Equilibrium Studies of the Ternary Complex Systems M^{n+} + Dipicolinic Acid + *N*-(2-Acetamido)iminodiacetic Acid or Amino Acids

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Complex formation in the ternary systems M^{n+} + dipicolinic acid + amino acids or *N*-(2-acetamido)iminodiacetic acid (H_2ADA), where $M^{n+} = Cu^{II}$, Zn^{II}, Ni^{II}, Co^{II}, Hg^{II}, Cd^{II}, Pb^{II}, UO_2^{II}, Y^{III}, and Ce^{III}, have been investigated pH-metrically in aqueous media at 25 °C and at ionic strength $I = 0.10$ mol dm^{-3} (KNO_3). The stability constants of the different binary and ternary complexes formed in such systems have been determined and discussed in terms of the nature of both metal ion and secondary ligand (amino acids or H_2ADA). It was deduced that, except in the case of dicarboxylic amino acid, the stability of the ternary complex is lower than that of the corresponding binary M^{n+} + amino acid or H_2ADA.

Introduction

Mixed ligand complexes play a significant role in biological processes as exemplified by many instances in which enzymes are known to be activated by metal ions (Sigel *et al.*, 1977). On the other hand, some metal complexes containing 2,6-pyridinedicarboxylic acid showed anti-inflammatory activities (Sing *et al.*, 1986). Carboxylic acid derivatives of pyridine, *N*-(2-acetamido)iminodiacetic acid (H_2ADA), and amino acids have a considerable activity in biological and chemical applications (Bridger *et al.*, 1982). Results have been published for the ternary metal complexes containing both H_2ADA and amino acid ligands (Mahmoud *et al.*, 1989; Nakon *et al.*, 1986). Binary complexes of 2,6-pyridinedicarboxylic acid have been studied (Bridger *et al.*, 1982; Aruga, 1979; Sarin and Munshi, 1977; Chandra, 1977; Shelke and Jahagirdar, 1979; Nathan *et al.*, 1989; Sandro *et al.*, 1978), but there have been few studies of equilibria in ternary systems containing this ligand with amino acids (Shelke and Jahagirdar, 1978), and no measurements appear to have been made on ternary systems containing dipicolinic acid and H_2ADA. In this paper a systematic study on the complex formation among some metal ions (Cu^{II}, Zn^{II}, Ni^{II}, Co^{II}, Hg^{II}, Cd^{II}, Pb^{II}, UO_2^{II}, Y^{III}, and Ce^{III}) and 2,6-pyridinedicarboxylic acid (dipicolinic acid), H_2L, as a primary ligand and some amino acids (aspartic, asparagine, and serine) as well as H_2ADA as secondary ligands in aqueous media has been carried out pH-metrically. The study involves the determination of the formation constants of the different 1:1 binary and 1:1:1 ternary complexes formed in such systems using the Irving and Rossotti technique (Irving and Rossotti, 1953, 1954). The stability of the ternary complexes formed has been examined and discussed in terms of the nature of both the metal ion and secondary ligands used as well as in relation to that of the corresponding binary complexes.

Experimental Section

Materials and Solutions. Pyridine-2,6-dicarboxylic acid (dipicolinic acid), amino acids, and *N*-(2-acetamido)iminodiacetic acid (H_2ADA) were analytical grade (BDH) products with a high purity and were used without further purification. All other chemicals used were of A.R. grade. Solutions of Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Hg^{II}, Cd^{II}, UO_2^{II}, Pb^{II}, Y^{III}, and Ce^{III} were prepared from their nitrate salts. Stock solutions (2×10^{-2} mol dm^{-3}) of the dipicolinic acid, amino acids, and metal salts were prepared in CO_2-free doubly distilled water. CO_2-free NaOH solution (≈0.20 mol dm^{-3}) was prepared and standardized by a standard potassium hydrogen phthalate solution. However, since the solubility of the free acid H_2ADA in pure aqueous media is very small, the monosodium salt was prepared by titration with a standard NaOH solution. HNO_3 solution (≈0.10 mol dm^{-3}) was prepared and used after standardization. A stock solution (0.20 mol dm^{-3}) of KNO_3 was prepared in doubly distilled water and used as a supporting electrolyte. The required concentrations were then obtained by an accurate dilution.

