CALORIMETRIC DETERMINATION OF THE HEATS OF FORMATION OF COMPETITIVE TERNARY MIXED-LIGAND COMPLEX COMPOUNDS. COPPER(II)–N-ACETYLGLYCINE–α-AMINO ACID SYSTEM *

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ABSTRACT

The heats of protonation of eight α-amino acids (N-acetylglycine, proline, threonine, serine, valine, glycine, isoleucine and α-aminoisobutyric acid) have been determined in aqueous solution at $25.0 \pm 0.1°C$ and I (ion strength) $= 0.1 \text{ mol dm}^{-3}$ ($NaClO_4$) by means of a model RD-1 automatic conduction calorimeter. The heats of the stepwise formation of binary complex compounds of these ligands with copper(II) have also been determined under identical conditions. By utilizing the calorimetric data, the heats of formation of the ternary complex compounds of the type copper(II)–N-acetylglycine–α-amino acid have been evaluated through "overall calculation". Some linear enthalpy and entropy relationships have been found to exist between the ternary and the parent binary systems.

INTRODUCTION

We have previously reported [1] the calorimetric determination of the heats of formation of copper(II)–2,2′-bipyridyl–α-amino acid ternary complex compounds which were treated essentially as ordinary binary systems because of the very high stability of the $Cu(bipy)^{2+}$ species formed in the pH range studied as a single moiety. The mathematical treatment in this case was rather simple. However, the situation is different in the copper(II)–N-acetylglycine–α-amino acid system [2], which is similar to the copper(II)–oxalate–ethylenediamine system we reported earlier [3], where both the first and second ligands form competitive complexes with the copper ion and the binary complex compounds of one ligand can be replaced by another in a different pH range owing to the difference in acidity or basicity of the ligands. In other words, when we consider the

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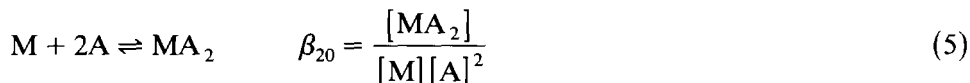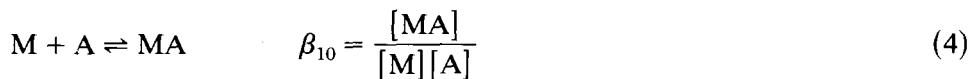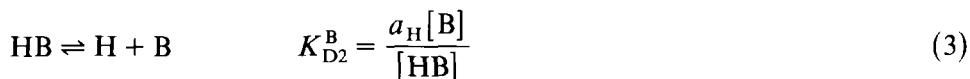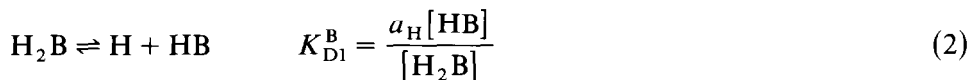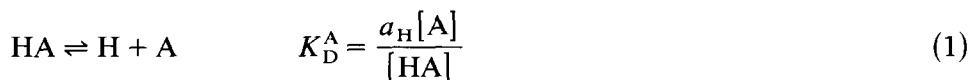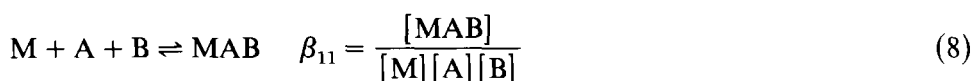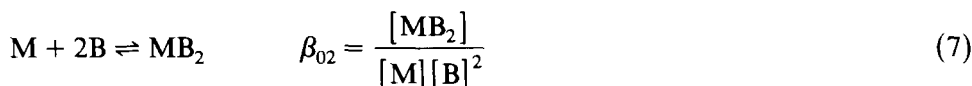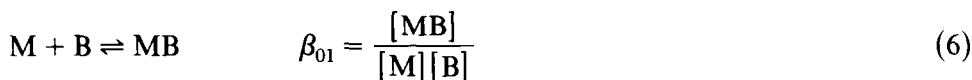** To whom correspondence should be addressed.

formation of a ternary complex compound, we must take into account the binary complexation equilibria of both ligands with the copper ion. The mathematical treatment is indeed more complicated, but it is theoretically practical. In addition, this kind of consideration and treatment are more or less close to the reality of many biochemical equilibrium systems existing in nature and may be of some value to certain biochemical and medical investigations.

