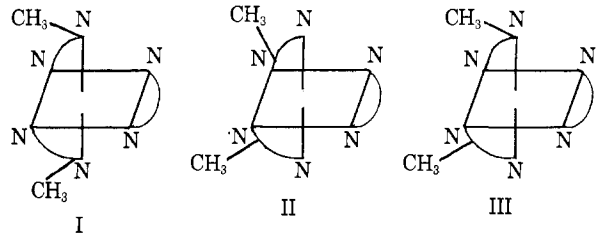
The complex L[Co(en)((−)pn)$_2$]Br$_2$ showed some structure in the methyl region. This may be due to a mixture of the possible geometrical isomers I, II, and III. The racemate D[Co((+)pn)$_2$((−)pn)]Cl$_3$·L[Co((−)pn)$_2$((+)pn)]Cl$_3$ also showed a trace of structure in this region, possibly for the same reason.



I II III

For the complexes containing (−)1,2-diaminopropane all the D isomers gave at least two bands in the NH region whereas the L isomers showed only a single band. It seems unlikely that this separation in the D series is due to a mixture of *cis* and *trans* isomers since D[Co(en)$_2$((−)pn)]$^{3+}$ exists only in one geometrical form. It is conceivable that the different chemical shifts indicate the presence of the less stable conformer which is consistent with our knowledge of the stereochemistry in these systems. The ions D[Co(en)$_2$((−)pn)]$^{3+}$, D[Co(en)((−)pn)$_2$]$^{3+}$, and D[Co((−)pn)$_3$]$^{3+}$ have one, two, and three rings, respectively, in the less stable k′ conformation and the separation of the NH chemical shift increases from the first complex to the last. The spectrum for the racemate L[Co((−)pn)$_2$((+)pn)]$^{3+}$·D[Co((+)pn)$_2$((−)pn)]$^{3+}$ is also consistent with this proposal since both ions contain ligands in both conformations and the peaks in the N–H region are separated about the same as for D[Co(en)$_2$((−)pn)]$^{3+}$.

The discussion above suggests an explanation for the two N–H signals observed with the [Co(en)$_3$]$^{3+}$ ion. Both L[Co(en)$_3$]$^{3+}$ k′k′k′ and L[Co(en)$_3$]$^{3+}$ k′k′k would be expected to be present in solution probably in the ratio of about 2:1.[15] The presence of both the stable and the less stable conformer then could give rise to the two bands in the N–H region.

Fine structure which would allow the assignment of coupling constants between the various protons in the chelate rings is shown only for two complexes, L- and D[Co((−)pn)$_3$]$^{3+}$ (Figure 4). Decoupling at the CH peak relaxes the methyl doublet to a single peak in both cases but the reverse sharpens the CH peak only for the L complex perhaps because the CH signal is so broad. Deuteration of the amine groups sharpens the CH–CH$_2$ region some.

The results of this study indicate the kind of information that may be obtained about chelate ring conformations and some of the problems involved. Although the results as they stand would not allow unambiguous ring conformation assignments, they are completely consistent with what is known about these complexes. Work in progress shows that ring conformation of L[Co((−)pn)$_3$]$^{3+}$ may be assigned on the basis of its nmr spectrum.

Acknowledgment.—S. T. S. wishes to thank Dr. W. B. Schwabacher for experimental assistance and helpful discussions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH

Formation Constants and Enthalpy and Entropy Values for the Association of H^+ and Cu^{2+} with Glycinate and Phenylalanate Ions in Aqueous Solution at 10, 25, and 40° [1a]

BY KEITH P. ANDERSON,[1b] WILBUR O. GREENHALGH, AND REED M. IZATT

Received February 23, 1966

Enthalpy change, entropy change, and equilibrium constant values at 10, 25, and 40° are reported for the formation in aqueous solution of glycine and phenylalanine from their respective ions and for the stepwise formation of the copper(II) chelates of glycine and phenylalanine from Cu^{2+} and the ligand anions. The $\Delta H°$ values were determined by a calorimetric method. Comparison data from the literature are listed for pK, $\Delta H°$, and $\Delta S°$ values.

Introduction

This paper is another in a series[2,3] involving the determination of the thermodynamic properties associated with copper(II)–amino acid interaction in aqueous solution. The present work is a continuation[2] of a calorimetric study of the temperature dependence of the thermodynamic quantities associated with metal–amino acid chelation.