pH-metric Titration. Numerous titrations of the different M^{n+} + H_2L and/or amino acids or $(HADA)^-$ mixtures in a 1:1:1 molar ratio (1×10^{-3} mol dm^{-3} for each) with a relatively concentrated standard CO_2-free NaOH solution were performed at 25 °C. A constant ionic strength, $I = 0.10$ mol dm^{-3} (KNO_3), was maintained, and the total volume was kept constant (50 cm^3). The pH measurements were carried out with an Orion 701A digital pH meter accurate to ±0.005 pH unit. The accuracy of the pH meter was checked by making use of buffers with pH values of 4.008 and 9.180 at 25 °C. The different solutions titrated can be represented according to the following scheme: HNO_3 + KNO_3 (a); solution a + an amino acid or $(HADA)^-$ (b); solution b + M^{n+} (c); solution a + dipicolinic acid (d); solution d + M^{n+} (e); solution e + an amino acid or $(HADA)^-$ (f). The equations used for various calculations were programmed using an IBM computer.

Results and Discussion

Figure 1 displays a typical set of experimental titration curves obtained according to the sequence described in the Experimental Section for the different metal ions + dipicolinic acid (H_2L) + amino acids or $(HADA)^{1-}$ systems

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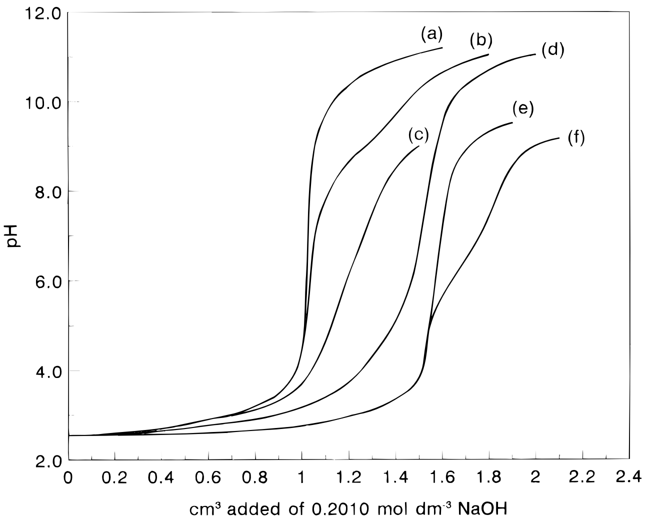

Figure 1. pH-metric titration curves for the Ni^{II} + H_2L + asparagine system at 25 °C and $I = 0.10$ mol dm^{-3} KNO_3: (a) 0.0042 mol dm^{-3} HNO_3; (b) solution a + 0.001 mol dm^{-3} asparagine; (c) solution b + 0.001 mol dm^{-3} Ni^{II}; (d) solution a + 0.001 mol dm^{-3} H_2L; (e) solution d + 0.001 mol dm^{-3} Ni^{II} and (f) solution e + 0.001 mol dm^{-3} asparagine.

studied. Examination of the different titration curves obtained reveals that the different 1:1 binary $M^{n+} + H_2L$ complexes are formed at lower pH values (2.50−2.90). This is attained from the divergence of each of the 1:1 binary $M^{n+} + H_2L$ titration curves from that of the corresponding free acid (H_2L) solution. With respect to the titration curves of the 1:1 binary M^{n+} + amino acids complexes, these complexes begin to form in the pH ranges 3.60−4.30 and 3.20−4.20 for mono- and dicarboxylic amino acids, respectively. For the 1:1 binary $[M(ADA)]^{(n-2)+}$ complexes, the titration curves indicate that they begin to form at a pH ranging from 2.60 to 3.50. Moreover, except in the case of the [Cu(ADA)] titration curve, investigation of the titration curves obtained of the different 1:1 binary M^{n+} + $(HADA)^{-}$ solutions does not show any buffer zones at high pH values (up to pH ≈ 10), denoting no possibility for the deprotonation of the amide proton in the formed $[M(ADA)]^{(n-2)+}$ complexes (Aruga, 1979; Lance *et al.*, 1983). On the other hand, except in the case of Pb^{II} + serine, the titrated solutions of all other different 1:1 binary M^{n+} + ligand complexes do not show a precipitate in the pH range of complex formation, denoting that hydrolysis reactions do not interfere in the determination of the formation constants for these binary complexes. However, the titration curve of the 1:1 binary Pb^{II} + serine complex solution shows a precipitate at a relatively low pH value. This is attributed to the formation of hydroxo complex species resulting from the possible hydrolysis of this complex. Thus, further study beyond the precipitation point could not be possible for this complex.

