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# Linear Free Energy Relationships Between Reaction Rate Constants and Equilibrium Constants of Complex Compounds. Cu(II)–Heteroaromatic Bases–Aminoacids Systems

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## Abstract

The temperature-jump technique has been used to determine the rate constants for the formation and dissociation of the mixed complex compounds Cu(II)–2,2′-bipyridyl–α-aminoacids and Cu(II)–1,10-phenanthroline–α-aminoacids at 25 °C and I = 0.10 mol $dm^{-3}$ $NaClO_4$. The α-aminoacids used as the second ligand are proline, α-aminoisobutyric acid, valine and threonine. The formation constants of these ternary systems were determined by the pH method under the same experimental conditions. It has been found that the Brönsted type linear free energy relationships (LFER) do exist between the reaction rate constants and the equilibrium constants of these ternary complex compounds. With bipy** and phen in the inner coordination sphere of the copper ion, the rate-determining step involves both bond making and bond breaking processes and the mechanism likely falls into the $S_N2$ category. The enhancement of stability of these ternary complex compounds relative to the parent binary systems was interpreted in terms of kinetic processes of complexation.

## Introduction

The existence of linear free energy relationships (LFER) between the stability of complex compounds and the acid and base strengths of the ligands has been amply reported in the literature [1–7]. These are mostly of the Hammett type of LFER, that is, LFER between equilibrium constants. Recently we have investigated a series of ternary mixed ligand complex compounds both thermodynamically and kinetically and found the existence of the Brönsted type LFER in these systems, that is, LFER between the rate constants and the equilibrium constants of these ternary complex compounds. The ternary systems investigated are Cu(II)–2,2′-bipyridyl–α-aminoacids and Cu(II)–1,10-phenanthroline–α-aminoacids. The α-aminoacids used are proline, α-aminoisobutyric acid, valine and threonine.

## Experimental

The stability constants of these ternary complexes of Cu(II) were measured by the pH method at 25 °C and $I = 0.10$ mol $dm^{-3}$ $NaClO_4$ [7]. The kinetic study of these systems was carried out by means of the temperature-jump technique with a Union Giken Model RA-401 stopped-flow spectrophotometer. The ligands used were of reagent grade with a purity over 99.5%. 2,2′-bipyridyl and 1,10-phenanthroline were of A.R. grade. Sodium perchlorate was of A.R. grade and further purified in 90% ethanol. Copper(II) perchlorate was prepared and the concentration of its stock solution was analyzed by the EDTA titration method [7]. The course of the relaxation process was followed through use of methyl red as an indicator. The experimental procedures were similar to that described by Pasternack and Sigel [8]. The solutions for the different experiments, which were made within an hour of the time in which they were studied by temperature-jump, were prepared such that the copper and bipy or phen concentration was kept equal while the concentration of the aminoacids was varied. The ionic strength was adjusted to 0.10 mol $dm^{-3}$ with $NaClO_4$ and all solutions were $2.5 \times 10^{-5}$ mol $dm^{-3}$ in methyl red. The solutions were degassed and then the pH was adjusted with small amounts of NaOH and/or $HClO_4$ solution. The equilibrium temperature of these studies was 25 °C. Temperature-jump measurements were made at $\lambda = 520$ nm, slit width 1.4, measuring time 10 ms, response bypass, voltage 15 kV, initial temperature 15 °C, temperature jump 10 °C, final temperature 25 °C.

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**Abbreviations and legend: 2,2′-bipyridyl, bipy; 1,10-phenanthroline, phen; $pK_2$ denotes the negative logarithm of dissociation constant of aminoacid, $pK_{NH_3^+}$; $pK_1$ denotes that of $pK_{COOH}$.

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All the solutions containing copper(II), bipy or phen, aminoacid, neutral salt and indicator showed a single relaxation effect. Blank tests containing either only copper(II), bipy or phen, indicator and neutral salt or only aminoacid, indicator and neutral salt showed no relaxation effect. The relaxation time of at least three determinations had the relative error of these experiments at ±10%. Calculations were carried out on Casio FX-702P calculator.

