Calorimetric determination of the heats of formation of competitive ternary mixed-ligand complex compounds. Copper(II)-12-(2′-hydroxy-benzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione-α-aminoacids and 5-substituted phenanthrolines systems

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Abstract

The heats of protonation of 12-(2′-hydroxy-benzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (HTADO) have been determined in aqueous solution at $25 \pm 0.1°C$ and $I = 0.1$ mol dm^{-3} KNO$_3$ by conduction calorimetry. The heats of formation of the binary complex compound of this ligand with Cu(II) and the ternary complex compounds of this ligand with Cu(II)-5-substituted phenanthrolines have also been determined under identical conditions. By utilizing the calorimetric data, the heats of formation of the ternary complex compounds Cu(II)-α-aminoacids-HTADO have been evaluated through "overall calculation". Some linear enthalpy relationships have been found between the heats of protonation of the ligands and the heats of formation of the ternary complex compounds.

Keywords: Additivity; Heat of formation; LER; Tetraazacyclotridecane-dione
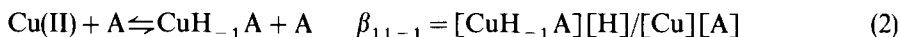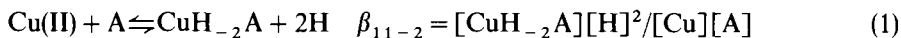
1. Introduction

The structures and properties of macrocyclic dioxotetraamine are similar to those of tripeptide. They are able to coordinate a divalent 3d cation with simultaneous release of two hydrogen ions from the amido groups [1, 2]. Transition metal(II) complexes of macrocyclic dioxotetraamine have shown some interesting properties and important

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biological functions including being used as models for metalloproteins and oxygen carriers [3–6]. Copper(II) complexes can be oxidized at moderately positive potential to give authentic trivalent copper species that are stable in aqueous solution [7–9]. Such compounds can serve as models for some enzymes, e.g. galactose oxidase [10], and may be used as effective oxidants and redox catalysts [11]. Unsubstituted macrocyclic dioxotetraamines of different ring sizes have been reported [12,13]. In a previous paper [14], the calorimetric determination of the heats of formation of competitive ternary mixed-ligand complex compounds, Cu(II)-1,4,7,10-tetra-azacyclotridecane-11,13-dione (TADO)-α-aminoacids (AA) and of 5-substituted phenanthroline (RPhen) systems was reported. Relationships between structures and properties have been reported for the 13-membered macrocyclic dioxotetraamine, bearing the pendent coordination group, 12-(2'-hydroxy-benzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione [15, 24]. In this paper, we report the calorimetric measurement of the heats of protonation of 12-(2'-hydroxy-benzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione(HTADO) and of the heats of formation of the binary complex compound copper(II)-HTADO and of the ternary complex compounds Cu(II)-RPhen-HTADO and Cu(II)-AA-HTADO.

2. Theoretical

Because two hydrogen ions have been released from the amido group in the coordination of these macrocyclic dioxotetraamines with metal(II) ions, the following two equations must be considered in the overall calculation

$$Cu(II) + A \rightleftharpoons CuH_{-2}A + 2H \quad \beta_{11-2} = [CuH_{-2}A][H]^2/[Cu][A] \quad (1)$$

$$Cu(II) + A \rightleftharpoons CuH_{-1}A + A \quad \beta_{11-1} = [CuH_{-1}A][H]/[Cu][A] \quad (2)$$

where A denotes HTADO and H denotes the hydrogen ion. The remainder of the calculation is as in the literature [16–18].

3. Experimental

12-(2'-Hydroxy-benzyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione(HTADO) was prepared as reported earlier [15]. The structure of HTADO has been confirmed to be as shown by means of elemental analysis, IR, NMR, and MS. Copper(II) nitrate
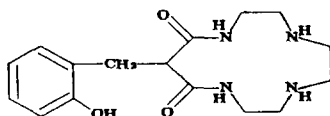
(Tianjin Second Chemical Reagent Factory, A.R.) and potassium nitrate (Tianjin Third Chemical Reagent Factory, A.R) were recrystallized before use. The concentration of Cu(II) in the stock solution was analysed by the conventional method. The potassium nitrate (Tianjin Third Chemical Reagent Factory, A.R.) was recrystallized. 5-Methyl-

