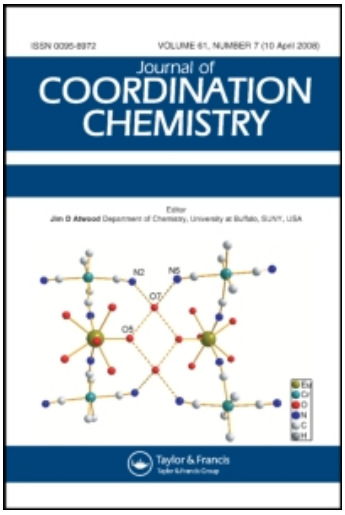

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Synthesis, characterization and thermodynamic properties of metal complexes of a phenanthroline-bridging macrocyclic ligand

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SYNTHESIS, CHARACTERIZATION AND THERMODYNAMIC PROPERTIES OF METAL COMPLEXES OF A PHENANTHROLINE-BRIDGING MACROCYCLIC LIGAND

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A macrocyclic ligand incorporating phenanthroline has been synthesized by the reaction of 2,9-dichloromethyl-1,10-phenanthroline with dioxo[13]aneN_4(dioxo[13]aneN_4 = 1,4,7,11-tetraazacyclotridecane-8,10-dione). The stability constants of its Cu^{2+}, Co^{2+}, Hg^{2+} and Pd^{2+} metal complexes have been measured by potentiometric pH titration technique. It was found that a π-*dp* electrostatic interaction between Cu^{2+} and the phenanthroline moiety does exist in the binary systems. Stability constants of ternary systems containing Cu^{2+}, ligand L(L_1) and α-amino acids (AA, L_2) in aqueous solution were also determined. Linear free energy relationships (LFER) exist in the ternary systems.

Keywords: Phenanthroline; Dioxotetraamine macrocycles; α-Amino acids; Metal complexes; Thermodynamics; LFER

INTRODUCTION

1,10-Phenanthroline, one of the earliest and most extensively studied bidentate ligands, is widely employed as a metal-binding component in coordination chemistry, supramolecular chemistry and bioinorganic chemistry. The inlay of the 1,10-phenanthroline unit in polydentate macrocycles or linear ligands is of great interest in the design of new receptors in view of its ability to act as a powerful photosensitizer, catalyst and chelator [1]. Its larger aromatic electron-deficient system makes phenanthroline an excellent π acceptor [2] and some substitution-inert octahedral metal complexes derived from it are capable of selectively binding DNA through intercalation [3]. On the other hand, amide macrocyclic complexes have been widely investigated in recent years [4]. Some metal complexes of the macrocyclic amide, prepared by the ammoniation of a polyamine with either a dicarboxylic diester or a dicarboxylic chloride [5], have been used to construct supramolecular architecture [6] and have also been developed as effective oxidants and biomimetic redox catalysts [7]. Macrocycles, for instance dioxo[13]aneN_4

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(1,4,7,11-tetraazacyclotridecane-8,10-dione), bear the dual structural features of polyaza macrocycles and oligopeptides and have been reported to have peculiar properties and important functions both in inorganic chemistry and in biochemistry. However, an amide group can coordinate with a metal ion using either or both of its two competitive binding atoms, carboxylic oxygen and amino nitrogen atoms [8]. Furthermore, the amide group can deprotonate by an ene–ketone configuration interchange and hence lose a proton from the amide nitrogen under the influence of a 3d metal ion.

More recently, polynuclear complexes have generated interest because they are good models for polynuclear metalloenzymes as well as being multi-electron redox catalysts. The bridging macrocycle is believed to have the ability to form two and more metal centres, either heteronuclear or homonuclear. Since the chemical properties of the metal centres depend on the ligational properties of the chelating sites, such a situation has led to the synthesis of a number of macrocycles linked with a variety of bridges [9]. Moreover, these complexes often show special characters in magnetoelectricity and electrochemistry which are different from those of acycles [10]. At this point, it is of interest to synthesize new macrocyclic receptors containing heteroaromatic moieties as bridging units. The incorporation of a phenanthroline moiety can provide a further binding site for both metal cations and inorganic anions through the two aromatic nitrogens whose unshared electron pairs are expected to act cooperatively in binding.

Metal ions play a very important role in life. For example, Cu(II) is the activation centre of several Cu(II) proteins, while Co(II) is the redox site of the well-known oxygen transfer species $Co(salen)^{2+}$. In addition, Hg(II) can cause the deprotonation of amides at low pH values, while Pd(II) has application as an anticancer pharmaceutical. The function of the metal ions are believed to be relevant to the stabilities of their complexes, so the determination of stability constants is obligatory for studies of solution properties. All four metal ions have the potential ability to coordinate with phenanthroline and are expected to form stable trinuclear complexes with L, offering the facility to investigate the thermodynamic properties of polynuclear complexes. Other studies involving redox and photochemical characteristics are continuing and these may provide further insight into the coordination chemistry.

EXPERIMENTAL

Synthesis

Materials

Most of the starting materials and solvents for synthesis were obtained commercially and purified prior to use. The compounds 2,9-dicarboxaldehydro-1,10-phenanthroline, 2,9-dihydroxylmethyl-1,10-phenanthroline and 2,9-dichloromethyl-1,10-phenthroline were prepared according to literature methods [11]. Dioxo[13]aneN_4 was prepared from triethylenetetraamine and diethyl malonate as reported previously [12].

