

Synthesis and Stability of Nitrilotrimethylenephosphonic Acid Mixed Ligand Complexes of Zn(II) and Cd(II) in Solution

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Abstract: The acid-dissociation constants of Nitrilotrimethylenephosphonic acid, $C_3H_{12}O_9N$ (NTPA) and its binary complexing equilibria as well as ternary chelates tendency with Zn(II) and Cd(II) ions involving some other chelating agents such as glycine (Gly) or β -alanine (Ala) (N-O type donors), 5-sulphosalicylic acid (5SSA), oxalic acid (Oxa) or catechol (Cat) (O-O type donors), 2,2 bipyridyl (Bipy) or 1, 10-phenanthroline (Phen) (N-N type donors) and iminodiacetic acid (imda) N-N-O type donor have been determined potentiometrically in aqueous medium containing a supporting electrolyte (0.10 M KNO_3) at different temperatures. All the ternary formation systems follow stepwise equilibria in which NTPA behaves as a primary ligand in presence of Gly, Ala or Cat and as a secondary ligand in presence of the remaining few other chelating agents, i.e., 5SSA, Oxa, Bipy, Phen or imda. The stability constants ($\log K_1$, $\log K_2$, $\log \beta_2$, $\log K_T$ and $\log K_T'$), the percentage of relative stabilization values ([%RS]) and the distribution of total metal ions in different chelated species as a function of pH have been evaluated and discussed.

Keywords: NTPA; Mixed ligand complexes; stability constants; [%RS].

1. Introduction

Phosphonic acid group will have an effective donor tendency [1] and one of such examples is nitrilotrimethylenephosphonic acid (NTPA) which has an immense importance in the fields of industry and biology [2,3]. Hence, the formation, stability and reactivity of these complexes have been an effective field of research [4,5]. Present communication reports the results of the studies on the binary (M-L and M-L₂) and ternary (M-A-L) complexes of Zn (II) and Cd (II) with NTPA (A) and other chelating agents (L), viz., Gly, Ala, 5SSA, Oxa, Cat, Phen, Bipy and imda in aqueous medium at 30° C and 0.10 M (KNO_3) ionic strength.

2. Experimental

The ligand NTPA was synthesized by reacting phosphoric acid with ammonium chloride at 108° C and then treated with formaldehyde, gave crystalline NTPA. The metal ion solutions were standardized by chelatometric titrations and gravimetric analysis [6,7]. The pH-metric titrations of the binary systems were carried out at 20, 30, 40 and 50° C and that of ternary systems at 30° C. An ionic strength of 0.10 M (KNO_3) was maintained in all the systems.

The binary as well as ternary formation constants were evaluated with the help of suitable computer programs. Various models were fitted to the data and the model selected was that which gave the best statistical fit. BEST [8] computer program was used to generate the complete species distribution curves (Fig. 2) at various pH values.

3. Results and Discussion

The ligand NTPA possesses three phosphonic acid groups attached to tertiary nitrogen atom through three methylene groups. When all the functional groups are considered, it

behaves as a hexadentate ligand. The acid-dissociation constants of NTPA determined were $pK_1=12.30$; $pK_2=6.66$; $pK_3=5.46$; $pK_4=4.30$; pK_5 and $pK_6 < 2$ and these are in good agreement with those values reported by Iraniet. al., [9, 10, 11]. The lowest three acid-dissociation constants (viz., pK_6 , pK_5 and pK_4) have not been considered in the stability constant evaluation procedure. This simplification is due to the fact that these acid forms of the ligand are completely dissociated at the lowest pH values of lowest metal titration curves. Experimental conditions were streamlined by adding equivalent amounts of potassium hydroxide to make sure that a tripotassium salt of NTPA exists before the actual titration.

Binary systems: The metal-ligand binary formation constants have been evaluated by Irving-Rossotti [12, 13] pH-metric and various other computational techniques and linear plots. The acid-dissociation constants and stability constants of both Zn (II) and Cd (II) metal ions with other chelating agents employed in the ternary chelate formation studies have been re-determined under the present experimental conditions and presented in Table-1 along with NTPA binary formation constant values. The \bar{n} values (0.1 – 0.9) obtained for metal-NTPA binary systems indicate the formation of both 1:1 (M-L) and 1:2 (M-L₂) complexes. The buffer region representing complex formation of M(II)-NTPA is at pH range 5.0 – 10.5. The standard deviation for all the constants reported are within ± 0.50 log units. The values of $\log K_2$ (1:2 complexes) are far-less than the values of $\log K_1$ (1:1 complexes) of NTPA with metal ions (Table-1) may be due to the complex structure of the ligand NTPA (Fig.1), which provides lesser coordination in 1:1 complex for second ligand to form 1:2 complex.