The titration curves (f) obtained for the different 1:1:1 ternary complexes and that of the 1:1 binary complex $[M(L)]^{(n-2)+}$, curve e, are strongly overlapped at the lower pH values where the binary complex $[M(L)]^{(n-2)+}$ is formed, indicating that the amino acids (aa) and $(HADA)^{1-}$ ligands do not bind with the metal ion in this pH range. Generally, at a high pH value which is largely dependent on the nature of the two secondary ligands [amino acids or $(HADA)^{-}$] as well as the nature of the metal ion used, a divergence of the ternary titration curve (f) from that of the binary $[M(L)]^{(n-2)+}$ titration curve (e) is observed. This behavior indicates that the binary complex $[M(L)]^{(n-2)+}$ is firstly formed and it coordinates with an amino acid or $(ADA)^{2-}$ moiety as a secondary ligand, affording the ternary complex in a stepwise manner as represented by the following equations:

$$M^{n+} + H_2L \rightleftharpoons [M(L)]^{(n-2)+} + 2H^+$$

$$[M(L)]^{(n-2)+} + (aa)^{m-} \rightleftharpoons [M(L)(aa)]^{(n-2-m)+}$$

$$[M(L)]^{(n-2)+} + (HADA)^{-} \rightleftharpoons [M(L)(ADA)]^{(n-4)+} + H^+$$

where M = Cu^{II}, Zn^{II}, Ni^{II}, Co^{II}, Cd^{II}, Hg^{II}, Pb^{II}, UO_2^{II}, Y^{III}, and Ce^{III}, $m = 1$ for monocarboxylic amino acids, and $m = 2$ for the dicarboxylic amino acid (aspartic acid).

It is assumed that the secondary ligand [amino acids or $(HADA)^{-}$] would combine with $[M(L)]^{(n-2)+}$ binary complex species in the ternary systems as it does with $[M(H_2O)_X]^{n+}$ in a binary system. The divergence of curve f from curve e on using the dicarboxylic amino acid (aspartic) and $(HADA)^{-}$ as secondary ligands occurred at lower pH values relative to that on using the monocarboxylic amino acids. This behavior could be ascribed to the available additional coordination site that can be exerted by the additional carboxylate group which tends to promote the binding of these ligands to the binary $[M(L)]^{(n-2)+}$ complex even at lower pH values. The binary $[M(L)]^{(n-2)+}$ complexes are stable up to the pH value where the attachment of the secondary ligand takes place, forming the ternary mixed ligand complexes.

On the other hand, the different titration curves of the 1:1:1 ternary system $M^{n+} + H_2L + (HADA)^{-}$ do not show any buffer zones at high pH values, suggesting that the formed $[M(L)(ADA)]^{(n-4)+}$ ternary complexes have no tendency to undergo deprotonation of the amide group belonging to the secondary ligand $(HADA)^{-}$. Further, all ternary metal complex solutions under investigation do not show any precipitation up to the pH value corresponding to complete complex formation. This reveals that the different 1:1:1 mixed ligand ternary complexes studied have no tendency to form hydroxo complex species.