The glycine, copper(II)–glycine, phenylalanine, and copper(II)–phenylalanine systems were investigated in the present study at 10, 25, and 40°. The reactions studied are represented by eq 1–4, respectively.

(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, D. A. Newell, and R. M. Izatt, *Inorg. Chem.*, **5**, 62 (1966).

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

$$H_2L^+ \rightleftharpoons HL + H^+ \quad (1)$$

$$HL \rightleftharpoons H^+ + L^- \quad (2)$$

$$Cu^{2+} + L^- \rightleftharpoons CuL^+ \quad (3)$$

$$CuL^+ + L^- \rightleftharpoons CuL_2 \quad (4)$$

The symbols, K_{D_1}, K_{D_2}, K_1, and K_2 represent the thermodynamic equilibrium constants corresponding to eq 1–4, respectively. The ligand anion (glycinate or phenylalanate ion) is represented by L^-.

Values of pK_{D1}, pK_{D2}, log K_1, and log K_2 for the glycine and copper–glycine systems at 10, 25, and 40° have been reported by a number of workers.[3,4–12] Enthalpy change values $\Delta H_{D_2}°$, $\Delta H_1°$, and $\Delta H_2°$ for reactions 2–4, respectively, have also been reported.[3–5,8,10,12]

Data for the phenylalanine and copper–phenylalanine systems are much fewer than for the glycine and copper–glycine systems. Other than those data previously reported from this laboratory,[13] pK_{D1} and pK_{D2} values have been reported at 20, 24, and 25° [14–17] and log K_1 and log K_2 values at 20 and 25°.[14,17,18] The only enthalpy change values in the literature for these systems are those reported from temperature-coefficient experiments performed in this laboratory.[13]

Experimental Section

Materials.—Solutions of NaOH and $HClO_4$ were prepared from reagent grade chemicals (J. T. Baker Chemical Co.) and were standardized using recognized analytical procedures. Stock copper(II) perchlorate solutions were prepared as described previously.[2] Glycine (Matheson Coleman and Bell) and phenylalanine (Eastman Organic Chemical) were used without further purification to prepare stock ligand solutions. Titration of the carboxyl group of glycine and phenylalanine in the presence of HCOOH[19] showed these reagents to be 99.7 and 99.2% pure, respectively.

Buffer solutions were prepared both by the method of Bates[20] and from packaged powders formulated according to National Bureau of Standards specifications by Beckman Instruments, Inc. Buffer solutions prepared to maintain a given pH value by the two methods were indistinguishable; that is, cross checking of pH values of pairs of buffer solutions prepared by the two methods gave values within ±0.002 pH unit of each other.

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.[2] Temperature differences of 0.0002° were detectable. Calibration was both electrical and chemical as described previously.[2] A microtimer (Dimco-Gray Co. 201) was used to measure the duration of heat input during electrical calibration runs. Values for the hydrogen ion activities of a number of the calorimetric solutions were determined by means of a Beckman Model GS battery-operated pH meter. A Beckman Model 76 expanded-scale pH meter was used to measure the hydrogen ion activities of the remainder of the solutions. The titrations performed to determine the values of the equilibrium constants were carried out under a nitrogen atmosphere in a temperature-controlled (±0.02°), 10-l. water bath using the method of Block and McIntyre.[21] The output of a Leeds and Northrup 7664-A1 pH meter was expanded by and recorded on a Leeds and Northrup Speedomax H 177181 continuously adjustable recorder for these titrations. At least three separate titrations consisting of at least ten points for which equilibrium constants could be calculated were performed to evaluate each constant at each of the three temperatures. Activity coefficients 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[22] and Harned and Owen[23] as described previously.[2] Crouthamel and Martin[22] assumed that the activity coefficients of all singly charged ions (γ_1) were equal as were the activity coefficients of all doubly charged ions (γ_2) in solutions of ionic strength μ less than 0.1 where the activity coefficient is independent of the specific nature of the electrolyte apart from the charge of the ions. The measured values of $\gamma^{\pm}$ for HCl in KCl solutions[23] of given μ values were assumed to be equal to γ_1 for any singly charged ion in any aqueous solution of the same μ value. The differences between γ_1^4 and γ_2 at 25° are small in these dilute solutions. These differences are probably very nearly the same at 10 and 40° as at 25°. This assumption permits the calculation of γ_2 values at 10 and 40° with the same accuracy with which the measured values at 25° were determined.

