J. Chem. Eng. Data **1998,** *43,* 459−464 **459**

Mixed-Ligand Complexes of Some Divalent Transition Metal Ions with Dicarboxylic Amino Acids and 8-Hydroxyquinoline

Iman T. Ahmed and Ahmed A. Ahmed Boraei*

Department of Chemistry, Faculty of Science, Minia University, El-Minia 61519, Egypt

Omar M. El-Roudi

Department of Chemistry, Faculty of Science, Helwan University, Helwan, Egypt

---

Mixed-ligand complexes of Co^{II}, Ni^{II}, and Cu^{II} with dicarboxylic amino acids (aspartic and glutamic or H_2ADA) as primary ligands and 8-hydroxyquinoline as a secondary ligand were prepared and characterized. Formation constants of the different complexes were determined acidimetrically at 25 °C and at ionic strength $I = 0.1$ mol dm^{-3} (KNO_3) and were discussed in terms of the nature of both the metal ion and the ligand used. The thermodynamic functions (ΔH, $\Delta G°$, and $\Delta S°$) associated with the formation of [M^{II} + $(HADA)^{1-}$ + 8-hydroxyquinoline] complexes were also calculated and discussed.

Introduction

In recent years metal complexes of 8-hydroxyquinoline derivatives (Basudhar et al., 1996; Ibrahim et al., 1992, 1994; Islam et al., 1995) and *N*-(2-acetamido)iminodiacetic acid (H_2ADA) (Hamed et al., 1994; Ibrahim et al., 1994; Mahmoud et al., 1996; Ahmed et al., 1996, 1997) have been studied because of their established biological activity. However, a survey of the literature reveals that studies of systems containing the two ligands H_2ADA and 8-hydroxyquinoline have not been carried out. Extending our studies on ternary metal complexes (Ahmed et al., 1996, 1997; Boraei and Abd Alla, 1993), we report in this article the synthesis and characterization of complexes of Co^{II}, Ni^{II}, and Cu^{II} with dicarboxylic amino acids [aspartic **(I)** and glutamic **(II)** or H_2ADA **(III)**] as primary ligands and 8-hydroxyquinoline **(IV)** as a secondary ligand. The structures of the ligands used are as follows:

$HOOC\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$

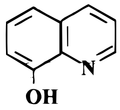
(I)

$HOOC\text{-}CH_2\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$

(II)

$H_2N\text{-}CO\text{-}CH_2\text{-}N(CH_2COOH)_2$

(III)



(IV)

The formation constants of the different binary and ternary complexes formed in such systems have been determined acidimetrically and discussed in terms of the nature of both the metal ion and the primary ligands used. The thermodynamic functions ΔH, $\Delta G°$, and $\Delta S°$ associated with the complex formation of M^{II} + $(HADA)^{1-}$ + 8-hydroxyquinoline were determined and are discussed here.

Experimental Section

All chemicals were analytical reagent-grade products. Stock solutions (2×10^{-2} mol dm^{-3}) of amino acids (aspartic and glutamic) and the divalent transition metal salts {$Cu(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $Co(NO_3)_2{\cdot}6H_2O$} were prepared by dissolving an accurate mass in the appropriate volume of CO_2-free doubly distilled H_2O. 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. 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. Since the solubility of free *N*-(2-acetamido)iminodiacetic acid (H_2ADA) in H_2O is low, the monosodium salt was prepared and used. The metal ion concentrations were determined by complexometric titrations (Vogel, 1975). The 8-hydroxyquinoline solution was prepared in a redistilled and purified EtOH. Generally, the concentrations of the acids were checked by titration using the standardized KOH.

Synthesis of the Ternary Complexes. The following general procedure (Masson et al., 1987) has been used for the synthesis of the ternary complexes reported in Table 1. An EtOH solution of $CuCO_3{\cdot}Cu(OH)_2$, $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$, or $CoCO_3{\cdot}Co(OH)_2{\cdot}6H_2O$ (5 mmol) was added slowly to an equimolar EtOH solution of a dicarboxylic amino acid (aspartic, glutamic, or H_2ADA) with stirring. An EtOH solution of 8-hydroxyquinoline containing 5 mmol was added to the above mixture dropwise with constant stirring. For each an accurate mass corresponding to the (5 mmol) concentration was dissolved in 10 cm^3 EtOH. The mixture was refluxed for 2 h, evaporated, and cooled; the solid ternary complex precipitated out. The precipitate was filtered off and washed thoroughly with absolute EtOH. The solid ternary complexes were dried in vacuo over P_4O_{10}.

Acidimetric Titrations. In a typical run a solution made from metal ion, primary ligand dicarboxylic amino acid (aspartic, glutamic, or $(HADA)^{1-}$) and/or secondary ligand 8-hydroxyquinoline in a 1:1:1 molar ratio was stirred and titrated with 0.1982 mol dm^{-3} CO_2-free KOH solution at 25 °C (Figure 1). A constant ionic strength was maintained with 0.10 mol dm^{-3} KNO_3, and a total volume of 50 cm^3 was used for each titration. The various solutions titrated were as follows: (a) 2 cm^3 of (0.10 mol dm^{-3}) HNO_3;

---

* To whom correspondence should be addressed. Fax: 02 086 34 2601.

