give only a small energy difference (0.1–0.3 kcal/mole) between the isomers of the wrong sign. The calculations were carried out using the distances measured from Dreiding scale models for the D configuration about cobalt with the k conformation for both Co–en rings. The amino acid conformation found in the $[Co(en)_2(sar)]^{2+}$ ion was used in one calculation (0.3 kcal/mole) while keeping the isopropyl group in its most equatorial position, and in the other the interactions between the amino acid NH_2 and the neighboring apical NH groups were minimized (0.1 kcal/mole). These differences arise from the sum of a number of small interactions, and it is conceivable that the equilibrium conformers in solution could be different from those proposed. Also it is possible that slightly different solvation energies for the two ions decide the isomeric stability. Some support for the last possibility might be derived from the fact that the calculations showed no difference between the corresponding alanine and valine isomers.

It would appear that the results support the thesis that planar or near-planar optically active chelates are less effective in determining the degree of stereospecificity in the D and L complexes than those with more pronounced conformational characteristics.

Acknowledgment. We thank the Microanalytical Unit of the John Curtin School of Medical Research for C, H, and N analyses.

Nickel(II) Complexes of Glycine Peptides in Aqueous Solution[1,2]

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Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois. *Received February 11, 1967*

Abstract: Nickel(II) complexes of diglycine, triglycine, and tetraglycine in aqueous solution are studied by potentiometric pH, visible spectral, and infrared spectral measurements. Coordination sites of these glycine peptides for the nickel(II) ion are nitrogen atoms of amino and peptide groups and an oxygen atom of the carboxylate group. As with the corresponding Cu(II) complexes, the formation of nickel(II) complexes promotes the dissociation of a proton from each peptide linkage; direct evidence for this reaction is provided by a frequency shift of the infrared absorption of the peptide carbonyl group from 1670 (free ligand) to 1610 cm^{-1} (coordinated ligand). Unlike copper(II) complexes, the displacement of peptide protons by the nickel(II) ion occurs in a single dissociation step, with simultaneous conversion of the paramagnetic octahedral nickel(II) complexes to diamagnetic planar chelates.

In previous studies of copper(II) complexes of glycine peptides[4,5] it was possible to obtain structural information on the chelates formed and equilibrium constants for all microscopic reaction steps, by combining potentiometric pH measurements with infrared and visible spectral studies. Frequency changes of the infrared absorption bands of the peptide carbonyl groups provide the first direct proof of the dissociation of a proton from the peptide linkage in the course of chelate formation.

From a study of potentiometric titration curves, Martin, *et al.*,[6] suggested that reactions of the nickel(II) ion with glycine peptides are similar to those of the copper(II) ion. In the present paper, the methods used for the study of copper(II) complexes, that is, potentiometric pH measurements combined with the infrared and visible spectral studies, are extended to nickel(II) complexes.

Experimental Section

Methods. All the measurements, potentiometric pH, visible spectral, and infrared spectral, were carried out as described previously.[4]

Reagents. The ligands used are the same as those reported previously.[7] Nickel(II) nitrate and chloride were certified reagent chemicals purchased from Fisher Scientific Co., Fair Lawn, N. J.

Results

Potentiometric Titrations and Visible Spectra. Nickel(II)–Diglycine System. Potentiometric titration curves for solutions containing 1:1 and 1:2 molar ratios of nickel(II) to diglycine in 0.10 *M* KNO_3 media are shown in Figure 1. About 5–10 min was required to reach equilibrium after each increment of base. Contrary to what had been observed for the interaction of diglycine with copper(II), nickel(II) does not show a strong tendency to coordinate with this ligand, except at relatively high pH precipitation of nickel(II) hydroxide begins. For solutions having a 1:2 molar ratio of metal ion to ligand, the addition of base was accompanied by a relatively small color change (deepening of the blue color), and no inflection was observed in the potentiometric titration curve, indicating further reaction with base.

The reactions taking place involve the formation of simple 1:1 and 1:2 complexes of the mononegative form

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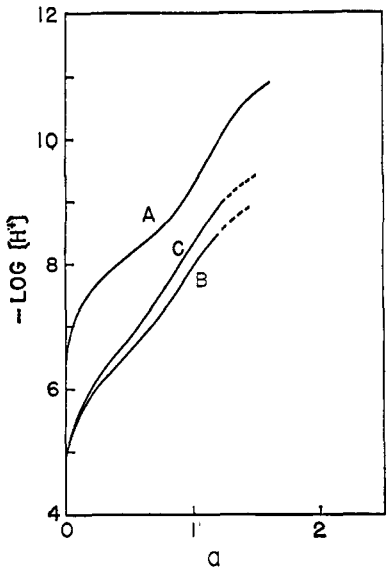


Figure 1. Potentiometric titration curves for nickel(II)-diglycine system: (A) GG, 3.98 × 10^{-3} *M*; (B) 1:1 Ni(II)-GG, 3.97 × 10^{-3} *M* in Ni(II); (C) 1:2 Ni(II)-GG, 3.97 × 10^{-3} *M* in Ni(II) (24.9°, μ = 0.10 *M* (KNO_3)).

