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Equilibrium Studies of Ternary Systems Involving Divalent Transition Metal Ions, Aliphatic Acids, and Triazoles

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The binary and ternary complexes of some M(II) ions with dicarboxylic aliphatic acids as primary ligands and some triazole compounds as secondary ligands have been studied pH-metrically in aqueous media at 25 °C and at a constant ionic strength of $I = 0.10$ mol dm^{-3} (KNO_3). The formation of the different 1:1 binary and 1:1:1 ternary complexes is inferred from the corresponding titration curves. The stability constants of the different complexes formed were determined and are discussed in terms of the nature of both the ligand and metal ion used. The stability of the ternary complexes is also discussed in relation to that of the binary complexes of secondary ligands.

Introduction

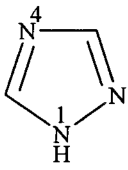
Mixed-ligand ternary complexes are well-known to play a significant role in biological processes.[1] Triazole complexes are very important in the production of pharmaceutical compounds used to inhibit the growth of tumors and cancer in mammals.[2−4] Such compounds are also used to treat viral as well as bacterial infections.[5] Moreover, the importance of the metal complexes of these compounds in biological fields is well-recognized in the literature.[6] The bioactivities of such compounds have been correlated with their ability to form complexes with metal ions.[7] Extensive studies have been performed on the synthesis and characterization of binary metal complexes of triazole compounds.[8−12] Binary complexes of 1,2,4-triazole and its alkyl, amino, methylthio, and mercapto derivatives with some metal ions have been studied in aqueous solution by means of pH-metric titration and absorption spectra.[13−16] However, a survey of the literature revealed that little work has been done on mixed-ligand ternary complexes containing triazole compounds.[17,18] In addition, no measurements appear to have been made on ternary systems containing triazoles and aliphatic acids. This fact provided a reasonable inducement for the investigation of the ternary complex formation of such ligands. Accordingly, continuing our work on ternary complexes,[19−22] a systematic study of the complex formation of some divalent transition metal ions [Cu(II), Ni(II), and Co(II)] with some dicarboxylic aliphatic acids (succinic, malic, and tartaric) as primary ligands and some triazoles [1,2,4-triazole (TRZ), 3-amino-1,2,4-triazole (TRZAM), and 3-mercapto-1,2,4-triazole (TRZSH)] as secondary ligands in aqueous media has been carried out pH-metrically at (25 ± 0.1) °C and a constant ionic strength of $I = 0.10$ mol dm^{-3} (KNO_3). The study adopts the Irving and Rossotti technique[23] for the determination of the stability constants of the different 1:1 binary and 1:1:1 ternary complexes formed in such systems. The stabilities of the different 1:1 binary and 1:1:1 ternary complexes are discussed in terms of the nature of both the ligands and the metal ion used.

The structures of the ligands are

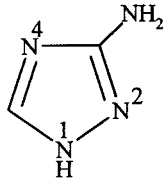
$HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$
Succinic acid

$HOOC\text{-}CH_2\text{-}CH(OH)\text{-}COOH$
Malic acid

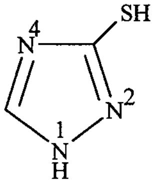
$HOOC\text{-}CH(OH)\text{-}CH(OH)\text{-}COOH$
Tartaric acid



(TRZ)



(TRZAM)



(TRZSH)

Experimental Section

Materials and Solutions. The triazole compounds (TRZ, TRZAM, and TRZSH) and aliphatic acids (succinic, malic, and tartaric) were analytical-grade (Aldrich or Merck) products. The purities of these compounds exceeded 99.4%, as verified by the TLC method. The metal salts used [$Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}2.5H_2O$] were BDH (England) analytical-grade products. All other chemicals used were A. R. analytical-grade (BDH) products.