S0021-9568(97)00192-1 CCC: $15.00

Table 1. Analytical Data, Physical Properties, Molar Conductance and UV−Vis Spectra for the Different Isolated Ternary Complexes[a]

complex	mol. wt.	color	dec. temp./°C	found (calcd) % C	H	N	Λ_m cm^2 mol^{-1} (DMSO)	λ_{max}/nm (ϵ_{max} × 10^{-3}/mol^{-1} cm^2)
H[(Co(ADA)(8-hydroxyquinoline)H_2O]H_2O	428.25	pink	220	41.85	4.32	9.88	105	405 (6.50), 528b (0.015)
$H[Co(C_6H_8N_2O_5)(C_9H_6NO)H_2O]H_2O$				(42.03)	(4.21)	(9.81)		
H[Co(aspartic)(8-hydroxyquinoline)H_2O]H_2O	371.19	pale-violet	260	42.17	3.98	7.76	102	407 (3.30), 525b (0.028)
$H[Co\ (C_4H_5NO_4)(C_9H_6NO)H_2O]H_2O$				(42.03)	(4.04)	(7.54)		
H[Co(glutamic)(8-hydroxyquinoline)H_2O]H_2O	385.22	pink	230	43.56	4.25	7.43	98	406 (5.80), 338 (1.20), 530b (0.012)
$H[Co(C_5H_7NO_4)(C_9H_6NO)H_2O]H_2O$				(43.61)	(4.41)	(7.27)		
H[Ni(ADA)(8-hydroxyquinoline)H_2O]H_2O	428.01	pale-green	225	41.98	4.18	9.60	89	411 (9.40), 340 (7.32), 575b (0.084)
$H[Ni(C_6H_8N_2O_5)(C_9H_6NO)H_2O]H_2O$				(42.06)	(4.21)	(9.81)		
H[Ni(aspartic)(8-hydroxyquinoline)H_2O]H_2O	370.95	pale-green	233	42.46	3.97	7.32	97	413 (22.21),338 (17.41), 578b (0.04)
$H[Ni(C_4H_5NO_4)(C_9H_6NO)H_2O]H_2O$				(42.05)	(4.04)	(7.55)		
H[Ni(glutamic)(8-hydroxyquinoline)H_2O]H_2O	384.98	pale-green	222	43.49	4.49	7.58	103	409 (27,30), 580b (0.012)
$H[Ni(C_5H_7NO_4)(C_9H_6NO)H_2O]H_2O$				(43.64)	(4.42)	(7.27)		
H[Cu(ADA)(8-hydroxyquinoline)H_2O]H_2O	432.86	blue	252	41.19	4.24	9.90	103	415 (6.70), 610b (0.017)
$H[Cu(C_6H_8N_2O_5)(C_9H_6NO)H_2O]H_2O$				(41.59	(4.16)	(9.70)		
H[Cu(aspartic) (8-hydroxyquinoline)H_2O]H_2O	375.76	blue	224	41.44	3.64	7.52	99	420 (11.23),343 (5.70), 630b (0.016)
$H[Cu(C_4H_5NO_4)(C_9H_6NO)H_2O]H_2O$				(41.52)	(3.99)	(7.45)		
H[Cu(glutamic) (8-hydroxyquinoline)H_2O]H_2O	389.79	blue	226	43.38	4.41	7.29	87	418 (6.63),344 (1.23), 612b (0.052)
$H[Cu(C_5H_7NO_4)(C_9H_6NO)H_2O]H_2O$				(43.10)	(4.36)	(7.18)		

[a] b = broad; dec. temp. = decomposition temperature.

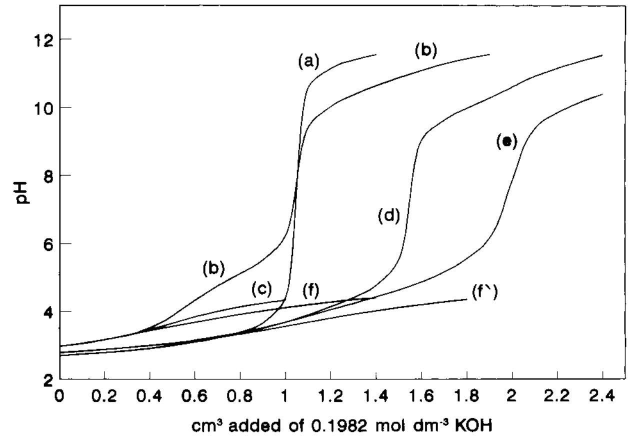


Figure 1. Titration curves for the [Ni^{II} + aspartic acid + 8-hydroxyquinoline] system at 25 °C and an ionic strength I = 0.10 mol dm^{-3} (KNO_3) with (0.1982 mol dm^{-3}) KOH. (a) (4 × 10^{-3} mol dm^{-3}) HNO_3; (b) solution a + (2 × 10^{-3}) mol dm^{-3} 8-hydroxyquinoline; (c) solution b + (2 × 10^{-3} mol dm^{-3}) Ni^{II}; (d) solution a + (2 × 10^{-3} mol dm^{-3}) aspartic acid; (e) solution d + (2 × 10^{-3} mol dm^{-3}) Ni^{II}; (f) solution e + (2 × 10^{-3})mol dm^{-3} 8-hydroxyquinoline; (f`) solution f + volume of KOH equivalent to the concentration (2 × 10^{-3} mol dm^{-3}) of 8-hydroxyquinoline base.

