fit was obtained using the rate expression $R = k[\mathrm{ReCl_6}^{2-}][\mathrm{H}^+]$. Using this equation all of the data gave a value of $k = (0.659 \pm 0.221) \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$, having a range of $(0.413\text{–}1.188) \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$.

Rate laws using the activities of the various species present[13–17] did not provide a better fit to the data than the use of concentrations.

In view of the lack of a quantitative fit to a single rate law, no positive conclusions can be reached concerning the mechanism of reaction.

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(13) G. Åkerlöf and J. W. Teare, *J. Am. Chem. Soc.*, **59**, 1855 (1937).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p 603.

(15) G. Åkerlöf and H. C. Thomas, *J. Am. Chem. Soc.*, **56**, 593 (1934).

(16) R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948). Values of constants for HCl at 90° from H. M. Feder, *ibid.*, **70**, 3525 (1948).

(17) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

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Formation Constant, Enthalpy, and Entropy Values for the Association of Nickel(II) Ion with Glycinate, Alanate, and Phenylalanate Ions at 10, 25, and 40°[1a]

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Previous studies[2–5] dealing with metal ion–amino acid interaction with Cu^{2+} ion are extended in this work to include interaction with Ni^{2+} ion. The effects of changes of temperature and ligand have been investigated in this study of the nickel(II)–glycine, –alanine, and –phenylalanine systems at 10, 25, and 40°. Values for constants for the association of Ni^{2+} ion with the anions of glycine[6–9] and alanine[7] appear in the literature but no data for the nickel(II) phenylalanine system are available. Apparently no previous calorimetric studies of enthalpy changes associated with the formation of nickel complexes of these three amino acids have been made.

Experimental Section

Materials.—Solutions of NaOH and $\mathrm{HClO_4}$ were prepared from reagent grade chemicals obtained from the J. T. Baker Chemical Co. and standardized using recognized analytical procedures. Stock nickel(II) perchlorate solutions were prepared by dissolving reagent grade nickel perchlorate (The G. Frederick Smith Chemical Co.) in distilled water and determining the metal formality by dimethylglyoxime gravimetric analysis. Stock ligand solutions were prepared by dissolving weighed quantities of glycine (Matheson Coleman and Bell) and alanine and phenylalanine (East Organic Chemicals) in water without further purification. Titration of the carboxyl group of the amino acid in the presence of HCOOH[10] shows these reagents to be 99.7, 99.9, and 99.2% pure, respectively. Buffer solutions were prepared both as discussed by Bates[11] and from packaged powders formulated according to National Bureau of Standards specifications by Beckman Instruments, Inc. The measured pH values of buffer solutions prepared to maintain a given pH value by the two methods were identical within ±0.002 pH unit.

Apparatus.—The submarine isothermal calorimeter operating in a well-stirred, constant-temperature water bath controlled to ±0.005° at 10, 25, and 40° has been described.[3] Temperature differences of 0.0002° were detectable using a Wheatstone bridge assembly, power supply, and timing device described previously.[2,3] A 200-ml round-bottom flask, modified with five 0.75-in. diameter necks spaced about the main neck, served as the container for metal–ligand solutions during titrations for the determination of stepwise constants for the association of metal ion with ligand anion. This container was immersed in a 10-l. water bath whose temperature was controlled to ±0.02°. Hydrogen ion activity values were determined by means of a Beckman Model 76 expanded-scale pH meter for calorimetric runs and by means of a Leeds and Northrup 7664-A1 pH meter whose output was expanded on a Leeds and Northrup Speedomax H 177181 recorder for titration studies.

Association Constants.—Titrations to determine values for the thermodynamic equilibrium constants, K_1 and K_2, for the reactions represented by eq 1 and 2, respectively, were carried out under a nitrogen atmosphere.[3]

$$\mathrm{M}^{2+} + \mathrm{L}^- \rightleftharpoons \mathrm{ML}^+ \qquad (1)$$

$$\mathrm{ML}^+ + \mathrm{L}^- \rightleftharpoons \mathrm{ML_2} \qquad (2)$$

M^{2+} represents the metal ion, L^- represents the anion of the appropriate amino acid, and ML^+ and $\mathrm{ML_2}$ represent the species resulting from the stepwise association of ligand and metal ions. The calculation methods of Block and McIntyre[12] were used. Activity coefficient values for singly and doubly charged ions, γ_1 and γ_2, were calculated by means of equations derived from the data of Crouthamel and Martin[13] and Harned and Owen[14] as previously described.[2,3] Values of γ_1 and γ_2 calculated by this method agree well with those of Kielland.[15] Values for the thermodynamic equilibrium constants, K_{D_1} and K_{D_2}, for the reactions represented by eq 3 and 4, respectively, are those reported from this laboratory.[2,3]

$$\mathrm{H_2L}^+ \rightleftharpoons \mathrm{H}^+ + \mathrm{HL} \qquad (3)$$

$$\mathrm{HL} \rightleftharpoons \mathrm{H}^+ + \mathrm{L}^- \qquad (4)$$

Calorimetric Determinations.—Two types of calorimetric runs, type y and type z, were performed to measure enthalpy values. These runs measured the heats evolved when alkaline solutions of a ligand were mixed with solutions of nickel(II) ions. The formality ratios of ligand to metal ion in the final mixed solutions were 2:1 for y runs and 1:1 for z runs.