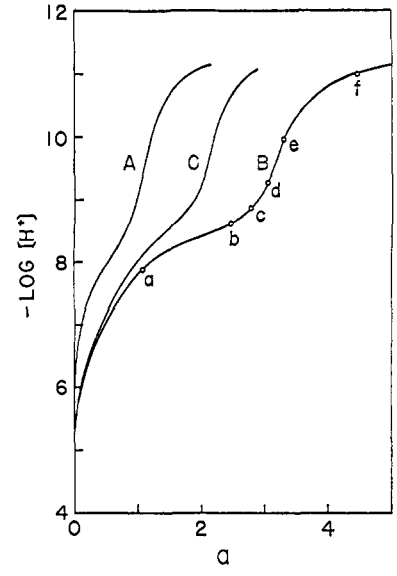


Figure 2. Potentiometric titration curves for the nickel(II)-triglycine system: (A) GGG, 3.43 × 10^{-3} *M*; (B) 1:1 Ni(II)-GGG, 1.71 × 10^{-3} *M* in Ni(II); (C) 1:2 Ni(II)-GGG, 1.71 × 10^{-3} *M* in Ni(II) (24.9°, μ = 0.10 *M* (KNO_3)).

of the ligand. The 1:3 complex seems to form at high ligand to metal ratios. The pertinent equilibrium constant expressions are

$$M^{2+} + L^- \rightleftharpoons ML^+ \quad K_1 = [ML^+]/[M^{2+}][L^-] \qquad (1)$$

$$ML^+ + L^- \rightleftharpoons ML_2 \quad K_2 = [ML_2]/[ML^+][L^-] \qquad (2)$$

$$ML_2 + L^- \rightleftharpoons ML_3^- \quad K_3 = [ML_3^-]/[ML_2][L^-] \qquad (3)$$

where HL = diglycine. The K_1 and K_2 values were determined graphically from potentiometric data taken on the 1:2 system, and the value of K_3 was obtained directly from the 1:3 potentiometric titration data. These results are listed in Table I.

Table I. Equilibrium Constants for the Interaction of Nickel(II) with Glycine Peptides[a]

System	K_x	Equilibrium quotient, K_x	Log K_x
Ni(II)-GG	K_1	$[ML^+]/[M^{2+}][L^-]$	3.34
	K_2	$[ML_2]/[ML^+][L^-]$	4.07
	K_3	$[ML_3^-]/[ML_2][L^-]$	2.5
Ni(II)-GGG	K_1	$[ML^+]/[M^{2+}][L^-]$	3.76
	K_2	$[ML_2]/[ML^+][L^-]$	3.10
	K_{1ab}	$[MB^-][H^+]^2/[MH_2B^+]$	−16.9
	K_{1c}	$[M(OH)B^{2-}][H^+]/[MB^-]$	−10.5
Ni(II)-GGGG	K_1	$[ML^+]/[M^{2+}][L^-]$	3.65
	K_2	$[ML_2]/[ML^+][L^-]$	3.3
	K_{1abc}	$[MC^{2-}][H^+]^3/[MH_3C^+]$	−24.4
	K_{1d}	$[M(OH)C^{3-}][H^+]/[MC^{2-}]$	−10.0

[a] μ = 0.1 *M* (KNO_3); *t* = 24.9°.

Nickel(II)–Triglycine System. The potentiometric titration curves of solutions containing 1:1 and 1:2 molar ratios of nickel(II) to triglycine in 0.10 *M* KNO_3 media are given in Figure 2. The 1:1 curve shows a distinct inflection at a = 3. All the experimental points between a = 0 and a = 3 on the nickel(II)–triglycine curve are much higher (*i.e.*, hydrogen ion concentrations are lower) than those of the corresponding copper(II) curve,[5] which also has an inflection at a = 3. The inflection of the 1:2 curve occurs at a = 2 but is not very sharp. In the region between a = 0 and a = 1, 5–10 min is required to obtain steady pH readings after each addition of base to the solution.

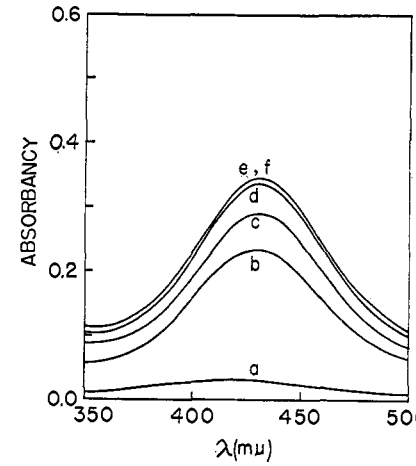


Figure 3. Visible spectra of 1:1 nickel(II)-triglycine solution: (a) pH 7.88, (b) pH 8.63, (c) pH 8.87, (d) pH 9.29, (e) pH 9.98, (f) pH 11.01. Designations on the spectral curves correspond to the points on Figure 2.