Stock solutions (5×10^{-2} mol dm^{-3}) of triazoles and aliphatic acids were prepared by dissolving an accurate mass in the appropriate volume of CO_2-free doubly distilled H_2O. Solutions (5×10^{-2} mol dm^{-3}) of the divalent transition metal ions were also prepared from their nitrate salts. The metal ion concentrations were checked by a standard method.[24] A CO_2-free KOH solution (~0.20 mol dm^{-3}) was prepared and standardized with a standard solution (0.10 mol dm^{-3}) of potassium hydrogen phthalate. A solution (~0.10 mol dm^{-3}) of HNO_3 was also prepared. Generally, the concentrations of the acids were checked by titrations using the standardized KOH solution. A stock solution (1.0 mol dm^{-3}) of KNO_3 was also prepared by dissolving the required mass in the appropriate volume of CO_2-free doubly distilled H_2O.

Procedure. The following solutions were made from a metal ion, a primary ligand (succinic, malic, or tartaric acid), and/or a secondary ligand (TRZ, TRZSH, or TRZAM) in a 1:1:1 molar ratio: (a) (0.003−0.004) mol dm^{-3} HNO_3,

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(b) solution a + 0.004 mol dm^{-3} a triazole ligand, (c) solution b + 0.004 mol dm^{-3} M(II), (d) solution a + 0.004 mol dm^{-3} aliphatic acid, (e) solution d + 0.004 mol dm^{-3} M(II), and (f) solution e + 0.004 mol dm^{-3} a triazole ligand. The uncertainty in the concentrations ranged from 5 to 8%. The various solutions were stirred and titrated individually against a standard CO_2-free KOH solution. Generally, a constant ionic strength of 0.10 mol dm^{-3} (KNO_3) was maintained, and the volume was kept constant at 25 cm^3 for each titration. All titrations were performed in a thermostat cell at (25 ± 0.1) °C. The titrated solutions were purged with nitrogen gas before and during titrations. The titration was repeated at least three times for each titration curve.

Apparatus. The pH measurements were made with a model SM 702 Metrohm automatic titrator with a combined pH glass electrode equipped with a magnetic stirrer (Switzerland). 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). Because the potentiometric couple is calibrated under the experimental conditions of constant ionic strength, the hydrogen-ion activity can be expressed in terms of concentration.[25] Thus, all constants determined in this study are concentration constants. A water thermostat (Fisher Scientific Isotemp Refrigerated Circulator model 9000) with a temperature uncertainty of ±0.1 °C was used to adjust the temperature to 25 °C.

Calculations. Part of the information required for determining the metal complex stability constants is the acid dissociation constants (pK_a). Therefore, the pK_a values were calculated from the relationship[23]

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

where β is the proton−ligand formation constant (K_a) of the ligand and n_H is the average number of protons associated per mole of ligand at several pH values. The following equation[23] was used for calculation the n_H values from the titration curves corresponding to solutions a, b, and d

$$n_H = \left[yC_L + \frac{(V_a - V_b \text{ or } V_a - V_d)C_b}{V_o}\right\}(C_L)^{-1} \qquad (2)$$

where y is the number of dissociable protons ($y = 1$ for TRZ and TRZSH, and $y = 2$ for TRZAM and aliphatic acids). V_a, V_b, and V_d are the volumes of KOH consumed to reach the same pH values in curves a, b, and d, respectively. C_b and C_L are the concentrations of KOH and ligand, respectively, and V_o is the original volume (25 cm^3).

Titration curves b, c and d, e (Figures 1 and 2) were used to calculate the stability constants of the binary metal complexes of triazoles and aliphatic acids, respectively. The average number of ligand molecules (n_b) coordinated to the metal ion and the free ligand exponent (pL) at several pH values were calculated according to[23]

$$n_b = \frac{[(V_c - V_b) \text{ or } (V_e - V_d)][C_a + C_b + C_L(y - n_H)]}{[(V_o + V_b) \text{ or } (V_o + V_d)]n_H C_M} \qquad (3)$$

$$pL = \log\left[\frac{\sum_{y=0}^{y=1 \text{ or } 2} \beta_y^H\left(\frac{1}{10^B}\right)}{C_L - n_b C_M}\,\frac{V_o + (V_c \text{ or } V_e)}{V_o}\right] \qquad (4)$$

V_c and V_e are the volumes of KOH consumed to reach the same pH values in curves c and e, respectively. C_a is the concentration of HNO_3, and C_M is the initial concentration of the metal ion used. β_y^H represents the proton−ligand dissociation constants of the ligands, and B is the pH value. n_H values were available from the determination of the proton−ligand formation constant. It is worth mentioning that the values of n_b do not exceed unity, indicating the formation of only 1:1 binary complexes.

