

# First Investigation at Elevated Pressures To Confirm the Exact Nature of the Gated Electron-Transfer Systems: Volume Profiles of the Gated Reduction Reaction and Nongated Reverse Oxidation Reaction Involving a $[\text{Cu}(\text{dmp})_2(\text{solvent})]^{2+}/[\text{Cu}(\text{dmp})_2]^+$ Couple (dmp = 2,9-Dimethyl-1,10-phenanthroline)

Sumitaka Itoh, Kyoko Noda, Ryouhei Yamane, Nobuyuki Kishikawa, and Hideo D. Takagi\*

Graduate School of Science and Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8602, Japan

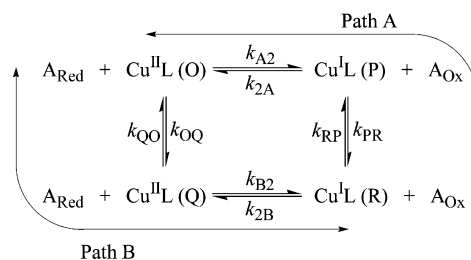
Received August 22, 2006

Redox reactions involving the  $[\text{Cu}(\text{dmp})_2]^{2+/+}$  couple (dmp = 2,9-dimethyl-1,10-phenanthroline) in acetonitrile were examined at elevated pressures up to 200 MPa. Activation volumes were determined as  $-8.8$  and  $-6.3$   $\text{cm}^3 \text{mol}^{-1}$  for the reduction cross-reaction by  $[\text{Co}(\text{bipy})_3]^{2+}$  (bipy = 2,2'-bipyridine) and for the oxidation cross-reaction by  $[\text{Ni}(\text{tacn})_2]^{3+}$  (tacn = 1,4,7-triazacyclononane), respectively. The activation volume for the hypothetical gated mode of the self-exchange reaction estimated from the reduction cross-reaction was  $-13.9$   $\text{cm}^3 \text{mol}^{-1}$ , indicating extensive electrostrictive rearrangement of solvent molecules around the  $\text{Cu}^{\text{II}}$  complex during the change in the coordination geometry before the electron-transfer step. On the other hand, the activation volume for the self-exchange reaction estimated from the oxidation cross-reaction was  $-2.7 \pm 1.5$   $\text{cm}^3 \text{mol}^{-1}$ . Although this value was within the range that can be interpreted by the concept of the ordinary concerted process, from theoretical considerations it was concluded that the reverse (oxidation) cross-reaction of the gated reduction reaction of the  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}/[\text{Cu}(\text{dmp})_2]^+$  couple proceeds through the product excited state while the direct self-exchange reaction between  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^+$  proceeds through an ordinary concerted process.

## Introduction

Gated electron-transfer (ET) reactions involving  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  centers are related to the biologically important catalytic processes.<sup>1,2</sup> Among investigations carried out to date, systematic studies by Rorabacher and co-workers have largely improved the understanding of the gated phenomena: they postulated a dual-pathway square scheme (Scheme 1).<sup>3–5</sup> In the square scheme, only one of the reactants  $[\text{Cu}^{\text{I}}\text{L}(\text{R})]$  or  $\text{Cu}^{\text{II}}\text{L}(\text{O})$ , where L stands for the coordinated ligands] changes its structure before the ET step, and the choice of

Scheme 1



path A or path B depends on the energy of the deformed species, P or Q. In general, ET reactions of copper(II)/copper(I) polythioether complexes proceed through path A in Scheme 1, and the direction in which the estimated self-exchange rate constant is much smaller than that directly measured by NMR is gated. Rorabacher and co-workers attributed the cause of the gated phenomena to the sluggish conformational change of the coordinated multidentate macrocyclic polythioether ligands<sup>3–5</sup> because structures of  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  species should come close to each other at the

\* To whom correspondence should be addressed. E-mail: h.d.takagi@chem.nagoya-u.ac.jp.

- (1) Williams, R. P. *J. Eur. J. Biochem.* **1995**, *234*, 363–381.
- (2) Kaim, W.; Schwederski, B. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*; Wiley: Chichester, U.K., 1994.
- (3) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012–3022.
- (4) Rorabacher, D. B.; Meagher, N. E.; Juntunen, K. L.; Robandt, P. V.; Leggett, G. H.; Salhi, C. A.; Dunn, B. C.; Schroeder, R. R.; Ochrymowycz, L. A. *Pure Appl. Chem.* **1993**, *65*, 573–578.
- (5) Rorabacher, D. B. *Chem. Rev.* **2004**, *104*, 651–697.

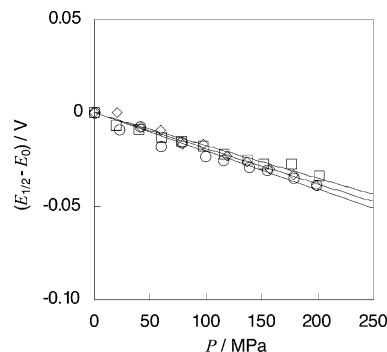
transition state, according to the Marcus theory for the outer-sphere ET reactions.<sup>6,7</sup>

On the other hand, for redox reactions involving Cu<sup>II</sup>/Cu<sup>I</sup> complexes with polypyridine ligands, the reduction direction is always gated,<sup>8–10</sup> although no sluggish conformational change of the coordinated ligands is necessary for the alterations of the coordination geometries around the Cu<sup>II</sup> and Cu<sup>I</sup> centers in the case of these bidentate ligands. In the most recent publication,<sup>11</sup> we reported that consideration of the direction for structural changes on the basis of the second-order perturbation theory (symmetry rules and the principle of least motion, PLM)<sup>12,13</sup> successfully explains the gated phenomena exhibited, at least, by copper(II)/copper(I) polypyridine complexes. However, the pathway of the reverse direction of the gated reaction as well as the direct self-exchange reaction has to be confirmed for the better understanding of the gated reactions.