## Results and Discussion

In the pH range studies (pH 4.5–5.4) the complexation of bipy or phen with copper ion has been considered to be complete [9]. The rate constants of complexation reactions (1) and (2) can be evaluated by coupling to the more rapid processes (3)–(5), where HIn is the acidic form of the indicator, methyl red, B denotes bipy or phen, L stands for aminoacid.

$$\mathrm{CuB} + \mathrm{L} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{CuBL} \qquad (1)$$

$$\mathrm{CuB} + \mathrm{HL} \underset{k'_{21}}{\overset{k'_{12}}{\rightleftharpoons}} \mathrm{CuBL} + \mathrm{H} \qquad (2)$$

$$\mathrm{H_2L} \rightleftharpoons \mathrm{H} + \mathrm{HL} \qquad (3)$$

$$\mathrm{HL} \rightleftharpoons \mathrm{H} + \mathrm{L} \qquad (4)$$

$$\mathrm{HIn} \rightleftharpoons \mathrm{H} + \mathrm{In} \qquad (5)$$

The charges are omitted for the sake of simplicity.

The derivation for relaxation time $\tau$ was essentially the same as that reported by Pasternack *et al.* [10].

Tables I–VIII show the results of the relaxation experiments for the ternary complexation reaction Cu(II)–bipy/phen–α-aminoacids. Tables IX and X include the equilibrium constants of the reactions involved in the individual complex formations of the particular ligands and the reaction rate constants for eqns. (1) and (2). The reverse reaction rate constants were calculated from the equilibrium constants and forward reaction rate constants.

It was found that in these ternary systems linear relationships do exist between the rate constant of the formation of the complexes and the stability constant of the complexes and the dissociation constant of the aminoacids as well. The correlation equations for these parameters are listed below, where $r$ is the correlation coefficient.

$$\log k_{12} = 3.74 + 0.641 \log K^{\mathrm{Cu\cdot bipy}}_{\mathrm{Cu\cdot bipy\cdot L}} \quad r = 0.983$$

TABLE I. Results of the Relaxation Spectra Cu(II)–bipy–proline Ternary System

| No. | [Cu–bipy] $\times 10^3$ | [HL] $\times 10^3$ | pH | $\tau$ (ms) | $X \times 10^6$ | $Y \times 10^{-3}$ |
|---|---|---|---|---|---|---|
| 1 | 2.692 | 10.00 | 4.585 | 3.25 | 0.7793 | 2.044 |
| 2 | 2.692 | 10.00 | 5.280 | 1.03 | 3.869 | 7.621 |
| 3 | 2.692 | 10.00 | 4.848 | 2.02 | 1.428 | 3.273 |
| 4 | 2.692 | 10.00 | 5.040 | 1.55 | 2.223 | 4.513 |
| 5 | 2.692 | 5.000 | 5.202 | 1.41 | 3.203 | 5.521 |
| 6 | 2.692 | 5.000 | 5.005 | 1.87 | 2.035 | 3.899 |
| 7 | 2.692 | 5.000 | 4.540 | 3.99 | 0.6980 | 1.945 |
| 8 | 2.692 | 5.000 | 4.760 | 2.97 | 1.158 | 2.425 |
| 9 | 1.346 | 5.000 | 5.300 | 1.65 | 4.051 | 9.266 |
| 10 | 1.346 | 5.000 | 5.080 | 2.14 | 2.438 | 6.485 |
| 11 | 1.346 | 5.000 | 4.800 | 3.87 | 1.279 | 3.400 |
| 12 | 1.346 | 5.000 | 4.510 | 5.22 | 0.6568 | 2.704 |
| 13 | 1.346 | 2.500 | 5.085 | 2.68 | 2.449 | 6.209 |
| 14 | 1.346 | 2.500 | 4.780 | 5.30 | 1.214 | 3.166 |
| 15 | 1.346 | 2.500 | 5.380 | 1.90 | 4.831 | 9.507 |
| 16 | 1.346 | 2.500 | 4.555 | 5.13 | 0.7242 | 3.605 |
| 17 | 4.023 | 10.00 | 4.825 | 1.85 | 1.347 | 2.426 |
| 18 | 4.023 | 10.00 | 4.520 | 3.15 | 0.6676 | 1.483 |
| 19 | 4.023 | 10.00 | 4.775 | 1.79 | 1.200 | 2.499 |
| 20 | 4.023 | 10.00 | 5.060 | 1.35 | 2.315 | 3.540 |
| 21 | 4.023 | 7.500 | 4.522 | 3.44 | 0.6692 | 1.423 |
| 22 | 4.023 | 7.500 | 5.010 | 1.42 | 2.057 | 3.333 |
| 23 | 4.023 | 7.500 | 5.330 | 0.73 | 4.300 | 7.469 |
| 24 | 4.023 | 7.500 | 4.720 | 2.09 | 1.055 | 2.205 |

