Formation Constants of Complexes of Manganese(II), Cobalt(II), Nickel(II), Copper(II) & Zinc(II) with 2-(Phenyl-hydrazino)-, 2-(p-Tolylhydrazino)- & 2-(p-Nitrophenylhydrazino)-propionic Acids

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The formation constants of complexes of 2-(phenylhydrazino) propionic acid, 2-(p-tolylhydrazino)propionic acid and 2-(p-nitrophenylhydrazino)propionic acid with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been studied at various ionic strengths, temperatures and in different ethanol-water mixtures (v/v) using the potentiometric technique. Thermodynamic parameters have been evaluated and discussed.

Phenylhydrazones of pyruvic acid are of immense use because of their antituberculosis activity[1], and the *p*-nitro derivative is used as an acid-base indicator[2]. With a view to understanding the nature of metal-ligand interactions and bonding in this type of complexes, formation constants of complexes of 2-(p-tolylhydrazino)propionic acid, 2-(p-nitrophenylhydrazino) propionic acid and 2-(phenylhydrazino)propionic acid with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been determined in ethanol-water medium (40%, v/v) at different temperatures and ionic strengths, employing Calvin-Bjerrum[3,4] *p*H titration technique as modified by Irving and Rossotti[5]. From the formation constants obtained at various temperatures, the values of the thermodynamic parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$, and $\Delta S^{\neq}$ have been evaluated. $\Delta G^{\neq}$ and $\Delta H^{\neq}$ have been separated into the corresponding electrostatic $\left(\Delta G_{e}^{\neq} \text{ and } \Delta H_{e}^{\neq} \right)$ and non-electrostatic or cratic $\left(\Delta G_{c}^{\neq} \text{ and } \Delta H_{c}^{\neq} \right)$ components with a view to understanding the extent of ionic and covalent nature of the complexes. An attempt has been made to determine the thermodynamic ligand field stabilization energy δH and the transition series contraction energy E_r (Mn-Zn) of divalent metal complexes.

All the reagents and chemicals used and the method employed to determine the formation constants in the present work were similar to those reported in an earlier paper[6]. 2-(Phenylhydrazino)propionic acid and its *p*-methyl and *p*-nitro derivatives were synthesized in our laboratory by known methods[7-9]. As these ligands had low solubilities in water, the solutions of the ligands were prepared in ethanol.

Since *p*H titrations were carried out in 40% (v/v) ethanol-water medium, appropriate corrections in all *p*H meter readings were made as suggested by Van Uitert and Haas[10,11].

The stability constants of metal complexes calculated by Irving and Rossotti expressions are presented in Table 1; these follow the order: Mn(II) < Co(II) < Ni (II) < Cu(II) > Zn(II), which is in accordance with the Irving and Williams series[12]. A study of the dependence of stability constants on ionic strengths at constant temperature shows that there is a regular and slow decrease in the values with increase in ionic strength. The values of $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ have been calculated using Gibbs-Helmholtz equation from the stability constants obtained at various temperatures at constant ionic strength (0.1 *M*) and the values are given in Table 2. These reactions are exothermic and spontaneous as supported by the negative values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ respectively. $\Delta S^{\neq}$ values are positive for all the chelates indicating that entropy change is favourable for complex formation. To know the extent of ionic and covalent nature of bonding in these complexes, the $\Delta H^{\neq}$ and $\Delta G^{\neq}$ were separated into their electrostatic $\left(\Delta G_{e}^{\neq} \text{ and } \Delta H_{e}^{\neq} \right)$ and cratic $\left(\Delta G_{c}^{\neq} \text{ and } \Delta H_{c}^{\neq} \right)$ components as suggested by Digischer and Nancollas[13]. Comparison of the electrostatic and cratic components for the equilibrium(1),

$$M^{2+}(aquo) + L^{-} \rightleftharpoons ML^{+} \qquad \ldots(1)$$

indicates that $\Delta G_{c}^{\neq}$ values are significantly more negative than $\Delta G_{e}^{\neq}$ values (Table 3). This trend suggests that the non-electrostatic forces are stronger than the electrostatic forces in 1:1 chelates. The difference in the electrostatic and cratic components