In this study, we took advantage of the preciseness of the volume analyses to clarify the exact nature of the gated reaction systems: it has been proven that the volume analyses are effective to precisely determine profiles of outer-sphere ET reactions.<sup>14–16</sup> We also revisited the results reported in 1989<sup>17</sup> for the activation volume of the direct self-exchange reaction of the [Cu(dmp)<sub>2</sub>]<sup>2+/+</sup> (dmp = 2,9-dimethyl-1,10-phenanthroline) couple in acetonitrile (Appendix A).

## Experimental Section

**Chemicals.** Acetonitrile was obtained from Wako Pure Chemicals Inc. and purified by distillation from phosphorus pentoxide and from 4A molecular sieves. The content of residual water in thus purified acetonitrile was examined by a Mitsubishi Chemical CA-07 Karl Fischer apparatus, by which the amount of residual water was determined to be less than 1 mmol kg<sup>-1</sup>. Tetrabutylammonium perchlorate (*n*Bu<sub>4</sub>NClO<sub>4</sub>, TBAP) from Aldrich was twice recrystallized from the mixture of an ethyl acetate/pentane solution and dried under reduced pressure. All other chemicals from Wako and Aldrich were used without further purification. [Cu(dmp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Cu(dmp)<sub>2</sub>](ClO<sub>4</sub>) were synthesized by the reported methods.<sup>11</sup> Anal. Calcd for CuC<sub>28</sub>H<sub>24</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 49.5; N, 8.25; H, 3.56. Found: C, 50.5; N, 8.16; H, 3.65. Anal. Calcd for CuC<sub>28</sub>H<sub>24</sub>N<sub>4</sub>ClO<sub>4</sub>: C, 58.0; N, 9.67; H, 4.17. Found: C, 58.6, N, 9.87; H, 4.10. We were able to obtain [Cu(dmp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> by removing the loosely coordinated solvent molecule using a vacuum



**Figure 1.** Pressure dependence of the electrode potentials for various redox couples in acetonitrile: (○) [Cu(dmp)<sub>2</sub>]<sup>2+/+</sup> = 1.0 × 10<sup>-3</sup> mol kg<sup>-1</sup>; (□) [Ni(tacn)<sub>2</sub>]<sup>2+/+</sup> = 1.0 × 10<sup>-3</sup> mol kg<sup>-1</sup>; (◇) [Co(bipy)<sub>3</sub>]<sup>3+/2+</sup> = 1.0 × 10<sup>-3</sup> mol kg<sup>-1</sup>. The sweep rate is 0.1 V s<sup>-1</sup>. T = 298 ± 1 K. I = 0.1 mol kg<sup>-1</sup> (TBAP). E<sub>0</sub> denotes the redox potential at 0.1 MPa.

oven. However, it was shown that the complex exists as a five-coordinate [Cu(dmp)<sub>2</sub>(solvent)]<sup>2+</sup> species in donor solvents.<sup>11</sup>

[Co(bipy)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub><sup>18</sup> (bipy = 2,2'-bipyridine) and [Ni(tacn)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (tacn = 1,4,7-triazacyclononane) were synthesized by the literature methods.<sup>19</sup> Anal. Calcd for CoC<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 49.6; H, 3.33; N, 11.6. Found: C, 50.0; H, 3.23; N, 11.6. Anal. Calcd for NiC<sub>12</sub>H<sub>30</sub>N<sub>6</sub>Cl<sub>3</sub>O<sub>12</sub>: C, 23.42; H, 4.91; N, 13.66. Found: C, 23.42; H, 4.96; N, 13.55. **Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive.

**General Procedures.** All manipulations were carried out in an atmosphere of dry nitrogen to avoid possible contamination of water and oxygen from the environment. The reaction volumes were measured by the pressure dependence of the redox potentials at 25 °C by using a BAS 100B/W electrochemical analyzer. The pressure vessel for the measurements was reported previously.<sup>10</sup> We used a glass electrochemical cell equipped with a 2.0-mm-diameter Pt disk and a 1.0-mm-diameter Pt wire as the working and counter electrodes, respectively. A silver/silver nitrate electrode used as a reference was made by placing a solution (1.0 × 10<sup>-3</sup> mol kg<sup>-1</sup> of AgNO<sub>3</sub> with 0.10 mol kg<sup>-1</sup> of *n*Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte) in a collapsible Teflon tube equipped with a vicor plug. Kinetic measurements at ambient pressure were carried out by a Unisoku RA401 stopped-flow apparatus, while the measurements at elevated pressures were carried out by a Hi-Tech HPSF-50 apparatus. The reactions were monitored by observation of the absorption change at 456 nm (the absorption band maximum of [Cu(dmp)<sub>2</sub>]<sup>+</sup>). Paraffin oil was used as the pressurizing fluid, after deaeration by dry nitrogen for 1 h.

## Results

The reaction volumes of the redox couples used in this study were determined from the pressure dependence of the redox potentials at 298 K.

