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LINEAR ENTHALPY RELATIONSHIPS BETWEEN THE HEATS OF FORMATION OF COORDINATION COMPOUNDS AND THE HEATS OF PROTONATION OF THE LIGANDS. THE COPPER(II)–*N*-(*meta*-SUBSTITUTED PHENYL)-IMINODIACETIC ACID–α-AMINO ACID COMPETITIVE TERNARY SYSTEM

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ABSTRACT

The heats of formation of the ternary complex compounds of Cu^{II} – *N*-(*meta*-substituted phenyl)iminodiacetic acid–α-amino acid (*m*-RPhIDA, *N*-(*meta*-substituted phenyl)iminodiacetic acid, R ≡ CH_3, H, CH_3O or Cl; AA, α-amino acid, AA ≡ proline, α-aminoisobutyric acid, isoleucine, glycine, valine or serine) have been determined in aqueous solution at 25.0 ± 0.2 °C and $I = 0.1$ mol dm^{-3} (KNO_3) by means of an automatic conduction calorimeter, model RD-1. The results show the existence of linear enthalpy relationships between the heats of formation of these ternary compounds and the heats of protonation of the *m*-RPhIDA ligands.

INTRODUCTION

The linear enthalpy relationships in the ternary systems of Cu^{II}–2,2′-bipyridylphenanthroline–*N*-(*meta*-substituted phenyl)iminodiacetic acid have been reported previously [1]. In order to explore further the nature of the complex compounds formed with competitive multidentate mixed ligands in biological systems, we have investigated calorimetrically the formation reaction of the competitive ternary complex compounds Cu^{II}-*N*-(*meta*-substituted phenyl)iminodiacetic acid–α-amino acid (*m*-RPhIDA, *N*-(*meta*-substituted phenyl)iminodiacetic acid, R ≡ CH_3, H, CH_3O, or Cl; AA, α-amino acid, AA ≡ proline, α-aminoisobutyric acid, isoleucine, valine, glycine or serine) in aqueous solution. Some linear enthalpy relationships have been found to exist between the relevant thermodynamic parameters.

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THEORETICAL

Calorimetric studies of the copper(II)–oxalate–ethylenediamine [2] and nickel(II)–oxalate–ethylenediamine [3] competitive ternary systems have been carried out under the experimental conditions of a high molar ratio of both ligands to the metal ion, using acid balance in the calculation. In this work, however, on investigating the formation reaction of the copper(II)–*m*-RPhIDA–AA ternary system, we used a comparable molar ratio of ligand to metal in the experiment without taking account of acid balance in the calculation. In the system investigated, the following eight independent equilibria must be considered: A denotes the first ligand (*m*-RPhIDA) and B the second ligand (AA)

$$H_2A = H + HA \qquad K_1^A = [H][HA]/[H_2A] \tag{1}$$

$$HA = H + A \qquad K_2^A = [H][A]/[HA] \tag{2}$$

$$H_2B = H + HB \qquad K_1^B = [H][HB]/[H_2B] \tag{3}$$

$$HB = H + B \qquad K_2^B = [H][B]/[HB] \tag{4}$$

$$M + A = MA \qquad \beta_{10} = [MA]/[M][A] \tag{5}$$

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

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

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

Here the charges are omitted for the sake of convenience. K_1^A, K_2^A, K_1^B and K_2^B denote the first and second dissociation constants of ligands A and B, respectively. β_{ij} denotes the consecutive formation constants of copper(II) with ligands A and B ($i = 0, 1$; $j = 0, 1, 2$). According to mass balance, we have

$$T_A = [A] + [HA] + [H_2A] + [MA] + [MAB] \tag{9}$$

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

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

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

$$n_A = 1 + [H]/K_2^A + [H]^2/K_1^AK_2^A$$

$$n_B = 1 + a_H/K_2^B + a_H/K_1^BK_2^B \qquad (a_H = \text{activity of hydrogen ion})$$