(b) solution a + 5 cm^3 of (2 × 10^{-2} mol dm^{-3}) 8-hydroxyquinoline; (c) solution b + 5 cm^3 of 2 × 10^{-2} mol dm^{-3} metal ion; (d) solution a + 5 cm^3 of (2 × 10^{-2} mol dm^{-3}) (HADA)$^{1-}$ or a dicarboxylic amino acid; (e) solution d + 5 cm^3 of (2 × 10^{-2} mol dm^{-3}) metal ion; (f) solution e + 5 cm^3 of (2 + 10^{-2} mol dm^{-3}) 8-hydroxyquinoline.

The titrations were carried out in 20 mass % EtOH + H_2O mixture. Accordingly, the measured pH values were corrected according to the procedure of Douhéret (1967, 1968), where a value of 0.04 pH units is subtracted from the pH-meter reading to obtain the corrected value for this EtOH concentration.

Physical Measurements. The C, H, and N contents of the ternary metal complexes were determined in the microanalytical unit of Cairo University. Values are given in Table 1. The molar conductance of DMSO solutions of the synthesized ternary complexes were measured at 25 °C (cf. Table 1) by a YSI conductivity bridge model 31 with a conductivity cell constant K_{cell} = 0.10 m^{-1}. The IR spectra were recorded over a 400−4000 cm^{-1} range on a Shimadzu 470 spectrophotometer using KBr pellets. Electronic spectra were recorded in the 250−1000 nm range by a Perkin-Elmer Lambda 2 spectrophotometer using 1 cm^3 matched silica cells. Thermogravimetric analysis of the solid ternary complexes were automatically carried out using a DuPont 9000 thermal analyzer with a computer at a heating rate 10 °C min^{-1} in a dynamic air atmosphere.

The pH measurements were made using an Orion model 701A digital pH meter accurate to ±0.005 pH unit with a glass-calomel electrode assembly. The pH meter was standardized against 4.008 and 9.180 buffers. A Fisher Scientific Isotemp Refrigerated Circulator model 9000 water thermostat accurate to ±0.1 °C was used to adjust the temperature. The equations utilized for various calculations were programmed using an IBM computer.

Results and Discussion

Characterization of the Solid Ternary Complexes. The analytical data given in Table 1 for the isolated ternary complexes are consistent with the general molecular formula $H[M(L)(L')H_2O]H_2O$, where M = Cu^{II}, Ni^{II}, or Co^{II}, L is the divalent anion of (ADA)$^{2-}$, aspartate, or glutamate, and L′ is the monovalent anion of 8-hydroxyquinoline. The measured molar conductances Λ_m of the DMSO solutions of the isolated ternary complexes given in Table 1 are found to be in the range consistent with a 1:1 electrolyte (Geary, 1971).

Assignment of the most important IR bands providing conclusive structural evidence for the coordination mode in the isolated ternary complexes is presented in Table 2. The broad OH stretching band appearing in the 3200−3100 cm^{-1} region for 8-hydroxyquinoline is missing in the IR spectra of the complexes. Instead two broad bands appeared in the 3450−3550 and 3320−3220 cm^{-1} ranges in the IR spectra of all complexes. These two bands are

Table 2. Assignment of the Most Important IR Frequencies (cm^{-1}) for the Various Synthesized Ternary Complexes

$[M^{II} + (HADA)^{1-} +$ 8-hydroxyquinoline]			$[M^{II}$ + aspartic + 8-hydroxyquinoline]			$[M^{II}$ + glutamic + 8-hydroxyquinoline]			
Co^{II}	Ni^{II}	Cu^{II}	Co^{II}	Ni^{II}	Cu^{II}	Co^{II}	Ni^{II}	Cu^{II}	assignment
3505	3495	3455	3495	3550	3490	3510	3505	3500	ν_{OH} of hydrated H_2O molecules
3310	3320	3225	3315	3250	3290	3310	3290	3220	ν_{OH} of coordinated H_2O molecules
3180	3105	3050	3050	3050	3090	3100	3150	3120	ν_{NH} of free NH_2 of ADA moiety
2950	2980	2960	2990	2980	2910	1980	3050	3095	ν_{NH} of coordinated NH_2 of aspartic and glutamic acids
1675	1685	1685	1680	1690	1680	1680	1680	1685	ν_{CO} free CO of coordinated ADA
1610	1600	1638	1600	1585	1590	1575	1580	1575	ν_{COO} of asymm. COO^- of ADA, aspartate, or glutamate
1410	1420	1410	1420	1410	1390	1405	1395	1410	ν_{symm} COO^- of ADA, aspartate, or glutamate
1590	1585	1575	1590	*a*	*a*	*a*	*a*	*a*	$\nu_{(-C=N-)}$ of quinoline moiety
890	915	875	865	850	890	950	915	870	ν of rocking mode of coordinated H_2O

[a] Band is buried under the $\nu_{\mathbf{symm}}$ of coordinated carboxylate group.