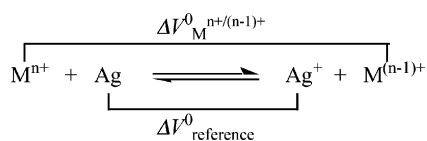
$$\Delta V_{\text{cell}}^{\circ} = \left( \frac{\partial \Delta G^{\circ}}{\partial P} \right)_T = -nF \left( \frac{\partial E^{\circ}}{\partial P} \right)_T \quad (1)$$

All redox couples examined in this study were either electrochemically reversible or quasi-reversible. The pressure dependence of the electrode potentials is shown in Figure 1 for each redox couple (Table S1 in the Supporting Informa-

- (6) Cannon, R. D. *Electron Transfer Reactions*; Butterworth: London, 1980.
- (7) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441–498.
- (8) Koshino, N.; Kuchiyama, Y.; Ozaki, H.; Funahashi, S.; Takagi, H. D. *Inorg. Chem.* **1999**, *38*, 3352–3360.
- (9) Itoh, S.; Funahashi, S.; Koshino, N.; Takagi, H. D. *Inorg. Chim. Acta* **2001**, *324*, 252–265.
- (10) Itoh, S.; Funahashi, S.; Takagi, H. D. *Chem. Phys. Lett.* **2001**, *344*, 441–449.
- (11) Itoh, S.; Kishikawa, N.; Suzuki, T.; Takagi, H. D. *Dalton Trans.* **2005**, 1066–1078.
- (12) Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley: New York, 1976.
- (13) Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489–496.
- (14) Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 5017–5025.
- (15) Grace, M. R.; Takagi, H. D.; Swaddle, T. W. *Inorg. Chem.* **1994**, *33*, 1915–1920.
- (16) Swaddle, T. W. In *Inorganic High Pressure Chemistry*, van Eldik, R., Ed.; Elsevier: Amsterdam, The Netherlands, 1985; Chapter 4.
- (17) Doine (Takagi), H.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1989**, *28*, 2319–2322.

- (18) Davies, G.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 694–700.
- (19) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, *23*, 1938–1943.

## Scheme 2



tion). The overall reaction volumes ( $\Delta V_{\text{cell}}^{\circ}$ ) corresponding to Scheme 2, calculated from the slopes of the plots in Figure 1, are listed in Table 1. To determine the reaction volume of a cross-reaction, it is not necessary to isolate  $\Delta V_{\text{M}^{n+/(n-1)+}}^{\circ}$ , provided that the identical reference electrode is used for all measurements of  $\Delta V_{\text{cell}}^{\circ}$ .<sup>20</sup>

$$\Delta V_{\text{cell}}^{\circ} = \Delta V_{\text{M}^{n+/(n-1)+}}^{\circ} + \Delta V_{\text{reference}}^{\circ} \quad (2)$$

Pressure dependences of the rate constants are shown in Figures 2 and 3 (Tables S2 and S3 in the Supporting Information) for the examined oxidation and reduction cross-reactions. The activation volumes corresponding to the hypothetical electron self-exchange reaction between  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^+$  were then calculated by the following volume cross-relation, which has been verified by Grace et al.<sup>15</sup>

$$\Delta V_{12}^* = \frac{\Delta V_{11}^* + \Delta V_{22}^* + \Delta V_{12}^{\circ}}{2} + C$$

$C =$

$$\frac{X \Delta V_{12}^{\circ} \ln K_{12} - 2(\ln K_{12})^2 (\Delta V_{11}^* + \Delta V_{22}^* - \Delta V_{11}^{\text{W}} - \Delta V_{22}^{\text{W}})}{X^2}$$

$$X = 4 \left[ \ln \left( \frac{k_{11} k_{22}}{Z^2} \right) + \frac{w_{11} + w_{22}}{RT} \right] \quad (3)$$

where  $\Delta V_{12}^*$  is the activation volume of the cross-reaction,  $\Delta V_{11}^*$ ,  $\Delta V_{22}^*$ ,  $k_{11}$ , and  $k_{22}$  are the activation volumes and corresponding rate constants for each electron self-exchange reaction,  $\Delta V_{12}^{\circ}$  is the reaction volume of the cross-reaction,  $Z$  is the collision frequency, which is usually taken to be  $10^{11}$ , and  $w_{ii}$  and  $\Delta V_{ii}^{\text{W}}$  are the Coulombic work terms and the corresponding volumes, respectively. Because the contribution of the  $C$  term in the above equation was less than  $1 \text{ cm}^3 \text{ mol}^{-1}$  for both of the examined cross-reactions, this term was ignored in the calculation: it has been known that the uncertainty in the estimated activation volumes is generally  $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$ . In Table 2, listed are the activation volumes for the self-exchange reaction between  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^+$  calculated from both directions of the cross-reactions, together with the measured activation volumes for each cross-reaction.

## Discussion

We reported in the previous study that  $[\text{Cu}(\text{dmp})_2]^{2+}$  crystallized in two different forms, depending on the solvent used for the syntheses:<sup>11</sup> the complex with a five-coordinate pseudo-trigonal-bipyramidal structure,  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$ ,

Table 1. Reaction Volumes for Various Redox Couples in Acetonitrile<sup>a</sup>

redox couple	$\Delta V_{\text{cell}}^{\circ}/\text{cm}^3 \text{ mol}^{-1}$
$[\text{Cu}(\text{dmp})_2]^{2+/+}$	$19.8 \pm 0.7$
$[\text{Ni}(\text{tacn})_2]^{3+/2+}$	$16.9 \pm 0.5$
$[\text{Co}(\text{bipy})_3]^{3+/2+}$	$18.4 \pm 0.4$

<sup>a</sup>  $I = 0.1 \text{ mol kg}^{-1}$  (TBAP).

