ELSEVIER

Thermochimica Acta, 242 (1994) 51–64

thermochimica
acta

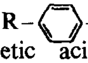
Linear thermodynamic function relationships in coordination chemistry: calorimetric study on nickel(II)–, cobalt(II)–, zinc(II)–*N*-(*p*-substituted phenyl)iminodiacetic acid binary systems and nickel(II)–, cobalt(II)–, zinc(II)–nitrilotriacetic acid–*N*-(*p*-substituted phenyl)iminodiacetic acid ternary systems

Hua-Kuan Lin *, Zong-Xin Gu, Yun-Ti Chen

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

(Received 4 October 1993; accepted 15 February 1994)

Abstract

The heats of protonation of *N*-(*p*-substituted phenyl)iminodiacetic acids (B, R––$N(CH_2COOH)_2$, RPhIDA: R is CH_3O, CH_3, H, Cl) and nitrilotriacetic acid (A, $N(CH_2COOH)_3$, NTA) and the heats of formation of the M(II)–B and M(II)–A binary systems (M is Ni, Co, Zn), and of the M(II)–A–B ternary systems have been determined at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} ($NaClO_4$) in aqueous solution using an improved model RD-1 automatic conduction calorimeter. The entropies of protonation and of formation for these binary and ternary systems have been calculated from their free energies. The results show that both linear enthalpy relationships (LERs) and linear entropy relationships (LSRs) exist between the heat (and entropy) of protonation of B and the heat (and entropy) of formation of both binary and ternary complex compounds.

It is noted that the heats of protonation of RPhIDA and the heat of formation for their metal complexes are all positive, i.e. endothermic, and a hypothetical structure of the polyring for the hydrated ligands B has been suggested to interpret the experimental results.

Keywords: Binary system; Entropy; Enthalpy; Heat of protonation; Ligand; RETE; Ternary system; Tunnelling

---

* Corresponding author.

SSDI 0040-6031(94)01776-D

1. Introduction

We have previously reported the LERs of the Cu(II)–N-(*p*-substituted phenyl) iminodiacetic acid (RPhIDA) binary system and the Cu(II)–RPhIDA–α-amino acid ternary system [1] and the LFERs of the Ni(II)–, Co(II)–, and Zn(II)–RPhIDA binary and ternary systems formed by the former with NTA in aqueous solution, $I = 0.1$ mol dm^{-3} ($NaClO_4$) [2]. But the LERs of these Ni(II)–, Co(II)–, and Zn(II)–RPhIDA binary and ternary systems have not been reported previously.

In this paper, we report the results of the calorimetric study on these systems. Both LERs and LSRs are found to exist in these systems. We also discuss the phenomenon of the positive values of $\Delta H_{HB}(\Delta H_{MB})$ in detail.

We have previously reported the calculation method for the calorimetric determination of the heats of formation of Cu(II)–RPhIDA–α-amino acid competitive ternary complex compounds [1]. A similar calculation method was used in this paper.

2. Experimental

Nickel(II), cobalt(II), and zinc(II) perchlorates were prepared by the conventional method from their nitrate salts. Sodium perchlorate (C.P., Shanghai Second Chemical Reagent Factory) was recrystallized from 90% ethanol solution. Perchloric acid (G.R., Tianjin Dongfang Chemical Factory) and sodium hydroxide (A.R., Tianjin Third Chemical Reagent Factory) were used without further purification.

An improved model RD-1 automatic conduction calorimeter with a precision of ±0.5% [3] was used to measure the heat effects. The instrumental constant K was determined to be $(3.00 \pm 0.02) \times 10^{-3}$ J mm^{-2} (n, the number of tests was 11) using electrical power calibration and was checked again with the neutralization reaction ($HClO_4(aq) + NaOH(aq)$) at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} ($NaClO_4$) (see Table 1). The average value of ΔH_N obtained was -56.32 ± 0.10 kJ mol^{-1}, which is in good agreement with the literature value (-56.44 kJ mol^{-1}) [4]. With this value, the heats of formation of H_2O in the reaction vessel were calibrated.

The pH values of both solutions (before and after the reaction) were measured by a model 71Φ Beckman pH-meter (precision ±0.001).

The procedure for the calorimetric measurements was the same as reported previously [3].

3. Results and discussion

All the experimental data are given in Tables 1–6. The apparent thermodynamic parameters of protonation and formation for ligands A and B and for these binary and ternary complex compounds are listed in Tables 7 and 8.

The existence of LFERs for these systems has been reported [2]. From the calorimetric study of the systems under identical conditions, we also found linear

Table 1
Measurement of the heat of formation of water at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} (NaClO$_4$) in aqueous solution

$C_{HClO_4} \times 10^3$/mol dm^{-3}	$C_{NaOH} \times 10^3$/mol dm^{-3}	S/mm^2	Q_m/J	Q_c/J	ΔH_N/kJ mol^{-1}
96.05$_5$	9.910	− 3567.2 ± 0.02	− 10.70 ± 0.02	− 10.82 ± 0.02	− 56.32 ± 0.10
96.05$_5$	0	+ 40	+ 0.12		

Table 2
Measurements of the heats of step-wise protonation of NTA at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} (NaClO$_4$) in aqueous solution

n	$C_H \times 10^3$/mol dm^{-3a}	$C_A \times 10^3$/mol dm^{-3}	pH$_i$	pH$_f$	Q_c/J	pK_{D1}	pK_{D2}	pK_{D3} [5]	ΔH_p/kJ mol^{-1}
5	8.732	9.610	10.53	7.82	− 4.14 ± 0.02	1.80			− 20.5 ± 0.10
6	8.732	6.407	10.42	3.02	− 2.89 ± 0.01		2.48		− 3.25 ± 0.23
5	8.732	3.203	10.25	2.43	− 1.53 ± 0.01			9.65	− 2.62 ± 0.05

[a] C_H denotes the concentration of HClO$_4$.