The following three expressions for [M] can then be obtained

$$[M] = (T_A - n_A)/(\beta_{10}[A] + \beta_{11}[A][B]) \tag{12}$$

$$[M] = (T_B - n_B)/\left(\beta_{01}[B] + 2\beta_{02}[B]^2 + \beta_{11}[A][B]\right) \tag{13}$$

$$[M] = T_M/\left(1 + \beta_{10}[A] + \beta_{01}[B] + \beta_{02}[B]^2 + \beta_{11}[A][B]\right) \tag{14}$$

From eqns. (12) and (13) we obtain

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

where

$$u = 2\beta_{02}(T_\mathrm{A} - n_\mathrm{A}[\mathrm{A}]) + n_\mathrm{B}\beta_{11}[\mathrm{A}] \tag{15a}$$

$$v = -\beta_{11}n_\mathrm{A}[\mathrm{A}]^2 + [(T_\mathrm{A} - T_\mathrm{B})\beta_{11} + n_\mathrm{B}\beta_{10} - n_\mathrm{A}\beta_{01}][\mathrm{A}] + T_\mathrm{A}\beta_{01} \tag{15b}$$

$$w = -T_\mathrm{B}\beta_{10}[\mathrm{A}] \tag{15c}$$

Further, let a and b denote the denominators of eqns. (12) and (14) respectively. We then obtain

$$aT_\mathrm{M} - b(T_\mathrm{A} - n_\mathrm{A}[\mathrm{A}]) = 0 \tag{16}$$

If an initial value of [A] is assumed, we can obtain a set of u, v and w values using eqns. (15a) to (15c), and a reasonable value of [B] may be calculated readily. If a and b values do not fit eqn. (16) satisfactorily, a new [A] value must be assumed and the computation repeated until the absolute value of the left-hand side of eqn. (16) is close to zero. The concentrations of free ligands A and B were obtained. Consequently, the concentrations of other species in the equilibrium system could be evaluated, provided that all equilibrium constants expressed by eqns. (1) to (8) are known [4–6]. The concentration of the species existing in initial solution may be also evaluated using the equilibrium constants of eqns. (1) to (4), the pH value of the initial solution and the total concentrations of ligands A and B.

For energy balance, the following thermochemical equation can be established

$$\begin{aligned} Q_\mathrm{c} &= Q_\mathrm{m} - Q_\mathrm{b} \\ &= R + \{([\mathrm{HA}]_\mathrm{f} + [\mathrm{H_2A}]_\mathrm{f})V_\mathrm{f} - ([\mathrm{HA}]_\mathrm{i} + [\mathrm{H_2A}]_\mathrm{i})V_\mathrm{i}\}\ \Delta H_1^\mathrm{A} \\ &\quad + ([\mathrm{H_2A}]_\mathrm{f}V_\mathrm{f} - [\mathrm{H_2A}]_\mathrm{i}V_\mathrm{i})\ \Delta H_2^\mathrm{A} \\ &\quad + \{([\mathrm{HB}]_\mathrm{f} + [\mathrm{H_2B}]_\mathrm{f})V_\mathrm{f} - ([\mathrm{HB}]_\mathrm{i} + [\mathrm{H_2B}]_\mathrm{i})V_\mathrm{i}\}\ \Delta H_1^\mathrm{B} \\ &\quad + ([\mathrm{H_2B}]_\mathrm{f}V_\mathrm{f} - [\mathrm{H_2B}]_\mathrm{i}V_\mathrm{i})\ \Delta H_2^\mathrm{B} + [\mathrm{MA}]_\mathrm{f}V_\mathrm{f}\ \Delta H_\mathrm{A}^\mathrm{M} + [\mathrm{MB}]_\mathrm{f}V_\mathrm{f}\ \Delta H_\mathrm{B1}^\mathrm{M} \\ &\quad + [\mathrm{MB_2}]_\mathrm{f}V_\mathrm{f}\ \Delta H_\mathrm{B2}^\mathrm{M} + [\mathrm{MAB}]_\mathrm{f}V_\mathrm{f}\ \Delta H_\mathrm{MAB} \end{aligned} \tag{17}$$

