordination. The population of the octahedral configuration follows the order $F < Cl < Br > I$. The parameters ΔH° (and ΔS°) for the equilibria are found to be positive. A possible rationalization is discussed on the basis of a simple model.

Introduction

Triazene 1-oxides act as versatile ligands forming nonelectrolytic chelates with many metal ions.^{1,2} However, there is a surprising paucity of data on structural aspects of these extremely interesting complexes. The syntheses, stereochemistry, and electronic spectra of some cobalt(III),³ rhodium(III),⁴ and chromium(III)⁴ chelates derived from bidentate triazene 1-oxides were reported recently from this laboratory. All these complexes have a *trans*- MN_3O_3 coordination sphere. In this paper complexes of the structural type 1 are characterized using spectroscopic and magnetic data. In 1 the dotted line indicates that the donor group X may or may not be coordinated to the central metal atom. In what follows, the complexes 1 will be abbreviated as $(RX)_2M$.



R = CH₃, C₂H₅, n-C₃H₇
X = F, Cl, Br, I, OCH₃, OC₂H₅, SCH₃
M = Co, Ni

Experimental Section

Preparation of Compounds.—The ligands were synthesized by treating the appropriate diazonium salts with substituted hydroxylamines.³ The complexes were prepared as crystalline solids by treating an ethanolic or methanolic solution of the ligand (0.02 mol) with an aqueous or methanolic solution of the appropriate metal acetate (0.01 mol). In the case of $(CH_3F)_2Co$ the reaction was carried out under nitrogen. Recrystallizations were done from acetone.

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