was isolated from solvents with relatively large basicity such as water and acetonitrile, while the complex with a four-coordinate  $D_2$  structure was isolated from solvents with low basicity such as nitromethane. In the former structure, one of the coordination sites in the trigonal plane is occupied by a solvent molecule. Kinetic measurements revealed that the reduction reaction of the latter species in nitromethane was the first example of the fully gated reaction: the reduction reaction was completely regulated by the rate of the slow (symmetrically forbidden) structural change ( $k_{\text{OQ}} = 1.17 \text{ s}^{-1}$  at  $25 \text{ }^{\circ}\text{C}$ ).<sup>11</sup> On the other hand, it was reported<sup>8,9</sup> that the reductions of the five-coordinate complex in acetonitrile proceeded through the gated mechanism with a faster structural change ( $k_{\text{OQ}} = \text{ca. } 30 \text{ s}^{-1}$  at  $25 \text{ }^{\circ}\text{C}$ ) followed by the rapid ET.<sup>8</sup> With these results, we postulated two essential factors that are necessary for the occurrence of gated reactions:<sup>9,11</sup> (1) the nonadiabatic nature of the direct ET reactions involving the ground-state species ("O" in Scheme 1) and (2) slow structural changes so as to induce better electronic coupling with the counter-reagent through the charge-transfer (CT)-perturbed superexchange-type interaction. According to the theoretical discussion by Brunshwig and Sutin, the structural change is required to take place prior to the formation of the encounter complex because a high-energy (slow) structural activation before the ET process within the encounter complex cannot compete with the ordinary concerted reaction,<sup>21</sup> which is nonadiabatic and very slow for the reaction systems that exhibit gated behaviors.

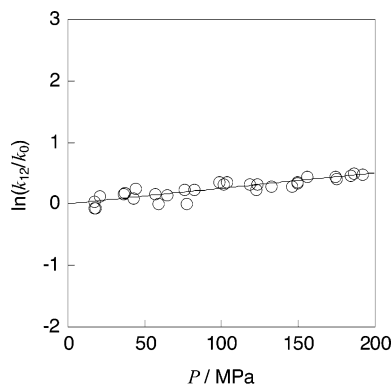
The activation process of a redox-active species is independent of the counter-reagent when the cross-relation holds for cross-reactions with various counter-reagents:<sup>22</sup> the activation volume for the hypothetical self-exchange reaction estimated from a cross-reaction reflects the activation mode of the reactant in the cross-reaction. As shown in Table 2, the activation volumes corresponding to the same hypothetical self-exchange process estimated from the oxidation and reduction cross-reactions were different from each other for the  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}/[\text{Cu}(\text{dmp})_2]^+$  couple. This indicates that the activation process/mode is certainly different for the Cu species in two directions because the counter-reactants are typical outer-sphere reagents for which the activation process is always the same for all redox reactions.

In the gated reduction cross-reactions, two consecutive structural activation steps are expected for  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  so as to maximize the electronic coupling with the counter-reagent: (1) a change from the pseudo- $D_{3h}$  structure of the ground-state geometry for  $\text{Cu}^{\text{II}}$  to the  $C_{2v}$  structure by

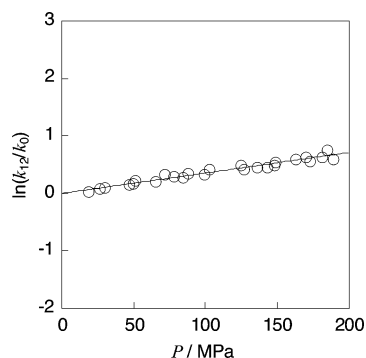
(21) Brunshwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454–7465.

(22) Ratner, M. A.; Levine, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 4898–4900.

(20) Doine (Takagi), H.; Whitcombe, T. W.; Swaddle, T. W. *Can. J. Chem.* **1992**, *70*, 81–88.



**Figure 2.** Pressure dependence of the rate constant for the cross-reaction between  $[\text{Cu}(\text{dmp})_2]^+$  and  $[\text{Ni}(\text{tacn})_2]^{3+}$  in acetonitrile.  $[\text{Cu}(\text{dmp})_2]^+ = (1.44\text{--}1.71) \times 10^{-5} \text{ mol kg}^{-1}$ .  $[\text{Ni}(\text{tacn})_2]^{3+} = (1.48\text{--}1.72) \times 10^{-4} \text{ mol kg}^{-1}$ .  $T = 298 \pm 1 \text{ K}$ .  $I = 0.1 \text{ mol kg}^{-1}$  (TBAP).



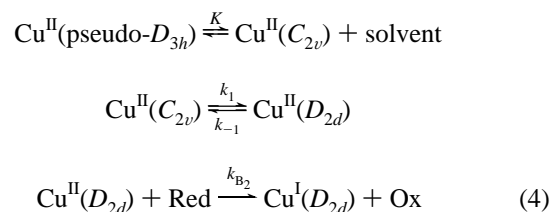
**Figure 3.** Pressure dependence of the rate constant for the cross-reaction between  $[\text{Cu}(\text{dmp})_2]^{2+}$  and  $[\text{Co}(\text{bipy})_3]^{2+}$  in acetonitrile.  $[\text{Cu}(\text{dmp})_2]^{2+} = (1.05 \text{ or } 5.19) \times 10^{-4} \text{ mol kg}^{-1}$ .  $[\text{Co}(\text{bipy})_3]^{2+} = (2.57 \text{ or } 4.93) \times 10^{-5} \text{ mol kg}^{-1}$ .  $T = 298 \pm 1 \text{ K}$ .  $I = 0.1 \text{ mol kg}^{-1}$  (TBAP).

releasing the loosely coordinated solvent molecule and (2) a further structural change to achieve the same symmetry as that of  $\text{Cu}^{\text{I}}$  in the ground state, the  $D_{2d}$  structure. Therefore, it is necessary for the five-coordinate  $\text{Cu}^{\text{II}}$  species,  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$ , to form a four-coordinate intermediate ( $C_{2v}$ ), in the first stage of the structural activation.

