

## Thermodynamics of Complex Formation: Part I—Complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) & Cd(II) with N-2'-Diphenylacetohydroxamic Acid

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Received 19 October 1983; revised and accepted 12 November 1984

Thermodynamic functions for the formation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with N-2'-diphenylacetohydroxamic acid (N-2'-DPAHA) in solution have been analysed in terms of electrostatic ( $\Delta G_e$ ,  $\Delta H_e$ ) and non-electrostatic or cratic ( $\Delta G_c$ ,  $\Delta H_c$ ) components. The non-electrostatic forces are stronger than the electrostatic forces in the mono-complexes. Electrovalent nature of metal-ligand bond significantly decreases when the second molecule of N-2'-DPAHA coordinates to metal ion. The proton-ligand and metal-ligand stability constants have also been calculated in solvent media of different dielectric constants. The ion-solvent interactions play more important role than that done by the dielectric constant of the medium.

In continuation of our earlier work on hydroxamic acids<sup>1-4</sup>, we report here the determination of stability constants and thermodynamic parameters of the complex formation reactions of N-2'-diphenylacetohydroxamic acid (N-2'-DPAHA) with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II). The electrostatic and cratic components of  $\Delta G$  and  $\Delta H$  values have been evaluated to study the nature of metal-ligand bond. Solvent effects on the ionization of ligand and complex stability have also been studied and discussed.

### Materials and Methods

N-2'-Diphenylacetohydroxamic acid was prepared by a known method<sup>5</sup>. The instrument used, the experimental procedures employed, and the method of calculating stability constants and thermodynamic parameters were the same as described earlier<sup>2</sup>. The pH correction for aquo-organic solvent was carried out by the method of Van Uitert and Haas<sup>6</sup>. All calculations were computed on a TDC-12 computer.

### Results and Discussion

The stepwise stability constants are given in Table 1. Positive  $\Delta S$  and negative  $\Delta H$  values (Table 2) for the formation of mono- and bis-complexes of N-2'-DPAHA with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) indicate that both the enthalpy and entropy factors favour complex formation. Most of the negative  $\Delta H$  values may be due to the covalent interaction of metal ion with oxygen atom of carbonyl group of N-2'-DPAHA. The positive entropy change probably arises from the displacement of water dipoles from the hydration shells of the interacting ions.

Comparison of the electrostatic and cratic parts of thermodynamic parameters (Table 3) for the

equilibrium-1 representing formation of 1:1 complex indicates that  $\Delta G_c$  values are significantly more



negative than  $\Delta G_e$  values suggesting that non-electrostatic forces are stronger than the electrostatic forces in 1:1 complexes. The difference in the electrostatic and cratic components decrease in the order Cu(II) > Ni(II) > Co(II) > Mn(II), indicating that the order in the ionic character of the complexes increases in the order: Cu(II) < Ni(II) < Co(II) < Mn(II). Since the number of unpaired electrons also increases in the same order, it may be concluded that the ionic character of the complexes increases with the increase in the number of unpaired electrons. The enthalpy data also support the above contention.

Table 1—Stepwise Stability Constants of Metal Chelates of N-2'-DPAHA at Different Temperatures

[ $\mu = 0.1 M$ ; 50% (v/v) Water-Ethanol Mixtures]

Metal ion	Stability constant	Temperature			
		293 K	303 K	313 K	323 K
H	$H_{\beta_1}$	10.2	9.98	9.80	9.63
Mn(II)	$\log K_1$	4.60	4.46	4.31	4.20
	$\log K_2$	3.76	3.63	3.50	3.40
Co(II)	$\log K_1$	5.39	5.24	5.10	4.96
	$\log K_2$	3.96	3.82	3.69	3.52
Ni(II)	$\log K_1$	6.44	6.30	6.17	6.01
	$\log K_2$	4.45	4.30	4.16	4.02
Cu(II)	$\log K_1$	9.35	9.20	9.05	8.85
	$\log K_2$	6.85	6.70	6.55	6.43
Zn(II)	$\log K_1$	6.68	6.55	6.43	6.30
	$\log K_2$	4.65	4.50	4.37	4.23
Cd(II)	$\log K_1$	4.64	4.50	4.35	4.20
	$\log K_2$	3.50	3.34	3.20	3.10