The color changes observed during the titration of this system are quite remarkable. The initial pale blue solution has a yellowish tint at a = 1. The yellow color deepens as more base is added and finally the solution becomes bright yellow. The visible spectra of 1:1 solutions obtained during the titration are shown in Figure 3. The absorption maximum appears at 430 mμ at a = 1, and at larger "a" values the absorption band increases in intensity with no shift in frequency of absorption maximum, showing one-step formation of the ultimate yellow chelate. This behavior contrasts that reported for the corresponding copper(II)–peptide chelate, for which the absorption maxima undergoes a gradual shift in frequency.

The following reaction steps were found necessary for correlation with spectrophotometric and potentiometric data.

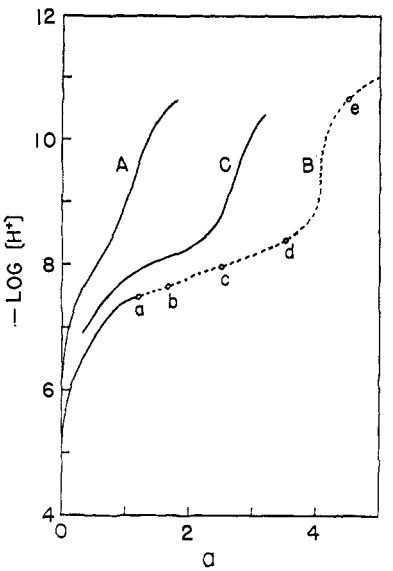


Figure 4. Potentiometric titration curves for nickel(II)–tetraglycine system: (A) GGGG, 1.99×10^{-3} *M*; (B) 1:1 Ni(II)–GGGG, 2.98×10^{-3} *M* in Ni(II); (C) 1:2 Ni(II)–GGGG, 8.49×10^{-4} *M* in Ni(II) (24.9°, $\mu = 0.10$ *M* (KNO_3)).

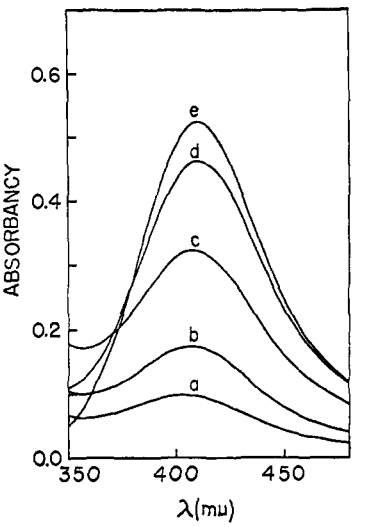


Figure 5. Visible spectra of 1:1 nickel(II)–tetraglycine solution: (a) pH 7.48, (b) pH 7.65, (c) pH 7.97, (d) pH 8.40, (e) pH 10.65. Designations on the spectral curves correspond to the points on Figure 4.

$$M^{2+} + L^- \rightleftharpoons ML^+ \quad K_1 = [ML^+]/[M^{2+}][L^-] \quad (4)$$

$$ML^+ + L^- \rightleftharpoons ML_2 \quad K_2 = [ML_2]/[ML^+][L^-] \quad (5)$$

$$MH_2B^+ \rightleftharpoons MB^- + 2H^+ \quad K_{1ab} = [MB^-][H^+]^2/[MH_2B^+] \quad (6)$$

$$MB^- \rightleftharpoons M(OH)B^{2-} + H^+ \quad K_{1c} = [M(OH)B^{2-}][H^+]/[MB^-] \quad (7)$$

The values of K_1 and K_2 were obtained in the same way as described above for the nickel(II)–diglycine system. For the 1:1 Ni(II)–triglycine system, attempts were made to calculate K_1, K_{1a}, and K_{1b}, involving stepwise displacement of peptide protons, with the graphical method employed for copper(II)–triglycine,[5] but the equilibrium constants obtained were not consistent. This is not unexpected from the relative shapes of the 1:1 nickel(II)–triglycine and copper(II)–triglycine titration curves. In the latter case the titration curve rises gradually by 3–3.5 pH units from $a = 0$ to $a = 3$, whereas in the case of nickel(II) a large increase of 2.5 pH units occurs from $a = 0$ to $a = 1$, and thereafter the rise of titration curve is a mere 1.5 pH units from $a = 1$ to $a = 3$. Therefore, it was concluded that stepwise proton displacement reactions of the type that occurs in the copper(II)–triglycine system do not occur in the formation of the analogous nickel(II) complex MB^-, and both protons are displaced in a single step, as indicated by eq 6. The value of K_{1c} was calculated directly from potentiometric data with the aid of the known equilibrium constants, K_1 and K_{1ab}. The results are included in Table I.

