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AN OVER VIEW OF POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANTS OF METAL COMPLEXES

D. M. JANRAO[a], JAMIL PATHAN[*], D. D. KAYANDE[b] and JABBER J. MULLA[c]

S. R. College, GHANSAWANGI, Dist.: Jalna (M.S.) INDIA
[a]J. E. S. College, JALNA (M.S.) INDIA
[b]S. B. E. S. College, AURANGABAD (M.S.) INDIA
[c]Adarsh College, UMARGA, Dist.: Usmanabad (M.S.) INDIA

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ABSTRACT

This paper deals with review of stability constants of some metal complexes. The review is divided into two parts, a theoretical aspects and literature survey. In this paper, complexes of metal ions particularly transition metals & lanthanides are reviewed.

Key words: Potentiometry, Stability constant, Metal, Complexes.

INTRODUCTION

Recently, most of the workers used complexation for the purification of amino acids and in the synthesis. The complex formation has wide applicability in different field of drugs containing metal complexes in the form of chelate. There are various advanced techniques to separate chiral compounds from the racemic mixture. It is a challenging job to have pure isomeric compounds in order to avoid the multiple product formation in newer techniques. Complexation is also used for the separation of isomer.

The acid base protonation constant of two recently introduced chelating ligands for protein purification, O-phosphoserine and 8-hydroxy quinoline immobilized into sepharose CL-4B, and the stability constant of their derived immobilized metal ion chelate complexes have been reported using the potentiometric methods.[1] The study confirmed that immobilization thermodynamically constrains the ligands, with electron withdrawing characteristics of the group linking the ligand to the support material affecting the magnitude of the stability constant of the immobilized metal ion complex vis-à-vis the free ligand-metal ion complexes in solution. The buffer composition, ionic strength and pH influences on the stability constant of the immobilized hard metal ion chelate complexes. The coordination complexes with stoichiometries, other than the simply 1:1 ML type exist with these systems with hard metal ion exhibiting a preference for hydrolytic $M(OH)_mL_n$ complexes where m or n > 1. These finding on the participation of coordination complexes of different stoichiometry depending on the characteristics of the chelating ligand and metal ion have fundamental implications for the interpretation of immobilized metal ion affinity in chromatographic separation of proteins.

Available online at www.sadgurupublications.com
[*]Author for correspondence; E-mail: mazahar_64@rediffmail.com

The stoichiometry and stability constant of the manganese (II), cobalt (II) and nickel (II) complexes with seven aminodiphosphonates [RN $(CH_2PO_3H_2)_2L$) containing iminomethylene phosphonate moieties have been determined pH metrically at 25^0C and at an ionic strength of 0.20 mol.^{2} dm^{-3} (KCl). The results suggest equimolar species $[M(H_2L)]$, $[M(HL)]^-$ $[ML]^{-2}$ and hydroxo $[MH_{-1}\ L]^{3-}$, in the pH range of 3-11.5. The ligands coordinate to the metal ions only by the phosphonate group(s) in a monodentate or bidentate manner.

Reaction of the fluoroquinolone antimicrobial ciprofloxacin with copper (II) nitrate in the presence of 2, 2'-bipyridine resulted in the isolation of the complex $[Cu(cip)\ (bipy)\ (C_1)_{0\text{-}7}(NO_3)_{0\text{-}3}](NO_3)2H_2O$. Reaction at an aqueous solution of ciprofloxacin HCl and NaCl with $CuCl_2$ at pH 5.0 resulted in the isolation of $[CuCCiP)_2]Cl_2.11H_2O$. The complex $[Cu(cip)(bipy)(Cl)_{0.7}(NO_3)_{0.3}]$ $(NO_3).2H_2O$ crystallizes in the monoclinic space group P2/n; with a = 13.955 (8), b = 14.280 (8), C = 14.192 (6) Å, β = 93.10 $(4)^0$, Z = 4 with R = 0.046. The selective broadening of resonance in the ^{13}C NMR spectrum of ciprofloxacin by the addition of Cu^{2+} (aq.) was employed to probe metal ion binding sites in the ligand. The protonation contents of norfloxacin & ciprofloxacin and the formation constant with copper (II) were determined by potentiometric titrations at 25^0C. The additions of ciprofloxacin to metal to form ML and ML_2 complexes exhibit stepwise formation constants of log K_1 6.2 & K_2 11.1, respectively.[3]

The full speciation of the vanadium (V) complexation systems with two aminohydroxamic acids, aspartic-β- and glutamic-γ-hydroxamic acid, has been reported using potentiometric and spectroscopic techniques. The two ligands have a carboxylic group in the structure and show comparable biological activities. Analogous complexation behaviour at physiological conditions was found despite the presence of two or three methylenic groups between the amino and hydroxamate groups. The carboxylic groups are quite different from the hydroxamic groups and are not involved directly in the coordination process. Therefore, the coordination structures are related to that found in the vanadium (v)-β-alanine hydroxamic acid, where there is not a carboxylic group[4].