General Techniques

C, H, N elemental analyses were carried out on a Perkin-Elmer 240C instrument. Proton NMR spectra were recorded on a Bruker AC-P200 spectrometer (25°C in d^6-DMSO solution with tetramethylsilane as internal reference). IR spectra were recorded on a Bruker Euinox 55 FT spectrometer.

Synthesis of 2,9-di[4-(1,4,7,10-tetraazacyclotridecane-11,13-dione)methyl]-1,10-phenanthroline (L)

To a suspension of dioxo[13]aneN_4 (2.6 g, 12 mmol) in anhydrous DMF (60 cm^3), dried, powdered K_2CO_3 (2 g) was added and then 2,9-dichloromethyl-1,10-phenanthroline (1.1 g, 4 mmol) was introduced with stirring under N_2 at 35°C for three days. After filtration, the filtrate was evaporated to less than 10 cm^3 and redissolved in 20 cm^3 of $CHCl_3$. The product was purified on silica gel by elution with $CHCl_3/CH_3OH/NH_3$ (aq) (300/200/15), and then $MeOH/NH_3$ (80/20). The second band was evaporated to dryness and recrystallized from ethanol to produce buff coloured crystals. Yield: 31.5%; m.p.: 240°C (decomposition); ^{1}H NMR (d^6-$CDCl_3$): δ2.67–δ3.35 (m, 28H, 14CH_2 of dioxo[13]aneN_4); δ4.06 (s, 4H, 2Phen-CH_2-N); δ7.76, δ7.81 (d, 2H Phen H-3, H-8); δ8.31, δ8.27 (d, 2H, Phen H-5, H-6); δ8.57 (m, 2H, Phen H-4, H-7); IR (KBr pellet): 1627 cm^{-1}($\nu_{C=O}$), 3289(ν_{N-H}), 1059, 1448(ν_{C-N}), 862.7(Ar). Anal. Calc. for $C_{32}H_{44}N_{10}O_4 \cdot H_2O$ (%): H, 7.12; C, 59.06; N, 21.52. Found H, 7.40; C, 58.82; N, 21.35.

Potentiometric Titrations

Apparatus

Potentiometric determinations were measured in a 50-cm^3 jacketted cell thermostatted at 25.0 ± 0.1°C by a refrigerated, circulating water bath. Titration was carried out with a Beckman pH meter (model Φ71) equipped with a type 39481 combination glass electrode. Anaerobic conditions were maintained using pre-purified N_2 as an inert atmosphere, and ionic strength was maintained through the addition of KNO_3 to each solution to achieve $I = 0.1$ mol dm^{-3}. The concentrations of Cu^{2+}, Co^{2+}, Hg^{2+} and Pd^{2+} in the stock solution were analyzed by EDTA titration.

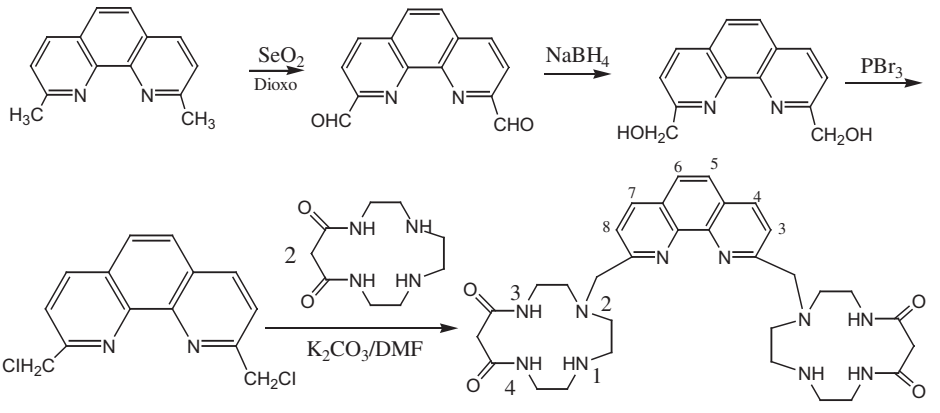
Procedure

In each system studied, the starting volume was 20.00 ± 0.05 cm^3 and pH measurements were recorded by adding base to the acid forms of the ligand. The ligand concentration, 1.00×10^{-3} mol dm^{-3}, was one-third of that of the metal ion. The ligand was dissolved in an adequate amount of dilute HNO_3 and then was titrated with approximately 0.10 M KOH. Stability constants were calculated using the TITFIT program as reported previously [13]. In all cases, the δ_{fit} value, the sum of squared deviations of experimental equilibrium constants, was less than 10^{-3}.

RESULTS AND DISCUSSION

Ligand Synthesis

The reaction sequence is shown in Scheme 1. 2,9-Dichloromethyl-1,10-phenanthroline was synthesized according to literature [11]. 2,9-Dimethyl-1,10-phenanthroline was oxidized using selenium dioxide to give 2,9-dicarboxaldehydro-1,10-phenanthroline. The product was reduced to 2,9-dihydroxylmethyl-1,10-phenanthroline by $NaBH_4$ and was then treated with PCl_3 to give 2,9-dichloromethyl-1,10-phenanthroline.