Nickel(II)–Tetraglycine System. The potentiometric titration method was modified for the nickel(II)–tetraglycine system, since complex formation requires several hours to reach equilibrium at *a* values greater than unity. Sample solutions of equimolar metal ion and ligand, but with different amounts of sodium hydroxide, were prepared and allowed to stand in a constant-temperature water bath. When equilibrium had been attained, the pH values and the spectra were measured. The results are shown in Figures 4 and 5. The "titration" curve in Figure 4 is partially drawn with a broken line, because a small amount of precipitate was present in the region between $a = 2$ and $a = 5$, and the high pH values may not be absolutely accurate because nitrogen gas was not bubbled through the sample solution. However, it seems reasonable to conclude that an inflection occurs at $a = 4$ for this system. When the 1:1 curve is compared to the corresponding copper(II) curve,[5] the latter has the lower pH values until the value of *a* reaches 3, after which a reversal occurs. This demonstrates that the tendency of nickel(II) to combine with tetraglycine at high pH is greater than that of copper(II). The solution starts to show a yellow color at $a = 1$, and becomes very intense yellow at higher *a* values. These observations are in accord with the visible spectra in Figure 5, for which the absorption maximum is seen to occur at 410 mμ.

In another modification of the potentiometric titration method, sodium hydroxide was added to the solution to make the pH of the solution ~11, and the titration was carried out with hydrochloric acid (back titration). The 1:2 titration curve shown in Figure 4 was obtained in this way. Because of the slowness of the reaction at low *a* values, there are no data from $a = 0$ to $a = 0.5$. The 1:2 solution has a less well-defined inflection at $a = 2.5$, which can be explained as resulting from the displacement of four hydrogen ions from half of the ligand (which is coordinated) and of one hydrogen ion from the remaining uncoordinated ligand.

The following interesting observations were made during the titration of nickel(II)–tetraglycine systems. (1) The precipitate which separated from the 1:1 solution reached a maximum amount at $a = 3.0$–4.0 and has a brownish yellow color, rather than the green color of nickel(II) hydroxide. (2) The visible spectra of 1:1 nickel(II)–tetraglycine solution with *a* values of 1–4 change their shape soon after the systems reach equilibrium. The results of rough paper chromatographic separations suggested hydrolysis of the peptide at this pH in the presence of free nickel(II) ion. (3) No precipitate appeared in the solutions containing 1:1.5 and 1:2 molar ratios of metal ion to ligand. (4) The time required to reach equilibrium for back titration increases from ~5 min at high pH to ~30 min at

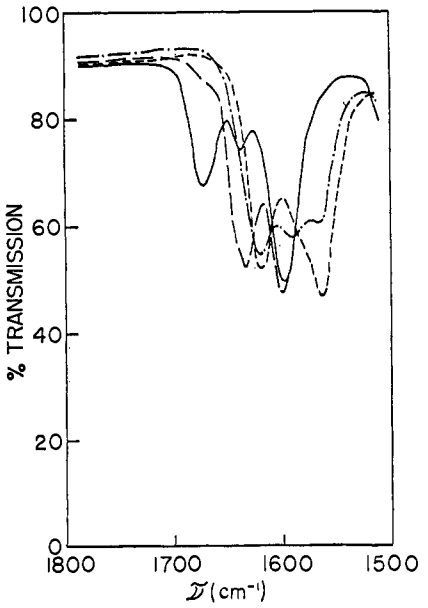


Figure 6. Infrared spectra of nickel(II)–diglycine complexes in aqueous (D_2O) solution: ———, pD 5.05; — — —, pD 6.93; — · —, pD 10.46; - - - -, pD ~12 ($T_M = T_L = 0.198$ *M*, μ = 1.0 *M* (KCl)).

relatively low pH. At very low pH, several hours are required. These results are contrary to normal titrations, in which the time required to reach equilibrium is usually shorter at low pH than at high pH.

The equilibrium constants corresponding to the following reaction steps were calculated and are listed in Table I.

$$M^{2+} + L^- \rightleftharpoons ML^+ \quad K_1 = [ML^+]/[M^{2+}][L^-] \qquad (8)$$

$$ML^+ + L^- \rightleftharpoons ML_2 \quad K_2 = [ML_2]/[ML^+][L^-] \qquad (9)$$

$$MH_3C^+ \rightleftharpoons MC^{2-} + 3H^+ \quad K_{1abc} = [MC^{2-}][H^+]^3/[MH_3C^+] \qquad (10)$$

(where HL = H_4C)

$$MC^{2-} \rightleftharpoons M(OH)C^{3-} + H^+ \quad K_{1d} = [M(OH)C^{3-}][H^+]/[MC^{2-}] \qquad (11)$$

The graphical method did not give good results for the determination of K_1 and K_2. A preliminary K_1 value was determined at low pH with 1:1 titration data and was used for calculating K_2 from 1:2 titration data. With this value of K_2, a better value of K_1 was determined. Although this process was repeated several times, the values obtained for K_2 were not as accurate as the values determined for K_1. The direct algebraic method was used to calculate K_{1abc}, with the assumption that ML^+ and MC^{2-} are the only species present in the pH range 8.0–8.5. The value of K_{1d} was calculated from data obtained at high pH.