Table 3
Measurement of the heats of step-wise protonation of RPhIDA at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} (NaClO$_4$) in aqueous solution

R	n	$C_H \times 10^3$/mol dm^{-3}	$C_B \times 10^3$/mol dm^{-3}	pH$_i$	pH$_f$	Q_c/J	pK_1	pK_2 [2]	ΔH_p/kJ mol^{-1}
CH$_3$O	4	8.732	9.009	7.20	4.43	+ 0.61	3.97		+ 3.20 ± 0.03 (1)
	4	8.732	4.325	7.38	2.99	+ 0.35		5.36	+ 0.57 ± 0.80 (2)
CH$_3$	4	8.732	7.632	10.70	3.55	− 0.36	2.04		+ 4.65 ± 0.05 (1)
	4	8.732	3.816	10.44	2.44	− 0.21		5.18	+ 0.80 ± 0.21 (2)
H	4	8.732	8.324	6.85	3.65	+ 1.02	2.41		+ 5.83 ± 0.05 (1)
	4	8.732	4.162	6.77	2.61	+ 0.54		5.05	+ 0.49 ± 0.15 (2)
Cl	4	8.732	8.324	6.94	3.58	+ 1.25	2.40		+ 7.31 ± 0.04 (1)
	4	8.732	4.162	6.81	2.53	+ 0.60		4.82	− 1.43 ± 0.14 (2)

Table 4

Measurement of the heats of formation of Ni(II)–, Co(II)–, and Zn(II)–NTA binary systems at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} ($NaClO_4$) in aqueous solution

M(II)	*n*	$C_M \times 10^3$/mol dm^{-3}	$C_A \times 10^3$/mol dm^{-3}	pH_i	pH_f	Q_c/J mol dm^{-3}	log K_1	log K_2 [4]	ΔH_{MA}/kJ mol^{-1}	
Ni	4	3.568	3.844	10.28	6.68	−1.03	11.50		−9.56 ± 0.26	(1)
	4	3.568	9.610	10.55	9.96	−2.90		4.82	−21.2 ± 0.5	(2)
Co	4	3.876	3.844	10.28	8.15	−0.26	10.38		−2.36 ± 0.23	(1)
	4	3.891	9.610	10.55	9.44	−2.22		3.95	−15.3 ± 0.23	(2)
Zn	4	3.541	3.844	10.28	7.15	−0.48	10.66		−3.64 ± 0.26	(1)
	5	3.541	9.610	10.55	9.97	−1.44		3.58	−9.35 ± 0.26	(2)

Table 5
Measurement of the heats of formation of M(II)–RPhIDA binary systems at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} ($NaClO_4$)

R	n	$C_M \times 10^3$/mol dm^{-3}	$C_B \times 10^3$/ mol dm^{-3}	pH_i	pH_f	Q_c/J	log K_1	log K_2 [2]	ΔH_{MB}/kJ mol^{-1}	
Ni(II)–RPhIDA										
CH_3O	4	3.568	4.325	7.64	7.06	+0.72	4.06		+10.3 ± 0.2	(1)
	4	3.568	8.649	7.63	7.05	+0.96		3.46	+2.35 ± 0.1	(2)
CH_3	5	3.568	3.816	9.80	7.96	+0.73	3.77		+12.6 ± 0.2	(1)
	5	3.568	7.635	5.23	4.68	+0.94		2.97	+7.60 ± 0.2	(2)
H	5	3.568	4.162	6.77	5.66	+0.96	3.62		+14.2 ± 0.2	(1)
	4	3.568	8.324	6.85	6.18	+1.36		2.58	+7.09 ± 0.1	(2)
Cl	4	3.568	4.162	6.81	5.67	+0.96	3.27		+16.1 ± 0.2	(1)
	4	3.568	8.324	6.94	6.21	+1.32		2.07	+6.75 ± 0.2	(2)
Co(II)–RPhIDA										
CH_3O	4	3.876	4.325	7.38	6.88	+0.84	3.81		+14.1 ± 0.2	(1)
	4	3.502	9.009	7.20	6.19	+0.84		3.09	−4.36 ± 0.1	(2)
CH_3	4	3.891	3.816	10.40	5.19	+0.35	3.37		+17.3 ± 0.3	(1)
	6	3.891	7.632	10.62	7.24	+0.43		2.93	+0.24 ± 0.2	(2)
H	5	3.502	4.162	6.77	5.00	+0.94	2.94		+19.9 ± 0.4	(1)
	5	3.502	8.324	6.85	5.49	+1.56		2.91	+3.24 ± 0.4	(2)
Cl	4	3.502	4.162	6.81	4.86	+0.92	2.67		+22.0 ± 0.5	(1)
	4	3.502	8.324	6.94	5.30	+1.52		2.50	+2.42 ± 0.6	(2)
Zn(II)–RPhIDA										
CH_3O	5	3.541	4.321	7.52	7.23	+1.01	3.95		+12.4 ± 0.2	(1)
	4	3.541	8.649	7.63	7.32	+1.54		3.46	+8.75 ± 0.1	(2)
CH_3	5	3.541	3.816	9.96	7.14	+0.81	3.70		+14.2 ± 0.2	(1)
	5	3.541	7.632	10.12	7.29	+1.31		2.68	+13.6 ± 0.1	(2)
H	4	3.541	4.160	6.77	6.01	+1.08	3.45		+15.8 ± 0.2	(1)
	4	3.541	8.324	6.85	6.56	+1.62		2.42	+13.4 ± 0.1	(2)
Cl	5	3.541	4.162	6.81	6.48	+1.04	3.07		+18.2 ± 0.4	(1)
	4	3.541	8.324	6.94	6.65	+1.55		1.91	+17.7 ± 0.3	(2)