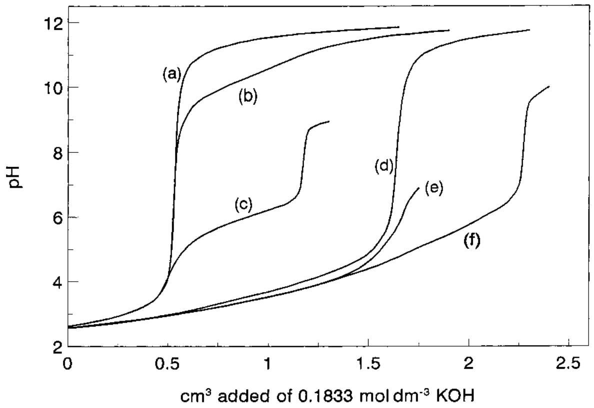

Figure 1. pH-Metric titration curves for the [Ni(II) + (tartaric acid) + (TRZ)] system at 25 °C and a constant ionic strength of $I = 0.10$ mol dm^{-3} (KNO_3): (a) 0.003 97 mol dm^{-3} HNO_3, (b) solution a + 0.004 mol dm^{-3} TRZ, (c) solution b + 0.004 mol dm^{-3} Ni(II), (d) solution a + 0.004 mol dm^{-3} tartaric acid, (e) solution d + 0.004 mol dm^{-3} Ni(II), and (f) solution e + 0.004 mol dm^{-3} TRZ.

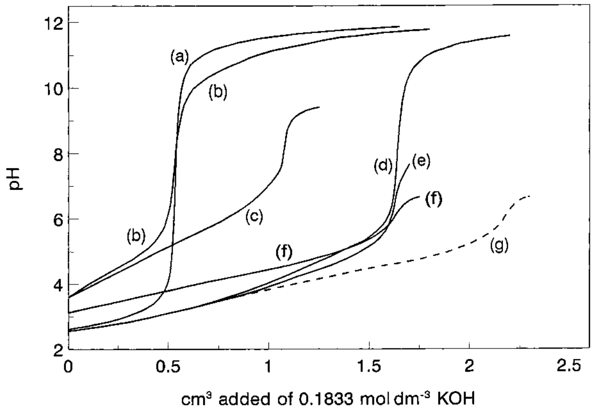

Figure 2. Titration curves for the [Co(II) + (malic acid) + (TRZAM)] system at 25 °C and a constant ionic strength of $I = 0.10$ mol dm^{-3} (KNO_3): (a) 0.004 mol dm^{-3} HNO_3, (b) solution a + 0.004 mol dm^{-3} TRZAM, (c) solution b + 0.004 mol dm^{-3} Co(II), (d) solution a + 0.004 mol dm^{-3} malic acid, (e) solution d + 0.004 mol dm^{-3} Co(II), (f) solution e + 0.004 mol dm^{-3} TRZAM, and (g) solution f + volume of KOH equivalent to the concentration (0.004 mol dm^{-3}) of TRZAM.