Support for the validity of the assumptions of Crouthamel and Martin in solutions with μ = 0.025 is given by the work of Kielland,[24] who calculated approximate radii and activity coefficients for a number of hydrated ions. The values for γ_1 given by Kielland for ions with effective radii varying from 3.5 to 6 A (those present in this study) ranged from 0.900 to 0.907 at μ = 0.01 (our value was 0.904), and at μ = 0.025 they ranged from 0.855 to 0.870 (our values were about 0.877 near μ = 0.02). The value for γ_2 for hydrated Ni^{2+} and Cu^{2+} ions is given by Kielland as 0.57 at μ = 0.025 (our values were about 0.58 near μ = 0.02).

A change in the value of γ_1 from 0.875 to 0.831 (5%) for a typical copper–glycine run changed the calculated value for the concentration of the CuL^+ species by only 1.26%. A change in the value of γ_2 from 0.576 to 0.634 (10%) also made a 1.26% change in the calculated value of this quantity. Changes of 5 and 10% in γ_1 and γ_2 for a typical copper–phenylalanine run each resulted in about a 3% change in the calculated value of the concentration of CuL^+.

It is interesting to note that Kielland's data indicate that a 3.6-fold change in the effective ionic radius of a singly charged ion results in only a 1.8% change in γ_1 at μ = 0.01 and a 3.6% change at μ = 0.025. A twofold change in the effective radius of a doubly charged ion results in only a 4.5% change in γ_2 at μ = 0.01 and a 9.2% change at μ = 0.025.

Calorimetric Determinations.—Three types of calorimetric determinations (x, y, and z) were performed. Type x measured the heats evolved when alkaline solutions of the amino acids were mixed with perchloric acid solutions. Types y and z measured the heats evolved when alkaline solutions of the amino acids were mixed with copper(II) perchlorate solutions at different Cu^{2+}:L^- ratios. These formality ratios in the mixed solutions for y runs were about 2:1 for glycine and 1.5:1 for phenylalanine. They were about 1:1 for all z runs. Molar heats of formation of the ligand from its ions H^+ and L^- ($-\Delta H_{D_2}°$) at μ values near 0.01

(4) H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939).
(5) E. J. King, *J. Am. Chem. Soc.*, **73**, 155 (1951).
(6) W. Corker and J. O. Harris, *J. Chem. Soc.*, 1290 (1940).
(7) J. T. Edsall and M. H. Blanchard, *J. Am. Chem. Soc.*, **55**, 2337 (1933).
(8) N. C. Li, J. M. White, and R. L. Yoest, *ibid.*, **78**, 5218 (1956).
(9) C. B. Monk, *Trans. Faraday Soc.*, **47**, 297 (1951).
(10) J. Sturtevant, *J. Am. Chem. Soc.*, **63**, 88 (1941).
(11) R. M. Keefer, *ibid.*, **70**, 476 (1948).
(12) S. P. Datta and A. K. Gryzbowski, *Trans. Faraday Soc.*, **54**, 1179 (1958).
(13) R. M. Izatt, J. W. Wrathall, and K. P. Anderson, *J. Phys. Chem.*, **65**, 1914 (1961).
(14) A. Albert, *Biochem. J.*, **47**, 531 (1950).
(15) E. L. Bennett and C. Niemann, *J. Am. Chem. Soc.*, **72**, 1804 (1950).
(16) J. C. Nevenzel, W. E. Shelberg, and C. Niemann, *ibid.*, **71**, 3024 (1949).
(17) N. C. Li and E. Doody, *ibid.*, **74**, 4184 (1952).
(18) J. Curchod, *Compt. Rend.*, **241**, 1124 (1955).
(19) "Specifications and Criteria for Biochemical Compounds," National Academy of Sciences–National Research Council, Washington, D. C., June 1960, p AAvii.
(20) R. G. Bates, *Chimia* (Aarau), **14**, 111 (1960).
(21) B. P. Block and G. H. McIntyre, *J. Am. Chem. Soc.*, **75**, 5667 (1953).
(22) C. E. Crouthamel and D. S. Martin Jr., *ibid.*, **73**, 570 (1951).
(23) 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.
(24) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

were determined from x-run data. Heats for the stepwise formation of metal chelates from the ions Cu^{2+} and L^- ($\Delta H_1°$ and $\Delta H_2°$) at μ values near 0.02 were calculated from the data obtained in y and z runs. A number of calorimetric determinations were made to measure thermal effects accompanying dilution of reactant solutions. In no case were thermal effects detectable.