Infrared Spectra. Infrared spectra of D_2O solutions of 1:1 nickel(II)–diglycine, nickel(II)–triglycine, and nickel(II)–tetraglycine are shown in Figures 6–8, respectively. A trace of precipitate that appeared at high pD was removed before the spectra were measured. For the nickel(II)–diglycine system the bands at low pD are similar to those of the ligand alone, but at high pD three bands at 1620, 1590, and 1565 cm^{-1} were found. As pD is further increased, the 1565-cm^{-1} band becomes very intense, with simultaneous decrease of the 1590-cm^{-1} band.

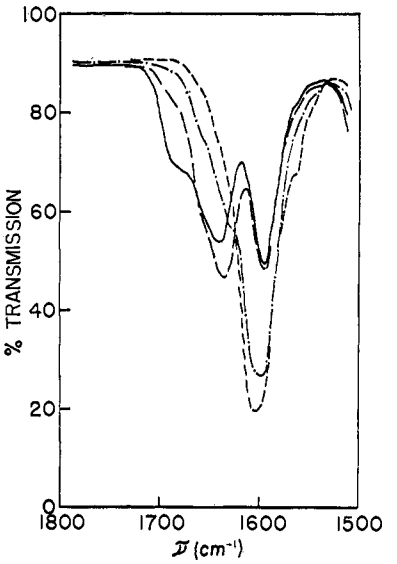


Figure 7. Infrared spectra of nickel(II)–triglycine complexes in aqueous (D_2O) solution: ———, pD 5.68; — — —, pD 6.91; — · —, pD 9.60; - - - -, pD 11.88 ($T_M = T_L = 0.200$ *M*; μ = 1.0 *M* (KCl)).

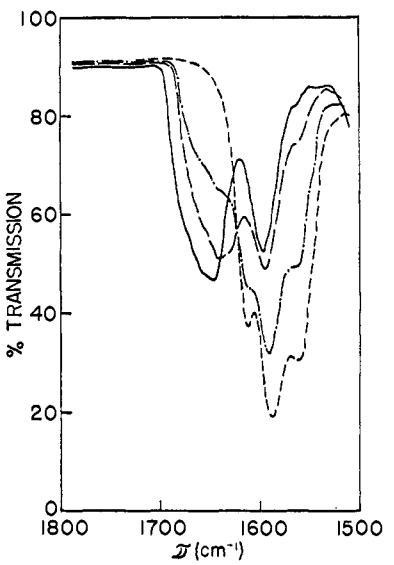


Figure 8. Infrared spectra of nickel(II)–tetraglycine complexes in aqueous (D_2O) solution: ———, pD 4.90; — — —, pD 8.53; — · —, pD 8.96; - - - -, pD ~12 ($T_M = T_L = 0.200$ *M*, μ = 1.0 *M* (KCl)).

The nickel(II)–triglycine spectrum shows three bands at low pD with maxima at 1680, 1640, and 1595 cm^{-1}. The 1680-cm^{-1} shoulder disappears at high pD and only two bands remain, at 1635 and 1595 cm^{-1}, until pD reaches 9.5. As the pD is further increased, these two bands are replaced by one strong band at 1603 cm^{-1}. This 1603-cm^{-1} band has a shoulder at 1565 cm^{-1} which becomes apparent as a separate band at very high pD.

The spectra of nickel(II)–tetraglycine solutions are very similar to those of the ligand itself until pD reaches 8.5. At higher pD there appear three bands at 1610, 1590, and 1565 cm^{-1}, in addition to a shoulder at 1645 cm^{-1}. Only the three main bands remain when the pD is further increased to very high values.

The frequencies of the infrared absorption bands of Ni(II) chelates of glycine peptides, together with corresponding assignments, are given in Table II.

Table II. Antisymmetric Carboxyl and Peptide Carbonyl Bands of Nickel(II) Complexes of Glycine Peptides as a Function of pD

System	pD	Observed bands, cm^{-1}				
		Peptide carbonyl			Carboxylate	
		HNC=O	HNC=O-Ni	$(NCO)^-$-Ni	$-COO^-$-Ni	$-COO^-$
Ni-GG	5.05	1672	1637		1597	
	6.93	1670 (sh)[a]	1633		1600	
	10.46		1620		1590	1565
	~12		1618		1590 (sh)	1564
Ni-GGG	5.68	1680	1640		1595	
	6.91		1635		1595	
	9.60		1632 (sh)	1598[b]	1598[b]	
	11.88			1603[b]	1603[b]	1565 (sh)
Ni-GGGG	4.90	1650 (B)[c]			1596	
	8.53	1643 (B)			1595	
	8.96		1645 (sh)	1610	1590	1565
	~12			1610	1587	1560

[a] Shoulder. [b] Mergence of two neighboring bands. [c] Broad band.

Discussion

Nickel(II) Complexes of Diglycine. Potentiometric measurements shown in Figure 1 cannot be applied to reactions beyond the displacement of a proton from the ammonium group of the dipolar ion. Only complexes of the type ML^+, ML_2, and ML_3 are formed. Also, at low pD, no significant changes are found in the infrared spectra of nickel(II)–diglycine complexes compared to the spectra of the free ligand.