The symmetry rules and PLM<sup>12,13</sup> indicate that the dissociation of the solvent molecule from the trigonal plane of the five-coordinate  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  in pseudo- $D_{3h}$  symmetry is allowed to form a species in  $C_{2v}$  symmetry through the  $E$  normal-mode vibration. This kind of dissociation process is quite common for transition-metal complexes with  $D_{3h}$  symmetry such as *trans*- $[\text{Ni}(\text{CN})_2(\text{triphenylphosphine})_3]$ .<sup>23</sup> Although this solvent dissociation from  $\text{Cu}^{\text{II}}$  in pseudo- $Tbp$  symmetry is as rapid as ca.  $10^6 \text{ s}^{-1}$ ,<sup>24,25</sup> it may not take place within the encounter complex (the lifetime of the encounter complex is in a range of  $10^{-10}$ – $10^{-12} \text{ s}$ , depending on the charges on the reactants). On the other hand, structural deformation from pseudo- $D_{3h}$  to  $C_{2v}$  symmetry *without* dissociation of the coordinated solvent molecule is also allowed to occur within the encounter complex because this type of deformation through the

allowed  $E$  normal-mode vibration takes place with a time scale of  $10^{-13} \text{ s}$ , which is much shorter than the lifetime of the encounter complex, ca.  $10^{-10} \text{ s}^{-1}$ .

Because the observed overall reduction cross reaction is gated,<sup>8</sup> it is certain that the  $\text{Cu}^{\text{II}}$ –solvent bond completely breaks at the first stage of the reaction. However, this solvent dissociation process is not the sole reason for the observed gated behavior: (1) the observed  $k_{\text{OQ}}$  value (ca.  $30 \text{ s}^{-1}$ ) is much smaller than the rate constant for this solvent dissociation,  $10^6 \text{ s}^{-1}$ ,<sup>24,25</sup> and (2)  $\text{Cu}^{\text{II}}$  in  $C_{2v}$  symmetry does not exhibit a low-energy CT band, which is necessary for the rapid ET reactions to occur.<sup>10</sup> The succeeding structural change from  $[\text{Cu}(\text{dmp})_2]^{2+}$  in  $C_{2v}$  symmetry (the solvent  $\text{CH}_3\text{CN}$  molecule is already removed) to the  $D_{2d}$  structure is also allowed through the normal  $B_2$  twist mode. Therefore, the structural change that regulates the overall ET process includes both of the pseudo- $D_{3h}$  to  $C_{2v}$  and  $C_{2v}$  to  $D_{2d}$  interconversions before the formation of the encounter complex in which a rapid ET takes place. This situation is expressed by the following mechanism.



The observed rate constant  $k_{\text{obs}}$  is then expressed by the following equation, by assuming a steady state for  $\text{Cu}^{\text{II}}$  in  $D_{2d}$  symmetry.

$$k_{\text{obs}} = \frac{Kk_1k_{B_2}[\text{Red}]}{k_{B_2}[\text{Red}] + k_{-1}} \quad (5)$$

In this case,  $Kk_1$  corresponds to  $k_{\text{OQ}}$  in Scheme 1. The equilibrium constant  $K$  is small because  $\text{Cu}^{\text{II}}(C_{2v})$  is considered to be an intermediate for the solvent-exchange reaction: when the solvent-exchange (dissociation) rate constant is ca.  $10^6 \text{ s}^{-1}$ ,<sup>24,25</sup> the  $K$  value is estimated as ca.  $1 \times 10^{-5} \text{ M}$  because the back reaction is expected to be diffusion-controlled (ca.  $10^{11} \text{ kg mol}^{-1} \text{ s}^{-1}$ ). Therefore, when  $Kk_1$  is ca.  $30 \text{ s}^{-1}$ ,<sup>8</sup>  $k_1$  is ca.  $3 \times 10^6 \text{ s}^{-1}$ . As a result, the time scale of this twisting process,  $> 10^{-7} \text{ s}$ , is longer than the ordinary lifetime of the encounter complex (ca.  $10^{-10}$ – $10^{-12} \text{ s}$  depending on the charges on the reactants), and this twist process also takes place prior to the formation of the encounter complex. However, it should be noted that the bond stretching by the  $E$  mode combined with the *partial* twisting through the  $B_2$  mode may be acceptably rapid for the concerted reaction to occur if the electronic coupling between  $\text{Cu}^{\text{II}}$  and the counter-reagent is sufficiently large. Such a case may be met when the counter-reagent is also a copper polypyridine complex: the pseudo-self-exchange rate constant for the reduction reaction of  $[\text{Cu}(\text{dmbp})_2(\text{CH}_3\text{CN})]^{2+}$  by  $[\text{Cu}(\text{dmp})_2]^+$  ( $\text{dmbp} = 6,6'$ -dimethyl-2,2'-bipyridine, and the reduction reaction of  $[\text{Cu}(\text{dmbp})_2(\text{CH}_3\text{CN})]^{2+}$  has been known to be gated) was as fast as  $\log k_{12} = 4.4$ .<sup>11</sup>

(23) Grimes, C. G.; Pearson, R. G. *Inorg. Chem.* **1974**, *13*, 970–977.

(24) Powell, D. H.; Merbach, A. E.; Fabian, I.; Schindler, S.; van Eldik, R. *Inorg. Chem.* **1994**, *33*, 4468–4473.

(25) Nubrand, A.; Thaler, F.; Korner, M.; Zahl, A.; Hubbard, C.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **2002**, 957–961.



