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Synthesis and Equilibrium Studies of Mixed-Ligand Complexes of Co(II), Ni(II), and Cu(II) with Some Aliphatic Dicarboxylic Acids and Creatinine

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis and Equilibrium Studies of Mixed-Ligand Complexes of Co(II), Ni(II), and Cu(II) with Some Aliphatic Dicarboxylic Acids and Creatinine

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ABSTRACT

Ternary mixed-ligand metal complexes $[M(L^1)(L^2)_2](H_2O)_n$, where M = Co(II), Ni(II), or Cu(II), L^1 = the dianion of succinic, malic, or tartaric acid, and L^2 = creatinine, were synthesized and characterized using microchemical and thermal analyses, molar conductance, infrared, and electronic spectral measurements. A square–planar structure is suggested for the Co(II) and Cu(II) ternary complexes, whereas Ni(II) ternary complexes have tetrahedral stereochemistry. Formation constants of the binary and ternary complexes in such systems were determined by pH-metric titrations at $25 \pm 0.1\,^\circ C$ and at a constant ionic strength $I = 0.1\,M$ (KNO_3). The stability of the various complexes was discussed in terms

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of the nature of both the ligands and metal ions. The thermodynamic functions (ΔH, ΔG^o, and ΔS^o) associated with the complex formation of [Cu(II) + aliphatic acids + creatinine] were also determined and examined.

Key Words: Mixed-ligand complex; Creatinine; Aliphatic acids; Complex formation.

INTRODUCTION

2-Amino-1-methyl-4-imidazolidinone (commonly known as creatinine) is an important end product of nitrogen metabolism in vertebrates.[1] Moreover, its levels in urine are clinically important as indicators of a variety of disease states.[1] The investigation of the complexing ability of creatinine with various metal ions might be of interest in connection with creatinine metabolism studies.[1,2] The possibility of it existing in imino- or/and amino-tautomeric forms and the presence of several donor groups determines its strong coordination capacity.[3,4] A literature survey indicates that very few pH-metric studies on creatinine complexes were made.[5] Great interest was devoted to the synthesis, characterization and structural studies of binary complexes of creatinine with the following metal ions; Ag(I), Hg(II), Cd(II), Zn(II), Co(II), Ni(II), Cu(II), Pt(II), and Pd(II).[6–12] The results obtained indicate that the complexation ability of this ligand and the types of complexes formed depend strongly on the reaction conditions.[7,9–12] However, no studies have been made on ternary systems containing divalent metal ions as well as creatinine, and aliphatic acids. Therefore, extending the studies on ternary metal complexes,[13–23] this article reports the synthesis of the ternary complexes of Co(II), Ni(II), and Cu(II) ions with aliphatic acids (H_2L^1) as primary ligands and creatinine (L^2) as a secondary ligand, as shown in Fig. 1. The prepared complexes were characterized by elemental, thermogravimetric analyses, molar conductance, infrared, and electronic spectral measurements. The formation constants of the various binary and ternary complexes were also determined and discussed in terms of the nature of both the ligand and metal ion. The thermodynamic functions (ΔH, ΔG^o, and ΔS^o) associated with the complex formation of [Cu(II) + aliphatic acids + creatinine] were also determined.

EXPERIMENTAL

Materials

The aliphatic acids and creatinine were of analytical grade and were purchased from Aldrich. The purity of these compounds was verified by thin layer

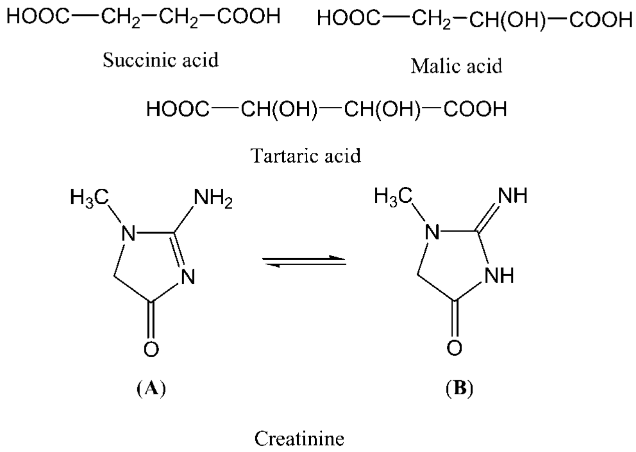

Figure 1. Structures of the ligands.

chromatography (TLC). The metal salts [$Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 6H_2O$] and all other chemicals used were also of analytical grade. Spectroscopic grade DMSO purchased from Aldrich was used for the electronic spectral measurements.