Table 6

Measurement of the heats of formation of M(II)–NTA–RPhIDA ternary systems at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} (NaClO$_4$) in aqueous solution

R	n	$C_M \times 10^3$/mol dm^{-3}	$C_B \times 10^3$/mol dm^{-3}	$C_A \times 10^3$/mol dm^{-3}	pH$_i$	pH$_f$	Q_c/J	$\log \beta_{11}$ [2]	ΔH_{MAB}/kJ mol^{-1}
Ni(II)									
CH_3O	4	3.568	4.162	4.805	10.35	7.48	−1.26	13.80	−1.24 ± 0.41
CH_3	5	3.568	3.816	3.817	10.53	8.92	−1.24	13.59	+1.25 ± 0.51
H	5	3.568	4.162	4.805	10.37	7.62	−1.35	13.38	+3.11 ± 0.75
Cl	4	3.568	4.162	4.805	10.35	7.55	−1.37	13.07	+5.46 ± 1.3
Co(II)									
CH_3O	5	3.502	4.162	4.805	10.35	8.25	−0.47	12.65	+11.3 ± 0.4
CH_3	3	3.502	3.816	3.817	10.53	6.04	−0.55	12.41	+14.0 ± 0.6
H	6	3.502	4.162	4.805	10.41	7.26	−0.71	12.20	+16.3 ± 0.7
Cl	4	3.502	4.162	4.805	10.35	7.39	−0.66	11.95	+18.7 ± 1.1
Zn(II)									
CH_3O	4	3.541	4.162	4.805	10.17	8.11	−0.36	12.59	+8.38 ± 0.61
CH_3	6	3.541	3.816	3.817	10.40	8.98	−0.46	12.38	+10.2 ± 0.9
H	6	3.541	4.162	4.805	10.37	8.62	−0.72	12.12	+12.4 ± 1.5
Cl	4	3.541	4.162	4.805	10.32	8.76	−0.64	11.77	+15.1 ± 3.2

Table 7

The apparent thermodynamic parameters of protonation for NTA and RPhIDA at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} (NaClO$_4$) in aqueous solution

L	ΔG_{P1}/kJ mol^{-1}	ΔG_{P2}/kJ mol^{-1}	ΔG_{P3}/kJ mol^{-1}	ΔH_{P1}/kJ mol^{-1}	ΔH_{P2}/kJ mol^{-1}	ΔH_{P3}/kJ mol^{-1}	ΔS_{P1}/J K^{-1} mol^{-1}	ΔS_{P2}/J K^{-1} mol^{-1}	ΔS_{P3}/J K^{-1} mol^{-1}
NTA	−55.1	−14.2	−10.3	−20.5	−3.25	−2.62	116	36.6	25.7
CH_3O	−30.6	−22.7		+3.20	+0.57		113	77.9	
CH_3	−29.6	−11.6		+4.65	+0.80		115	41.7	
H	−28.8	−13.8		+5.83	+0.49		116	47.8	
Cl	−27.5	−13.7		+7.31	−1.34		117	41.1	

Table 8
The apparent thermodynamic parameters of formation for M(II)–NTA (or RPhIDA) binary and M(II)–NTA–RPhIDA ternary systems at 25.0 ± 0.2°C, $I = 0.1$ mol dm^{-3} ($NaClO_4$) in aqueous solution