Table 1: Proton-ligand and binary formation constants of M(II)-NTPA systems in aqueous medium at 30°C and 0.10 M (KNO₃) ionic strength

Ligand	pK ₁ (pK ₂)	Zn(II) log K ₁ (log K ₂)	Cd(II) log K ₁ (log K ₂)
Gly	9.50 (2.35)	5.00 (3.50)	4.14 (3.40)
Ala	9.75 (3.40)	5.00 (3.60)	4.25 (3.60)
Cat	11.50 (9.70)	9.54 (7.50)	7.70 (6.20)
5SSA	11.60 (2.60)	6.00 (4.40)	4.50 (3.50)
Oxa	3.80 (1.40)	3.88 -	4.00 (1.77)
Phen	4.95 (1.92)	5.65 (4.10)	5.78 (5.04)
Bipy	4.47 (1.50)	5.30 (3.80)	4.12 (3.20)
imda	9.38 (2.65)	7.03 (5.14)	5.35 (4.18)
NTPA	6.66 (5.46)	9.85 (4.69)	9.30 (4.45)

Ternary systems: The formation of ternary complexes as studied under the same conditions as for the binary complexes at 30° C, except that the solutions contained equivalent amounts of metal solution. The complex formation in systems such as those under study is the result of competition between metal ions and portions towards the ligands. At higher pH, the hydroxyl ions compete with the ligands for the metal ions so that hydroxo complexes are present in appreciable concentrations. The nature of the species present in the solution is therefore highly pH dependent. In the present investigation, a pH range of 3.0 – 9.0 has been chosen for complexation so that the protonated and hydroxyl species are kept at minimum to non-existence. Stability constants of all the ternary systems were calculated using Santappa-Ramamoorthy pH-metric method [14, 15].

In the ternary systems, M-A-L or M-L'-A (where M=Zn (II) or Cd (II); A=NTPA; L=Ala, Gly or Cat; L'=5SSA, Oxa, Phen, Bipy or imda), the mixed ligand curves follow those of 1:1 M-A or M-L' curves in the lower pH region, until the protons of ligands A or L' are completely neutralized, indicating [M-A] or [M-L'] complex formation in this region. The deviation of ternary curve from binary curve above this pH region results in the formation of M-A-L or M-L'-A ternary complex in a two-step equilibria. The formation of ternary complex can also be seen on comparison of the mixed ligand titration curve with the

theoretical composite curve obtained by the graphical addition of the secondary ligand [L] or [A] titration curve to the 1:1 [M-A] or [M-L'] titration curve. The clear difference between them indicate the formation of a stable ternary complex species. The formation constants of ternary complexes are presented in Table-2.

The stability constants of ternary complexes are characterized by $\Delta \log K$ values which are in accordance with statistically expected values. The $\Delta \log K'$ values for M(II)-5SSA/Phen/Bipy-NTPA systems are found to be less negative than other related systems which can be explained as follows: The ligands 5SSA, Phen and Bipy are bound to metal ion by decreasing the concentration of electron density on the metal ion as a result of the delocalization of electrons into the phenyl rings of these ligands. In other words, the electronegativity of the metal ion in [M-5SSA/Phen/Bipy]²⁺ is almost same as in [M_{aq}]²⁺ which facilitates stronger interaction between these primary complexes and secondary ligand and hence the ternary complex stabilities for these systems are higher than the other systems under study. Another explanation was extended by Griesser and Sigel [16] in terms of Pearson's hard and soft acid-base rule. As a result of back donation of electrons from d-orbitals of metal ions to ligands, the metal ion becomes harder acid and this favors coordination with oxygen donor ligands. The stability values of M(II)-NTPA-Cat systems are greater than those of

M(II)-NTPA-Ala/Gly systems. This order is in accordance with their basicities. The $\Delta \log K'$ values of M(II)-oxa/imda-NTPA systems are found to be more negative than the other systems containing same metal ions. Since these ligands are negatively charged, charge neutralization takes place when Oxa/imda interacts with metal ion lower the interaction of metal ion with NTPA. In addition to charge neutralization, steric factors may also influence the formation of ternary complexes. Thus Oxa/imda less stable ternary complexes.