Calculations.—The equations for K_{D1}, K_{D2}, K_1, and K_2 were combined with the mass balance equations for M_T, the total metal formality, and L_T, the total ligand formality in a mixed solution, to produce a cubic equation in the concentration of ML^+ from which the concentrations of all chemical species other than the hydrogen ion were calculated. This equation has been reported.[2] The heat measured in a given calorimetric run, Q_m (eq 5), is the sum of terms arising from the association of ions to form H_2O, HL, H_2L^+, ML_2, and ML^+.

$$Q_m = R + [[HL]V_f - T]Q_{HL} + [H_2L^+]V_fQ_{H_2L^+} + [ML_2]V_fQ_{ML_2} + [ML^+]V_fQ_{ML^+} \quad (5)$$

In this equation, R represents the heat produced by the formation of water from its ions, T represents the number of moles of HL present in the initial ligand solution, V_f represents the volume the final mixed solution, the bracketed quantities are the molar concentrations of the indicated species in the final solution, and each Q represents the heat produced when 1 mole of subscript species is formed from its ions, *total*, not stepwise. This equation contains a term in H_2L^+ not present in the previously reported equation for Q_m.[2] Many of the final pH values for the calorimetric determinations reported herein were low enough (<5) for the heat contributed by the formation of H_2L^+ to become measurable.

$Q_{H_2L^+}$ was represented in the equation used in calculations performed by the computer for the heat of formation of H_2L^+ from HL and H^+. This additive term was calculated from the variation of pK_{D1} with $1/T$ and was less than one-tenth the value of Q_{HA}. The contribution of $Q_{H_2L^+}$ was as large as 0.15 cal in very acid solutions but usually was of the order of a few hundredths of a calorie. Q_m was evaluated from the first three terms (eq 5) for x runs and from all terms for y and z runs.

The pH values of the initial amino acid solutions, pH_L, and of the final mixed solutions, pH_f, were such that the clear-cut distinction between y and z runs reported for copper alanine[2] no longer obtained. The z-type equation[2] for Q_m (modified to include $Q_{H_2L^+}$) was used for both y- and z-type runs. A y and z pair could be solved simultaneously to calculate Q_{ML_2} and Q_{ML^+} values.

The ratios of the concentrations of CuL_2 to CuL^+ in copper glycine solutions were about 2.2:1 for y runs and 1:6 for z runs. At a given temperature every z run was matched in turn with a given y run to obtain a "best" Q_{ML_2} value for that run. These "best" values for Q_{ML_2} were averaged and this average value substituted back into each z run to produce an average Q_{ML^+} value.

The CuL_2:CuL^+ ratios in copper phenylalanine solutions were about 1:4 and 1:6 for y and z runs, respectively. The unfavorable ratio for y runs was unavoidable because of the formation of insoluble substances in very alkaline solutions of phenylalanine. Because the pH_L values sometimes differed only slightly from the value for pK_{D2}, variations of a few thousandths of a unit in measured pH_L values caused appreciable variations in calculated Q values for these runs.

The average deviations of measured values of pH_L for phenylalanine solutions measured at 40° were ±0.006 and ±0.003 for y and z runs, respectively. Average values for all y and z data at 40° were used to calculate a value for Q_{ML^+} inasmuch as ML^+ was present in much greater quantities than was ML_2. This value for Q_{ML^+} was substituted into the heat equation for each y and each z run individually to obtain an average value for Q_{ML^+}. A value for Q_{ML^+} was also determined by setting limits on Q_{ML_2} as a function of Q_{ML^+}. It was possible to set limits because the concentrations of ML^+ were much greater than those of ML_2 so that large variations of Q_{ML_2} produced relatively small variations in Q_{ML^+}. The value of Q_{ML^+} determined in this manner differed by only 0.04 kcal from that obtained by the more conventional procedure.

The final mixed solutions for determinations involving phenylalanine at 10 and 25° were of necessity more acidic than were those at 40° because insoluble substances formed at lower pH values as the temperature was lowered. In these solutions the CuL_2:CuL^+ ratios for y and z runs became so nearly the same that only the limit-setting method used at 40° was feasible at 10 and 25°. An analysis of the ratios of Q_{ML_2} to Q_{ML^+} for copper glycine, copper alanine, and copper phenylalanine was made to ascertain any observable trends. The results of this analysis predicted Q_{ML_2}:Q_{ML^+} ratios of about 1.20 and 1.07 for copper phenylalanine at 25 and 10°, respectively. The results obtained from the limit-setting method gave ratios of 1.21 and 1.07, in excellent agreement with the predicted values.

