Inorg. Chem. **1999,** *38,* 3352−3360

An Interpretation of Gated Behavior: Kinetic Studies of the Oxidation and Reduction Reactions of Bis(2,9-dimethyl-1,10-phenanthroline)copper(I/II) in Acetonitrile

Nobuyoshi Koshino, Yoshio Kuchiyama, Hiroshi Ozaki, Shigenobu Funahashi, and Hideo D. Takagi*

Inorganic and Analytical Chemistry Division, Department of Chemistry and Physics, Graduate School of Sciences, Nagoya University, Furocho, Chikusa, Nagoya, 464-8602 Japan

Received September 4, 1998

Reduction reactions of $Cu(dmp)_2^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) by ferrocene ($Fe(Cp)_2$ = bis(cyclopentadienyl)iron(II)), decamethylferrocene ($Fe(PMCp)_2$ = bis(pentamethylcyclopentadienyl)iron(II)), and $Co(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and oxidation reactions of $Cu(dmp)_2^{+}$ by $Ni(tacn)_2^{3+}$ (tacn = 1,4,7-triazacyclononane) and $Mn(bpyO_2)_3^{3+}$ ($bpyO_2$ = *N*,*N*′-dioxo-2,2′-bipyridine) were studied in acetonitrile for the purpose of interpreting the gated behavior involving copper(II) and -(I) species. It was shown that the electron self-exchange rate constants estimated for the $Cu(dmp)_2^{2+/+}$ couple from the oxidation reaction of $Cu(dmp)_2^{+}$ by $Ni(tacn)_2^{3+}$ (5.9×10^2 kg mol^{-1} s^{-1}) and $Mn(bpyO_2)_3^{3+}$ (2.9×10^4 kg mol^{-1} s^{-1}) were consistent with the directly measured value by NMR (5×10^3 kg mol^{-1} s^{-1}). In contrast, we obtained the electron self-exchange rate constant of $Cu(dmp)_2^{2+/+}$ as 1.6 kg mol^{-1} s^{-1} from the reduction of $Cu(dmp)_2^{2+}$ by $Co(bpy)_3^{2+}$. The pseudo-first-order rate constant for the reduction reaction of $Cu(dmp)_2^{2+}$ by $Fe(Cp)_2$ was not linear against the concentration of excess amounts of $Fe(Cp)_2$. A detailed analysis of the reaction revealed that the reduction of $Cu(dmp)_2^{2+}$ involved the slow path related to the deformation of $Cu(dmp)_2^{2+}$ (path B in Scheme 1). By using $Fe(PMCp)_2$ (the $E°$ value is 500 mV more negative than that of $Fe(Cp)_2^{+/0}$) as the reductant, the mixing with another pathway involving deformation of $Cu(dmp)_2^{+}$ (path A in Scheme 1) became more evident. The origin of the “Gated Behavior” is discussed by means of the energy differences between the “normal” and deformed Cu(II) and Cu(I) species: the difference in the crystal field activation energies corresponding to the formation of pseudo-tetrahedral Cu(II) from tetragonally distorted Cu(II) and the difference in the stabilization energies of the tetrahedral and tetragonal Cu(I) for the activation of Cu(I) species. The reduction reaction of $Cu(dmp)_2^{2+}$ by $Fe(PMCp)_2$ confirmed that the mixing of the two pathways takes place by lowering the energy level corresponding to the less favorable conformational change of Cu(I) species.

Introduction

Concerted inner- and outer-sphere reorganizations are assumed to occur for most of the outer-sphere electron-transfer reactions.[1,2] Therefore, the electron-transfer reaction is slow when the reaction involves a large change in the coordination geometry during the electron-transfer process. Vallee and Williams pointed out for the electron exchange reactions involving copper(II/I) couples that the rate of the electron transfer is slow for the redox couple with normally preferred coordination geometries, i.e., the tetrahedral four coordination for copper(I) and the tetragonal five- or six-coordination for copper(II).[3]