THEORETICAL

We have previously reported [3] the calorimetric study of the copper(II)–oxalate–ethylenediamine competitive ternary system under the chosen experimental conditions of a high molar ratio of both ligands to metal ion. It was presumed that no free metal ion or monocoordinated binary complex compounds would be present in the system, thus making the mathematical treatment rather simple. For this paper, however, on investigating the formation reactions of the copper(II)–N-acetylglycine–α-amino acid ternary system, we took a comparable molar ratio of ligands to metal and neglected any species in the system which would lead to a serious error in the subsequent results. Therefore, we adopted the following method for the data treatment which may be called "overall calculation". In this treatment all charges are omitted for the sake of convenience. A, B and M represent the first and second ligand and the metal ion, copper(II), respectively.

No matter how the reactant solutions are mixed, either by mixing copper(II) with (A + B), (copper(II) + A) with B or (copper(II) + B) with A, the following eight independent equilibria must be taken into consideration in the final equilibrium system:

$$HA \rightleftharpoons H + A \qquad K_D^A = \frac{a_H[A]}{[HA]} \qquad (1)$$

$$H_2B \rightleftharpoons H + HB \qquad K_{D1}^B = \frac{a_H[HB]}{[H_2B]} \qquad (2)$$

$$HB \rightleftharpoons H + B \qquad K_{D2}^B = \frac{a_H[B]}{[HB]} \qquad (3)$$

$$M + A \rightleftharpoons MA \qquad \beta_{10} = \frac{[MA]}{[M][A]} \qquad (4)$$

$$M + 2A \rightleftharpoons MA_2 \qquad \beta_{20} = \frac{[MA_2]}{[M][A]^2} \qquad (5)$$

$$M + B \rightleftharpoons MB \qquad \beta_{01} = \frac{[MB]}{[M][B]} \tag{6}$$

$$M + 2B \rightleftharpoons MB_2 \qquad \beta_{02} = \frac{[MB_2]}{[M][B]^2} \tag{7}$$

$$M + A + B \rightleftharpoons MAB \qquad \beta_{11} = \frac{[MAB]}{[M][A][B]} \tag{8}$$

K_{D1}^B and K_{D2}^B denote the first and second dissociation constants of ligand B respectively. β_{ij} denotes the consecutive complexity constants of copper(II) with ligand A and B. The values of (i and j) vary from 0 to 2. For mass balance, we have

$$T_A = [A] + [HA] + [MA] + 2[MA_2] + [MAB] \tag{9}$$

$$T_B = [B] + [HB] + [H_2B] + [MB] + 2[MB_2] + [MAB] \tag{10}$$

$$T_M = [M] + [MA] + [MA_2] + [MB] + [MB_2] + [MAB] \tag{11}$$

where T_A, T_B and T_M are the total concentrations of A, B and M respectively. Let

$$n_A = 1 + \frac{a_H}{K_D^A}$$

and

$$n_B = 1 + \frac{a_H}{K_{D_1}^B} + \frac{a_H^2}{K_{D_1}^B K_{D_2}^B}$$

Then the following three expressions for [M] can be obtained:

$$[M] = \frac{T_A - n_A[A]}{\beta_{10}[A] + \beta_{11}[A][B] + 2\beta_{20}[A]^2} \tag{12}$$

$$[M] = \frac{T_B - n_B[B]}{\beta_{01}[B] + \beta_{11}[A][B] + 2\beta_{02}[B]^2} \tag{13}$$

$$[M] = \frac{T_M}{1 + \beta_{10}[A] + \beta_{20}[A]^2 + \beta_{01}[B] + \beta_{02}[B]^2 + \beta_{11}[A][B]} \tag{14}$$

