

## Reaction of Copper(II) with Ferrocene and 1,1'-Dimethylferrocene in Aqueous Acetonitrile: The Copper(II/I) Self-Exchange Rate

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The kinetics of the reactions of copper(II) with ferrocene (Fc) and 1,1'-dimethylferrocene (Dmfc) have been studied at 25 °C in aqueous acetonitrile (AN) containing 50–97.5 vol % AN. With increasing % AN, the rate constant increases along with the driving-force for the reaction. The results are analyzed in terms of Marcus theory to estimate the Cu(II/I) electron self-exchange rate constant ( $k_{11}$ ) for the system. Over the solvent range studied, the calculated  $k_{11}$  changes from  $1.1 \times 10^{-9}$  to  $17 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ , with an average value of  $5 \times 10^{-9}$ . In addition, the structures of the trifluoromethanesulfonate salts of  $[\text{Cu}(\text{AN})_4]^+$ ,  $[\text{Cu}(\text{OH})_2(\text{AN})_2]^{2+}$ , and  $[\text{Cu}(\text{AN})_4]^{2+}$  are reported. It is found that the Cu–NCCH<sub>3</sub> bond-length difference between the Cu(I) and Cu(II) oxidation states is only  $\sim 0.02 \text{ \AA}$ .

### Introduction

Since the introduction of Marcus theory<sup>1</sup> in the 1960s, it has been recognized that knowledge of the rates of electron self-exchange reactions is fundamental to understanding and predicting the rates of outer-sphere electron-transfer reactions. Consequently, the self-exchange rates have been measured by direct methods for many solvated transition metal ions and their complexes. For the first transition metal series, the exchange rates in water are known for the common oxidation states, with the glaring exception of the Cu(II/I) system. Unless the rate is moderately fast, it is unlikely that this system will ever be studied in water because of the instability of aqueous Cu(I) with respect to disproportionation.

The general area of Cu(II/I) redox chemistry has been reviewed recently by Rorabacher.<sup>2</sup> There have been several applications of the Marcus cross-relationship to estimate the Cu(II/I) electron self-exchange rate in water. Sutin and co-workers<sup>3</sup> studied the reaction of Cu(I) with various Ru(III) polypyridyl complexes and estimated a rate constant of  $\sim 1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ . Shortly thereafter, Davies<sup>4</sup> measured the rates for Cu(I) reacting with several Ru(III) ammine com-

plexes and obtained an estimate of  $\sim 2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . More recently, Sisley and Jordan<sup>5</sup> studied the reduction of Cu(II) by Co(II)(sep) and found a self-exchange rate constant of  $\sim 5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  (sep = 1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane). These authors also corrected the  $E^\circ$  values for ionic strength effects and applied these to the results of Davies<sup>4</sup> to obtain self-exchange rate constants in the range of  $(2-9) \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ . Espenson and co-workers<sup>6</sup> studied the oxidation of aqueous V(II) and Cr(II) by aqueous Cu(II), and obtained rate constants of 26.6 and  $0.17 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These give self-exchange rate constants of  $3 \times 10^{-2}$  and  $7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ , respectively, from the Marcus cross-relationship. The latter value is reasonably consistent with the range calculated by Sisley and Jordan,<sup>5</sup> whereas the V(II)/Cu(II) system would appear to be using an inner-sphere mechanism. Rorabacher and co-workers<sup>7</sup> also concluded that the oxidation of Cu(I) by Co(TIM)(OH)<sub>2</sub><sup>3+</sup> (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) proceeds by an inner-sphere mechanism because it yields a large self-exchange rate constant of  $\sim 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for aqueous Cu(II/I). It would appear that the aqueous Cu(II/I) self-exchange rate constant is in the range of  $10^{-6}$ – $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ , and the rate would not be competitive with disproportionation of aqueous Cu(I).

The situation is different in acetonitrile (AN), where Cu(I) is quite stable.<sup>8</sup> Therefore, it is at least chemically feasible

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to measure directly the Cu(II/I) self-exchange rate in AN. In fact, Manahan<sup>9</sup> reported in 1967 that radiochemical tracer methods gave a self-exchange rate constant of  $\geq 0.3 \text{ M}^{-1} \text{ s}^{-1}$  in AN. This value seems anomalously large as compared to more recent estimates in water, and this was confirmed in our preliminary experiments which failed to detect any  $^{63}\text{Cu(I)}$  NMR line broadening in the presence of Cu(II). However, before attempting any direct measurements, it obviously would be helpful to have some idea of the magnitude of the rate of Cu(II/I) exchange to choose the appropriate experimental method and time scale.

The present work describes experiments to estimate the Cu(II/I) electron exchange rate in AN by applying the Marcus cross-relationship<sup>1</sup> to the reduction of Cu(II) with ferrocene (Fc) and 1,1'-dimethylferrocene (Dmfc) in AN/water mixtures. Reactions of ferrocenes are generally thought to be outer-sphere, and necessary background information is available from studies of the Cu(II) and ferrocenium ion ( $\text{Fc}^+$ ) reduction potentials in AN/water mixtures by Cox and co-workers<sup>10</sup> and the electron self-exchange studies in AN of the  $\text{Fc}/\text{Fc}^{+11-13}$  and  $\text{Dmfc}/\text{Dmfc}^{+11}$  couples. In the present study, the driving force for the reaction is varied by changing the reductant, but primarily by changing the AN/water composition, and the variation of the rate will be analyzed in terms of Marcus theory to obtain an estimate of the Cu(II/I) self-exchange rate constant.