1,10-phenanthroline (CH$_3$Phen) and 5-chloro-1,10-phenanthroline (ClPhen) were obtained from Aldrich Chemical Company; 5-nitro-1,10-phenanthroline (NO$_2$Phen) and 1,10-phenanthroline (Phen) from Shanghai Chemical Reagent Factory; L-proline (Pro) from Sigma Chemical Reagent Factory; 2-aminoisobutyric acid (Aib) from BDH; glycine (Gly), L-serine (Ser), L-isoleucine (iLe) and L-valine (Val) from Shanghai Chemical Reagent Factory. All α-aminoacids were biochemical reagents. All 5-substituted phenanthrolines (RPhen) and α-aminoacids (AA) were used without further purification. All solutions were prepared by weight except Cu(II) stock solution. All solutions of the Cu(II) binary complexes with 5-substituted phenanthrolines were prepared in warm redistilled water. The ionic strength was adjusted to 0.1 mol dm^{-3} by KNO$_3$ stock solution (1 mol dm^{-3}).

A model RD-1 automatic conduction calorimeter with a precision of ± 0.5% [19] was used to measure the heat effect. The instrumental constant K was determined to be $(3.00 \pm 0.01) \times 10^{-3}$ J mm^{-2} (n(number of tests) = 11), using electric power calibration, and was checked again by chemical calibration (NaOH (aq) + HClO$_4$(aq)). An average value for the heat of neutralization, $\Delta H_N = -56.57 \pm 0.09$ kJ mol^{-1} ($I = 0.1$ mol dm^{-3} (NaClO$_4$)) ($n = 9$), was obtained which is in good agreement with the literature value [20]. The pH values of the solutions were measured by means of a Beckman Φ 71 pH-meter equipped with a type 39841 combination electrode.

The methods of the determination of the heats of protonation of ligand A (HTADO), of the formation heats of binary complex compounds of Cu(II) with ligand A, and of the formation heats of ternary complex compounds Cu(II)-AA-HTADO are the same as reported previously [17, 18].

All determinations were carried out at 25.0 ± 0.1°C, $I = 0.1$ mol dm^{-3} (KNO$_3$). An average value for the heat of neutralization (HNO$_3$(aq.) + KOH(aq.)) under the same conditions as above was obtained ($\Delta H_N = -59.78 \pm 0.1$ kJ mol^{-1}); this was used for calibration of the formation of H$_2$O in all the main reactions [21], and the activity coefficient r_H(0.8318) was used for calculation of the concentration of hydrogen ion [22].

4. Results and discussion

The experimental data and the results for the heats of protonation of ligand A and the heats of formation of the binary complex compounds Cu(II)-HTADO are tabulated in Tables 1 and 2. The results of the heats of formation of the ternary complex compounds Cu(II)-RPhen-HTADO and Cu(II)-AA-HTADO are tabulated in Tables 3 and 4.

It is seen from Table 1 that the heat of the first protonation of ligand HTADO, i.e. the heat of coordination of the hydrogen ion to the oxygen atom of the pendent group (phenol group), is -32.7 ± 0.3 kJ mol^{-1}. This value is slightly larger than the heat of protonation of phenol, -25.5 kJ mol^{-1} [27]. This result is reasonable, because–CH$_2$ is introduced to benzyl which increases the electron cloud of phenol oxygen. From Table 2, the heat of formation of the binary complex compounds CuH$_{-2}$A and CuH$_{-1}$A are -15.1 ± 0.2 and -16.1 ± 0.5 kJ mol^{-1}, which indicates that the overall heat effects of

Table 1
Determination of the heat of protonation (kJ mol^{-1}) of ligand HTADO (temperature $25 \pm 0.1°C$; $I = 0.1$ mol dm^{-3} KNO$_3$; $\Delta H = -59.78$ kJ mol^{-1}; $r_H = 0.8318$)

n	$10^3 T_A/$ mol dm^{-3}	$10^3 T_H/$ mol dm^{-3}	pH$_i$	pH$_f$	$Q_c/$J	pK_{D1}	pK_{D2}	pK_{D3}	ΔH_{HA}	ΔH_{H2A}	ΔH_{H3A}
4	1.378	4.730	9.93	2.24	-1.70 ± 0.01	3.66 [23]			-32.7 ± 0.3		
4	1.818	4.730	10.30	2.34	-2.72 ± 0.01		9.06			-22.8 ± 1.1	
4	2.927	4.730	10.45	2.77	-4.44 ± 0.01			10.01			-19.6 ± 1.4

