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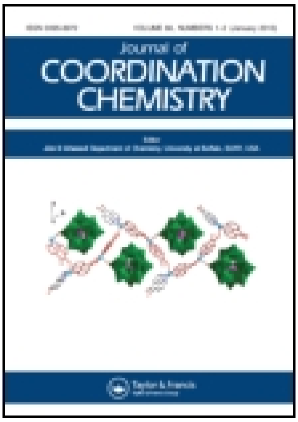

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Electroanalytical, kinetic, and mechanistic investigations of coordination-inspired electron transfer between Fe(II)/Cu(II)

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Accepted author version posted online: 25 Feb 2013.Published online: 05 Apr 2013.

To cite this article: Syed Raashid Maqsood , Mohsin Ahmad Bhat & Badruddin Khan (2013) Electroanalytical, kinetic, and mechanistic investigations of coordination-inspired electron transfer between Fe(II)/Cu(II), Journal of Coordination Chemistry, 66:7, 1211-1219, DOI: 10.1080/00958972.2013.778987

To link to this article: http://dx.doi.org/10.1080/00958972.2013.778987

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Journal of Coordination Chemistry, 2013
http://dx.doi.org/10.1080/00958972.2013.778987

Electroanalytical, kinetic, and mechanistic investigations of coordination-inspired electron transfer between Fe(II)/Cu(II)

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(*Received 8 September 2012; in final form 20 December 2012*)

Herein, we report that the thermodynamic barrier for solution-phase electron transfer (ET) between Cu(II) and Fe(II) in aqueous acidic media can be overcome through the addition of 2,9-dimethyl-1,10-phenanthroline (Neocuproine [NC]) to the reaction mixture. A detailed discussion of the kinetic and mechanistic aspects of this coordination-inspired ET is presented. We attribute the observed change in the thermodynamic feasibility to the change in the reduction potential of Cu(II)–Cu(I) couple on its ligation with NC. The reaction was found to be slow, following first-order kinetics with respect to each Cu(II) and Fe(II). In the presence of excess NC, the reaction was observed to proceed with a pseudo-second-order rate constant of $3.37 \pm 0.05\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ at 298 K, with an activation barrier of ca. $26.22\,\mathrm{kJ\,mol^{-1}}$. The slow reaction is attributed to the significant reorganization energy associated with large-scale changes in the coordination sphere of the oxidant. A two-step mechanism that explains the experimental observations is proposed for the investigated reaction.

Keywords: Neocuproine; Metalloproteins; Redox potential; Nonspontaneous; Activation energy

1. Introduction

Coordination complexes of transition metal ions [1–3] have established roles as metalloproteins in life processes. Analytical and other applications of coordination complexes make studies related to redox properties, mechanistic, kinetic, and applied aspects of inner and outer sphere electron transfers in coordination complexes important [4, 5]. Few reports [6–8] using transition metal ion complexes as model systems for understanding electron-transfer processes in metalloproteins have been demonstrated. A long-standing challenge related to electron-transfer processes in metalloproteins is to unravel the basic cause for the metal ion center in electron transfer proteins that allows them to mediate a huge number of electron transfer reactions with high sensitivity and accuracy [9, 10]. XRD and other structural studies in blue copper proteins have established that this ability of metalloproteins can be partly attributed to a large variation in the redox potential of metal ion center (190–780 mV) due to the nature and complexation geometry specific to the redox tuning properties of ligands [11, 12].

In continuation to our work on coordination-inspired redox systems [13, 14], we investigated redox titration between Fe(II) and Cu(II) in the presence of 2,9-dimethyl-1,