The electron-transfer regulated by the slowness of the change in coordination geometry has been reported for some copper(II/I) couples with tetrathiamacrocyclic ligands.[4−8] Rorabacher et al. precisely explored such “gated behavior” caused by sluggishness in the geometric interconversion and discovered that the oxidation of tetrahedral Cu(I) to tetragonal Cu(II) is slow in most cases when macrocyclic thioether ligands were used. In such cases, the electron exchange rate constant estimated by the application of the Marcus cross relation to the oxidation reaction of Cu(I) was not consistent with the directly measured electron exchange rate constant by using NMR. However, when the energy required for the geometric change from the tetrahedral to the tetragonal structure is not large, such gated behavior diminishes and the Marcus cross relation is successfully applied to the estimation of the self-exchange rate constant.[9]

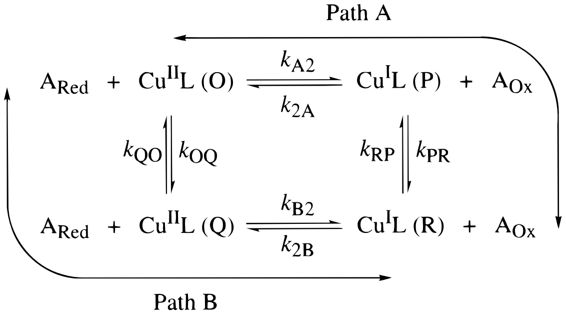
Early works on the outer-sphere reactions of copper cpmplexes centered on reactions of $Cu(bpy)_2^{2+/+}$, $Cu(phen)_2^{2+/+}$, and its derivative $Cu(dmp)_2^{2+/+}$.[10−12] In 1983, Lee and Anson pointed out that the steric interconversion may have an important

---

(1) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(2) Cannon, R. D. *Electron-Transfer Reactions*; Butterworth: London, 1980.
(3) Vallee, B. L.; Williams, R. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *58*, 498.
(4) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012.
(5) Meagher, N. E.; Juntunen, K. L.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 10411.
(6) 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.
(7) Meagher, N. E.; Juntunen, K. L.; Heeg, M. J.; Salhi, C. A.; Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1994**, *33*, 670.
(8) Salhi, C. A.; Yu, Q.; Heeg, M. J.; Villeneuve, N. M.; Juntunen, K. L.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 6053.
(9) Vande Linde, A. M. Q.; Westerby, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1993**, *32*, 251.
(10) Yoneda, G. S.; Blackmer, G. L.; Holwerda, R. A. *Inorg. Chem.* **1977**, *16*, 3376.
(11) Augustin, M. A.; Yandell, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 370.

10.1021/ic9810687 CCC: $18.00

Scheme 1



role in the electron-transfer processes of the $Cu(bpy)_2{}^{2+/+}$ and $Cu(phen)_2{}^{2+/+}$ couples.[13] The studies of electron-transfer reactions for $Cu(dmp)_2{}^{2+/+}$ with various reaction partners in aqueous solution were reported.[14-19] The studies of the reduction of the water-soluble $Cu(dpsmp)_2{}^{2-}$ (dpsmp = 2,9-dimethyl-4,7-bis-((sulfonyloxy)phenyl)-1,10-phenanthroline) by Sykes et al. indicated the involvement of such steric interconversion.[20-22] However, there are some cases where electron exchange is slow even for the near-tetrahedral Cu(II/I) couples.[23-25] Most recently Stanbury et al. reported the slow electron-exchange reaction of $Cu(bib)_2{}^{2+/+}$ (bib = 2,2′-bis(2-imidazoly)biphenyl).[26] The estimated electron self-exchange rate constant of $Cu(bid)_2{}^{2+/+}$ is 0.16 kg mol^{-1} s^{-1}. Takagi and Swaddle have been studying Cu(II/I) electron-exchange couples by NMR where the coordination geometries of Cu(I) and Cu(II) are constrained to be similar, the kinetic behavior is expected to follow the context of the moderately fast electron-transfer case, and no significant change in coordination number or coordination geometry was expected prior to the electron-transfer processes.[27,28]