The binary and ternary systems 2.2'-bipyridine (bpy)-M(II)-NO_2 psglyH_2 (M(II) = magnesium(II), cobalt(II), copper(II), zinc(II), cadmium(II), lead(II), NO_2, psglyH_2 = N-2(nitrophenyl sulphonyl glycine) were reported in aqueous solution by means of potentiometry and electron spectroscopy in order to identify the type, number and stability of complex species as a function of pH and metal to ligand molar ratio. A substituent on the phenyl ring of the N-sulphonyl amino acid affects their coordination properties. The prevailing species in the binary systems is the (ML) [M= cobalt(II), nickel (II), copper (II), cadmium(II), lead(II), where the amino acid molecule is in the dianionic form and coordinates the metal ion through both; carboxylic oxygen and deprotonated sulphonamidic nitrogen, while in the Mn(II) and Zn(II) containing binary system, the only complex species found are those with the amino acid in the monoanionic form. In the ternary 2.2'-bipyridine containing systems, the chelating coordination mode of the dianionic amino acid is maintained with M(II) = cobalt(II), nickel (II), copper (II), cadmium(II), lead(II) and the addition of aromatic base also enables the zinc(II) ion to substitute for the sulfonamide nitrogen bound hydrogen of NO_2 PsglyH_2[5].

Complex or coordination compound and any substance, which can accept a pair of electron is called as Lewis acid whereas any substance donating a pair of electrons is commonly called as Lewis base. When a ligand contains two or more donor atoms close to each other, the metal complex formed is said to be a chelate and the process is referred as chelating. The chelating ring may be ionic or covalent depending on the nature of ligands. The history of complexes and the interpretation of complexes begin with Alfred

Werner. Coordinating agents are used in metal-ion sequestration or removal, solvent extraction, dyeing, leather tanning, electroplating, catalysis, water softening, and in other industrial processes. For example, vitamin B_{12} is a coordination compound of cobalt, the heamoglobin of human blood is a coordination compound of iron, the haemocyanin of invertebrate animal blood is a coordination compound of copper, and the chlorophyll of green plants is a coordination compound of magnesium.

Importance of stability constants

The stability constant of complexes has been found to be greater than zero, which is perhaps one of the most convincing pieces of evidence for the existence of the complex species ML_n in solution. Moreover, if all the possible stability constants for a given system have been determined, it is possible, in principle, to calculate the equilibrium concentration or activity of each of the species present under a known set of experimental conditions. Such exact knowledge of the composition of a solution is essential for a correct interpretation of its optical and kinetic properties of partition equilibria and its biological behavior.

Factors affecting the stability of metal complexes

There are many factors, which assist the formation of a complex and sometimes hidden factors are working against the same. The capacity of a metal ion to form a complex with a ligand is mainly decided by its environment, which decides the stability of the complex. Some of the factors, which affect the stability of the complexes are solvents, tempreture, effect of metal ions, nature of ligands etc.

Determination of stability constant of binary complexes

The stability constant of complex in the solution is usually determined by the knowledge of measurement of equilibrium constants (K) for complex forming reaction. The knowledge of stability constant is, therefore, of immense help to rationalize our understanding of the behaviors of metal chelate in the solution.

Bjerrum method

Bjerrum technique is use to determine the stability constant of metal-complexes from the concentration of metal, free ligand and total ligand concentration. The equilibrium constant of the free ligand is a prerequisite to the occurrence of the following equilibria:

$$H_2L^+ \rightleftharpoons HL + H^+ \qquad K_1 = \frac{\left[H^+\right][HL]}{[H_2L^+]} \qquad \ldots(1)$$

$$HL \rightleftharpoons L^- + H^+ \qquad K_2 = \frac{\left[H^+\right][HL^-]}{[HL]} \qquad \ldots(2)$$

Where H_2L^+, HL and L^- are the diprotonated, monoprotonated and the ligand anion, respectively. The values of pK_1 and pK_2 were determined according to the equations: $pK_1 = - \log K_2$ and $pK_2 = \log K_2$ and to calculate the concentration of H_2L^+, HL and L^-, which are present in the reaction medium. Most previous studies consider that the complexation processes were carried out by one of these species.