An equation representing the concentration of the species ML^+, as a function of K_{D_1}, K_{D_2}, K_1, K_2, γ_1, γ_2, and the hydrogen ion activity, and an equation for the heat measured during a

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(1) (a) Supported in part by Public Health Research Grant AM-02170 from the National Institute of Arthritis and Metabolic Diseases; (b) to whom inquiries concerning this article should be sent.

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

(3) K. P. Anderson, D. A. Newell, and R. M. Izatt, *ibid.*, **5**, 62 (1966).

(4) R. M. Izatt, J. J. Christensen, and V. Kothari, *ibid.*, **3**, 1565 (1964).

(5) R. M. Izatt, J. W. Wrathall, and K. P. Anderson, *J. Phys. Chem.*, **65**, 1914 (1961).

(6) N. C. Li, J. M. White, and R. L. Yoest, *J. Am. Chem. Soc.*, **78**, 5278 (1956).

(7) C. B. Monk, *Trans. Faraday Soc.*, **47**, 297 (1951).

(8) A. Albert, *Biochem. J.*, **47**, 531 (1950).

(9) H. Flood and V. Loras, *Tidsskr. Kjemi, Bergvesen. Met.*, **5**, 83 (1945).

(10) "Specifications and Criteria for Biochemical Compounds," National Academy of Sciences, National Research Council, Washington, D. C., June 1960, p AA vii.

(11) R. G. Bates, *Chimia* (Aarau), **14**, 111 (1960).

(12) B. P. Block and G. H. McIntyre, *J. Am. Chem. Soc.*, **75**, 5667 (1953).

(13) C. E. Crouthamel and D. S. Martin, Jr., *ibid.*, **73**, 570 (1951).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 469.

(15) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

calorimetric run, Q_m, as a function of the heat produced by the association of the appropriate ions to produce the species HL, H_2L^+, ML^+, ML_2, and H_2O have been given.[2,3] In theory, any pair of equations for Q_m for a y and a z run at a given temperature could be solved for values of $\Delta H_1°$ and $\Delta H_2°$, the stepwise enthalpies of formation of ML^+ and ML_2 from their ions (eq 1 and 2). In practice, more complex methods of data treatment were necessary to minimize uncertainties in the measured enthalpy values.

For the nickel(II)–glycine and –alanine systems at a given temperature, every z run was matched in turn with each y run and the results averaged to produce a "best" $\Delta H_2°$ value for that z run. The $\Delta H_2°$ values obtained in this manner were averaged and this average value substituted in turn into the equation for Q_m for each z run to produce a set of $\Delta H_1°$ values from which an average was calculated.

TABLE I

pK AND LOG K VALUES FOR IONIZATION AND COMPLEX FORMATION, RESPECTIVELY. $\Delta H_1°$, $\Delta H_2°$, $\Delta S_1°$, AND $\Delta S_2°$ FOR COMPLEX FORMATION AT $\mu = 0$[h]

Temp, °C	pK_{D_1}	pK_{D_2}	Log K_1	Log K_2	$\Delta H_1°$, kcal/mole	$\Delta H_2°$, kcal/mole	$\Delta S_1°$, eu	$\Delta S_2°$, eu
	Glycine		Nickel(II)–glycine					
10	2.41	10.20	6.36	5.29	−5.2 ± 0.1	−5.8 ± 0.1	10.7	3.7
20			6.1[a]	4.9[a]				
			5.77[b]	4.80[b]				
25	2.39	9.77	6.18	5.07	−4.9 ± 0.1	−4.7 ± 0.2	11.9	7.6
			6.18[c]	4.96[c]				
			6.12[d]	5.03[d]				
			5.86[e]	4.78[e]				
			5.97[f]	4.95[f]				
30			5.88[f]	4.86[f]				
40	2.33	9.46	6.09	4.92	−4.3 ± 0.2	−4.7 ± 0.3	14.2	7.4
			5.72[f]	4.70[f]				
25[g]					−3.6 ± 1.0	−5.1 ± 0.8	16.1	6.1
	Alanine		Nickel(II)–alanine					
10	2.60	10.29	5.93	4.87	−3.4 ± 0.2	−4.6 ± 0.2	15.1	5.9
25	2.63	9.89	5.81	4.73	−3.3 ± 0.2	−3.9 ± 0.3	15.5	8.7
			5.96[c]	4.70[c]				
40	2.65	9.51	5.69	4.50	−3.6 ± 0.2	−2.6 ± 0.2	15.4	11.4
25[g]					−3.2	−5.1	15.9	4.7
	Phenylalanine		Nickel(II)–phenylalanine					
10	2.14	9.75	5.61	4.95	−3.4 ± 0.3	−3.6 ± 1.0	13.8	10.0
25	2.20	9.31	5.56	4.66	−3.2 ± 0.2	−3.3 ± 0.4	14.8	10.3
40	2.21	8.96	5.52	4.39	−2.6 ± 0.3	−2.9 ± 0.8	17.0	10.7
25[g]					−1.2	−7.6	21.6	−4.4