The gated electron-transfer process has been successfully interpreted by the square scheme, postulated by Rorabacher et al., as shown in Scheme 1. The theoretical studies of the gated electron transfer have been reported.[29,30] However, the energetic origin of conformational change has not yet been well understood to date. In this article, we have observed inconsistency of the electron exchange rate constants estimated from the oxidation and reduction cross reactions involving sterically constrained complex ions, $Cu(dmp)_2{}^{2+/+}$. The results indicate that the electron-transfer reactions of $Cu(dmp)_2{}^{2+/+}$ proceed through path B. The energetic origin of the "gated behavior" is explained on the basis of the ligand field activation energy corresponding to the deformation of $Cu(dmp)_2{}^{2+}$, and the energetic inter-mixing of the two independent reaction pathways corresponding to path A and path B for the $Cu(dmp)_2{}^{2+/+}$ redox couple was demonstrated in acetonitrile. The expression for the electron self-exchange rate constant was derived for path B in Scheme 1, and the estimated electron self-exchange rate constant for the $Cu(dmp)_2{}^{2+/+}$ couple was compared with that reported previously.[27] The free-energy profile of the gated electron-transfer process involving $Cu(dmp)_2{}^{2+/+}$ was discussed on the basis of the experimental and calculated results.

Experimental Section

Chemicals. Acetonitrile was obtained from Wako Pure Chemicals Inc. and purified by distillation twice from phosphorus pentoxide. The content of the residual water in thus purified acetonitrile was examined by a Mitsubishi Kasei CA01 Karl Fischer apparatus, by which the amount of residual water was determined to be less than 1 mmol/dm^3. Ferrocene (Wako) and decamethylferrocene (Aldrich) were purified by sublimation. All other chemicals from Wako and Aldrich were used without further purification. $Cu(dmp)_2(ClO_4)_2$ and $Cu(dmp)_2ClO_4$ were synthesized by reported methods.[27,31] Anal. Calcd for $CuC_{28}H_{24}N_4Cl_2O_8$: C, 49.5; N, 8.25; H, 3.56. Found: C, 50.5; N, 8.16; H, 3.65. Anal. Calcd for $CuC_{28}H_{24}N_4ClO_4$: C, 58.0; N, 9.67; H, 4.17. Found: C, 58.6; N, 9.87; H, 4.10.

$[Co(bpy)_3](ClO_4)_2$,[32] $[Ni(tacn)_2](ClO_4)_3$,[33] and $[Mn(bpyO_2)_3](ClO_4)_2$[34] were synthesized by literature methods. Anal. Calcd for $CoC_{30}H_{24}N_6Cl_2O_8$: C, 49.6; H, 3.33; N, 11.6. Found: C, 50.0; H, 3.23; N, 11.6. Anal. Calcd for $NiC_{12}H_{30}N_6Cl_3O_{12}$: C, 23.42; H, 4.91; N, 13.66. Found: C, 23.42; H, 4.96; N, 13.55. Anal. Calcd for $MnC_{30}H_{24}N_6O_{14}Cl_2$: C, 44.0; H, 2.96; N, 10.3. Found: C, 43.2; H, 2.87; N, 9.87. (**Caution!** *Perchlorate salts of metal complexes with organic ligands are potentially explosive.*)

General. All manipulations were carried out in an atmosphere of dry nitrogen to avoid any possible contamination of water and oxygen from the environment. A Unisoku stopped-flow apparatus was used for the kinetic measurements at various temperatures controlled by a Hetofrig circulation bath. The reservoirs for the reactant solutions were kept under nitrogen atmosphere during the experiments. At least 10 kinetic traces were collected for each run, and the results were analyzed by an NEC personal computer fitted with an interface for the stopped-flow apparatus. Unisoku software was used for the data analysis. Preliminary experiments revealed that $Cu(dmp)_2{}^{2+}$ releases a small amount of dmp after several hours. However, this decomposition was suppressed successfully by the addition of excess amounts of dmp in the solution. Moreover, no electroactive species other than $Cu(dmp)_2{}^{2+}$ was observed within the redox window of acetonitrile (-2 V ∼ $+2$ V) by cyclic voltammetry, which strongly indicates that neither $Cu(dmp)^{2+}$ nor Cu^{2+} produced by the decomposition of $Cu(dmp)_2{}^{2+}$ oxidizes ferrocene or decamethylferrocene used in this study. The absorbance increase at *ca.* 456 nm, corresponding to the absorption maximum of $Cu(dmp)_2{}^{+}$, was monitored for the kinetic measurements.

