

methanol around the equatorial, pyridine ligands, but the reverse occurs at the axial oxo ligands. Should H-bonding at the oxo ligands facilitate equatorial ligand loss as it does oxo exchange in  $trans\text{-}[\text{O}_2(\text{en})_2\text{Re}]^{+2}$ , then ligand replacement by DMF would be favored over a given range of  $X_{\text{MeOH}}$ .

In conclusion, (1) complexes of the type  $trans\text{-}[\text{O}_2(\text{Py})_4\text{Tc}]^+$  tend to undergo substitution via dissociative mechanisms, which may be strongly solvent mediated, (2) in aqueous solvents, in which these complexes rapidly form an intractable  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  complex, the leaving ligand must be present to stabilize the complex, and (3) specific solvation effects can significantly alter substitution rates in mixed solvents. Finally, while the effects exerted by minor alkyl substitutions on the pyridine ring may produce only a factor of 2-3 difference in the substitution rates, synthetic technetium reactions frequently proceed through several steps with side reactions often present. Small effects in individual steps or in siphoning off product into other reactions can be multiplied

through successive intermediates, resulting in the large differences in yields noted in some reactions.

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**Registry No.** Apy, 504-24-5; DMApy, 1122-58-3;  $[(n\text{-Bu})_4\text{N}][\text{TcOCl}_4]$ , 71341-65-6;  $trans\text{-}[\text{O}(\text{OCH}_3)(\text{py})_2\text{Cl}_2\text{Tc}]$ , 120610-32-4;  $trans\text{-}[\text{O}(\text{OCH}_3)(\text{pic})_2\text{Cl}_2\text{Tc}]$ , 120610-33-5;  $trans\text{-}[\text{O}(\text{OCH}_3)(\text{lut})_2\text{Cl}_2\text{Tc}]$ , 120610-34-6;  $trans\text{-}[\text{O}_2(\text{py})_4\text{Tc}]\text{Cl}$ , 93383-85-8;  $trans\text{-}[\text{O}_2(\text{pic})_4\text{Tc}]\text{Cl}$ , 93383-86-9;  $trans\text{-}[\text{O}_2(\text{lut})_4\text{Tc}]\text{Cl}$ , 93383-87-0;  $trans\text{-}[\text{O}_2(\text{Apy})_4\text{Tc}]\text{Cl}$ , 120610-35-7; ethylenediamine, 107-15-3; imidazole, 288-32-4; cyanide, 57-12-5; cyclam, 295-37-4.

**Supplementary Material Available:** A plot of  $k_{\text{obs}}$  versus mole fraction of methanol in toluene for the substitution reaction of Apy onto  $trans\text{-}[\text{O}_2(\text{Py})_4\text{Tc}]^+$  and an analogous plot but with methanol added in a 50% methanol/DMF mixture, a plot of  $1/k_{\text{obs}}$  versus  $[\text{Py}]$  for the substitution of Apy onto  $trans\text{-}[\text{O}_2(\text{Py})_4\text{Tc}]^+$ , a plot of  $1/k_{\text{obs}}$  versus  $[\text{Apy}]$  for the substitution of Apy onto  $trans\text{-}[\text{O}_2(\text{Py})_4\text{Tc}]^+$ , Eyring plots for activation parameters in Table II, listings of data for all graphs, derivations of rate equations, and the kinetic simulation program (34 pages). Ordering information is given on any current masthead page.

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## Kinetics of the Bis(2,9-dimethyl-1,10-phenanthroline)copper(I/II) Self-Exchange Reaction in Solution

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The rate of the  $\text{Cu}(\text{dmp})_2^{+2}$  electron-transfer reaction has been measured by <sup>1</sup>H NMR spectroscopy in the perdeuterated solvents water (with the chloride salts), acetonitrile, and acetone (with the  $\text{CF}_3\text{SO}_3^-$  salts). The respective kinetic parameters  $k_{\text{ex}}^{298}/\text{kg mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger/\text{kJ mol}^{-1}$ , and  $\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$ , at ionic strength  $I/\text{mol kg}^{-1}$ , are as follows: for  $\text{D}_2\text{O}$ ,  $2.0 \times 10^3$ , 24, and -63, at 0.002; for  $\text{CD}_3\text{CN}$ ,  $4.9 \times 10^3$ , 29.6, and -75, at 0.1; for  $(\text{CD}_3)_2\text{CO}$ ,  $3.0 \times 10^3$ , 29.2, and -80, at 0.1. For acetonitrile and acetone, respectively, variable-pressure studies gave  $\Delta V^\ddagger = -3.4$  and  $-7.8 \text{ cm}^3 \text{ mol}^{-1}$ . No significant concentration dependencies of these parameters were observed. With these data, the measured rate of the oxidation of  $\text{Ru}^{\text{II}}(\text{CF}_3\text{COCHCOCF}_3)_3^-$  by  $\text{Cu}(\text{dmp})_2^{2+}$  in  $\text{CH}_3\text{CN}$  can be satisfactorily accounted for, by using the Marcus cross relation. There is evidence that the  $\text{Cu}^{\text{II}}$  complex contains coordinated solvent in solution; with this qualification, the characteristics of the electron-transfer reactions conform to the Marcus outer-sphere adiabatic model.