SCHEME 1 Synthetic scheme adopted for the ligand.

TABLE I Protonation constants for lignad L ($25 \pm 0.1^{\circ}C$, $I = 0.1\,mol\,dm^{-3}$ KNO_3)

$log\,\beta_n$				$log\,K_n$			
$log\,\beta_1$	$log\,\beta_2$	$log\,\beta_3$	$log\,\beta_4$	$log\,K_1$	$log\,K_2$	$log\,K_3$	$log\,K_4$
8.73	16.31	20.04	21.09	8.73	7.58	3.73	1.05

The bridging ligand L was prepared by refluxing 2,9-dichloromethyl-1,10-phenthroline with dioxo[13]aneN$_4$ using the high dilution technique. The final product was purified by column chromatography to give the required ligand.

Protonation Constants

The acid–base behaviour of the ligand in aqueous solution (0.10 M KNO_3) at 25°C was investigated by pH titration. The stepwise protonation equilibrium constants determined are shown in Table I.

$$H_{n-1}L^{(n-1)+} + H^+ \rightarrow H_nL^{n+} \qquad K_n = [H_nL^{n+}]/([H_{n-1}L^{(n-1)+}][H^+]) \tag{1}$$

In the pH range studied (2.6–10.4), ligand L has four protonation steps. The term $n = 4$ refers to the four nitrogen atoms, one on the phenanthroline moiety and others on dioxo[13]aneN$_4$ macrocycles, that can be protonated. As shown in Table I, both the first two protonation constants $\log K_1 = 8.73$ and $\log K_2 = 7.58$ are significantly larger than the last two protonation constants $\log K_3 = 3.73$ and $\log K_4 = 1.05$. However, the protonation constant $\log K_1$ (8.73) is similar to that of free dioxo[13]aneN$_4$ ($\log K_1 = 8.865$) [14], but is much larger than the first protonation constant of the phenanthroline nitrogen, with a value of 4.748 [15]. Thus the protonation constant $\log K_1$ belongs to the more basic secondary nitrogen atom N(1) on the 13-membered macrocycle. In addition, $\log K_2$ (7.58) is larger than either the second protonation constant of the same dioxo[13]aneN$_4$ ($\log K_2 = 3.60$) [14] or the first protonation constant of phenanthroline (4.748). Therefore, $\log K_2$ corresponds to

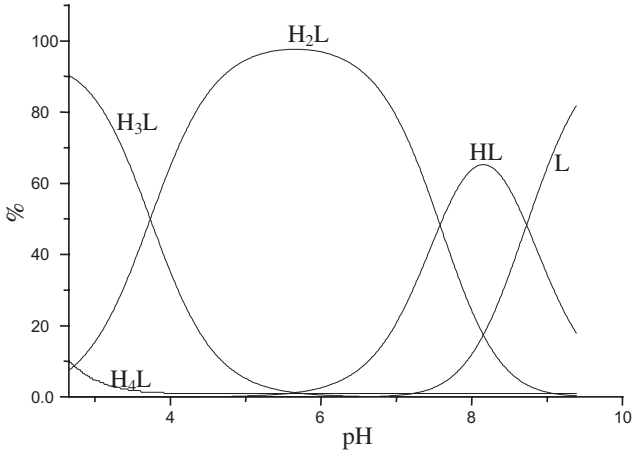


FIGURE 1 Distribution curves for the protonated species of L as a function of pH in 0.1 mol dm^{-3} KNO_3 at 298.15 K.

protonation of the N(1)′ atom of the other macrocycle. At the same time, log K_3 and log K_4 are considered to refer to the bridging phenanthroline and the tertiary nitrogen atom N(2) respectively. The stepwise protonation constants log K_2, log K_3 and log K_4 decrease (1.15, 3.85 and 2.68) gradually, due to electrostatic repulsive effects between the prior protonated nitrogens and approaching H^+. The significant drop (3.85) for log $K_2 \rightarrow$ log K_3 indicates the large difference in basicities between N(1)′ and phenanthroline nitrogen.

The protonation constant of N(1) is 0.14 log units lower than that of free dioxo[13]aneN_4 and this may be due to the electron density flow from the lone pair of N(1) on the electron-rich dioxo[13]aneN_4 macrocycle to the electron-deficient phenanthroline nitrogen; this makes the interaction of N(1) with a proton weaker.

The percentage distribution curve for all protonated species in aqueous solution as a function of pH is shown in Fig. 1. As seen from the figure, the protonated species H_1L^+, H_2L^{2+} and H_3L^{3+} are particularly concentrated in solution, but the concentration of H_4L^{4+} is extraordinary small. This indicates that the tetra-protonated species cannot exist when pH > 3 and only forms in significant quantities in strongly acidic solution. The protonated species exist over a pH range of 2.5–10. However, the species H_2L^{2+}, containing H^+ on N(1) and N(1)′, is dominant in the pH range 4–7.5 with a maximum contribution at pH around 6.