attributed to the OH stretching vibration of hydrated and coordinated H_2O molecules, respectively. The appearance of a strong band in the range 950−850 cm^{-1} in the IR spectra of the complexes, which is assignable to the rocking mode ofvibration of coordinated H_2O (Nakamoto, 1986), where the free ligands lack such band, substantiates the presence of coordinated H_2O in the isolated complexes. This is in harmony with the results of chemical analyses (cf. Table 1) as well as the thermal analyses described later. The NH_2 stretching vibration band centered in the vicinity of 3200 cm^{-1} for the ADA moiety is found to be at the same position in the IR spectra of the complexes, indicating that this group is probably not coordinated to the metal ion. A weak broad band appearing in the range 3150−2910 cm^{-1} is assigned to the stretching vibration of the coordinated NH_2 group belonging to the aspartate and glutamate moieties. The distinct band appearing in the range 1690−1675 cm^{-1} in the IR spectra of complexes is attributable to the stretching vibration of the CO group of the ADA moiety (Ibrahim et al., 1994). The characteristic band appearing in the 1610−1575 cm^{-1} region is assigned to the stretching vibration of the coordinated carboxylate group (Nakamoto, 1986). This assignment is based on the fact that the unionized and uncoordinated COO stretching band appears at 1750−1700 cm^{-1} whereas the ionized and coordinated COO stretching band occurs at 1650−1590 cm^{-1} (Nakamoto, 1986). Further, the band responsible for the symmetric stretching vibration of the coordinated carboxylate appeared in the 1410−1390 cm^{-1} region, suggesting that the carboxyl groups of the amino acid moieties (aspartate and glutamate) as well as of the ADA moiety are involved in the coordination to the central metal ion via the oxygen atom. Moreover, the absence of any band in the region 1750−1700 cm^{-1} in the IR spectra of the complexes is considered as a further evidence for the participation of the carboxylate groups in the complex formation. The stretching vibration band of the azomethine linkage (−C=N−) appearing at 1605−1630 cm^{-1} (Lambert et al., 1976) for 8-hydroxyquinoline is shifted to lower frequency in the IR spectra of complexes, revealing the involvement of this group in the coordination. However, in some cases this band is probably obscured under the symmetric stretching vibration of coordinated carboxylate.

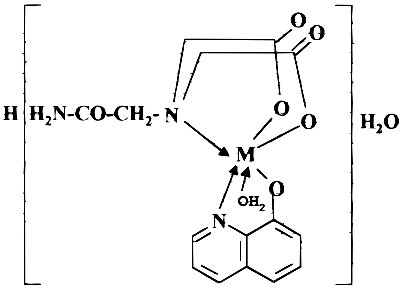
From the foregoing discussion, one can conclude that the primary ligand, H_2ADA, aspartic, or glutamic acid, is chelated to the metal ion as dinegative tridentate ligand through the two oxygen atoms of the two COO groups belonging to the three ligands as well as through the nitrogen atom of NH_2 group of amino acids (aspartic and glutamic) and the nitrogen atom of the tertiary amine of the ADA moiety. On the other hand, the secondary ligand 8-hydroxyquinoline is coordinated to the metal ion as a mononegative bidentate ligand through its −C=N− nitrogen atom and the oxygen atom of the deprotonated phenolic OH group. This conclusion is consistent with the results of chemical analyses (cf. Table 1).

Thermogravimetric analyses of the different synthesized ternary complexes have been carried out to obtain a diagnostic structural evidence for the suggested molecular formula. Generally, the TG curves show two successive mass loss steps over the temperature range (50−300 °C). The overall mass loss is consistent with the removal of two H_2O molecules, where the low-temperature mass loss (50−150 °C) corresponds to the removal of one hydrated H_2O molecule and the other mass loss (at 200−300 °C) is due to the removal of one coordinated H_2O molecule. This is in accordance with the suggested structural formula as well as the microanalytical data and the infrared spectra cited in Tables 1, and 2, respectively.

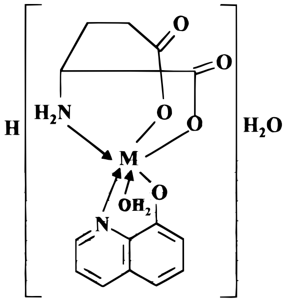
The λ_{max} and ϵ_{max} values of the absorption bands recorded for DMSO solutions of the different synthesized ternary complexes are listed in Table 1. Generally, the spectra of all complexes are characterized by one or two bands in the region 338−420 nm. These bands can be assigned to intermolecular CT-transitions from the ligand molecule to the vacant orbital localized on the metal ion (L → M CT-transition) (Mahmoud et al., 1986). This assignment is based on the observation that these bands are characterized by high molar extinction coefficients (cf. Table 1). Further, the L → M CT-transition character of such bands is also substantiated by the fact that the λ_{max} of the L → M CT-band of the same ligand is red-shifted on changing the metal ion from $Co^{II} \rightarrow Ni^{II} \rightarrow Cu^{II}$. This behavior is in accordance with the fact that the third ionization potentials of these metal ions increase in the same direction (Mahmoud et al., 1986); therefore, the electron-accepting character of the metal ion is expected to increase in the same order, i.e., low-energy L → M CT-transition. The absence of the shorter wavelength band in the recorded spectra of some complexes is attributed to its overlap with the strong $\pi \rightarrow \pi^*$ transition of the ligands.