### Introduction

Copper(I/II) couples are important in many biological redox systems<sup>1-3</sup> and in other contexts, and their self-exchange rates have been estimated from the Marcus cross relationship for a variety of ligand environments.<sup>4-13</sup> Kinetic data for redox reactions of simple copper complexes are relatively sparse, partly because of limitations imposed by the poor water solubility of many copper(I) species and their tendency to disproportionate,<sup>14</sup> but also because the coordination numbers, bond lengths, and stereochemistry of the two oxidation states are often very different, resulting in severe retardation of outer-sphere electron transfer through the large internal rearrangement contribution  $\Delta G_{\text{IR}}^*$  to the free energy of activation.<sup>15</sup>

The Marcus cross relationship, however, often gives discordant values of the self-exchange rate constant  $k_{\text{ex}}$  for a given pair of copper(I/II) complexes when different redox partners are used<sup>6,8,10-13</sup> or when  $k_{\text{ex}}$  values obtained from oxidation reactions are compared with those from the corresponding reductions.<sup>4,9</sup> It could be that, in these cases, the mechanism of reaction is inner sphere<sup>14</sup> or outer sphere but multistep.<sup>4</sup> Whatever the reason, there is a clear need for direct experimental determination of  $k_{\text{ex}}$  for some typical copper(I/II) couples.

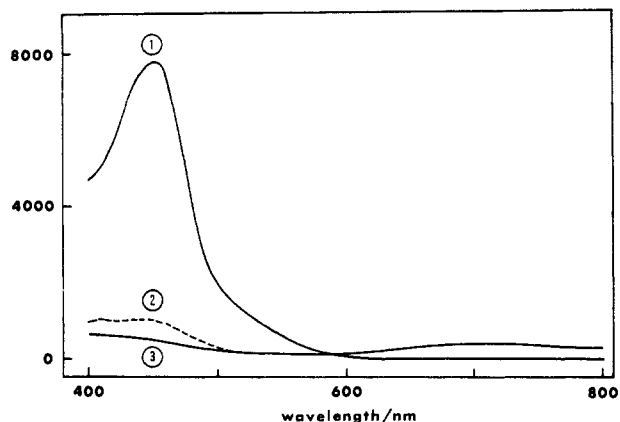
To date, direct measurements of  $k_{\text{ex}}$  for copper(I/II) couples have been reported only for (i)  $\text{Cu}^{\text{I}}\text{Cl}_x/\text{Cu}^{\text{II}}\text{Cl}_y$  in concentrated

aqueous HCl,<sup>16</sup> which probably proceeds by an inner-sphere mechanism<sup>14</sup> and may not be pertinent to copper(I/II) reactions generally, most of which are thought to be outer-sphere processes, (ii)  $\text{Cu}(\text{TAAB})^{+2}$  in methanol-*d*<sub>4</sub>, where TAAB is the rather rigid quadridentate macrocycle tetrabenzotetraazacyclo-

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**Figure 1.** Absorption spectra of  $[\text{Cu}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_n$  in acetonitrile: (1)  $\text{Cu}(\text{dmp})_2^+$ , before and after electrochemical redox cycle; (2) solution of solid preparation of anhydrous  $[\text{Cu}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_2$ , without electrochemical treatment; (3)  $\text{Cu}(\text{dmp})_2^{2+}$ , after full electrochemical oxidation. Spectra 1 and 3 are reproducible through several electrochemical cycles.

hexadecine,<sup>17</sup> (iii) pentacoordinate  $\text{Cu}(\text{py})_2(\text{DAP})^{+/2+}$  in acetonitrile-*d*<sub>3</sub>, where py is pyridine and DAP is a terdentate ligand that coordinates through three pyridyl functions<sup>5</sup> and (iv)  $\text{Cu}(\text{phen})_2^{+/2+}$  (phen = 1,10-phenanthroline) in aqueous chloride media.<sup>18</sup> The first three studies used NMR line broadening, whereas the fourth used electrochemical methods and gave only an approximate value for  $k_{\text{ex}}$ .

We report here a proton NMR study of the kinetics of the  $\text{Cu}(\text{dmp})_2^{+/2+}$  self-exchange reaction (dmp = 2,9-dimethyl-1,10-phenanthroline, "neocuproine") in water, acetonitrile, and acetone, these being apparently the only common solvents in which the copper(I) complex salts were sufficiently soluble for NMR work (this was marginal in water) and the copper(II) compounds did not undergo spontaneous reduction before completion of the experiment. The  $\text{Cu}(\text{dmp})_2^{+/2+}$  couple was chosen because steric hindrance by the 2,9-methyl groups can be expected to enforce maintenance of the approximately tetrahedral disposition of the dmp ligands in  $\text{Cu}(\text{dmp})_2^{+/19}$  when it is oxidized, so that  $\Delta G_{\text{IR}}^*$  should be minimized and redox reactions involving this couple should be relatively rapid—as is indeed the case,<sup>6,8-12,20</sup> although it has been pointed out<sup>8,9,21</sup> that the copper(II) complex may be pentacoordinate in aqueous solution at least. We also report measurements of the kinetics of the oxidation of  $\text{Ru}(\text{hfac})_3^-$  (hfac<sup>-</sup> = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) by  $\text{Cu}(\text{dmp})_2^{2+}$  in acetonitrile, made as a test of the applicability of the Marcus cross relation in this solvent. These studies complement the extensive work of McMillin on the photochemistry and photophysics of  $\text{Cu}(\text{dmp})_2^+$ .<sup>22-24</sup>