The speciation of solvated Cu(II) ions in AN/water solutions was studied by Funahashi and co-workers<sup>14</sup> for  $[\text{H}_2\text{O}]$  between 0 and 0.84 M (98.5% AN), and they reported formation of  $[\text{Cu}(\text{OH})_n(\text{NCCH}_3)_{6-n}]^{2+}$  ( $n = 0-3$ ) with  $[\text{Cu}(\text{OH})_2(\text{NCCH}_3)_4]^{2+}$  as the dominant species for  $[\text{H}_2\text{O}]$  as low as 0.5 M ( $\sim 99\%$  AN). For Cu(I), the formation constants determined by Kamau and Jordan<sup>15</sup> suggest that  $\text{Cu}(\text{OH})_2(\text{NCCH}_3)_3^+$  is the dominant species for  $> 50\%$  AN, but the point at which this converts to  $\text{Cu}(\text{NCCH}_3)_4^+$  is uncertain. Our study<sup>16</sup> of  $^{63}\text{Cu(I)}$  NMR line widths in AN revealed that there is significant line broadening for  $> 0.5 \text{ M H}_2\text{O}$ , suggesting the formation of at least some  $\text{Cu}(\text{OH})_2(\text{NCCH}_3)_3^+$  at this point, and that the latter is the dominant species for the 50–97.5% AN of this study. The electrochemical studies of Cox and co-workers<sup>10</sup> show that the Cu(II/I) reduction potential increases smoothly with increasing % AN (50–100%) and do not suggest any abrupt change in species.

## Experimental Section

**Materials.** Acetonitrile (Caledon, Fisher or BDH), perchloric acid (Fisher), trifluoromethanesulfonic acid (triflic acid, Aldrich), copper(II) nitrate trihydrate (Allied Chemicals), and 1,1'-dimeth-

ylferrocene (Alfa Inorganics) were used as supplied. Ferrocene (Strem Chemicals) was purified by sublimation. The copper content of the various products was determined by iodimetry.

Tetraaquacopper(II) triflate  $[\text{Cu}(\text{OH})_4(\text{F}_3\text{CSO}_3)_2]$  (**I**) was prepared typically by adding 5.0 mL (26.5 mmol) of 5.3 M triflic acid to a slurry of 1.04 g (13.0 mmol) of cupric oxide in 25 mL of water. The mixture was heated at  $\sim 60^\circ\text{C}$  until the solid had dissolved, and then filtered and evaporated to dryness on a steam bath. The blue, crystalline product was redissolved in a minimum volume of water on the steam bath and recrystallized by cooling. This product was dissolved in acetonitrile ( $\sim 10 \text{ mL}$ ) and precipitated with ether, filtered, and washed with ether and dried in air. Anal. Calcd for  $\text{CuC}_2\text{F}_6\text{H}_8\text{O}_{10}\text{S}_2$ : Cu, 14.65; C, 5.54; H, 1.86. Found: Cu, 14.50; C, 5.20; H, 1.67.

Anhydrous Cu(II) triflate,  $\text{Cu}(\text{F}_3\text{CSO}_3)_2$  (**II**), was obtained as a fine, white hygroscopic powder by heating the tetrahydrate salt in air at  $\sim 100^\circ\text{C}$ . This solid was stored in a vial with a plastic cap in a desiccator. Anal. Calcd for  $\text{CuC}_2\text{F}_6\text{O}_6\text{S}_2$ : Cu, 17.5; C, 6.64. Found: Cu, 17.6; C, 6.30.

Tetraacetonitrilecopper(I) triflate  $[\text{Cu}(\text{NCCH}_3)_4](\text{F}_3\text{CSO}_3)$  (**III**) was prepared by a modification of the methods by Ogura<sup>17</sup> and Jenkins and Kochi.<sup>18</sup> A mixture containing 50 mL of acetonitrile, 1.0 g (2.3 mmol) of **I**, and 0.3 g (4.7 mmol) of copper foil was stirred in a capped parafilm-sealed Erlenmeyer flask until the solution turned colorless. Filtration on a  $4-8 \mu$  sintered glass frit gave a clear solution. Addition of anhydrous ether produced a white powder, which was collected by filtration under argon. Argon was sucked through the product until it looked reasonably dry, and then it was sealed under argon. Anal. Calcd for  $\text{CuC}_9\text{F}_3\text{H}_{12}\text{N}_4\text{O}_3\text{S}$ : Cu, 16.86; N, 14.87; C, 28.69; H, 3.21. Found: Cu, 17.10; N, 14.18; C, 27.64; H, 2.98.

The Cu(II) solvates,  $[\text{Cu}(\text{H}_2\text{O})_2(\text{NCCH}_3)_2](\text{F}_3\text{CSO}_3)_2$  (**IV**) and  $[\text{Cu}(\text{NCCH}_3)_4(\text{F}_3\text{CSO}_3)_2]$  (**V**), were obtained as blue crystals by slow evaporation of acetonitrile solutions of the tetrahydrate (**I**) and the anhydrous (**II**) Cu(II) triflates, respectively. The crystals from the solution of the tetrahydrate were obtained in an air atmosphere, whereas those from the solution of the anhydrous salt were obtained under an argon atmosphere. Single crystals for the structure determination were selected from the solution-crystal mixture in the X-ray crystallography laboratory.

The AN/water solvent was made by transferring an appropriate volume of doubly distilled water, and sometimes standardized aqueous perchloric or triflic acid, to a 500 mL or 1.00 L volumetric flask and diluting to volume with AN (99.7% or 99.5%). Therefore, the % AN refers to volume percentage. The acid added was prepared by diluting the concentrated acid with doubly distilled water and analyzed by titration with 0.100 M NaOH. The mixed solvents were stored in volumetric flasks and used within 2 days. The densities and molarities as a function of volume % AN are given in the Supporting Information.