In addition to the above transitions, the synthesized Co^{II}-complexes are characterized by a broad band within the range 500−520 nm with a shoulder over a wide range in the visible region. In terms of previous work (Lever, 1968), an octahedral structure can be suggested for such ternary complexes, where the broad band is ascribed to the ${}^4T_{1g}(f) \rightarrow {}^4T_{1g}(p)$ transition in admixture with spin-forbidden transitions to doublet states (Lever, 1968). The electronic spectra of Ni^{II}-complexes displayed a main broad absorption band in the wavelength range 550−640 nm, which is indicative of a distorted octahedral structure where the band observed is assigned to the ${}^3A_{2g}(f) \rightarrow {}^3T_{1g}(f)$ transition (Lever, 1968). The Cu^{II}-complex spectrum showed a broad band with λ_{max} within the wavelength range 600−650 nm followed by a broad band into the near-infrared region. On the basis of the fact that six-coordinate Cu^{II} tetragonal distorted complexes have one absorption band near 625 nm (Lever, 1968), a tetragonal distorted structure could be suggested for these complexes, where the observed bands is assigned to the combination of $^2B_{1g} \rightarrow {}^2A_1$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2E_g$ transitions (Lever, 1968).

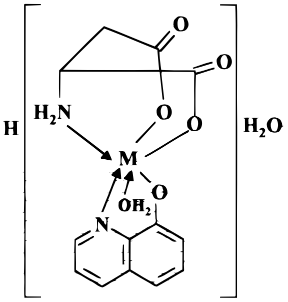
On the basis of the above discussion, the following structures are suggested for the synthesized ternary complexes of Cu^{II}, Ni^{II}, and Co^{II} with H_2ADA **(a)**, glutamic acid **(b)**, and spartic acid **(c)** as primary ligands and 8-hydroxyquinoline as a secondary ligand.



(a)



(b)



(c)

Formation Constants. A typical set of experimental titration curves, obtained according to the sequence described in the Experimental Section for the systems under investigation, is shown in Figure 1. Examination of the titration curves obtained reveals that 1:1 binary [M(ADA)] complexes are formed at low pH values ≤ 2.50. Except in case of [Cu(ADA)], the titration curves for the different 1:1 binary $M^{II} + (HADA)^{1-}$ solutions do not show any buffer zones at high pH value (~10), denoting no possibility for the deprotonation of the amide proton in the formed [M(ADA)] complexes (Nakon et al., 1986). The titration curves of the 1:1 binary M^{II} + dicarboxylic amino acids complexes indicated that they are formed at pH ranging from 2.60 to 3.50. The titration curves of the 1:1 binary M^{II} + 8-hydroxyquinoline reveals that these complexes begin to be formed in the pH range 3.00−4.50. These complexes are stable up to the pH range 4.90−5.20, and above this pH range a precipitation was observed owing to the formation of hydroxo complex species. A further study beyond this pH range was not possible. Generally, the formation of a 1:1 binary complex is indicated by the divergence of its titration curve from that of the corresponding free ligand solution.

The titration curves (f′) obtained for the different 1:1:1 ternary systems under investigation indicated that the 1:1 binary complex [M(a.a)] or [M(ADA)] is first formed and then subsequently coordinates with 8-hydroxyquinoline, HL, as a secondary ligand affording the mixed-ligand complex $[M(ADA)(L)]^{1-}$ or $[M(a.a)(L)]^{1-}$ in a stepwise manner as represented by the following equations:

$$M^{II} + (HADA)^{1-} \rightleftharpoons M(ADA) + H^+$$

$$M^{II} + (a.a) \rightleftharpoons M(a.a) + 2H^+$$

$$M(a.a) \quad \text{or} \quad M(ADA) + [H_2L]^+ \rightleftharpoons [M(a.a)(L)]^{1-} \quad \text{or} \quad [M(ADA)(L)]^{1-} + 2H^+$$

where $M^{II} = Cu^{II}$, Ni^{II}, or Co^{II}; a.a = a dicarboxylic amino acid (aspartic or glutamic); $[H_2L]^+$ = protonated 8-hydroxyquinoline.

It is assumed that the secondary ligand, H_2L^+, would combine with [M(ADA)] or [M(a.a)] binary complex species in the ternary system as it does with $[M(H_2O)_6]^{2+}$ in a binary one. This behavior is supported by observation that the titration curves (f′) for the different 1:1:1 ternary complexes (obtained after addition of a KOH volume equivalent to the concentration of free protonated 8-hydroxyquinoline present in the medium) are strongly overlapped with the corresponding titration curves of the 1:1 binary $M^{II} + (HADA)^{1-}$ or M^{II} + (a.a) complexes, curve e, at low pH values. At a high pH value; which is largely dependent on the nature of both the metal ion and primary ligand, a divergence of the 1:1:1 titration curve (f′) from that of the corresponding binary $M^{II} + (HADA)^{1-}$ or M^{II} + (a.a) is observed. The different titration curves of the 1:1:1 ternary complexes containing (ADA) moiety do not show any buffer zones at high pH values suggesting that the formed $[M(ADA)(L)]^{1-}$ ternary complexes have no tendency to undergo deprotonation of the amide group belonging to the primary ligand $(HADA)^{1-}$. Further, all ternary metal complex solutions do not show any precipitation up to the pH value corresponding to complete complex formation. However, a precipitation takes place in the pH range 5.00−5.60 owing to the formation of hydroxo complex species.