25.0 ± 0.2 °C; $I = 0.10$ mol dm$^{-3}$ $\mathrm{NaClO_4}$; (methyl red) = $2.5 \times 10^{-5}$ mol dm$^{-3}$.

TABLE II. Results of the Relaxation Spectra for Cu(II)–bipy–α-aminoisobutyric acid Ternary System

| No. | (Cu–bipy) $\times 10^3$ | (HL) $\times 10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 2.692 | 10.00 | 5.340 | 1.20 |
| 2 | 2.692 | 10.00 | 4.800 | 2.67 |
| 3 | 2.692 | 10.00 | 4.995 | 1.97 |
| 4 | 2.692 | 10.00 | 4.535 | 4.00 |
| 5 | 2.692 | 5.000 | 4.515 | 4.20 |
| 6 | 2.692 | 5.000 | 5.297 | 1.15 |
| 7 | 2.692 | 5.000 | 4.805 | 2.66 |
| 8 | 2.692 | 5.000 | 5.000 | 1.82 |
| 9 | 1.346 | 5.000 | 5.345 | 1.66 |
| 10 | 1.346 | 5.000 | 5.045 | 2.65 |
| 11 | 1.346 | 5.000 | 4.835 | 3.46 |
| 12 | 1.346 | 5.000 | 4.528 | 5.88 |
| 13 | 1.346 | 2.500 | 5.375 | 1.59 |
| 14 | 1.346 | 2.500 | 5.040 | 2.89 |
| 15 | 1.346 | 2.500 | 4.525 | 6.25 |
| 16 | 1.346 | 2.500 | 4.816 | 4.39 |
| 17 | 4.038 | 10.00 | 5.325 | 0.94 |
| 18 | 4.038 | 10.00 | 5.085 | 1.29 |
| 19 | 4.038 | 10.00 | 4.855 | 1.89 |
| 20 | 4.038 | 10.00 | 4.590 | 2.86 |
| 21 | 4.038 | 7.500 | 5.340 | 0.76 |

*(continued)*

TABLE II. *(continued)*

| No. | (Cu–bipy) × $10^3$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 22 | 4.038 | 7.500 | 5.105 | 1.19 |
| 23 | 4.038 | 7.500 | 4.765 | 2.05 |
| 24 | 4.038 | 7.500 | 4.570 | 2.85 |

