Thermodynamic Parameters for the Interaction of Metal - Thiamineorthophosphate with a Series of Secondary Ligands

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Interaction of Cu(II), Ni(II), Zn(II) and Co(II) with thiamineorthophosphate (TOP) and a series of N donating, O-O donating and N-O donating secondary ligands have been studied by potentiometry. The enthalpy and entropy changes for the formation of 1:1:1 ternary complexes are reported. The overall negative contribution to the enthalpy can be attributed to the formation of M-N bonds, while the positive entropy to the charge neutralisation in the secondary ligands. The enhanced stabilities of the ternary system have been explained in terms of their $\Delta\Delta H$ and $\Delta\Delta S$. ^{13}CNMR spectra was recorded in D_2O for free TOP and Zn(II)-TOP in D_2O solution to understand the binding site.

The study of ternary metal ion complexes simulating ternary enzyme substrate-metal complexes [1] has received considerable attention [2] in recent years. In our earlier papers [3], we have reported the stability constants of ternary 1:1:1 metal - TOP. In the present paper, thermodynamic parameters have been evaluated for the interaction of Cu(II), Ni(II), Zn(II) and Co(II) with Thiamineorthophosphate (TOP) and a series of N donating (imidazole, benzimidazole, 5,6-dimethyl benzimidazole), O-O donating (oxalic acid, malonic acid and pyrocatechol) and N-O donating (glycine, alanine, phenylalanine, tryptophan and tyrosine) secondary ligands by evaluating stability constant of 1:1:1 complexes at different temperatures.

EXPERIMENTAL

Experimental method, conditions and procedure for evaluating stability constants are similar to those employed in our earlier paper [3].

Preparation of Samples for NMR

A solution of about 0.15 M thiamine-orthophosphate was prepared in D_2O for each run. A 0.15 M analytical grade $ZnCl_2$ was added to this solution by weighing out appropriate quantities of anhydrous $ZnCl_2$. The pH was adjusted to 7.0 by adding NaOD. The ^{13}CNMR spectra of the complex was recorded on Varian Gemini 200 MHz NMR. Spectra were recorded with reference to TPS locking the D_2O signal.

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RESULTS AND DISCUSSION

Stability constants of different complex species are calculated & presented in Table 1.

The Δ log K values are given in Table 2.

Table 1

Stability constants (log K) of 1:1:1 Ternary Complexes
μ = 0.1 M KNO_3

Complex	Co(II)			Ni(II)			Cu(II)			Zn(II)		
At Temp °C	25	35	45	25	35	45	25	35	45	25	35	45
M:TOP:Gly	4.33	4.2	4.08	5.11	4.95	4.80	6.14	5.95	5.77	5.01	4.86	4.71
M:TOP:Ala	4.14	4.01	3.89	4.91	4.76	4.62	6.27	6.07	5.88	5.20	5.04	4.89
M:TOP:Ph Ala	4.03	3.90	3.78	4.93	4.78	4.64	7.07	6.85	6.64	4.34	4.20	4.07
M:TOP:Tryp	4.44	4.31	4.18	5.38	5.21	5.05	7.90	7.65	7.42	4.99	4.83	4.68
M:TOP:Tyro	3.90	3.78	3.67	4.24	4.11	3.98	7.25	7.02	6.80	4.44	4.30	4.17
M:TOP:Pyrocat	4.43	4.29	4.16	4.67	4.52	4.38	6.63	6.42	6.22	4.95	4.79	4.64
M:TOP:Imd	5.78	5.62	5.48	6.90	6.72	6.55	9,10	8.88	8.65	7.05	6.86	6.68
M:TOP:Bimd	5.61	5.46	5.32	6.38	6.20	6.04	8.20	7.98	7.77	7.39	7.18	6.98
M:TOP:DmBimd	6.50	6.33	6.17	6.96	6.76	6.58	8.55	8.32	8.10	7.91	7.69	7.49
M:TOP:Oxa	6.27	6.07	5.88	6.11	5.92	5.74	6.44	6.24	6.05	6.30	6.10	5.91
M:TOP:Maa	5.64	5.46	5.29	5.52	5.35	5.19	6.21	6.01	5.83	4.78	4.63	4.49