L	ΔG_{M1}/kJ mol^{-1}	ΔG_{M2}/kJ mol^{-1}	ΔG_{MAB}/kJ mol^{-1}	ΔH_{M1}/kJ mol^{-1}	ΔH_{M2}/kJ mol^{-1}	ΔH_{MAB}/kJ mol^{-1}	ΔS_{M1}/kJ mol^{-1}	ΔS_{M2}/J K^{-1}	ΔS_{MAB}/J K^{-1} mol^{-1}
Ni(II)– binary and Ni(II)–NTA– ternary system									
NTA	−65.6	−27.5		−9.56	−21.2		188	21	
CH_3O	−23.2	−19.7	−78.7	+10.3	+2.35	−1.24	112	74	260
CH_3	−21.5	−17.0	−77.9	+12.6	+7.60	+1.25	114	82	264
H	−20.7	−14.7	−76.3	+14.2	+7.09	+3.11	117	73	266
Cl	−18.6	−11.8	−74.6	+16.1	+6.75	+5.46	117	62	268
Co(II)– binary and Co(II)–NTA– ternary									
NTA	−59.2	−22.5		−2.36	−15.3		191	127	
CH_3O	−21.7	−17.6	−72.2	+14.1	−4.36	+11.3	120	45	280
CH_3	−19.2	−16.7	−70.8	+17.3	+0.24	8.38	123	57	285
H	−16.8	−16.6	−69.6	+19.9	+3.24	+16.3	123	67	288
Cl	−15.2	−14.3	−68.2	+22.0	+2.42	+18.7	125	56	292
Zn(II)– binary and Zn(II)–NTA– ternary									
NTA	−60.8	−20.4		−3.64	−9.35		192	37	
CH_3O	−22.5	−19.7	−71.8	+12.4	+8.75	+8.38	117	96	269
CH_3	−21.1	−15.3	−70.6	+14.2	+13.6	+10.2	118	97	271
H	−19.7	−13.8	−69.2	+15.8	+13.4	+12.4	119	91	274
Cl	−17.5	−10.9	−67.2	+18.2	+17.7	+15.1	120	96	276

enthalpy relationships (LERs) and linear entropy relationships (LSRs) in both binary systems and ternary systems, and even some cross-linear relationships bewteen the enthalpy of formation of the complexes and the entropy of protonation of the ligand (see Figs. 1–3). The relevant linear regression equations and their correlation coefficients are shown as follows.

3.1. LERs of binary systems

Ni(II)–RPhIDA $\Delta H_{\mathrm{MB}} = 5.92 + 1.41\Delta H_{\mathrm{HB}}$ $(r = 0.999)$

Co(II)–RPhIDA $\Delta H_{\mathrm{MB}} = 8.13 + 1.94\Delta H_{\mathrm{HB}}$ $(r = 0.994)$

Zn(II)–RPhIDA $\Delta H_{\mathrm{MB}} = 7.76 + 1.41\Delta H_{\mathrm{HB}}$ $(r = 0.998)$

3.2. LERs of ternary systems

Ni(II)–NTA–RPhIDA $\Delta H_{\mathrm{MAB}} = -6.39 + 1.63\Delta H_{\mathrm{HB}}$ $(r = 1.000)$

Co(II)–NTA–RPhIDA $\Delta H_{\mathrm{MAB}} = 5.57 + 1.81\Delta H_{\mathrm{HB}}$ $(r = 0.999)$

Zn(II)–NTA–RPhIDA $\Delta H_{\mathrm{MAB}} = 2.84 + 1.65\Delta H_{\mathrm{HB}}$ $(r = 0.996)$

3.3. LSRs of binary systems

Ni(II)–RPhIDA $\Delta S_{\mathrm{MB}} = -43.1 + 1.37\Delta S_{\mathrm{HB}}$ $(r = 0.956)$

Co(II)–RPhIDA $\Delta S_{\mathrm{MB}} = -12.3 + 1.17\Delta S_{\mathrm{HB}}$ $(r = 0.970)$

Zn(II)–RPhIDA $\Delta S_{\mathrm{MB}} = 32.9 + 0.74\Delta S_{\mathrm{HB}}$ $(r = 0.983)$

3.4. ESRS of ternary systems

Ni(II)–NTA–RPhIDA $\Delta S_{\mathrm{MAB}} = 34.0 + 2.00\Delta S_{\mathrm{HB}}$ $(r = 1.000)$

Co(II)–NTA–RPhIDA $\Delta S_{\mathrm{MAB}} = -5.29 + 2.94\Delta S_{\mathrm{HB}}$ $(r = 0.994)$

Zn(II)–NTA–RPhIDA $\Delta S_{\mathrm{MAB}} = 68.3 + 1.77\Delta S_{\mathrm{HB}}$ $(r = 0.973)$

3.5. Linear enthalpy–entropy relationships of binary systems

Ni(II)–RPhIDA $\Delta H_{\mathrm{MB}} = -151 + 1.43\Delta S_{\mathrm{HB}}$ $(r = 0.992)$

Co(II)–RPhIDA $\Delta H_{\mathrm{MB}} = -211 + 1.99\Delta S_{\mathrm{HB}}$ $(r = 0.994)$

Zn(II)–RPhIDA $\Delta H_{\mathrm{MB}} = -146 + 1.40\Delta S_{\mathrm{HB}}$ $(r = 0.971)$

3.6. Linear enthalpy–entropy relationships of ternary systems

Ni(II)–NTA–RPhIDA $\Delta H_{\mathrm{MAB}} = -187 + 1.64\Delta S_{\mathrm{HB}}$ $(r = 0.988)$

Co(II)–NTA–RPhIDA $\Delta H_{\mathrm{MAB}} = -196 + 1.83\Delta S_{\mathrm{HB}}$ $(r = 0.988)$

Zn(II)–NTA–RPhIDA $\Delta H_{\mathrm{MAB}} = -177 + 1.64\Delta S_{\mathrm{HB}}$ $(r = 0.964)$