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10-phenanthroline, also known as Neocuproine (NC). NC is used as Cu(I) stabilizing ligand for its tendency to form a very stable $[Cu(NC)_2]^{1+}$ complex [15–17]. Formation of this complex has been explored for analytical monitoring of many bioactive molecules like cysteine, ascorbic acid, dazomet, and carpital [18–23]. Cu(I) stabilization and tuning of redox properties of Cu(II) by NC are the underlying principles for CUPric Reducing Antioxidant Capacity-based hydroxyl–scavenging antioxidant assay of various antioxidants [22, 24, 25]. Reduction of Cu(II) to Cu(I) by Fe(II) is thermodynamically a nonspontaneous process [26]. We report here that the unfavorable electron transfer (ET) between Cu (II) and Fe(II) can be made thermodynamically feasible by the presence of NC in the reaction mixture. We propose that owing to its tendency to stabilize Cu(I), NC modifies the redox behavior of Cu(II)–Cu(I) system by increasing its apparent redox potential. A detailed discussion of kinetic and mechanistic aspects of this coordination-inspired ET is presented and a probable mechanism that justifies the feasibility and associated observations of the investigated process is also presented. Spectrophotometric and potentiometric investigations were used for the estimation of various kinetic and thermodynamic parameters of the investigated redox process.

2. Experimental

Research-grade ferrous ammonium sulfate, copper sulfate, and NC were purchased from Merck India and used without purification. In view of the poor solubility of NC in water and possible hydrolysis complications for Fe(II) in neutral water, all solutions were prepared in 1×10^{-3} M H_2SO_4 in water. Spectrophotometric measurements were carried out on a Shimadzu 1650 UV–visible spectrophotometer with thermostatic control (±0.2 °C). Potentiometric measurements were done on a Eutech PC5500 ion analyzer over a thermostatic magnetic stirrer. All experiments were repeated at least five times to ensure reproducibility of the reported observations.

3. Results and discussion

3.1. *Redox titration between Cu(II) and Fe(II)*

ET between Cu(II) and Fe(II) in H_2O is thermodynamically nonspontaneous [26, 27], and hence expectedly, we observed no significant potential break during potentiometric titration of Cu(II) with Fe(II). However, a marked change in potentiometric behavior in terms of a significant potential break in emf *versus* volume of titrant added was observed when the titration was carried out in the presence of NC (figure 1). This observed change in potentiometric response clearly indicates spontaneity of ET between the Cu(II) and Fe(II) in the presence of NC in aqueous solutions.

Expecting ligation effect of NC to be responsible for the previously mentioned observation, UV–visible spectra for Fe(II), Cu(II) and their solutions with NC were recorded (figure 2). From these recorded UV–visible spectra, it is clear that, while Fe(II) aq. shows no significant absorbance in the 900–300 nm region, Cu(II) shows a broad absorbance peak around 815 nm, and NC shows the absorbance in UV region at 285 nm. Fe(II) and NC taken together showed no prominent changes in their absorption characteristics in

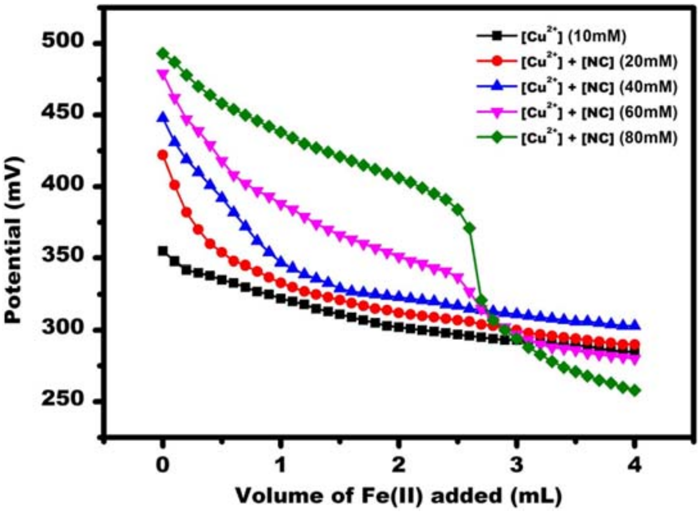


Figure 1. Potentiometric titration of Cu(II) (10 mM, 5 mL) with Fe(II) (20 mM) in the presence of varying concentrations of neocuproine.