---

(12) Yandell, J. K. *Copper Coordination Chemistry*: Biochemical and Inorganic Perspectives; Adenine Press: Guilderland, NY, 1983; p 157 and references therein.
(13) Lee, C.-W.; Anson, F. C. *J. Phys. Chem.* **1983**, *87*, 3360.
(14) Augustin, M. A.; Yandell, J. K. *Inorg. Chem.* **1979**, *18*, 577.
(15) Clemmer, J. D.; Hogaboom, G. K.; Holwerda, R. A. *Inorg. Chem.* **1979**, *18*, 2567.
(16) Holwerda, R. A. *Inorg. Chem.* **1982**, *21*, 2107.
(17) Davies, K. M. *Inorg. Chem.* **1983**, *22*, 615.
(18) Davies, K. M.; Byers, B. *Inorg. Chem.* **1987**, *26*, 3823.
(19) Lappin, A. G.; Youngblood, M. P.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 407.
(20) Al-Shatti, N.; Lappin, A. G.; Sykes, A. G. *Inorg. Chem.* **1981**, *20*, 1466.
(21) Leupin, P.; Al-Shatti, N.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1982**, 927.
(22) Allan, A. E.; Lappin, A. G.; Laranjeira, M. C. M. *Inorg. Chem.* **1984**, *23*, 477.
(23) Lappin, A. G.; Peacock, R. D. *Inorg. Chim. Acta* **1980**, *46*, L71.
(24) Knapp, S.; Keenan, T. P.; Zhang, X.; Fikar, R.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1990**, *112*, 3452.
(25) Flanagan, S.; Dong, J.; Haller, K.; Wang, S.; Scheidt, W. R.; Scott, R. A.; Webb, T. R.; Stanbury, D. M.; Wilson, L. J. *J. Am. Chem. Soc.* **1997**, *119*, 8857.
(26) Xie, B.; Elder, T.; Wilson, L. J.; Stanbury, D. M. *Inorg. Chem.* **1999**, *38*, 12.
(27) Doine (Takagi), H.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1989**, *28*, 2319.
(28) Metelski, P. D.; Hinman, A. S.; Takagi, H. D.; Swaddle, T. W. *Can. J. Chem.* **1995**, *73*, 61.
(29) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237.
(30) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7457. The authors of refs 29 and 30 dealt with the energetics of the gated *intramolecular* electron-transfer processes and concluded that the process with high energy intermediate never compete with the direct outer-sphere process. However, the reactions investigated in this study and by Rorabacher *et al.* involve intermolecular electron-transfer process after deformation of one of the reactants.
(31) Davies, G.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 694.
(32) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.
(33) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, *23*, 1938.
(34) Simpson, P. G.; Vinciguerra, A.; Quagliano, J. V. *Inorg. Chem.* **1963**, *2*, 283.

Table 1. Calculated Electron Self-Exchange Rate Constants for $Cu(dmp)_2^{2+/+}$ at 298 K in Acetonitrile[a]

	$E°$/V vs $Fc^{+/0}$	r/pm	k_{12}[b]	k_{22}[c]	k_{11}[d]	ΔH*/kJ mol^{-1}	ΔS*/J mol^{-1} K^{-1}
$Cu(dmp)_2^{2+} + Cu(dmp)_2^{+}$	0.28	650	−	−	5.0×10^3 [e]	28 ± 1	−81 ± 4
oxidant							
$Ni(tacn)_2^{3+}$	0.555	380	$(2.7 \pm 0.2) \times 10^5$	6.0×10^3 [f]	5.9×10^2	24 ± 1	−60 ± 2
$Mn(bpyO_2)_3^{3+}$	0.435	400	$(2.9 \pm 0.1) \times 10^4$	80[g]	2.9×10^4	−	−
reductant							
$Co(bpy)_3^{2+}$	−0.081	700	$(7.0 \pm 0.2) \times 10^2$	0.645[h]	1.6	36 ± 2	−68 ± 6