From eqns. (12) and (14), we obtain eqn. (15):

$$u[B]^2 + v[B] + w = 0 \tag{15}$$

where

$$u = 2\beta_{02}(T_A - n_A[A]) + n_B\beta_{11}[A] \tag{15a}$$

$$v = (2n_B\beta_{20} - n_A\beta_{11})[A]^2 + [(T_A - T_B)\beta_{11} + n_B\beta_{10} - n_A\beta_{01}][A] + T_A\beta_{01} \tag{15b}$$

$$w = -T_B(\beta_{10} + 2\beta_{20}[A])[A] \tag{15c}$$

Furthermore, if a and b denote the denominator of eqn. (12) and eqn. (14) respectively, then we obtain eqn. (16):

$$aT_M - (T_A - n_A[A])b = 0 \tag{16}$$

We have previously determined [2] the equilibrium constants expressed by eqns. (1)–(8). If an initial value of [A] is assumed, we can obtain a set of u, v and w values by using eqns. (15a)–(15c) and a reasonable value of [B] may be obtained by solving eqn. (15). From the assumed [A] value and the [B] value obtained, a and b values can be calculated readily. If a and b values do not fit eqn. (16), a new [A] value may be assumed and the computation repeated again and again until the absolute value of the left-hand side of eqn. (16) is a minimum (close to zero). In this way the concentrations of the free ligands A and B as well as of other species in the equilibrium system can be evaluated. The concentration of the species existing in the initial solutions may be obtained in accordance with the way the reactant solutions are mixed. Thus, since the equilibrium constants expressed by eqns. (1)–(8) are known [2], and using the experimental data, the molar concentrations of all species in equilibrium before and after the determination can be calculated.

Then, for energy balance, the following thermochemical equation can be established:

$$\begin{aligned}
Q_c = \overline{Q}_m - \overline{Q}_b &= R + ([HA]_f V_f - [HA]_i V_i)\Delta H^A + \big[([HB]_f + [H_2B]_f)V_f \\
&\quad - ([HB]_i + [H_2B]_i)V_i\big]\Delta H_1^B + ([H_2B]_f V_f - [H_2B]_i V_i)\Delta H_2^B \\
&\quad + \big[([MA]_f + [MA_2]_f)V_f - ([MA]_i + [MA_2]_i)V_i\big]\Delta H_{M_1}^A \\
&\quad + ([MA_2]_f V_f - [MA_2]_i V_i)\Delta H_{M_2}^A + \big[([MB]_f + [MB_2]_f)V_f \\
&\quad - ([MB]_i + [MB_2]_i)V_i\big]\Delta H_{M_1}^B + ([MB_2]_f V_f \\
&\quad - [MB_2]_i V_i)\Delta H_{M_2}^B + [MAB]_f V_f \Delta H_{MAB} \tag{17}
\end{aligned}$$

where Q_c denotes the corrected heat; $\overline{Q}_m$ denotes the average value of the measured heat effects of the reaction under investigation; $\overline{Q}_b$ denotes the average heat of the blank tests; R represents the heat produced by the association of H^+ and OH^- to form H_2O; ΔH^A denotes the heat of protonation of ligand A; ΔH_1^B (ΔH_2^B) denotes the heats of the first (second) step protonation of ligand B; $\Delta H_{M_1}^A$ ($\Delta H_{M_2}^A$) and $\Delta H_{M_1}^B$ ($\Delta H_{M_2}^B$) denote the heats of the first (second) step complexation of ligand A and B with copper(II) respectively; ΔH_{MAB} denotes the heat of formation of ternary complex compounds; $[\ ]_f$ and $[\ ]_i$ represent the molar concentrations (mol dm^{-3}) of the indicated species after and before the reaction respectively; V_f and V_i represent the total volume of the final mixed solution and the volume of the initial solution respectively.

After the heats of protonation of both ligands and the heats of formation of binary complex compounds have been determined experimentally, the

heat of formation of the ternary mixed-ligand complex compound can be calculated from a set of calorimetric measurements by means of eqn. (17).

The method used to determine and calculate the heats of stepwise complexation of the copper(II)–α-amino acid binary system is the same as that described previously [4]. However, the determination and calculation of the heats of stepwise protonation of α-amino acids is somewhat different. In the present work, the α-amino acid was reacted with an equimolar standard acid or base. The concentrations of all species before and after reaction can be calculated by using previously determined pK values and the pH values of the solution before and after reaction. The heat produced by the formation of water was calculated in accordance with the decrease in the amount of acid or base. From two sets of calorimetric data, the values of ΔH_1 and ΔH_2 can be obtained by solving the simultaneous eqns. (18)

$$Q_c = \overline{Q}_m - \overline{Q}_b = R + \{([HL]_f + [H_2L]_f)V_f - ([HL]_i + [H_2L]_i)V_i\}\Delta H_1$$
$$+ ([H_2L]_f V_f - [H_2L]_i V_i)\Delta H_2 \tag{18}$$

where ΔH_1 and ΔH_2 represent the heats of first step and second step protonation respectively and L represents the ligand A or B. The meanings of the other symbols are the same as those of the symbols of eqn. (17).