On the other hand, the titration curves e and f or g (obtained in the case of TRZAM after the addition of a KOH volume equivalent to the concentration of this ligand present in the ternary complex solution) were used to calculate the number of triazole secondary ligands attached to one binary [M(II) + aliphatic acid] complex molecule (n_{mix}) for a mixed-ligand ternary complex. The following equation was used for this calculation[23]

$$n_{mix} = \frac{[(V_f \text{ or } V_g) - V_e)][C_b + C_a + C_L(y - n_H)]}{(V_o + V_e)n_H C_M} \qquad (5)$$

where C_M is the concentration of the binary complex, which equals the concentration of M(II) used; C_L is the concentration of the secondary ligand; ; y is the number of dissociable

Table 1. Ionization Constant Values of the Ligands Used and the Stability Constants (log *K*)[a] for Their 1:1 Binary Complexes Formed at 25 °C and $I = 0.10$ mol dm^{-3} (KNO$_3$)

			$\log K^{M}_{M(L)}$ or $\log K^{M}_{M(A)}$		
ligand	pK_{a1}	pK_{a2}	Co(II)	Ni(II)	Cu(II)
succinic acid	4.20 ± 0.02	5.65 ± 0.02	*b*	*b*	*b*
malic acid	3.45 ± 0.03	5.10 ± 0.03	3.10 ± 0.06	3.25 ± 0.05	4.22 ± 0.03
tartaric acid	3.10 ± 0.02	4.50 ± 0.02	2.88 ± 0.10	2.95 ± 0.08	4.10 ± 0.04
1,2,4-triazole		9.95 ± 0.03	6.10 ± 0.04	6.93 ± 0.04	9.14 ± 0.02
3-amino-1,2,4-triazole	4.20 ± 0.03	10.72 ± 0.03	5.54 ± 0.06	6.14 ± 0.04	8.80 ± 0.02
3-mercapto-1,2,4-triazole		7.10 ± 0.04	3.02 ± 0.06	3.60 ± 0.05	*b*

[a] Stability constants were calculated using the equilibria $\mathrm{M(II)} + \mathrm{L}^{2-} \Leftrightarrow [\mathrm{M(L)}]$ and $\mathrm{M(II)} + \mathrm{A}^{1-} \Leftrightarrow [\mathrm{M(A)}]^{1-}$, where L and A refer to aliphatic acid and triazole moieties, respectively. [b] Could not be determined because of precipitation.

protons per molecule of the secondary ligand. V_f or V_g is the volume of KOH consumed to reach the same pH values in curve f or curve g, respectively. In this case, the n_H values are the average number of protons associated with the secondary ligand at different pH values. The values obtained were in the range $1 \geq n_{mix} \geq 0$, indicating the formation of 1:1:1 ternary complexes in which only one secondary ligand molecule combines with the binary complex.

The free secondary ligand exponent, pL$_{mix}$, was calculated from the obtained values of n_{mix} using the equation[23]

$$\mathrm{pL}_{mix} = \log\left[\frac{\sum_{y=0}^{y=1}\beta_y^H\left(\frac{1}{10^B}\right)}{C_L - n_{mix}C_M}\,\frac{V_o + V_f \text{ or } V_g}{V_o}\right] \tag{6}$$

Here, β_y^H represents the proton−ligand dissociation constants of the secondary ligand triazoles. All other terms have the same meanings as above.

A computer program based on unweighted linear least-squares fits was used for all calculations.

Results and Discussion

A representative set of experimental titration curves obtained according to the sequence described in the Experimental Section for the different [M(II) + aliphatic acids + triazoles] systems under investigation are displayed in Figures 1 and 2. The *N*-unsubstituted 1,2,4-triazoles (HA) are considered to be protonated at low pH at the imidazolic nitrogen atom (N4), producing the protonated form $(\mathrm{H_2A})^+$.[16,26] Accordingly, such compounds are expected to have two ionization constants relevant to the following ionization steps[16,26]

$$(\mathrm{H_2A})^+ \Leftrightarrow \mathrm{HA} + \mathrm{H}^+ \tag{7}$$

$$\mathrm{HA} \Leftrightarrow (\mathrm{A})^{1-} + \mathrm{H}^+ \tag{8}$$

On the other hand, the dicarboxylic aliphatic acids can generally be represented by $\mathrm{H_2L}$, thus also having two ionization constants. The ionization constant values obtained for the various ligands (Table 1) are in good agreement with the literature values determined under similar experimental conditions.[27] However, the first ionization constant values for 1,2,4-triazole (TRZ) and 3-meracpto-1,2,4-triazole (TRZSH) are very low (≤2.4); therefore, they could not be determined and were not used in the calculations.