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 8-hydroxyquinoline molecules as a secondary ligand associated with one molecule of binary [M(ADA)] or [M(a.a)] complex by the method of Irving and Rossotti (Irving and Rossotti, 1953, 1954). The equation given is

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

where $V_{f'}$ and V_e are the volumes of KOH consumed to reach the same pH values in curves f′ and e, respectively (cf. Figure 1). C_b and C_a are the concentrations of KOH and HNO_3, respectively. C_M is the concentration of [M(ADA)] or [M(a.a)] which is equal to the concentration of M^{II} used, C_L is the concentration of a ligand, y is the number of dissociable protons of the secondary ligand 8-hydroxyquinoline ($y = 2$ for such molecule), and V_o is the original volume (50 cm^3). $\bar{n}_H$ values (the average number of protons associated with the ligand) for 8-hydroxyquinoline at different pH values were available from the determination of its formation constant. The $\bar{n}_{mix}$ values do not exceed unity, indicating that only one secondary ligand molecule combines with the binary [M(ADA)] or [M(a.a)] complex. From the values of $\bar{n}_{mix}$, the free secondary ligand exponent (pL_{mix}) was calculated using the following equation (Irving and Rossotti, 1953, 1954):

$$pL_{mix} = \log\left\{\frac{\sum_{y=0}^{y=1or2} \beta_y^H\,(1/10^B)}{C_L - \bar{n}_{mix}C_M}\,\frac{V_o + V_{f'}}{V_o}\right\}$$

Here β_y^H are the formation constant values of the second-

Table 3. Mean Formation Constants Values[a] of the Different (1:1) Binary and (1:1:1) Ternary Metal Complexes Formed at (25 ± 0.1) °C and an Ionic Strength $I = 0.10$ mol dm^{-3} (KNO$_3$)

		$\log K^{M}_{M(ADA)}$				$\log K^{M(a.a)}_{M(a.a)(L)}$	
metal ion	$\log K^{M}_{M(ADA)}$	$\log K^{M}_{M(aspart)}$	$\log K^{M}_{M(glut)}$	$\log K^{M}_{M(L)}$	$\log K^{M(ADA)}_{M(ADA)(L)}$	$\log K^{M(aspart)}_{M(aspart)(L)}$	$\log K^{M(glut)}_{M(glut)(L)}$
Cu^{II}		8.78 ± 0.04 (8.81)[c]	8.32 ± 0.03 (8.34)[c]	9.12 ± 0.02	9.62 ± 0.03	9.89 ± 0.05	8.70 ± 0.04
Ni^{II}	6.73 ± 0.03 (6.73)[b]	7.42 ± 0.03 (7.41)[b]	5.40 ± 0.06 5.58[d]	8.45 ± 0.05	8.38 ± 0.05	9.02 ± 0.03	8.15 ± 0.06
Co^{II}	6.48 ± 0.05 (6.50)[b]	6.65 ± 0.02 (6.74)[b]	4.68 ± 0.04 4.56[d]	8.16 ± 0.02	8.22 ± 0.03	8.38 ± 0.02	7.98 ± 0.07

[a] aspart = aspartic acid, glut = glutamic acid, and L = 8-hydroxyquinoline. [b] Ahmed et al., 1996. [c] Boraei and Abd Alla, 1993. [d] Martel and Sillen, 1971.

ary ligand 8-hydroxyquinoline, and B is the pH meter reading. All other terms have the same meanings as defined above.

The formation constants of the different binary complexes (Table 3) were determined by applying the original equations of Irving and Rossotti (1953, 1954) to the binary complex solution systems (curves b, c and d, e for [M(ADA)] or [M(a.a)], and [M(L)]$^+$, respectively).

The mean $\log K^{M}_{M(ADA)or(a.a)}$, $\log K^{M}_{M(L)}$, and $\log K^{M(ADA)or(a.a)}_{M(ADA)or(a.a)(L)}$ values obtained from the corresponding experimental formation curves using the average value and straight line methods along with the error as obtained by applying the least-squares fits are listed in Table 3. Some of the log K values of the binary complexes under investigation are in good agreement with the literature values (cf. Table 3) (Ahmed et al., 1996; Boraei and Abd Alla, 1993; Martel and Sillen, 1971). The results cited in Table 3 reveal that the stability of binary or ternary complexes of the same metal ion, in terms of the nature of the primary ligand, varies according to the order: aspartic acid (pK_{a_2} = 3.86, pK_{a_3} = 9.80) > (HADA)$^{1-}$ (pK_{a_2} = 6.62) > glutamic acid (K_{a_2} = 4.31, pK_{a_3} = 9.67) (Perrin and Dempsey, 1974; Weast, 1973). 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 the ligand chain would result in more strain on its bending, i.e., relatively low stability. In addition, though each of the three ligands acts as a tridentate ligand (NOO donor), and glutamic acid is highly basic relative to (HADA)$^{1-}$, the observed low stability of the metal complexes containing glutamate relative to those containing ADA moiety can be ascribed to the formation of two five- and seven-membered metal chelate rings in the case of glutamic acid and two five-membered metal chelate rings in the case of (HADA)$^{1-}$. The high stability of the binary or ternary complexes containing the dicarboxylic amino acid (aspartic) can be ascribed, in addition to the effective high basicity of aspartic acid, i.e., a good σ-donor, to the formation of two five- and six-membered metal chelate rings. Moreover, the order of stability of the different binary or ternary complexes in the systems under investigation, in terms of the nature of metal ion, follows the usual sequence Co^{2+} < Ni^{2+} < Cu^{2+} (Cotton and Wilkinson, 1976).