[a] Ionic strength of the solutions was adjusted to 0.1 mol kg^{-1} by $(n\text{-}Bu_4N)ClO_4$. [b] The rate constant for each cross reaction (kg mol^{-1} s^{-1}). [c] The self-exchange rate constant for oxidizing or reducing reagent (kg mol^{-1} s^{-1}). [d] The self-exchange rate constant for $Cu(dmp)_2^{2+/+}$ (kg mol^{-1} s^{-1}). [e] Reference 27. [f] Macartney, D. H. *Inorg. Chim. Acta* **1987**, *127*, 9. [g] Macartney, D. H.; Thompson, D. W. *J. Chem. Res., Synop.* **1992**, 344. [h] Reference 58.

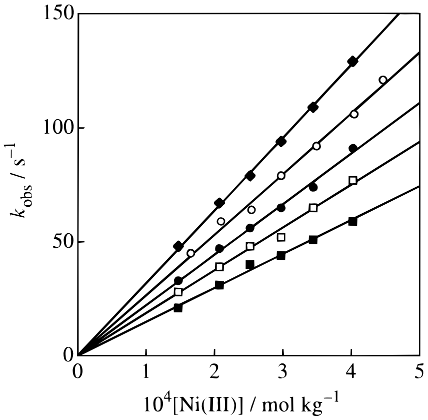


Figure 1. Dependence of k_{obs} on the concentration of $Ni(tacn)_2^{3+}$ for the oxidation reaction of $Cu(dmp)_2^{+}$. $[Cu(dmp)_2^{+}] = 1.50 \times 10^{-5}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). The symbols represent the data obtained at 303.2 (closed lozenges), 298.2 (open circles), 293.2 (closed circles), 288.2 (open squares), and 283.2 K (closed squares).

Electrochemical measurements were carried out by a BAS 100BW electrochemical analyzer with a 1.5 mm ϕ platinum disk or glassy carbon as the working electrode, and a 0.5 mm ϕ platinum wire as the counter electrode. A silver/silver nitrate electrode with 0.1 mol kg^{-1} tetrabutylammonium perchlorate (TBAP) in acetonitrile was used as a reference electrode. A solution of $Mn(bpyO_2)_3^{3+}$ was prepared electrochemically in CH_3CN, containing 0.10 mol kg^{-1} TBAP at carbon electrode (Hokuto Denko HX-201).

Results

Oxidation Reactions of $Cu(dmp)_2^{+}$ by $Ni(tacn)_2^{3+}$ and $Mn(bpyO_2)_3^{3+}$. The reaction of $Cu(dmp)_2^{+}$ with $Ni(tacn)_2^{3+}$ in acetonitrile shows pseudo-first-order behavior up to 3 half-lives under conditions where $[Cu(dmp)_2^{+}]_0 \ll [Ni(tacn)_2^{3+}]_0$.

$$Cu(dmp)_2^{+} + \text{oxidant} \xrightarrow{k_{Ox}} Cu(dmp)_2^{2+} + \text{reductant} \quad (1)$$

$$rate = k_{Ox}[Cu(dmp)_2^{+}][\text{oxidant}] \quad (2)$$

Figure 1 shows the dependence of k_{obs} ($=k_{Ox}$[oxidant]) on the concentration of $Ni(tacn)_2^{3+}$ at various temperatures. The second-order rate constant at 298 K, $I = 0.1$ mol kg^{-1} is listed in Table 1, together with the activation parameters of the reaction. The reaction of $Cu(dmp)_2^{+}$ with $Mn(bpyO_2)_3^{3+}$ was observed under the conditions of $[Cu(dmp)_2^{+}]_0 \gg [Mn(bpyO_2)_3^{3+}]_0$. The estimated electron self-exchange rate constants for the $Cu(dmp)_2^{2+/+}$ couple by the Marcus cross relation from the oxidation reactions of $Cu(dmp)_2^{+}$ by $Ni(tacn)_2^{3+}$ and $Mn(bpyO_2)_3^{3+}$ were 5.9×10^2 and 2.9×10^4 kg mol^{-1} s^{-1}, respectively. These values were in agreement with the reported value (5.0×10^3 kg mol^{-1} s^{-1}) obtained from the NMR measurement considering the accuracy of the Marcus relation.[35,36]