### Experimental Section

**Materials.** Orange  $[\text{Cu}(\text{dmp})_2]\text{CF}_3\text{SO}_3$ , which was prepared by a straightforward adaptation of literature methods<sup>20,25</sup> for the perchlorate salt, gave good microanalyses (Galbraith Laboratories) for C, H, N, and F, and its UV-visible spectrum in solution in acetonitrile (Figure 1) was in close agreement with spectra reported for other  $\text{Cu}(\text{dmp})_2^+$  salts of noncomplexing anions.<sup>8,20,22-24</sup>

Like its perchlorate analogue,<sup>20</sup>  $[\text{Cu}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_2$  is hygroscopic and difficult to prepare completely free of the copper(I) complex. Copper(II) trifluoromethanesulfonate was first made by adding  $\text{CF}_3\text{SO}_3\text{H}$  to a concentrated solution of  $\text{CuCl}_2$  in water until no more HCl was evolved, boiling the mixture until the greenish color disappeared and  $\text{Cl}^-$  was undetectable, and then cooling and filtering the suspension. The light blue crystals of the product were washed with ether and dried in vacuo. About 0.5 g of this material was dissolved in 200 mL of water, 0.5 g of dmp was added, and the suspension was agitated vigorously for 1 h. To the light green filtered solution was added an excess of solid  $\text{CF}_3\text{SO}_3\text{K}$ , and the resulting green precipitate was filtered and washed with ice-cold water. The solid became pale brown after drying in vacuo at 50 °C; the color change probably reflected the loss of a coordinated water molecule.<sup>8,9,21</sup> Microanalyses were close to those expected for  $[\text{Cu}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_2$  but suggested some minor contamination, probably with the very poorly soluble salt of the copper(I) complex, which forms slowly in aqueous solutions of  $\text{Cu}(\text{dmp})_2^{2+}$ .<sup>25</sup> Anal. Calcd: C, 46.3; H, 3.11; N, 7.20. Found: C, 47.4; H, 3.19; N, 7.11. The UV-visible spectrum of the product in  $\text{CH}_3\text{CN}$  (Figure 1) is similar to those reported by James et al.<sup>26</sup> for  $\text{Cu}(\text{dmp})_2^{2+}$  and by McMillin and co-workers<sup>23</sup> for the photooxidation product of  $\text{Cu}(\text{dmp})_2^+$  in dichloromethane.

It would appear, however, that the spectrum published by James et al.<sup>26</sup> is of a sample of  $\text{Cu}(\text{dmp})_2^{2+}$  that contained a few percent of  $\text{Cu}(\text{dmp})_2^+$ . A cyclic voltammogram of a solution of our preparation of  $[\text{Cu}(\text{dmp})_2]\text{CF}_3\text{SO}_3$  in acetonitrile with  $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$  as supporting electrolyte gave a half-wave potential of 680 mV vs a saturated calomel electrode, and the observed wave was highly reversible (scanning rate 100 mV s<sup>-1</sup>). A spectrum (also shown in Figure 1) was therefore obtained of a solution of  $[\text{Cu}(\text{dmp})_2]\text{CF}_3\text{SO}_3$  with  $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$  in acetonitrile in an electrochemical cell with quartz windows in which the potential was varied from 400 to 850 mV vs SCE and back, several times; oxidation was complete at 850 mV, as judged by the current, and the spectra of the reduced and oxidized forms were fully reproducible. However, the molar absorbance of the oxidized complex at 454 nm (where  $\text{Cu}(\text{dmp})_2^+$  has an absorption maximum,  $\epsilon = 7800 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) was lower than for the solution of the solid  $[\text{Cu}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_2$  (530 vs 945  $\text{L mol}^{-1} \text{ cm}^{-1}$ , respectively; James et al.<sup>26</sup> reported 1250  $\text{L mol}^{-1} \text{ cm}^{-1}$  at 460–470 nm for their  $\text{Cu}^{\text{II}}$  complex). The excellent reversibility of the redox cycle indicated that the electrochemically produced spectrum of  $\text{Cu}(\text{dmp})_2^{2+}$  is definitive and that the solid  $[\text{Cu}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_2$  sample contained about 5.7% unoxidized copper(I) complex. Attempts to purify the solid copper(II) complex further were unsuccessful; where it was used for kinetic experiments, an appropriate correction was applied in calculating concentrations.

$\text{Cu}(\text{dmp})_2\text{Cl}\cdot\text{H}_2\text{O}$  was made by the method of Hall et al.;<sup>25</sup> the water molecule was not removed by desiccation. The oxidized chloride,  $\text{Cu}(\text{dmp})_2\text{Cl}_2$ , remained green in the solid phase even after desiccation, suggesting that a chloride ion is coordinated to the  $\text{Cu}^{\text{II}}$  center.