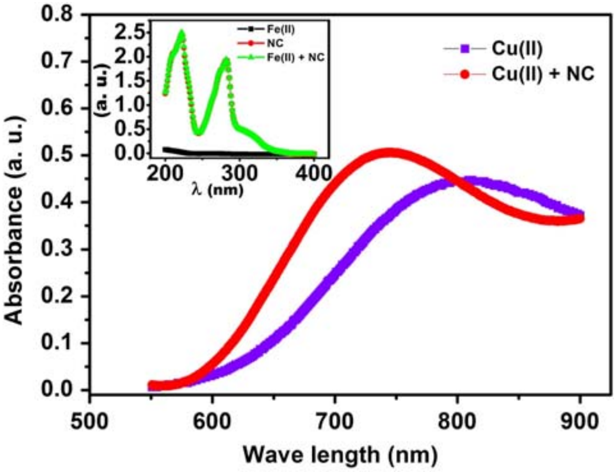


Figure 2. Effect of Neocuproine (100 mM) on the absorbance spectra of Cu(II) (10 mM) and Fe(II) (10 mM).

comparison to their absorption behavior when they are present individually. This indicates that there is no significant interaction between Fe(II) and NC in aqueous solution. However, the absorbance band characteristic to Cu(II) (aq.) was shifted hypsochromically by ca. 70 nm in the presence of NC, indicating a possible complex formation between Cu(II) and NC. Using Job's method, we established a stoichiometry of 1 : 2 ($[Cu(NC)_2]^{2+}$) for this precursor complex (inset figure 3). It was found that the addition of Fe(II) solution to the solution of Cu(II) and NC results in the disappearance of absorbance band at 745 nm characteristic to $[Cu(NC)_2]^{2+}$ and the appearance of a new band at 450 nm. Compared to the band at 815 nm (for Cu(II) aq.) and 745 nm (for $[Cu(NC)_2]^{2+}$), this new band at 450 nm

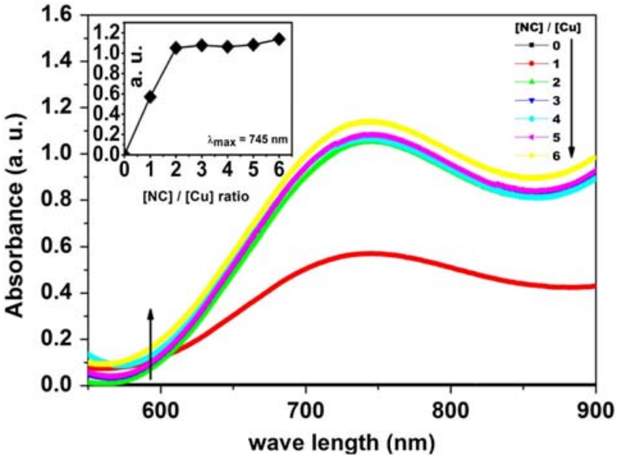


Figure 3. Absorption spectra recorded for Cu(II)+NC solutions of varying compositions. (Inset) Job's plot that establishes a 1 : 2 stoichiometry for Cu(II)-NC complex.

was narrower and more intense ($\varepsilon_{\max} = 7.5 \times 10^{-3}\,\mathrm{L\,cm^{-1}\,mol^{-1}}$). These features are characteristic of a charge transfer band. These prominent changes in absorbance, wavelength, and absorbtivity coefficient indicate that some significant changes in the electronic and bonding pattern of $[\mathrm{Cu(NC)_2}]^{2+}$ complex occur on its interaction and spontaneous reduction by Fe(II). In light of these observations, it can be safely argued that breaking of non-spontaneity of the the investigated ET (from Fe(II) to Cu(II)) is on account of the complexation of NC. We propose that the addition of NC to Cu(II) aqueous solutions alters the reduction potential of Cu(II)–Cu(I) couple to a level wherein ΔG associated with ET from Fe(II) to Cu(II)-NC complex is sufficiently negative that ET proceeds spontaneously. The spectral and potentiometric results indicate complexation-driven ET between Fe(II) and $[\mathrm{Cu(NC)_2}]^{2+}$ to form highly stable $[\mathrm{Cu(NC)_2}]^{1+}$.