25.0 ± 0.2 °C; $I = 0.10$ mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

TABLE III. Results of the Relaxation Spectra for Cu(II)–bipy–valine Ternary System

| No. | (Cu–bipy) × $10^3$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 2.692 | 10.00 | 4.840 | 1.37 |
| 2 | 2.692 | 10.00 | 5.347 | 0.73 |
| 3 | 2.692 | 10.00 | 5.040 | 1.04 |
| 4 | 2.692 | 10.00 | 4.585 | 2.15 |
| 5 | 2.692 | 5.000 | 5.324 | 0.72 |
| 6 | 2.692 | 5.000 | 4.780 | 1.46 |
| 7 | 2.692 | 5.000 | 4.500 | 2.33 |
| 8 | 1.346 | 5.000 | 5.342 | 1.09 |
| 9 | 1.346 | 5.000 | 5.080 | 1.50 |
| 10 | 1.346 | 5.000 | 4.830 | 2.07 |
| 11 | 1.346 | 5.000 | 4.505 | 3.42 |
| 12 | 1.346 | 2.500 | 5.282 | 1.19 |
| 13 | 1.346 | 2.500 | 5.070 | 1.72 |
| 14 | 1.346 | 2.500 | 4.507 | 3.60 |
| 15 | 1.346 | 2.500 | 4.800 | 2.32 |
| 16 | 4.023 | 10.00 | 5.050 | 0.87 |
| 17 | 4.023 | 10.00 | 4.827 | 1.17 |
| 18 | 4.023 | 10.00 | 4.522 | 1.95 |
| 19 | 4.023 | 7.500 | 5.300 | 0.56 |
| 20 | 4.023 | 7.500 | 5.060 | 0.93 |
| 21 | 4.023 | 7.500 | 4.542 | 1.91 |
| 22 | 4.023 | 7.500 | 4.830 | 1.18 |

25.0 ± 0.2 °C; $I = 0.10$ mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

TABLE IV. Results of the Relaxation Spectra for Cu(II)–bipy–threonine Ternary System

| No | (Cu–bipy) × $10^3$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 2.692 | 10.00 | 5.082 | 4.05 |
| 2 | 2692 | 10.00 | 4.500 | 1.30 |
| 3 | 2.692 | 10.00 | 4.833 | 0.71 |
| 4 | 2.692 | 5.000 | 5.340 | 0.54 |
| 5 | 2.692 | 5.000 | 4.825 | 0.81 |
| 6 | 2.692 | 5.000 | 4.575 | 1.07 |
| 7 | 2.692 | 5.000 | 5.025 | 0.60 |
| 8 | 1.346 | 5.000 | 5.082 | 0.79 |
| 9 | 1.346 | 5.000 | 4.510 | 1.85 |
| 10 | 1.346 | 5.000 | 4.877 | 1.03 |
| 11 | 1.346 | 2.500 | 4.515 | 2.17 |
| 12 | 1.346 | 2.500 | 5.360 | 0.72 |
| 13 | 1.346 | 2.500 | 5.060 | 0.92 |
| 14 | 1.346 | 2.500 | 4.840 | 1.30 |
| 15 | 4.023 | 10.00 | 5.340 | 0.28 |
| 16 | 4.023 | 10.00 | 5.070 | 0.33 |
| 17 | 4.023 | 10.00 | 4.582 | 0.86 |
| 18 | 4.023 | 10.00 | 4.862 | 0.57 |
| 19 | 4.023 | 7.500 | 4.549 | 0.96 |
| 20 | 4.023 | 7.500 | 4.805 | 0.64 |
| 21 | 4.023 | 7.500 | 5.035 | 0.49 |
| 22 | 4.023 | 7.500 | 5.245 | 0.36 |

25.0 ± 0.2 °C; $I = 0.10$ mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

TABLE V. Results of the Relaxation Spectra for Cu(II)–phen–proline Ternary System