Synthesis of the Ternary Metal Complexes

In a round bottom flask an ethanolic solution (10 mL) containing 5 mmol (0.566 g) of creatinine was added to an EtOH solution (10 mL) containing 5 mmol of each of the following metal salts: $Co(NO_3)_2 \cdot 6H_2O$ (1.455 g); or $Ni(NO_3)_2 \cdot 6H_2O$ (1.454 g); or $Cu(NO_3)_2 \cdot 6H_2O$ (1.163 g). To this mixture was added slowly with stirring an EtOH solution (10 mL) containing 5 mmol of one of the following aliphatic acids: succinic (0.590 g), malic (0.670 g), or tartaric (0.750 g). The ternary mixture was refluxed for 5 hr and then evaporated to half of its volume and left to cool. The ternary complexes precipitated out, were filtered and washed thoroughly with distilled H_2O and EtOH and dried *in vacuo* over P_4O_{10}.

Solutions

Stock solutions of the aliphatic acids and creatinine were prepared in CO_2-free, doubly distilled H_2O. Solutions of the divalent transition metal ions were prepared from their nitrate salts in doubly distilled H_2O, and the metal ion concentrations were checked by compleximetric titration as recommended elsewhere.[24] Stock solutions of HNO_3 and CO_2-free ($\approx 0.2\,M$) KOH were prepared and used after standardization. A stock solution of KNO_3 was also prepared in doubly distilled H_2O.

pH-Metric Titration

Numerous titrations of M(II) + aliphatic acids and/or creatinine mixture in the 1 : 1 : 1 molar ratio (1.5 mL of 0.05 M of each) with a standard (0.1878 M) KOH solution were performed at $25 \pm 0.1\,^\circ C$. The titrations were carried out 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 (0.1 M) using a KNO_3 solution, and a total mixture volume of 25 mL was used for each titration. The titration was carried out in a closed titration jacket. The titrations were repeated three times for each titration curve to ensure consistency. More than 40 data points were collected for each curve.

The various solutions titrated were made according to the following sequence: (a) 2.5 mL of 9.4×10^{-2} M HNO_3; (b) solution (a) + 1.5 mL of 0.05 M creatinine; (c) solution (b) + 1.5 mL of 0.05 M M(II); (d) solution (a) + 1.5 mL of 0.05 M aliphatic acids; (e) solution (d) + 1.5 mL of 0.05 M M(II); (f) solution (e) + 1.5 mL of 0.05 M creatinine; and (g) solution (f) + 0.4 mL of KOH (0.1878 M) equivalent to the concentration of creatinine.

Apparatus

The C, H, and N contents of the prepared ternary complexes were determined by the Microanalytical Unit at Cairo University. Molar conductances of DMSO solutions of the synthesized ternary complexes were measured at 25 °C using a model 31 YSI conductivity bridge with a conductivity cell constant = 0.10 M. Thermogravimetric (TG) analyses were performed automatically using a DuPont 9000 thermal analyzer with a computer and at a heating rate of $10\,^\circ C\,min^{-1}$ in a dynamic air atmosphere. Infrared spectra were recorded in the 4000–400 cm^{-1} range on a Shimadzu IR-470 spectrophotometer using KBr pellets. Electronic spectra of freshly prepared solutions of the complexes in DMSO were recorded at 25 °C in the 200–1000 nm range by a model UVA 1000E Unicam Scanning UV-VIS spectrophotometer with an accuracy of ±1 nm using matched silica cells of 1.0 cm path length. The spectrophotometer and its accessories were controlled by software based on Windows to provide advanced operational facilities. The pH-measurements were performed by means of a model SM 702 Metrohm automatic titrator (Switzerland) with a combined pH glass electrode equipped with a magnetic stirrer. The accuracy of the pH-meter is ± 0.001 pH units. The glass electrode and the pH-meter were calibrated before each series of measurements using aqueous standard buffers of pH 4.00 (phthalate buffer) and 9.20 (borate buffer). A Fischer Scientific Isotemp Refrigerator Circulator Model 9000 was used for adjusting the temperature.

RESULTS AND DISCUSSION

Characterization of the Ternary Metal Complexes

Microanalysis

The microanalytical data for the prepared ternary complexes along with their physical properties are listed in Table 1. The general molecular formula of the ternary complexes was found to be $[M(L^1)(L^2)_2](H_2O)_n$, where $n = 1$ for the Co(II) and Cu(II) complexes, $n = 2$ for the Ni(II) complexes.