Calculations on the basis of equation (1),

$$E_{\text{Complex}} = E^{0}_{\text{aqua}} - (59.16\ \text{mV}) \log \frac{\beta^{\text{II}}}{\beta^{\text{I}}} \tag{1}$$

where E_{Complex} is the reduction potential of Cu(II) in complexed form, E^{0}_{aqua} is the standard electrode potential of Cu(II) as aqua complex, $\beta^{\text{II}}(11.7)$ and $\beta^{\text{I}}(19.1)$ are the stability constants of oxidized and reduced form of Cu(II) with NC, respectively [28], suggest that in the presence of NC, the reduction potential of Cu(II)–Cu(I) couple increases from 153 mV [29] to 709 mV. This much variation in reduction potential ensures spontaneous ET from Fe(II) to Cu(II).

Though the thermodynamic feasibility attained by the complexation effect predicted smooth ET from Fe(II) to Cu(II), fluctuations in the emf readings were observed during potentiometric titrations of Cu(II)+NC solution with Fe(II). After the addition of Fe(II) to Cu(II) and NC solution, the potential readings stabilized only after at least 10–20 s. Hence, all emf readings used for the present study were recorded with a 20-s delay. These fluctuations in potential readings during potentiometric titrations are suggestive of the slow ET between the titrant (Fe(II)) and the titrand (Cu(II)-NC complex). We attribute this slow

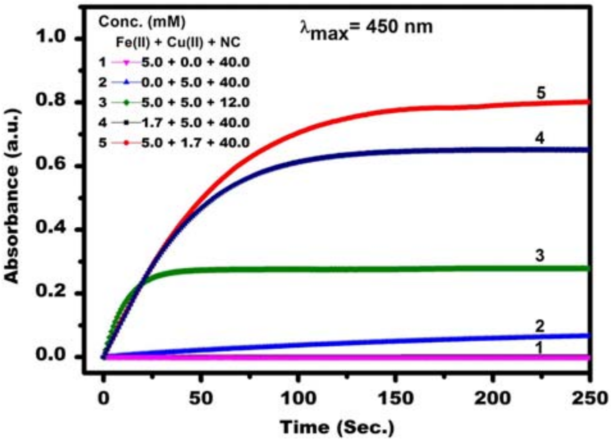


Figure 4. Change in absorbance with time and with different concentrations of reactants.

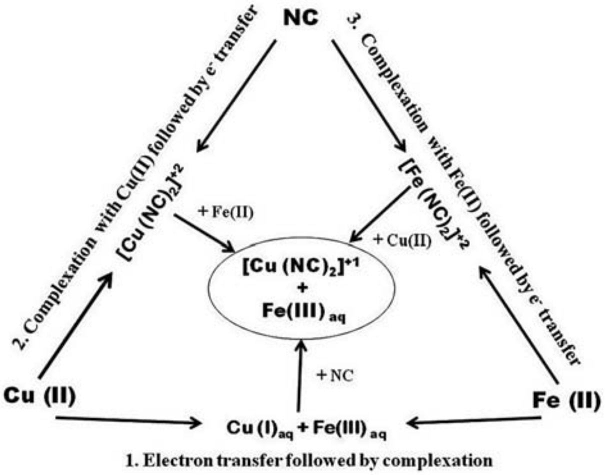
kinetics of ET to unusually large changes in coordination geometry attending the reduction of $[Cu(NC)_2]^{2+}$ due to which the investigated ET will be associated with an appreciable kinetic barrier and hence, slow kinetics. Cu(II) complexes prefer to exist as Jahn–Teller distorted octahedra (though other configurations are known), while Cu(I) complexes usually are four-coordinate tetrahedra or linear species [30]. Hence, large changes in the complex geometry are expected during redox, which in turn slow down the rate of ET. It is due to this effect that the choice of ligands has a major effect on the rates of Cu(II)-mediated catalytic processes like the Ullmann reaction [31]. The slow kinetics of the ET in the present case allow us to carry out detailed kinetic investigations through conventional kinetic methods.