Reduction Reaction of $Cu(dmp)_2^{2+}$ by $Co(bpy)_3^{2+}$. The reaction was observed under the conditions of $[Cu(dmp)_2^{2+}]_0 \gg [Co(bpy)_3^{2+}]_0$. The monitored absorption increase at 456 nm for every run confirmed that the decomposition of $Co(bpy)_3^{2+}$ before mixing was minimal. The kinetic trace was satisfactorily first-order for up to 3 half-lives. The dependence of the pseudo-first-order rate constant on the concentration of $Cu(dmp)_2^{2+}$ was linear at various temperatures as shown in Figure 2. The second-order rate constant at 298 K and the corresponding activation parameters are listed in Table 1. From the reduction of $Cu(dmp)_2^{2+}$ by $Co(bpy)_3^{2+}$, we obtained the self-exchange rate constant of $Cu(dmp)_2^{2+/+}$ as 1.6 kg mol^{-1} s^{-1}. This value is smaller than those estimated from the NMR measurement and from the oxidation reactions of $Cu(dmp)_2^{+}$, which strongly indicates that the reduction of $Cu(dmp)_2^{2+}$ is "gated." As it is shown later, this reaction is also gated through path B: $k_{B2}[Co(bpy)_3^{2+}] \ll k_{QO}$ in Scheme 1.

Reduction Reaction of $Cu(dmp)_2^{2+}$ by $Fe(Cp)_2$. The kinetic traces were excellently first-order for $Cu(dmp)_2^{2+}$ up to 3 half-lives.

$$\frac{d[Cu(dmp)_2^{+}]}{dt} = k_{obs}[Cu(dmp)_2^{2+}] \quad (3)$$

$$[Fe(Cp)_2]_0 \gg [Cu(dmp)_2^{2+}]_0$$

However, the dependence of k_{obs} on the concentration of $Fe(Cp)_2$ was not linear. This tendency may be explained by the following two-step mechanism including a conformational change of Cu(II) *prior to* the fast outer-sphere electron-transfer reaction (k_{B2}).

$$Cu(dmp)_2^{2+} \underset{k_{QO}}{\overset{k_{OQ}}{\rightleftharpoons}} Cu(dmp)_2^{2+}* \quad (4)$$

$$Cu(dmp)_2^{2+}* + A_{Red} \xrightarrow{k_{B2}} Cu(dmp)_2^{+} + A_{Ox} \quad (5)$$

where A_{Red} and A_{Ox} represent $Fe(Cp)_2$ and $Fe(Cp)_2^{+}$, respectively. When the reduction reaction is gated as suggested from the results for the reaction with $Co(bpy)_3^{2+}$, the conformational change corresponding to the k_{OQ} process may be slow. In such a case, the rate law is expressed by eq 6.

$$rate = \frac{k_{B2}k_{OQ}}{k_{B2}[A_{Red}] + k_{QO}}[A_{Red}][Cu^{II}L] = k_{obs}[Cu^{II}L] \quad (6)$$

Therefore, the plot of the reciprocal value of k_{obs} against $[A_{Red}]^{-1}$

---

(35) Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems*; Oxford University Press: New York, 1991.
(36) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: New York, 1991.