This study takes into account that all of these species could act as a legating species. Due to the presence of positive charge of the metal ions, an expected repulsion between H_2L^+ is there and these were

excluded as a ligating species. In this case, most probable ligating species are HL and/or L^-. The stoichiometry stability constants of the possible suggested reactions; the deprotonated ligand anion L^-, could act as a ligating species according to the following equilibria.

$$M + L^- \rightleftharpoons ML \qquad \beta_1^{[L^-]} = \frac{[ML]}{[ML][L^-]} \qquad \ldots(3)$$

$$M + 2\,L^- \rightleftharpoons ML_2 \qquad \beta_2^{[L^-]} = \frac{[ML_2]}{[M][L^-]^2} \qquad \ldots(4)$$

The $\beta_1^{[L^-]}$ and $\beta_2^{[L^-]}$ are the overall stability constants of the complexes formed from the reaction between ligand and metal ion. From equation (1), (2), (3), (4) one gets –

$$[L^-] = K_1\,K_2\,[H_2L^+]/[H^+]^2 \qquad \ldots(5)$$

But the monoprotic amino acid HL could act as interacting ligating species and the complexation process could proceeds with proton release as follows.

$$M + HL \rightleftharpoons ML + H^+ \qquad \beta_{[HL]}^{[HL]} = \frac{[ML][H^+]}{[M][HL]} \qquad \ldots(6)$$

$$M + 2\,HL \rightleftharpoons ML + 2\,H^+ \qquad \beta_{2_{[H^-]}}^{[HL]} = \frac{[ML_2][H^+]^2}{[M][HL]^2} \qquad \ldots(7)$$

Where $\beta_{[HL]}^{[HL]}$, $\beta_{2_{[H^-]}}^{[HL]}$ are the overall stability constant of the complexes formed from the reaction between HL and M with proton release. In this case, [H] calculated from (2) and substituted in equation (6), (7), one gets –

$$[HL] = K_1[H_2L]/[H^+] \qquad \ldots(8)$$

Where [L] is the concentration of free ligand and n- is the average number of ligand bound per metal ion concentrations (CM) that expressed as –

$$\bar{n} = \text{Bound ligand/total metal ligand concentration} \qquad \ldots(9)$$

$$\bar{n} = \frac{\sum_{i=0}^{n} i[ML]_i}{\sum_{i=0}^{n} [ML_i]} \qquad \ldots(10)$$

The average number of hydrogen ions bound to the ligand at different pH value :

$$\bar{n}_A = \gamma + \frac{E^0 - N + [OH^-] - [H^+]}{T_A^0} \qquad \ldots(11)$$

Where E^0, N and T^0 are the concentrations of acid, alkali and ligand added, respectively, $[H^+]$ = antilog (- pH) and $[^-OH] = Kw/[H^+]$. When $\bar{n}_A$ versus pH was plotted, the values of pK_1 and pK_2 are equated to the values of pH, at which the values of nA =1.5 and 0.5, respectively.

Kruck and Sarkar method

Kruck and Sarkar performed a series of titrations of weak acid, each differing in CA (CA is the total concentration of ligand) in all forms and used the following expression to calculate the values of $\bar{n}$ at different pH values:

$$n_A^- = \gamma - (\frac{\delta C_{NaOH}}{\delta C_A})H \quad ...(12)$$

Sarkar and Kruck recently extended a procedure developed by Osterberg to determine pL in the presence of metal ions by pH. The complexation reactions occurring between C_M moles of metal ion M, C_H moles of hydrogen H, and C_L moles of ligand anion L can be represented by general equilibrium reaction.

$$pM + qH + rL \rightleftharpoons Mp\ Hq\ Lr \quad ...(13)$$

Where p, q and r are the stoichiometry quantities of M, H and L, respectively. The stabilities of the species formed are represented by the stoichiometry equilibrium constant β expressed in terms of concentrations, ionic strength, temperature and pressure:

$$\beta_{pqr} = \frac{M_p H_q L_r}{m^p h^q l^r} \quad ...(14)$$

Where m, h and l are the concentration of free metal ion, hydrogen ion and ligand, respectively. Osterberg showed that the differential quotient of two external coordinates of a titration could be evaluated experimentally at selected values of pH, and that this function could be used to determine the difference in pL between two points differing in pH.

$$pL - pL_0 = \int_{pH}^{pH_0} (\delta C_H / \delta C_A)_{H.C_M} dpH \quad ...(15)$$

If pH_0 is selected such that at it pL_0 is known, eg., a value low enough that no metal complex formation occurs, then (eq. 17) can be used to find pL at any other chosen pH. Sarkar and Kruck showed the analogues function ($\delta C_H/\delta C_M$) could be determined experimentally and used to determine pM at a selected pH provided that at some reference pH_0 the value of pM_0 was known –

$$pM - pM_0 = \int_{pH}^{pH_0} (\delta C_H / \delta C_M)_{H.C_L} dpH \quad ...(16)$$

Where pM = – log [Free metal M], pL= – log [Free ligand L], pH = – log [H^+] and H = moles of OH^- consumed in the titration of the hydrogen ion liberated from the complexation reactions. This is a method used with computer program to calculate of the stability constant and species distribution of the complexes formed.