**NMR Measurements.** The 2D COSY <sup>1</sup>H NMR spectrum of  $[\text{Cu}(\text{dmp})_2]\text{CF}_3\text{SO}_3$  in  $\text{CD}_3\text{CN}$ , obtained at 200 MHz on a Bruker AC-E 200 spectrometer, showed that negligible coupling exists between the 2,9-methyl protons ( $\delta = 2.4 \text{ ppm}$  vs TMS) and the 5,6-protons ( $\delta = 8.1 \text{ ppm}$ ) or 3,4,7,8-protons (strongly coupled amongst themselves,  $\delta = 7.8$  and 8.7 ppm). Line broadening of the 2,9-methyl proton resonances was therefore used to follow the copper(I/II) self-exchange kinetics. Overlap of the 2,9-methyl proton resonances with those of the methyl groups of acetonitrile and acetone, however, necessitated the use of  $\text{CD}_3\text{CN}$  (MSD Isotope) and  $(\text{CD}_3)_2\text{CO}$  (Sigma Chemical Corp.) of high (>99.96 atom % <sup>2</sup>H) isotopic purity as solvents for the NMR studies.

Dynamic NMR measurements on  $\text{CD}_3\text{CN}$  and  $(\text{CD}_3)_2\text{CO}$  solutions were made at 90 MHz with a Bruker WH-90 spectrometer and on  $\text{D}_2\text{O}$  solutions at 400 MHz with a Bruker AM-400 instrument. Variable-pressure measurements were carried out with the pressurizable probehead for the Bruker WH-90 instrument as described elsewhere.<sup>27</sup> The pressurizing fluid was perfluorohexane. Temperature readings were calibrated against the temperature dependence of the proton chemical shifts of ethylene glycol. The self-exchange rate was found to lie in the slow-exchange region, so the ratio  $[\text{Cu}^{\text{II}}]/[\text{Cu}^{\text{total}}]$  was always made <0.1. There was no observable change in the chemical shift of the 2,9-methyl protons in the presence of the copper(II) complex. Rate constants  $k_{\text{ex}}$  were extracted in the usual way<sup>28</sup> from the  $\text{Cu}^{\text{II}}$ -induced change in the 2,9-methyl <sup>1</sup>H line width of the  $\text{Cu}^{\text{I}}$  complex, measured by Lorentzian curve fitting; in  $\text{CD}_3\text{CN}$  in the absence of  $\text{Cu}^{\text{II}}$ , this line width was 1.0–1.5 Hz and was independent of temperature from -30 to +50 °C. For  $\text{CD}_3\text{CN}$  and  $(\text{CD}_3)_2\text{CO}$  as solvents, the  $\text{CF}_3\text{SO}_3^-$  salts were used, as the solubility of the  $\text{Cu}^{\text{I}}$  complex (which is very stable with respect to

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**Table I.** Temperature Dependence of  $k_{ex}$  for  $\text{Cu}(\text{dmp})_2^{+/2+}$  in  $\text{D}_2\text{O}^a$ 

$[\text{Cu}^I]/$ $\text{mmol kg}^{-1}$	$[\text{Cu}^{II}]/$ $\text{mmol kg}^{-1}$	$I/$ $\text{mmol kg}^{-1}$	temp/ $^\circ\text{C}$	$k_{ex}/10^5$ $\text{kg mol}^{-1} \text{s}^{-1}$
1.59	0.227	2.27	29.1	2.0
			36.3	2.5
			41.8	2.9
			47.8	3.4
0.695	0.0098	0.72	29.1	1.9
			36.3	3.0
			41.8	3.8
			49.1	4.3
			24.9	2.3
1.55	0.213	2.19	34.3	3.2
			43.8	4.8
			40.8	3.7
			34.3	2.7
			26.9	2.2

<sup>a</sup>The anion is chloride.

oxidation in these solvents) exceeded 0.1 mol  $\text{kg}^{-1}$  and the  $\text{Cu}^{II}$  complex was not significantly reduced on the time scale of the NMR experiments.

For water ( $\text{D}_2\text{O}$ , 99.8 atom %  $^2\text{H}$ ; Aldrich) as solvent, however,  $[\text{Cu}(\text{dmp})_2]\text{CF}_3\text{SO}_3$  was very poorly soluble, and the chloride salt had to be used. Even so, the total Cu concentration was limited to less than 2 mmol  $\text{kg}^{-1}$ , and some 10% of the total Cu was found to be present as  $\text{Cu}(\text{dmp})_2^{2+}$  in aqueous solutions of  $[\text{Cu}(\text{dmp})_2]\text{Cl}$ ; thus, it was unnecessary to add further  $\text{Cu}^{II}$  for the line-broadening experiments so long as the  $[\text{Cu}^{II}]/[\text{Cu}_{\text{total}}]$  ratio and the  $\text{Cu}^{II}$ -free line width of the 2,9-methyl protons in  $\text{Cu}(\text{dmp})_2^+$  could be measured. The fraction of  $\text{Cu}^{II}$  was obtained by measuring the concentration of  $\text{Cu}(\text{dmp})_2^+$  spectrophotometrically before and after reduction of  $\text{Cu}^{II}$  with hydroxylammonium sulfate (cf. Figure 1). The 2,9-methyl proton line width of the  $\text{Cu}^{II}$ -free  $\text{Cu}^I$  complex (ca. 2 Hz) was obtained from 400-MHz NMR spectra of solutions of  $[\text{Cu}(\text{dmp})_2]\text{Cl}$  (1 mmol  $\text{kg}^{-1}$ ) in  $\text{D}_2\text{O}$  containing an equimolar amount of hydroxylammonium sulfate to reduce all traces of  $\text{Cu}^{II}$ . It was not possible to obtain meaningful line-broadening data for the very dilute aqueous solutions in the pressurizable probehead, which has relatively low sensitivity and operates on the Bruker WH-90 instrument only.