EXPERIMENTAL

Copper perchlorate was prepared and the concentration of copper(II) in the stock solution was analysed by means of a conventional method. The concentration of free acid in the copper(II) solution was calibrated with a standard base solution by pH measurement. The standard acid (perchloric acid obtained from Tianjin Dongfang Chemical Reagent Factory, G.R.) and the base (NaOH obtained from Tianjin Third Chemical Reagent Factory, A.R.) solution were prepared according to standard procedures. All the α-amino acids (biochemical reagents) were obtained commercially (from Shanghai Chemical Reagent Station). Sodium perchlorate (obtained from Beijing Nanshangle Chemical Reagent Factory, A.R.) was recrystallized from 90% ethanol solution.

A model RD-1 automatic conduction calorimeter with a precision of $\pm 0.5\%$ [5] has been used to measure the heat effect. The instrumental constant K was determined to be $(3.51 \pm 0.06) \times 10^{-3}$ J mm^{-2} (n (number of tests) = 11) by using electrical power calibration and was again checked by chemical calibration (Tris(aq) + HCl(aq)). An average value for the heat of neutralization, $\Delta H_N = -11.36 \pm 0.06$ kcal mol^{-1} ($n = 7$), was obtained which is in good agreement with the literature value [6]. The pH values of the solutions were measured by a model pHS-2 pH meter (precision: 0.02 pH units).

TABLE 1

Determination of the heats of protonation of α-amino acids (temperature, 25.0±0.2°C; $I = 0.1$ mol dm⁻³ (NaClO₄); $\Delta H_N = -56.4$ kJ mol⁻¹ [1]; $v_\pm = 0.796$ [7])

α-Amino acid	n[a]	T_L (×10² mol dm⁻³)	T_H (T_{OH}) (×10² mol dm⁻³)	pH$_i$	pH$_f$	Q_c (J)	pK_1 [2]	pK_2 [2]	ΔH_1 (kJ mol⁻¹)	ΔH_2 (kJ mol⁻¹)
N-Acetylglycine	5	1.384	(1.384)	2.74	6.72	−17.3 ±0.03	3.51		0.15±0.11	
Proline	5 5	1.384	(1.384) 1.406	5.89 6.05	11.21 2.19	−3.56 ±0.02 0.010±0.020	1.77	10.39	−43.3 ±0.1	0.1 ±0.2
Threonine	5 5	1.384	(1.384) 1.406	5.68 5.72	10.36 2.23	−4.14 ±0.02 −0.658±0.020	2.20	8.98	−43.9 ±0.1	−3.99±0.06
Serine	6 4	1.384	(1.384) 1.406	5.69 5.88	10.33 2.25	−3.86 ±0.03 −0.709±0.020	2.29	9.02	−45.5 ±0.1	−3.99±0.06
Valine	5 5	1.384	(1.384) 1.406	5.99 5.90	10.69 2.28	−3.27 ±0.02 0.064±0.020	2.34	9.57	−47.3 ±0.1	0.35±0.11
Glycine	5 5	1.384	(1.384) 1.406	5.92 5.85	10.67 2.28	−3.23 ±0.02 −0.695±0.020	2.36	9.56	−47.7 ±0.2	−3.81±0.10
Isoleucine	4 4	1.384	(1.384) 1.406	5.98 6.19	10.89 2.31	−3.01 ±0.2 −0.147±0.01	2.26	9.60	−48.5 ±0.1	−0.9 ±0.1
α-Aminoiso-butyric acid	5 5	1.384	(1.384) 1.406	6.30 6.08	10.97 2.32	−2.12 ±0.02 −0.287±0.020	2.44	10.08	−51.9 ±0.1	−1.5 ±0.1

[a] Number of tests.