Stability Constants

The stability constants for complexes of ligand L with Cu^{2+}, Co^{2+}, Hg^{2+} and Pd^{2+} were measured in aqueous solution; the mol ratio of M^{2+} : L was 3 : 1. The constants obtained are shown in Table II.

$$M^{2+} + L + 3H^+ = MLH_3^{5+} \quad \beta_{113} = [MLH_3^{5+}]/[M^{2+}][L][H^+]^3 \tag{2}$$

$$M^{2+} + L + 2H^+ = MLH_2^{4+} \quad \beta_{112} = [MLH_2^{4+}]/[M^{2+}][L][H^+]^2 \tag{3}$$

TABLE II Formation constants for complexes of M(II) ions coordinated with ligand L (0.1 mol dm^{-3} KNO_3 if 298.15 K)

	Cu(II)	*Co(II)*	*Hg(II)*	*Pd(II)*
$\log \beta_{113}$	25.99 ± 0.13	25.88 ± 0.11	28.38 ± 0.08	–
$\log \beta_{112}$	19.94 ± 0.08	19.87 ± 0.15	–	19.82 ± 0.22
$\log \beta_{210}$	12.23 ± 0.12	11.90 ± 0.17	16.20 ± 0.12	15.83 ± 0.20
$\log \beta_{31-2}$	6.89 ± 0.15	5.56 ± 0.09	12.30 ± 0.13	9.93 ± 0.18
$\log \beta_{31-3}$	-3.08 ± 0.13	-7.62 ± 0.07	1.18 ± 0.04	-3.52 ± 0.15
$\log \beta_{31-4}$	-10.34 ± 0.06	-16.20 ± 0.10	-10.08 ± 0.11	-13.72 ± 0.13

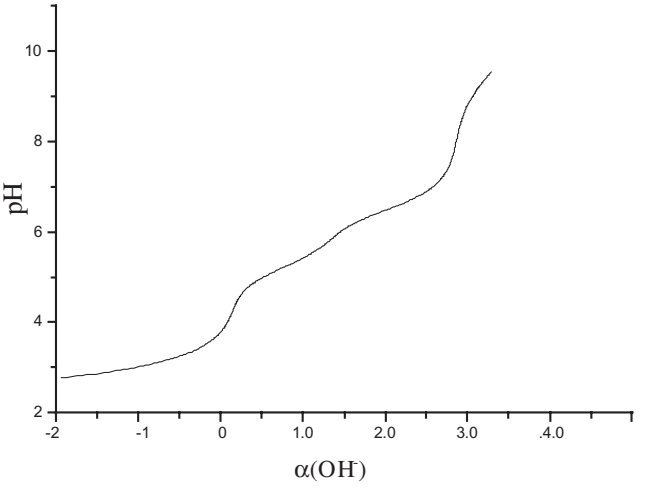


FIGURE 2 pH titration curves for pH *vs* B/L (base/ligand) for the Cu^{+2}–L system.

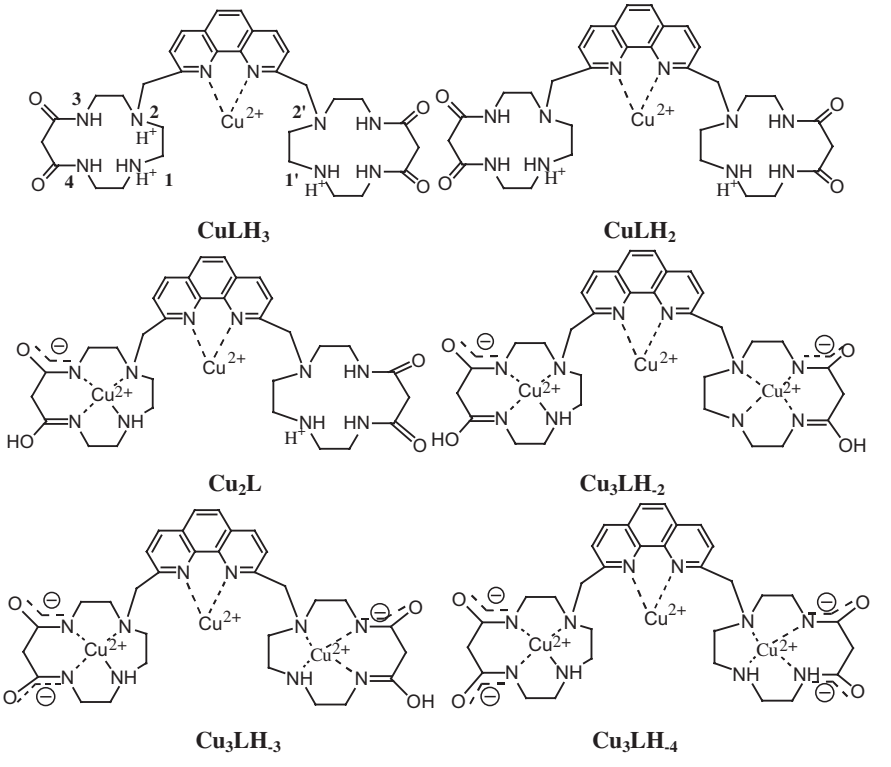
$$2M^{2+} + L = M_2L^{4+} \qquad \beta_{210} = [M_2L^{4+}]/[M^{2+}]^2[L] \tag{4}$$

$$3M^{2+} + L = M_3LH_{-2}^{4+} + 2H^+ \qquad \beta_{31-2} = [M_3LH_{-2}^{4+}][H^+]^2/[M^{2+}]^3[L] \tag{5}$$

$$3M^{2+} + L = M_3LH_{-3}^{3+} + 3H^+ \qquad \beta_{31-3} = [M_3LH_{-3}^{3+}][H^+]^3/[M^{2+}]^3[L] \tag{6}$$

$$3M^{2+} + L = M_3LH_{-4}^{2+} + 4H^+ \qquad \beta_{31-4} = [M_3LH_{-4}^{2+}][H^+]^4/[M^{2+}]^3[L] \tag{7}$$