| No. | (Cu–phen) × $10^4$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 9.616 | 1.250 | 5.075 | 4.48 |
| 2 | 9.616 | 2.500 | 5.070 | 4.18 |
| 3 | 9.616 | 2.500 | 5.333 | 2.13 |
| 4 | 9.616 | 2.500 | 4.883 | 5.23 |
| 5 | 9.616 | 2.500 | 4.680 | 5.83 |
| 6 | 9.616 | 3.750 | 5.395 | 1.92 |
| 7 | 9.616 | 3.750 | 5.120 | 3.06 |
| 8 | 9.616 | 3.750 | 4.920 | 4.36 |
| 9 | 9.616 | 3.750 | 4.735 | 4.93 |
| 10 | 4.808 | 2.500 | 5.360 | 4.04 |
| 11 | 4.808 | 2.500 | 5.145 | 5.81 |
| 12 | 7.212 | 3.750 | 5.385 | 2.65 |
| 13 | 7.212 | 3.750 | 5.077 | 4.69 |
| 14 | 7.212 | 3.750 | 4.840 | 6.30 |
| 15 | 4.808 | 3.750 | 4.980 | 5.70 |
| 16 | 4.808 | 3.750 | 5.170 | 4.57 |
| 17 | 4.808 | 3.750 | 4.795 | 7.14 |
| 18 | 7.212 | 5.000 | 5.388 | 2.45 |
| 19 | 7.272 | 5.000 | 5.170 | 3.59 |
| 20 | 7.212 | 5.000 | 4.975 | 4.63 |
| 21 | 7.212 | 5.000 | 4.760 | 5.01 |
| 22 | 7.212 | 2.500 | 4.970 | 6.21 |

25.0 ± 0.2 °C; I = 0.10 mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

$$\log k'_{12} = 18.62 - 1.85 \log K^{\mathrm{Cu \cdot bipy}}_{\mathrm{Cu \cdot bipy \cdot L}} \quad r = -0\ 992$$

$$\log k_{21} = 3.79 - 0.366 \log K^{\mathrm{Cu \cdot bipy}}_{\mathrm{Cu \cdot bipy \cdot L}} \quad r = -0.948$$

$$\log k'_{21} = 11.52 - 0.777 \log K^{\mathrm{Cu \cdot bipy}}_{\mathrm{Cu \cdot bipy \cdot L}} \quad r = -0.992$$

$$\log k_{12} = 3.57 + 0.664 \log K^{\mathrm{Cu \cdot phen}}_{\mathrm{Cu \cdot phen \cdot L}} \quad r = 0.988$$

TABLE VI. Results of the Relaxation Spectra for Cu(II)–phen–α-aminoisobutyric acid Ternary System

| No. | (Cu–phen) × $10^4$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 9.616 | 2.500 | 5.380 | 2.04 |
| 2 | 9.616 | 2.500 | 5.180 | 3.40 |
| 3 | 9.616 | 2.500 | 4.969 | 4.25 |
| 4 | 9.616 | 2.500 | 4.740 | 6.17 |
| 5 | 9.616 | 3.750 | 5.360 | 2.13 |
| 6 | 9.616 | 3.750 | 5.170 | 2.81 |
| 7 | 9.616 | 3.750 | 4.980 | 4.22 |
| 8 | 9.616 | 3.750 | 4.768 | 5.66 |
| 9 | 7.212 | 5.000 | 5.380 | 2.85 |
| 10 | 7.212 | 5.000 | 5.190 | 3.26 |
| 11 | 7.212 | 5.000 | 4.990 | 4.11 |
| 12 | 7.212 | 5.000 | 4.775 | 4.89 |
| 13 | 7.212 | 3.750 | 5.400 | 2.51 |
| 14 | 7.212 | 3.750 | 5.200 | 3.32 |
| 15 | 7.212 | 3.750 | 4.995 | 4.36 |
| 16 | 7.212 | 3.750 | 4.785 | 6.00 |
| 17 | 7.212 | 2.500 | 5.386 | 2.82 |
| 18 | 7.212 | 2.500 | 5.158 | 3.92 |
| 19 | 7.212 | 2.500 | 4.969 | 4.76 |
| 20 | 7.212 | 2.500 | 4.780 | 5.29 |
| 21 | 4.808 | 5.000 | 5.400 | 3.23 |
| 22 | 4.808 | 5.000 | 5.200 | 4.06 |
| 23 | 4.808 | 2.500 | 5.375 | 3.30 |
| 24 | 4.808 | 3.750 | 5.390 | 3.11 |

