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Linear enthalpy relationships. Zinc(II), cobalt(II), nickel(II), copper(II)–bipyridyl/phenanthroline–N-(*meta*-substituted phenyl) iminodiacetic acid ternary systems [a]

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Abstract

According to a method reported earlier (Chen et al., J. Inorg. Chem., 1 (1985) 13) the heat of protonation of the ligands (N-(*meta*-substituted phenyl) iminodiacetic acids) (*m*-$RC_6H_4N(COOH)_2$, R = CH_3, CH_3O, H, Cl), the heat formation of complex compounds formed from these ligands with Cu(II), and the heats of formation of ternary complex compounds formed from Zn(II), Co(II), Ni(II), Cu(II) with 2,2′-bipyridyl or 1,10-phenanthroline and N-(*meta*-substituted phenyl) iminodiacetic acids have been determined by a calorimetric method. The results showed the existence of linear enthalpy relationships between the heats of formation of these complex compounds and the heats of protonation of ligands conforming to the equation $\Delta H_M = Q - \beta \Delta H_{HL}$.

INTRODUCTION

We have previously [1–3] reported the existence of linear enthalpy relationships on the system N-(*meta*-substituted phenyl) glycines–M(II) binary systems and N-(*meta*-substituted phenyl) glycines–2,2′-bipyridyl/1,10-phenanthroline–M(II) ternary systems. In order to explore this phenomenon further, we found that linear enthalpy relationships also exist between the heat of protonation of the ligands, N-(*meta*-substituted phenyl) iminodiacetic acids (*m*-RPhIDA), and the heats of formation of complex compounds formed from Zn(II), Co(II), Ni(II), Cu(II) with 2,2′-bipyridyl or 1,10-phenanthroline and *m*-RPhIDA conforming to the equation $\Delta H_M = Q - \beta \Delta H_{HL}$.

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EXPERIMENTAL

Reagents and Instruments

N-(*meta*-substituted phenyl) iminodiacetic acids were prepared as reported earlier [4]. The concentration of metal ions was determined by EDTA titration. The pH values of the solutions were measured by a Beckman pH meter model ϕ71 (precision 0.001 pH unit). 2,2′-Bipyridyl and 1,10-phenanthroline (A.R.) were obtained from the Shanghai Chemical Reagent Factory.

Calorimetric measurement

A conduction automatic calorimeter, Model RD-1, was employed to make all the heat measurements. The heat of ionisation of water was determined from the neutralisation of nitric acid by sodium hydroxide with an ionic strength 0.1 mol kg^{-1} at 25 ± 0.2 °C, which provides a check on the conventional electrical calibration. The ΔH_N value so obtained was -13.29 ± 0.06 kcal mol^{-1}. When it was converted to that at $I = 0$ from the L value [5] a new value of $\Delta H_N^\circ = -13.24$ kcal mol^{-1} was obtained, which is in good agreement with the standard heat of ionisation of water which is -13.34 kcal mol^{-1} at 25 °C and $I = 0$ [6] under the same conditions. However the ΔH_N value obtained from neutralization of standard potassium hydroxide solution with standard nitric acid solution at $I = 0$ and 25 °C was -14.29 ± 0.023 kcal mol^{-1}.

Determination of the heat of protonation of the ligands m-*RPhIDA*

According to the method described previously [7], 2.00 cm^3 of nitric acid solution was put in the sample tube and 20.00 cm^3 of the *m*-RPhIDA solution was put in the reaction chamber (the two sets of experiments $L/H^+ = 1:1$ and $1:2$ molar ratio) with the former being placed in the latter and the whole set was put into the calorimeter vessel. The vessel was then inserted into the calorimeter for several hours to attain thermal equilibrium with the base line of the photo-pen recorder in its 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. To offset the influence of the heat other than reaction heat, blank tests were made under the same conditions.

*Determination of the heats of formation of copper(II)–*m-*RPhIDA binary complex compounds*

Two cubic centimeters of Cu(II) solution was mixed with 20.00 cm^3 of *m*-RPhIDA solution. The experimental procedures are the same as those described above. The results obtained are tabulated in Table 1.