Formation Constants. The horizontal distance between curves e and f in the pH range of ternary complex formation was measured and used for the calculation of $\bar{n}_{mix}$ [average number of secondary ligand molecules (amino acids or ADA) bound to one binary $[M(L)]^{(n-2)+}$ complex]. The equation used for the calculation of $\bar{n}_{mix}$ was the same as reported in the original papers (Irving and Rossotti, 1953, 1954):

$$\bar{n}_{mix} = \frac{(V_f - V_e)\,[C_b + C_a + C_L(y - \bar{n}_H)]}{(V_o + V_e)\bar{n}_H C_M}$$

Here C_M is the concentration of $[M(L)]^{(n-2)+}$ which is equal to the concentration of M^{n+} used, C_L is the concentration of a ligand, y = the number of dissociable protons of the secondary ligand ($y = 1$ in the case of monocarboxylic amino acids and $(HADA)^{-}$ and $y = 2$ in the case of aspartic acid), and V_o = the original volume (50 cm^3). V_f and V_e are the volumes of alkali (NaOH) consumed to reach the same pH values in curves f and e, respectively. C_b and C_a are the concentrations of NaOH and HNO_3, respectively. $\bar{n}_H$ values (the average number of protons associated with the ligand) for secondary ligands at different pH values were available from the determination of their formation constants. The $\bar{n}_{mix}$ values do not exceed unity, indicating that only one secondary ligand molecule combines with the complex $[M(L)]^{(n-2)+}$. The free secondary ligand exponent, pL_{mix}, was calculated from the values of $\bar{n}_{mix}$ by the equation

$$\mathrm{pL}_{\mathrm{mix}} = \log\left(\frac{\sum_{y=0}^{y=1\text{ or }2}\beta_y^{\mathrm{H}}\left(\frac{1}{10^{\mathrm{B}}}\right)}{C_{\mathrm{L}} - \bar{n}_{\mathrm{mix}}C_{\mathrm{M}}}\,\frac{V_{\mathrm{o}} - V_{\mathrm{f}}}{V_{\mathrm{o}}}\right)$$

where β_y^{H} are the formation constant values of the applying secondary ligands and B is the pH value. All other terms have the same meanings as defined above.

The second acid dissociation constants of all secondary ligands studied as well as the third acid dissociation constant of aspartic acid were determined from the titration curves a and b, making use of the Irving and Rossotti method (Irving and Rossotti, 1953, 1954). However, the first acid dissociation constant values of the secondary ligands as well as that of the primary ligand are very low (≈2.00), occurring only in strongly acidic solutions; therefore, they were not used in the calculations. The second acid dissociation constant for dipicolinic acid (H_2L) has been determined from the titration curves a and d. Generally, the obtained values are in good agreement with the literature values (Shelke and Jahagirdar, 1978, 1979; Albert and Serjeant, 1984; Weast, 1973; Perrin and Dempsey, 1974).

The formation constants of the different binary complexes (Table 1) were determined by applying the original equations of Irving and Rossotti (Irving and Rossotti, 1953, 1954) to the binary complex solution systems (curves b, c and d, e for $[\mathrm{M(aa)}]^{(n-m)+}$ or $[\mathrm{M(ADA)}]^{(n-2)+}$ and $[\mathrm{M(L)}]^{(n-2)+}$, respectively.