**Table 2.** Activation Volumes for the Self-Exchange Reaction of  $[\text{Cu}(\text{dmp})_2]^{2+/+}$  Estimated from the Cross-Reactions of Oxidation and Reduction Directions<sup>a</sup>

cross-reaction	$\Delta V_{12}^*$	$\Delta V_{22}^*$	$\Delta V_{12}^\circ$	$\Delta V_{11}^*$
$[\text{Cu}(\text{dmp})_2]^+ + [\text{Ni}(\text{tacn})_2]^{3+}$	$-6.3 \pm 0.3$	$-7 \pm 1^b$	$-2.9 \pm 1.2$	$-2.7 \pm 2.8$
$[\text{Cu}(\text{dmp})_2]^{2+} + [\text{Co}(\text{bipy})_3]^{2+}$	$-8.8 \pm 0.1$	$-5.1 \pm 1.4^c$	$1.4 \pm 0.9$	$-13.9 \pm 2.5$

<sup>a</sup>  $\text{cm}^3 \text{mol}^{-1}$ . <sup>b</sup> Estimated value using the SHM equation.<sup>14,16</sup> <sup>c</sup> Braum, P.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1349–1350.

In the current reduction reaction of  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  by  $[\text{Co}(\text{bipy})_3]^{2+}$ ,  $k_{\text{obs}}$  is given by eq 6, by defining new  $K_{\text{OQ}}$  as  $Kk_1/k_{-1}$ , under the experimental conditions  $[\text{Red}] \ll [\text{Cu}^{\text{II}}]$ .

$$k_{\text{obs}} = K_{\text{OQ}}k_{B_2} \quad (6)$$

In this equation,  $k_{B_2}$  stands for the rate constant of ET between  $[\text{Cu}(\text{dmp})_2]^{2+}$  in  $D_{2d}$  symmetry,  $\text{Cu}^{\text{II}}\text{L}(\text{Q})$ , and the counter-reagent (Scheme 1). Because the observed rate constant is defined by eq 6, the calculated activation volume for the reduction reaction is expressed by eq 8. Because the  $\Delta V_{12}$  value (and, hence,  $K_{12}$  and  $\Delta E_{12}$ ) reflects the difference of the volume (free energy) between the initial and final states, it does not include any information of the reaction pathway. Therefore, the following discussion is valid, as the hypothetical self-exchange reaction between  $\text{Cu}^{\text{II}}$  and  $\text{Cu}^{\text{I}}$  both in the ground states is discussed.

$$\Delta V_{\text{obs}}^* = -RT \left( \frac{\partial \ln k_{\text{obs}}}{\partial P} \right)_T \quad (7)$$

$$\Delta V_{\text{obs}}^* = \Delta V_{\text{OQ}} + \Delta V_{B_2}^* \quad (8)$$

where  $\Delta V_{\text{OQ}}$  and  $\Delta V_{B_2}^*$  are the volume change from pseudo- $D_{3h}$  to  $D_{2d}$  for  $\text{Cu}^{\text{II}}$  and the activation volume for the succeeding ET between  $\text{Cu}^{\text{II}}$  in  $D_{2d}$  symmetry and  $[\text{Co}(\text{bipy})_3]^{2+}$ , respectively. Because the  $k_{B_2}$  process is governed essentially by the outer-sphere contributions to the activation process,  $\Delta V_{B_2}^*$  is expected to be ca.  $-5 \text{ cm}^3 \text{mol}^{-1}$  according to the Stranks–Hush–Marcus (SHM) theory:<sup>15,17</sup>  $\Delta V_{\text{OQ}} \sim -9 \text{ cm}^3 \text{mol}^{-1}$ . This large negative  $\Delta V_{\text{OQ}}$  may be attributed to the solvation of the released solvent molecule from  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  and the solvent reorganization around  $[\text{Cu}(\text{dmp})_2]^{2+}$ , the latter of which is a result of the increased CT interaction in  $D_{2d}$ - $[\text{Cu}(\text{dmp})_2]^{2+}$  compared with that in  $C_{2v}$ - $[\text{Cu}(\text{dmp})_2]^{2+}$ .

On the other hand, the estimated activation volume for the hypothetical self-exchange reaction,  $-2.7 \pm 1.5 \text{ cm}^3 \text{mol}^{-1}$ , by application of eq 3 to the result of the oxidation cross-reaction of  $[\text{Cu}(\text{dmp})_2]^+$  by  $[\text{Ni}(\text{tacn})_2]^{3+}$ , is consistent with the activation volume calculated on the basis of the SHM equation<sup>14,16</sup> within experimental uncertainty. If the oxidation reaction requires a large structural change of  $\text{Cu}^{\text{I}}$ , from  $D_{2d}$  to  $C_{2v}$ , a large positive activation volume is expected: Path A requires a structural change from  $D_{2d}$  to  $C_{2v}$  and the polarity change in this activation process is the reverse process to the activation of  $\text{Cu}^{\text{II}}$ . Therefore, we can conclude that the oxidation cross-reaction of  $[\text{Cu}(\text{dmp})_2]^+$  by  $[\text{Ni}(\text{tacn})_2]^{3+}$  does not proceed through path A: this oxidation process proceeds either through the concerted mechanism or through the product excited state (path B).

However, it has been pointed out by Brunshwig and Sutin that a process through the product excited state is preferred to the concerted process in the normal region. We, therefore, safely conclude that the oxidation cross-reactions of  $[\text{Cu}(\text{dmp})_2]^+$  proceed through the product excited state ( $\text{Cu}^{\text{II}}$  in  $D_{2d}$  symmetry) without much change in the coordination structure of  $D_{2d}$ - $\text{Cu}^{\text{I}}$ : this process corresponds to path B in Scheme 1 (see also path B' in Scheme 3-1 and Appendix B). At this point, it is clear that the volume analyses cannot distinguish the reaction through path B from the concerted process because neither mechanism involves a significant volume change at the rate-determining ET step.