TABLE 2

Determination of the heats of complexation of copper(II) with α-amino acid (temperature, 25.0±0.2°C; I = 0.1 mol dm⁻³ (NaClO₄))

α-Amino acid	n	T_L (×10³ mol dm⁻³)	T_M (×10³ mol dm⁻³)	pH_i	pH_f	Q_c (J)	Log K_{M_1} [2]	Log K_{M_2} [2]	ΔH_{M_1} (kJ mol⁻¹)	ΔH_{M_2} (kJ mol⁻¹)
N-Acetylglycine	5	17.42	8.741	7.33	5.52	0.43±0.03	2.40	2.14	1.9±0.4	1.9±0.4
	5	8.709	8.741	6.73	5.37	0.24±0.03				
Proline	5	8.709	7.010	11.10	6.39	−5.67±0.04	8.80	7.50	−27.9±0.3	−28.5±0.1
	4	8.709	5.070	11.12	6.62	−5.88±0.03				
Threonine	5	8.709	8.741	10.21	5.63	−4.97±0.04	8.02	6.66	−27.5±0.3	−28.0±0.3
	6	8.709	4.370	10.21	7.24	−5.05±0.02				
Serine	4	8.709	7.010	10.26	7.23	−4.73±0.04	7.95	6.57	−26.1±0.2	−27.3±0.2
	5	8.709	5.070	10.20	6.19	−4.79±0.04				
Valine	4	8.709	8.741	10.58	5.82	−4.67±0.02	8.15	6.82	−26.0±0.3	−27.3±0.3
	5	8.709	4.370	10.58	7.60	−4.77±0.02				
Glycine	5	8.709	8.741	10.65	5.92	−5.23±0.02	8.16	6.81	−28.0±0.4	−28.3±0.6
	4	8.709	4.370	10.65	7.75	−5.27±0.03				
Isoleucine	5	8.709	8.741	10.47	5.76	−4.71±0.04	8.16	6.86	−28.9±0.4	−28.7±0.2
	4	8.709	4.370	10.47	7.55	−4.71±0.02				
α-Aminoiso-butyric acid	5	8.709	8.741	10.86	6.00	−4.47±0.02	8.34	7.01	−25.8±0.3	−27.6±0.3
	5	8.709	4.370	10.86	7.89	−4.57±0.02				

TABLE 3

Determination of the heats of complexation of copper(II)–N-acetylglycine–α-amino acid ternary systems

α-Amino acid	n	T_A (×10³ mol dm⁻³)	T_B (×10³ mol dm⁻³)	T_M (×10³ mol dm⁻³)	pH_i (A)	pH_i (MB)	pH_f	Q_c (J)	Log β_{11} [2]	ΔH_{MAB} (kJ mol⁻¹)
Proline	4	27.25	9.173	4.370	4.09	9.63	4.84	-1.63 ± 0.02	11.28	-25.9 ± 0.3
	5	22.00	9.173	4.370	4.16	9.67	5.19	-1.44 ± 0.03		-26.4 ± 0.5
Threonine	5	26.22	9.173	4.370	3.83	8.31	4.22	-1.77 ± 0.02	10.35	-25.0 ± 0.4
	5	20.17	9.173	4.370	4.14	8.31	4.82	-1.27 ± 0.01		-25.3 ± 0.2
Serine	5	26.22	9.173	4.370	3.83	8.54	4.28	-2.12 ± 0.02	10.30	-24.2 ± 0.4
	3	22.00	9.173	4.370	4.16	8.56	4.95	-1.56 ± 0.03		-24.1 ± 0.5
Valine	5	26.22	9.173	4.370	3.83	9.66	4.38	-2.72 ± 0.02	10.53	-23.9 ± 0.4
	4	22.00	9.173	4.370	4.16	9.18	5.02	-1.91 ± 0.03		-23.4 ± 0.5
Glycine	3	22.00	9.091	4.370	4.16	9.46	5.14	-1.81 ± 0.05	10.52	-25.6 ± 0.9
Isoleucine	5	26.22	9.173	4.370	3.83	9.64	4.36	-2.72 ± 0.02	10.51	-27.6 ± 0.4
	5	20.17	9.173	4.370	4.14	9.64	5.11	-1.89 ± 0.02		-25.6 ± 0.4
α-Aminoiso-butyric acid	4	27.25	9.182	4.370	4.09	9.56	4.95	-2.90 ± 0.04	10.76	-24.3 ± 0.7
	5	22.00	9.182	4.370	4.16	9.56	5.16	-2.59 ± 0.03		-24.3 ± 0.5