The mean log $K^{\mathrm{M}}_{\mathrm{M(L)}}$, log $K^{\mathrm{M}}_{\mathrm{M(aa)\ or\ (ADA)}}$, and log $K^{\mathrm{M(L)}}_{\mathrm{M(L)(aa)\ or\ (ADA)}}$ values obtained from the corresponding experimental formation curves using the average value and straight line methods along with the error as obtained by applying least-squares fits are given in Tables 1 and 2. However, the stability constant of the binary $\mathrm{Pb^{II}}$ + serine complex could not be calculated due to the precipitation of the complex at a pH value lower than that corresponding to $\bar{n} = 0.50$. On the other hand, the stability constants of 1:1:1 ternary $\mathrm{Y^{III}}$ + H_2L + serine and + asparagine and $\mathrm{Ce^{III}}$ + H_2L + serine could not be calculated due to the small divergence of curve f from curve e. Some of the log K values of the binary complexes studied are in good agreement with the literature values, where the obtained log K values for $[\mathrm{Zn^{II}(ADA)}]$, $[\mathrm{Ni^{II}}$(aspartic acid)], $[\mathrm{Co^{II}}$(aspartic acid)], and $[\mathrm{Co^{II}}$(serine)] are in good accordance with the corresponding literature values 6.85, 7.35, 6.20, and 4.50, respectively (Mahmoud *et al.*, 1989). Our log K values obtained for $[\mathrm{UO_2^{II}(L)}]$, $[\mathrm{UO_2^{II}}$(aspartic acid)] and $[\mathrm{Hg^{II}}$(aspartic acid)] binary complexes are consistent with the log K values 5.44 and 8.71 (Shelke and Gahagirdar, 1978) and 7.14 (Martel and Sillen, 1971) reported for these complexes. Moreover, the values 8.10, 5.80, and 8.00 (Abd El-Gaber *et al.*, 1992) reported for the binary complexes $[\mathrm{Cu^{II}}$(serine)], $[\mathrm{Ni^{II}}$(serine)], and $[\mathrm{Cu^{II}}$(asparagine)], respectively, as well as the values 8.81, 5.62, and 4.50 (Boraei and Abd Alla, 1993) for $[\mathrm{Cu^{II}}$(aspartic acid)], $[\mathrm{Ni^{II}}$(asparagine)], and $[\mathrm{Co^{II}}$(asparagine)] complexes are reproduced in our own experiments (cf. Table 1).

The data cited in Tables 1 and 2 show that the stability constants of the binary and ternary complexes of the same metal ion, in terms of the nature of the secondary ligand, follow the order aspartic acid ($\mathrm{p}K_{\mathrm{a2}} = 3.86$, $\mathrm{p}K_{\mathrm{a3}} = 9.80$) > $(\mathrm{HADA})^-$ ($\mathrm{p}K_{\mathrm{a2}} = 6.62$) > serine ($\mathrm{p}K_{\mathrm{a2}} = 9.21$) > asparagine ($\mathrm{p}K_{\mathrm{a2}} = 8.80$) (Albert and Serjeant, 1984; Weast, 1973; Perrin and Dempsey, 1974). This behavior can be explained on the basis of the effective basicity of the conjugate base of these ligands as well as a steric effect. Generally, increasing the length of the ligand chain would result in more strain on its bending, i.e., relatively low stability. In

Table 1. Acid Dissociation Constant Values of the Ligands Used in This Study and the Stability Constants of Their 1:1 Binary Metal Complexes Formed at 25 °C and I = 0.10 mol dm^{-3} ($\mathrm{KNO_3}$)

			log $K^{\mathrm{M}}_{\mathrm{M(L)}}$, log $K^{\mathrm{M}}_{\mathrm{M(ADA)}}$, and log $K^{\mathrm{M}}_{\mathrm{M(aa)}}$									
ligand	pK_{a2}	pK_{a3}	$\mathrm{UO_2}$(II)	Cu(II)	Zn(II)	Ni(II)	Co(II)	Hg(II)	Cd(II)	Pb(II)	Y(III)	Ce(III)
2,6-pyridinedicarboxylic acid (dipicolinic acid)	4.80 ± 0.02		5.70 ± 0.10	5.66 ± 0.08	5.63 ± 0.05	5.60 ± 0.05	5.54 ± 0.07	5.45 ± 0.10	5.31 ± 0.09	5.26 ± 0.10	5.56 ± 0.09	5.50 ± 0.03
$(\mathrm{HADA})^-$	6.52 ± 0.04		6.89 ± 0.03		6.86 ± 0.02	6.73 ± 0.05	6.50 ± 0.12	6.44 ± 0.03	6.34 ± 0.04	5.89 ± 0.11	7.05 ± 0.12	6.08 ± 0.05
aspartic acid	3.90 ± 0.04	9.82 ± 0.02	8.89 ± 0.03	8.85 ± 0.02	8.01 ± 0.02	7.41 ± 0.05	6.74 ± 0.04	6.72 ± 0.05	6.62 ± 0.06	6.08 ± 0.10	8.42 ± 0.02	8.70 ± 0.06
serine	9.25 ± 0.03		8.41 ± 0.01	8.16 ± 0.03	6.40 ± 0.04	5.80 ± 0.07	4.58 ± 0.06	4.42 ± 0.08	4.13 ± 0.08		5.53 ± 0.06	5.21 ± 0.03
asparagine	8.90 ± 0.02		8.12 ± 0.05	8.05 ± 0.03	5.82 ± 0.03	5.57 ± 0.06	4.38 ± 0.07	4.16 ± 0.07	4.11 ± 0.04	3.71 ± 0.12	5.46 ± 0.10	5.14 ± 0.02