The titration curves c obtained for the different 1:1 binary [M(II) + triazoles] complex solutions reveal that these complexes begin to form in the pH ranges 3.90−4.40, 3.40−3.90, and 3.00−3.50 for Co(II), Ni(II), and Cu(II), respectively. These values were obtained from the appearance of divergence of the titration curve of each of the 1:1 binary [M(II) + triazole] complexes from that of the free triazole ligand (curve b). The pH value at which the binary complex begins to form decreases in the direction TRZSH → TRZ → TRZAM, indicating a higher tendency of triazole ligands toward binary complex formation in the same order. Except in the case of the 1:1 binary complex [Cu(II) + TRZSH], the different 1:1 binary [M(II) + triazoles] complex solutions do not give rise to a precipitate, indicating that hydrolysis reactions do not interefere in the formation of such complexes. On the other hand, an inflection was observed in the different 1:1 binary [M(II) + triazoles] titration curves at a pH value corresponding to the addition of 1 mol of base per 1 mol of triazole ligand. This behavior suggests that the triazole ligands bind to the metal ions as monovalent anions according to the equations

$$\mathrm{M(II)} + \mathrm{HA} \Leftrightarrow [\mathrm{MA}]^+ + \mathrm{H}^+$$

and

$$\mathrm{M(II)} + [\mathrm{H_2A}]^+ \Leftrightarrow [\mathrm{MA}]^+ + 2\mathrm{H}^+$$

for TRZ or TRZSH and TRZAM, respectively. However, the 1:1 binary [Cu(II) + TRZSH] complex solution could not be studied as a result of the formation a precipitate at low pH values (<2.5). Generally, studies beyond the precipitation point were not performed.

The titration curves e of the 1:1 binary [M(II) + aliphatic acids] complex solutions clearly reveal that the different 1:1 binary complexes begin to form at a lower pH range (2.50−3.00). It is noteworthy that the titration curves of the binary [M(II) + succinic acid] complex solutions form precipitates at low pH values, so they could not be studied.

The titration curve f or g (obtained in the case of TRZAM as the secondary ligand) for the different 1:1:1 ternary [M(II) + aliphatic acids + triazoles] complex solutions and that of the 1:1 binary [M(II) + aliphatic acid] complex solutions (curve e) strongly overlap at lower pH values, indicating that the triazole ligands do not bind with the metal ion in this pH range. Generally, at high pH, which depends on the nature of the secondary ligand triazole and metal ion used, the ternary titration curve (f or g) diverges from that of the corresponding 1:1 binary metal complexes of aliphatic acids. The titration curves of all of the mixed-ligand complex solutions display an inflection at the titration point corresponding to the addition of a base concentration equivalent to 2 mol of aliphatic acid and 1 mol of triazole ligand. This clearly indicates that the aliphatic acids coordinate to the central metal ion via the carboxylate oxygens as divalent bidentate anions (OO donors) and that triazoles bind to the metal ion as monovalent monodentate anions (N donors) through the pyrrolic nitrogen after deprotonation. This behavior suggests the

Table 2. Stability Constant Values (log K)[a] for the Different Mixed-Ligand Complexes Formed at 25 °C and $I = 0.10$ mol dm^{-3} (KNO_3) along with the Δ log K Values[b]