The foregoing kinetic analysis presupposes that the dmp ligands of  $\text{Cu}(\text{dmp})_2^+$  and  $\text{Cu}(\text{dmp})_2^{2+}$  are not significantly dissociated in solution and do not exchange rapidly (on the NMR time scale) with any free dmp that may be present. To address these points, it was shown that the addition of up to 2/1 molar excess of free dmp over  $\text{Cu}^I$  had no effect on the optical or  $^1\text{H}$  NMR spectra of  $\text{Cu}(\text{dmp})_2^+$  (up to 0.2 mmol  $\text{kg}^{-1}$ ) in  $\text{CD}_3\text{CN}$ ,  $(\text{CD}_3)_2\text{CO}$ , or  $\text{D}_2\text{O}$ ; separate resonances due to protons in bound and free dmp were observed, and no significant changes due to the presence of free dmp could be detected in either the line widths or chemical shifts of the 2,9-methyl protons or 3,4,7,8- or 5,6-protons. More importantly, the rates of electron transfer as measured above were unaffected, within the experimental uncertainty of ca. 5%, by the introduction of free dmp in concentrations up to equimolar with the total  $[\text{Cu}]$ . Thus, the reaction kinetics reported here are unaffected by dmp loss or exchange from either  $\text{Cu}(\text{dmp})_2^+$  or  $\text{Cu}(\text{dmp})_2^{2+}$ .

**Stopped-Flow Kinetics.** The rate of oxidation of  $(n\text{-C}_4\text{H}_9)_4\text{N}[\text{Ru}^{II}(\text{hfac})_3]^{2-}$  by  $\text{Cu}(\text{dmp})_2^{2+}$  in HPLC-grade  $\text{CH}_3\text{CN}$  was measured by following the disappearance of the absorption band of the  $\text{Ru}^{II}$  complex at 530 nm on a Hi-Tech Model SF-51 stopped-flow spectrophotometer. The products were shown spectrophotometrically to be  $\text{Ru}(\text{hfac})_3^0$  and  $\text{Cu}(\text{dmp})_2^+$ .

## Results

The kinetic data for the self-exchange reaction are summarized in Tables I–III, in which  $I$  is the ionic strength and the uncertainties cited are standard deviations. Full details of the measurements in acetonitrile and acetone, in which  $k_{ex}$  was reproducible to  $\pm 6\%$  or better, are given in the supplementary material. The data for aqueous solutions were limited in quantity and accuracy by redox instability and solubility and are given in full in Table I.

**Self-Exchange in Water.** Solubility and redox limitations in aqueous solutions confined the kinetically useful measurements to the temperature range 298–322 K. Despite the limited precision of the data of Table I, it can be seen that  $k_{ex}$  is quite reproducible and is not significantly dependent on concentration or on the history of the solution. One can therefore be confident that the derived quantity  $k_{ex}$  does genuinely represent the self-exchange rate of  $\text{Cu}(\text{dmp})_2^{+/2+}$ . The data can be represented adequately

**Table II.** Temperature and Ionic Strength Dependence of the Self-Exchange Kinetics of  $\text{Cu}(\text{dmp})_2^{+/2+}$  in Acetonitrile and Acetone<sup>a</sup>

solvent	$I/$ $\text{mol kg}^{-1}$	temp/ $^\circ\text{C}$	$\Delta H^*/$ $\text{kJ mol}^{-1}$	$\Delta S^*/$ $\text{J K}^{-1} \text{mol}^{-1}$	$k_{ex}^{298} / 10^3$ $\text{kg mol}^{-1} \text{s}^{-1}$
$\text{CD}_3\text{CN}$	0.068	7–44	$31.1 \pm 1.5$	$-70 \pm 5$	5.1
	0.099	7–48	$27.9 \pm 1.0$	$-81 \pm 4$	5.0
	0.145	3–44	$28.8 \pm 1.9$	$-78 \pm 6$	4.7
$(\text{CD}_3)_2\text{CO}$	0.424 <sup>c</sup>	5–48	$30.5 \pm 1.0$	$-73 \pm 3$	4.5
	0.049	3–35	$27.3 \pm 0.9$	$-87 \pm 3$	3.0
	0.067	9–43	$26.6 \pm 1.4$	$-89 \pm 5$	3.1
	0.130	5–54	$30.3 \pm 0.6$	$-76 \pm 2$	3.3
	0.139	14–48	$29.9 \pm 1.1$	$-78 \pm 4$	3.1

<sup>a</sup>The anion is  $\text{CF}_3\text{SO}_3^-$ . <sup>b</sup>Interpolated. <sup>c</sup>Includes 0.302 mol  $\text{kg}^{-1}$   $\text{CF}_3\text{SO}_3\text{K}$ .