Table 2. Formation Constants of the Ternary Complexes Formed at 25 °C and $I = 0.10$ mol dm^{-3} (KNO$_3$) as Well as the Values of Δ log *K*

			$\log K^{\mathrm{M(L)}}_{\mathrm{M(L)(aa)}}$					
	$\log K^{\mathrm{M(L)}}_{\mathrm{M(L)(ADA)}}$		aspartic acid		serine		asparagine	
metal ion	log *K*	Δ log *K*	log *K*	Δ log *K*	log *K*	Δ log *K*	log *K*	Δ log *K*
UO_2(II)	6.79 ± 0.06	−0.10	9.15 ± 0.03 (9.21)[a]	+0.17	5.99 ± 0.08	−2.42	4.97 ± 0.10	−3.15
Cu(II)	6.69 ± 0.05		8.89 ± 0.05	+0.04	5.26 ± 0.07	−2.90	4.62 ± 0.11	−3.43
Zn(II)	5.83 ± 0.07	−1.03	8.59 ± 0.02	+0.58	5.12 ± 0.05	−1.28	4.22 ± 0.09	−1.60
Ni(II)	5.18 ± 0.06	−1.55	8.47 ± 0.01	+1.06	4.76 ± 0.06	−1.40	4.12 ± 0.12	−1.05
Co(II)	4.83 ± 0.09	−1.67	8.40 ± 0.02	+1.66	4.11 ± 0.11	−0.47	4.07 ± 0.08	−0.11
Hg(II)	4.38 ± 0.11	−2.06	8.37 ± 0.10	+1.65	4.08 ± 0.11	−0.34	4.01 ± 0.06	−0.15
Cd(II)	4.24 ± 0.10	−2.10	8.12 ± 0.01	+1.50	3.78 ± 0.12	−0.35	3.70 ± 0.12	−0.41
Pb(II)	3.85 ± 0.12	−2.04	7.48 ± 0.08	+1.40	3.80 ± 0.11		3.53 ± 0.09	−0.19
Y(III)	6.49 ± 0.10	−0.56	8.94 ± 0.02	+0.52				
Ce(III)	5.70 ± 0.08	−0.90	8.83 ± 0.03	+0.46			4.80 ± 0.08	−0.39

[a] Shelke and Jahagirdar (1978).

addition, the stability of the different binary and ternary complexes containing the dicarboxylic amino acid (aspartic acid) is higher than that of the corresponding one containing monocarboxylic amino acids (serine and asparagine). This can be ascribed primarily to the effective high basicity of aspartic acid, i.e., a good σ-donor, where it can probably act as a tridentate ligand (NOO donor) whereas monocarboxylic amino acids act only as bidentate ligands (NO donors). On the other hand, the observed higher stability of the different complexes containing the ADA moiety relative to that of the corresponding ones containing monocarboxylic amino acids can be attributed to the possibility of the former ligand (ADA) to act as a tridentate ligand (NOO ligand). Furthermore, the formation of two chelate rings in the complex containing aspartate or ADA moieties accounts for their relatively high stability.