The prepared ternary complexes were found to be insoluble in water as well as in most common organic solvents (such as ethanol, methanol, chloroform, acetonitrile). However, they are slightly soluble in DMF and DMSO. The measured molar conductance values (Λ_m) of 10^{-3} M DMSO solutions of the ternary complexes shown in Table 1 are in the range 13–19 $\text{ohm}^{-1}\,\text{cm}^{-1}\,\text{M}^{-1}$, indicating the nonelectrolytic nature of these complexes.[25]

TG Analysis

Thermogravimetric (TG) analyses of the various ternary complexes have been carried out to obtain diagnostic structural evidence of the suggested molecular formula. Generally, the TG curves exhibit one smooth weight loss step over the temperature range 75–115 °C. This weight loss is in good agreement with the removal of one or two water molecules, depending on the nature of the metal ion, indicating that the various synthesized ternary complexes contain only water of hydration. This is in accordance with the elemental analyses data as shown in Table 1, as well as the IR spectra of the ternary complexes shown in the following section. At high temperature (>300 °C) a steep weight loss step is observed pointing out to a rapid decomposition of the ternary complexes.

Table 1. Microanalytical data, physical properties, molar conductance, and electronic spectra of the prepared ternary complexes.[a]

Complex (empirical formula)	M. wt.	Color	M.p. (°C)	Yield (%)	Found (calcd, %)			Λ_m ($\mathrm{ohm^{-1}\,cm^{-1}\,mol^{-1}\,L}$)	λ_{max} (nm) [$\varepsilon_{max} \times 10^{-3}$ ($\mathrm{M^{-1}\,cm^{-1}}$)]
					C	H	N		
[Co(succinate)(creatinine)$_2$]H$_2$O ($C_{12}H_{20}CoN_6O_7$)	419.26	Deep pink	330 d	53	34.57 (34.38)	4.63 (4.81)	19.87 (20.04)	19	524 br (220)
[Ni(succinate)(creatinine)$_2$](H$_2$O)$_2$ ($C_{12}H_{22}N_6NiO_8$)	437.04	Pale green	212	64	33.16 (32.98)	5.31 (5.07)	19.44 (19.23)	15	720 br (30.4)
[Cu(succinate)(creatinine)$_2$]H$_2$O ($C_{12}H_{20}CuN_6O_7$)	423.87	Pale blue	196	46	33.78 (34.00)	4.63 (4.76)	19.69 (19.83)	17	770 br (39.75)
[Co(malate)(creatinine)$_2$](H$_2$O)$_2$ ($C_{12}H_{20}CoN_6O_8$)	435.26	Deep pink	223	51	30.95 (31.11)	4.89 (4.63)	19.56 (19.31)	13	490 br (235)
[Ni(malate)(creatinine)$_2$](H$_2$O)$_2$ ($C_{12}H_{22}N_6NiO_9$)	453.03	Pale green	335 d	52	32.11 (31.81)	5.07 (4.89)	18.38 (18.55)	17	696 br (28.5)
[Cu(malate)(creatinine)$_2$]H$_2$O ($C_{12}H_{20}CuN_6O_8$)	439.87	Pale blue	320 d	64	32.64 (32.77)	4.77 (4.58)	19.29 (19.11)	14	755 br (44.00)
[Co(tartarate)(creatinine)$_2$]H$_2$O ($C_{12}H_{20}CoN_6O_9$)	451.26	Deep pink	232	62	32.21 (31.94)	4.32 (4.47)	18.77 (18.62)	19	515 br (260)
[Ni(tartarate)(creatinine)$_2$](H$_2$O)$_2$ ($C_{12}H_{22}N_6NiO_{10}$)	469.03	Pale green	316 d	53	30.92 (30.73)	4.56 (4.73)	18.18 (17.92)	15	680 br (26.5)
[Cu(tartarate)(creatinine)$_2$]H$_2$O ($C_{12}H_{20}CuN_6O_9$)	455.87	Pale blue	254	55	31.49 (31.62)	4.63 (4.42)	18.26 (18.44)	16	708 br (37.5)

[a] br = broad; d = decomposed.