[a] See ref. 8. [b] See ref 9. [c] See ref 7. [d] L. E. Maley and D. P. Mellor, *Australian J. Sci. Res.*, **A2**, 579 (1949). [e] F. Basolo and Y. T. Chen, *J. Am. Chem. Soc.*, **76**, 953 (1954). [f] See ref 6. [g] These values were obtained from log K *vs.* $1/T$ plots. [h] Experimental data for the calorimetric runs have been deposited as Document No. 9273 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

The treatment of data obtained for the nickel–phenylalanine system was more involved and the results more uncertain than for the other two systems. It was necessary to use experimental conditions which produced final solutions for y and z runs differing little in their concentration ratios of ML_2 and ML^+ because of the formation of insoluble substances at high pH values when Ni^{2+} and phenylalanine solutions were mixed. Relatively small concentrations of ML_2 as compared to those of ML^+ were present in all of these mixed solutions. An analysis of the results of nickel–glycine and nickel–alanine experiments indicated that it would be extremely unlikely for the value of $\Delta H_2°$ for nickel–phenylalanine to be outside the limits of two-thirds to three-halves the value of $\Delta H_1°$. The small value of the ML_2/ML^+ ratio in this system permitted the calculation of $\Delta H_1°$ with reasonable certainty by the imposition of these limits on $\Delta H_2°$ as a function of $\Delta H_1°$ in the equations for Q_m. The value for $\Delta H_1°$ obtained in this manner was then substituted into the equation for Q_m for each y and each z run to obtain a value for $\Delta H_2°$.

Several calorimetric determinations were made to measure thermal effects accompanying dilution of the reactant solutions. In no case were thermal effects detectable. It was therefore assumed that measured enthalpy changes were standard enthalpy changes.

Results

Values of pK_{D_1}, pK_{D_2}, log K_1, log K_2, $\Delta H_1°$, $\Delta H_2°$, $\Delta S_1°$, and $\Delta S_2°$ for the nickel(II)–glycine, –alanine and –phenylalanine systems at 10, 25, and 40° are given in Table I. Only those values for pK_{D_1} and pK_{D_2} reported previously from this laboratory[2,3] are listed. Comparison data from the literature for log K_1 and log K_2 are given.

Discussion

The data presented in Table I are in good agreement with previous results in the few instances where these are available. The $\Delta H°$ and $\Delta S°$ values calculated for 25° from log K *vs.* $1/T$ plots are included because many of the thermodynamic data appearing in the literature for similar systems have been arrived at by means of this temperature coefficient method. For these values to have any real meaning measurements would have to be made at more than three points. Even then the basic assumption of invariance of ΔH with temperature is false and only an approximate value for the midpoint of the temperature range could be obtained.

The decrease in the magnitude of $\Delta H_n°$ with increasing complexity of α-amino acid in the formation of metal complexes is much more pronounced for nickel than for copper.[2,3] Seven of the nine $\Delta H_2°$ values determined were more negative than were the corresponding $\Delta H_1°$ values, probably indicating differences in solvation of the NiL^+ ions. It is noteworthy that the values of $\Delta S_1°$ for Cu^{2+} and Ni^{2+} complexes and of $\Delta S_2°$ for Cu^{2+} complexes were more positive for alanine complexes than for either glycine or phenylalanine complexes, while the value of $\Delta S_2°$ for Ni^{2+} complexes increased from glycine to alanine to phenylalanine.

As one might expect, the formation constants for ML^+ decrease with increasing ligand complexity. This trend is not so pronounced for the formation of NiL_2 complexes.