The stability of the ternary complex compared to that of the corresponding binary M^{n+} + amino acid or + ADA complex is expressed in terms of Δ log *K*. From Tables 1 and 2, except for the case of aspartic acid, the stability of the ternary complex of the same metal ion is lower than that of the corresponding binary complex; i.e., Δ log *K* is negative. This behavior can be explained on the basis of the principle that there are fewer sites available for bonding on the binary $[M(L)]^{(n-2)+}$ complex than on the aquatic M^{n+}. Thus, the secondary ligand is expected to bind the $[M(L)]^{(n-2)+}$ complex with a smaller formation constant than that with the aquatic M^{n+}. The observed positive value of Δ log *K* for the different 1:1:1 ternary complexes containing the dicarboxylic amino acid (aspartic acid) can be ascribed to the fact that aspartic acid is more prone to show complex formation. This is due to the effective high basicity of this ligand (i.e., its good σ-donor character) as well as its tendency to act as an NOO tridentate ligand, leading to the formation of two metal chelate rings (as discussed above). However, the observed lower stability of the ternary complexes containing the ADA moiety relative to that of the corresponding $[M(L)]^{(n-2)+}$ binary complex (Δ log *K* is negative), though ADA can act as an NOO tridentate ligand, forming two metal chelate rings, can be attributed to the relatively low basicity of this ligand ($pK_{a2} = 6.62$) (Perrin and Dempsey, 1974). Therefore, one can conclude that the basicity of the secondary ligand as well as the structure of the complex formed has a significant role in determining the stability of the mixed ligand ternary complex.

The stability constants of the binary and ternary complexes of the divalent oxygenated cation $[UO_2^{II}]$ have higher values than those of the other divalent cations. This may be attributed to the bonded oxygen atoms which may increase the electrostatic attraction between the metal ion and the coordinated ligand which overcome the expected steric hindrance offered by the oxygen of the oxygenated cation (Abdel-Moez *et al.*, 1990). Such behavior was observed for other metal complexes of oxygenated cations (Abdel-Moez *et al.*, 1990; Trujillo and Brito, 1956). The results in Tables 1 and 2 reveal that the stabilities of the different binary or ternary complexes in the systems under investigation, in terms of the nature of the metal ion, follow the order Cu > Zn > Ni > Co > Hg > Cd > Pb for the divalent metal ions and Y > Ce for the trivalent metal ions. This order is in good agreement with the order of stabilities of such metal ion complexes (Grinberg and Yatsimerski, 1952; Irving and Williams, 1953; Cotton and Wilkenson, 1972).

Literature Cited

Abd El-Gaber, A. A.; Saleh, M. B.; Ahmed, I. T. Potentiometric Studies on the Ternary Complex Systems: Metal(II)-Salicylic Acid-Amino Acids. *J. Indian Chem. Soc.* **1992**, *69*, 17−20.

Abdel-Moez, M. S.; Stefan, S. L.; El-Behairy, M. M.; Mashely, M. M.; El-Shetary, B. A. Studies on Complexes of VO(II), Mn(II), Cu(II), Ni(II), Co(II), Zn(II), Fe(III) and UO_2(II) with Hydrazone β-Diketone Ligands. *Can. J. Chem.* **1990**, *68*, 774−781.

Albert, A.; Serjeant, E. P. *The determination of Ionization Constants*, 3rd ed.; Chapman and Hall: London, New York, 1984; pp 167−173.

Aruga, R. Coordinating Properties of Pyridinecarboxylate Anions with Metals in Aqueous Solution. *J. Inorg. Nucl. Chem.* **1979**, *41*, 845−848.

Boraei, A. A. A.; Abd Alla, E. M. Stability Constants of the Ternary Complexes System: M(II)-Amino Acids-Quinolines. *J. Indian Chem. Soc.* **1993**, *70*, 197−201.

Bridger, K.; Patel, R. C.; Matijevic, E. Thermodynamics and Kinetics of Complexation of Iron(III) Ion by Picolinic and Dipicolinic Acids. *Polyhedron* **1982**, *1*, 269−275.

Chandra, T. N. Studies of Complex Compounds of Uranium(IV) and Uranium(VI) with Pyridine and Quinoline Carboxylic Acid. Part 1. *J. Coord. Chem.* **1977**, *7*, 9−11.

Cotton, F. A.; Wilkenson, C. *Advanced Inorganic Chemistry*; Wiley (Eastern): New Delhi 1972; p 569.

Grinberg, A. A.; Yatsimerski, K. B. The Periodic Law of D. I. Mendeleev and the Stability of Complex Compounds. *Bull. Acad. Sci., USSR Div. Chim. Sci.* **1952**, 239−244.