IR Spectra

Table 2 shows the important IR bands of the prepared ternary complexes, which provided good evidence for the coordination mode of the ligands. The broad bands in the range of 3560–3500 cm^{-1} in the IR spectra of the various ternary complexes can be most likely attributed to the OH-stretching vibration of water of hydration. This band overlapped with the stretching vibration of the OH group of malate or tartarate. However, the absence of sharp band in the IR spectra of free OH group belonging to malate or tartarate could likely be ascribed to its being buried under the broad band due to the antisymmetric and symmetric OH-stretching of hydrated water molecules. On the other hand, the IR spectra of malate and tartarate complexes showed strong absorptions at 1370–1350 cm^{-1} range due to the vibration bending of the free OH group. In addition, the IR spectra displayed bands in the ranges 1075–1060 and 1125–1115 cm^{-1} for C–O stretching of –CH_2OH (malate) and $>$CHOH (tartarate), respectively. This is another evidence for the nonparticipation of hydroxyl groups in case of malate and tartarate complexes. Furthermore, it had been reported earlier that the transition metal ions Co(II), Ni(II), and Cu(II) formed seven-membered ring structures with malate and tartarate with the oxygen of carboxyl groups.[15] A number of bands were observed in the 3450–3400 cm^{-1} range, in which $\nu(NH_2)$ symmetric and asymmetric vibrations of creatinine appear.[26] These data show that creatinine is mainly present in the complex as its amino-tautomer (A) as shown in Fig. 1. The bands in the 2990–2900 cm^{-1} range (medium to weak) could be assigned to the C–H stretching vibrations in both primary and secondary ligands. The ν(C=O) bands of creatinine were observed in the range 1710–1690 cm^{-1} showing that the C=O groups of creatinine are not involved in the coordination. The assignment of this band is in a good agreement with those previously reported for creatinine on the basis of characteristic vibrations.[4,27] The stretching modes of C=N of free creatinine observed[10] at 1680 cm^{-1} is shifted to lower frequency at the 1645–1665 cm^{-1} range in the IR spectra of the complexes, revealing the involvement of this group in the coordination with the metal ion. The suggested structure of the complexes in Fig. 2 indicates the possible formation of intramolecular hydrogen bonding between C=O and exocyclic NH_2 groups, which may stabilize the structure.[10] A distinct band appearing in the 1640–1600 cm^{-1} region in all complexes is typical of coordination carboxylate stretching.[26] This assignment is based on the fact that the ionized and coordinated COO$^-$ stretching band appears[26] at 1650–1590 cm^{-1}. The fact that the band appeared in the 1450–1400 cm^{-1} range is likely ascribed to the symmetric vibration of the coordinated carboxylates.[26] The above findings are consistent with the conclusion that the divalent anions of aliphatic acids are coordinated to the central metal ion as bidentate ligands, whereas, creatinine coordinated as a monodentate ligand through the endocyclic N-atom.

Table 2. The most important infrared bands (cm^{-1}) of the ternary complexes.[a]

[M(II)–succinate–(creatinine)$_2$](H$_2$O)$_n$			[M(II)–malate–(creatinine)$_2$](H$_2$O)$_n$			[M(II)–tartarate–(creatinine)$_2$](H$_2$O)$_n$			
Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Assignment of IR bands
3540 br	3500 br	3560 br	3520 br	3530 br	3560 br	3565 br	3520 br	3550 br	ν(OH) of hydrated H_2O molecules + ν(OH) free of malate and tartarate.
3375 br	3440 br	3430 br	3450 m	3450 m	3420 m	3400 br	3410 br	3400 m	$\nu(NH_2)$ symm. and asymm. vibration.
2980 m	2980 m	2930 w	2900 m	2930 w	2920 w	2990 m	2940 w	2960 m	CH-stretching vibration of aliphatic acids and creatinine.
1695 s	1700 s	1705 s	1720 s	1690 s	1710 s	1705 s	1700 s	1705 s	ν(CO) of creatinine.
1645 s	1650 m	1650 s	1660 s	1655 s	1665 m	1660 s	1660 s	1660 m	ν(C=N) of creatinine.
1620 m	1590 m	1630 m	1620 s	1620 m	1630 s	1630 m	1625 m	1630 m	Ionized and coordinated COO^- stretching.
1450 s	1430 s	1440 m	1400 m	1435 m	1440 s	1420 m	1450 m	1440 m	Symm. stretching vibration of coordinated COO^-.
—	—	—	1360 s	1365 s	1350 s	1370 s	1360 s	1365 s	Free OH bending.
—	—	—	1075 s	1060 s	1070 s	—	—	—	C–O stretching of $-CH_2-OH$.
—	—	—	—	—	—	1125 s	1115 s	1120 s	C–O stertching of $>CH-OH$.

[a] $n = 1$ for Co(II) and Cu(II) complexes and $n = 2$ for Ni(II) complexes. s = strong, m = medium, w = weak, and br = broad.