Table 2
Determination of the heats of formation (kJ mol^{-1}) of binary complex compound Cu(II)–HTADO (temperature $25.0 \pm 0.1°C$; $I = 0.1$ mol dm^{-3} KNO$_3$)

n	$10^3 T_A$ mol dm^{-3}	$10^3 T_{Cu}$ mol dm^{-3}	pH$_i$	pH$_f$	$Q_c/$J	Log$\beta_{CuH_{-2}A}$	Log$\beta_{CuH_{-1}A}$	$\Delta H_{CuH_{-2}A}$	$\Delta H_{CuH_{-1}A}$
4	3.636	1.807	10.71	8.76	-1.40 ± 0.01	1.58[23]	7.01	-15.1 ± 0.2	
4	1.818	1.807	10.34	5.34	-0.80 ± 0.01				-16.1 ± 0.5

Table 3
Determination of the heats of formation (kJ mol⁻¹) of ternary complex compounds Cu(II)-RPhen-HTADO and Cu(II)-RPhen-TADO (temperature 25.0 ± 0.1 °C; $I = 0.1$ mol dm⁻³ KNO₃)

| R	n	$10^3 T_A$/mol dm⁻³	$10^3 T_{CuRPhen}$/mol dm⁻³	pH₁	pH_f	Q_c/J	Log $\beta_{CuRPhen}$	$\Delta H_{CuRPhen}$
Cu(II)-RPhen-HTADO								
CH₃	4	1.818	1.807	10.46	7.18	−0.48 ± 0.01	10.24 [25]	−12.0 ± 0.3
H	4	1.818	1.800	10.44	6.80	−0.54 ± 0.01	10.30	−13.8 ± 0.3
Cl	4	1.818	1.807	10.44	6.95	−0.65 ± 0.01	10.42	−16.8 ± 0.3
NO₃	4	1.818	1.807	10.42	6.75	−0.72 ± 0.01	10.51	−19.3 ± 0.3
Cu(II)-RPhen-TADO [14]								
CH₃	6	1.892	1.807	10.76	6.83	−0.97 ± 0.01	6.20	4.90 ± 0.31
H	5	1.892	1.800	10.76	6.75	−1.04 ± 0.01	6.22	3.46 ± 0.31
Cl	5	1.892	1.807	10.43	6.61	−0.72 ± 0.01	6.25	−0.15 ± 0.32
NO₂	6	1.892	1.807	10.43	6.53	−0.83 ± 0.01	6.28	−3.14 ± 0.32

Table 4
Determination of the heats of formation (kJ mol⁻¹) of ternary complex compounds Cu(II)-AA-HTADO (temperature 25.0 ± 0.1°C; $I = 0.1$ mol dm⁻³ KNO₃)

α-Aminoacid	n	$10^3 T_A$/mol dm⁻³	$10^3 T_B$/mol dm⁻³	$10^3 T_{Cu}$/mol dm⁻³	pH₁	pH_f	Q_c/J	Log β_{CuAB}	ΔH_{CuAB}
Proline	5	1.725	1.805	1.807	10.50	6.30	−1.64 ± 0.01	20.20 [23]	−64.6 ± 2.3
α-Aminoisobutyric acid	5	1.725	1.805	1.807	9.97	5.34	−1.04 ± 0.01	19.89	−72.2 ± 1.5
Isoleucine	5	1.810	1.805	1.807	9.68	5.28	−0.99 ± 0.01	19.70	−68.3 ± 1.3
Glycine	5	1.810	1.805	1.807	9.76	5.35	−1.17 ± 0.01	19.43	−67.5 ± 1.8
Valine	6	4.342	4.718	4.517	9.72	5.27	−2.41 ± 0.01	19.64	−67.5 ± 0.4
Serine	5	1.810	1.804	1.807	9.54	5.40	−1.09 ± 0.01	19.32	−66.0 ± 1.2