**Table III.** Pressure Effect on the  $\text{Cu}(\text{dmp})_2^{+/2+}$  Exchange Kinetics in Acetonitrile and Acetone<sup>a</sup>

solvent	temp/ $^\circ\text{C}$	pressure/ $\text{MPa}$	$I/$ $\text{mol kg}^{-1}$	$k_{ex}(P \rightarrow 0)/$ $10^3 \text{kg mol}^{-1} \text{s}^{-1}$	$\Delta V^*/$ $\text{cm}^3 \text{mol}^{-1}$
$\text{CD}_3\text{CN}$	38.4	0.1–202	0.094	8.0	$-3.3 \pm 0.7$
		0.1–200	0.059	8.6	$-3.5 \pm 0.6$
$(\text{CD}_3)_2\text{CO}$	29.5	0.1–184	0.121	4.1	$-7.8 \pm 0.6$
		0.1–190	0.108	4.4	$-7.0 \pm 1.1$

<sup>a</sup>The anion is  $\text{CF}_3\text{SO}_3^-$ .

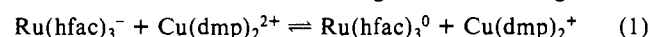
by the activation parameters  $\Delta H^* = 24 \pm 3 \text{ kJ mol}^{-1}$ ,  $\Delta S^* = -63 \pm 10 \text{ J K}^{-1} \text{mol}^{-1}$ , and  $k_{ex}^{298} = (2.0 \pm 0.2) \times 10^5 \text{ kg mol}^{-1} \text{s}^{-1}$ .

**Self-Exchange in Acetonitrile.** Table II shows that the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange is about 40 times slower at 25  $^\circ\text{C}$  in acetonitrile with  $\text{CF}_3\text{SO}_3^-$  as the anion than in water with chloride. A very slight *inverse* dependence of  $k_{ex}$  on  $I$  or  $[\text{CF}_3\text{SO}_3^-]$  is discernible, but it is not significant in terms of the likely error limits ( $\pm 6\%$ ) in  $k_{ex}$  and is not apparent in  $\Delta H^*$  and  $\Delta S^*$ . For practical purposes, all the variable-temperature data may be combined to give  $\Delta H^* = 29.6 \pm 0.8 \text{ kJ mol}^{-1}$ ,  $\Delta S^* = -75 \pm 3 \text{ J K}^{-1} \text{mol}^{-1}$ , and  $k_{ex}^{298} = (4.9 \pm 0.2) \times 10^3 \text{ kg mol}^{-1} \text{s}^{-1}$  for the title reaction in acetonitrile with  $\text{CF}_3\text{SO}_3^-$  as the anion over the range  $I = 0.07\text{--}0.42 \text{ mol kg}^{-1}$ .

**Self-Exchange in Acetone.** No systematic dependence of either  $k_{ex}$  or the activation parameters upon ionic strength  $I$  is evident in Table II when acetone is the solvent. The kinetic data may therefore be combined to give  $\Delta H^* = 29.2 \pm 0.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^* = -80 \pm 2 \text{ J K}^{-1} \text{mol}^{-1}$ , and  $k_{ex}^{298} = (3.0 \pm 0.2) \times 10^3 \text{ kg mol}^{-1} \text{s}^{-1}$  for the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange reaction in acetone with  $\text{CF}_3\text{SO}_3^-$  as the anion. These parameters are very similar to those for acetonitrile solutions.

**Pressure Effect on Self-Exchange Rates.** The precision of  $k_{ex}$  values obtained in the pressurizable probehead, which has a small sample tube, was inevitably poorer than in the variable-temperature study, and this is reflected in rather large uncertainties in the volumes of activation  $\Delta V^*$  given in Table III. These volumes were calculated on the assumption that they are independent of pressure  $P$ , i.e., that  $\ln k_{ex}$  is a linear function of  $P$ , which is probably not strictly correct<sup>27,28</sup> but is adequate in view of the limited precision of the data. Thus, the  $\Delta V^*$  values should be regarded as mean values for the pressure range 0.1–200 MPa. In the absence of evidence of significant concentration effects, the data may be combined to give  $\Delta V^* = -3.4 \pm 0.6 \text{ cm}^3 \text{mol}^{-1}$  for acetonitrile at 38  $^\circ\text{C}$  and  $-7.8 \pm 0.6 \text{ cm}^3 \text{mol}^{-1}$  for acetone at 30  $^\circ\text{C}$ .

**Oxidation of  $\text{Ru}(\text{hfac})_3^-$  by  $\text{Cu}(\text{dmp})_2^{2+}$  in Acetonitrile.** Measurements by cyclic and ac voltammetry with a silver/silver ion reference electrode gave an electrode potential difference of +150 mV and hence an equilibrium constant  $K_{12}$  of 340 for reaction 1 at 21  $^\circ\text{C}$  and ionic strength  $I = 0.1 \text{ mol kg}^{-1}$ .