Thermodynamic Functions of Complex Formation. The formation constants of [M^{II} + (HADA)$^{1-}$ + 8-hydroxyquinoline] complex (where M = Co, Ni, or Cu) were determined acidimetrically at 10, 25, 35, and 55 °C and at a constant ionic strength $I = 0.1$ mol dm^{-3} (KNO$_3$) in 20 mass % EtOH + H$_2$O mixture. The overall reaction of the ternary complex formation can be represented by the following equation:

$$\mathrm{M(ADA)} + [\mathrm{H_2L}]^+ \rightleftharpoons [\mathrm{M(ADA)(L)}]^{1-} + 2\mathrm{H}^+$$

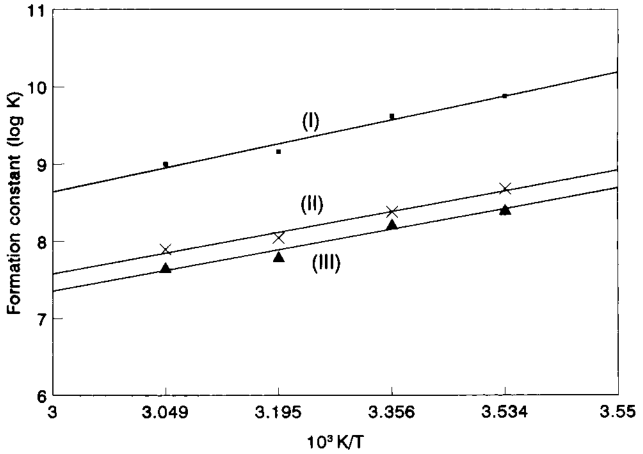


Figure 2. Plot of log K against $1/T$ for [M^{II} + (HADA)$^{1-}$ + 8-hydroxyquinoline] complex solutions for Cu^{II}-complex (**I**), Ni^{II}-complex (**II**), and Co^{II}-complex (**III**) at a constant ionic strength I = 0.10 mol dm^{-3} (KNO$_3$).

Table 4. Thermodynamic Functions[a] of M^{II}–(AdA)$^{1-}$–8-Hydroxyquinoline Ternary Complexes at an Ionic Strength $I = 0.10$ mol dm^{-3} (KNO$_3$)

metal	log K values at t/°C				$-\Delta H$/kJ	-$\Delta G°$/kJ	$\Delta S°$/J
ion	10	25	40	55	mol^{-1}	mol^{-1}	mol^{-1} K^{-1}
Cu^{II}	9.88	9.62	9.16	9.00	36.75	54.89	60.79
Ni^{II}	8.68	8.38	8.04	7.89	32.22	11.43	52.38
Co^{II}	8.41	8.22	7.80	7.66	31.63	46.90	51.25

[a] $\Delta G°$ and $\Delta S°$ values are calculated at 25 °C.

The values of the enthalpy change (ΔH) are determined graphically by plotting log K values at different temperatures vs $1/T$ (Figure 2) and equating the gradient with $-\Delta H/19.15$. The values of the free energy ($\Delta G°$) and entropy ($\Delta S°$) changes associated with the complex formation are calculated at 25 °C using the following equations: $\Delta G° = -2.303RT \log K$ and $\Delta S° = (\Delta H - \Delta G°)/T$, respectively.

The formation constants values along with the values of ΔH, $\Delta G°$, and $\Delta S°$ are given in Table 4. The results obtained reveal that the metal–ligand complexation reaction is less favored with increasing the temperature, indicating the exothermic nature of the complex formation reactions. The negative $\Delta G°$ values for complex formation indicate that the metal–ligand chelates are formed spontaneously. The $\Delta S°$ values for formation of all complexes are positive indicating that the entropy is favorable for the formation of the complexes studied. This is interesting and must be a result of solvation and charge changes. Normally, one expects a decrease in randomness (i.e., negative value of $\Delta S°$) when separate components are combined into a complex for the combining process involving all gaseous ions. However, Williams has pointed out that a high positive value for the entropy of the formation reaction is observed when positive and negative ions combine to give a complex of a different charge in solution (Williams, 1954). Moreover, the relatively large values of ΔS° compared with the values of ΔH indicate entropy as the principal driving force for the complex formation of the investigated systems. Therefore, the positive ΔS° values obtained substantiate the conclusion (cf. above *Characterization of the Solid Ternary Complexes*) that the ternary metal chelates are formed owing to the coordination of the divalent anion of the tridentate primary ligand $(\mathrm{ADA})^{2-}$ and the monovalent anion of the bidentate secondary ligand 8-hydroxyquinoline $(\mathrm{L})^{1-}$ to the central divalent transition metal ion (M^{II}). Further, the magnitude of the ΔS° value of of the complexes, in terms of the nature of metal ion, increases in the order $\mathrm{Co}^{\mathrm{II}} \rightarrow \mathrm{Ni}^{\mathrm{II}} \rightarrow \mathrm{Cu}^{\mathrm{II}}$. This is consistent with the order of increasing the electron-accepting character of these metal ions (Cotton and Wilkinson, 1976).

Literature Cited

(1) Ahmed, I. T.; El-Roudi, O. M.; Boraei, A. A. A.; Ibrahim, S. A. Equlibrium Studies of the Ternary Complexes Systems M^{n+} + Dipicolinic Acid + *N*-(2-Acetamido)iminodiacetic Acid or Amino Acids. *J. Chem. Eng. Data* **1996**, *41*, 386−390.