Table 2

Δ log K Value of 1:1:1 Ternary Complexes
μ = 0.1 M KNO_3

Complex	Co(II)			Ni(II)			Cu(II)			Zn(II)		
At Temp °C	25	35	45	25	35	45	25	35	45	25	35	45
M:TOP:Gly	-1.02	-1.01	-0.97	-0.96	-0.95	-0.93	-2.58	-2.56	-2.53	-0.64	-0.64	-0.64
M:TOP:Ala	-0.51	-0.50	-0.49	-0.52	-0.50	-0.48	-1.99	-1.94	-1.89	-0.45	-0.45	-0.44
M:TOP:Ph Ala	-0.31	-0.30	-0.30	-0.43	-0.42	-0.42	-0.94	-0.93	-0.91	-0.45	-0.44	-0.43
M:TOP:Tryp	-0.05	-0.04	-0.04	-0.30	-0.29	-0.28	-0.35	-0.36	-0.36	-0.06	-0.07	-0.07
M:TOP:Tyro	-0.28	-0.27	-0.26	-1.14	-1.10	-1.07	-0.60	-0.58	-0.58	-0.31	-0.30	-0.29
M:TOP:Pyrocat	-0.17	-0.17	-0.17	-0.02	-0.02	-0.02	-0.07	-0.07	-0.08	-0.25	-0.26	-0.26
M:TOP:Imd	+0.03	+0.02	+0.01	+0.32	+0.27	+0.25	+0.76	+0.73	+0.73	+0.63	+0.58	+0.52
M:TOP:Bimd	+0.37	+0.35	+0.33	+0.26	+0.21	+0.18	+0.85	+0.83	+0.82	+1.68	+1.24	+1.17
M:TOP:DmBimd	+0.95	+0.92	+0.90	+0.61	+0.56	+0.52	+0.98	+0.97	+0.94	+1.63	+1.55	+1.48
M:TOP:Oxa	-1.35	-1.34	-1.33	-2.17	-2.15	-2.14	-2.82	-2.75	-2.69	-1.79	-1.79	-1.80
M:TOP:Maa	-1.60	-1.68	-1.69	-1.30	-1.31	-1.31	-3.01	-2.94	-2.87	-1.72	-1.73	-1.75

Thermodynamic Constants

The values of the enthalpy of complex formation ΔH^{o}_{f} were obtained at each temperature interval using the relationship [6]:

$$\Delta H^{o}_{f} = \frac{2.303\ RT_1T_2\ \log\ (K_2/K_1)}{T_2 - T_1}$$

The values of ΔG^{o}_{f} and ΔS^{o}_{f} for various reactions involved were calculated using:

$$\Delta G^{o}_{f} = -RT\ \ln K \quad \text{and}$$

$$\Delta S^{o}_{f} = \frac{\Delta H^{o}_{f} - \Delta G^{o}_{f}}{T}$$

where ΔH^{o}_{f} = standard enthalpy change, R = gas constant, T = absolute temperature and K = equilibrium constant, ΔG^{o}_{f} = standard free energy change, ΔS^{o}_{f} = standard entropy change. Enthalpy changes are affected by the medium; its effect is minimised by extrapolating a set of values to infinitely dilute solutions. On this basis, all constants reported here are close to thermodynamic constants.

The thermodynamic quantities associated with the formation constants are presented in Table 3. The negative contributions to the enthalpy can be ascribed to the formation of M-N bonds while the positive entropy to the charge neutralization during bonding with secondary ligand [7].

Table 3

Thermodynamic Parameters Associated with Formation of 1:1:1 Ternary Complexes

μ = 0.1 M KNO_3; Temp 35°

Complex	Co(II)			Ni(II)			Cu(II)			Zn(II)		
Therm.Parameter	ΔG^{o}_{f}	ΔH^{o}_{f}	ΔS^{o}_{f}	ΔG^{o}_{f}	ΔH^{o}_{f}	ΔS^{o}_{f}	ΔG^{o}_{f}	ΔH^{o}_{f}	ΔS^{o}_{f}	ΔG^{o}_{f}	ΔH^{o}_{f}	ΔS^{o}_{f}
M:TOP:Gly	-6.09	-5.41	+2.20	-6.97	-6.72	+0.81	-8.38	-8.02	+1.16	-6.84	-6.50	+1.10
M:TOP:Ala	-5.65	-5.42	+0.75	-6.70	-6.28	+1.36	-8.55	-8.45	+0.32	-7.10	-6.72	+1.23
M:TOP:Ph Ala	-5.49	-5.42	+0.22	-6.73	-6.28	+1.46	-9.65	-9.32	+1.07	-5.92	-5.85	+0.22
M:TOP:Tryp	-6.07	-5.63	+1.42	-7.34	-7.15	+0.64	-10.8	-10.4	+1.23	-6.80	-6.72	+0.25
M:TOP:Tyro	-5.32	-4.98	+1.10	-5.79	-5.59	+0.64	-9.89	-9.75	+0.45	-6.06	-5.85	+0.68
M:TOP:Pyrocat	-6.04	-5.85	+0.61	-6.37	-6.28	+0.29	-9.04	-8.88	+0.51	-6.75	-6.72	+0.10
M:TOP:Imd	-7.92	-6.50	+4.15	-9.47	-7.58	+6.13	-12.5	-9.66	+9.25	-9.66	-8.02	+5.32
M:TOP:Bimd	-7.69	-6.28	+4.57	-8.73	-7.51	+3.96	-11.2	-9.32	+6.23	-10.1	-8.88	+3.99
M:TOP:DmBimd	-8.92	-7.15	+5.74	-9.52	-8.23	+4.18	-11.7	-9.75	+6.39	-10.8	-9.10	+5.61
M:TOP:Oxa	-8.55	-8.45	+0.32	-8.34	-8.02	+1.03	-8.79	-8.45	+1.10	-8.59	-8.45	+0.45
M:TOP:Maa	-7.69	-7.58	+0.35	-7.54	-7.15	+1.26	-8.47	-8.23	+0.77	-6.52	-6.28	+0.77