	$\log K^{M(L)}_{M(L)(A)}$								
	1,2,4-triazole			3-amino-1,2,4-triazole			3-mercapto-1,2,4-triazole		
	succinic	malic	tartaric	succinic	malic	tartaric	succinic	malic	tartaric
metal ion	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)	log K (Δ log K)
Co(II)	5.61 ± 0.03 (−0.49)	5.17 ± 0.04 (−0.93)	5.03 ± 0.05 (−1.07)	7.76 ± 0.03 (+2.22)	7.26 ± 0.03 (+1.72)	7.02 ± 0.04 (+1.48)	2.95 ± 0.09 (−0.07)	2.83 ± 0.10 (−0.19)	2.78 ± 0.05
Ni(II)	6.86 ± 0.02 (−0.07)	6.71 ± 0.04 (−0.22)	6.58 ± 0.04 (−0.35)	9.23 ± 0.02 (+3.09)	8.60 ± 0.02 (+2.46)	8.07 ± 0.04 (+1.93)	3.40 ± 0.07 (−0.20)	3.25 ± 0.08 (−0.35)	3.17 ± 0.04 (−0.43)
Cu(II)	9.03 ± 0.03 (−0.11)	8.95 ± 0.02 (−0.19)	8.80 ± 0.03 (−0.34)	10.52 ± 0.02 (+1.72)	10.28 ± 0.02 (+1.48)	9.94 ± 0.03 (+1.14)	*c*	*c*	*c*

[a] Stability constants were calculated using the chemical equilibrium $[M(L)] + A^{1-} \Leftrightarrow [M(L)(A)]^{1-}$, where L and A refer to aliphatic acid and triazole moieties, respectively. [b] $\Delta \log K = \log K^{M(L)}_{M(L)(A)} - \log K^{M}_{M(A)}$. [c] Could not be determined because of precipitation.

coordination of a triazole moiety $(A)^{1-}$ as a secondary ligand to the binary complex [M(L)], which is first formed, affording the mixed-ligand 1:1:1 ternary complex $[M(L)(A)]^{1-}$ in a stepwise manner, as represented by

$$M(II) + H_2L \Leftrightarrow [M(L)] + 2H^+$$

Accordingly, one can consider the triazole moiety to

$$[M(L)] + A^{1-} \Leftrightarrow [M(L)(A)]^{1-}$$

combine with the binary complex species [M(L)] in the ternary systems as it does with $[M(H_2O)_6]^{2+}$ in a binary system. The 1:1:1 mixed-ligand complexes are stable up to the pH values where the primary and secondary ligands are completely attached to the central divalent metal ion, forming the ternary complexes, i.e., the hydrolysis reactions have no role in complex formation. However, the ternary $[Cu(II) + H_2L + TRZSH]$ complexes could not be studied because of the extensive hydrolysis of these complexes at low pH values, yielding the hydroxo complex species.

Stability Constants. The mean formation constant values (log K) of the various 1:1 binary and 1:1:1 ternary complexes, obtained from the corresponding titration curves 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.

Examination the results in Tables 1 and 2 indicates that the stability of the binary or the mixed-ligand complex of the same metal ion varies in terms of the nature of the primary ligand, dicarboxylic aliphatic acid anion, according to the order: succinate ($pK_{a1} = 4.21$, $pK_{a2} = 5.64$) > malate ($pK_{a1} = 3.40$, $pK_{a2} = 5.05$) > tartarate $pK_{a1} = 3.03$, $pK_{a2} = 4.36$).[27] This behavior is consistent with the decrease in the σ-donor character (expressed in pK_a values) of these anions in the same order. On the other hand, the stability constant values obtained (Table 1) for the different 1:1 binary [M(L)] complexes are in good agreement with the corresponding literature values, where the values 3.10, 3.25, 4.22, 2.88, 2.95, and 4.10 obtained for the 1:1 binary [Co(II) + malic], [Ni(II) + malic], [Cu(II) + malic], [Co(II) + tartaric], [Ni(II) + tartaric], and [Cu(II) + tartaric] complexes are in accordance with the corresponding literature values[19,28] of 3.00, 3.39, 4.00, 2.80, 2.96, and 4.00, respectively.