Irving and Rossotti method

The proton-ligand equilibrium constant for the ligand L under experimental conditions were determined by Calvin-Bjerrum pH –titration, as modified by Irving and Rossotti for calculation of $\bar{n}$ and pH

from proton-ligand formation. The proton-ligand formation curve was obtained by plotting $\bar{n}$ values against pH. This indicates that the ligand has one dissociable proton. The pK values were estimated from formation curve by noting the pH at which $\bar{n}$ = 0.5 and $\bar{n}$ = 1.5. In Irving and Rossotti method, the pH titration of the three sets of mixtures against a carbonate free standard alkali, were performed. These are –

(i) Free acid A

(ii) Free acid + Ligand A + L

(ii) Free acid + Ligand + Metal A + L + M

On plotting the observed pH against the volume of alkali, different trends were obtained in the titration curves, the acid curve (A) and the ligand curve (A + L) and a metal complex titration curve (A + L + M) lies below the ligand curve indicating the complex formation. For the present investigation, only Calvin-Bjerrum method, as modified by Rossotti-Rossotti was used, because of their advantages such as comparative simple calculation, less time consuming and economical viable method.

Calculation of pK and log K

From the titration curves, the average number of protons associated with the ligand $\bar{n}_A$ at different pH values was calculated utilizing the acid and ligand curves. The average number of metal ions associated with the ligand $\bar{n}$ at different pH values is calculated from the metal ions and ligand titration curves, where the proton-ligand $\bar{n}_A$ are evaluated as:

$$\bar{n}_A = \gamma \frac{(V_L - V_a)(N + E^0)}{(V_0 + V_a)T_L} \quad \ldots(17)$$

Where V_a and V_L are the volumes of alkali required to reach the same pH in acid and ligand titration curves. T_L is the total ligand concentration. γ is the total number of replaceable protons free attached to the ligand molecule, N is the normality of the alkali, E^0 is the initial concentration of free acid and V_0 is the total volume of the titration solution. The average number of metal ions associated with the ligand $\bar{n}$ - at different pH values is calculated from the metal ions and ligand titration curves using:

$$\bar{n} = \frac{\text{Total number of ligand (L) bound to metal (M)}}{\text{Total number of metal present in system}} \quad \ldots(18)$$

$$\bar{n} = \frac{(V_M - V_L)(N + E^0)}{(V_0 + V_L)n_A^- T_m} \quad \ldots(19)$$

and

$$pL = \log_{10}\left[\frac{\sum_{n=0}^{n=i} \beta_a^H (_{anti\log pH})}{T_L - n^- T_M} . \frac{V_0 + V_M}{V_0}\right] \quad \ldots(20)$$

Where T_M denotes the total concentration of metal present in solution, V_M is the volume of metal ions present in solution and β_o^H is the overall proton ligand stability constant. There are three most commonly used methods for the calculation of stability constant. Out of these three, we have used two methods i.e. point wise calculations and half integral method for calculation of stability constant.

Method of point wise calculation

This method is used to calculate K_1 and K_2 values of the proton ligand formation by using the following expressions:

$$K_2 = \frac{\bar{n}_A}{(1-\bar{n}_A)[H^+]} \quad \ldots(21)$$

For monobasic acid:

$$\log K_2 = pH + \frac{\bar{n}_A}{1-\bar{n}_A} \qquad (\bar{n}_A = 0.2 - 0.8) \quad \ldots(22)$$

For dibasic acid:

$$\log K_1 = pH + \log \frac{\bar{n}_A - 1}{2-\bar{n}_A} \quad (\bar{n}_A = 1.2 - 1.8) \quad \ldots(23)$$

$$\log K_1 = pH + \log \frac{\bar{n}_A - 1}{2-\bar{n}_A[H^+]} \quad \ldots(24)$$

Half integral method of calculation

In the case of proton-ligand, one can calculate the stability constant by plotting $\bar{n}_A$ against pH, the value of pH where $\bar{n}_A = 1.5$ and $\bar{n}_A = 0.5$ corresponds to the values of pK_1 and pK_2, respectively, and in the case of a metal ligand curve by plotting $\bar{n}$ against pL, log K_1 and log K_2 were calculated from the formation curve by the known values of pL at which $\bar{n} = 0.5$ and $\bar{n} = 1.5$ corresponds to the values of log K_1 and log K_2, respectively.