^{13}C NMR Chemical Shifts

^{13}C NMR Chemical shifts are listed in Table 4. The ^{13}C signals for thiamine-orthophosphate (TOP) have been assigned from the earlier work [8,9]. The spectra of free thiamineorthophosphate (TOP) and Zn(II)-TOP complexes were recorded in D_2O The downfield shift of C_2^1-CH_3, C_2^1- and C_6^1, OCH_2 and C_5-CH_2 indicates coordination of TOP to Zn(II) through N_1 and phosphate group. Theophanides *et.al.* [10] observed much larger downfield chemical shift for carbon adjacent to the coordination site.

Table 4

^{13}CNMR Chemical Shifts of thiamineorthophosphate (TOP) and Zn(II)-TOP system in ppm (δ)

Group	TOP	Zn(II)-TOP
4-CH_3	13.76	13.80
C-5	137.22	152.25
2-CH_3	29.26	29.80
C-4	144.46	144.50
5-CH_2	51.24	52.14
C-6^1	145.76	147.10
5'-CH_2	65.26	65.31
C-2	157.51	159.41
OCH_2	67.92	69.97
C-4^1	164.30	165.0
C-5^1	107.71	107.80
C-2^1	164.63	166.50

DISCUSSION

The enthalpy value for the formation of mixed ligand complex in every case is negative and entropy values are positive. The extent of change in these values depend on the nature of secondary ligands. The ligand-ligand interactions are known to be most effective in stabilizing the ternary systems in solutions. The effect so called "secondary bond", results in more entropy and enthalpy contributions [6]. Enthalpy change for complexes with N donors and O^--O^- donors are more negative than those of N-O^- donors.

The enthalpy changes for 1:1:1 mixed ligand complex formation of metal(TOP)(N-O^-) complexes are higher than those of 1:1 (binary) metal(N-O^-) complexes. Higher negative enthalpy changes indicated favourable mixed ligand complex formation. Higher stabilities in these cases are due to their stacking interactions.

The enthalpy of 1:1:1 metal-TOP-N complexes are more exothermic than those of 1:1 metal-N complexes [11]. The formation of 1:1:1 complexes is also accompanied by larger positive entropy values as compared to 1:1 metal-N complexes. The high positive entropy and high negative enthalpy are due to the stacking interactions between the two aromatic systems. The entropy values in all the cases of the mixed ligand complexes of N donors with TOP are more positive than those of NO^- donors with TOP. This indicates that mixed ligand complexes of N donors with TOP are stabilised by entropy and those of N-O^- and O^--O^- donors with TOP are stabilised by enthalpy [12].

The enthalpies of 1:1:1 ternary system with NO^-, N and O^--O^- do not-follow a regular

trend. This may be due to difference in the solvation energies of the ligands involved in mixed complex formation. The entropy values of the ternary systems are less positive than those of the corresponding binary 1:1 metal secondary ligand system and this follows a regular trend. The less positive entropy values are responsible for the lower stability of the ternary systems as compared to binary ones.

The Δ log K values decreases in the order: metal-TOP-N donors > metal-TOP-O⁻-O⁻ donors > metal-TOP-NO⁻ donors. The Δ log K values of complex with N donors and TOP are more positive than those of O⁻-O⁻ donors which are more negative than NO⁻ donors indicating that there is no extra stabilization due to the ligand interaction. The positive Δ log K values in metal-TOP-N donors may be due to difference in the solvation energies of the mixed ligand and binary system.

The enhanced stability in case of ternary complexes can be measured in terms of ΔΔH values. These values for metal(TOP)(NO⁻) and metal(TOP)(O⁻-O⁻) donors are positive and for metal(TOP)(N) donors the values are negative. The exothermic enthalpy in the formation of 1:1:1 ternary complexes can be associated with the energy of stacking which is purely a van der Waals (London type) interaction. This interaction is much smaller than a hydrogen bond formation (This energy is in the range 1.0 to 5.0 kcals. mol^{-1}). The entropy change values may be negative and positive and indicate no regular trend. Such complexes follow the normal statistical consideration so that the higher stabilities are favoured by positive ΔΔH values.

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