For kinetic studies, stock solutions of Cu(II) were prepared by dissolving  $\sim 1.0 \text{ g}$  ( $\sim 2.3 \text{ mmol}$ ) of (**I**) or  $\sim 0.6 \text{ g}$  ( $\sim 2.5 \text{ mmol}$ ) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 50.0 mL of the appropriate solvent. The Cu(II) content was determined by standard iodimetry. Aliquots from these solutions were diluted to 25.0 mL with the solvent and used for the kinetic runs.

Solutions of Fc and Dmfc were prepared by dissolving weighed amounts of Fc ( $\sim 10 \text{ mg}$ ) or Dmfc ( $\sim 11 \text{ mg}$ ) in the appropriate solvent in 25.0 mL volumetric flasks. Next, 10.0 mL aliquots of these solutions were diluted in 50.0 mL with the same solvent to give stock solutions for the kinetic runs.

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**Table 1.** Summary of Crystallographic Data for [Cu(NCCH<sub>3</sub>)<sub>4</sub>](F<sub>3</sub>CSO<sub>3</sub>) (III), [Cu(H<sub>2</sub>O)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>](F<sub>3</sub>CSO<sub>3</sub>)<sub>2</sub> (IV), and [Cu(NCCH<sub>3</sub>)<sub>4</sub>](F<sub>3</sub>CSO<sub>3</sub>)<sub>2</sub> (V)

	III	IV	V
empirical formula	C <sub>9</sub> H <sub>12</sub> CuF <sub>3</sub> N <sub>4</sub> O <sub>3</sub> S	CuC <sub>6</sub> F <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub>	CuC <sub>10</sub> F <sub>6</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>
molecular mass	376.83	479.82	525.90
temp (K)	193	193	193
cryst syst	monoclinic	triclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	15.2062 (14)	5.7426 (9)	13.5406 (17)
<i>b</i> (Å)	14.1400 (13)	7.2723 (11)	10.8441 (14)
<i>c</i> (Å)	22.399 (2)	10.5221 (16)	27.725 (4)
$\alpha$ (deg)		79.855 (3)	
$\beta$ (deg)	94.527 (2)	84.183 (3)	
$\gamma$ (deg)		78.537 (3)	
<i>V</i> (Å <sup>3</sup> )	4801.2 (8)	422.92 (11)	4071.1 (9)
<i>Z</i>	12	1	8
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.564	1.884	1.716
cryst size, mm	0.81 × 0.69 × 0.58	0.40 × 0.25 × 0.07	0.46 × 0.41 × 0.27
collecn 2 $\theta$ limit (deg)	52.76°	52.84°	52.82°
wavelength (Å)	0.71073	0.71073	0.71073
reflns collected	9759	1710	4170
indep reflns	6972	1523	3565
final <i>R</i> indices <sup>a</sup>			
<i>R</i> <sub>1</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2 $\sigma$ ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.0827	0.0420	0.0391
<i>wR</i> <sub>2</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 3 $\sigma$ ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.2706	0.1236	0.1083

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

**Kinetic Measurements.** Runs under pseudo-first-order, and a few under second-order, conditions were done in 50%, 80%, 90%, 95%, or 97.5% AN. The rates were too fast in 99.5% AN to give reliable data. Measurements were done on a Tritech Dynamic Instruments stopped-flow spectrophotometer, in which the storage and drive syringes, the observation cell, and all connecting tubing are in a circulating, thermostated water bath at 25 ± 0.5 °C. The temperature was monitored via a Fluke 2180A digital thermometer. Most runs were under pseudo-first-order conditions with [Cu(II)] > 10 [Fc] or [Dmfc].

The rate of formation of the Fc<sup>+</sup> or Dmfc<sup>+</sup> product was monitored by measuring the change in absorbance with time at 616 nm. The voltage/time data from the photomultiplier were stored on a transient recorder and transferred to a 486 PC using the manufacturer's software and stored as a text file. A locally developed program read this file, converted the data to absorbance/time, and fitted it by iterative least-squares to a first-order, or second-order when appropriate, rate law to obtain the rate constants. At least 120 points were used in the analysis of each run, and the rate constants are the average of 8–12 kinetic runs.

**X-ray Structures.** The crystal data are summarized in Table 1. For Cu(NCCH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(F<sub>3</sub>CSO<sub>3</sub>)<sub>2</sub> (IV) and Cu(NCCH<sub>3</sub>)<sub>4</sub>(F<sub>3</sub>CSO<sub>3</sub>)<sub>2</sub> (V), crystals were obtained by slow evaporation of acetonitrile solutions of I in air and of II under argon, respectively. A sample of III was dissolved in acetonitrile, concentrated under argon, and cooled at ~5 °C to yield a white, crystalline product. In each case, a crystal was selected for the structure determination. Data were collected at -80 °C on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation using 0.2°  $\omega$  scans of 20 or 25 s exposures.<sup>19</sup> Empirical or multiscan (SADABS) methods were used to correct the intensity data for decay and absorption. A summary of the crystal and refinement data for all of these crystals is given in the Supporting Information. Hydrogen atoms were not apparent in the electron density maps and thus were not included in the fitting models.