Method of least squares

Irving and Rossotto showed the better set of stability constants from different experimental data that can be solved by least squares method after algebraic transformation. More over, when the difference between log K_1 and log K_2 was less than 1.8, the exact values were evaluated by this method. For a system consisting of (1:1) and (1:2) complex species, the following expression was employed.

$$\frac{\bar{n}}{(\bar{n}-1)} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)} . K_1K_2 - K_1 \quad \ldots(25)$$

A plot of $g\frac{\bar{n}}{(\bar{n}-1)(L)}$ against $\frac{(2-\bar{n})[L]}{(\bar{n}-1)}$ give the best straight line with slope = K_1K_2 and the intercept K_1. The method was also utilized to confirm the presence and absence of 1:2 complex species. In one of the report, researchers have also attempted to simplify the approach for calculating various parameters required for stability constant.

Calculation of stability constant of ternary complexes

There are some methods used to calculate of the stability constant of ternary complexes:

Stepwise method

The stepwise equilibria in solution would be confirmed, when the mixed ligand curve could be superimposed over the binary ML_P or ML_s titration cure. The method of Thomson and Loraas for calculation

of stepwise stability constants is widely used. The stabilities of the mixed-ligand complexes can be calculated by the replacement of M = L_p = L_s by ML_p or ML_s in the following expression :

For monobasic acid as primary ligand

$$K_{ML_pL_S}^{ML_P} = \frac{T_M - AX}{A^2 X} \quad \ldots(26)$$

Where $$A = \frac{T_{LS} - T_{OH} - [H^+] + [OH^-]}{[H^+]/K_1}$$

And $$X = \frac{[H^+]}{K_1} + 1$$

For dibasic acids as secondary ligand

Where $$A = \frac{2T_R - T_{OH}{}^{-}[OH^-] + [H^+]}{\frac{[H^+]}{K_1} + \frac{2[H^+]^2}{K_1K_2}} \quad \ldots(27)$$

and $$X = 1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1K_2}$$

Simultaneous equilibria

When the mixed ligand curve does not coincide with either of the simple binary curves (MLp or Mls), the equilibria involved is simultaneous one. Irving and Rossotti have developed a number of equations for the evaluation of stability constants of mixed complexes involving number of ligands. Following expressions (modification of Thomson and Loraas) are utilized for the determination of stability constants of ternary complexes.

For monobasic-monobasic acids ($T_M = T_{LS} = T_{LP}$)

$$K_{ML_SL_P} = \frac{T_M - (0.5.[A].X}{0.5^9[A]^9 X} \quad \ldots(28)$$

Where $$A = \frac{2T_M + P - T_{OH} - [H^+]}{\frac{[2H^+]}{K_1K_2}} \quad (T_M = T_R = T_L)$$

and $$X = 1 + \frac{2[H^+]}{K_1 + K_1^-}$$

For dibasic-dibasic acids:

$$K_{ML_SL_P}^{ML_S} = \frac{(T_M - \{0.5[A]X\})}{0.5^9[A]^3 X} \quad \ldots(29)$$

Where $$A = \frac{4T_M + P - T_{OH} - [H^-]}{\frac{[2H^+]}{K_2K_2^-} + \frac{4[H^+]^2}{(K_1K_2) + K_1K_2^-)}} (T_M = T_L = T_{LP})$$

$$X = 1 + \frac{2[H^+]}{(K_2 + K_2^-)} + \frac{2[H^+]^2}{K_1K_2) + (K_1^-K_2^-)}$$

For monobasic-dibasic ligands ($T_{LP} = T_{LS} = T_{LP}$)

$$K_{ML_SL_P}^{ML_S} = \frac{(T_M - 0.5[A]X)}{0.5^9 A^9 X} \quad \ldots(30)$$

Where $$A = \frac{3T_M + P - T_{OH} - [H^+]}{\frac{[2H^+]}{K_2K_1^-} + \frac{2[H+]^2}{K_1K_2}}$$

and $$X = 1 + \frac{2[H^+]}{K_2 + K_1^-} + \frac{[H^+]^2}{K_1K_2}$$

Where, T_M = Concentration of total metal ion,

T_{LP} = Concentration of primary ligand,

T_{LS} = Concentration of secondary ligand,

P = Initial concentration of $HClO_4$

and T_{OH} = Concentration of alkali [NaOH]

K_1 and K_2 are the first and second dissociation constants of two ligands. In the present investigation, it was observed that in all mixed ligand systems, the mixed curve did not coincide with either ML_p or ML_s curve since from the initial existence of complex species was confirmed by simultaneous equilibria.