TABLE 1

Heat of formation and apparent thermodynamic parameters of formation of complex compounds Cu(II)–*m*-RPhIDA

R	No. runs	$T_L(T_M)$ $\times 10^3$ (mol l^{-1})	pH_i	pH_f	Q (J)	K_M * $\times 10^{-5}$	ΔG_M * (kJ mol^{-1})	ΔH_M (kJ mol^{-1})	ΔS_M (J K^{-1} mol^{-1})
CH_3	5	9.782	8.681	6.674	3.56 ±0.01	23.44	−36.37	16.69 ±0.05	177.93 ±0.00
H	5	9.782	8.105	6.283	3.67 ±0.01	6.457	−33.17	17.29 ±0.04	169.22 ±0.13
CH_3O	5	9.782	8.681	6.700	3.72 ±0.01	4.266	−32.15	17.59 ±0.05	166.80 ±0.17
Cl	5	9.782	8.947	6.337	3.74 ±0.02	1.349	−29.29	17.93 ±0.05	158.35 ±0.00

25.0±0.2°C, $I = 0.1$ mol l^{-1} (KNO_3).

* Data taken from ref. 4.

Determination of the heats of formation of ternary complex compounds

A volume of 20.00 cm^3 of Cu(II)–bipy(phen) with molar ratio ($Cu^{2+}/L = 1:1$) was placed in the reaction chamber and 5.00 cm^3 of an *m*-RPhIDA

TABLE 2

Heat of formation and apparent thermodynamic parameters of formation of complex compounds M(II)–bipy–*m*-RPhIDA

M(II)	R	No. runs	$T_M(T_L)$ $\times 10^3$ (mol l^{-1})	pH_i		pH_f	K^{MA}_{MAL} $\times 10^{-4}$ *	Q (J)
				MA	L			
Zn(II)	CH	5	5.034	2.966	7.190	4.202	2.344	1.36±0.01
	H	6	5.034	2.966	6.864	4.385	1.023	1.53±0.01
	CH_3O	6	5.034	2.966	10.675	4.485	0.8511	0.86±0.01
	Cl	5	5.034	2.966	6.801	3.890	0.5888	1.53±0.01
Co(II)	CH	6	5.034	2.858	7.518	4.653	1.585	1.28±0.01
	H	6	6.034	2.880	7.190	4.902	0.6310	1.43±0.01
	CH_3O	5	5.034	2.880	6.620	4.355	0.6026	1.37±0.01
	Cl	5	5.034	2.880	7.270	4.655	0.3548	1.51±0.01
Ni(II)	CH	5	5.034	2.887	7.190	4.004	1.318	1.04±0.01
	H	5	5.034	2.887	6.864	4.154	0.5248	1.20±0.01
	CH_3O	6	5.034	2.887	10.305	4.356	0.3981	0.96±0.01
	Cl	5	5.034	2.887	6.801	4.253	0.2089	1.27±0.01
Cu(II)	CH	5	5.034	2.556	7.330	2.944	1738	0.81±0.01
	H	5	5.034	2.556	7.031	3.065	141.3	0.98±0.01
	CH_3O	5	5.034	2.556	7.382	2.979	933.3	1.10±0.01
	Cl	6	5.034	2.556	7.475	3.014	660.7	1.22±0.01

25.0±0.2°C, $I = 0.1$ mol l^{-1} (KNO_3).

* Data taken from ref. 4.

TABLE 3

Heat of formation and apparent thermodynamic parameters of formation of complex compounds M(II)–phen–*m*-RPhIDA

M(II)	R	No. runs	$T_M(T_L)$ $\times 10^3$ (mol l^{-1})	pH_i		pH_f	K^{MA}_{MAL} $\times 10^{-4}$ *	Q (J)
				MA	L			
Zn(II)	CH_3	5	5.034	2.584	7.330	3.506	5.248	1.32±0.01
	H	5	5.034	2.584	7.031	3.701	2.089	1.49±0.01
	CH_3O	5	5.034	2.584	7.382	3.545	1.778	1.44±0.01
	Cl	4	5.034	2.584	7.475	3.704	1.122	1.59±0.01
Co(II)	CH_3	5	5.034	2.573	7.330	3.690	2.818	1.20±0.01
	H	5	5.034	2.573	6.864	3.920	1.122	1.37±0.01
	CH_3O	5	5.034	2.573	7.382	3.839	0.8710	1.35±0.01
	Cl	3	5.034	2.573	7.475	4.070	0.5888	1.50±0.01
Ni(II)	CH_3	5	5.034	2.610	7.330	3.834	1.259	1.02±0.01
	H	5	5.034	2.610	7.031	3.870	0.6166	1.16±0.01
	CH_3O	5	5.034	2.610	7.382	3.941	0.5129	1.20±0.01
	Cl	5	5.034	2.610	7.475	3.928	0.3020	1.23±0.01
Cu(II)	CH_3	5	5.034	2.556	7.330	2.910	457.1	0.83±0.01
	H	5	5.034	2.556	7.031	3.015	72.44	1.06±0.01
	CH_3O	5	5.034	2.556	7.382	2.920	134.9	1.01±0.01
	Cl	6	5.034	2.556	7.475	2.947	74.13	1.12±0.01