(2) Ahmed, I. T.; Boraei A. A. A.; Ibrahim, S. A. Mixed-Ligand Complexes of Some Metal Ions with *N*-(2-Acetamido)iminodiacetic and Salicylic Acid Derivatives: Synthesis, Solution Equilibria and Characterization Studies. *Synth. React. Inorg. Met.-Org. Chem.* **1997**, *27*, 169−186.

(3) Basudhar, P. R.; Sinha S.; Das P. K.; Ghosh, B. K. Mixed-Ligand Complexes of Osmium(III/IV)8-Quinolinolates with One Ketoximate Ligand. *Transition Met. Chem.* **1996**, *21*, 154−157.

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

(5) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley (Eastern): New Delhi, 1976; p 596.

(6) Douhéret, G. Dissociation of Organic Compounds in Aqueous Organic Media. I. Determination of the Liquid Junction Potential and the Effect of the Medium on the Hydrogen Ion in These Systems, and the Study of the Dissociation of Some Acid−Base Couples. *Bull. Soc. Chim. Fr.* **1967**, 1412−1419.

(7) Douhéret, G. Liquid Junction Potentials and Medium Effects in Mixed Solvents (Water-Dipolar Aprotic Solvents). Application to the Standardization of the Glass-Calomel Electrodes Systems in These Mixtures. Dielectric Properties of These Mixtures. *Bull. Soc. Chim. Fr.* **1968**, 3122−3131.

(8) Geary, W. J. Use of Conductivity Measurements in Organic Solvents for the Characterization of Coordination Compounds. *Coord. Chem. Rev.* **1971**, *7*, 81−122.

(9) Hamed, M. M. A.; Saleh, M. B.; Ahmed, I. T.; Mahmoud, M. R. Formation Constants of Ternary Complexes of Some Heavy Metal Ions with *N*-(2-Acetamido)iminodiacetic Acid and Aliphatic or Aromatic Acids. J. *Chem. Eng. Data* **1994**, *39*, 565−567.

(10) Ibrahim, S. A.; El-Gahami, M. A.; Awad, I. M. A. New Biologically Active Four Coordinate Complexes Involving Some Divalent Transition Metal Ions and 5-(substitutedimino)-8-Hydroxyquinolines. *Ann. Quim.* **1992**, *88*, 657−660.

(11) Ibrahim, S. A.; El-Gyar, S. A.; Abdel-Hafez, A. A.; Rabia, M. K. Divalent Transition Metal Complexes of Potentially Polynucleating 8-hydroxyquinoline-5-sulfonyl Hydrazone. *Collect. Czech. Chem. Commun.* **1994**, *59*, 1800−1808.

(12) Ibrahim, S. A.; Mahmoud, M R.; Saleh M. B.; Ahmed, I. T. $\mathrm{H_2O}$ Soluble Ternary Complexes of Divalent Transition Metal Ions with *N*-(2-Acetamido)iminodiacetic Acid and Heterocyclic Diimines. *Transition Met. Chem.* **1994**, *19*, 494−497.

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

(14) 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.

(15) Islam, M. S.; Ahmed, M. S.; Pal, S. C.; Reza Y.; Jesmin, S. Synthesis and Characterization of Platinum(IV) and Gold(III) Complexes of Amino Acids and 8-Hydroxyquinoline. *Indian J. Chem.* **1995**, *34A*, 816−818.

(16) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks R. G.; Stout, G. H. *Organic Structural Analysis*; MacMillan: New York, 1976; p 275.

(17) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968; pp 318, 321, 333, and 3523.

(18) Mahmoud, M. R.; Hammam, A. M.; El-Gyar, S. A.; Ibrahim, S. A. Coordination Compounds of Heterocyclic Azo Derivatives. III. Co(II), Ni(II) and Cu(II) Complexes of Some Arylazo-4,5-diphenylimidazole Derivatives. *Monatsh. Chem.* **1986**, *117*, 313−325.

(19) Mahmoud, M. R.; Ibrahim, S. A.; Hassan, A. M. A.; Ahmed, I. T. Ternary Complexes of *N*-(2-Acetamido)iminodiacetic Acid and Some Aromatic Acids. Isolation and Stability Constants in Solution. *Transition Met. Chem.* **1996**, *21*, 1−4.

(20) Martel A. E.; Sillen L. G. *Stability Constants of Metal Ion Complexes*; The Chemical Society: London, 1971; p 317.

(21) Masson, J.; Busnot, A.; Busnot, F.; Hamidy, J. F.; Le Querler, J. F. Study of Copper(II) Succinate Complexes with Imidazole or Methyl-Substituted Imidazoles. *Thermochim. Chim. Acta* **1987**, *122*, 221−229.

(22) Nakamoto,K.; *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; pp 228, 229, 237−239.

(23) Nakon, R.; Krishnamoorthy, C. R.; Townshend, S.; Grayson, J. Direct Evidence for an $\mathrm{S_N1CB}$ Mechanism III. Observation of Deprotonated Mixed Ligand Chelates of *N*-(2-Acetamido)iminodiacetatocopper(II). Evidence for the Intermediate. *Inorg. Chim. Acta* **1986**, *124*, L5−L7.

(24) Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal ion Control*; Chapman & Hall: London, 1974; p 92.

(25) Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 3rd ed.; Longman: London, 1975; pp 435, 441, 443.

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

(27) Williams, R. J. P. The Stability of Complex Ion with Special Reference to Hydration. *J. Phys. Chem.* **1954**, *58*, 121−126.

Received for review August 7, 1997. Accepted February 25, 1998.

JE970192M