Since the coordination number of nickel(II) is six, and the maximum number of coordination sites in diglycine is three, the first complex ML^+ is expected to combine with a second ligand very readily to form the complex ML_2. This is shown by the equilibrium constants listed in Table I, where it is seen that K_1 and K_2 are very similar in magnitude. Octahedral structures are suggested for ML^+ and ML_2. The small value of K_3 indicates that the third ligand combines much less strongly, and in the resulting complex ML_3^- each ligand coordinates to metal ion as a bidentate donor, probably through amino and peptide carbonyl groups.

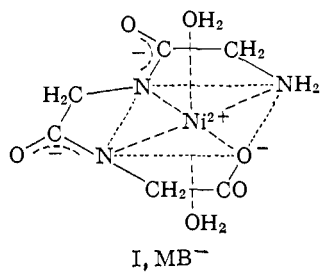
The infrared spectra at high pD show a decrease in the intensity of the 1590-cm^{-1} band, with simultaneous increase in intensity of the 1565-cm^{-1} band and a slight shift of the peptide carbonyl band. At high hydroxide ion concentrations, formation of the ML_3^- species leaves the carboxylate group displaced from the first coordination sphere, and thus the frequency of the free carboxylate group appears at 1565 cm^{-1}. Comparison of the 1630-cm^{-1} band of the free ligand at high pD[7] with the 1620-cm^{-1} band of nickel(II)–diglycinate indicates association of the protonated peptide linkage with the nickel(II) ion, though the interaction is not so strong as in the case of copper(II).

Nickel(II) Complexes of Triglycine. When equimolar amounts of nickel(II) ion and triglycine are treated with base, a total of three protons are displaced from the ligand. But unlike the corresponding copper(II) case, the first displacement reaction occurs in a lower pH range, 5–7.8, and the second and third displacement reactions, involving the peptide linkages, occur simultaneously over a higher pH range, 7.8–9.2. Martin, *et al.*,[6] reported the dissociation constants for two individual steps, each involving the displacement of a single proton by Ni(II). It is, however, interesting that the equilibrium constant obtained in the present investigation for the two-equivalent displacement of peptide protons from the nickel(II)–triglycine system is very close to the product of the dissociation constants obtained by Martin, *et al.*,[6] for the corresponding stepwise reactions.

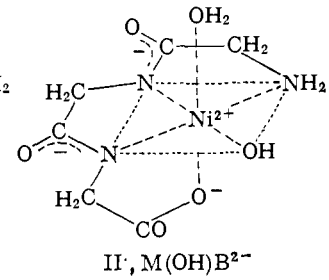
Since no appreciable extent of complex formation occurs at low pD values, the infrared spectra at pD 5.68 in Figure 7 are not significantly different from those of the free ligand.[7] At higher pD, however, the complex ML^+ is formed. The infrared spectra at pD 6.91 has two maxima, at 1635 and 1595 cm^{-1}, the first being due to weak coordination of nickel(II) to the peptide linkage, and the second being due to coordination of the carboxylate group to the metal ion. The fact that these two bands (1635 and 1595 cm^{-1}) persist up to a pD of ~8 indicates that this 1:1 complex, ML^+, is the predominant species at low pD values.

Since the ligand has four coordination sites and the maximum coordination number of nickel(II) is six, several structures can be drawn for the 2:1 complex, ML_2. So far no information is available to distinguish between the possible arrangements of the mononegative ligands about the nickel(II) ion.

As pD is further increased for the 1:1 system, the metal coordinates with the negative peptide group as a result of proton displacement from the peptide nitrogen, and the 1635-cm^{-1} band of the neutral peptide group, therefore, shifts to lower frequency. At pD 9.60 the 1635-cm^{-1} band is very weak and the coordinated negative peptide absorption is superimposed on the carboxylate band at 1598 cm^{-1}, since the main species at this pD is MB^- (structure I). At still higher pD, all the peptide linkages exist in the negative coordinated form, and the increased intensity of its absorption band results in a shift of the frequency of the maximum of the composite band toward the coordinated negative amide frequency of 1610 cm^{-1}. This corresponds closely to the 1603-cm^{-1} band observed at pD 11.88. The small shoulder at 1565 cm^{-1} that appears at this pD is again due to displacement of the carboxylate group from the



I, MB^-



II, $M(OH)B^{2-}$

coordination sphere by the hydroxide ion in the formation of $M(OH)B^{2-}$, as shown by structure II.

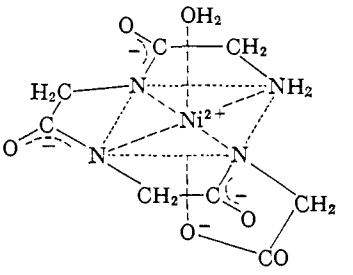
When the complex ML^+ loses two protons from its peptide nitrogens, the resulting metal–peptide bonds become quite strong. A chelate compound is formed that probably has four strong coordinate bonds (a metal–amino nitrogen, a metal–carboxylate oxygen, and two metal–negative peptide nitrogen bonds) arranged around the nickel(II) ion in a planar fashion. The original octahedral configuration of the nickel(II) ion is easily distorted under the influence of the planar donor groups, and the structure of MB^- is either planar or tetragonal. Such a structural change is indicated by the potentiometric titration data, whereby the reaction with added base was observed to become instantaneous at a values larger than 1.0, in contrast to the slow rates observed at a between 0 and 1.0. Also the dissociation of second and third protons (from the peptide linkages) in the presence of the metal ion was observed to occur simultaneously, indicating the formation of a very stable complex.