It is seen that the titration curve increases sharply at α (B/L, the mol ratio of base added to ligand) = 0 and 3 and changes gently at $\alpha = 2$, 4 (see Fig. 2). This behaviour is consistent with the formation of species $[Cu_2L]$ (210), $[Cu_3LH_{-2}]$ (31 − 2), $[Cu_3LH_{-3}]$ (31 − 3) and $[Cu_3LH_{-4}]$ (31 − 4), respectively. The charges on the complexes are omitted for clarity, and the symbol (m 1 n) is equal to the molecular formula $M_mL_1H_n$. However, all four metal ions, Cu^{2+}, Co^{2+}, Hg^{2+} and Pd^{2+}, can coordinate with ligand L to give species (210), (31 − 2), (31 − 3) and (31 − 4). For both Cu^{2+} and Co^{2+}, there are two more species, (113) and (112). The possible configurations of $Cu_mL_1H_n$ species are shown in Scheme 2. At the same time, in the Hg^{2+}–L system species (113) exists while the Pd^{2+}–L system has the species (112). As an example, we show the distribution curve of Cu(II) with L as a function of pH in Fig. 3.



SCHEME 2 Possible configurations of binary species in the Cu–L system.

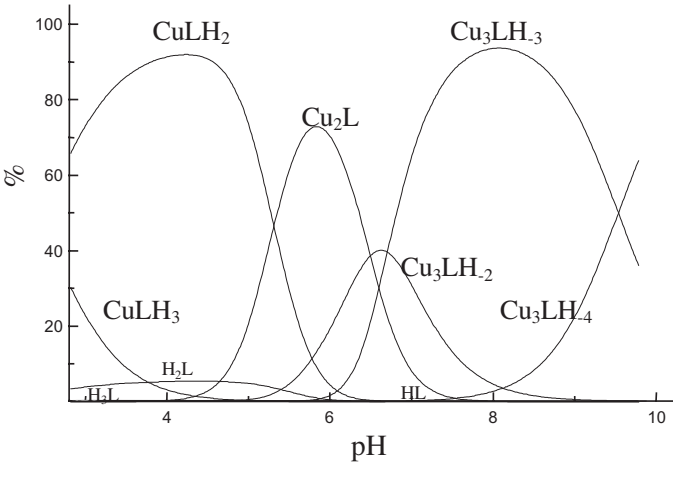


FIGURE 3 Distribution curves for the Cu^{2+}–L system as a function of pH in 0.1 mol dm^{-3} KNO_3 solution at 298.15 K.

As shown in Scheme 2, only the phenanthroline moiety significantly coordinates with Cu(II) in species $CuLH_3$ (113) while the two secondary N(1) and N(1)′ atoms and a tertiary nitrogen N(2) atom of the macrocycles carry three protons. The sum of the stability constant of Cu^{2+}–phenanthroline ($\log K = 9.08$) [16] and the three protonation

constants of ligand L, $\log K_1 = 8.73$, $\log K_2 = 7.58$, $\log K_4 = 1.05$ has a value (26.44) slightly higher than the stability constant $\log \beta_{113}$ (25.99) and this indicates that Cu^{2+} truly takes part in coordination with the two phenanthroline nitrogens. This is confirmed by the work of Walker, who found that phenanthroline interacts with Cu^{2+} at almost 100% capacity even when the pH is lower than 2.0 and d–pπ interaction occurs between Cu^{2+} and the π-system of the phenanthroline unit. Successively, species (113) releases the proton bound to the tertiary N(2) atom to form $CuLH_2$ with increase of pH. Species (112) is proposed such that each 13-membered macrocycle has its N(1) or N(1)′ atom protonated while the Cu^{2+} ion remains coordinated to phenanthroline. Thereafter, further interest arises for the species (210) as shown in Scheme 2. One amide group of the macrocycle changes into the enolic configuration and then releases H^+ under the influence of a second Cu^{2+} ion; at the same time the other macrocycle is still protonated.

There were several opinions concerning coordination models of dioxo[13]aneN_4 with Cu^{2+}. Kimura [17] thought the system has two species, (112) and (110), while Fabbrizzi [18] used the three models (110), (11 − 1) and (11 − 2); there was no evidence for (11 − 1) in his studies. Only recently, Chen and co-workers [19] obtained the single-crystal X-ray structure of (11 − 1) with two amide groups in the enolic configuration with one amide deprotonated and the other in the "ketone–ene" configuration with a copper(II) complex of a substituted dioxo[14]aneN_4. Thus, we considered model (210) and found that only if it were used in the calculation would the result be accurate. It is interesting and important to point out which amide group deprotonates first. In fact, the attack of Cu^{2+} is always at the more nucleophilic receptor and thus N(1) and N(2) no doubt take part in coordination. With species (112), as shown in Scheme 2, it is a question of whether N(3) or N(4) amide groups lose a proton. As is known, both the amide groups coordinate to metal ion through a "ketone–ene" configuration interchange, so the hydrogen bound to oxygen more weakly will be lost first. H^+ on the N(3) carboxyl oxygen is bound more loosely than that of the N(4) amide group owing to the double inductive effects of the positive charge on the metal ion and the adjacent π-system of phenanthroline.