25.0±0.2°C, $I = 0.1$ mol l^{-1} (KNO_3).

* Data taken from ref. 4.

solution was put in the sample tube. The experimental procedures were the same as those described above. The measurement of the heats of ternary complex compounds Zn(II). Co(II), and Ni(II) were determined in the same manner and the data obtained are summarized in Tables 2 and 3.

All calculations were programmed on a CASIO FX-702P calculator. The heats of protonation of *m*-RPhIDA and the heats of formation of these complex compounds were calculated by utilising the dissociation constants of *m*-RPhIDA (R = CH_3, CH_3O, H, Cl); the formation constants of complex compounds M(II)–*m*-RPhIDA and M(II)–bipy(phen)–*m*-RPhIDA are reported in a previous paper [1].

RESULTS AND DISCUSSION

The experimental data of heats of protonation of *m*-RPhIDA and their thermodynamic properties are summarised in Table 4. The experimental data of heats of formation of Cu(II)–*m*-RPhIDA and their thermodynamic properties are shown in Table 1. The experimental data of heats of forma-

TABLE 4

Heat of protonation of *m*-RPhIDA and thermodynamic parameters of protonation of *m*-RPhIDA

	R							
	CH_3		H		CH_3O		Cl	
	No. run							
	6	5	4	5	5	7	5	5
$T_L \times 10^3$ (mol l^{-1})	9.091	9.091	9.091	0.091	9.091	9.091	9.091	9.091
$T_M \times 10^3$ (mol l^{-1})	9.091	18.18	9.091	18.18	9.091	18.18	9.091	18.18
pH_i	9.543	9.543	9.141	9.141	7.951	7.951	7.766	7.766
pH_f	4.127	2.448	4.055	2.469	4.067	2.459	3.894	2.475
Q (J)	0.95	1.05	1.19	1.22	1.24	1.24	1.36	1.35
	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01
$K_1^a \times 10^3$	2.951		3.802		4.467		4.677	
$K_2^a \times 10^6$	4.677		7.762		8.913		13.18	
ΔG_{L1}^b (kJ mol^{-1})	−30.43		−29.18		−28.83		−27.86	
ΔG_{L2}^b (kJ mol^{-1})	−14.45		−13.82		−13.42		−13.30	
ΔH_{L1} (kJ mol^{-1})	5.32±0.05		6.60±0.05		6.88±0.05		7.55±0.05	
ΔH_{L2} (kJ mol^{-1})	0.38±0.01		−0.81±0.01		−1.49±0.02		−1.84±0.01	
ΔS_{L1} (J K^{-1} mol^{-1})	119.89±0.17		119.99±0.17		119.75±0.17		118.75±0.17	
ΔS_{L2} (J K^{-1} mol^{-1})	49.73±0.03		43.63±0.03		40.00±0.07		38.43±0.03	

25.0±0.2°C, $I = 0.1$ mol l^{-1} (KNO_3).

* a, b data taken from ref. 5. Note: pH_i: intial pH; pH_f: final pH.