Literature survey

Stability constant of the complexes formed in the reaction of $[Pd (bpma)]^{2+}$ [bpma = bis (pyridine 2-yl-methyl) amine] with monodentate nitrogen and thioether ligands including uridine, MeUH, cytidine, MeC, EtGH, AcHis, AcHM, AcLys and AcMet were determined by potentiometric method. The coordination chemistry of $[bp (bpma)]^{2+}$ shows significant similarity to that of $[Pd (terpy)]^{2+}$, but it is different from $[Pd (dien)]^2$. The formation of hydro and dinuclear complexes is especially enhanced in the case of $[Pd (bpma)]^{2-}$ and $[Pd (terpy)]^{2+}$ but the affinity of palladium (II) ion for the coordination of thioether residues is reduced in the presence of pyridine nitrogen atom. Stopped flow kinetic measurements reveal that the substitution reactions of thioether ligand AcMet are much faster than those of N-donor cytidine. The presence of two pyridyl residues significantly enhances the kinetic reactivity of $[Pd (bpma)]^2$ as compaired to that of $[Pd (dien)]^{2+}$. The Pd-S(thioether) banded species can be important intermediates in multicomponent system, but the equilibrium state is characterized by the formation Pd-N bonded species. The complex $[Pd (bpma) NO_3] NO_3$ has been prepared in solid state and its structure was elucidated by single crystal X-ray diffraction method[6].

Taking into the account the low stability of the Sm (III) amino acids compounds and search for thermodynamically stable compounds, which contain biologically relevant ligands in the coordination sphere of mixed ligand compounds have been reported. They used a stable case with Sm (III) and polycarboxylates (edta, nta, ida, etc.) and to substitute the labile positions (occupied by water molecules) by amino acid. Experiments were performed in aqueous solution at 37.0°c and 0.15M $NaClO_4$, resembling in physiological medium. In all cases, mixed ligand species were detected in solution[7].

The stability constant N-(pyridine-2-yl-methylene) isonicotinohydrazide pmINH basis of elemental & spectral data. The protonation constants of Pm INH and stability constants of the base with trivalent La, Pr, Nd, Sm, Eu & Gd at constant ionic strength (I, mole. dm^{-3} = 0.05 M $NaClO_4$) and at different temperatures, T = (293, 303 and 313) K, were reported potentiometrically in water dioxane (30%) medium. The ligands form only 1:1 complexes with lanthanides. Both protonation and complexation reactions are exothermic in nature. The trends in the formation constants follow the order: $La^{3+} < Pr^{3+} < Nd^{3+} < Gd^{3+} < Sm^{3+} < Eu^{3+}$ and a break at gadolinium was also calculated. The values of ΔG, ΔH and ΔS are negative for all the system indicating that all the reaction are enthalpy driven. The thermodynamic parameters of the complexation are correlated with reciprocal ionic radii of the metal ions[8].

The properties of the iron(III) complexes of the ditopic macrocyclic ligand with three aminopropyl pendant arms, L^1= 3,7,11-tris-(3-aminopropyl)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene were investigated in aqueous solution. Potentiometric studies indicated the presence of mononuclear $[FeH_h\ L\ ^1]^{h+3}$ (h = 0–3), and dinuclear $[Fe_2L^1]^{6+}$$[Fe_2L^1(OH)]^{5+}$ and $[Fe_2L^1(OH)\ _2]^{4+}$ complexes. The log K values of mononuclear protonated species indicated the consecutive deprotonation of the aminopropyl arms, suggesting the nitrogen donor atoms from the macrocycle as the preferred coordination environment for the first metal centre, and the amines from the pendant arms for the second one. The dinuclear complex is formed at about 85% of the total amount of the metal ion for 2:1 Fe: L^1 ratio solutions at pH 4.0-4.5. The log K values of the deprotonation of dinuclear hydrolyzed species are consistent with the presence of two water molecules directly bound to the metal centers[9].