Results

Values of pK_{D1}, pK_{D2}, log K_1, and log K_2 are given in Table I. Comparison data from the literature are included. The experimental data are presented in Table II.

TABLE I

pK AND LOG K VALUES FOR IONIZATION AND COMPLEX FORMATION, RESPECTIVELY[a]

t, °C	pK_{D1}	pK_{D2}	Log K_1	Log K_2	Log (K_1K_2)
	Glycine		Copper–Glycine		
10	2.41	10.20	8.85	7.36	
	2.404[3]	10.20[3]			
	2.397[6]	10.193[6]			
		10.194[13,b]			
25	2.39	9.77	8.58	7.09	
	2.35[5]	9.78[5]			
	2.35[6]	9.78[6]			
	2.41[7]	9.75[7]			
	2.31[8]	9.72[8]			
		9.68[9]			15.10[9]
	2.35[10]	9.78[10]	8.62[10]	6.97[10]	
		9.78[13]	8.28[12]	7.70[12]	
40	2.33	9.46	8.42	6.85	
	2.324[5]	9.49[5]			
	2.327[6]	9.412[6]			
		9.21[9]			14.60[9]
		9.214[13,b]			
	Phenylalanine		Copper–Phenylalanine		
10	2.14	9.75	8.48	7.43	
	2.21[14]	9.66[14]	8.45[14]	7.26[14]	
			8.38[14]	7.21[14]	
25	2.20	9.31	8.25	7.13	
	2.16[17]	9.15[17]	7.70[19]	6.94[19]	
		9.13[18]			14.7[18]
40	2.21	8.96	8.13	6.94	
	2.20[14]	8.89[14]	8.12[14]	6.79[14]	
			8.03[14]	6.78[14]	
			8.02[14]	6.76[14]	

[a] For ref 9, μ = 0.15 and for ref 17 and 18, μ = 0.1. [b] Interpolated values.

Inasmuch as no detectable thermal effects accompanied the dilution of reactants at these low initial concentrations, measured enthalpy changes were considered to be standard or "infinite dilution" enthalpy changes.

The uncertainty in the determination of pK_D values was about ±0.01 unit while for log K values it was about ±0.03 unit. Table III summarizes the calori-

TABLE II[a]

CALORIMETRIC DATA FOR TYPES x, y, AND z RUNS FOR THE REACTION OF GLYCINATE AND PHENYLALANATE IONS WITH H^+ AND Cu^{2+} AT 10, 25, AND 40°. THE REACTION FOR x RUNS WAS $H^+ + L^- = HL$, AND FOR y AND z RUNS IT WAS $Cu^{2+} + (2 - n)L^- = nCuL^+ + (1 - n)CuL_2$ $(0 \leq n \leq 1)$

Run type	t, °C	$10^4\mu$	No. of runs	V_L, ml	V_{a-M}, ml	10^2F_{a-M}	10^3F_L	10^3F_{NaL}	pH_L	pH_f	Q_m, cal	$\Delta H°$, kcal/mole
						Glycine						
x	10	88	6	99.69	9.97	9.64	9.95	9.77	10.994	7.029	10.42 ± 0.06	−11.57 ± 0.11
	25	89	6	99.96	10.00	9.61	9.90	9.74	10.650	6.949	10.19 ± 0.05	−10.76 ± 0.05
	40	86	6	100.01	10.05	9.86	9.90	9.68	10.277	6.999	9.64 ± 0.09	−10.22 ± 0.08
y	10	185	7	99.69	9.97	9.94	19.87	16.89	10.727	5.809	11.00 ± 0.06	−14.20 ± 0.07
	25	185	6	99.96	10.00	9.91	18.65	16.84	10.521	5.830	10.79 ± 0.12	−13.18 ± 0.16
	40	185	5	100.45	10.05	9.86	19.49	16.77	10.034	5.550	10.36 ± 0.04	−13.08 ± 0.02
z	10	185	6	99.69	9.97	9.94	9.94	9.39	10.868	5.329	5.92 ± 0.08	−7.28 ± 0.04
	25	202	6	99.96	10.00	9.91	9.92	9.37	10.557	5.160	5.69 ± 0.04	−6.22 ± 0.08
	40	202	6	100.45	10.05	9.86	9.88	9.32	10.203	5.027	5.43 ± 0.06	−5.75 ± 0.06
						Phenylalanine						
x	10	88	3	99.69	9.97	9.64	9.90	9.77	10.650	6.682	10.28	−11.42
		88	4	99.04	4.50	20.06	9.06	8.98	10.699	4.116	9.48	−11.38
	25	89	5	99.96	10.00	9.61	9.97	9.74	10.333	6.877	10.14	−10.72
		86	7	99.27	4.40	20.00	9.03	8.96	10.17	5.24	8.70	−10.61
	40	88	5	100.45	10.05	9.56	9.89	9.51	9.914	4.817	9.85	−10.54
		86	6	99.21	4.51	19.92	8.99	8.92	9.581	6.399	7.73	−10.51
y	10	190	6	99.04	8.40	10.21	12.99	7.60	9.717	4.055	3.54	
	25	190	5	99.27	8.40	10.18	12.95	7.58	9.34	3.88	3.35	
	40	182	7	99.21	8.41	10.14	12.90	7.99	9.038	3.823	3.29	
z	10	190	6	99.04	8.40	10.21	9.06	6.74	9.725	4.238	2.33	
	25	193	5	99.27	8.40	10.18	9.03	7.72	9.53	4.10	2.92	
	40	190	6	99.21	8.41	10.14	8.99	6.99	9.206	3.967	2.54	