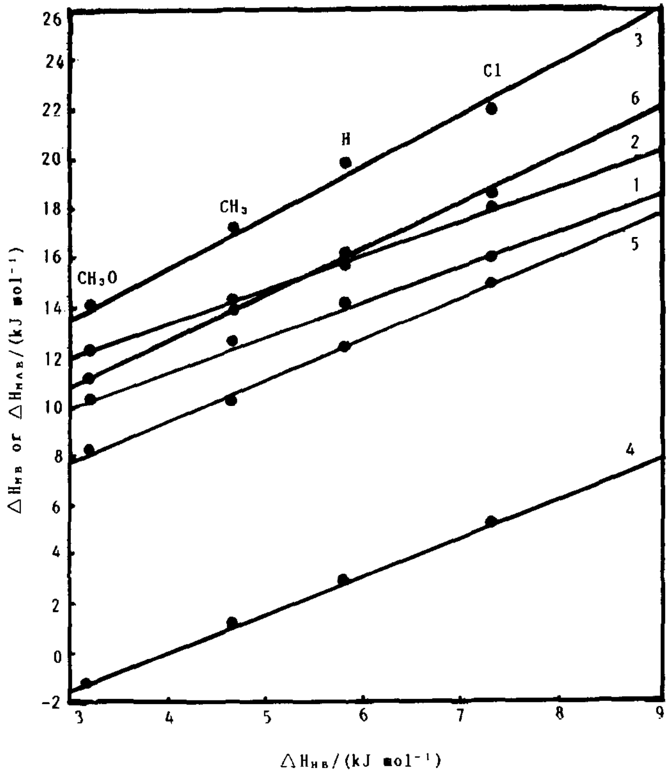


Fig. 1. Linear enthalpy relationships: 1, Ni(II)-*p*-RPhIDA; 2, Zn(II)-*p*-RPhIDA; 3, Co(II)-*p*-RPhIDA; 4, Ni(II)-NTA-*p*-RPhIDA; 5, Zn(II)-NTA-*p*-RPhIDA; 6, Co(II)-NTA-*p*-RPhIDA.

For a chemical reaction, in general, the change in enthalpy reflects a change in the binding energy of a compound; the change in entropy directly reflects a change in energy level and space structure distribution. But a chemical reaction is, in fact, a mutual reaction of an atom (or group of atoms) in a compound and a redistribution of space structure. Thus, enthalpy–enthalpy, entropy–entropy and enthalpy–entropy relationships are basic relationships of thermodynamics.

LFERs are a direct result of LERs and LSRs; LERs and LSRs ought to have the same slope, but many experimental results indicate that this is not true. Actually, LFERs, LERs and LSRs may have different slopes, which is in agreement with experimental results. Therefore, we can understand that LERS, LSRs and linear enthalpy–entropy relationships are more basic thermodynamic relationships than LFERs [6].

The experimental results show that ΔH_{HB} and ΔH_{MB} have positive values, i.e. they are endothermic. We have previously reported calorimetric studies on *N*-(substituted phenyl)glycine (RPhGly) [7–10], for which either the heats of protonation of the ligands (ΔH_{HB}) or the heats of formation of the complexes (ΔH_{MB}) are negative, i.e. exothermic. So the appearance of positive values for RPhIDA is