where Q_c denotes the corrected heat quantity, Q_m denotes the average value of the measured heat effects of the reaction under investigation, Q_b denotes the average heat of the blank tests, R represents the heat of neutralization when H and OH form H_2O, ΔH_1^A (ΔH_2^A) and ΔH_1^B (ΔH_2^B) denote the heats of the first (second) protonation steps of ligands A and B, respectively, H_A^M denotes the heat of complexation of ligand A with copper(II), $\Delta H_\mathrm{B1}^\mathrm{M}$ ($\Delta H_\mathrm{B2}^\mathrm{M}$) denotes the heat of the first (second) complexation step of ligand B with copper(II), ΔH_MAB denotes the heat of formation of the ternary complex compounds, V represents the total volume of the solution and the subscripts f and i denote after and before reaction, respectively.

Since ΔH^{A} (ΔH^{B}) and ΔH_{A}^{M} (ΔH_{B}^{M}) are known [1,7], the heat of formation of the ternary mixed-ligand complex compounds can be calculated from a set of calorimetric measurements using eqn. (17).

EXPERIMENTAL

Reagents

m-RPhIDA compounds were prepared using the method reported in the literature [8]. Copper(II) nitrate (AnalaR) was recrystallized and the concentration of copper ion in the stock solution was determined by EDTA titration. All the α-amino acids (biochemical reagents) were obtained commercially (Beijing Chemical Reagent Station). Potassium nitrate (Tianjin Third Chemical Reagent Factory) was recrystallized from redistilled water. A potassium hydroxide (AnalaR, Tianjin Third Chemical Factory) standard solution was prepared and standardized by a conventional method. An automatic conduction calorimeter model RD-1 [9] (with a precision of 0.5%) was used to measure the heats of formation of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds at $25.0 \pm 0.2\,°C$ and $I = 0.1$ mol dm^{-3} (KNO_3) in aqueous solution. The instrumental constant K of the calorimeter was found to be $(3.66 \pm 0.09) \times 10^{-3}$ J mm^{-2} ($n = 16$) using electrical power calibration, and this was further checked by chemical calibration. A value of -13.24 kcal mol^{-1} for $\Delta H_{N}^{\ominus}$ was obtained, which is in good agreement with the literature value [10] within experimental error. Under the same conditions, 2.00 ml of a standard nitric acid solution (0.1207 mol dm^{-3}) was neutralized with 20.00 ml of a standard sodium hydroxide solution (0.015 29 mol dm^{-3}) at $I = 0.1$ mol dm^{-3} KNO_3. The ΔH_N value was determined to be -59.78 ± 0.095 kJ mol^{-1} (or -14.29 ± 0.02 kcal mol^{-1}). The pH values before and after reaction were measured by means of a pH-meter, model pHS-2. 2.00 ml of a $Cu(NO_3)_2$ solution (0.051 49 mol dm^{-3}) were placed in the sample tube and 20.00 ml of a mixed solution of *m*-RPhIDA (0.017 88 mol dm^{-3}) and AA (0.010 38 mol dm^{-3}) were placed in the reaction chamber. Both solutions were maintained at 0.1 mol dm^{-3} with KNO_3. The heat of dilution in the sample tube was calibrated by means of a blank test. However, the heat of dilution of the ligand solution was neglected on account of the fact that the change in concentration on mixing was very small. The heat evolved in the reaction cell was calculated from the area under the curve measured by a planimeter, and the instrumental constant K.

TABLE 1

Determination of the heats of formation of Cu^{II}–*m*-RPhIDA–proline ternary systems at 25.0±0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	n	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH_i	pH_f	Q (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3	7	1.625	9.435	4.680	10.86	8.23	−4.72±0.02	−13.25±0.50
H	5	1.625	9.432	4.680	10.78	7.95	−4.15±0.02	−11.56±0.52
CH_3O	6	1.625	9.432	4.680	10.80	7.77	−4.27±0.02	−11.14±0.53
Cl	5	1.625	9.433	4.680	10.82	7.46	−4.38±0.02	−10.31±0.55

Units for T_A, T_B and T_M are mol dm^{-3}.