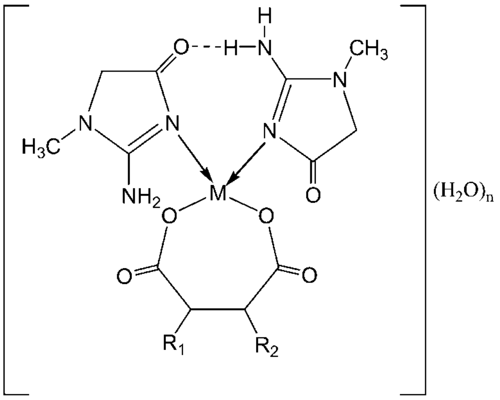

Figure 2. The suggested structures of the prepared ternary complexes $[M(L^1)(L^2)_2](H_2O)_n$, where $n = 1$ for M = Co(II) and Cu(II) and $n = 2$ for M = Ni(II). L^1 = succinate ($R_1 = R_2 = H$), malate ($R_1 = OH$, $R_2 = H$), and tartarate ($R_1 = R_2 = OH$).

Electronic Spectra

In order to shed some light on the geometrical structure of the ternary metal complexes, the electronic absorption spectra of the complex solutions in DMSO were recorded (Fig. 3). The wave length maxima and the molar extinction coefficients of the various bands in the recorded spectra were collected in

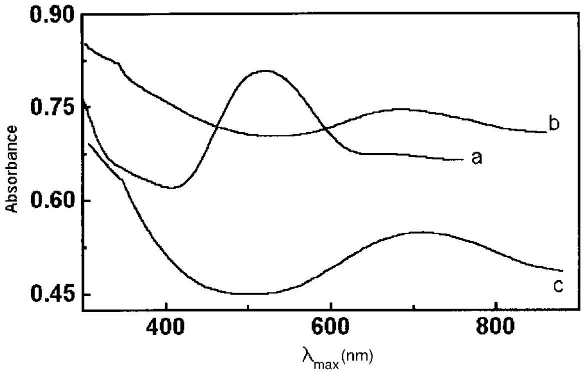

Figure 3. Visible electronic absorption spectra of Co(II), Ni(II), and Cu(II) ternary complexes containing creatinine as secondary ligand: (a) [Co(succinate)(creatinine)$_2$]-H_2O, (b) [Ni(tartarate)(creatinine)$_2$]$(H_2O)_2$, and (c) [Cu(tartarate)(creatinine)$_2$]H_2O.

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Table 1. The Co(II)-complexes are characterized by a broad absorption band with λ_{max} in the 490–524 nm range ($\varepsilon_{max} = 220–260\,cm^{-1}\,M^{-1}$). In terms of previous work, a square–planar structure may be suggested for the ternary complexes of Co, Ni, and Cu with O_2N_2 ligands.[28–32] Accordingly, this band can be assigned to an electronic transition from the lower orbital (e_g) to the empty (b_{1g}) $dx^2 - y^2$ σ-anti-bonding orbital.[32]

The electronic absorption spectra of the Ni(II)-complexes display a broad band in the visible region in the range 680–720 nm ($\varepsilon_{max} = 26.5–30.4\,cm^{-1}\,M^{-1}$), followed by a weak shoulder at the low-energy side. Based on previous work, this is indicative of a tetrahedral stereochemical configuration of the Ni(II) ion, where the recorded broad band is assigned to the $^3T_1 \rightarrow {}^3T_1(P)$ transition.[28]

It was reported previously that four-coordinate Cu(II)-complexes have d–d transitions at about 1112–1250, 1175–740, and 699–917 nm for a regular tetrahedral, pseudo-tetrahedral, or square–planar structure, respectively.[28] Considering this fact that the absorption maximum related to four-coordinate Cu(II)-complexes shifts to higher energy as the regular tetrahedral structure is distorted towards square–planar.[28] Thus, one may suggest a square–planar structure for the present synthesized Cu(II) complexes having an absorption band in the range 708–770 nm ($\varepsilon_{max} = 37.50–44.00$), where this band is attributed to the $^2B_{2g} \rightarrow {}^2E_{1g}$ and $^2B_{2g} \rightarrow {}^2A_{1g}$ transitions.[28]

Formation Constants of the Various Complexes

Formation of the Complexes

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 Fig. 4. Similar curves were obtained for the other metal ions.

