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Formation Constants of Ternary Complexes Involving Some Metal Ions, Tricine, Dicarboxylic Amino Acids, as Well as *N*-(2-Acetamido)iminodiacetic Acid and 3-Amino-5-mercapto-1,2,4-triazole

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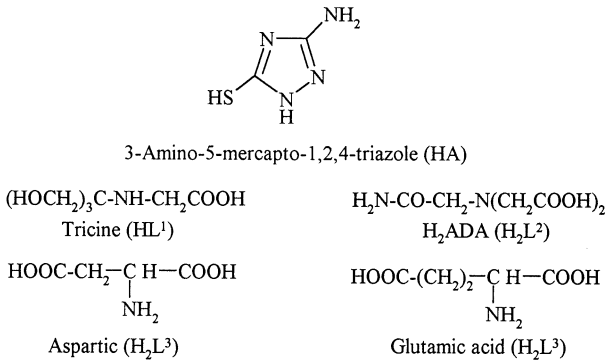
Solution equilibria of the ternary systems of Zn^{II}, Ni^{II}, Co^{II}, Cd^{II}, Pb^{II}, UO_2^{II}, Ce^{III}, and La^{III} with *N*-[tris(hydroxymethyl)methyl]glycine (tricine), *N*-(2-acetamido)iminodiacetic acid (H_2ADA), and dicarboxylic amino acids (aspartic and glutamic) as primary ligands and 3-amino-5-mercapto-1,2,4-triazole as a secondary ligand have been studied pH-metrically at (25 ± 0.1) °C, and a constant ionic strength $I = 0.1$ mol dm^{-3} (KNO_3). The formation of various binary and ternary complexes has been inferred from the corresponding titration curves. The stability constants of the different complexes are determined and discussed in terms of the nature of both the ligands and metal ions.

Introduction

Considerable interest in the synthesis of the complexes of some transition metals with 1,2,4-triazoles has increased. Because 1,2,4-triazoles are used to inhibit the growth of tumors and cancer in mammals[1] and to treat the viral as well as bacterial infection.[2] Recently, the importance of their metal complexes in the biological fields was reported.[3] The complexes of 3-amino-5-mercapto-1,2,4-triazole with Co^{II} and Ni^{II} were previously investigated in aqueous solutions by means of the pH-metric method and absorption spectra.[4] The metal complexes of this ligand with Hg^{II}, Ag^{I}, Co^{II}, Ni^{II}, Zn^{II}, and Cd^{II} were also prepared and characterized on the basis of chemical analysis, IR, and visible spectroscopy.[5−7] It has been reported that 3-amino-5-mercapto-1,2,4-triazole has five potential coordination sites: three *N*-cyclic atoms, one exocyclic NH_2 group, and one exocyclic SH group.[5] A number of studies on ternary complex systems including *N*-[tris(hydroxymethyl)methyl]glycine (tricine), *N*-(2-acetamido)iminodiacetic acid (H_2ADA), and dicarboxylic amino acids (aspartic and glutamic) appeared in the literature.[8−20] However, a survey the literature reveals that no study has been made on the complexes containing these ligands and 3-amino-5-mercapto-1,2,4-triazole. The present paper is devoted to the study of the ternary 1:1:1 complexes of some divalent metal ions (Zn^{II}, Ni^{II}, Co^{II}, Cd^{II}, and Pb^{II}) and some heavy metal ions (UO_2^{II}, Ce^{III}, and La^{III}) with tricine (HL^1), H_2ADA (H_2L^2), and dicarboxylic amino acids (aspartic and glutamic) (H_2L^3) as primary ligands and 3-amino-5-mercapto-1,2,4-triazole (HA) as a secondary ligand. The structures of the ligands used are seen in Scheme 1.

The stability constants of various binary and ternary complexes formed were determined and are discussed in relation to the nature of the ligands and metal ion used. Moreover, the stability of the ternary metal complexes are discussed in relation to that of the corresponding binary metal complexes of the primary ligands.

Scheme 1



Experimental Section

Materials and Solutions. Tricine (HL^1) and amino acids (aspartic and glutamic, H_2L^3) were purchased from (Sigma), and H_2ADA (H_2L^2) from Aldrich and 3- amino-5-mercapto-1,2,4-triazole (HA) from Janssen were analytical grade products. The purity of these compounds exceeded 99%, as verified by the TLC method and were used without further purification. All other chemicals used were of A. R. analytical-grade (BDH, England) reagents.