The results obtained clearly indicate that, for a given metal ion, the stability of the 1:1 binary $[M(A)]^+$ complex is influenced by changing the nature of the triazole ligand as follows: TRZ ($pK_{a2} = 9.95$) > TRZAM ($pK_{a2} = 10.72$) > TRZSH ($pK_{a2} = 7.10$). Although TRZAM is a stronger base than TRZ, the 1:1 binary complexes of TRZAM are less stable than those of TRZ. This behavior can likely be ascribed to the electrostatic repulsive interactions established during the formation of the binary complex TRZAM-$(H_2A)^+$ $\{M(II) + (H_2A)^+ \Leftrightarrow [M(A)]^+ + 2H^+\}$ compared to those in the formation of the binary complex TRZ(HA) $\{M(II) + (HA) \Leftrightarrow [M(A)]^+ + H^+\}$. However, the log K values obtained for the 1:1 binary complexes [Co(II) + TRZ], [Co(II) + TRZAM], [Ni(II) + TRZ], and [Ni(II) + TRZAM] are more than 4 orders of magnitude greater than the log K values 1.32, 1.40, 1.90, and 2.34, respectively, reported previously[15,16] for the Co(II) and Ni(II) binary complexes. This discrepancy can be explained in terms of the different experimental conditions and, therefore, the different coordination modes of the ligands. In the previous studies,[15,16] the measurements were carried out in a low pH range, suggesting the coordination of these ligands to the metal ion as neutral molecules. The measurements in the present study were performed over a wide range of pH, and the studied triazole ligands bind to the metal ion as anions rather than neutral molecules. The difference in the ionic strength can be considered an additional factor (the previous studies are carried out in aqueous solutions of 0.50 ionic strength) for the high stability constant values obtained for the 1:1 binary [Co(II) + TRZSH] and [Ni(II) + TRZSH] complexes (cf. Table 1) compared to the values of 2.58 and 3.09 reported previously[13] for the Co(II) and Ni(II) complexes, respectively.

On the other hand, in terms of the effect of the secondary ligand, the data cited in Table 2 show that the stabilities of the ternary complexes of the same metal ion follow the sequence TRZAM ($pK_{a2} = 10.72$) > TRZ ($pK_{a2} = 9.95$) > TRZSH ($pK_{a2} = 7.10$). This behavior can be interpreted on the basis of the effective basicity of the conjugate base of these ligands, where the ligand basicity decreases on going from TRZAM to TRZSH in the above sequence. Moreover, the stability of the mixed-ligand complex compared to that of the corresponding binary $[M(A)]^+$ complex is expressed in terms of Δ log K, which represents the difference in stability for the addition of a triazole $(A)^-$ as the secondary ligand to the binary complex [M(L)] to yield the ternary complex $[M(L)(A)]^{1-}$ and that for its binding with the aquatic metal ion $[M(H_2O)_6]^{2+}$ to form the binary complex $[M(A)]^+$. It is evident that, except for the case of TRZAM, the stability of the ternary complex of the same metal ion is lower than that of the corresponding binary complex, i.e., the association of TRZ or TRZSH with the aquatic metal ion is more favored than that with the binary complex [M(L)] (i.e., Δ log K is negative). This behavior is likely to be due to the smaller number of sites available for bonding on the binary [M(L)] complex than on the aquatic M(II) complex. In contrast, the positive value of Δ log K obtained for the different 1:1:1 ternary complexes containing TRZAM can presumably be attributed to the high electrostatic repulsive forces in the binary complex formation between the positive charge carried by protonated TRZAM $(H_2A)^+$ and the aquatic metal ion $\{M(II) + (H_2A)^+ \Leftrightarrow [M(A)]^+ + 2H^+\}$. Such forces are low during mixed-ligand complex formation $\{M(L) + (HA) \Leftrightarrow [M(L)(A)]^{1-} + H^+\}$.

Moreover, in terms of the nature of the metal ion used, the results obtained reveal that the stability of the different binary and ternary complexes follows the order: Cu(II) > Ni(II) > Co(II). This order is in conformity with the order of stabilities of such metal ion complexes.[29]

Note Added after ASAP Posting

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