The stability constants of the ternary uranyl ion complexes involving dicarboxylic acids show the discriminating qualities of uranyl ion-dibasic acid 1:1 complex toward the secondary ligand to be coordinated. The values of log K_{2rx} are inversely related to the product of the acid dissociation constants of the secondary ligands. The overall stability is found to be dependent on the binary stabilities. Ring size of the chelates formed by the secondary ligands is found to influence the formation of ternary complexes.[10]

The stability constants of the ternary complexes [MAL] [where M" refers to nickel (II), copper (II), A refers to diethylenetriamine (det) and dipropylenetriamine (dpt) and L refers to catecholate, o-amino phenolate, o-phenylenediamine, oxalate, malonate, glycinate, β-alaninate, ethylenediamine and 1,3-diaminopropane] indicated reason for the more negative A log K. The complexes $[Cu(DET)en](C10_4)_2$ and $[Ni(DET)en]\ (C10_4)_2$ have been obtained and the crystal structure of the former was determined by single crystal X-ray diffraction[11].

The stability constants of mixed ligand complexes of the type M(Phen)(ACA), where M = Copper(II) or zinc(II), Phen = 1, 10-phenanthroline and ACA^- = propionate, valerate and 2-cyclohexylacetate, in 50% (v/v) dioxane-water and compared with the stabilities of the corresponding ternary complexes formed with formate and acetate. The ternary complexes containing the alkane carboxylates (ACA^-) are significantly more stable, due to intramolecular hydrophobic interactions between the alkyl residue of the ACA^- ligands and the 1,10-phenanthroline molecule. The stability data for the Cu^{2+}/leucinate (Leu^-) system shows that

addition of some dioxane to an aqueous solution favors the intramolecular interaction between the two isopropyl residues in $Cu(Leu^-)_2$ considerably. The formation degree of the closed isomer reaches about 80% in 40 to 50% aqueous dioxane. Higher concentrations of the organic solvent destabilize the hydrophobic interaction. The overall stability of Cu(Leu)' and $Cu(Leu^-)_2$ as well as of $Cu(alaninate)^+$ and $Cu(alaninate)_2$, is governed by the polarity of the solvent while the extent of the intra-molecular ligand-ligand interaction is influenced by the hydrophobic properties of the solvent molecules. Based on stability data, it is shown that intra-molecular ligand-ligand interactions are quite a common feature for many binary and ternary amino acid complexes: e.g., $M(norvalinate)_2$, $M(phenyl\ alaninate)_2$, $M(tyrosinate)_2$ [M = Cobalt(II), nickel (II), copper (II), zinc(II)] or $Cu(tryptophanate)_2$ and M(phenylalaninate)(norvalinate) or M(phenylalaninate) (tyrosinate) [M = cobalt(II), nickel (II), copper (II),][12].

The interaction of Be, Mg, Ca, Sr and Ba ions with tetracycline was also followed by pH-metry. The stability constants of the 1:1 complexes formed decrease in the order Be > Mg > Ca > Sr > Ba[13]. The strength of complexation to form binary and ternary complexes can be interpreted in terms of cationic hydration and structural effects in the interaction of metal cations with aminopolycarboxylate ligands[14].

The stability constants and coordination modes of the mixed-ligand complexes formed by copper(II), nickel(II), zinc(II), with ethylenediamine (en), 2,2-bipyridine (bpy), glycinate (Gly), disodium salt of 4,5-dihydroxybenzene 1,3-disulfonate (Tiron), diethylenetri-amine (dien) or 2,2:6,2|-terpyridine (terpy) (ligand B) and acetohydroxamate (Aha), N-methylacetohydroxamate (MeAha) or N-phenylacetohydroxamate (PhAha) (ligand A) are shown in water (25°C, I = 0.2 M KCl). Mixed-ligand complexation with typical hydroxamate type chelation mode involves the NHO^- moiety. However, further copper(II) induced deprotonation of the NHO^- moiety of Aha in the presence of en or bpy results in the formation of mixed-ligand complexes with hydroximato chelates at high pH. The coordination was of a hydroxamate to metal(II) – en and especially to a metal(II)-bpy moiety. If ligand B is Gly, the increase of stability of the mixed-ligand complexes is as expected on statistical basis, whereas the formation of complexes involving O,O-coordinated hydroxamate and O,O-coordinated Tiron is norfavoured. The tridentate coordination of dien or terpy results in five-coordinated mixed-ligand copper(II) complexes in which, most probably, the hydroxamate moiety adopts an equatorial-axial coordination mode[15].