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The Reactions of Dimethylaminophosphines with Dimethylchloramine

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It has been well established that the chloramination of tertiary phosphines in the presence of ammonia yields aminophosphonium chlorides.[1-4] Several tertiary phosphines, including some dialkylaminophosphines,[2-4] were chloraminated in our laboratory and invariably analogous results were obtained. It was of interest to know whether dimethylchloramine also behaves toward the dimethylaminophosphines in an analogous way giving phosphonium salts according to the equations

$$(CH_3)_2NP(CH_3)_2 + (CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_2P(CH_3)_2]Cl \quad (1)$$

$$[(CH_3)_2N]_2P(CH_3) + (CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_3P(CH_3)]Cl \quad (2)$$

If so, it was thought that the proton magnetic resonance spectra of the reaction products of eq 1 and 2 might provide a further proof of the chloramination occurring on the phosphorus atom as has been observed in the earlier studies.[2-4]

The results of the present investigation show that except in the case of tris(dimethylamino)phosphine, the reactions of dimethylchloramine with dimethylaminophosphines yield the expected phosphonium salts, the chloramination occurring on the phosphorus atom of the aminophosphines. The analogous reactions of tris(dimethylamino)phosphine with ammonia plus chloramine and with ammonia-free chloramine were carried out. A different result was obtained for the reaction of tris(dimethylamino)phosphine with dimethylchloramine, and a mechanism for this reaction has been suggested.

Experimental Section

All operations were conducted in a moisture-free nitrogen atmosphere.

Materials.—Solvents were dried over calcium hydride. Dimethylamine used in the preparation of aminophosphines was obtained from the Matheson Co. Phosphorus trichloride, obtained from J. T. Baker Co., was redistilled before use. The aminophosphines[5,6] and dimethylchloramine[7] were synthesized by previously reported procedures.

Analyses.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus.

Infrared Spectra.—Infrared spectra were recorded with a Beckman Model IR-10 grating infrared spectrophotometer. The spectra of solids were taken in the form of Kel-F mulls for the range 2.5–7.5 μ and as Nujol mulls for the range 7.5–20 μ using KBr plates. A summary of spectral bands is presented in Table I.

TABLE I[a]
INFRARED DATA (CM^{-1})

$[\{(CH_3)_2N\}_3PCH_3]Cl$

2940–2800 b, s, 2620 w, 2425 w, 2240 w, 1600 w, 1450 s, 1420 m, 1327 s, 1315 s, 1280 sh, 1185 s, 1165 sh, 1155 sh, 1115 w, 1080 sh, 1060 s, 990 b, vs, 922 m, 810 vs, 735 vs, 615 w, 450 m

$[\{(CH_3)_2N\}_2P(CH_3)_2]Cl$

2925 s, 2800 s, 2800 s, 2310 vw, 1440 s, 1420 m, 1410 m, 1320 m, 1305 s, 1288 m, 1178 s, 1110 vw, 1068 s, 995 b, vs, 970 m, 952 m, 898 s, 775 m, 770 s, 720 m

$[\{(CH_3)_2N\}_3PNH_2]Cl$

3175–2800 b, vs, 2550 b, w, 2320 b, vw, 1565 s, 1540 sh, 1480 sh, 1450 vs, 1410 sh, 1300 vs, 1176 vs, 1166 sh, 1114 w, 1066 vs, 993 m, 758 s, 745 s, 626 m, 470 m

$[\{(CH_3)_2N\}_3PNH_2]PF_6$

3470 s, 3300 s, 3045 m, 3025 m, 2995 m, 2940 w, 2820 w, 1575 w, 1530 w, 1478 s, 1460 w, 1425 m, 1312 s, 1176 s, 1076 s, 1000 vs, 937 m, 833 b, s, 758 s, 741 s, 625 w, 557 vs, 465 b, w

$[\{(CH_3)_2N\}_3PNH_2]B(C_6H_5)_4$

3450 vs, 3360 vs, 3000 sh, 2945 sh, 2920 s, 2865 m, 2830 m, 1565 vs, 1485 s, 1460 b, s, 1418 w, 1302 s, 1266 w, 1167 s, 1147 m, 1144 sh, 1064 m, 1027 m, 1000 vs, 951 m, 858 w, 846 m, 758 m, 743 vs, 735 vs, 717 m, 708 vs, 625 w, 615 m, 605 s

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra for protons were recorded with a Varian Associates A-60A spectrometer at 60 Mcps. The spectra were run in $CDCl_3$ solutions with tetramethylsilane as external standard. ^{31}P chemical shifts were determined with respect to H_3PO_4 (85%) as external standard using a Varian Model V-4300-2 high-resolution spectrometer at 19.3 Mcps in chloroform solution. A summary of the nmr data is given in Table II.

Reaction of Dimethylaminodimethylphosphine with Dimethyl-

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[1] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. S. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

[2] W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

[3] D. F. Clemens and H. H. Sisler, *ibid.*, **4**, 1222 (1965).

[4] S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *ibid.*, **6**, 515 (1967).

[5] A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

[6] E. M. Evleth, L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, **27**, 2192 (1962).

[7] A. Berg, *Ann. Chim. Phys.*, **3**, 319 (1894).