Solutions of Zn^{II}, Ni^{II}, Co^{II}, Cd^{II}, Pb^{II}, UO_2^{II}, Ce^{III}, and La^{III} were prepared from their nitrate salts. Concentrations of the metal ions were checked using the standard method.[21] Stock solutions (5×10^{-2} mol dm^{-3}) of tricine, dicarboxylic amino acids, 3-amino-5-mercapto-1,2,4-triazole, and metal salts were prepared in CO_2-free doubly distilled water. The uncertainty in the concentrations ranged from 5 to 8%. CO_2-free KOH solution (≈0.20 mol dm^{-3}) was prepared and standardized by a standard solution (0.10 mol dm^{-3}) of potassium hydrogen phthalate. However, because the solubility of the free acid H_2ADA in a pure aqueous medium is very small, the mono sodium salt $(HADA)^{1-}$ was prepared by titration with a standard KOH solution. HNO_3 solution (≈0.10 mol dm^{-3}) was prepared and used after standardization. A stock solution (1.0 mol dm^{-3}) of KNO_3 was also prepared and used as a supporting electrolyte. The required concentrations were obtained by an accurate dilution.

Apparatus. The pH measurements were performed by means of a Metrohm automatic titrator model SM 702

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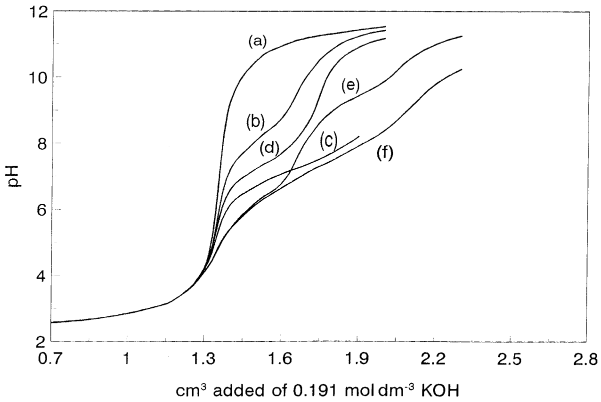

Figure 1. Titration curves of [Ni^{II} + (tricine) + (HA)] at 25 °C and at the constant ionic strength $I = 0.10$ mol dm^{-3} (KNO_3). (a) 0.010 mol dm^{-3} HNO_3, (b) solution a + 0.002 mol dm^{-3} of HA, (c) solution b + 0.002 mol dm^{-3} of Ni^{II}, (d) solution a + 0.002 mol dm^{-3} tricine, (e) solution d + 0.002 mol dm^{-3} of Ni^{II}, and (f) solution e + 0.002 mol dm^{-3} of HA.

(Switzerland) with a combined pH glass electrode equipped with a magnetic stirrer. The accuracy of the instrument was ±0.001 pH unit. The instrument was calibrated using aqueous standard buffers of pH 4.00 (phthalate buffer) and 9.20 (borate buffer). The electrode system was calibrated in terms of hydrogen ion concentrations instead of activities,[22] where a constant ionic strength was used. Thus, all equilibrium constants determined in this work are concentration constants. A water thermostat (Fischer Scientific Isotemp Refrigerated Circulator model 9000) accurate to ±0.1 °C was used to control temperature.

pH Measurements. The pH-metric titrations were carried out in aqueous media, where the following solutions were made from metal ion a primary ligand [HL^1, $(HL^2)^-$, or H_2L^3] and/or HA as a secondary ligand in a 1:1:1 molar ratio (2×10^{-3} mol dm^{-3} of each) titrated with a standard KOH solution at (25 ± 0.1) °C. The titrations were performed in an inert atmosphere where nitrogen gas was bubbled through the titrated solutions before and during the pH measurements. The ionic strength was kept constant (0.10 mol dm^{-3}) using a KNO_3 solution, and a total volume of 25 cm^3 was used for each titration. The different solutions titrated were as follow: (a) (0.010 to 0.012) mol dm^{-3} HNO_3, (b) solution a + 0.002 mol dm^{-3} HA, (c) solution b + 0.002 mol dm^{-3} M^{n+}, (d) solution a + 0.002 mol dm^{-3} HL^1, $(HL^2)^-$ or H_2L^3, (e) solution d + 0.002 mol dm^{-3} M^{n+}, and (f) solution e + 0.002 mol dm^{-3} HA.