25.0 ± 0.2°C; $I = 0.10$ mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

TABLE VII. Results of the Relaxation Spectra for Cu(II)–phen–valine Ternary System

| No. | (Cu–phen) × $10^4$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 9.616 | 2.500 | 5.372 | 1.44 |
| 2 | 9.616 | 2.500 | 5.190 | 1.64 |
| 3 | 9.616 | 2.500 | 4.987 | 2.37 |
| 4 | 9.616 | 2.500 | 4.758 | 2.45 |
| 5 | 9.616 | 3.750 | 5.350 | 1.35 |
| 6 | 9.616 | 3.750 | 5.162 | 1.85 |
| 7 | 9.616 | 3.750 | 4.960 | 2.22 |
| 8 | 9.616 | 3.750 | 4.780 | 2.30 |
| 9 | 7.212 | 5.000 | 5.380 | 1.55 |
| 10 | 7.212 | 5.000 | 5.190 | 1.93 |
| 11 | 7.212 | 5.000 | 4.980 | 2.50 |
| 12 | 7.212 | 5.000 | 4.780 | 3.07 |
| 13 | 7.212 | 3.750 | 5.380 | 1.59 |
| 14 | 7.212 | 3.750 | 5.172 | 2.04 |
| 15 | 7.212 | 3.750 | 4.970 | 2.75 |
| 16 | 7.212 | 3.750 | 4.786 | 3.31 |
| 17 | 7.212 | 2.500 | 5.355 | 1.59 |
| 18 | 7.212 | 2.500 | 5.180 | 2.09 |
| 19 | 7.212 | 2.500 | 4.940 | 2.96 |
| 20 | 7.212 | 2.500 | 4.650 | 3.64 |
| 21 | 4.808 | 5.000 | 5.395 | 1.64 |
| 22 | 4.808 | 5.000 | 4.752 | 3.82 |
| 23 | 4.808 | 3.750 | 5.365 | 2.08 |
| 24 | 4.808 | 3.750 | 4.735 | 3.35 |

25.0 ± 0.2 °C; $I = 0.10$ mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

TABLE VIII. Results of the Relaxation Spectra for Cu(II)–phen–threonine Ternary System

| No. | (Cu–phen) × $10^4$ | (HL) × $10^3$ | pH | $\tau$ (ms) |
|---|---|---|---|---|
| 1 | 9.616 | 2.500 | 5.346 | 0.89 |
| 2 | 9.616 | 2.500 | 5.175 | 1.00 |
| 3 | 9.616 | 2.500 | 4.920 | 1.39 |
| 4 | 9.616 | 2.500 | 4.750 | 1.51 |
| 5 | 9.616 | 3.750 | 5.165 | 0.86 |
| 6 | 9.616 | 3.750 | 4.755 | 1.33 |
| 7 | 9.616 | 3.750 | 4.963 | 0.89 |
| 8 | 9.616 | 3.750 | 4.546 | 1.70 |
| 9 | 7.212 | 5.000 | 4.740 | 1.36 |
| 10 | 7.212 | 5.000 | 4.573 | 1.68 |
| 11 | 7.212 | 5.000 | 4.975 | 1.05 |
| 12 | 7.212 | 5.000 | 5.200 | 0.90 |
| 13 | 7.212 | 3.750 | 5.250 | 1.02 |
| 14 | 7.212 | 3.750 | 4.560 | 1.62 |
| 15 | 7.212 | 3.750 | 4.775 | 1.62 |
| 16 | 7.212 | 3.750 | 4.990 | 1.10 |
| 17 | 7.212 | 2.500 | 5.390 | 0.99 |
| 18 | 7.212 | 2.500 | 4.928 | 1.37 |
| 19 | 7.212 | 2.500 | 4.740 | 2.04 |
| 20 | 4.808 | 5.000 | 5.135 | 1.00 |
| 21 | 4.808 | 5.000 | 4.563 | 2.31 |
| 22 | 4.808 | 2.500 | 5.360 | 1.17 |