3.2. *Kinetic studies*

Investigated redox reaction was monitored spectrophotometrically for kinetic investigations. During kinetic investigations, the absorbance of the reaction mixture at 450 nm (λ_{max} for $[Cu(NC)_2]^{1+}$ (product of redox reaction)) was recorded as a function of time with time interval of 0.1 s over a period of 5 min; typical absorbance *versus* time plots are presented in figure 4. From the recorded absorbance *versus* time plot, it appeared that the investigated ET reaction approached 95% completion in 120–130 s. The absorbance plot at varying reactant concentrations (Cu(II) (1.5–5.0 mM) and Fe(II) (1.5–5.0 mM) with NC (1.5–12.0 mM)) was recorded and the order with respect to each reactant was calculated. From these calculations, it appears that in the presence of excess of NC (12.0 mM), the reaction follows pseudo-second-order kinetics with order with respect to both Fe(II) and Cu(II) equal to one. Order for NC was calculated by comparing the initial rates for two reactant mixtures which were similarly concentrated for Fe(II) and Cu(II) but differed in the concentration of NC, which was, however, kept in excess in both cases. From these calculations, it was observed that the investigated reaction follows second-order kinetics with respect to NC.

3.3. *Mechanistic aspects*

In view of the kinetic investigations, it appears that the investigated redox reaction between Fe(II) and Cu(II) in the presence of NC can take place through three possible



Scheme 1. Schematic representation for the three possible pathways in favor of the studied electron transfer reaction.

pathways (scheme 1). Complexation of either of the two redox species (Fe(II) or Cu(II)) with NC followed ET, or stabilization of the product/s of ET by complexation with NC. Absorption spectra recorded for Fe(II) and Cu(II) in the presence of NC clearly establish complexation of NC with Cu(II) but rule out complexation of Fe(II) with NC (see figure 2). Similarly, in view of our observations during potentiometric titrations and the reported value of standard redox potentials of Cu(II) and Fe(II) [29], the possibility of ET prior to complexation can be safely ruled out. In light of these facts, we propose that the investigated redox reaction follows complexation-mediated ET pathway.

We propose that the reaction involves complexation of Cu(II) with NC that leads to formation of a less stable Cu–NC precursor complex, which in turn is reduced by Fe(II), which is oxidized to Fe(III).

Formation of Cu–NC complex was shown by shift in the absorbance maximum for Cu (II) by 70 nm on the addition of NC in the aqueous solution. Following Job's method, the stoichiometry of the resulting complex was (1 (Cu) : 2 (NC)) (see figure 3). We propose that the investigated NC-mediated redox reaction between Cu(II) and Fe(II) in aqueous media involves an initial complexation of Cu(II) with NC to form $[\mathrm{Cu(NC)_2}]^{2+}$, which in turn is reduced by aqueous phase Fe(II) to a more stable $[\mathrm{Cu(NC)_2}]^{1+}$. The proposed mechanism for the overall process can be summarized as below:

$$\mathrm{Cu}^{2+}_{\mathrm{aq}} + 2\mathrm{NC}\ \frac{k_1}{k_{-1}}\ [\mathrm{Cu(NC)_2}]^{2+} \quad (\mathrm{fast}) \tag{2}$$

$$[\mathrm{Cu(NC)_2}]^{2+} + \mathrm{Fe}^{2+}_{\mathrm{aq}} \xrightarrow{k_2} [\mathrm{Cu(NC)_2}]^{1+} + \mathrm{Fe}^{3+}_{\mathrm{aq}} \quad (\mathrm{slow}) \tag{3}$$

$$K_{\mathrm{eq}} = \frac{[\mathrm{Cu(NC)_2}]^{2+}}{[\mathrm{Cu}^{2+}_{\mathrm{aq}}][\mathrm{NC}]^2} \tag{4}$$