## Results

The electronic spectra of the reactants and products in acetonitrile (AN) (see details in the Supporting Information)

reveal that the reactants Fc and Dmfc have maxima at 440 and 432 nm, with extinction coefficients of 95 and 102 M<sup>-1</sup> cm<sup>-1</sup>, respectively, while the corresponding values for the oxidized forms are 616 and 644 nm, 482 and 357 M<sup>-1</sup> cm<sup>-1</sup>. The extinction coefficients show minor variations ( $\pm 10$  M<sup>-1</sup> cm<sup>-1</sup>) with the % AN in 80%, 90%, and 95% AN. For Cu(II) triflate, the extinction coefficients at 616 and 644 nm are 3.65 and 6.81 M<sup>-1</sup> cm<sup>-1</sup>, respectively. The latter decrease significantly with decreasing % AN. These observations for Cu(II) agree well with those of Funahashi and co-workers.<sup>14</sup> Cu(I) is essentially transparent in the visible region. Overall, these results led to the selection of 616 nm for observation of the oxidation of Fc and Dmfc by Cu(II) for conditions of [Cu(II)]  $\gg$  [Fc] or [Dmfc].

It has been shown by Kratochvil and co-workers<sup>20</sup> that the reaction of Cu(II) with Fc in AN proceeds with 1:1 stoichiometry. For [Cu(II)]  $\gg$  [Fc] or [Dmfc], it is shown here that the rate is first-order in [Cu(II)], and a few runs under second-order conditions indicate that the rate is also first-order in Fc.

Although plots of the pseudo-first-order rate constant versus [Cu(II)] were always linear, they sometimes showed a significant intercept. It was found that this intercept could be greatly reduced if  $\geq 0.2$  mM perchloric or triflic acids were present.<sup>21</sup> The effect is illustrated in Figures 1 and 2 for reactions in 80% and 95% AN, respectively.

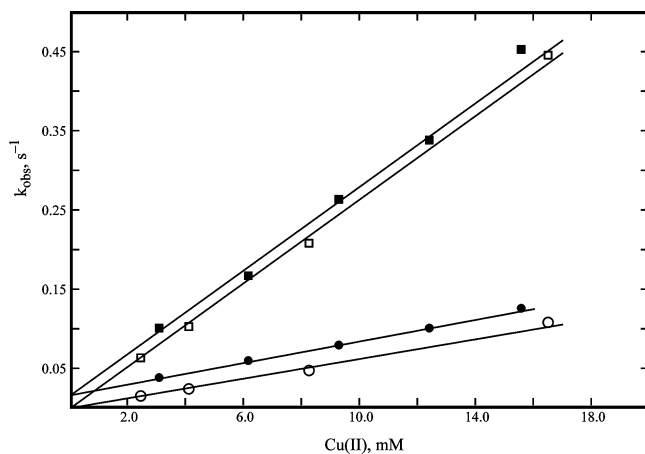
Analogous plots for other runs are given in the Supporting Information. The second-order rate constants (*k*<sub>12</sub>) reported in Table 2 were obtained by least-squares fitting of the pseudo-first-order rate constants (*k*<sub>obs</sub>) to eq 1.

$$k_{\text{obs}} = k_0 + k_{12}[\text{Cu(II)}] \quad (1)$$

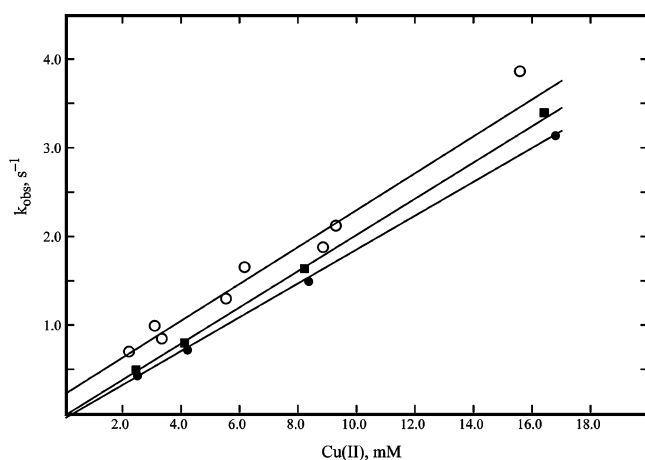
It is important to note that the slopes (*k*<sub>12</sub>) of plots such as those in Figures 1 and 2 are not affected by the addition or

(19) Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

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**Figure 1.** Variation of  $k_{\text{obs}}$  with  $[\text{Cu(II)}]$  for reactions of  $\text{Cu(II)}$  triflate in 80% AN at 25 °C with: Fc, no  $\text{H}^+$  added (●); Fc and 0.202 mM  $\text{HClO}_4$  (○); Dmfc, no  $\text{H}^+$  added (■); Dmfc and 0.202 mM  $\text{HClO}_4$  (□).



**Figure 2.** Variation of  $k_{\text{obs}}$  with  $[\text{Cu(II)}]$  for reactions of  $\text{Cu(II)}$  triflate in 95% AN at 25 °C with Fc: no  $\text{H}^+$  added (○); 0.285 mM  $\text{HClO}_4$  (●); 0.423 mM triflic acid (■).

nature of the acid. This also is true if the acid is varied within a particular set of runs, as can be seen from the results in Table 2 in both 90% and 95% AN.

Although the ionic strength ( $\mu$ ) was not controlled, the values of  $k_{12}$  in 80% AN (see Table 2) suggest that there is no significant difference between 1.2 or 1.8 mM and 8–50 mM  $\mu$ , as might be expected because one of the reactants is uncharged. The values of  $k_{12}$  do change substantially with the solvent composition, increasing by a factor of  $\sim 5 \times 10^2$  between 50% and 97.5% AN. This variation will be the subject of the following discussion.

## Discussion

It will now be shown that the variation of  $k_{12}$  with solvent composition can be reasonably understood in terms of Marcus theory and can be used to estimate the  $\text{Cu(II/I)}$  electron-exchange rate for AN/water solvates. Some structural parameters for these solvates also are discussed with regard to the inner-sphere reorganization energy for such systems.