Results and Discussion

Figures 1 and 2 display a representative set of experimental titration curves obtained according to the above-described sequence for the different M^{n+} + [HL^1, $(HL^2)^-$, or H_2L^3] + HA systems studied. Examination the titration curve corresponding to the 1:1 binary M^{n+} + HL^1 complex solution displays two inflections after the addition of 1 mol and 3 mol of base per 1 mol of the ligand at pH values 8.5 and 10.5, revealing the stepwise dissociation of one and three protons from coordinated ligand, respectively. This behavior could be interpreted on the basis of the formation of a 1:1 binary complex $[M(L^1)]^{(n-1)+}$ at the addition of 1 mol of base per 1 mol of ligand. The observed buffer zone at the high pH ranges 8.50−10.50 (cf. Figure 1) suggests that the 1:1 binary complex formed having a tendency to undergo deprotonation of coordinated L^1, where two protons are successively released affording the 1:1 binary metal complexes $[M(L^1)]^{(n-3)+}$. Accordingly, one may suggest that tricine acts as an OON tridentate ligand, where it chelates to the metal ion through the carboxylic oxygen and amide nitrogen in addition to one of the $(-CH_2OH)_3$ alcoholic oxygen atoms after deprotonation.

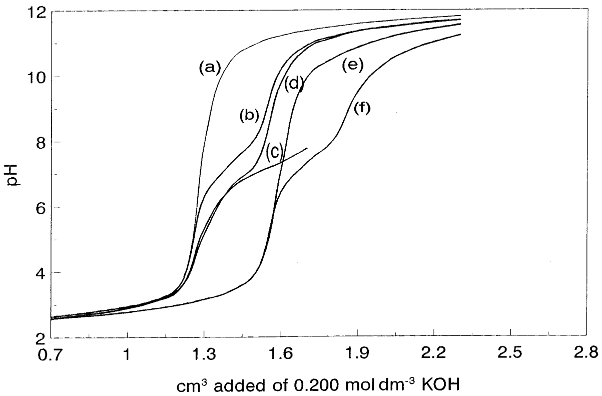

Figure 2. Titration curves of [Ni^{II} + $(HADA)^{1-}$ + (HA)] at 25 °C and at the constant ionic strength $I = 0.10$ mol dm^{-3} (KNO_3). (a) 0.011 mol dm^{-3} HNO_3, (b) solution a + 0.002 mol dm^{-3} of HA, (c) solution b + 0.002 mol dm^{-3} of Ni^{II}, (d) solution a + 0.002 mol dm^{-3} $(HADA)^{1-}$, (e) solution d + 0.002 mol dm^{-3} of Ni^{II}, and (f) solution e + 0.002 mol dm^{-3} of HA.

The titration curve e (Figure 2) indicates that the different 1:1 binary $[M(ADA)]^{(n-2)+}$ complexes are formed at a lower pH range 2.60−3.20. This is attained from the observed divergence of the 1:1 binary M^{n+} + $(HADA)^{1-}$ titration curve (curve e) from that of the free ligand $(HADA)^{1-}$ (curve d). The complex solutions of these binary systems do not show any precipitation up to the pH value (≥6) corresponding to the complete complex formation. This behavior strongly suggests that the ligand $(HADA)^{1-}$ is characterized by a high tendency to form metal complexes. On the other hand, the titration curves obtained of the different binary [M^{n+} + $(HADA)^{1-}$] solutions do not show any buffer zone up to a high pH value, denoting no possibility for the deprotonation of the amide proton of the ligand in the formed $[M(ADA)]^{(n-2)+}$ complexes.[23,24]

From the titration curves of the different binary M^{n+} + H_2L^3 compex solutions studied, it is evident that these complexes begin to form at a pH range of 3.90−5.30, where no buffer zone was observed up to the pH value of complete complex formation. However, the binary complexes of the dicarboxylic acids under investigation with the lanthanide metal ions (La^{III} and Ce^{III}), and the binary complex of glutamic acid with $UO_2{}^{II}$ could not be studied because of the hydrolysis at low pH values.