Binary Complexes

The titration curves (c) in Fig. 4 corresponding to the 1 : 1 binary M(II)-creatinine complex solutions indicate that the binary complexes are formed at a pH range 5.0–6.5. This is concluded from the observed difference of the titration curve (c) of the binary complex solution from the curve (b) of the free ligand. The binary metal complex solutions show precipitation at a pH range of 7.0–8.0 depending on the nature of metal ion. This behavior can be attributed to the interference of hydrolysis reaction. Therefore, beyond this point, the calculation of the binary stability constant could not be made.

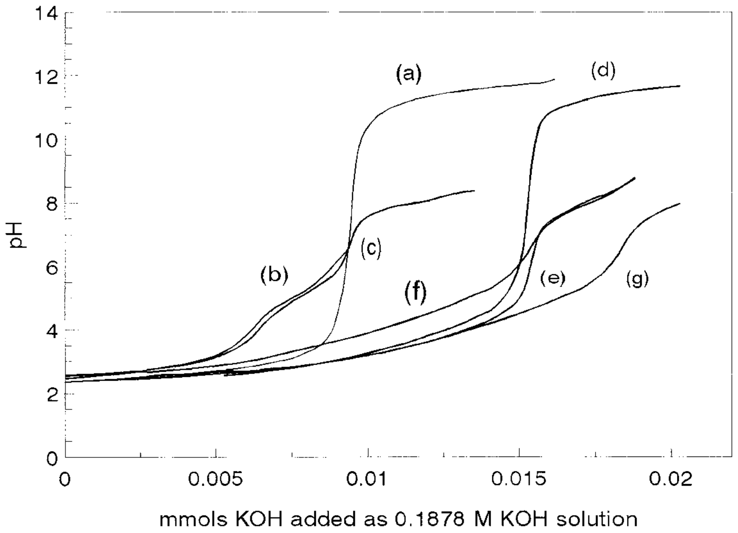

Figure 4. Titration curves of [Co(II)–tartaric acid–creatinine] at 25 °C and constant ionic strength $I = 0.10\,\mathrm{M}$ KNO_3. (a) 2.5 mL of 9.4×10^{-2} M HNO_3; (b) solution (a) + 1.5 mL of 0.05 M of creatinine; (c) solution (b) + 1.5 mL of 0.05 M of Co(II); (d) solution (a) + 1.5 mL of 0.05 M tartaric acid; (e) solution (d) + 1.5 mL of 0.05 M of Co(II); (f) solution (e) + 1.5 mL of 0.05 M of creatinine; and (g) curve (f) after addition of 0.4 mL of KOH (0.1878 M) equivalent to creatinine concentration present in the solution.

The titration curve (e) in Fig. 4 of the 1 : 1 binary [M(II) + aliphatic acids] complex solutions clearly reveal that the various 1 : 1 binary complexes begin to form at the lower pH range 3.0–4.5. Examination of the various titration curves of the investigated binary M(II)–aliphatic acid complexes reveals that the pH at which the binary complex is formed is largely dependent on the nature of each of the aliphatic acids and metal ion. For the same metal ion the pH value, at which the 1 : 1 binary complex of an aliphatic acid begins to form, is lowered according to the following order: succinic > malic > tartaric. This indicates a high tendency of the hydroxy aliphatic acid towards complex formation along the same sequence.

Ternary Complexes

The titration curve (g) in Fig. 4 (obtained after addition of KOH equivalent to the creatinine ligand present in the ternary solution) of the mixed-ligand system under investigation overlaps with those corresponding to the 1 : 1 binary M(II)–aliphatic acids, (curve e) at the lower pH value. This pH value is largely dependent on the nature of both the M(II) ion and aliphatic acid. At a pH range 3.4–4.5, the curve (g) diverges from curve (e) indicating the attachment of the secondary ligand creatinine producing the mixed-ligand ternary complex. This revealed that the binary complex of the aliphatic acid $[ML^1]$, is formed first and, accordingly, combines with creatinine in the protonated form $(HL^2)^+$ as a secondary ligand producing the mixed-ligand complex $[ML^1L^2]$ in a stepwise manner as represented by the following equations:

$$M(II) + H_2L^1 \rightleftharpoons [ML^1] + 2H^- \qquad (1)$$

$$[ML^1] + [HL^2] \rightleftharpoons [ML^1L^2] + H^- \qquad (2)$$

where $M(II) = Co(II), Ni(II), Cu(II)$; H_2L^1 = aliphatic acid (succinic, malic, tartaric); and L^2 = creatinine.