The theory predicts that  $k_{12}^1$  is given by eq 2,

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (2)$$

where  $k_{11}$  and  $k_{22}$  are the self-exchange rate constants for

the  $\text{Cu(II/I)}$  and  $\text{Fc(+0)}$  or  $\text{Dmfc(+0)}$  systems, and  $K_{12}$  is the equilibrium constant for the redox reaction. The correction factor  $f_{12}$  is given by eq 3,

$$\ln f_{12} = \frac{(\ln K_{12} + (w_{12} - w_{21})/RT)^2}{4 \ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT} \quad (3)$$

where  $Z$  is the collision number ( $\sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ), and the individual work term corrections ( $w_{ij}$ ) at 25 °C are given by eq 4,

$$w_{ij} = \frac{331.7z_i z_j}{\epsilon_s r(1 + r\sqrt{8.50\mu/\epsilon_s})} \quad (4)$$

where  $r$  is the sum of the radii ( $\text{\AA}$ ) of the reaction partners,  $\mu$  is the ionic strength (M), and  $\epsilon_s$  is the dielectric constant of the solvent. The overall work term correction in eq 2 is given by eq 5,

$$W_{12} = \exp\left(\frac{-(w_{12} + w_{21} - w_{11} - w_{22})}{2RT}\right) \quad (5)$$

For the present system, it should be noted that  $w_{12} = w_{22} = 0$  because one of the reaction partners has  $z = 0$ .

To estimate  $k_{11}$ , known or good estimates of  $k_{22}$  and  $K_{12}$  will be used in eq 2, and the correction factors  $f_{12}$  and  $W_{12}$  will be calculated to give a best estimate of  $k_{11}$ . The dominant factor determining the variation of  $k_{12}$  with solvent composition is  $K_{12}$ , and this can be obtained from the electrochemical measurements of Cox and co-workers<sup>10</sup> for the  $\text{Cu(II/I)}$  and  $\text{Fc(+0)}$  couples over the range of solvent compositions used here. The same information is not available for Dmfc, but it is known<sup>22</sup> to have a reduction potential  $\sim 0.10$  V more positive than Fc in acetonitrile, and that the difference in reduction potential for several methyl-substituted ferrocenes is the same in many solvents.<sup>23</sup> Therefore, it will be assumed that a difference of 0.10 V is maintained for the AN/water solutions.

The self-exchange rate constant ( $k_{22}$ ) for  $\text{Fc(+0)}$  in acetonitrile has been the subject of several recent studies; the values of Kirchner et al.<sup>12</sup> ( $k_{22} = 9.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\mu = 0$ ) and McManis et al.<sup>13</sup> ( $k_{22} = 9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\mu = 0.65$  M) are in excellent agreement and show very little ionic strength effect on  $k_{22}$ . Earlier, Yang, Chan, and Wahl<sup>11</sup> reported values of  $5.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  ( $\mu = 0.035$  M) for

(21) The source of the  $k_0$  term has not been exhaustively investigated. It is not due to an impurity introduced with the  $\text{Cu(II)}$ , because then it would be proportional to  $[\text{Cu(II)}]$  and would simply make the rate faster than the true  $\text{Cu(II)}$  oxidation rate. The latter possibility has been checked by showing that a number of different preparations of copper(II) triflate and copper(II) nitrate give the same values for  $k_2$ . Different sources and resublimation of Fc have no effect. The fact that  $k_0$  is suppressed by  $\text{H}^+$  at first seems to suggest proton equilibria of the reactants (protonation of Fc or formation of  $\text{Cu(OH)}^+$ ), but these should be rapidly established equilibria and would not lead to eq 1. Dioxygen is a possible oxidant for Fc, but the reaction is quite slow in aqueous AN. The  $\text{O}_2/\text{Fc}$  reaction would need to be activated by some species in solution whose concentration either does not directly affect the rate or is not proportional to the  $\text{Cu(II)}$  concentration.

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**Table 2.** Kinetic Results for the Reaction of Cu(II) with Ferrocene (Fc) and 1,1'-Dimethylferrocene (Dmfc) in Aqueous Acetonitrile (AN) at 25 °C and Variable Ionic Strength ( $\mu$ )

% AN	[Cu(II)], mM <sup>a</sup> range	[H <sup>+</sup> ], mM <sup>b</sup>	$\mu$ , mM range	$k_{12}$ , M <sup>-1</sup> s <sup>-1</sup> <sup>c</sup>	
				Fc	Dmfc
50	2.19–14.6	0	6.6–44	4.34 ± 0.07	17.1 ± 0.6
50	2.61–17.4 <sup>d</sup>	0	7.8–52	3.95 ± 0.18	15.0 ± 0.4
80	2.48–16.5	0.202	7.6–50	6.14 ± 0.40	26.3 ± 0.9
80	3.09–15.6	0	9.3–47	6.84 ± 0.09	26.4 ± 1.3
80	0.385	0	1.2		28.5 ± 0.5 <sup>e</sup>
80	0.505	0.254	1.8	6.22 ± 0.15	25.6 ± 0.5 <sup>f</sup>
80	2.52–15.0 <sup>d</sup>	0.254	7.8–45	5.63 ± 0.26	21.2 ± 0.4
80	2.85–9.96 <sup>d</sup>	0	8.6–30		24.2 ± 1.4
90	2.51–16.7	0.096 × [Cu(II)]	7.8–52	23.8 ± 1.0	110 ± 3
90	2.34–15.6	0.103 × [Cu(II)]	7.3–48	21.4 ± 2.4	98.4 ± 3
90	2.33–15.7	0.0208 × [Cu(II)]	7.5–50	21.3 ± 1.8	101 ± 2
95	2.21–1.6	0	6.6–47	207 ± 17	
95	2.46–16.4	0.285	7.7–50	203 ± 5	829 ± 33
95	2.52–16.8	0.423 <sup>g</sup>	8.0–51	185 ± 4	872 ± 9
95	2.68–17.9	0.0095 × [Cu(II)] <sup>g</sup>	8.1–54	178 ± 13	794 ± 21
95	2.52–16.8	0.025 × [Cu(II)] <sup>g</sup>	7.6–51	185 ± 3	795 ± 24
95	2.64–19.8	0.071 × [Cu(II)]	8.1–61	195 ± 9	842 ± 19
97.5	2.04–8.15	0.202	6.3–25	1970 ± 50	7780 ± 380
97.5	1.98–7.91	0	5.9–24	1790 ± 70	8070 ± 260