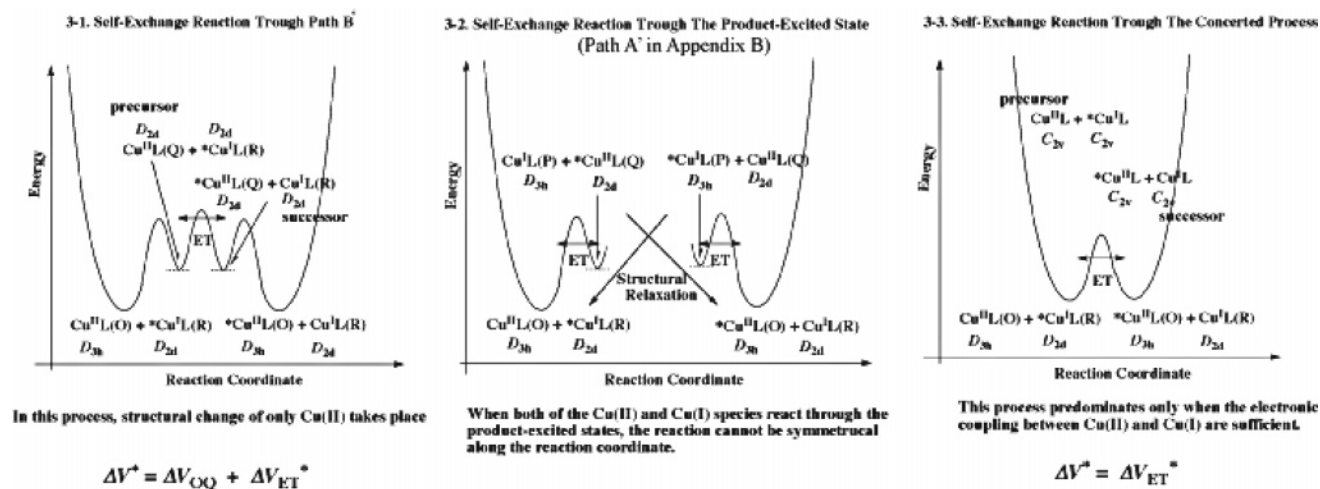
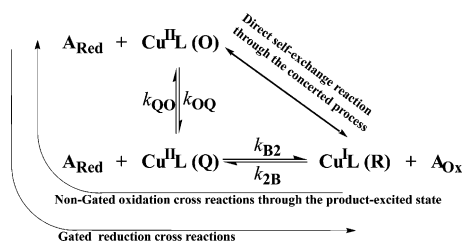
On the other hand, we will encounter a difficulty when the direct self-exchange reaction between  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^+$  is considered: the direct self-exchange reaction cannot proceed through the product excited state for both  $\text{Cu}^{\text{II}}$  and  $\text{Cu}^{\text{I}}$  species because the overall reaction profile of the self-exchange reaction should be *symmetric along the reaction coordinate*. This situation is graphically described in Scheme 3-2 (path A'; see also Appendix B). As a result, the direct self-exchange reaction may proceed through path B, as was shown in the previous article (Scheme 3-1).<sup>8</sup> However, the self-exchange rate constant through path B is expressed by eq 9,<sup>8</sup> and hence the observed activation volume should exhibit the contribution of  $\Delta V_{\text{OQ}}$ .

$$k_{\text{ex}} = K_{\text{OQ}}k_{\text{ET}} \quad (9)$$

$$\Delta V_{\text{ex}}^* = \Delta V_{\text{OQ}} + \Delta V_{\text{ET}}^* \quad (10)$$

where  $k_{\text{ET}}$  corresponds to the rate constant for the ET process between  $[\text{Cu}(\text{dmp})_2]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^+$ , both of which are in  $D_{2d}$  symmetry, and hence the activation volume for this process is ca.  $-5 \text{ cm}^3 \text{mol}^{-1}$  from the SHM theory.<sup>15,17</sup> From eq 10, the activation volume for the self-exchange reaction should be ca.  $-14 \text{ cm}^3 \text{mol}^{-1}$ , which is much more negative compared with the directly measured activation volume,  $-3.4 \text{ cm}^3 \text{mol}^{-1}$ .<sup>17</sup> We, therefore, have to conclude that the direct self-exchange reaction does not proceed through path B (see also path B' in Scheme 3-1), from the results obtained in this study (Appendix B).

When the self-exchange reaction is concerted, both  $D_{2d}$ - $\text{Cu}^{\text{I}}$  and pseudo- $D_{3h}$ - $\text{Cu}^{\text{II}}$  structurally activate within the encounter complex, without dissociation of the solvent molecule from  $\text{Cu}^{\text{II}}$  (Scheme 3-3). As noted above, the time scale for the bond stretching between  $\text{Cu}^{\text{II}}$  and the solvent molecule (without the bond rupture) by the *E* mode ( $10^{-13}$  s), together with the *partial* twisting through the normal  $B_2$  mode ( $10^{-11}$ – $10^{-13}$  s), is sufficiently rapid to occur within the encounter complex. However, this type of activation leads

**Scheme 3.** Modes of the Electron Self-Exchange Reaction between  $[\text{Cu}(\text{dmp})_2(\text{solvent})]^{2+}(\text{pseudo-}D_{3h})$  and  $[\text{Cu}(\text{dmp})_2]^{+}(D_{2d})^2$ **Scheme 4.** Reactions Involving a  $[\text{Cu}(\text{dmp})_2(\text{solvent})]^{2+}/[\text{Cu}(\text{dmp})_2]^{+}$  Couple

the ET reaction *only when the electronic coupling between the two reactants is sufficiently large*. We believe that the electronic coupling between  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^{+}$  is sufficiently large because the energy levels of the d orbitals are much closer to each other compared with those for the cross-reactions of  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  with other metals. Such a situation was demonstrated by the previously reported pseudo-self-exchange reaction between  $[\text{Cu}(\text{dmbp})_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^{+}$ .<sup>11</sup>