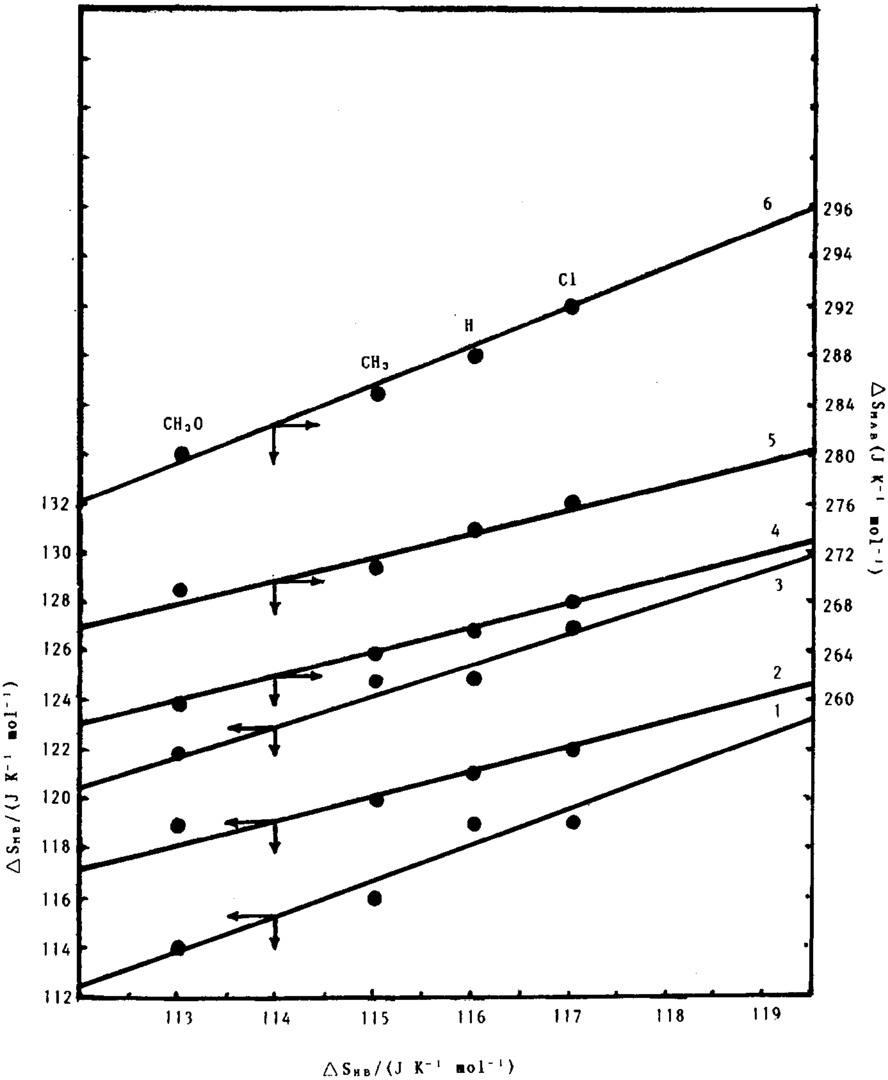


Fig. 2. Linear entropy relationships: 1, Ni(II)-*p*-RPhIDA; 2, Zn(II)-*p*-RPhIDA; 3, Co(II)-*p*-RPhIDA; 4, Ni(II)-NTA-*p*-RPhIDA; 5, Zn(II)-NTA-*p*-RPhIDA; 6, Co(II)-NTA-*p*-RPhIDA.

puzzling. Why should the addition of a carboxyl group on the nitrogen atom of RPhGly, i.e. RPhIDA, change the heat of protonation (ΔH_{HB}) and the heat of formation of the complex compound (ΔH_{MB}) so much that even the sign is changed?

First, consider the structure of the four ligands: NH_3, NH_2CH_2COOH, $NH(CH_2COOH)_2$ and $N(CH_2COOH)_3$. Their constants of protonation on the nitrogen atom, $\log K_{HL}$, are respectively 9.24 [5], 9.56 [11], 9.34 [5] and 9.65 [5]; the

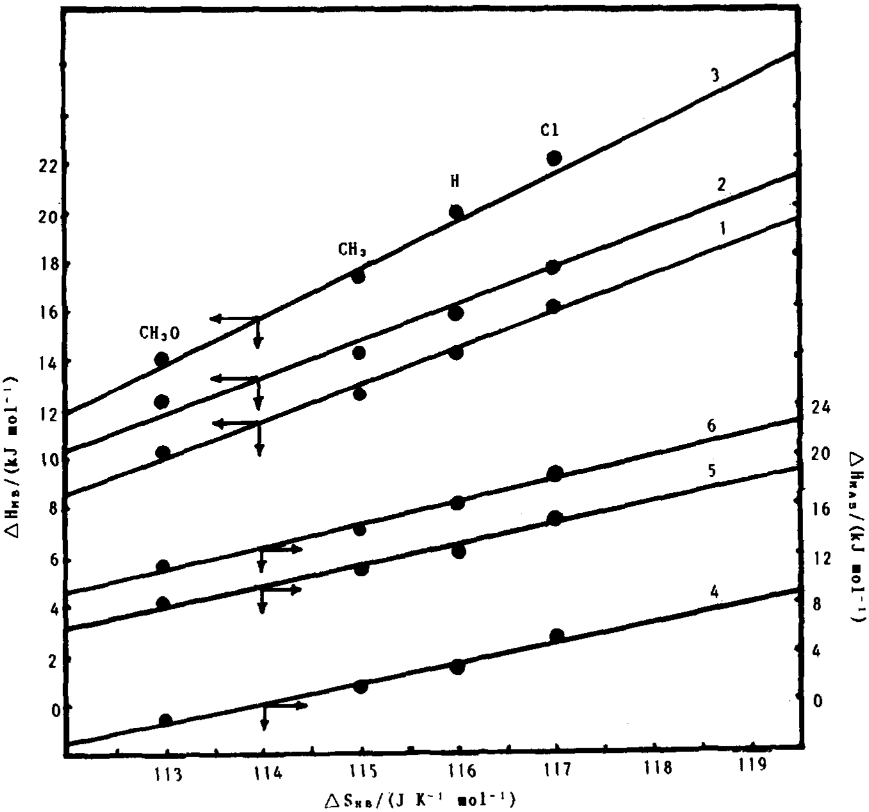


Fig. 3. Linear enthalpy–entropy relationships: 1, Ni(II)-*p*-RPhIDA; 2, Zn(II)-*p*-RPhIDA; 3, Co(II)-*p*-RPhIDA; 4, Ni(II)-NTA-*p*-RPhIDA; 5, Zn(II)-NTA-*p*-RPhIDA; 6, Co(II)-NTA-*p*-RPhIDA.

differences are not significant. But their heats of protonation are -52.1 [5], -47.7 [11], -34.4 [5] and -20.5 kJ mol^{-1} respectively; the differences are very distinct. The log K values of protonation on the oxygen atom of a carboxyl group are 2.36 [11], 2.61 [5] and 2.48 [5], while their heats of protonation are -3.81 [11], -5.02 [5] and -3.25 kJ mol^{-1} [8], respectively. We can see that when the number of carboxyl groups on the nitrogen atoms is increased, the log K values of protonation on the nitrogen atom do not change much, but their heats of protonation are decreased by -4.4, -13.4, -13.9 kJ mol^{-1}, respectively, the protonation constants and the heats of protonation on the oxygen atom of the carboxyl group remaining almost unchanged. From an energetic viewpoint, any formation of a chemical bond (involving a coordination bond) should evolve an amount of heat corresponding to the bonding energy. Conversely, breaking a bond should expend on equal amount of energy. From this we know that a large expense of energy should occur in the reaction system of RPhIDA during the calorimetric measurement. The evolved heat of formation of coordination bonding cannot compensate for this large expenditure of energy; therefore the apparent enthalpies obtained have positive values, i.e. they