Determination of the heats of protonation of α-amino acids

2.00 cm^3 of NaOH solution (0.1522 mol dm^{-3}) was put in the sample tube and 20.00 cm^3 of the α-amino acid solution (0.01522 mol dm^{-3}) was put in the reaction chamber with the former being placed in the latter and the whole set was put into the calorimetric vessel. The vessel was then inserted into the calorimeter for several hours to attain thermal equilibrium when the base line of the photo-pen recorder was in normal position. The solutions were thoroughly mixed and the heat evolved in the reaction cell was calculated from the area under the curve by means of a model KP-39 zero-setting compensating planimeter. The equivalent heat amount (J) was calculated from the instrumental constant K. The pH values before and after reaction were measured at the same time. In this way, the first set of data was obtained. By replacing NaOH solution with HClO$_4$ solution (0.1547 mol dm^{-3}) for the run, the second set of data was then obtained.

For blank tests, the blank solution of NaClO$_4$ (0.1 mol dm^{-3}) was mixed with the acid or base solution to measure the heat of dilution. The heats of dilution of α-amino acids were neglected because the change in concentration on mixing was very small.

From the pK values previously reported [2] and the measured pH values, the heats of protonation of all the eight α-amino acids were calculated. The experimental data and results are tabulated in Table 1.

Determination of the heats of complexation of the copper(II)–α-amino acid binary system

The experimental procedures are the same as those described earlier [4]. The results of the heats of stepwise complexation of the eight α-amino acids with copper(II) are shown in Table 2.

Determination of the heats of formation of copper(II)–N-acetylglycine–α-amino acid ternary complex compounds

2.00 cm^3 of *N*-acetylglycine (A) was reacted with 20.00 cm^3 of copper(II)–α-amino acid (MB). The experimental procedures are the same as those described above. The results obtained are tabulated in Table 3.

RESULTS AND DISCUSSION

The results in Tables 1 and 2 are in good agreement with those reported in the literature [8].

It is seen from Table 3 that the results of the two sets of experiments, except those involving glycine, agree satisfactorily. The heats of replacement,

TABLE 4

The apparent thermodynamic functions of copper(II)–N-acetylglycine–α-amino acid ternary systems (temperature, $25.0 \pm 0.2\,°C$; $I = 0.1$ mol dm^{-3} (NaClO$_4$))

α-Aminoacid	ΔG_{MAB} (2) (kJ mol^{-1})	ΔH_{MAB} (kJ mol^{-1})	ΔS_{MAB} (J K^{-1} mol^{-1})	ΔH_{R1} (kJ mol^{-1})	ΔH_{R2} (kJ mol^{-1})
Proline	−64.4	−26.2 ± 0.7	128 ± 2	30.2	30.0
Threonine	−59.1	−25.2 ± 0.6	114 ± 2	30.3	29.0
Serine	−58.8	−24.2 ± 0.6	116 ± 2	29.2	28.0
Valine	−60.1	−23.7 ± 0.8	122 ± 2	29.6	27.5
Glycine	−60.1	−25.6 ± 0.9	116 ± 3	30.7	29.4
Isoleucine	−60.1	−26.6 ± 1.4	112 ± 5	31.0	30.4
α-Aminoiso-butyric acid	−61.4	−24.3 ± 0.7	124 ± 2	29.1	28.1

ΔH_{R1} and ΔH_{R2}, for reactions (19) and (20) were calculated from the average ΔH_{MAB} values according to Hess' Law and were tabulated with other apparent thermodynamic functions of the ternary complex compounds in Table 4.

$$MB_2 + A \rightleftharpoons MAB + B \qquad \Delta H_{R1} \tag{19}$$

$$MAB + A \rightleftharpoons MA_2 + B \qquad \Delta H_{R2} \tag{20}$$

From Table 4 it is seen that the heats of the two stepwise replacement reactions are comparable, with ΔH_{R1} slightly larger than ΔH_{R2}, which is in agreement with the heats of formation of binary complex compounds shown in Table 2. Linear enthalpy relationships are found to exist between ΔH_{1+2} and ΔH_{R1} and between ΔH_{1+2} and ΔH_{R2} as expressed by the following regression equations:

$$\Delta H_{R1} = -8.24 - 0.395\Delta H_{1+2} \qquad r = -0.947 \tag{21}$$

$$\Delta H_{R2} = -4.44 - 0.605\Delta H_{1+2} \qquad r = -0.976 \tag{22}$$

ΔH_{R1} (ΔH_{R2}) denotes the heat of replacement of B in MB$_2$ (MAB) by A.