Then, it is a dilemma whether the next species is (31 − 2) as shown in Scheme 2, or the species (21 − 1) whose two amide groups on one macrocycle are deprotonated and while H^+ is bound to N(1)′ on the other macrocycle. It seems reasonable to admit the former because the excess Cu^{2+} attacks N(1)′ to give the arrangement depicted for formula (Cu_3LH_{-2}) rather than promoting the deprotonation of the N(4) amide group to give the arrangement depicted for formula (Cu_2LH_{-1}). The same applies to the formation of species (31 − 3) and (31 − 4). In complex Cu_3LH_{-4}, all four amide groups of the two dioxo[13]aneN_4 macrocycles are deprotonated.

As seen from the percentage distribution diagram in Fig. 3, there are three major species in solution. $CuLH_2$ (112), Cu_2L (210) and Cu_3LH_{-3} (31 − 3) come to a maximum at pH 4.5, 6 and 8, respectively. The species 113 exists only in strongly acidic pH and contributes no more than 30%, even at pH 2.5. The species (31 − 2) reaches a maximum of 40% at pH 7; this may be due to the species (31 − 2) not being stable towards deprotonation at only one protonated enolic group of the macrocycles. Thus species (210) is dominant in the pH range 3–5 while species (31 − 2) is lesser. In addition, the macrocycles have all of their four amide groups deprotonated only when pH is above 8.

The stability constants of Cu^{2+} and Co^{2+} when compared conform to the Irving–Williams order $Co^{2+} < Cu^{2+}$. The stability of this system is dependent on two effects,

the coordination ability of the metal ion and the match between the metal ion and the cavity size of the macrocycle. The higher crystal field stabilization energy of Cu^{2+} compared with that of Co^{2+} is the main factor that enhances the coordination ability of Cu^{2+} with phenanthroline and dioxo[13]aneN_4 nitrogens, although dioxo[13]aneN_4 (192 pm) prefers Co^{2+} (74 pm) rather than Cu^{2+} (72 pm). Similar to Cu^{2+}, Hg^{2+} can also promote the deprotonation of amide groups at low pH. Comparing the stability constants $\log \beta_2 = 19.65$ for Hg^{2+} with phenanthroline and 15.76 [16] for Cu^{2+}, we find that both Hg^{2+} and Cu^{2+} are strongly electrophilic metal ions. However, sometimes Hg^{2+} can form more stable complexes than Cu^{2+}. For example, in this system studied the stability of Hg^{2+} is larger than of Cu^{2+} (see Table II) because dioxo[13]aneN_4 (192 pm) prefers Hg^{2+} (110 pm) rather than Cu^{2+} (72 pm). Hg^{2+} and Pd^{2+} in this system studied have higher stability owing to the suitable ionic radius and strong ionic affinity: Hg^{2+} (ionic radius: 110 pm; electron affinity: 98 kJ mol^{-1}); Pd^{2+} (ionic radius: 86 pm; electron affinity: 108 kJ mol^{-1}) [20].

Ternary Systems

Cu^{2+}–L–AA Systems

Complex formation constants for Cu^{2+} with ligand L (L_1) and *L*-α-amino acids (AA, L_2) were measured in aqueous solution, the mol ratio of Cu(II) : L_1 : L_2 being 3 : 1 : 3. Stability constants [relating to Eqs. (8)–(11)] are shown in Table III. The Cu(II)–L–serine distribution curve as an example is shown in Fig. 4.

$$Cu + L_1 + L_2 + 2H = CuL_1L_2H_2 \qquad \beta_{1112} = [CuL_1L_2H_2]/[Cu][L_1][L_2][H]^2 \tag{8}$$

$$2Cu + L_1 + 2L_2 = Cu_2L_1(L_2)_2 \qquad \beta_{2120} = [Cu_2L_1(L_2)_2]/[Cu]^2[L_1][L_2]^2 \tag{9}$$

$$3Cu + L_1 + 3L_2 = Cu_3L_1(L_2)_3H_{-2} + 2H \quad \beta_{313-2} = [Cu_3L_1(L_2)_3H_{-2}][H^+]^2/[Cu]^3[L_1][L_2]^3 \tag{10}$$

$$3Cu + L_1 + 3L_2 = Cu_3L_1(L_2)_3H_{-4} + 4H \quad \beta_{313-4} = [Cu_3L_1(L_2)_3H_{-4}][H]^4/[Cu]^3[L_1][L_2]^3 \tag{11}$$

The experimental data obtained for the 3 : 1 : 3 Cu–L–AA systems and other data determined above were used in refinement of the constants for interactions in the ternary system. Figure 4 reveals the presence of four ternary species in the pH range from

TABLE III Formation constants for complexes in the ternary of $Cu(II)^+$–L–amino acid system (0.1 mol dm^{-3} KNO_3 at 298.15 K)