In the systems containing a 2:1 or higher molar ratio of ligand to metal ion, in the medium to high pH range where the chelate MB^- is formed in the 1:1 system, no 2:1 chelate can be detected. The potentiometric data are completely accounted for by the formation of MB^-, and the excess ligand remains uncoordinated in solution. Also, infrared data indicate formation of the chelate MB^-, with a coordinated carboxylate group (or a free carboxylate and a hydroxide ion for $MOHB^{2-}$) with uncoordinated excess ligand in solution.

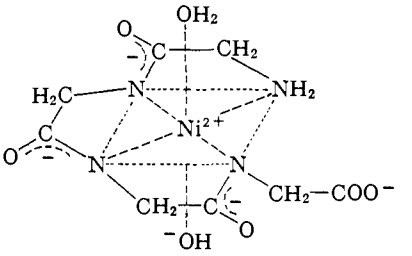
Nickel(II) Complexes of Tetraglycine. As in the nickel(II)–triglycine case the 1:1 nickel(II)–tetraglycine system forms a blue octahedral complex, ML^+, at low a values (a less than unity). At higher ratios of ligand to metal ion, a blue complex, ML_2, also seems to be formed at low pH. Of the two infrared bands found at pD 4.90 and 8.53 in Figure 8, the broad band at 1640–1650 cm^{-1} is due to the sum of the coordinated and uncoordinated protonated peptide carbonyl groups, while the other, at 1595 cm^{-1}, is due to the coordinated carboxylate group.

As seen from the equilibrium steps of this system described above, the second, third, and fourth proton dissociations from peptide linkages are simultaneous, contrary to the conclusions of Martin, *et al.*[6] This is further supported by the fact that the 1640-cm^{-1} band of the neutral protonated peptide carbonyl group persists until all the protons are removed from the peptide linkages. At pD 8.96, where the predominant species is MC^{2-} (III), the absorption band of the negative coordinated peptide carbonyl group appears at 1610 cm^{-1}. The 1645-cm^{-1} shoulder at this pD merely shows the presence of a small amount of ML^+. The remaining two bands, at 1590 and 1565 cm^{-1}, come from two different types of carboxylate groups. After proton displacement from all peptide nitrogens, the ligand has four nitrogens available for the formation of a very stable chelate ring system and would surround the nickel(II) ion in such a way that the four nitrogens occupy the corners of the plane, with the carboxylate group taking a remote position below the plane. The 1590–cm^{-1} band is this weakly coordinated carboxylate frequency.

The 1565-cm^{-1} band at pD 8.96, illustrated in Figure 8, is due to a carboxylate group completely displaced from the coordination sphere of the metal ion by the hydroxide ion. At very high pD, formation of the $M(OH)C^{3-}$ species IV occurs. The frequencies of the three infrared bands at pD ~12 are due to the co-



III, MC^{2-}



IV, $M(OH)C^{3-}$

ordinated negative peptide carbonyl group, 1610 cm^{-1}, to the weakly coordinated carboxylate group, 1587 cm^{-1}, and to the free carboxylate group, 1560 cm^{-1}.

It is interesting to note that in all of the copper(II) and nickel(II) polyglycine systems studied the peptide carbonyl and carboxylate frequencies occur as separate bands only in the cases of copper(II)–tetraglycine and nickel(II)–tetraglycine. For the copper(II)–diglycine,[4] copper(II)–triglycine,[5] and nickel(II)–triglycine complexes, the carboxylate group forms one of the strong primary coordinate bonds. The frequencies of the coordinated negative peptide carbonyl group and of the coordinated carboxylate group are close enough that their absorptions appear as one band at 1595–1610 cm^{-1}. In the tetraglycine complexes, however, the amino and three peptide groups provide a sufficient number of strongly coordinating nitrogen atoms, so that there is no strongly coordinated carboxylate group at and beyond $a = 4$, and their absorptions appear as separate bands. This evidence provides further confirmation of the nature of the square-planar coordination in these complexes.

For the nickel(II)–tetraglycine complex in which all peptide protons are displaced, the ligand field around the nickel(II) ion is stronger than is the case for the analogous triglycine complex, and the formation of a clearly diamagnetic planar or tetragonal complex thus seems reasonable for the tetraglycine complex. This change of configuration to square-planar is suggested from the considerable changes of absorption maximum in the visible spectra, the shape of the potentiometric titration curve, and the geometrical structure of the ligand. The diamagnetic nature of this complex was recently observed by Mathur and Martin[8] from the proton nmr spectra of the nickel(II) complex MC^{2-}. Further work on the proton nmr spectra is in progress and will be described in a subsequent paper.