25.0 ± 0.2 °C; $I = 0.10$ mol $dm^{-3}$ $NaClO_4$; (methyl red) = $2.5 \times 10^{-5}$ mol $dm^{-3}$.

$$\log k'_{12} = 18.97 - 1.879 \log K^{\mathrm{Cu \cdot phen}}_{\mathrm{Cu \cdot phen \cdot L}} \quad r = -0.969$$

$$\log k_{21} = 3.53 - 0.331 \log K^{\mathrm{Cu \cdot phen}}_{\mathrm{Cu \cdot phen \cdot L}} \quad r = -0.955$$

$$\log k'_{21} = 11.28 - 0.713 \log K^{\mathrm{Cu \cdot phen}}_{\mathrm{Cu \cdot phen \cdot L}} \quad r = -0.968$$

The correlation equations for rate constants and dissociation constants of the aminoacids are listed below

$$\log k^{\mathrm{bipy}}_{12} = 6.06 - 0.296\ \mathrm{p}K_2 \quad r = 0.954$$

$$\log k'^{\mathrm{bipy}}_{12} = 12.24 - 0.886\ \mathrm{p}K_2 \quad r = -1.000$$

$$\log k^{\mathrm{bipy}}_{21} = 2.57 - 0.179\ \mathrm{p}K_2 \quad r = -0.979$$

TABLE IX. Thermodynamic and Kinetic Data for Cu(II)–α,α′-bipy–α-aminoacid Ternary System

| Aminoacid | $pK_2$ | $pK_1$ | $\log K^{Cu \cdot bipy}_{Cu \cdot bipy \cdot L}$ | $\log k_{12}$ | $\log k'_{12}$ | $\log k_{21}$ | $\log k'_{21}$ |
|---|---|---|---|---|---|---|---|
| Proline | 10.60(7) | 1.77(7) | 8.55(7) | 9.25 | 2.85 | 0.700 | 4.90 |
| α-Aminoisobutyric acid | 10.08(7) | 2.44(7) | 8.23(7) | 8.97 | 3.29 | 0.740 | 5.14 |
| Valine | 9.57(7) | 2.34(7) | 8.00(7) | 8.84 | 3.76 | 0.840 | 5.33 |
| Threonine | 8.98(7) | 2.20(7) | 7.78(7) | 8.76 | 4.28 | 0.980 | 5.48 |

25.0 ± 0.2 °C; $I$ = 0.10 mol dm$^{-3}$ $NaClO_4$.

TABLE X. Thermodynamic and Kinetic Data for Cu(II)–phen–α-aminoacid Ternary System

| Aminoacid | $pK_2$ | $pK_1$ | $\log K^{Cu \cdot phen}_{Cu \cdot phen \cdot L}$ | $\log k_{12}$ | $\log k'_{12}$ | $\log k_{21}$ | $\log k'_{21}$ |
|---|---|---|---|---|---|---|---|
| Proline | 10.60(7) | 1.77(7) | 8.48(7) | 9.23 | 3.16 | 0.753 | 5.28 |
| α-Aminoisobutyric acid | 10.08(7) | 2.44(7) | 8.16(7) | 8.95 | 3.46 | 0.795 | 5.38 |
| Valine | 9.57(7) | 2.34(7) | 7.94(7) | 8.83 | 3.98 | 0.890 | 5.61 |
| Threonine | 8.98(7) | 2.20(7) | 7.74(7) | 8.74 | 4.56 | 1.000 | 5.80 |

25.0 ± 0.2 °C; $I$ = 0.10 mol dm$^{-3}$ $NaClO_4$.