Irving, H.; Rossotti, H. S. Methods for Computing Successive Stability Constants From Experimental Formation Curves. *J. Chem. Soc.* **1953**, 3397−3405.

Irving, H.; Rossotti, H. S. The Calculation of Formation Curves of Metal Complexes From pH-Titration Curves in Mixed Solvents. *J. Chem. Soc.* **1954**, 2904−2910.

Irving, H. M.; Williams, R. J. P. Stability of Transition Metal Complexes. *J. Chem. Soc.* **1953**, 3192−3210.

Lance, E. A.; Rhodes, W. C.; Nakon, R. Free Metal Ion Depletion by "Good's" Buffers III. N-(2-Acetamido)IminoDiacetic Acid, 2:1 Complexes With Zinc(II), Cobalt(II), Nickel(II) and Copper(II); Amide Deprotonation by Zn(II), Co(II) and Cu(II). *Anal. Biochem.* **1983**, *133*, 492−501.

Mahmoud, M. R.; Azab, H. A.; Mansour, H.; Mohamed, A. H. Potentiometric Studies on the Ternary Complex Systems: M(II)-N-(2-Acetamido)IminoDiacetic Acid-Amino Acids. *Chem. Scr.* **1989**, *29*, 347−350.

Martel, A. E.; Sillen, L. G. *Stability Constants of Metal Ion Complexes*; The Chemical Society: London, 1971; pp 339, 343, 504.

Nakon, R.; Krishnamoorthy, C. R.; Townshend, S.; Grayson, J. Direct Evidence for an S_N1CB Mechanism III. Observations of Deprotonated Mixed Ligand Chelates of N-Acetamidoiminodiacetatocopper(II). Evidence for the Intermediate. *Inorg. Chim. Acta* **1986**, *124*, L5−L7.

Nathan, L. C.; Zapien, D. C.; Mooring, A. M.; Doyle, C. A.; Brown, J. A. Anionic 2,6-Pyridinedicarboxylate Complexes with Some Divalent First-Row Transition Metals. *Polyhedron* **1989**, *8*, 745−748.

Perrin, D. D.; Dempsey, B. *Buffer for pH and Metal Ion Control*; Chapman and Hall: London, 1974; p 160.

Sandro, D.; Livio, B.; Rodolfo, G.; Eloise, C. Preparation and Characterization of Some Pyridine-2,6-dicarboxylatothorium(IV) Complexes. *Transition Met. Chem.* **1978**, *3*, 351−354.

Sarin, R.; Munshi, K. N. Stepwise Stability Constants and Thermodynamic Functions of In(III) Complexes with Some Substituted Derivatives of Quinoline and Pyridine. *Indian J. Chem.* **1977**, *15A*, 327−329.

Shelke, D. N.; Jahagirdar, D. V. Ternary Chelates of Zn(II) with Some Biological Active Ligands. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1635−1638.

Shelke, D. N.; Jahagirdar, D. V. Ternary Complexes: Equilibrium Studies of Mixed-Ligand Chelates of Uranyl Ion with Aspartic and Glutamic Acids as Primary Ligands and Some Dicarboxylic Acids as Secondary Ligands. *Indian J. Chem.* **1978**, *16A*, 60−62.

Sigel, H.; Fisher, B. E.; Prijs, B. Biological Implications From the Stability of Ternary Complexes in Solution. 1. Mixed-Ligand Complexes With Manganese(II) and Other 3d Ions. *J. Am. Chem. Soc.* **1977**, *99*, 4489−4495.

Singh, L.; Mohan, G.; Parashar, R. K.; Tripathi, S. P.; Sharma, R. C. Studies on Anti-inflammatory Activity of Some Lanthanon Complexes of Bioactive Organic Molecules. *Curr. Sci.* **1986**, *55*, 846−848.

Trujillo, R.; Brito, F. Complex of Quadrivalent Vanadium. III. Complexes With the β-Diketones (a) Acetylacetone. *An. R. Soc. Esp. Fis. Quim.* **1956**, *52B*, 407−416.

Weast, R. C. *Handbook of Chemistry and Physics*; CRC Press: Cleveland, OH, 1973; pp 126−129.

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