On the other hand, the titration curve c corresponding to the binary [M^{n+} + HA] complex solutions is diverged from that of the free ligand HA at a pH range of 4.00−6.50, indicating the formation of the binary complexes. The binary metal complex solutions show precipitation due to the interference of hydrolysis reaction at a pH range of 6.50−8.40 depending on the nature of metal ion used. Generally, further study beyond the precipitation point could not be made.

The titration curves f obtained for the different 1:1:1 [M^{n+} + (HL^1), $(HL^2)^{1-}$ or (H_2L^3) + (HA)] ternary complexes and that of the 1:1 binary complex of HL^1, $(HL^2)^{1-}$, or H_2L^3 (curve e) are strongly overlapped at lower pH values, where the binary complex $[M(L^1)]^{(n-1)+}$, $[M(L^2)]^{(n-2)+}$, and $[M(L^3)]^{(n-2)+}$ is formed suggesting that the HA ligand does 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 ligands HL^1, $(HL^2)^{1-}$, and H_2L^3 as well as the nature of the metal ion used, a divergence of the ternary titration curve f from that of the binary complexes (titration curves e) of these ligands is observed. The titration curves f are characterized by an inflection at the addition of 3 mol of base per 2 mol of a primary ligand HL^1 or H_2L^3 and 1 mol of a secondary ligand HA. On the other hand, the titration curves of the ternary complexes involving $(HADA)^{1-}$ as a primary ligand display an inflection at the addition of 2 mol of base per 1 mol of $(HADA)^{1-}$ and 1 mol of HA ligand. This clearly indicates that the primary ligands HL^1, $(HL^2)^{1-}$, and H_2L^3 act as divalent anion ligands, where HA coordinates to the metal ions as a monovalent anion ligand through the exocyclic sulfur after deprotonation. This behavior indicates that the binary complex $[M(L^1)]^{(n-2)+}$, $[M(L^2)]^{(n-2)+}$, or $[M(L^3)]^{(n-2)+}$ is first formed and it coordinates with HA as a secondary ligand, affording the ternary complex in a stepwise manner as represented by the following equation:

$$M^{n+} + HL^1 \Leftrightarrow [\,M(L^1)]^{(n-1)+} + H^+ \tag{1}$$

$$[M(L^1)]^{(n-1)+} \Leftrightarrow [\,M(L^1)]^{(n-2)+} + H^+ \tag{2}$$

$$M^{n+} + (HL^2)^{1-} \Leftrightarrow [ML^2]^{(n-2)+} + H^+ \tag{3}$$

$$M^{n+} + (H_2L^3) \Leftrightarrow [ML^3]^{(n-2)+} + 2H^+ \tag{4}$$

$$\begin{aligned}&[ML^1]^{(n-2)+},\ [ML^2]^{(n-2)+},\ \text{or}\ [ML^3]^{(n-2)+} + HA \Leftrightarrow \\ &\qquad [ML^1A]^{(n-3)+},\ [ML^2A]^{(n-3)+},\ \text{or}\ [ML^3A]^{[n-3)+} + H^+\end{aligned} \tag{5}$$

where $n = 2$ for UO_2^{II}, Zn^{II}, Ni^{II}, Co^{II}, Cd^{II}, and Pb^{II}; $n = 3$ for La^{III} and Ce^{III}; HL^1 = tricine, $(HL^2)^{1-} = (HADA)^-$, H_2L^3 = aspartic or glutamic acid, HA = 3-amino-5-mercapto-1,2,4-triazole.

Consequently, one can suggest that during ternary complex formation the $(HOH_2C)C-$ end of tricine does not participate in chelation where it acts as a bidentate dianion ligand through the carboxylic oxygen and amido nitrogen after deprotonation (i.e., NO ligand).

However, the stability constant of some ternary complexes such as $[UO_2^{II}$, Pb^{II} (aspartate)(HA)], $[UO_2^{II}$, Zn^{II}-(glutamate)(HA)], and $[Ce^{III}$(tricine)(HA)] could not be determined because of the extensive hydrolysis of the ternary complexes at low pH values. Other ternary metal complex solutions under investigation do not show a precipitation up to the pH value corresponding to the complete complex formation, revealing that these 1:1:1 mixed-ligand ternary complexes have no tendency to form hydroxo complex species.