TABLE 2

Determination of the heats of formation of Cu^{II}–*m*-RPhIDA–α-aminoisobutyric acid ternary systems at 25.0±0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	n	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH_i	pH_f	Q (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3	4	1.624	9.407	4.680	10.49	8.47	−3.44±0.02	−12.18±0.45
H	5	1.626	9.395	4.680	10.47	8.19	−3.23±0.02	−10.74±0.53
CH_3O	5	1.623	9.420	4.680	10.40	7.89	−2.85±0.02	−10.15±0.47
Cl	4	1.623	9.401	4.680	10.46	7.57	−3.22±0.02	−9.44±0.43

Units for T_A, T_B and T_M as in Table 1.

TABLE 3

Determination of the heats of formation of Cu^{II}–*m*-RPhIDA–isoleucine ternary systems at 25.0±0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	n	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH_i	pH_f	Q (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3	5	1.625	9.415	4.680	10.12	8.18	−3.97±0.02	−13.92±0.58
H	6	1.625	9.419	4.680	10.06	7.80	−3.67±0.02	−12.03±0.57
CH_3O	5	1.624	9.422	4.680	10.07	7.73	−3.71±0.02	−11.57±0.62
Cl	4	1.625	9.451	4.680	10.04	7.31	−3.59±0.02	−10.77±0.56

Units for T_A, T_B and T_M as in Table 1.

TABLE 4

Determination of the heats of formation of Cu^{II}–*m*-RPhIDA–valine ternary systems at 25.0±0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	n	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH_i	pH_f	Q (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3	5	1.625	9.423	4.680	10.15	8.26	−3.86±0.02	−12.30±0.63
H	4	1.624	9.422	4.680	10.08	7.83	−3.57±0.02	−10.71±0.58
CH_3O	5	1.625	9.418	4.680	10.06	7.66	−3.47±0.02	−10.17±0.58
Cl	6	1.625	9.423	4.680	10.06	7.32	−3.48±0.02	−9.44±0.47

Units for T_A, T_B and T_M as in Table 1.

RESULTS AND DISCUSSION

The experimental data for the heats of formation of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds are given in Tables 1–6. The formation constants of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds are shown in Table 7. The acid dissociation constants and the heats of protonation of the ligands AA are shown in Table 8. The formation constants and the heats

TABLE 5

Determination of the heats of formation of Cu^{II}–*m*-RPhIDA–glycine ternary systems at 25.0 ± 0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	n	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH_i	pH_f	Q (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3	6	1.625	9.387	4.680	10.17	8.03	-4.26 ± 0.02	-13.44 ± 0.51
H	5	1.624	9.378	4.680	10.06	7.59	-3.76 ± 0.02	-11.68 ± 0.47
CH_3O	6	1.626	9.388	4.680	10.05	7.39	-3.72 ± 0.02	-11.20 ± 0.46
Cl	5	1.624	9.377	4.680	10.12	7.19	-4.00 ± 0.02	-10.45 ± 0.53

Units for T_A, T_B and T_M as in Table 1.

TABLE 6

Determination of the heats of formation of Cu^{II}–*m*-RPhIDA–serine ternary systems at 25.2 ± 0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	n	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH_i	pH_f	Q (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3	6	1.638	9.375	4.680	9.80	8.02	-4.21 ± 0.02	-12.35 ± 0.72
	6	1.625	9.433	4.680	9.77	7.96	-4.17 ± 0.02	-12.18 ± 0.70
H	6	1.668	9.382	4.680	9.61	7.46	-3.62 ± 0.02	-10.68 ± 0.59
	7	1.836	9.216	4.680	9.21	6.71	-1.82 ± 0.02	-10.83 ± 0.35
CH_3O	7	1.713	9.368	4.680	9.39	6.86	-2.73 ± 0.02	-10.10 ± 0.43
	5	1.668	9.381	4.680	9.60	7.18	-3.60 ± 0.02	-10.12 ± 0.56
Cl	5	1.625	9.437	4.680	9.66	7.07	-3.84 ± 0.02	-9.47 ± 0.69
	5	1.664	9.363	4.680	9.68	7.10	-3.85 ± 0.02	-9.48 ± 0.68

Units for T_A, T_B and T_M as in Table 1.