the coordination of Cu(II) to ligand HTADO are exothermic. Because the coordination of Cu(II) with the four nitrogen atoms of the HTADO ligand would simultaneously release two hydrogen ions from the amido groups, a certain amount of energy was consumed. But an oxygen atom on the phenol group binding with Cu(II) (for $CuH_{-2}A$) or hydrogen ion (for $CuH_{-1}A$) will give out an energy (-21 [27] or $-32.7 \pm 0.3\,kJ\,mol^{-1}$) which is larger than the consumed energy ($-13.85 \pm 0.43\,kJ\,mol^{-1}$) [14]. Therefore, the heats of formation of binary complex compounds Cu (II)$H_{-2}A$ and Cu(II) $H_{-1}A$ are all negative values.
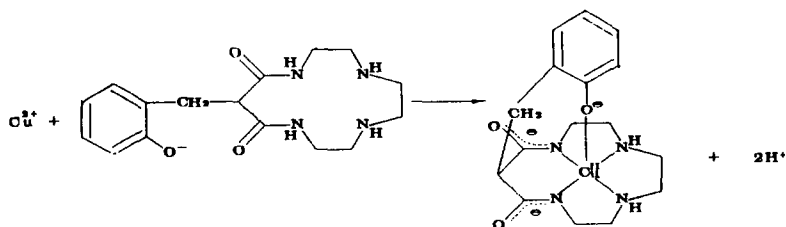
$$\Delta H = -15.1 \pm 0.2\,kJ\,mol^{-1}$$
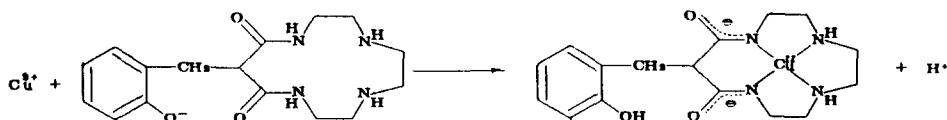
$$\Delta H = -16.1 \pm 0.5\,kJ\,mol^{-1}$$

It is also seen in Table 3 that the values of formation heats of the ternary complex compounds Cu(II)-RPhen-HTADO are -12.0 ± 0.3 (CH_3 Phen), -13.8 ± 0.3 (Phen), -16.8 ± 0.3 (ClPhen) and $-19.3 \pm 0.3\,kJ\,mol^{-1}$ (NO_2 Phen), respectively. Because the coordination tendency of Cu(II) toward RPhen is very strong, Cu(II)-RPhen does not dissociate in the pH range 2–7. So Cu(II)-RPhen can be taken as a stable species; the volume of Cu(II)-RPhen is too large to insert into the ring of macrocyclic dioxotetraamine. Therefore, when Cu(II)-RPhen coordinates with ligand HTADO, only two nitrogen atoms of HTADO can take part in the coordination and the Cu(II) ion cannot form a coplanar configuration with four nitrogen atoms of ligand HTADO. So the bonds of Cu(II)-RPhen with two nitrogen atoms are bent, and a certain amount of energy was consumed. Therefore, the reaction heats of Cu(II)-RPhen with two nitrogen atoms of ligand HTADO would be rather small, which ought to correspond to the values of the formation heats of Cu(II)-RPhen-TADO (4.90 ± 0.31 (CH_3 Phen), 3.46 ± 0.31 (Phen), -0.15 ± 0.32 (ClPhen) and $-3.14 \pm 0.32\,kJ\,mol^{-1}$ (NO_2 Phen)) [14]. But in HTADO, the oxygen atom of pendent phenolate took part in coordination with Cu(II) and released energy, so that the heats of formation of Cu(II)-RPhen-HTADO are larger than that of TADO (-12.0 ± 0.3 (CH_3 Phen), -13.8 ± 0.3 (Phen), -16.8 ± 0.3 (ClPhen) and -19.3 ± 0.3 $kJ\,mol^{-1}$ (NO_2 Phen), respectively).