Formation Constants. Part of the information required for determining the metal complex stability constants is the proton−ligand stability constants. Therefore, prior to determining the stability constants of metal−ligand complexes, the ionization constants of the ligands under investigation are determined.

From the titration curves corresponding to solutions a, b, and d, the average number of protons associated per one mole of a ligand (n_H) at several pH values was calculated using the following equation:[25]

$$n_H = \left\{yC_L + \frac{[(V_a - V_b)\ \text{or}\ (V_a - V_d)]C_b}{V_o}\right\}(C_L)^{-1} \tag{6}$$

The pK_a values were calculated from the following relationship:[26]

$$n_H = \beta[H^+]\,(1 + \beta[H^+])^{-1} \tag{7}$$

where β is the proton-ligand formation constant.

The calculated ionization constants of HL^1, $(HL^2)^{1-}$, and H_2L^3 are in fairly good agreement with literature values obtained under similar experimental conditions.[10,18,20] However, the obtained ionization constant value 7.38 for HA is higher than the value 7.28 reported previously[4] because of the difference in the ionic strength used.

Titration curves b, c and d, e were used for the calculation of the stability constants of the binary metal complexes of HA and the primary ligands $[(HL^1, (HL^2)^{1-}$, and $(H_2L^3)]$, respectively. The average number of ligand molecules coordinated to the metal ion (n_b) and the free ligand exponent at several pH values (pL) were calculated by the following equations:[25]

$$n_b = \frac{[(V_c - V_b)\ \text{or}\ (V_e - V_d)][C_b + C_a + C_L\,(y - n_H)]}{[(V_o + V_b)\ \text{or}\ (V_o + V_d)]n_H C_M} \tag{8}$$

$$pL = \log\left\{\frac{\sum_{y=0}^{y=1\ \text{or}\ 2} \beta_y^H\left(\frac{1}{10^B}\right)}{C_L - n_b C_M}\,\frac{V_o + (V_c\ \text{or}\ V_e)}{V_o}\right\} \tag{9}$$

where y is the number of dissociable protons ($y = 2$ for H_2L^3 and 1 for HA, HL^1, and $(HL^2)^{1-}$. C_a, C_b, and C_L are the concentrations of HNO_3, KOH, and a ligand, respectively, and V_0 is the original volume (25 cm^3). V_a, V_b, V_c, V_d, and V_e are the volumes of KOH consumed to reach the same pH values in curves a, b, c, d, and e, respectively. n_H values are the average number of protons associated with a ligand at different pH values were available from the determination of its proton-ligand formation constant. C_M is the initial concentration of the metal ion used. It is worth mentioning that the values of (n_b) do not exceed unity revealing the formation of only 1:1 binary complexes.

The formation constants for the different binary complexes of the ligands HL^1, $(HL^2)^{1-}$, and H_2L^3 are in good agreement with those reported previously under similar conditions.[10,14,18,20,27] However, the formation constant values obtained for the 1:1 binary $[Co(A)]^{1-}$ and $[Ni(A)]^{1-}$ complexes are higher that the corresponding values 1.68 and 2.49 reported previously for Co^{II} and Ni^{II} complexes,[4] respectively. This behavior could be attributed to the difference in the ionic strength, where an ionic strength of 0.5 mol dm^{-3} was used in the previous study.[4]

On the other hand, the horizontal distance between curves e and f (Figures 1 and 2) was measured and used for calculation of the number of the A^{1-} anion as a secondary ligand attached to one binary complex molecule of the primary ligands $[HL^1, (HL^2)^{1-}$, and $H_2L^3]$ (n_{mix}) for a mixed ligand ternary complex. The equation used for such a calculation was the same as reported elsewhere:[25,28,29]

$$n_{mix} = \frac{[(V_f - V_e)]\,[C_b + C_a + C_L\,(y - n_H)]}{(V_o + V_e)n_H C_M} \tag{10}$$