TABLE 5

Apparent thermodynamic parameters of complex compounds M(II)–bipy(phen)–*m*-RPhIDA

R	M(II)	M(II)–bipy–*m*-RPhIDA			M(II)–phen–*m*-RPhIDA		
		ΔG_M (kJ mol^{-1})	ΔH_M (kJ mol^{-1})	ΔS_M (J mol^{-1} K^{-1})	ΔG_M (kJ mol^{-1})	ΔH_M (kJ mol^{-1})	ΔS_M (J mol^{-1} K^{-1})
CH_3	Zn(II)	−24.95	13.37 ±0.11	128.50 ±0.37	−26.95	14.18 ±0.14	137.93 ±0.47
	Co(II)	−23.98	12.00 ±0.10	12.066 ±0.34	−25.41	12.95 ±0.14	128.64 ±0.47
	Ni(II)	−23.52	10.88 ±0.14	115.36 ±0.47	−23.41	11.27 ±0.17	116.30 ±0.57
	Cu(II)	−41.34	6.56 ±0.09	160.63 ±0.30	−38.03	6.82 ±0.09	150.40 ±0.30
H	Zn(II)	−22.90	15.08 ±0.12	127.36 ±0.40	−24.67	15.64 ±0.13	135.18 ±0.44
	Co(II)	−21.70	13.85 ±0.11	119.22 ±0.37	−23.12	14.46 ±0.14	126.02 ±0.47
	Ni(II)	−21.24	12.78 ±0.15	114.08 ±0.50	−21.64	12.81 ±0.17	115.53 ±0.57
	Cu(II)	−35.11	8.08 ±0.09	144.84 ±0.30	−33.46	8.99 ±0.09	142.35 ±0.30
CH_3O	Zn(II)	−22.44	15.56 ±0.11	127.43 ±0.37	−24.27	15.78 ±0.1	134.31 ±0.47
	Co(II)	−21.58	14.03 ±0.12	119.42 ±0.40	−22.50	14.52 ±0.14	124.14 ±0.47
	Ni(II)	−20.55	13.27 ±0.14	113.41 ±0.47	−21.18	12.99 ±0.16	114.59 ±0.54
	Cu(II)	−39.80	8.90 ±0.09	163.31 ±0.30	−35.00	8.32 ±0.10	145.27 ±0.34
Cl	Zn(II)	−21.53	16.72 ±0.14	128.27 ±0.47	−23.12	16.65 ±0.14	133.37 ±0.47
	Co(II)	−20.27	15.46 ±0.12	119.82 ±0.40	−21.53	15.46 ±0.13	124.04 ±0.44
	Ni(II)	−18.96	14.27 ±0.15	111.44 ±0.54	−19.87	13.84 ±0.18	113.04 ±0.60
	Cu(II)	−38.94	9.85 ±0.09	163.62 ±0.30	−33.52	9.25 ±0.10	143.43 ±0.34

25.0±0.2°C, $I = 0.1$ mol l^{-1} (KNO_3).

tion of M(II)–bipy/phen–*m*-RPhIDA and their thermodynamic properties are presented in Tables 2, 3 and 5.

It is seen from Tables 1–5 that the effect of substituting groups on the heats of reaction was reflected principally by the amino nitrogen atom rather than on the carboxyl oxygen atom, in agreement with what was found in the linear free energy relationships [4]. The order of magnitude of electron

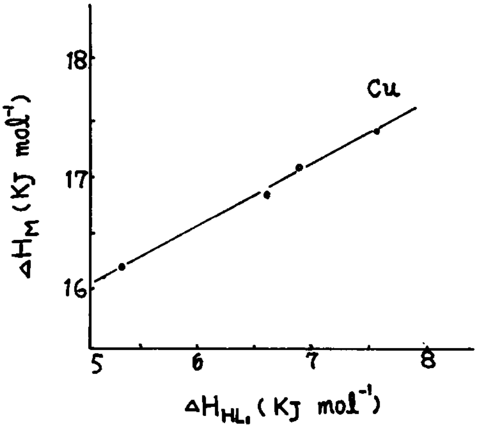

Fig. 1. Linear enthalpy relationship of the Cu(II)–*m*-RPhIDA binary system.

density on the nitrogen atom appears to be $CH_3 > H > CH_3O > Cl$. The greater the electron density, the greater the heat of ionisation. It is also noted in Table 4 that ΔH_{HL1} values are in the order $CH_3 > H > CH_3O > Cl$. When ΔH_M was plotted against ΔH_{HL1} a straight line was obtained (Fig. 1) with a correlation expression

$$\Delta H_M = 13.69 \pm 0.559\,\Delta H_{HL1} \qquad (\gamma = 0.993)$$

which is an indication of a linear enthalpy relationship.