Table 2—Thermodynamic Parameters for Formation of Mono- and Bis-metal Chelates of N-2'-DPAHA

[Temp. = 30° ± 0.1°C; μ = 0.1 M]

Central ion	ΔG <sub>1</sub> (kcal mol <sup>-1</sup> )	ΔH <sub>1</sub> (kcal mol <sup>-1</sup> )	ΔS <sub>1</sub> (e.u.)	ΔG <sub>2</sub> (kcal mol <sup>-1</sup> )	ΔH <sub>2</sub> (kcal mol <sup>-1</sup> )	ΔS <sub>2</sub> (e.u.)
Mn(II)	-6.18 ± 0.11	-5.22 ± 0.19	2.35 ± 0.04	-5.50 ± 0.12	-5.36 ± 0.21	0.578 ± 0.003
Co(II)	-7.26 ± 0.13	-5.56 ± 0.20	3.62 ± 0.09	-5.57 ± 0.13	-5.70 ± 0.22	0.771 ± 0.005
Ni(II)	-8.72 ± 0.16	-6.44 ± 0.22	7.20 ± 0.15	-6.03 ± 0.14	-6.58 ± 0.24	1.15 ± 0.012
Cu(II)	-12.72 ± 0.18	-7.81 ± 0.24	18.3 ± 0.34	9.28 ± 0.18	-7.47 ± 0.26	8.60 ± 0.109
Zn(II)	-9.07 ± 0.14	-6.59 ± 0.23	8.20 ± 0.22	6.49 ± 0.16	-6.79 ± 0.25	1.35 ± 0.028
Cd(II)	-6.23 ± 0.12	-5.74 ± 0.21	1.63 ± 0.02	-5.58 ± 0.13	-5.99 ± 0.23	0.623 ± 0.004

Table 3—Electrostatic and Cratic Components of Thermodynamic Parameters

(Values in kcal mol<sup>-1</sup>)

Metal ion	ΔG <sub>e</sub>	ΔG <sub>c</sub>	ΔH <sub>c</sub>	ΔE <sub>c</sub>
1:1 Complexes (Eqb-1)				
Mn(II)	-2.26 ± 0.06	-6.35 ± 0.15	0.867 ± 0.12	-6.08 ± 0.12
Co(II)	-2.54 ± 0.08	-7.16 ± 0.17	0.974 ± 0.15	-6.53 ± 0.14
Ni(II)	-3.32 ± 0.11	-7.83 ± 0.19	1.27 ± 0.17	-7.71 ± 0.17
Cu(II)	-5.77 ± 0.15	-9.42 ± 0.21	2.21 ± 0.19	-9.39 ± 0.21
Zn(II)	-3.54 ± 0.12	-7.96 ± 0.20	1.36 ± 0.18	-7.94 ± 0.19
Cd(II)	-2.10 ± 0.04	-6.56 ± 0.16	0.807 ± 0.11	-6.54 ± 0.15
1:2 Complexes (Eqb-2)				
Mn(II)	-1.87 ± 0.04	-6.06 ± 0.14	+0.719 ± 0.003	-6.07 ± 0.21
Co(II)	-1.89 ± 0.05	-6.31 ± 0.15	+0.726 ± 0.005	-6.42 ± 0.23
Ni(II)	-1.99 ± 0.07	-6.48 ± 0.16	+0.767 ± 0.009	-7.34 ± 0.26
Cu(II)	-3.63 ± 0.12	-8.08 ± 0.22	+1.39 ± 0.12	-8.86 ± 0.31
Zn(II)	-2.04 ± 0.09	-6.88 ± 0.19	+0.783 ± 0.008	-7.57 ± 0.25
Cd(II)	-1.88 ± 0.05	-6.13 ± 0.12	+0.722 ± 0.006	-6.71 ± 0.22

Thermodynamic data (Table 3) computed for the equilibrium-2 representing formation of 1:2 complexes show a marked decrease in the ionic character of the complexes and indicate that the metal-ligand bonds in bis-complexes are more covalent than those in the

$$M(II)-(N-2'-DPAHA) + N-2'-DPAHA \rightleftharpoons M(II)-(N-2'-DPAHA)_2 \quad \dots(2)$$

corresponding mono-complexes. For all the metal chelates, ΔG<sub>1</sub> was found to be more negative than ΔG<sub>2</sub> (Table 2) indicating that the mono-complexes are energetically favoured over the bis-complexes.