<sup>a</sup> Triflate salt unless otherwise indicated. <sup>b</sup> Perchloric acid unless otherwise indicated. <sup>c</sup> Errors are one standard deviation from fitting  $k_{\text{obs}}$  to eq 1. <sup>d</sup> Nitrate salt. <sup>e</sup> With [Dmfc] = 0.208 mM and analyzed by a second-order rate law. <sup>f</sup> With [Fc] = 0.266 mM and [Dmfc] = 0.297 mM and analyzed by a second-order rate law. <sup>g</sup> Triflic acid.

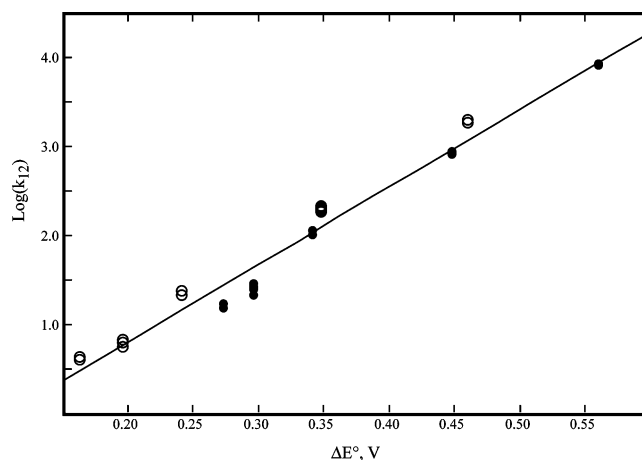
Fc(+/0) and  $8.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  ( $\mu = 0.016 \text{ M}$ ) for Dmfc(+/0). McManis et al. also found that  $k_{22}$  for Fc(+/0) has only a  $\sim 3$ -fold variation in a range of organic solvents. Nelsen et al.<sup>22</sup> have reported quite similar values for Fc(+/0), Dmfc(+/0), and pentamethylferrocene(+/0) in AN. For the present purpose of estimating  $k_{11}$  for Cu(II/I), we will assume that Fc and Dmfc have the same value of  $k_{22} = 9.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and that it is independent of the solvent composition.

It is now possible to determine if Marcus theory will even approximately describe these systems. For this, it is convenient to use the logarithmic form of eq 2 and substitute the usual thermodynamic relationship between  $\log(K_{12})$  and  $\Delta E^\circ$  to obtain eq 6.

$$\log(k_{12}) = 0.5 \log(k_{11}k_{22}) + 8.45\Delta E^\circ + 0.5 \log(f_{12}) + \log(W_{12}) \quad (6)$$

If one assumes, as a first approximation, that the  $f_{12}$  and  $W_{12}$  terms are insignificant, then eq 6 predicts that a plot of  $\log(k_{12})$  versus  $\Delta E^\circ$  should be linear with a slope of 8.45, and with  $k_{22}$  known, the intercept gives an estimate of  $k_{11}$ . Such a plot is shown in Figure 3, and it is linear with a slope of  $8.7 \pm 0.3$ , quite close to the theoretical prediction. The intercept of  $-0.93 \pm 0.09$  gives  $k_{11} \approx 1.4 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ .

The apparent close agreement of the plot in Figure 3 to the theoretical prediction may be somewhat accidental, because the nature of the Cu(II) solvate probably is changing with the solvent composition. The simplest explanation for this agreement would seem to be that the various Cu(II) solvates have similar self-exchange rate constants. In any case, the approximate analysis has been extended to include the  $f_{12}$  and  $W_{12}$  factors. The  $w_{11}$  and  $w_{12}$  were calculated using radii for the Cu(II) and Cu(I) solvates based on crystal structures reported here, and estimates of Murguia and Wherland<sup>24</sup> for Fc<sup>+</sup> and Dmfc<sup>+</sup>; dielectric constants were taken from Venables and Schmuttenmaer.<sup>25</sup> The results are summarized in Table 3.



**Figure 3.** Variation of  $\text{Log}(k_{12})$  with DE for the reaction of Cu(II) in aqueous acetonitrile (50–97.5%) with Fc (○) and Dmfc (●).

Ideally, the values of  $k_{11}$  from Fc and Dmfc should be the same, and they do agree to within a factor of  $< 3$ ; this difference could be removed by decreasing the  $E^\circ$  for Dmfc by only 0.015 V. There does seem to be a persistent increase in  $k_{11}$  with increasing % AN which might be attributed to replacement of coordinated  $\text{H}_2\text{O}$  by AN on Cu(II) and/or Cu(I), but the differences are within the uncertainties usually ascribed to the theory. Overall, the  $k_{11}$  values have a range of  $(1.1\text{--}17) \times 10^{-9}$ , with an average of  $5 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ .

The correlation in Figure 3 can be used to estimate that  $k_{12} \approx 4.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of Cu(II) with Fc in 100% AN ( $\Delta E^\circ = 0.646 \text{ V}$ ).<sup>10</sup> This value can be used to estimate that  $k_{11} \approx 4 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$  in 100% AN. The value of  $\geq 0.3 \text{ M}^{-1} \text{ s}^{-1}$  in AN determined by Manahan<sup>9</sup> seems to have been affected by separation-induced exchange. For

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**Table 3.** Summary of Kinetic and Thermodynamic Data for the Reactions of Cu(II) with Ferrocene (Fc) and 1,1'-Dimethylferrocene (Dmfc) in Aqueous Acetonitrile (AN)

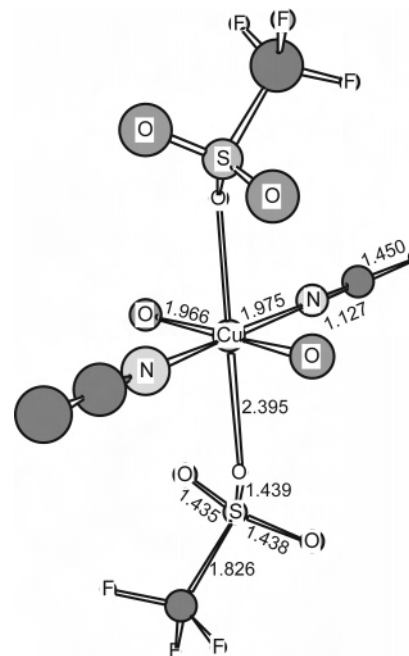
% AN	$k_{12}, \text{M}^{-1} \text{s}^{-1}$		$\Delta E^\circ, \text{V}$		$\log(K_{12})$		$\log(f_{12})^d$		$10^9 \times k_{11}, \text{M}^{-1} \text{s}^{-1}$	
	Fc <sup>a</sup>	Dmfc <sup>a</sup>	Fc <sup>b</sup>	Dmfc <sup>c</sup>	Fc	Dmfc	Fc	Dmfc	Fc <sup>e</sup>	Dmfc <sup>e</sup>
50	4.15	16.1	0.164	0.264	2.77	4.46	-0.068	-0.19	2.7	1.1
80	6.21	25.4	0.197	0.297	3.33	5.02	-0.10	-0.24	1.7	0.76
90	22.2	103	0.242	0.342	4.09	5.78	-0.15	-0.32	4.1	2.5
95	194	826	0.348	0.448	5.88	7.57	-0.34	-0.57	7.7	4.6
97.5	1880	7930	0.460	0.560	7.78	9.47	-0.62	-0.93	17	12

<sup>a</sup> Values are averages of those in Table 2 for each % AN. <sup>b</sup> Values from ref 10 at 25 °C in 0.10 M NaClO<sub>4</sub>; the value at 97.5% AN has been obtained by interpolation. <sup>c</sup> Values assume a 0.10 V difference from Fc, based on ref 20. <sup>d</sup> Calculated including  $w_{11}$  and  $w_{21}$  at  $\mu = 0.03 \text{ M}$  with radii of 6.00, 6.02, 3.75, and 4.25 Å for Cu(AN)<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub><sup>2+</sup>, Cu(AN)<sub>m</sub>(OH<sub>2</sub>)<sub>n</sub><sup>+</sup>, Fc<sup>+</sup>, and Dmfc<sup>+</sup>, respectively, and dielectric constants from ref 25. <sup>e</sup> Calculated including the log( $W_{12}$ ) term, although it is small and relatively constant, varying from 0.064 to 0.088 for Fc, and 0.073 to 0.10 for Dmfc.

attainable conditions with triflate salts of [Cu(II)] = [Cu(I)] = 0.1 M, the estimated value of  $k_{11}$  predicts a half-time for exchange of nearly 8 years, and it seems unlikely that anyone will have the patience to directly measure the Cu(II/I) self-exchange rate in acetonitrile.

There have been many studies of the Cu(II/I) electron exchange in various types of multidentate ligand complexes, as reviewed recently by Rorabacher.<sup>2</sup> For these systems,  $k_{11}$  ranges widely between  $2 \times 10^{-2}$  and  $8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , but none are nearly as small as the solvated aqueous and AN systems. It was originally suggested by Vallee and Williams<sup>26</sup> that Cu(II/I) electron exchange normally should be slow because of the much different coordination geometries of the two oxidation states, tetragonally distorted octahedral for Cu(II) and tetrahedral for Cu(I). A significant amount of the work on model systems has been devoted to designing ligands that would constrain the two oxidation states to have similar geometries and therefore faster electron exchange rates. It is somewhat ironic that some systems that seem to most nearly meet this goal have the smallest  $k_{11}$  values,<sup>27,28</sup> and the largest  $k_{11}$  is for a system in which the geometries are much different.<sup>29</sup>

Notwithstanding the difficulties encountered in structure–rate correlations for Cu(II/I) electron exchange, the structures of several species relevant to the present study have been determined. The structure of the triflate salt of Cu(AN)<sub>4</sub><sup>+</sup> (**III**) is generally similar to the previously determined structures of the perchlorate,<sup>30</sup> hexafluorophosphate,<sup>31</sup> and tetrafluoroborate<sup>32</sup> salts. All have three independent Cu–(AN)<sub>4</sub><sup>+</sup> ions showing somewhat different degrees of distortion from a tetrahedral arrangement of the AN ligands. In the triflate salt, the N–Cu–N angles range from 102.0° to 116.3° but average to the ideal tetrahedral angle of 109.4°. The Cu–NCCH<sub>3</sub> bond lengths range from 1.980 to 2.022 Å with an average of 2.002 Å, which is close to the average of 1.996 Å from the structures of the other salts mentioned

**Figure 4.** Perspective drawing based on the X-ray crystal structure of the trifluoromethanesulfonate salt of [Cu(OH<sub>2</sub>)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> (**IV**).

above. The AN in **III** is typically not linearly coordinated, with Cu–N–C angles ranging from 170.1° to 179.1° and averaging 173.8°. Full details are given in the Supporting Information.