TABLE 7

The formation constants log β_{11} [4] of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds at 25.0 ± 0.2°C and $I = 0.1$ mol dm^{-3} (KNO_3)

R	α-Amino acid					
	Proline	α-Aminoisobutyric acid	Isoleucine	Valine	Glycine	Serine
CH_3	13.08	12.76	12.34	12.32	12.32	11.97
H	12.76	12.32	12.00	12.00	12.02	11.66
CH_3O	12.57	12.17	11.85	11.85	11.86	11.50
Cl	12.23	11.89	11.58	11.56	11.52	11.18

TABLE 8

The dissociation constants [5] and the protonation heats [7] of some α-amino acids, and the formation constants [5] and formation heats [7] of Cu^{II}–AA binary complex compounds at $25.0 \pm 0.2\,^{\circ}C$ and $I = 0.1$ mol dm^{-3}

α-Amino acid	pK_1^B	pK_2^B	$\log \beta_{01}$	$\log \beta_{02}$	ΔH_1^B (kJ mol^{-1})	ΔH_2^B (kJ mol^{-1})	ΔH_{B1}^M (kJ mol^{-1})	ΔH_{B2}^M (kJ mol^{-1})
Proline	1.77	10.39	8.80	16.30	-43.3 ± 0.1	0.1 ± 0.2	-27.9 ± 0.3	-56.4 ± 0.4
α-Aminoiso-								
butyric acid	2.44	10.08	8.34	15.35	-51.9 ± 0.1	-1.5 ± 0.2	-25.8 ± 0.3	-53.4 ± 0.6
Isoleucine	2.30	9.60	8.16	15.02	-48.5 ± 0.1	-0.9 ± 0.1	-28.9 ± 0.4	-57.6 ± 0.6
Valine	2.34	9.57	8.15	14.97	-47.3 ± 0.1	0.35 ± 0.1	-26.0 ± 0.3	-53.3 ± 0.6
Glycine	2.36	9.56	8.16	14.97	-47.7 ± 0.2	-0.38 ± 0.1	-28.0 ± 0.4	-56.3 ± 1.0
Serine	2.29	9.05	7.95	14.52	-45.5 ± 0.1	-3.99 ± 0.1	-26.1 ± 0.2	-53.4 ± 0.4

TABLE 9

The dissociation constants [6] and protonation heats [1] of the ligands *m*-RPhIDA, and the formation constants [6] and formation heats [1] of Cu^{II}–*m*-RPhIDA binary complex compounds at $25.0 \pm 0.2°C$ and $I = 0.1$ mol dm^{-3}

R	pK_1^A	pK_2^A	$\log \beta_{10}$	ΔH_1^A (kJ mol^{-1})	ΔH_2^A (kJ mol^{-1})	ΔH_A^M (kJ mol^{-1})
CH_3	2.53	5.33	6.37	5.32 ± 0.05	0.38 ± 0.01	16.69 ± 0.05
H	2.42	5.11	5.81	6.60 ± 0.05	-0.81 ± 0.01	17.29 ± 0.05
CH_3O	2.35	5.05	5.63	6.88 ± 0.05	-1.49 ± 0.02	17.58 ± 0.05
Cl	2.33	4.88	5.13	7.55 ± 0.05	-1.84 ± 0.01	17.93 ± 0.05

of formation of Cu^{II}–*m*-RPhIDA binary complex compounds are shown in Table 9. The data in Tables 7–9 were used for calculation of the formation heats of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds. Plots of the heats of formation of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds against the heats of protonation of the ligands *m*-RPhIDA show very good linear enthalpy relationships (see Fig. 1) with a correlation coefficient *r* close to unity.