From Tables 2 and 3 the plots of ΔH_M values against ΔH_{HL1} give positive slopes (Figs. 2 and 3). Their correlation equations are shown in Table 6. From Figs. 2 and 3 the magnitude of enthalpy values of these ternary systems are found to be in the order Zn(II), Co(II), Ni(II), Cu(II). These might be ascribed to the difference of crystal field stabilization energy (CFSE).

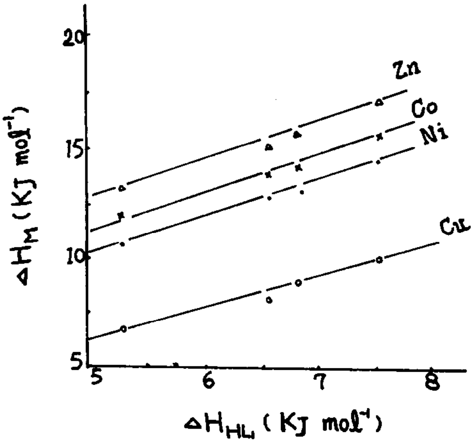

Fig. 2. Linear enthalpy relationships of the M(II)–bipy–*m*-RPhIDA ternary system.

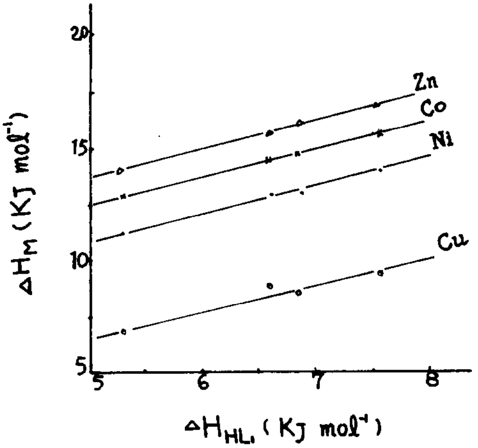

Fig. 3. Linear enthalpy relationships of the M(II)-phen-*m*-RPhIDA ternary system.

All these ΔH_M values of the above complex compounds are positive: this may be caused by solvation and rather loose bonding of M(II) to tertiary nitrogen atom. However the unfavourable factor of ΔH may partially offset the contribution of entropy effect. Furthermore, a rather poor linear entropy relationship was found to exist in these complex compounds. It would indicate that experimental errors due to ΔH and ΔG seemed to be responsible for the deviation from linearity.

From Tables 1 and 5, it is seen that large ΔS values of binary and ternary complexes may be explained in terms of greater chelation effect due to formation of two five-rings and one seven-ring in configuration. Moreover, the influence of substituent groups on entropy change are not important in the same complex (M(II)-bipy/phen) ion. This fact shows that the tridentate ligands *m*-RPhIDA have strong chelation tendency toward metal ions

TABLE 6

Correlation equations for the M(II)-bipy/phen-*m*-$RC_6H_4N(CH_2COOH)_2$ ternary systems

With bipy as the first ligand		
Zn(II)	$\Delta H_M = 5.406 + 1.484\,\Delta H_{HL1}$	$(\gamma = 0.997)$
Co(II)	$\Delta H_M = 3.906 + 1.507\,\Delta H_{HL1}$	$(\gamma = 0.992)$
Ni(II)	$\Delta H_M = 2.774 + 1.552\,\Delta H_{HL1}$	$(\gamma = 0.999)$
Cu(II)	$\Delta H_M = -1.305 + 1.480\,\Delta H_{HL1}$	$(\gamma = 0.999)$
With phen as the first ligand		
Zn(II)	$\Delta H_M = 8.359 + 1.094\,\Delta H_{HL1}$	$(\gamma = 0.997)$
Co(II)	$\Delta H_M = 7.067 + 1.105\,\Delta H_{HL1}$	$(\gamma = 0.995)$
Ni(II)	$\Delta H_M = 5.191 + 1.144\,\Delta H_{HL1}$	$(\gamma = 0.999)$
Cu(II)	$\Delta H_M = 1.105 + 1.067\,\Delta H_{HL1}$	$(\gamma = 0.999^*)$

* Omitting R = H.

and the electronic effect of substituting groups on the benzene ring is not significant with respect to this effect.

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