Here C_M is the concentration of the 1:1 binary complexes of the primary ligand which is equal to the concentration of M^{n+} used, C_L is the concentration of the secondary ligand (HA), and y is the number of dissociable protons of HA ($y = 1$). V_f is the volume of KOH consumed to reach the same pH values in curve f. In this case, the n_H values are the average number of protons associated with the secondary ligand HA at different pH values. The n_{mix} do not exceed unity indicating that only one secondary ligand molecule combines with the binary complex of HL^1, $(HL^2)^{1-}$, and

Table 1. Formation Constant Values for the Different 1:1 Binary Metal Complexes[a] Formed at (25.0 ± 0.1) °C and a Constant Ionic Strength $I = 0.10$ mol dm^{-3} (Kno$_3$)

metal ions	$\log K^{\mathrm{M}}_{\mathrm{M(aspt.)}}$	$\log K^{\mathrm{M}}_{\mathrm{M(ADA)}}$	$\log K^{\mathrm{M}}_{\mathrm{M(glu.)}}$	$\log K^{\mathrm{M}}_{\mathrm{M(tricine)}}$	$\log K^{\mathrm{M}}_{\mathrm{M(HA)}}$
$\mathrm{Zn^{II}}$	8.01 ± 0.02	6.85 ± 0.04	5.69 ± 0.02	5.59 ± 0.03	4.01 ± 0.05
$\mathrm{Ni^{II}}$	7.41 ± 0.01	6.70 ± 0.02	5.59 ± 0.03	5.51 ± 0.05	3.09 ± 0.03
$\mathrm{Co^{II}}$	6.74 ± 0.03	6.50 ± 0.05	4.56 ± 0.04	4.49 ± 0.04	2.77 ± 0.06
$\mathrm{Cd^{II}}$	6.62 ± 0.04	6.39 ± 0.01	4.45 ± 0.06	4.35 ± 0.02	2.56 ± 0.04
$\mathrm{Pb^{II}}$	6.08 ± 0.05	5.90 ± 0.02	4.39 ± 0.02	4.25 ± 0.01	2.37 ± 0.08
$\mathrm{UO_2{}^{II}}$	8.45 ± 0.03	7.05 ± 0.01	*b*	6.79 ± 0.04	5.95 ± 0.07
$\mathrm{Ce^{III}}$	*b*	6.76 ± 0.05	*b*	5.40 ± 0.03	4.05 ± 0.04
$\mathrm{La^{III}}$	*b*	6.65 ± 0.02	*b*	4.99 ± 0.05	3.39 ± 0.05

[a] aspt. = aspartic acid, glu. = glutamic acid, ADA = *N*-(2-acetamido)iminodiacetic acid, and HA = 3-amino-5-mercapto-1,2,4-triazole. [b] Could not be determined because of hydrolysis.

Table 2. Formation Constant Values for the Different 1:1:1 Ternary Metal Complexes[a] Formed at (25.0 ± 0.1) °C and a Constant Ionic Strength $I = 0.10$ Mol dm^{-3} (Kno$_3$)

metal ions	$\log K^{\mathrm{M(aspt.)}}_{\mathrm{M(aspt.)(HA)}}$	$\log K^{\mathrm{M(ADA)}}_{\mathrm{M(ADA)(HA)}}$	$\log K^{\mathrm{M(glu.)}}_{\mathrm{M(glu.)(HA)}}$	$\log K^{\mathrm{M(tricine)}}_{\mathrm{M(tricine)(HA)}}$
$\mathrm{Zn^{II}}$	3.90 ± 0.10	3.75 ± 0.08	*b*	3.59 ± 0.11
$\mathrm{Ni^{II}}$	3.82 ± 0.09	3.64 ± 0.10	3.61 ± 0.08	3.50 ± 0.12
$\mathrm{Co^{II}}$	3.75 ± 0.12	3.60 ± 0.11	3.54 ± 0.10	3.45 ± 0.12
$\mathrm{Cd^{II}}$	3.57 ± 0.12	3.45 ± 0.14	3.39 ± 0.12	3.30 ± 0.13
$\mathrm{Pb^{II}}$	*b*	3.40 ± 0.15	3.33 ± 0.12	3.25 ± 0.15
$\mathrm{UO_2{}^{II}}$	*b*	3.99 ± 0.07	*b*	3.65 ± 0.10
$\mathrm{Ce^{III}}$	3.69 ± 0.10	3.59 ± 0.09	3.45 ± 0.14	*b*
$\mathrm{La^{III}}$	3.53 ± 0.12	3.48 ± 0.12	3.37 ± 0.14	3.28 ± 0.12

[a] aspt. = aspartic acid, glu. = glutamic acid, ADA = *N*-(2-acetamido)iminodiacetic acid, and HA = 3-amino-5-mercapto-1,2,4-triazole. [b] Could not be determined because of hydrolysis.