Formation Constant Values

The formation constants for the various binary complexes [M(II)–aliphatic acid or M(II) + creatinine] in the system under investigation were also calculated by adopting the formula of Irving and Rossotti[33,34] to the results of the pH-titration curves of the binary complex solutions as shown in Fig. 4, curves (b), (c) and (d), (e) for creatinine and aliphatic acids, respectively. The formation constant values of the various 1 : 1 : 1 ternary complexes were calculated considering the titration curves (e) and (g) in the pH-range of ternary complex formation. The following equation was used for the calculation of n_{mix} (average number of creatinine molecules as a secondary ligand associated with one molecule of binary complex specie $[ML^1]$)[33,34]

$$n_{\text{mix}} = \frac{[(V_g - V_e)][C_b + C_a + C_L(y - n_H)]}{[V_o + V_e)]n_H C_M} \qquad (3)$$

V_g and V_e are the volumes of KOH consumed to reach the same pH values in curves (g) and (e), respectively (Fig. 4). C_b and C_a are the concentrations of KOH and HNO_3, respectively. C_M is the concentration of the binary $[ML^1]$ complex, which is equal to the concentration of M(II) used, C_L is the concentration of the ligand L^2, y is the number of dissociable protons of the secondary ligand $[HL^2]^-$ ($y = 1$ for such molecule), and V_o is the original volume (25 mL). n_H values are the average number of protons associated with the secondary ligand creatinine at different pH values and were available from the determination of the formation constant. The n_{mix} values do not exceed unity, indicating that only one secondary ligand molecule combines with the binary $[ML^1]$ complex forming the mixed-ligand complex $[ML^1L^2]$.

Table 3. Formation constant[a] values for the various 1 : 1 binary [M(II) + (aliphatic acids)] and [M(II) + (creatinine)] complexes formed at 25 °C and of $I = 0.1$ M KNO_3.

	$M(II)$ + aliphatic acids (L^1) or $M(II)$ + creatinine (L^2)		
Ligand	Cu(II)	Ni(II)	Co(II)
Succinic acid	4.65 ± 0.05	4.14 ± 0.09	3.65 ± 0.12
Malic acid	4.01 ± 0.07	3.35 ± 0.10	3.08 ± 0.11
Tartaric acid	3.90 ± 0.11	3.06 ± 0.10	2.85 ± 0.12
Creatinine	3.18 ± 0.10	3.07 ± 0.12	3.05 ± 0.11

[a] $M(II) + L^1 \text{ or } L^2 \rightleftharpoons ML^1 \text{ or } ML^2$; $K = [ML^1] \text{ or } [ML^2]/[M(II)][L^1 \text{ or } L^2]$.

From the values of n_{mix} the free secondary ligand exponent (pL_{mix}) was calculated using the following equation.[33,34]

$$pL_{\text{mix}} = \log\left\{\frac{\sum_{y=0}^{y=1 \text{ or } 2} \beta_y^{\text{H}}(1/10^B)}{C_L - n_{\text{mix}} C_M} \frac{V_o + V_g}{V_o}\right\} \tag{4}$$

Here β_y^{H} are the formation constant values of the secondary ligand creatinine, and B is the pH meter reading.

The various mean $\log K^{\text{M}}_{\text{ML}^1}$, $\log K^{\text{M}}_{\text{ML}^2}$, and $\log K^{\text{ML}^1}_{\text{ML}^1\text{L}^2}$ values determined along with the estimated errors using least-square fits are listed in Tables 3 and 4.

Examination of Tables 3 and 4 reveals that the stability constants of the binary or mixed-ligand complex for the same metal ion vary in terms of the nature of the primary ligand aliphatic acid according to the sequence: succinic > malic > tartaric. This behavior may be ascribed to the decrease in the basicity, as a measure of σ-donor character, of the corresponding anions in the same sequence.[35] Furthermore, it is evident that the mixed-ligand complex,

Table 4. Formation constant[a] values for the various 1 : 1 : 1 [M(II) + (aliphatic acids) + (creatinine)] ternary complexes at 25 °C and $I = 0.1$ M KNO_3.

	[M(II) + (aliphatic acids) + (creatinine, L^2)]		
Aliphatic acids (L^1)	Cu(II)	Ni(II)	Co(II)
Succinic acid	3.35 ± 0.11	3.26 ± 0.10	3.20 ± 0.09
Malic acid	3.29 ± 0.08	3.22 ± 0.11	3.16 ± 0.11
Tartaric acid	3.23 ± 0.11	3.16 ± 0.09	3.14 ± 0.10

[a] $M(L^1) + L^2 \rightleftharpoons ML^1L^2$; $K = [ML^1L^2]/[ML^1][L^2]$.