	$\log \beta_{1112}$	$\log \beta_{2120}$	$\log \beta_{313-2}$	$\log \beta_{313-4}$
Pro	30.94 ± 0.22	29.21 ± 0.09	22.85 ± 0.07	7.31 ± 0.12
Aib	28.83 ± 0.11	28.45 ± 0.17	20.88 ± 0.13	6.35 ± 0.04
Ile	27.81 ± 0.07	27.67 ± 0.09	19.83 ± 0.18	5.04 ± 0.015
Val	27.65 ± 0.15	27.51 ± 0.04	19.67 ± 0.10	5.04 ± 0.08
Gly	27.46 ± 0.21	27.42 ± 0.16	17.55 ± 0.11	4.96 ± 0.10
Ser	26.86 ± 0.19	26.67 ± 0.18	18.61 ± 0.13	4.25 ± 0.11
Thr	26.69 ± 0.23	26.53 ± 0.09	18.25 ± 0.14	3.75 ± 0.10

Pro = Proline; Aib = amino butyric acid; Ile = iso leucine; Val = valine; Gly = glycine; Ser = serine; Thr = threonine.

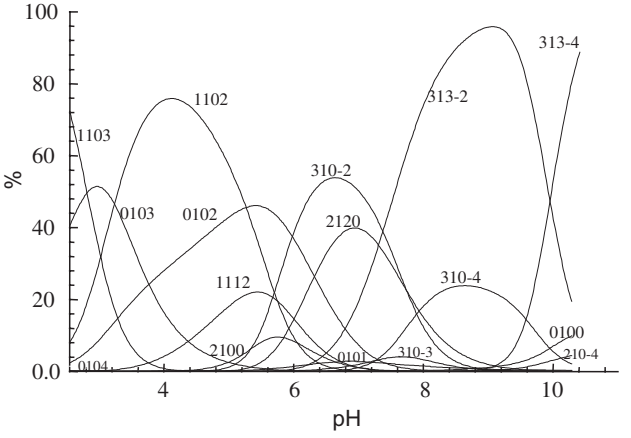
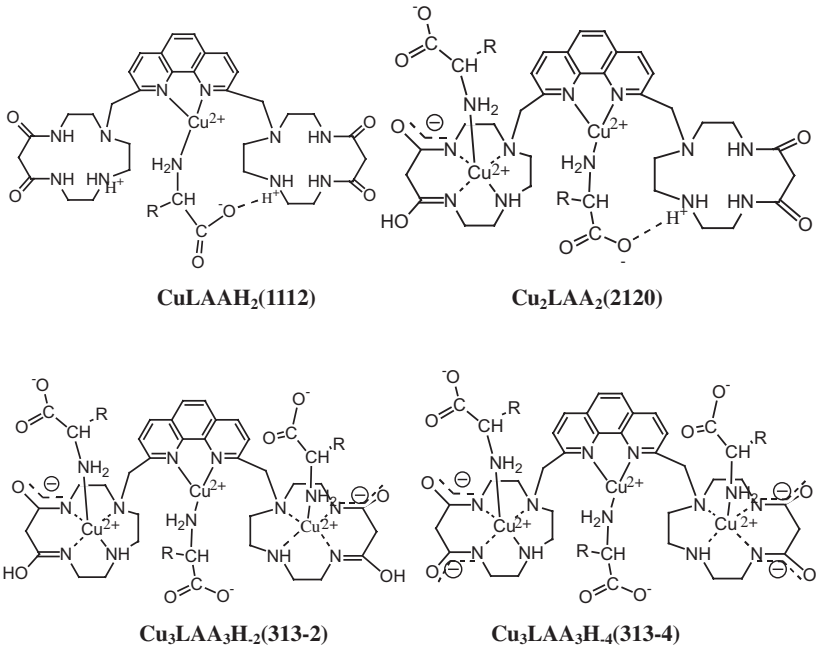


FIGURE 4 Distribution curves for the Cu(II)–L–AA acid system as a function of pH in 0.1 mol dm^{-3} KNO_3 solution at 298.15 K. The 1112 indicates species $CuLAAH_2$. The particular amino acid in this illustrative example is serine.

2.6 to 10.5. It is interesting to note that two ternary species dominate. Species $Cu_3LAA_3H_{-2}$ (313 −2) dominates from pH 6 to 10 and comes to a maximum at pH about 9.0, while complex $Cu_3LAA_3H_{-4}$ (313 −4 in Fig. 4) is a major species between pH 10 and 10.5.