The strong species of cadmium(II), copper(II), manganese(II) and nickel(II) in an Antarctic seawater sample are investigated by a method based on the sorption of metal ions on complexing resins. The resins compete with the ligands present in the sample to combine with the metal ions. Two resins with different adsorbing strengths were used. Very stable metal complexes were investigated with the strong sorbent Chelex 100 and weaker species with the less strong resin, Amberlite CG-50. Strong species were detected for three of the considered metal ions, but not for Mn(II). Cu(II) is completely linked to species with a side reaction coefficient as high as $\log \alpha_{M(I)} = 11.6$ at pH = 7.3[16].

The first solution studies at physiological pH for the formation of metal complexes of taurine, $^+NH_3CH_2CH_2SO_3^-$, one of the most abundant low molecular weight organic compounds in the animal kingdom, are reported. The complexes $Cu(Gly\text{-}GlyH^{-1})$ and $[Cu(Gly\text{-}AspH_{-1})]^-$ react with taurine to give the ternary complexes $[Cu(Gly\text{-}GlyH^{-1})\ taurine]^-$ ($\log K = 2.95 \pm 0.03$, I = 0.2 M, T = 25.0°C) and $[Cu(Gly\text{-}AspH^{-1})taurine]^{-2}$ ($\log K = 2.68 \pm 0.02$) in which taurine acts as an N-donor ligand, most likely monodentate, without involvement of the sulphonate group in coordination. The taurine complexes are less stable than the analogous complexes of β-alanine due to the decreased basicity of the amino group in the former ligand, and in the case of the $Cu(Gly\text{-}GlyH^{-1})$ complexes due to involvement of the carboxylate group of alanine in axial coordination[17].

Metal-ligand stability constants of 5, 7-substituted 1, 4-dizepines and 7-substituted 2, 4-dimethyl 1, 5-benzodiazepines with copper(II), cobalt(II) and nickel(II) have been determined in aqueous media at 25 ± 1°C and at constant ionic strength. It shows the log K and log β corresponds to copper(II) > nickel(II) ≈ cobalt(II), which is in agreement with Irving-Williams stability order. The $\bar{n}$ values suggest formation of ML_2 complexes[18].

The 1,5-disubstituted tetrazole ring, a mimetic of the cis-amide bond, is an unique element modifying the ability of peptides to chelate copper(II) ions. The position of the tetrazole ring system in the peptide back-bone plays a critical role in the stabilization of the metallopeptide molecule. The insertion of a tetrazole between amide groups leads to enhance the stability of the complex and to obtain a very effective peptide chelating agent. These findings can provide important information for modeling biologically relevant peptide–metal binding sites[19].

The dissociation constants for N-(l-naphthyl)ethylenediamine (NEN) and the formation constants for binary (ML) and ternary metal complexes (MLA), where M = Cu(II), L = alanine, phenylalanine, tryptophan, lysine, arginine, serine, threonine, aspartic acid or histidine and A = NEN or ethylenediamine (EN) are reported at 35°C (A = 0.2 M KNO_3)[20].

The 14-membered macrocyclic ligand containing the N_3O donor set, 1-oxa-4,8,12-triazacyclotetradecane([14]aneN_3O), has been synthesized and characterized. The copper atom is pentacoordinated by three nitrogens, one oxygen, and one bromide ion in a slightly distorted square-pyramidal coordination environment. The comparison of crystal structures with analogous [Cu(II)(13aneN_3O)Br]Br indicates that the copper(II) ion can fit into the macrocyclic ring of [14]aneN_3O better than into that of [13]aneN_3O. The former also has higher stability in aqueous solution than the latter. The smaller metal ion, Cu^{2+}, coordinates more strongly to the larger macrocycle [14]aneN_3O than to the smaller macrocyclic ligands [13]aneN_3O and [12]aneN_3O. The reverse is true of larger metal ions, such as Cd^{2+}. The protonation constants of [14]aneN_3O and the formation constants of its metal complexes with Cu(II), Ni(II), Zn(II), Co(II) and Cd(II) are determined potentiometrically at 25.0°C and ionic strength 0.10 M (KCl), with the stability order Cu(II) > Ni(II) > Zn(I1) > CoII) > Cd(II)[21].

The stability constant values of the following ligands were also determined and reported by various workers earlier, which includes 5-bromo -2 hydroxy acetophenone[22]; 3-chloro-2-hydroxy acetophenone[23]; amino-acids[24]; biologically active molecules[25]; cetrizine and benzoic acid[26]; metformin[27-29]; ciprofloxacin[30]; pyridoxine[31]; gabapentin[32]; atenolol[33]; nicotinamide[34]; nicotinic acid[35]; mandelic acid[36]; isoniazid[37,38]; imipramine[39,40]; gallic acid[41] and adenosine drug[42].

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