(8) R. Mathur and R. B. Martin, *J. Phys. Chem.*, **69**, 668 (1965).

In the formation of the stable square-planar tetraglycine complex, MC^{2-}, dissociation of three protons along with intramolecular rearrangement would be expected to require considerable time before the system can reach equilibrium. This behavior was observed in the potentiometric titration as base was added between $a = 1$ and $a = 4$. The same was true of the back titration for which association of three protons and the reverse intramolecular rearrangement to an octahedral complex occur.

Bis(triphenylphosphine)(π-allyl)rhodium Complexes

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Abstract: A series of novel bis(triphenylphosphine)(π-allyl)rhodium complexes is described. The nmr spectra of these compounds not only confirm their structures but also have some interesting features. Coupling is observed between rhodium and the hydrogen of the *central* carbon only of the allyl grouping (and even to the methyl protons in the methallyl complex), whereas only the hydrogens attached to the *terminal* carbons of the allyl grouping are coupled with the phosphorus nuclei. An explanation is given on the basis of simple MO theory. In the presence of excess triphenylphosphine the allyl group stays π-bonded, but rapid exchange occurs between free and complexed triphenylphosphine.

Until very recently allyl complexes of rhodium were unknown. The first example of an allylrhodium compound reported was dichloro(*trans,trans,trans*-1,5,9-cyclododecatrienyl)rhodium.[1] Subsequently, the addition of allyl chloride to chlorotris(triphenylphosphine)rhodium was reported to yield dichlorobis(triphenylphosphine)allylrhodium;[2] the reaction of allyl chloride with chlorodicarbonylrhodium in aqueous methanol was shown to give di-μ-chloro-tetrakis(allyl)-dirhodium[3] from which further derivatives were prepared.[3] Tris(allyl)rhodium finally could be obtained by treating di-μ-chloro-tetrakis(allyl)dirhodium with allylmagnesium chloride.[4] These compounds can be regarded in a formal sense to be derived from rhodium(III). So far only one example of a rhodium(I)–allyl compound has been reported, namely, (cyclooctadiene-1,5)(π-allyl)rhodium.[5] This paper is concerned with the preparation and properties of a series of new rhodium(I)–allyl complexes of the type bis(triphenylphosphine)-(π-allyl)rhodium.

Preparation of Bis(triphenylphosphine)(π-allyl)rhodium Complexes. The reaction of chlorotris(triphenylphosphine)rhodium[6] with allylmagnesium chloride in ether solution yields bis(triphenylphosphine)(π-allyl)-rhodium according to the equation

$$[P(C_6H_5)_3]_3RhCl + C_3H_5MgCl \longrightarrow [P(C_6H_5)_3]_2Rh(\pi\text{-}C_3H_5) + MgCl_2 + P(C_6H_5)_3$$

After recrystallization from a concentrated benzene solution by addition of diethyl ether the compound can be obtained as a crystalline yellow solid. In the same way bis(triphenylphosphine)(π-methallyl)rhodium and bis(triphenylphosphine)(π-crotyl)rhodium have been prepared.

The addition of a conjugated diolefin to hydridotetrakis(triphenylphosphine)rhodium[7] provides an alternative method for the preparation of bis(triphenylphosphine)(π-allyl)rhodium complexes. Bis(triphenylphosphine)(π-cyclohexenyl)rhodium, bis(triphenylphosphine)(π-cyclooctenyl)rhodium, and bis(triphenylphosphine)(π-crotyl)rhodium have been obtained in this manner from the addition of cyclohexadiene-1,3, cyclooctadiene-1,3, and butadiene, respectively. The reaction, as exemplified for the case of the cyclohexenyl complex, proceeds according to

$$[P(C_6H_5)_3]_4RhH + \bigcirc \longrightarrow [P(C_6H_5)_3]_2Rh\text{–}\bigcirc + 2P(C_6H_5)_3$$

All bis(triphenylphosphine)(π-allyl)rhodium complexes are yellow crystalline solids, thermally stable to ~170° where decomposition occurs without previous melting. Solvents, especially aromatic hydrocarbons and ethers, are easily incorporated into the crystals and could never be removed completely. The complexes are moderately soluble in aromatic hydrocarbons, sparingly soluble in ethers, and practically insoluble in aliphatic hydrocarbons. The compounds are highly sensitive to air in solution, much less so in the solid state. Protic solvents decompose bis(triphenylphosphine)(π-allyl) complexes in contrast to (cyclooctadiene-1)(π-allyl)rhodium.[5] This reaction has been used to obtain a chemical proof for the structure of the crotyl complex

$$[P(C_6H_5)_3]_2Rh(\pi\text{-}C_4H_7) + H^+ \longrightarrow \{[P(C_6H_5)_3]_2Rh\}^+ + C_4H_8$$

A mass spectroscopic analysis of the gas evolved showed that it contained butene as the only hydrocarbon. The infrared spectra of the bis(triphenylphosphine)(π-allyl)-

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