The rate of approach to equilibrium was measured with  $\text{Cu}(\text{dmp})_2^{2+}$  in large excess (up to  $1.9 \times 10^{-3} \text{ mol kg}^{-1}$ ) over  $\text{Ru}(\text{hfac})_3^-$  ( $6.7 \times 10^{-5} \text{ mol kg}^{-1}$ ); under these conditions, the reaction goes to  $>99.9\%$  completion. The reaction rate was first order with respect to each reactant but was too rapid to be measured precisely above 21  $^\circ\text{C}$ . Values of the forward reaction rate constant  $k_{12}$

**Table IV.** Rate Constants  $k_{12}$  for the Oxidation of  $n\text{-Bu}_4\text{N}[\text{Ru}^{\text{II}}(\text{hfac})_3]$  by  $[\text{Cu}^{\text{II}}(\text{dmp})_2](\text{CF}_3\text{SO}_3)_2$  in Acetonitrile<sup>a</sup>

temp/°C	$k_{12}/10^5 \text{ kg mol}^{-1} \text{ s}^{-1}$	temp/°C	$k_{12}/10^5 \text{ kg mol}^{-1} \text{ s}^{-1}$
0.1	0.91 ± 0.02	9.2	1.51 ± 0.03
4.7	1.10 ± 0.02	15.4	2.11 ± 0.05
9.0	1.53 ± 0.02	20.1	2.86 ± 0.05

<sup>a</sup>  $[\text{Cu}] = 1.39 \times 10^{-3} \text{ mol kg}^{-1}$ ;  $[\text{Ru}] = 6.7 \times 10^{-5} \text{ mol kg}^{-1}$ .

so obtained are listed in Table IV and may be summarized by the parameters  $\Delta H_{12}^* = 36.1 \pm 0.6 \text{ kJ mol}^{-1}$  and  $\Delta S_{12}^* = -17.4 \pm 2.1 \text{ J K}^{-1} \text{ mol}^{-1}$  at  $I \approx 0.04 \text{ mol kg}^{-1}$ . Following completion of the decrease in absorbance due to the oxidation reaction, a slight and much slower ( $k \approx 600 \text{ kg mol}^{-1} \text{ s}^{-1}$  at 10 °C) increase in absorbance was discernible; this minor phenomenon did not affect the reproducibility of  $k_{12}$  and may justifiably be disregarded.

### Discussion

A salient feature of the results reported here is the close similarity of  $k_{\text{ex}}$ ,  $\Delta H^*$ , and  $\Delta S^*$  values for the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange in acetonitrile to those in acetone. A similar correspondence was found for the  $\text{Ru}(\text{hfac})_3^{-/0}$  exchange in these same solvents and included  $\Delta V^*$ ; in fact, the  $\Delta V^*$  values for the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange are also not greatly different in view of the larger than usual experimental uncertainty involved. One would anticipate similarities in  $k_{\text{ex}}$ , at least, for these solvents on the basis of a simple Marcus adiabatic outer-sphere continuous-dielectric model,<sup>29</sup> since evaluation of eq 2–5 (assuming for the moment that  $\Delta G_{\text{IR}}^*$  is independent of the solvent) gives closely similar results for acetone and acetonitrile.

$$k_{\text{ex}} = (4000\pi N\sigma^3 \kappa_{\text{el}} \nu_n / 3) \exp[-(\Delta G_{\text{IR}}^* + \Delta G_{\text{SR}}^* + \Delta G_{\text{COUL}}^* + \Delta G_{\text{DH}}^*) / RT] \quad (2)$$

$$\Delta G_{\text{SR}}^* = (Ne^2 / 16\pi\epsilon_0)(r^{-1} - \sigma^{-1})(n^2 - D^{-1}) \quad (3)$$

$$\Delta G_{\text{COUL}}^* = (Nz_1z_2e^2 / 4\pi\epsilon_0) / D\sigma \quad (4)$$

$$\Delta G_{\text{DH}}^* = -2RTz_1z_2CI^{1/2} / (1 + BaI^{1/2}) \quad (5)$$

Here,  $n$  is the index of refraction and  $D$  the relative permittivity (dielectric constant) of the solvent, the Debye–Hückel (DH) and work (COUL) terms are incorporated into the free energy of activation along with the solvent rearrangement (SR) term, the reactants are assumed to behave as spheres of charges  $z_1$  and  $z_2$  and equal radii  $r$  (which may be set at 650 pm for  $\text{Cu}(\text{dmp})_2^{+/2+}$  ions<sup>19</sup>), which transfer an electron at the approach distance  $\sigma$ ,  $\kappa_{\text{el}}$  is the electronic transmission coefficient,  $\nu_n$  is the nuclear frequency, and the other symbols have their usual SI meanings. If  $\sigma$  is taken to be  $2r$ , eq 2–5 would reproduce  $k_{\text{ex}}$  if the internal reorganization term  $\Delta G_{\text{IR}}^*$  were about 40 kJ mol<sup>-1</sup> for both acetone and acetonitrile as solvents.

If the same  $\Delta G_{\text{IR}}^*$  value were to hold for water as solvent, eq 2–5 would predict  $k_{\text{ex}}$  to be somewhat slower, by a factor of about 2, for water than for acetone or acetonitrile; in fact, it is some 40 times faster. Experience, e.g., with the  $\text{Fe}(\text{phen})_3^{2+/3+}$  exchange in water and acetonitrile,<sup>30</sup> indicates that eq 2–5 should be equally valid in aqueous and nonaqueous solvents for simple outer-sphere electron transfer between large cations. This suggests that either the reaction mechanism is inner sphere in water (perhaps through the chloride ion that was necessarily present) but outer sphere for acetone and acetonitrile (where the anion was  $\text{CF}_3\text{SO}_3^-$ ) or else the internal reorganization required for electron transfer is different in water, leading to a  $\Delta G_{\text{IR}}^*$  contribution some 14 kJ mol<sup>-1</sup> less than in the nonaqueous solutions.