It seems that the smaller self-exchange rate constant for the  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}/[\text{Cu}(\text{dmp})_2]^{+}$  couple, ca.  $10^3 \text{ M}^{-1} \text{ s}^{-1}$ , than those for blue copper proteins such as plastocyanin or azurin, ca.  $10^5\text{--}10^6 \text{ M}^{-1} \text{ s}^{-1}$ , is a result of the extensive inner-sphere rearrangement within the encounter complex including (1) the elongation of the Cu<sup>II</sup>–solvent bond to induce structural activation to the  $C_{2v}$  structure and (2) the deformation of Cu<sup>I</sup> to  $C_{2v}$ , probably with the partial interaction of  $C_{2v}$ -Cu<sup>I</sup> with the solvent molecule that is to be released from  $C_{2v}$ -Cu<sup>II</sup>. The self-exchange rate constants estimated from the oxidation cross-reactions are almost always consistent with or slightly larger than the directly measured value by using NMR.<sup>8,26</sup> The difference in the activation free energies for the concerted process and for the reaction through the product excited state (path B) may have been obscured by the uncertainty inherent in the Marcus cross-relation (up to 2 orders of the magnitude for the estimated self-exchange rate constant). The redox reactions involving the  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}/[\text{Cu}(\text{dmp})_2]^{+}$  couple are summarized in Scheme 4.

## Appendix A

The gate behavior in the reduction reactions of  $[\text{Cu}(\text{dmp})_2]^{2+}$  was well established in the previous articles.<sup>8–11</sup> The hypothetical self-exchange rare constant ( $1.6 \text{ M}^{-1} \text{ s}^{-1}$ ), which was calculated by application of the Marcus cross-relation to the reduction cross-reaction by  $[\text{Co}(\text{bipy})_3]^{2+}$ , indicates that the reduction reaction is controlled by the structural change prior to the ET process because it is too small compared with the hypothetical self-exchange rate constant estimated from the oxidation cross-reactions.

## Appendix B

For the direct self-exchange reaction, three independent pathways may be considered in the current situation: (1) path B', in which structural change of only Cu<sup>II</sup> takes place prior to the ET process, (2) path A', in which the ET process takes place without structural change in both Cu<sup>I</sup> and Cu<sup>II</sup>, or (3) the concerted process (a process that involves the structural change of Cu<sup>I</sup> prior to the ET process may not have to be considered because this process requires much higher energy than path B'). When a nonconcerted self-exchange reaction takes place, the reaction profile should be symmetric along the reaction coordinate. Because the reaction profile of path A' does not fulfill this requirement (path A' corresponds to the middle figure in Scheme 3), the reaction through path A' is not allowed to occur. On the other hand, path B' is allowed as the nonconcerted process, according to the left-hand figure in Scheme 3.

Path B' is possible when the electronic coupling between the Cu<sup>II</sup> and Cu<sup>I</sup> species is not sufficient: this corresponds to the gated self-exchange process.<sup>8</sup> In such a case, it is known that the self-exchange rate constant is expressed by  $k_{\text{ex}} = K_{\text{OQ}}k_{\text{ET}}$ . Although  $K_{\text{OQ}}$  is small ( $\sim 10^{-5}$ ),  $k_{\text{ET}}$  may be large enough (ca.  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), and  $k_{\text{ex}}$  may not be distinguishable from the value expected for the concerted process (ca.  $10^3 \text{ M}^{-1} \text{ s}^{-1}$ ). On the other hand, the contribution of  $K_{\text{OQ}}$  may be clearly observed when the volume analysis of the reaction is carried out: the volume contribution of  $k_{\text{ET}}$  is expected to be small (ca.  $-3$  to  $-5 \text{ cm}^3 \text{ mol}^{-1}$ ) from the theory. In this study, it was shown that the volume

(26) Clemmer, J. D.; Hogaboom, G. K.; Holwerda, R. A. *Inorg. Chem.* **1979**, *18*, 2567–2572.

*Volume Profiles Involving [Cu(dmp)<sub>2</sub>(solvent)]<sup>2+</sup>/[Cu(dmp)<sub>2</sub>]<sup>+</sup>*

contribution of  $K_{OQ}$  is ca.  $-9 \text{ cm}^{-3} \text{ mol}^{-1}$ . Therefore, the overall activation volume should be ca.  $-12$  to  $-14 \text{ cm}^3 \text{ mol}^{-1}$  when the direct self-exchange reaction proceeds through path B'. On the other hand, the reported activation volume from the measurement of the direct self-exchange reaction is only  $-3.4 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>17</sup> Therefore, it is clear that the direct self-exchange reaction between  $[\text{Cu}(\text{dmp})_2(\text{solvent})]^{2+}$  and  $[\text{Cu}(\text{dmp})_2]^+$  proceeds through the concerted process.

**Supporting Information Available:** The pressure dependence of the electrode potential for the redox couples in acetonitrile (Table S1), the pressure dependence of the rate constant for the cross-reaction between  $[\text{Cu}(\text{dmp})_2]^+$  and  $[\text{Ni}(\text{tacn})_2]^{3+}$  in acetonitrile (Table S2), and the pressure dependence of the rate constant for the cross-reaction between  $[\text{Cu}(\text{dmp})_2]^{2+}$  and  $[\text{Co}(\text{bipy})_3]^{2+}$  in acetonitrile (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC061591I