Thermodynamic parameters<sup>7</sup> (Table 4), ΔG<sub>r</sub>, ΔH<sub>r</sub>, ΔS<sub>r</sub> for the formation of 1:1 complexes by the interaction of free metal ion and 1:2 complexes (equilibrium-3) show that the formation of 1:1 complex is highly favoured over that of 1:2 complex. For Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) the electrostatic forces involved in two mono-complexes are stronger than those in one bis-complex. In the case of Cd(II)



complex, the destabilization induced by electrostatic repulsions between two ligands is unimportant in the

Table 4—Thermodynamic Parameters of Equilibrium-3

Metal ion	ΔG <sub>r</sub> (kcal mol <sup>-1</sup> )	ΔH <sub>r</sub> (kcal mol <sup>-1</sup> )	ΔS <sub>r</sub> (e.u.)
Mn(II)	0.673 ± 0.004	0.317 ± 0.015	0.778 ± 0.009
Co(II)	1.49 ± 0.015	0.387 ± 0.023	2.84 ± 0.042
Ni(II)	2.29 ± 0.021	0.458 ± 0.031	6.04 ± 0.081
Cu(II)	3.46 ± 0.032	0.506 ± 0.042	9.74 ± 0.099
Zn(II)	2.58 ± 0.028	0.482 ± 0.036	6.83 ± 0.094
Cd(II)	0.652 ± 0.002	0.346 ± 0.019	1.08 ± 0.039

bis-complex, probably because of the large size of Cd(II). In the case of Co(II), Mn(II), Zn(II) and Cd(II) the non-electrostatic forces in one bis-complex are stronger than those in the corresponding two mono-complexes. The converse was found to be true in Cu(II) and Ni(II) complexes. ΔH<sub>2</sub> is more negative than ΔH<sub>1</sub>, indicating that covalent forces favour bis-complex formation even in the case of Cu(II) and Ni(II) complexes.

#### Effect of Dielectric Constant

The pK<sub>a</sub> values of N-2'-DPAHA and log K values (Table 5) of Ni(II)-N-2'-DPAHA and Co(II)-N-2'-DPAHA complexes were determined at 25, 35, 50, 65 and 75% of ethanol-water medium at 0.1 M ionic

Table 5— $pK_a$  Values of N-2'-DPAHA and Stability Constants of Ni(II), Co(II) Chelates in Different Percentages of Water-Ethanol Mixture

[Temp. = 303 K;  $\mu = 0.1 M$ ]

Organic solvent (% v/v)	Correction factor	$N_2$	$pK_a$	Ni(II)-(N-2'-DPAHA)	
				log $K_1$	log $K_2$
25.0	0.070	0.096	9.27	6.01 (4.98)	4.04 (3.68)*
35.0	0.170	0.147	9.50	6.12 (5.08)	4.14 (3.77)
50.0	0.235	0.242	9.80	6.30 (5.25)	4.30 (3.92)
65.0	0.305	0.373	10.2	6.55 (5.45)	4.53 (4.12)
75.0	0.370	0.490	10.6	6.78 (5.65)	4.71 (4.27)

\*Values in parentheses are for Co(II)-(N-2'-DPAHA)

strength and 303K. It is clear from Table 5 that the important factor that governs the extent of dissociation of acid is the ion-solvent interactions and not the dielectric constant of the medium. Since ethanol is more basic than water the  $pK_a$  value increases with the increase in mol fraction of ethanol. The stability constants of metal chelates were also found to be linearly dependent on the mol fraction of ethanol and not on the dielectric constant of the

medium suggesting that the predominant factor governing the dissociation equilibrium is again the solvating nature of the solvent.

The data from the Table 5 indicate that the difference between log  $K_1$  and log  $K_2$  continuously increases with the increase in percentage of ethanol. This shows that log  $K_2$  value relatively decreases as the dielectric constant is decreased. The lowering of dielectric constant would increase the electrostatic forces of attraction between the dipositive metal ion and the negatively charged or neutral ligand leading to formation of a more stable 1:1 complex. The formation of 1:2 complex on the other hand is not affected to a similar extent as it is formed by interaction of a monopositive 1:1 chelate with a negatively charged ion.

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