The structures of the Cu(II) species, **IV** and **V**, provide bond lengths that are helpful in assessing the inner-sphere ligand reorganization involved in the electron-exchange process. In **IV**, one obtains Cu–NCCH<sub>3</sub> and Cu–OH<sub>2</sub> bond lengths in the same ion, and both **IV** and **V** provide Cu–N bond lengths for comparison to Cu(AN)<sub>4</sub><sup>+</sup> (**III**). The perspective views and bond lengths of the structures of **IV** and **V** are shown in Figures 4 and 5, respectively.

In both structures, the bond angles at Cu are within 90 ± 2°, and the average Cu–O bond length to triflate in **V** (2.391 Å) is similar to that in **IV** (2.395 Å). In **IV**, the AN is close to linearly coordinated with Cu–N–C angles of 175.8°, but in **V**, this angle varies between 161.9° and 177.0°, with an average of 170.0°. In **IV**, the Cu–OH<sub>2</sub> bond length (1.966 Å) is slightly shorter than the Cu–N bond length (1.975 Å), and in **V**, the latter is slightly longer with an average of 1.989 Å. Full details are given in the Supporting Information.

The Cu(II)–NCCH<sub>3</sub> bond lengths are similar to those reported by Torrelli et al.<sup>33</sup> for two dimeric Cu(II) complexes

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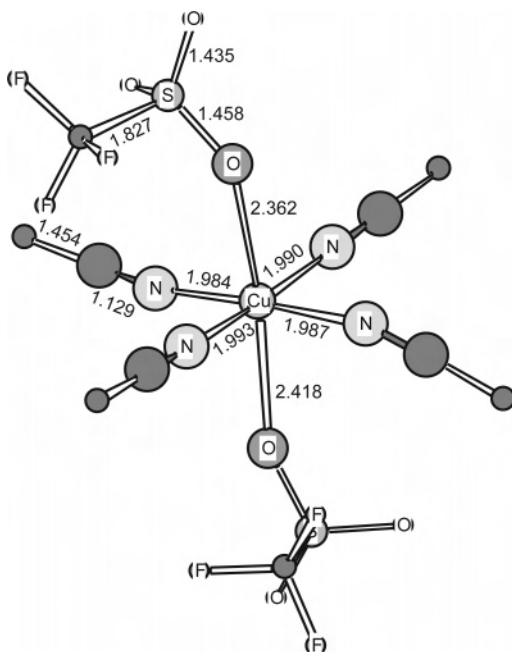
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**Figure 5.** Perspective drawing based on the X-ray crystal structure of the trifluoromethanesulfonate salt of  $[\text{Cu}(\text{NCCH}_3)_4]^{2+}$  (**V**).

in which the average equatorial Cu–NCCH<sub>3</sub> distance is 2.00 Å. There is longer distance of 2.355 Å to an axial NCCH<sub>3</sub>. The Cu–N–C angle for the latter is 159.0°, while it ranges between 164.3° and 175.3° for the equatorial NCCH<sub>3</sub> ligands. These systems contain both 5- and 6-coordinate Cu(II), and the other equatorial ligands are N-donors (pyridine, tertiary amine), while the axial ligands are O-donors (phenol, THF, perchlorate). It appears that the equatorial Cu(II)–NCCH<sub>3</sub> bond length is not very sensitive to the other donor types.

The relatively strong complexation of Cu(I) by AN in water,<sup>15</sup> and the stability of Cu(I) in pure acetonitrile, suggest

$\pi$ -back-bonding in the system. However, the C–N bond lengths in Cu(I)–AN complexes show no evidence of lengthening. In various  $\text{Cu}(\text{AN})_4^+$  salts, the average C–N bond length is 1.13 Å, and the same is found for  $[\text{Cu}(\text{AN})_2]\text{B}(\text{C}_6\text{F}_5)_4$ .<sup>34</sup> In the Cu(II) complexes, **IV** and **V**, where no  $\pi$ -back-bonding is expected, the average length is 1.129 Å.

With regard to the Cu(II/I) electron self-exchange kinetics, the theory suggests that one important consideration is the change in Cu–N bond length between the two oxidation states. The structures determined here indicate that this change will be  $\sim 0.02$  Å (1.98 (Cu(II)) vs 2.00 (Cu(I))), so that simple bond stretching and compression should not be important factors in making this exchange so slow in AN, and probably also in water. The model system studies described above, and the ease of tetrahedral–octahedral isomerization of Ni(II) complexes,<sup>35</sup> also suggest that coordination geometry differences between Cu(I) and Cu(II) may not be the controlling factors. Perhaps symmetry differences in the model systems affect electronic factors, which make electron exchange in the models so much faster and seemingly unrelated to the ligand geometry.

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**Supporting Information Available:** X-ray crystallographic details of the three compounds in CIF format, densities, mole fractions and molarities of solvent mixtures, electronic spectra (molar extinction coefficients), and dependence of  $k_{\text{obs}}$  on  $[\text{Cu}(\text{II})]$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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