Cu^{II}–*m*-RPhIDA–isoleucine ternary system:

$$\Delta H_{MAB} = -21.5 + 1.43\,\Delta H_1^A \qquad r = 0.999$$

Cu^{II}–*m*-RPhIDA–serine ternary system:

$$\Delta H_{MAB} = -19.0 + 1.27\,\Delta H_1^A \qquad r = 0.995$$

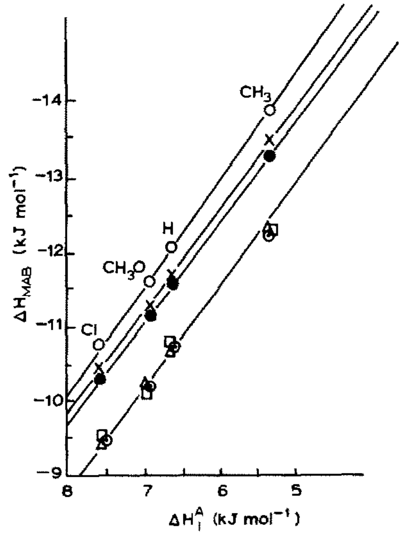

Fig. 1. Plot of the heats of formation of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds, ΔH_{MAB}, vs. the heats of protonation of the ligands *m*-RPhIDA, ΔH_1^A. ○, Isoleucine; ×, glycine; ●, proline; △, serine; □, valine; ⊙ α-aminoisobutyric acid.

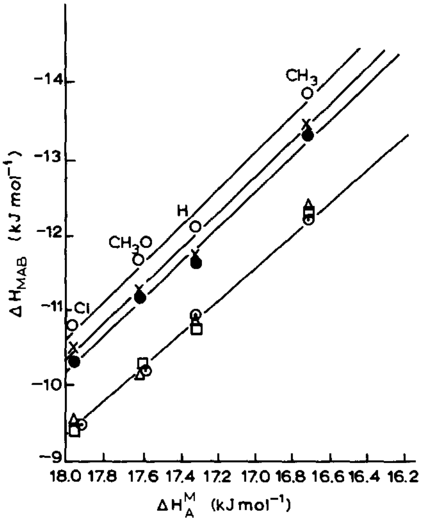

Fig. 2. Plot of the heats of formation of Cu^{II}-*m*-RPhIDA–AA ternary complex compounds, ΔH_{MAB}, vs. the heats of formation of Cu^{II}-*m*-RPhIDA binary complex compounds, ΔH_A^M. ○, Isoleucine; ×, glycine; ●, proline; △, serine; □, valine; ⊙, α-aminoisobutyric acid.

Cu^{II}–*m*-RPhIDA–proline ternary system:

$$\Delta H_{MAB} = -20.3 + 1.32\ \Delta H_1^A \qquad r = 1.00$$

Cu^{II}–*m*-RPhIDA–valine ternary system:

$$\Delta H_{MAB} = -19.2 + 1.30\ \Delta H_1^A \qquad r = 0.998$$

Cu^{II}–*m*-RPhIDA–α-aminoisobutyric acid ternary system:

$$\Delta H_{MAB} = -18.8 + 1.24\ \Delta H_1^A \qquad r = 0.996$$

Cu^{II}–*m*-RPhIDA–glycine ternary system:

$$\Delta H_{MAB} = -20.6 + 1.36\ \Delta H_1^A \qquad r = 0.999$$

On plotting the heats of formation of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds against the heats of formation of Cu^{II}–*m*-RPhIDA and Cu^{II}–AA binary complex compounds, respectively (Figs. 2 and 3), some clearly linear enthalpy relationships are also found to exist. The following regression equations with correlation coefficient r are obtained

Cu^{II}–*m*-RPhIDA–isoleucine ternary system:

$$\Delta H_{MAB} = -55.8 + 2.52\ \Delta H_A^M \qquad r = 0.991$$

Cu^{II}–*m*-RPhIDA–serine ternary system:

$$\Delta H_{MAB} = -50.1 + 2.27\ \Delta H_A^M \qquad r = 0.997$$

Cu^{II}–*m*-RPhIDA–proline ternary system:

$$\Delta H_{MAB} = -52.2 + 2.34\ \Delta H_A^M \qquad r = 0.994$$

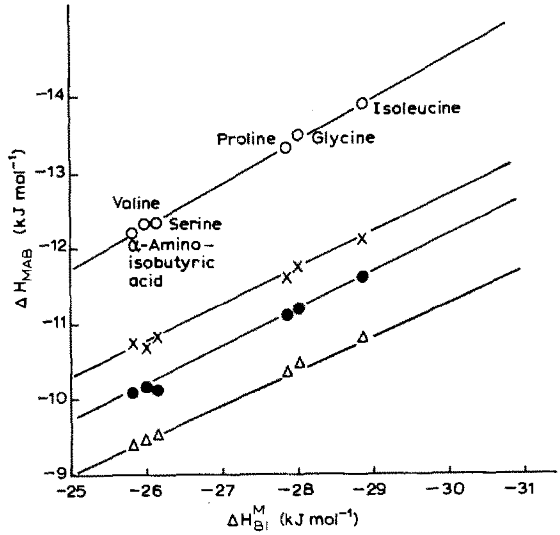

Fig. 3. Plot of the heats of formation of Cu^{II}-*m*-RPhIDA–AA ternary complex compounds, ΔH_{MAB}, vs. the heats of formation of Cu^{II}–AA binary complex compounds, ΔH^{M}_{B1}. ○, *m*-CH_3PhIDA; ×, PhIDA; ●, *n*-CH_3OPhIDA; △, *m*-ClPhIDA.

Cu^{II}-*m*-RPhIDA–valine ternary system:

$$\Delta H_{MAB} = -50.6 + 2.30\ \Delta H^{M}_{A} \qquad r = 0.997$$

Cu^{II}-*m*-RPhIDA–α-aminoisobutyric acid ternary system:

$$\Delta H_{MAB} = -49.0 + 2.21\ \Delta H^{M}_{A} \qquad r = 0.999$$

Cu^{II}-*m*-RPhIDA–glycine ternary system:

$$\Delta H_{MAB} = -53.3 + 2.40\ \Delta H^{M}_{A} \qquad r = 0.993$$

Cu^{II}-*m*-CH_3PhIDA–AA ternary system:

$$\Delta H_{MAB} = 2.35 + 0.56\ \Delta H^{M}_{B1} \qquad r = 0.997$$

Cu^{II}–PhIDA–AA ternary system:

$$\Delta H_{MAB} = 0.708 + 0.44\ \Delta H^{M}_{B1} \qquad r = 0.996$$

Cu^{II}-*m*-CH_3OPhIDA–AA ternary system:

$$\Delta H_{MAB} = 2.71 + 0.50\ \Delta H^{M}_{B1} \qquad r = 0.995$$

Cu^{II}-*m*-ClPhIDA–AA ternary system:

$$\Delta H_{MAB} = 2.35 + 0.45\ \Delta H^{M}_{B1} \qquad r = 0.997$$

From the data in Taoles 1 to 6 it is interesting to note that, first of all, the heats of formation of Cu^{II}-*m*-RPhIDA–AA ternary complex compounds, ΔH_{MAB}, like the heats of formation of Cu^{II}-*N*-acetylglycine–AA ternary complex compounds [7] was nearly equal to the sum ($\Delta H^{M}_{A} + \Delta H^{M}_{B1}$). This would mean that no π back-bonding and no interactions between ligands A and B exist in the ternary complex compounds. Secondly, the magnitude of the heats of formation of the Cu^{II}–*m*-RPhIDA–AA ternary complex compounds is largely dependent upon the magnitude of the heats of formation of Cu^{II}–*m*-RPhIDA and Cu^{II}–AA binary complex compounds. However, from the data in Tables 1 to 6, it may also be observed that no linear enthalpy relationships exist between the heats of formation of Cu^{II}–*m*-RPhIDA–AA ternary complex compounds and the the heats of protonation of the ligands B (AA). The heat of protonation of a ligand depends mainly on its strength of basicity and the extent of its solvation in solution, while the heat of formation of a complex compound depends not only on the basicity of the ligand and its degree of solvation but also on the steric effect due to the ligand. This steric effect might have an important role in these systems and thus linear enthalpy relationships will not be observed.

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