[a] Q_m represents the total measured heat. The subscripts L and f refer to initial ligand solutions and the final mixed solutions, respectively. V_{a-M} refers to the volume of the initial acid (x runs) or metal (y and z runs) solutions, while F_{a-M} refers to their formalities in acid or Cu^{2+}. F_L and F_{NaL} refer to the formalities of ligand and sodium ion, respectively, in the initial ligand solutions.

TABLE III

SUMMARY OF $\Delta H°$ AND $\Delta S°$ VALUES FOR HL^+ IONIZATION AND Cu^{2+}–L^- INTERACTION[a]

Temp, °C	$\Delta H_{D_2}°$, kcal/mole	$\Delta S_{D_2}°$, eu	$\Delta H_1°$, kcal/mole	$\Delta S_1°$, eu	$\Delta H_2°$, kcal/mole	$\Delta S_2°$, eu
			Ligand: Glycine			
10	11.57 ± 0.11	−5.8	−7.28 ± 0.04	14.8	−6.92 ± 0.08	9.2
25	10.76 ± 0.05	−8.6	−6.22 ± 0.08	18.4	−6.96 ± 0.19	9.1
	10.00[b]	−11.2[b]	−5.83[b]	19.7[b]	−6.83[b]	9.5
	10.6[3]	−9[3]	−6.0[3]	19[3]	−6.4	11[3]
	10.72[5]		(−21.0)[9,c]			
	10.55[6]					
	10.6[11]					
	10.56[13]					
40	10.22 ± 0.08	−10.7	−5.75 ± 0.06	20.2	−7.33 ± 0.07	7.9
			Ligand: Phenylalanine			
10	11.40 ± 0.11	−4.3	−6.0 ± 0.5	17.7	−6.4 ± 1.0	10.3
25	10.67 ± 0.09	−6.7	−5.3 ± 0.3	19.8	−6.4 ± 0.8	13.7
	10.63[b]	−7.3[b]	−4.48[b]	22.8[b]	−6.4[b]	10.9[b]
	10.3[14]	−7.8[14]	−5.1[14]	20.7[14]	−6.4[14]	10.7[14]
40	10.53 ± 0.12	−7.4	−4.85 ± 0.12	21.8	−5.5 ± 0.2	14.2

[a] Results reported in ref 3, 10, and 11 were obtained by calorimetric methods. [b] Calculated from pK and log K temperature dependence. [c] The sum of $\Delta H_1°$ and $\Delta H_2°$.

metric data obtained in this research as well as calculated $\Delta S°$ values. Estimated uncertainties for $\Delta H°$ values are given. For determinations involving glycine, these uncertainties are average deviations of calorimetric results and do not include contributions due to the uncertainties in log K and pK values. For determinations involving phenylalanine, the uncertainties given are over-all estimates.

Comparison values of $\Delta H°$ and $\Delta S°$ from the literature are given. Values of $\Delta H°$ obtained from the slopes of pK_2, log K_1, and log K_2 *vs.* $1/T$ plots are included for comparison purposes.

Discussion

The data in Tables I and III are in reasonable agreement with previous results where these are available.

An unusual feature of the present study is the inversion of the relative magnitudes of the $\Delta H_n°$ values for copper(II)–glycine interaction from 10 to 40°. Additional studies of metal–amino acid systems will