Table 9
Some correlative thermodynamic data of protonation for some amino acids

	$\log K_{P1}$	$\Delta H_{P1}/\mathrm{kJ\ mol^{-1}}$
Ammonia	9.24 [5]	−52.1 [5]
Glycine	9.56 [11] 9.52	−47.7 [11]
Iminodiacetic acid	9.34 [5] 9.49	−34.3 [5]
Nitrilotriacetic acid	9.65 [5] 9.51	−19.2 [5] −20.5
n-(phenyl)glycine	4.69 [8]	−10.37 [8]
N-(phenyl)iminoacetic acid	5.05 [2]	+5.83

are endothermic. This large expenditure of energy could well be caused by breaking the hydrated rings. Because of the solvation of NH_2CH_2COOH (or $NH(CH_2COOH)_2$ or $N(CH_2COOH)_3$), a nitrogen atom can form 1 (or 2 or 3) seven-membered rings with the oxygen atoms of the carboxyl groups intramolecularly with H_2O molecules through hydrogen bonding. It is obvious that those ligands with a different number of hydrated rings were coordinated either with hydrogen ions or with metal ions, the hydrated rings (1 or 2 or 3) being broken first. Because the breaking of a ring should expend a certain amount of energy, the more rings there are, the more energy consumed. The heat data in Table 9 show that the breaking of a ring requires the expenditure of 13–14 kJ mol^{-1}. The NH_3 molecule cannot form a ring structure, but it is still united with water molecules through hydrogen bonding. Therefore, when the nitrogen atom of an NH_3 molecule combines with a hydrogen ion, it needs to expend about 10 kJ mol^{-1}, which is less than that for glycine. When they combine with hydrogen ions, the number of seven-membered rings that are broken is 0, 1, 2, or 3, respectively. The energies expended breaking these rings are 10, 14, 28 and 42 kJ mol^{-1} respectively. The estimated value of the enthalpy change on combination of a nitrogen atom with a hydrogen ion is about −62 kJ mol^{-1}, provided its solvation energy is not considered. However, accounting for the solvation effect, their net energy changes are −52.1, −47.7, −34.3 and −20.5 kJ mol^{-1}, respectively. After breaking the ring, the combination of an oxygen atom of a carboxyl group with a hydrogen ion is about the same no matter how many carboxyl groups are attached to the nitrogen atom. Therefore, the constants of protonation and heats of protonation for an oxygen atom on a carboxyl group are roughly the same.

Why can a nitrogen atom and three carboxyl groups form three seven-membered rings with three water molecules through hydrogen bonding? That is to say, why can a nitrogen atom form another seven-membered ring when it is already attached to a carboxyl group, after the nitrogen atom and oxygen atom of a carboxyl group on glycine have formed a seven-membered ring with water molecules by hydrogen bonding? It may be that the electron density on the nitrogen atom or oxygen atoms becomes larger, and their basicity becomes stronger after the nitrogen atom or oxygen atom is attached to a carboxyl group. This tendency of increasing electron density makes it possible for the nitrogen or oxygen atom to form a seven-membered ring with a carboxyl group and H_2O molecule through hydrogen bonding. We suggest this in view of the following facts. Firstly, the constant of protonation, $\log K_{HL}$, of aniline is 4.65 [12], while that of benzoic acid is 4.21 [12]. However, the constant of protonation, $\log K_{HL}$, of the nitrogen atom of *o*-aminobenzene monocarbonic acid is 4.95 [12], and that of its oxygen atom is 2.05 [12]. Secondly, the constant of protonation for phenol, $\log K_{HL}$, is 9.99 [12], but that for the oxygen atom of salicylic acid is 12.38 [12], and that for the oxygen atom of the carboxyl group is 3.0 [12]. Thirdly, the constant of protonation of NH_3, $\log K_{HL}$, is 9.24 [5], and that of acetic acid is 4.76 [12]; however the constant of protonation of the nitrogen atom of glycine, $\log K_{HL}$, is 9.56 [11], and that of the oxygen atom of the carboxyl group is 2.36 [11]. From the above three examples we can see that the addition of a carboxyl group makes the density of the electron cloud on the nitrogen (or oxygen) atom increase significantly, so that it can form a seven-membered ring with the oxygen atom of a carboxyl group and a water molecule by hydrogen bonding. But when the seven-membered rings are broken, the degree of randomness of the H_2O molecule increases rapidly. This leads to a large entropy change, which compensates for the tendency to decrease the constant of protonation because of the energy that has been consumed breaking the seven-membered ring. Therefore, the constants of protonation of $NH_n(CH_2COOH)_{3-n}$ ($n = 0$, 1, 2 and 3) do not change much. It is obvious that when the ligands with different numbers of hydrated rings coordinate either with a hydrogen ion or metal ions, the hydrated rings must first be broken simultaneously. The breaking of the ring expends energy so that the more rings there are, the more energy will be consumed. The heat data in Table 9 indicate that the breaking of a hydrated ring expends about 13–14 $kJ\ mol^{-1}$. Because the phenyl ring was attached to the nitrogen atom, the heat of protonation decreased by 37–40 $kJ\ mol^{-1}$ during calorimetric measurement of the RPhGly and RPhIDA systems; the phenyl ring decreases markedly the density of the electron cloud on the nitrogen atom.