An important question for the Cu(II)–L–AA system is whether the carboxyl oxygen or the amino nitrogen atoms of AA participates in the coordination process. As is known, AA can use either of the two atoms to bind metal ions with formation of a chelate ring when AA alone binds metal ions. In this system studied, however, the α-amino acid cannot generate a coordinated cycle at axial positions and is constrained to act as unidentate towards the Cu(II) ion. Therefore, we consider that the amino nitrogen atom is coordinated to Cu(II) in solution. As shown in the percentage distribution curve in Fig. 4, when the complex $CuLAAH_2$ (1112) is formed, the pH value is about 4. Although the oxygen atom of the carboxylic group of AA is deprotonated due to its low $pK_0 = 2$–3, AA can still coordinate to Cu(II) at low pH (4–6) using the N atom. It would seem that $pK_N = 9$–10 of AA would make it difficult for N to participate in coordination at low pH, but in fact the presence of the divalent metal ion can displace the hydrogen ion on an amino nitrogen atom at pH about 5. In species $CuLAAH_2$ (1112) the O atoms is non-incorporated because its basicity is weaker than that of the free amino nitrogen. Such is also the case with species $CuLAA_2$ (2120). Without doubt, when species $Cu_3LAA_3H_{-2}$ (313 −2) becomes dominant at pH 6, the oxygen atom cannot coordinate with Cu(II) because of the more efficient nucleophilicity of the nitrogen atom at this pH. Thus we consider that it is the amino nitrogen atom of AA that coordinates to the metal ion in all four ternary complexes. Formation processes of the ternary complexes are represented in Scheme 3.

As seen in Scheme 3, the species $CuLAAH_2$ (1112) contains two hydrogen ions (one on each macrocycle) while Cu^{2+} binds to phenanthroline. At the same time, the amino acid coordinates with the metal ion using the amino nitrogen, and the carboxylic oxygen form an H-bond with the hydrogen atom of a macrocycle. The possible existence of an H-bond can confer additional stability on the ternary complex. With



SCHEME 3 Possible configurations of ternary species in the Cu–L–ser system.

regard to species Cu_2LAA_2 (2120), a second metal ion reacts with the macrocycle and causes deprotonation of the N(4) amide group as well as the incorporation of a second AA molecule. However, in the species $Cu_3LAA_3H_{-2}$ (313 −2) and $Cu_3LAA_3H_{-4}$ (313 −4) the H-bonds vanish. The former is a five-negative–six-positive charge system and the latter is a seven-negative–six-positive charge system. These species have more significant electrostatic interactions than the first two and this is reflected in their stabilities and the percentage distribution diagram of Fig. 4.

The percentage concentration of Cu_2LAA_2 is no higher than 40% and $CuLAAH_2$ is only 20% at its maximum. Species $Cu_3LAA_3H_{-2}$ (313 −2) and $Cu_3LAA_3H_{-4}$ (313 −4) read concentrations above 90%. The species (1112) come to a maximum at pH about 5.5, some 1.5 log units higher than for (1102). Similarly, species (2120) begins to form at pH 7 while its relative species (2100) forms at 5.5. On the other hand; the pH range of formation of 2120 is 5–10 compared with the 4–7 pH range of formation of 2100. It is obvious that the existence of the second AA ligand increases the stability of the complexes and widens the pH formation range. It is interesting to note that only the concentration of species 1112 is lower than that of 1102. This may due to the lignads L and AA interacting with Cu(II) at low pH; the phenanthroline nitrogens coordinate with Cu(II) at first because of its higher stability than with the amino nitrogen or carboxyl oxygen of AA. Thus the species 1102 is formed. The species 1112 is easily converted to species 2120 at pH 4–7. Thus, the concentration of species 1112 is lower than that of 1102 over this pH range. The fact that the other ternary species bond the AA molecule below or above the macrocycle plane with minimal steric interactions, and that the deprotonated amino nitrogen of the AA amino group dominates when pH increases to 7, leads to increasing stability and concentration of the ternary species.

Linear free energy relationships (LFER) [21] exist widely in many chemical systems. That is to say that there are linear relationships between stability constants of complexes and protonation constants of the ligands in the systems consisting of a metal ion and a series of ligands having similar structure. Chen and Lin [22] found LFER in tertiary systems and related these to previous studies. LFER also exist in the polynuclear systems studied. Stability constants of the species (2120), (313 −4) *vs* the first protonation constant of the seven α-amino acids, $\log \beta_{0011}$, leads to good linearity as shown below.

$$\log \beta_{2120} = -9.3974 + 1.8955 \ \log \beta_{0011} \quad R = 0.990$$
$$\log \beta_{313-4} = -17.6066 + 2.3767 \ \log \beta_{0011} \quad R = 0.978$$

LFER also exist between the stability constants of the four ternary complex species and the first equilibrium constants of the seven α-amino acids with the Cu(II) ions, $\log \beta_{1010}$. The reason for this is that the similar substituting groups of the α-amino acids bring about almost the same entropy effects in ternary and binary systems. Although chelates are formed in the Cu(II)–AA binary system, linear relationships between the stability constants $\log \beta_{1112}$, $\log \beta_{2120}$, $\log \beta_{313-2}$, $\log \beta_{313-4}$ for the ternary system and $\log \beta_{1010}$ for the binary system are evident. The reason again seems to be due to similar entropy effects. The linear relationships are shown below,

$$\log \beta_{1112} = -15.0890 + 5.2437 \ \log \beta_{1010} \quad R = 0.992$$
$$\log \beta_{2120} = -14.5554 + 5.1575 \ \log \beta_{1010} \quad R = 0.990$$
$$\log \beta_{313-2} = -24.3841 + 5.3902 \ \log \beta_{1010} \quad R = 0.990$$
$$\log \beta_{313-4} = -38.8672 + 5.3823 \ \log \beta_{1010} \quad R = 0.991$$

This study is the first to note that LFER exist in polynuclear complex systems.

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