$[ML^1L^2]$, formed is characterized by a high stability compared with that of the corresponding binary complex of the secondary ligand $[ML^2]^{2+}$. This result can be plausibly attributed to the low electrostatic repulsion forces during mixed-ligand complex formation $\{(ML^1 + [HL^2]^+ \rightleftharpoons [ML^1L^2] + H^+)\}$, compared to that for binary complex formation $(M^{2+}) + [HL^2]^+ \rightleftharpoons [ML^2]^{2+} + H^+)$.

The order of the stability of the various binary or mixed-ligand complexes under investigation in terms of the nature of the central divalent metal ion follows the usual sequence[36] Cu(II) > Ni(II) > Co(II).

Thermodynamic Function of Complex Formation

The formation constant of the 1 : 1 : 1 ternary [Cu(II) + aliphatic acid + creatinine] complexes were determined by pH-titrations at 5, 15, 25, 35, and 45 °C and at a constant ionic strength, $I = 0.1\,\mathrm{M}\ KNO_3$. The overall reaction of the ternary complex formation can be represented by the following equation:

$$[ML^1] + [HL^2]^+ \rightleftharpoons [ML^1L^2] + H^+ \tag{5}$$

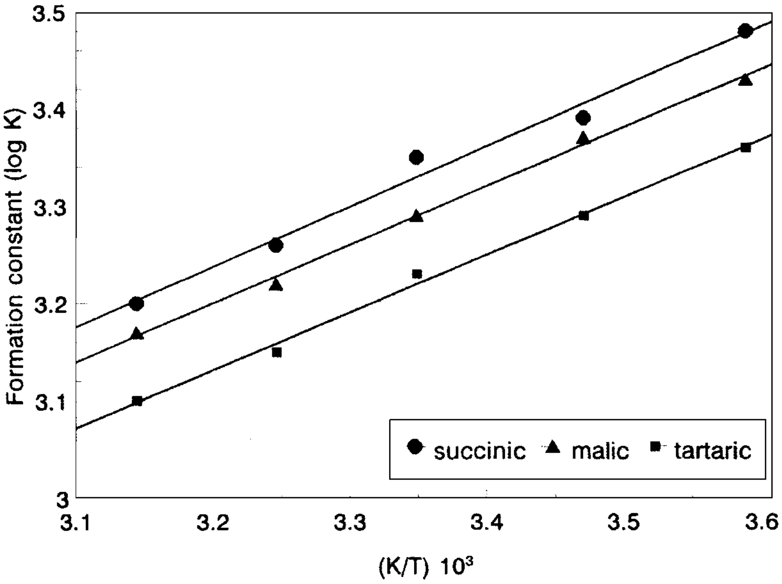

Figure 5. Plot of log K values against $1/T$ for [Cu(II) + (aliphatic acids) + (creatinine)] complex solutions at a constant ionic strength $I = 0.10\,\mathrm{M}\ KNO_3$.

Table 5. Thermodynamic functions[a] of [Cu(II) + (aliphatic acid) + (creatinine)] ternary complexes at a constant ionic strength $I = 0.10\,\mathrm{M\ KNO_3}$.

Aliphatic acid	log K values at T (°C)					$-\Delta H$ (kJ mol^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
	05	15	25	35	45			
Succinic acid	3.48	3.39	3.35	3.26	3.20	11.82	19.11	24.42
Malic acid	3.43	3.37	3.29	3.22	3.17	11.50	18.77	24.30
Tartaric acid	3.36	3.29	3.23	3.15	3.10	11.32	18.43	32.86

[a] ΔG° and ΔS° values were calculated for 25 °C.

The values of the enthalpy change (ΔH) were determined graphically using the van't Hoff relationship by plotting log K values at different temperatures vs. $1/T$ (Fig. 5) and equating the gradient with $-\Delta H/19.15$. The values of the free energy (ΔG°) and entropy (ΔS°) changes associated with the complex formation are calculated at 25 °C using the following equations: $\Delta G^\circ = -2.303\ RT \log K$, and $\Delta S^\circ = (\Delta H - \Delta G^\circ)/T$, respectively.

The formation constant values along with the ΔH, ΔG°, and ΔS° values are given in Table 5. The results obtained reveal that the metal–ligand complex formation is less favored with increasing temperature, coincident with the exothermic nature of the complex formation reaction. The negative ΔG° values obtained are consistent with the spontaneity nature of the complex formation processes. The values of entropy change ΔS° related to the formation of all complexes are positive indicating a favorable formation of the complexes studied. This behavior is in agreement with the metal–ligand complex formation reaction.[37]

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