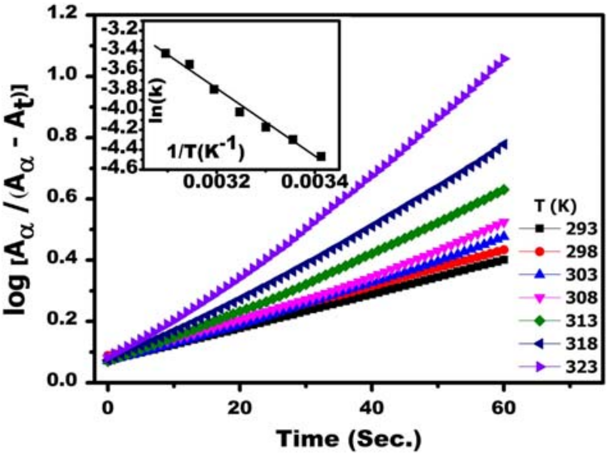


Figure 5. Effect of temperature on the rate of ($[Cu(NC)_2]^{1+}$) formation in a reaction mixture of Cu(II) (1.7 mM) + Fe(II) (5.0 mM) + NC (40 mM) at varying temperatures. (Inset) Arrhenius plot for the determination of activation energy.

$$[Cu(NC)_2]^{2+} = K_{eq}[Cu^{2+}_{aq}][NC]^2 \tag{5}$$

$$\text{Rate} = k_2[Cu(NC)_2]^{2+}[Fe^{2+}_{aq}] \tag{6}$$

$$\text{Rate} = k_2K_{eq}[Cu^{2+}_{aq}][NC]^2[Fe^{2+}_{aq}] \tag{7}$$

$$\text{Rate} = k'[Cu^{2+}_{aq}][NC]^2[Fe^{2+}_{aq}] \qquad k' = k_2K_{eq} \tag{8}$$

From the proposed mechanism, the investigated reaction should follow first-order kinetics with respect to each Cu(II) and Fe(II) and second-order kinetics with respect to NC, in agreement with our kinetic investigations. Substituting for the K_{eq} ($\log K_{eq} = 11.7$) [28] and experimentally determined rate, the average value for k_2 was ca. $3.37 \pm 0.05\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

Kinetics of the reaction at varying temperatures (temperature maintained with an accuracy of 0.2 °C) with two of the reactants in excess (NC and Cu(II) or Fe(II)) was followed for the estimation of temperature-dependent rate constant of the reaction (figure 5). For estimation of the rate constant, each experiment was repeated at least five times. The average value of rate constants at varying temperatures as estimated in these experiments is

Table 1. Variation of rate constant with change in temperature for the reaction of Cu(II) with Fe(II) in the presence of excess of neocuproine in 1×10^{-3} M H_2SO_4.

Temp. (°C)	Rate constant $k \pm 0.05$ (s^{-1})	1/T (K^{-1})	ln (k)
20.0	1.85	0.003413	0.62
25.0	1.99	0.003356	0.69
30.0	2.30	0.003300	0.86
35.0	2.60	0.003247	0.97
40.0	3.30	0.003195	1.19
45.0	4.24	0.003145	1.45
50.0	5.80	0.003096	1.76

listed in table 1. The Arrhenius plot corresponding to the data presented in table 1 led to an overall activation energy of ca. $26.22\,\mathrm{kJ\,mol^{-1}}$ for the redox reaction.

4. Conclusion

Kinetic, mechanistic, and electroanalytic aspects of coordination-inspired ET between Fe(II) and Cu(II) in the presence of Neocuproine (NC) were explored. The presence of NC ensures spontaneity of the otherwise nonspontaneous solution phase ET from Fe(II) to Cu (II) in aqueous acidic media. Besides being important for understanding the ligand effect in biologically important ET reactions, these studies present a new means for the potentiometric estimation of Cu(II)/Fe(II).

Acknowledgments

SRM would like to thank CSIR-New Delhi for the financial assistance in the form of Junior Research Fellowship and Professor Khaliquz Zaman Khan, Head Department of Chemistry, University of Kashmir, for his constant encouragement and inspiration.

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