Furthermore, d-p back-donation π-bonding exists between Cu(II) and RPhen; the electron cloud on the 3d-orbit of copper(II) was donated to the empty π-orbital of

RPhen. This donation decreases the density of the electron cloud on Cu(II). Thus, it diminishes the repulsion between the electron on Cu(II) and the coordinated electron pair of the HTADO; thus the strength of the bonding between Cu (II) and HTADO is increased. Consequently, the heats of formation of the ternary complex compounds Cu(II)-RPhen-HTADO should be increased, and tend to increase as the substituents vary from CH_3 to NO_2. Because the ability of the substituent of drawing an electron is stronger, the strength of back-donation π-bonding is larger. But the heats of protonation of ligands RPhen decrease with the substituents varying from CH_3 to NO_2. Therefore, when the heats of formation of ternary complex compounds Cu(II)-RPhen-HTADO are plotted against the heats of protonation of the ligands RPhen, a straight line with a negative slope was obtained (see Fig. 1). The linear enthalpy relationships presented in Fig. 1 indicate that the heats of formation of ternary complex compounds Cu(III)-RPhen-HTADO strongly depend on the heats of protonation of the ligands RPhen, which means that the substituents on RPhen not only affect the heats of protonation of the ligands RPhen, but also affect the heats of formation of the ternary complex compounds Cu(III)-RPhen-HTADO. Therefore, a linear enthalpy relationship appears to exist between the heats of formation of ternary
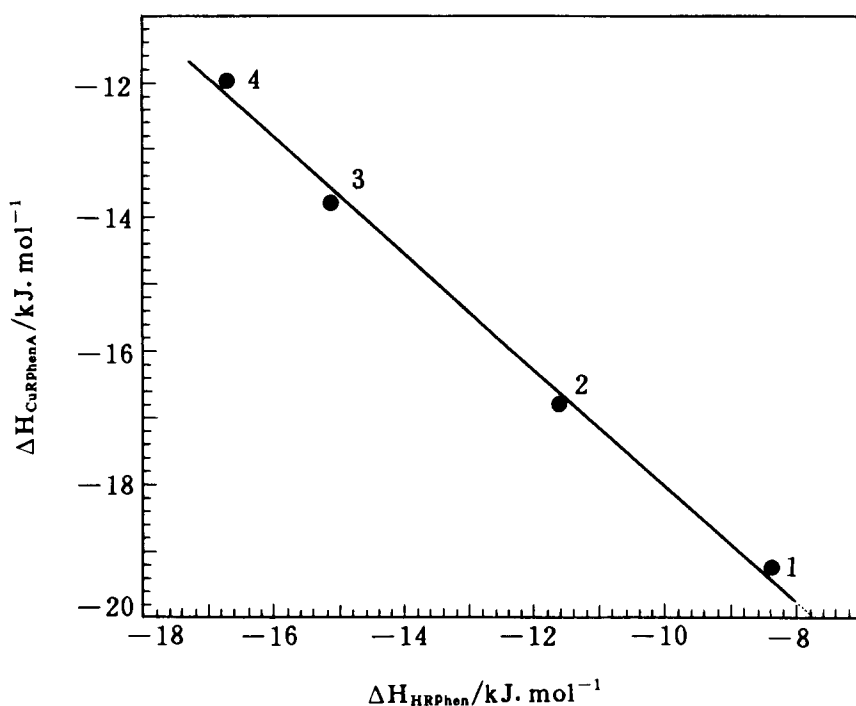

Fig. 1. Linear enthalpy relationship between the heats of formation of ternary complex compounds Cu(II)-RPhen-HTADO and the heats of protonation of ligands RPhen: 1, NO_2 Phen; 2, ClPhen; 3, Phen; 4, CH_3 Phen.

complex compounds Cu(II)-RPhen-HTADO and the heats of protonation of the ligands RPhen (ΔH_{HRPhen}:CH$_3$,-16.7; H, -15.1; Cl,-11.6; NO$_2$,-8.4 kJ mol^{-1}) [26] with the correlation equation: $\Delta H_{CuRPhenHTADO} = -26.73 - 0.8693\,\Delta H_{HRPhen}$ ($r = -0.9980$).