H_2L^3 ligands forming a 1:1:1 ternary complex. The free secondary ligand exponent, $\mathrm{pL_{mix}}$, was calculated from the obtained values of n_{mix} using the following equation:[25,28,29]

$$\mathrm{pL_{mix}} = \log\left\{\frac{\sum_{y=0}^{y=1} \beta_y^{\mathrm{H}}\left(\frac{1}{10^B}\right)}{C_{\mathrm{L}} - n_{\mathrm{mix}}C_{\mathrm{M}}}\,\frac{V_{\mathrm{o}} + V_{\mathrm{f}}}{V_{\mathrm{o}}}\right\} \tag{11}$$

where β_y^{H} are the proton−ligand dissociation constant values of HA and B is the pH value. All other terms have the same meaning as defined above. All calculations were performed using a computer program based on unweighted linear least-squares fits.

The mean formation constant values (log K) of the different 1:1 binary and 1:1:1 ternary complexes obtained using the average value and straight line methods, along with the errors as estimated by applying the least-squares fits are given in Tables 1 and 2. The results cited in Tables 1 and 2 reveal that the stability constant of the binary or mixed−ligand complex for the same metal ion varies in terms of the nature of the primary ligands, according to the following sequence: aspartic acid ($\mathrm{p}K_{\mathrm{a2}} = 3.86$, $\mathrm{p}K_{\mathrm{a3}} = 9.80$)[20] > $(\mathrm{HADA})^{1-}$ ($\mathrm{p}K_{\mathrm{a2}} = 6.62$)[18] > glutamic acid ($\mathrm{p}K_{\mathrm{a2}} = 4.31$, $\mathrm{p}K_{\mathrm{a3}} = 9.67$)[20] > tricine ($\mathrm{p}K_{\mathrm{a2}} = 8.20$).[10] This behavior can be related to the effective basicity of the conjugate base of these ligands as well as the steric effect. Generally, increasing the length of ligand chain would result in more strain on its binding, i.e., a relatively low stability. In addition, though, each of the three ligands [aspartic acid, $(\mathrm{HADA})^{1-}$, glutamic acid] can act as a tridintate dianion ligand (NOO donor). The high stability of the 1:1 binary or 1:1:1 ternary complexes containing aspartic acid moiety can be ascribed in addition to the effective high bascity of this ligand (a good σ donor) and to the formation of two five- and six-membered metal chelate rings.[20] Although, glutamic acid and tricine are highly basic relative to $(\mathrm{HADA})^{1-}$, the stability of the metal complexes containing glutamic acid or tricine is low compared with that containing $(\mathrm{HADA})^{1-}$. This can be attributed to the formation of two five- and seven-membered metal chelate rings in the case of glutamic acid,[20] and one five- membered metal chelate ring in the case of tricine, whereas two five-membered chelate rings are formed in the case of $[(\mathrm{HADA})^{1-}]$.[18] Moreover, the steric hindrance caused by the presence of the free bulky $(\mathrm{HOH_2C})_3\mathrm{C}-$ groups in the tricine ligand, which obstruct the approach of the secondary ligand HA to the metal ion, could be consider an additional factor for the low stability of tricine complexes.

The stability constants of the 1:1 binary and 1:1:1 ternary complexes of the divalent oxygenated cation $[\mathrm{UO_2{}^{II}}]$ 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.[30] Such behavior was also observed for other metal complexes of oxygenated cations.[30,31] The stability constants were found to increase with increasing ionic radii, electronegativity, and ionization potentials of the metal ions. The order of stability of the different binary or ternary complexes in the systems under investigations, in terms of the nature of metal ion, follows the usual sequence: Zn > Ni > Co > Cd > Pb (for the divalent metal ions) and Ce > La for the trivalent metal ions.[18] This behavior is consistent with the order of stability of such metal ion complexes as revealed in the Irving−Williams series,[32] which was confirmed recently.[33]

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