The ΔG_{1+2} and ΔS_{1+2} values of the binary complex compounds were calculated from the log β_{02} values obtained previously [2] and from the enthalpy values shown in Table 2. These results are tabulated in Table 5.

In contrast with previous reports [1–4] the present data show no obvious linear relationships between the heats of protonation of the α-amino acids (see Table 1) and the heats of binary complexation (ΔH_{1+2}) or heats of ternary complexation (ΔH_{MAB}), although linear free energy relationships do exist in the system [2]. However, a linear enthalpy relationship has been found to exist between the heats of formation of the ternary and the binary parent complex compounds (Fig. 1) with a correlation equation as follows:

$$\Delta H_{MAB} = 8.24 + 0.605\Delta H_{1+2} \qquad r = 0.976$$

TABLE 5

The apparent thermodynamic functions of copper(II)–α-amino acid binary systems (temperature, $25 \pm 0.2\,^\circ$C; $I = 0.1$ mol dm^{-3} (NaClO$_4$))

α-Aminoacid	Log β_{02}	ΔG_{1+2} (kJ mol^{-1})	ΔH_{1+2} (kJ mol^{-1})	ΔS_{1+2} (J K^{-1} mol^{-1})
Proline	16.30	-93.1	-56.4	123 ± 1
Threonine	14.68	-83.8	-55.5	95 ± 2
Serine	14.52	-82.9	-53.4	99 ± 1
Valine	14.97	-85.5	-53.3	108 ± 2
Glycine	14.97	-85.5	-56.3	98 ± 3
Isoleucine	15.02	-85.7	-57.6	94 ± 2
α-Aminoiso-butyric acid	15.35	-87.6	-53.4	115 ± 2

[a] The subscript $1+2$ indicates the sum of the thermodynamic functions of the first- and second-step reactions.
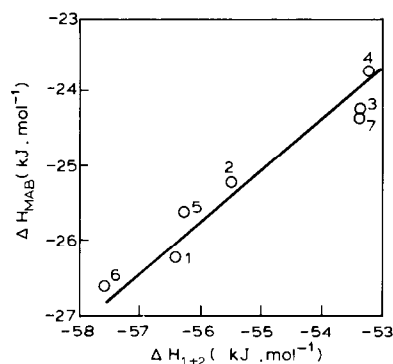

Fig. 1. Linear enthalpy relationships between ternary and binary systems for complexation reactions. The ligands are: 1, proline; 2, threonine; 3, serine; 4, valine; 5, glycine; 6, isoleucine; 7, α-aminoisobutyric acid.
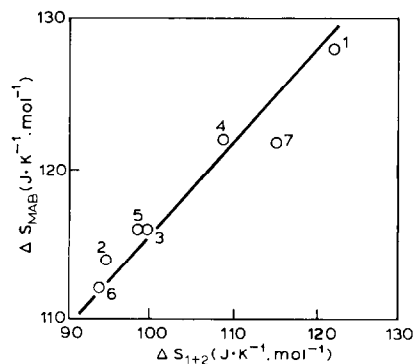

Fig. 2. Linear entropy relationships between ternary and binary systems for complexation reactions. The ligands are the same as those in Fig. 1.

Moreover, a good linear entropy relationship was also found to exist between the corresponding reactions (Fig. 2), with a correlation equation expressed as follows:

$$\Delta S_{MAB} = 64.1 + 0.524\Delta S_{1+2} \qquad r = 0.990$$

It is reasonable that the entropy effect existing in a binary complex system would also exist in a ternary system and thus linear enthalpy relationships are manifested between the heats of formation of the ternary and binary parent complex compounds.

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