Table 1—Stability Constants of Metal Chelates in 40% Ethanol-Water Medium at 0.1 *M* Ionic Strength at 30°C

Metal ion	2-(Phenyl-hydrazino)-propionic acid	2-(p-Tolyl-hydrazino propionic acid	2-(p-Nitrophenyl-hydrazino)-propionic acid
H+	5.15	5.42	4.53
Mn(II)	2.92	3.03	2.63
	(2.54)	(2.66)	
Co(II)	3.13	3.44	2.82
	(2.59)	(2.67)	
Ni(II)	3.42	3.72	3·06
	(2.68)	(2.98)	
Cu(II)	4.68	5.04	3.61
	(4.02)	(4.32)	(3.02)
Zn(II)	2.98	3.17	2.71
	(2.50)	(2.76)	

The figures in the parentheses indicate the values of $\log K_2$; the standard deviation of stability constants is ± 0.06; the limit of error for log K values is found to be ± 0.05.

Table 2—Thermodynamic Parameters for the Formation of 1:1 and 1:2 Metal Chelates at 30°C and 0.1 M Ionic Strength

Metal ion	$-\Delta G^{\neq}$ (k cal mol^{-1})	$-\Delta H^{\neq}$ (k cal mol^{-1})	$\Delta S^{\neq}$ (e.u.)
	2-(phenylhydrazino)propionic acid		
Mn(II)	4.05	3.27	3.05
	(3.52)	(3.16)	(1.19)
Co(II)	4.34	3.64	2.31
	(3.59)	(3.14)	(1.49)
Ni(II)	4.74	3.90	2.77
	(3.71)	(3.19)	(1.72)
Cu(II)	6.49	5.57	3.04
	(5.57)	(5.03)	(1.79)
Zn(II)	4.13	3.42	2.34
	(3.47)	(2.98)	(1.62)
	2-(p-Tolylhydrazino)propionic acid		
Mn(II)	4.22	3.71	1.69
	(3.69)	(3.22)	(1.55)
Co(II)	4.77	4.02	2.48
	(3.82)	(3.30)	(1.75)
Ni(II)	5.16	4.25	3.01
	(4.13)	(3.58)	(1.82)
Cu(II)	6.99	6.02	3.20
	(5.85)	(5.21)	(2.11)
Zn(II)	4.40	3.87	1.69
	(3.82)	(3.34)	(1.58)
	2-(p-Nitrophenylhydrazino)propionic acid		
Mn(II)	3.65	3.17	1.54
Co(II)	3.91	3.35	1.84
Ni(II)	4.24	3.68	1.87
Cu(II)	5.01	4.43	1.92
Zn(II)	3.76	3.29	1.61

The figures in the parentheses indicate the thermodynamic parameters for 1:2 complexes.

decreases in the order : Cu(II) > Ni(II) > Co(II) > Mn(II). This order indicates that the ionic character of the complexes is 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 data from Table 3 for the equilibrium(2),

$$ML^+ + L^- \rightleftharpoons ML_2 \qquad \ldots(2)$$

show a marked decease in the ionic character of the complexes and indicate that the metal-ligand bonds in bis complexes are more covalent than those in the corresponding mono complexes.