It is seen from Table 4 that the heats of formation of ternary complex compounds Cu(II)AB (A is HTADO, B is α-aminoacids) range from -65 to -72 kJ mol^{-1}. These values are much larger than the heat of formation of the binary complex compound Cu(II)-H$_{-1}$A, -16.1 ± 0.5 kJ mol^{-1}. To explain this phenomenon we consider that the ternary complex compounds Cu(II)AB may have the following structure.
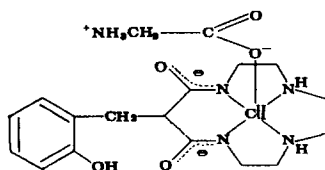
When the ligand HTADO is coordinated to Cu(II), there is simultaneous release of two hydrogen atoms from the amido group. While the pH values of the final solutions are 5.27–6.30, the oxygen atom of the carboxyl group of α-aminoacids cannot combine with the proton. Therefore, when α-aminoacids are coordinated to Cu(II), only the oxygen atom of the carboxyl group can attach to the metal ion. One of the two hydrogen ions released from the amido groups may join with the nitrogen atom of the amino group of α-aminoacids, and another one may join with the oxygen atom of the phenol group of ligand HTADO. When the stability constants of the ternary complex compounds Cu(II) AB were calculated using the TITFIT program, the resulting calculation converged only with the simulation of the model log β_{CuAB}. The heat of formation of the binary complex compound Cu(II)H$_{-1}$ A was -16.1 ± 0.5 kJ mol^{-1}, the protonation heat of α-aminoisobutyric acid was -51.9 ± 0.1 kJ mol^{-1} [18], and the heat of the coordination of the oxygen atom of the carboxyl group to Cu(II) was -4.2 kJ mol^{-1} [27]. Thus, the sum of the above three heat effects is -72.2 kJ mol^{-1}, which is in agreement with the heat of formation of the ternary complex compounds Cu(II)-Aib-HTADO, -72.2 ± 1.5 kJ mol^{-1}. A similar phenomenon is also found in other ternary complex compounds Cu(II)-AA-HTADO which also show that the heats of ternary complex compounds are approximately the sum of the heats of formation of the corresponding mother binary complex compounds if no d-p back π-bonding exists in the ternary systems. This further supports evidence that the heat of formation of ternary complex compounds has the property of additivity of the parent binary complex compounds [12]. Furthermore, a linear enthalpy relationship has been found to exist between the heats of formation of ternary complex compounds Cu(II) AB and the heats of protonation (ΔH_{HB}:-43.3 ± 0.1 (Pro); -51.9 ± 0.1 (Aib); -48.5 ± 0.1 (iLe); -47.7 ± 0.2 (Gly); -47.3 ± 0.1 (Val); -45.5 ± 0.1 (Ser) kJ mol^{-1} [18]) of the ligands and α-aminoacids, with the correlation equation (Fig. 2): $\Delta H_{CuAB} = -26.15 + 0.8769\,\Delta H_{HB}$ ($r = 0.9862$).
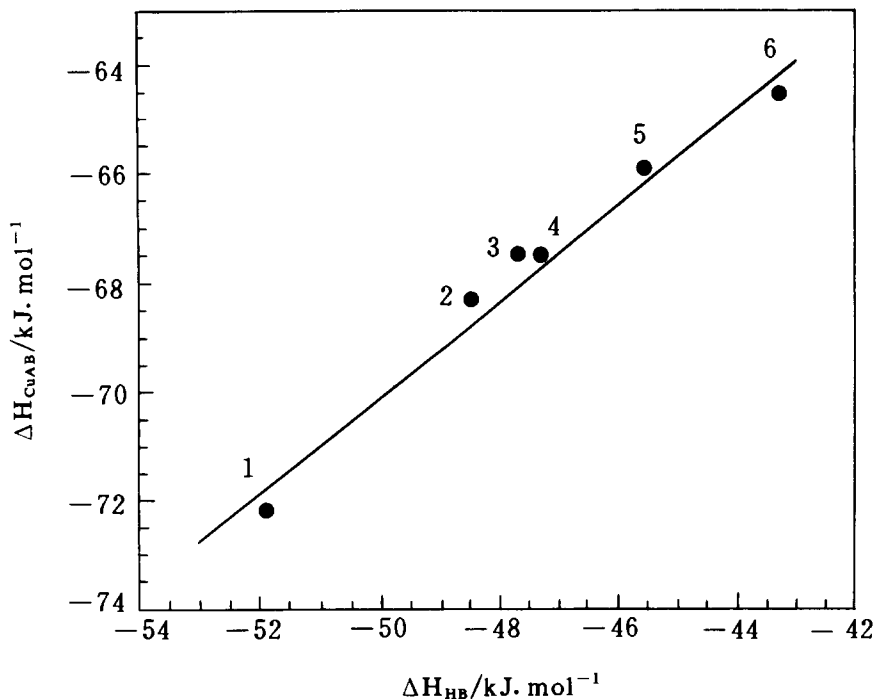
Fig. 2. Linear enthalpy relationship between the heats of formation of ternary complex compounds Cu(II)-α-aminoacids-HTADO and the heats of protonation of ligands α -aminoacids: 1, α-aminoisobutyric acid; 2, isoleucine; 3, glycine; 4, valine; 5, serine; 6, proline.

