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NOTE

Effect of Excess Concentration of Secondary Ligand on Stability of Mixed Ligand Complexes

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The formation constants of ternary complexes MAL where M = Ni(II), Cd(II) or Zn(II), A = 2,2′-bipyridyl amine as primary ligand and L = 1,2-diaminopropane or ethylene diamine have been determined in aqueous solution by potentiometric method at constant ionic strength, $\mu = 0.2$ M at 30 ± 0.1°C. The stability of the complexes is explained in terms of $M \rightarrow L$ π interaction, size of the chelate ring and steric factors. The effect of higher molar concentration of secondary ligand (1 : 1 : 2.5) on stability constants of complexes is compared with optimum molar concentration of L (1 : 1 : 1).

Ternary complexes involving bimolecules serve as a useful model for *in vivo* enzyme-metal ion substrate complexes involved in metalloenzyme catalysed biological reactions[1]. A detailed literature reivew reveals that there is a considerable interest in undertaking systematic studies on N and O/S donor systems because of their biological importance[2–5]. The formation, reactivity and stability of Ni(II)[6, 7] and Cd(II)[8] is the active field of research. The effects of various ligands on formation constants of Ni(II) are well studied[9].

In the present study mixed ligand formation constants, log K_{MAL}^{MA}, where M = Ni(II), Cd(II) or Zn(II), A = 2,2′-bipyridyl amine and L = 1,2-diaminopropane or ethylene diamine are determined by using modified form of Irving-Rossotti titration technique[10, 11].

It is interesting to study the effect of higher molar concentration of secondary ligand on ternary formation constants.

Ethylene diamine and 1,2-diaminopropane (AR grade), sodium perchlorate (Fluka), perchloric acid (Baker analysed) and sodium hydroxide were used.

A stock solution of Ni(II), Cd(II) and Zn(II) perchlorate was prepared. Acid and metal contents of solution under analysis were determined by acid-base[12] and complexometric[13] titrations. Ionic strength was maintained at 0.2 M dm^{-3} using

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sodium perchlorate. Systronics μpH system 361 with readability ± 0.01 was used for the potentiometric studies. μpH meter was calibrated with buffer solutions and calibration was checked intermittently. All potentiometric titrations were carried out at 30 ± 0.1°C using carbonate free sodium hydroxide[10, 14]. For titration five sets of solutions containing (I) known amount of free $HClO_4$, (II) free $HClO_4$ + known amount of primary ligand, (III) free $HClO_4$ + known amount of secondary ligand, (IV) free $HClO_4$ + primary ligand + metal perchlorate, (V) free $HClO_4$ + primary ligand + metal perchlorate + secondary ligand were prepared. Total volume was raised to 50 mL using double distilled water. From titration curves the proton-ligand and metal-ligand formation constants are calculated using Excel Computer Programme on the basis of literature method[11, 15].

Formation constant values of ternary complexes where molar ratios of M, A and L are 1 : 1 : 1 and 1 : 1 : 2.5 have been determined. The formation constant M-2,2′-bipyridyl amine-1,2-diaminopropane is higher than M-2,2′-bipyridyl amine-ethylene diamine for molar ratio of M, A and L as 1 : 1 : 1. Both secondary ligands are bidentate in nature. Basicity of 1,2-diaminopropane is higher than ethylene diamine which is in accordance with proton-ligand formation constant values[16].

2,2′-Bipyridylamine is of special nature. Besides N → M σ bonding there exists strong M → N π interaction due to back donation to vacant delocalised pπ orbitals over 2,2′-bipyridyl amine molecule. As a result of π-interaction in M—N bond, the concentration of electrons around the metal ion in $[M(bipy.A)]^{2+}$ complex does not increase significantly and electronegativity of metal ion in $[M(bipy.A)]^{2+}$ remais same as $[M(H_2O)_n]^{2+}$.[17, 18] Besides, basicity of ligand, size of metal ion and charge/size ratio also play an important role in values of formation constant[19]. The formation contant values are in accordance with the order Ni > Cd > Zn as expected with respect to configuration, size, Paulings electronegativity and ionic potential of divalent metal ions.

TABLE
FORMATION CONSTANTS OF SOME MIXED LIGAND COMPLEXES, MAL (1 : 1 : 1) AND MAL (1 : 1 : 2.5) AT 30 ± 0.1°C AND AT IONIC STRENGTH 0.2 M

Mixed ligand complexes	Molar ratio of M, A, L	
	1 : 1 : 1	1 : 1 : 2.5
Ni-2,2′-bipy. A-en	7.24	3.85
Zn-2,2′-bipy. A-en	6.13	3.55
Cd-2,2′-bipy. A-en	6.20	3.82
Ni-2,2′-bipy. A-1,2-dAp	7.36	3.78
Zn-2,2′-bipy. A-1,2-dAp	6.29	3.58
Cd-2,2′-bipy. A-1,2-dAp	6.39	3.56

2,2′-bipy.A = 2,2′ bipyridyl amine; en = ethylene diamine; 1,2-dAp = 1,2-diaminopropane

The mixed ligand formation constant values are lower when secondary ligand is used in 1 : 1 : 2.5 molar ratio as compared to 1 : 1 : 1 molar ratio[20]. The excess concentration of secondary ligand plays an important role and creates an unfavourable environment for the formation MAL.

Ethylene diamine and 1,2-diamino-propane both are aliphatic and strong bases; therefore electron donating capacity is more. Excess concentration of secondary ligand tends to reduce the acidity of metal ion which is surrounded in solution by secondary ligand. So there is decrease in the value of mixed ligand formation constant values in higher concentration of secondary ligand (L). Moreover, log K_{MAL}^{MA} values are slightly higher for ethylene diamine in higher concentration of secondary ligand when compared with 1,2-diaminopropane.

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