It can be seen that binary complexes are more stable than the ternary complexes resulting a negative $\Delta \log K$ values in all the ternary systems studied. Such a lowering of stability of ternary complexes compared to that of binary chelates may be due to the greater destabilization effects [17, 18] caused by ligand repulsions in mixed ligand complexes than that in binary systems, coupled with the availability of lesser number of coordination sites for second ligand on the primary complex [M-A] or [M-L'] compared to free $[M_{aq}]^{2+}$ ions. [%R.S.] values (Table-2) are used in the estimation of the relative stabilization of the ternary complex over that of its binary complex. The negative [%R.S.] values obtained, excepting Cd(II)-NTPA-Cat system, in the investigation indicate lesser stabilization of ternary complexes than those of binary ones.

Table 2: Formation constants of ternary metal chelates of NTPA with other chelating agents in aqueous medium at 30°C and 0.10 M (KNO₃) ionic strength

Other Chelating Agents	Zn(II)			Cd(II)		
	Stability Constant	$\Delta \log K$	[%R.S.]	Stability Constant	$\Delta \log K$	[%R.S.]
M-A-L						
Ala	4.90	-0.10	-2.00	4.16	-0.09	-2.07
Gly	4.90	-0.10	-2.00	3.93	-0.21	-5.02
Cat	9.50	-0.04	-0.42	9.19	+0.49	+6.36
M-L'-A						
5SSA	7.92	-1.93	-19.59	7.62	-1.68	-18.04
Oxa	7.54	-2.31	-23.47	7.22	-2.08	-22.39
Phen	8.83	-1.02	-10.42	8.29	-1.01	-10.84
Bipy	8.66	-1.19	-12.06	8.05	-1.25	-13.46
imda	7.27	-2.58	-26.21	7.00	-2.30	-24.69

In order to fully understand the coordination behavior of metal ions with ligands, it is of greater interest to examine some details of species distribution diagram to represent the distribution of various species present in the solution as a percentage of metal ion concentration and their variation with pH. The distribution curves for few representative systems, i.e., Zn(II)-Bipy-NTPA (a) and Cd(II)-NTPA-Ala (b) are given in Fig.2. It can be seen that the pH regions of primary complex formation of Zn(II)-Bipy or Cd(II)-NTPA are 2.0 – 3.0 or 2.0 – 6.0 for the binary complexes of Zn(II)-NTPA or Cd(II)-Ala are 3.0 – 4.0 or 8.0 – 10.0 respectively. Hence it becomes distinctly clear that the ligands interact in a stepwise manner for the formation of their corresponding ternary complexes. Hence the concentration of both the systems (a) and (b) reaches a maximum of 82% at pH 11. At lower pH regions, the primary complexes, Zn(II)-Bipy and Cd(II)-NTPA are the major species present.

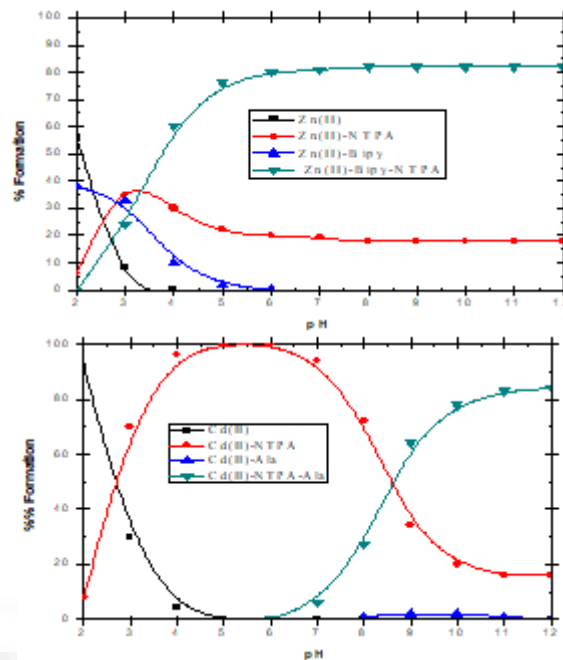


Figure 2a: Species distribution diagram of Zn(II)-Bipy-NTPA. **Fig. 2b:** Species distribution diagram of Cd(II)-NTPA-Ala

The order of stability constants of binary as well as ternary complexes with respect to metal ions is Zn(II) > Cd(II). This order is in agreement with the Irving-Williams (19) (natural) order.

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