$$\log k'^{bipy}_{21} = 8.82 - 0.369\, pK_2 \qquad r = -0.993$$

$$\log k^{phen}_{12} = 6.06 + 0.294\, pK_2 \qquad r = 0.956$$

$$\log k'^{phen}_{12} = 12.43 - 0.881\, pK_2 \qquad r = -0.993$$

$$\log k^{phen}_{21} = 2.39 - 0.156\, pK_2 \qquad r = -0.987$$

$$\log k'^{phen}_{21} = 8.79 - 0.334\, pK_2 \qquad r = -0.990$$

It is interesting to notice that LFER also exist between the rate constants of the ternary systems with common second ligands (aminoacids) but with different first ligands (bipy or phen). The correlation expressions for such linear relationships are shown as follows:

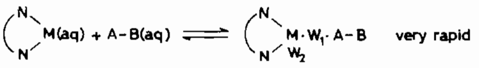
$$\log k^{bipy}_{12} = -0.053 + 1.008 \log k^{phen}_{12} \qquad r = 1.000$$

$$\log k'^{bipy}_{12} = -0.225 + 0.995 \log k'^{phen}_{12} \qquad r = 0.995$$

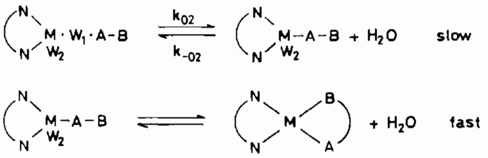
$$\log k^{bipy}_{21} = -0.177 + 1.156 \log k^{phen}_{21} \qquad r = 0.999$$

$$\log k'^{bipy}_{21} = -0.832 + 1.093 \log k'^{phen}_{21} \qquad r = 0.989$$

As to the mechanism of complexation reactions, the rate-determining step is usually regarded as the loss of a water molecule from the inner coordination sphere of a thermodynamically stable species [11]. A similar mechanism has also been proposed for the formation of higher order complexes [10], for example, in our case



(6)



(8)

The rate-determining step is again the loss of water molecule from the thermodynamically stable species (eqn. (7)). Since copper complexes in our case are most likely of the square coplanar configuration and the heteroaromatic bases are strong π-electron acceptors which allows for considerable π back donation from the copper ion, the net effect of which is the lowering of the electron density on the copper ion and then a slow down of the $S_N1$ process but enhancement of the $S_N2$ process [12]. This implies that the rate-determining step involves both bond making and bond breaking and therefore the mechanism falls into the $S_N2$ category.

As the deprotonated aminoacid is negatively charged ($L^-$), it favors a nucleophilic attack on $Cu(bipy)^{2+}$ and therefore the rate constants ($k_{12}$) are much larger than that ($k'_{21}$) of the protonated form (HL). It is also seen from Tables IX and X that the $k_{12}$ values increase with the increase of the base strength of the ligands ($pK_2$) while the $k'_{12}$ values decrease with the increase of the base strength of the ligands. The phenomena might be ascribed to the loss of a proton before the protonated ligand HL proceeds to attack the species $Cu(bipy)^{2+}$ and the process of deprotonation of the ligand affect the reaction rate constant $k'_{12}$, the more rapid is the process of deprotonation the larger is the reaction rate constant $k'_{12}$. The process of deprotonation is also related to the base strength of the ligand, as the stronger is the base the slower is the rate of deprotonation and hence the smaller the $k'_{12}$ values.

Since the extreme lability of aquated copper ion is ascribed to the Jahn–Teller effect, it has been suggested that the loss of a water molecule from the elongated axial position is the rate-determining process for complexation followed by a very rapid inversion with ligand attack bringing the ligand into the equatorial position [13]. In fact, for a ligand like bipy or phen, which provides a very large ligand field, it is more correct to consider the $CuB^{2+}$ species as square coplanar rather than a distorted octahedron. It is possible then that the first ligand in the inner coordination sphere so thoroughly inhibits the inversion that the incoming ligand must replace equatorial water, which is usually labile, to form a stable complex, and thus make these ternary mixed-ligand complexes particularly stable.

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