Due to the effect of the phenyl ring, PhGly with a seven-membered ring has a very small heat of protonation ($-10.37\ kJ\ mol^{-1}$ [7]) while the ΔH_{HL} of glycine is $-47.7\ kJ\ mol^{-1}$ [10] and the first-step heat of protonation of iminodiacetic acid is $-34.4\ kJ\ mol^{-1}$ [11]. However, when a phenyl group is substituted into iminodiacetic acid, yielding PhIDA and forming two seven-membered rings, it has a positive value ($+5.83\ kJ\ mol^{-1}$). Because the protonation energy cannot completely offset the energy consumed, the apparent enthalpies of protonation of PhIDA determined were positive.

The formation of a poly-ring structure was first suggested from our experimental results. According to the relevant bond theory, a lone pair of electrons on the nitrogen atom can form only one ring with it, even though it has two oxygen atoms from the carboxyl group as RPhIDA. However, from this viewpoint, it is difficult to interpret the fact that the $\log K_{HL}$ values are almost the same but the ΔH_{HL} values are quite different (see Table 9).

Therefore we are forced to hypothesize that some poly-ring structures are formed in these hydrated molecules, even though there is not enough evidence to

Table 10
Some correlative thermodynamic data for some amines

Amine	$\log K_1$	ΔH_1/kJ mol^{-1}
Ammonia	9.24 [5]	−52.1 [5]
Ethylenediamine	10.14 [5]	−49.0 [5]
Diethylenetriamine	9.88 [5]	−46.9 [5]
Tri(2-aminoethyl)amine	9.89 [5]	−51.0 [5]

confirm it. We believe that additional charges on the nitrogen atom already bound to the oxygen atom of the carboxyl group by hydrogen bonding, could be supplied by another lone pair electrons of the same oxygen atom. We propose to call this effect the "ring electron tunnel effect" (RETE). Thus, in the hydrated poly-ring, the electron cloud can flow from the oxygen atom of the carboxyl group on the nitrogen atom through the carbon linkage containing the carboxyl group, so that the basicity of the nitrogen atom already bound through hydrogen bonding in the hydrated ring does not decrease; it can form a second hydrated ring, and go on to form a third ring.

If we replace the oxygen atom of a carboxyl group by a nitrogen atom which has only one lone pair of electrons, instead of three on the oxygen atom, there are no surplus pairs of isolated electrons which can transfer to the central nitrogen atom so that no such trend would exist, as shown in Table 9. But, as seen in Table 10, we found that both $\log K_{HL}$ and ΔH_{HL} are almost the same because there is no formation of poly-ring structure. This would be another piece of evidence in favour of our assumption of poly-ring formation.

We believe that the poly-ring structure might be a common phenomenon in life systems and that the "ring electron tunnel effect" may play an important role in the formation of such a structure.

References

[1] Hua-Kuan Lin, Shu-Xiang Liu, Zong-Xin Gu and Yun-Ti Chen, Inorg. Chim. Acta, 175 (1990) 91–98.
[2] Hua-Kuan Lin, Zai-Jun Liu Xiang-Hai Tang and Yun-Yi Chen, Acta Phys. Chim. Sin., 9 (1993) 565.
[3] A.M. Tian, Z.M. Cin, X.Z. Zeng and Y. Deng, Chem. J. Chinese Univ., 2 (1981) 244.
[4] Yun-Ti Chen, Hua-Kuan Lin and Zong-Xin Gu, J. Inorg. Chem. (Chinese), 1 (1985) 13. Po I. Tian, E.J. Burhe, J.L. Meyer and G.H. Nancollas, Thermochim. Acta, 5 (1973) 463.
[5] A.E. Martell and R.M. Smith, Critical Stability Constants, Plenum Press, New York, 1974, Vol. 1, p. 139; Vol. 2, p. 36, 101, 137.
[6] F. Marsicano and R.D. Hancock, J. Chem. Soc. Dalton Trans., (1978) 228.
[7] Yun-Ti Chen, Hua-Kuan Lin and Zong-Xin Gu, Acta Phys. Chim. Sin., 1 (1985) 87.
[8] Yun-Ti Chen, Hua-Kuan Lin and Zong-Xin Gu, Sci. Sin. Ser. B, (1987) 816.
[9] Yun-Ti Chen, Hua-Kuan Lin and Zong-Xin Gu, Acta Phys. Chim. Sin., 2 (1986) 452.
[10] Yun-Ti Chen, Zong-Xin Gu, Hua-Kuan Lin, Gui-Fang Lu and Ji-Wei Tang, J. Inorg. Chem. (Chinese), 4 (1988) 102.
[11] Hua-Kuan Lin, Zong-Xin Gu and Yun-Ti Chen, Thermochim. Acta, 123 (1988) 201.
[12] Yun-Bing Yao, Tao Xie and Ying-Min Gao, Handbook of Physical Chemistry, Shanghai Science-Technique Publishing House, Shanghai, 1985, p. 783, 786, 788, 806.