The linear enthalpy relationships presented in Fig. 2 indicate that the heats of formation of ternary complex compounds Cu(II)-α-aminoacids-HTADO strongly depend on the heats of protonation of ligand α-aminoacids and the slope of the line in Fig. 2 is about unity.

References

[1] M. Kodama and E. Kimura, J. Chem. Soc., Dalton Trans. (1981) 694.
[2] M. Kodama and E. Kimura, J. Chem. Soc., Dalton Trans., (1979) 325.
[3] E. Kimura, T. Yatsunami, A. Watanabe, R. Michida et al., Biophys. Acta, 37 (1983) 745.
[4] M.C. Shen, Q.H. Lou, S.R. Zhu et al., Chem. J. Chinese Univ., Series B, 6 (1990), 354.
[5] Japan Kokai, 62-201361, 59-98074.
[6] R. Machida, E. Kimura and M. Kodama, Inorg. Chem., 22 (1983) 2055.
[7] L. Fabbrizzi and A. Poggi, J. Chem. Soc., Chem. Commun., 646 (1980).
[8] Y.D. Lampeka and S.P. Cavrish, J. Coord. Chem., 21 (1990) 351.
[9] R. Hay, R. Bembi and W. Sommerville, Inorg. Chim. Acta, 59 (1982) 147.
[10] B.J. Hathaway, in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry", Pergamon Press, Oxford, 1987, p. 533.

[11] D.M. Margerum and G.D. Owens, in H. Sigel (Ed.), Metal Ions in Biological Systems, Vol. 12, Marcel Dekker, New York, 1981, p. 75.
[12] I. Tabushi, Y. Taniguchi and H. Koto, Tetrahedron Lett., (1977) 1049.
[13] A. McAuley, K. Beveridge, S. Subramanian and T.W. Whitcombe, Can J. Chem., 67 (1989) 1657.
[14] H.K. Lin, S.R. Zhu, Z.X. Gu and Y.T. Chen, J. Indian Chem. Soc., submitted.
[15] S.R. Zhu, J.C. Xian, X.H. Bu, H.K. Lin and Y.T. Chen, Chinese Chem. Lett., 4 (1993) 669.
[16] Y.M. Rong, C.Y. Jin, H.K. Lin and Y.T. Chen, Thermochim. Acta, 183 (1991) 47.
[17] Y.T. Chen, Z.X. Gu, H.K. Lin and H.Q. Liu, Sci. Sinica (Ser. B), (1985) 518.
[18] H.K. Lin, Z.X. Gu and Y.T. Chen, Thermochim. Acta, 123 (1988) 201.
[19] A.M. Tian, Z.M. Qin, X.C. Zhen, Z.G. Zhan and Y. Den, Chem. J. Chinese Univ., 2 (1981) 244.
[20] P.I. Ting, E.J. Burch, J.L. Meyer and G.H. Nancollas, Thermochim. Acta, 5 (1973) 463.
[21] H.K. Lin, S.X. Lin, Z.X. Gu and Y.T. Chen, Thermochim. Acta, 164 (1990) 353.
[22] B.J. Wang, X.X. Fan and W.H. Wu, Titration Calorimetric Method, Advanced Teaching Publish House, Zhangchun, 1985, p. 13.
[23] J.C. Xian, S.R. Zhu, H.K. Lin and Y.T. Chen, Chem. J. Chin. Univ. 15 (1994) 163.
[24] S.R. Zhu, H.K. Lin, J.C. Xian and Y.T. Chen, Polyhedron, 13 (1994) 759.
[25] J.C. Xian, S.R. Zhu, H.K. Lin and Y.T. Chen, Acta Phys. Chim. Sinica, 10 (1994) 837.
[26] Y.T. Chen, H.K. Lin and J.Y. Zhu, J. Chem. Soc., Dalton Trans., (1990) 3445.
[27] A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 3, Plenum Press, New York and London, 1974, p. 3, p. 81, p. 183.