The lack of concentration dependence of  $k_{\text{ex}}$  in water would seem to rule out a chloride-mediated inner-sphere mechanism;

it is most unlikely that  $\text{Cu}(\text{dmp})_2^{2+}\text{-Cl}^-$  complexing could be saturated in such dilute aqueous solutions. It is, however, highly probable that a fifth ligand, specifically a water molecule, is indeed present in the oxidized complex  $\text{Cu}(\text{dmp})_2^{2+}$  in aqueous solution,<sup>8,9,21</sup> and this is supported by the observation of a color change from pale green to brown on desiccating the solid  $\text{CF}_3\text{SO}_3^-$  salt recovered from the green aqueous preparation. It is also likely that a solvent molecule is coordinated to  $\text{Cu}(\text{dmp})_2^{2+}$  in acetonitrile or acetone solutions, in which the  $\text{Cu}^{\text{II}}$  complex is again green. On the other hand,  $\text{Cu}(\text{dmp})_2^+$  occurs in its solid salts only as the four-coordinate distorted-tetrahedral ion, even when there is water present in the lattice,<sup>19</sup> and may be presumed to be four-coordinate in solution at equilibrium. Thus, the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange in solution may require a change from four-coordination in the  $\text{Cu}^{\text{I}}$  complex to five-coordination in the  $\text{Cu}^{\text{II}}$  species leading to a relatively high  $\Delta G_{\text{IR}}^*$  value that can be expected to show some dependence on solvent—as seems to be the case.

The observed value of  $k_{\text{ex}}$ <sup>29,8</sup> in  $\text{D}_2\text{O}$  at  $I = 0.002 \text{ mol L}^{-1}$  is about 5 times faster than predicted by Davies<sup>8</sup> from the Marcus cross relation for  $\text{H}_2\text{O}$  at  $I = 1.0 \text{ mol L}^{-1}$ . Correction for the ionic strength difference (eq 5) widens the discrepancy to over 10-fold, but this is not excessive in view of the approximations inherent in the cross relation and the scatter in the predictions made from it for the  $\text{Cu}(\text{dmp})_2^{+/2+}$  self-exchange. Conversely, for the net reaction 1 in acetonitrile, the available self-exchange rate constants  $k_{11}$  for  $\text{Cu}(\text{dmp})_2^{+/2+}$  and  $k_{22}$  for  $\text{Ru}(\text{hfac})_3^{-/0}$ <sup>27</sup> together with  $k_{12}$  and  $K_{12}$  for reaction 1 allow the validity of the Marcus cross relation

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (6)$$

where

$$\ln f_{12} = (\ln K_{12})^2 / [4 \ln (k_{11}k_{22}/Z^2)] \quad (7)$$

and  $Z$  is the collision frequency (ca.  $10^{11} \text{ kg mol}^{-1} \text{ s}^{-1}$ ) to be tested for that solvent. The predicted value of  $k_{12}$  is  $2.5 \times 10^6 \text{ kg mol}^{-1} \text{ s}^{-1}$  at 25 °C, which is in reasonable agreement with the extrapolated experimental value of  $3.6 \times 10^5 \text{ kg mol}^{-1} \text{ s}^{-1}$  in view of the differences in ionic strengths for the  $k_{11}$ ,  $k_{12}$ ,  $k_{22}$ , and  $K_{12}$  data used. Thus, in both water and acetonitrile, the kinetic behavior of the  $\text{Cu}(\text{dmp})_2^{+/2+}$  couple conforms quite well to the predictions of the Marcus theory despite the probable loss of a coordinated solvent molecule on going from  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ . Indeed, the slower, minor drift in absorbance noted after completion of reaction 1 in the stopped-flow noted after completion of reaction 1 in the stopped-flow experiments may have been due to such a solvational change, but this cannot be demonstrated, and the phenomenon may well be an artifact.

The lack of data on the pressure dependence of the refractive indices  $n$  for acetone and acetonitrile prevent tests of the consistency of the experimental  $\Delta V^*$  data for the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange in these two solvents with the predictions of theories of outer-sphere electron-transfer processes,<sup>27,28</sup> but we note that  $\Delta V^*$  values for the obligate outer-sphere  $\text{Ru}(\text{hfac})_3^{-/0}$  self-exchange in these same solvents<sup>27</sup> are similar to those reported here.

It may be concluded that the kinetics of the  $\text{Cu}(\text{dmp})_2^{+/2+}$  exchange in water, acetone, and acetonitrile are consistent with the operation of a common outer-sphere mechanism, if due recognition is given to the probable existence of differences in coordination chemistry of the copper(II) complex in the various solvents, and that they are adequately represented by the Marcus theory of adiabatic electron-transfer rates.

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**Supplementary Material Available:** Tables of  $k_{\text{ex}}$  values as functions of temperature, concentration, and pressure (4 pages). Ordering information is given on any current masthead page.

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