Ligand field stabilization energies (δH) of the complexes Co(II), Ni(II) and Cu(II) have been evaluated by using the expressions of George and McClure[14] (Table 4). The values of δH of the bivalent metal ions follow the order : Ni(II) > Cu(II) > Co(II). The low δH value of Cu(II) is ascribed to the steric hindrance preventing the formation of four coordinated structure. The stability constants of metal chelates are strongly affected by the dielectric constant of the medium and solvating property of the solvent[15,16]. An attempt has been made to investigate the effect of variation in dielectric constant on the stabilities of complexes in various ethanol-water

Table 3—Electrostatic and Cratic Components of Thermodynamic Parameters for the Formation of 1:1 and 1:2 Metal Chelates at 0.1 M Ionic Strength (Values in k cal mol^{-1})

Metal ion	Electrostatic components		Cratic components	
	$-\Delta G_e^{\neq}$	$\Delta H_e^{\neq}$	$-\Delta G_c^{\neq}$	$-\Delta H_c^{\neq}$
	2-(Phenylhydrazino)propionic acid			
Mn(II)	2.19	0.84	4.28	4.11
	(2.01)	(0.78)	(3.93)	(3.87)
Co(II)	2.25	0.87	4.51	4.47
	(2.07)	(0.81)	(3.95)	(3.88)
Ni(II)	2.34	0.91	4.82	4.78
	(2.12)	(0.83)	(4.01)	(3.96)
Cu(II)	2.41	0.94	9.57	9.53
	(2.14)	(0.84)	(5.85)	(5.83)
Zn(II)	2.25	0.87	4.30	4.27
	(2.09)	(0.81)	(3.80)	(3.79)
	2-(p-Tolylhydrazino)propionic acid			
Mn(II)	2.11	0.82	4.53	4.51
	(2.08)	(0.81)	(4.03)	(4.02)
Co(II)	2.28	0.89	4.91	4.87
	(2.12)	(0.83)	(4.13)	(4.10)
Ni(II)	2.40	0.93	5.18	5.13
	(2.14)	(0.84)	(4.41)	(4.37)
Cu(II)	2.44	0.95	6.97	6.96
	(2.20)	(0.86)	(6.07)	(6.04)
Zn(II)	2.12	0.83	4.70	4.65
	(2.08)	(0.82)	(4.16)	(4.13)
	2-(p-Nitrophenylhydrazino)propionic acid			
Mn(II)	2.08	0.82	3.99	3.97
Co(II)	2.12	0.82	4.18	4.15
Ni(II)	2.15	0.83	4.51	4.46
Cu(II)	2.17	0.85	5.27	5.02
Zn(II)	2.09	0.81	4.09	4.11

The figures in the parentheses indicate the values of electrostatic and cratic components for 1:2 complexes.

Table 4—Thermodynamic LFSE and Contraction Energy for $3d^n$ Divalent Metal Complexes

Metal ion	ΔG_r (k cal mol^{-1})	ΔH_L (k cal mol^{-1})	λE_r	δH (k cal mol^{-1})
	2-(Phenylhydrazino)propionic acid			
Mn(II)	—	—	—	—
Co(II)	0.40	43.40	18.82	24.58
Ni(II)	0.93	62.93	28.22	34.71
Cu(II)	4.56	67.56	37.63	29.93
Zn(II)	0.04	47.04	—	—
	2-(p-Tolylhydrazino)propionic acid			
Mn(II)	—	—	—	—
Co(II)	0.73	43.73	18.94	24.79
Ni(II)	0.75	62.75	28.41	34.34
Cu(II)	5.17	68.17	37.88	30.29
Zn(II)	0.35	47.35	—	—
	2-(p-Nitrophenylhydrazino)propionic acid			
Mn(II)	—	—	—	—
Co(II)	0.28	43.28	18.86	24.42
Ni(II)	0.64	62.64	28.28	34.36
Cu(II)	1.40	64.40	37.71	26.69
Zn(II)	0.41	47.14	—	—

mixtures. It is seen that with increase in the organic content of the solvent the stability constants are increased. Basolo et al.[17], reported the effect of solvent on complexes containing N-metal links and concluded that the organic content of the solvent had little influence on the stabilities of complexes. Van Uitert et al.[18], observed that the stabilities of complexes, which contained O-metal links, increased by an increase in the organic content of the solvent. The present complexes contain both O-metal and N-metal links; the observed increase in the stabilities may be due to the O-metal link which is strongly affected[19].

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