Table 2. Estimated Rate Constants for the Reactions of $Cu(dmp)_2^{2+}$ at 298 K[a]

reaction		
$Cu(dmp)_2^{2+} + Fe(Cp)_2$[b]	k_{OQ}	$33 \pm 3\ s^{-1}$
	k_{QO}[c]	$7.7 \times 10^7\ s^{-1}$
	$k_{OQ}/k_{QO} = K_{OQ}$[c]	4.3×10^{-7}
	k_{B2}[c]	3.0×10^{11} kg mol^{-1} s^{-1}
$Cu(dmp)_2^{2+} + Fe(PMCp)_2$[d]	k_{B2}	$(3.2 \pm 0.1) \times 10^{12}$ kg mol^{-1} s^{-1}
	k_{A2}	$(2.5 \pm 0.1) \times 10^4$ kg mol^{-1} s^{-1}

[a] Ionic strength of the solutions was adjusted to 0.1 mol kg^{-1} by $(n\text{-}Bu_4N)ClO_4$. [b] The rate constant were estimated from the slope and the intercept of Figure 3. [c] Calculated from the estimated value of the electron self-exchange rate constant for $Cu(dmp)_2^{2+*/+}$ (see text). [d] The rate constants were obtained by the least-squares analysis of the plot in Figure 4. k_{OQ} and k_{QO} values were fixed for the least-squares calculation.

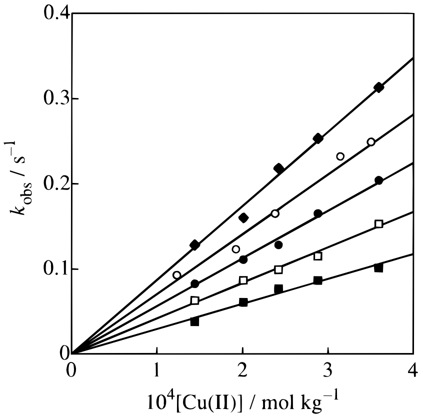


Figure 2. Dependence of k_{obs} on the concentration of $Cu(dmp)_2^{2+}$ for the reduction reaction of $Cu(dmp)_2^{2+}$ by $Co(bpy)_3^{2+}$. $[Co(bpy)_3^{2+}] = 1.50 \times 10^{-5}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). The symbols represent the data obtained at 302.9 (closed lozenges), 298.0 (open circles), 293.2 (closed circles), 288.1 (open squares), and 283.1 K (closed squares).

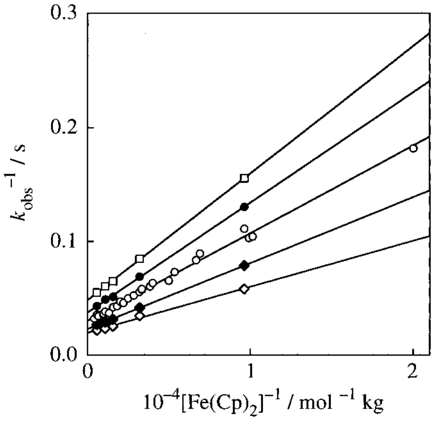


Figure 3. Plot of k_{obs}^{-1} vs $[Fe(Cp)_2]^{-1}$ for the reduction reaction of $Cu(dmp)_2^{2+}$ by $Fe(Cp)_2$. $[Cu(dmp)_2^{2+}] = 4.87 \times 10^{-6}-1.05 \times 10^{-5}$ mol kg^{-1}, $[dmp]_{free} = (1.0-1.1) \times 10^{-4}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). The symbols represent the data obtained at 308.2 (open lozenges), 303.2 (closed lozenges), 298.2 (open circles), 293.2 (closed circles), and 288.2 K (open squares).

should be linear with an intercept when $[A_{Red}]_0 \gg [Cu(dmp)_2^{2+}]_0$.

$$\frac{1}{k_{obs}} = \frac{k_{QO}}{k_{OQ}k_{B2}[A_{Red}]} + \frac{1}{k_{OQ}} \qquad (7)$$

The plots of $1/k_{obs}$ vs $1/[Fe(Cp)_2]_0$ at various temperatures are shown in Figure 3. The values of k_{OQ}, ΔH^*, and ΔS^* are 33 ± 3 s^{-1}, 31 ± 2 kJ mol^{-1}, and −110 ± 10 J mol^{-1} K^{-1}, respectively.

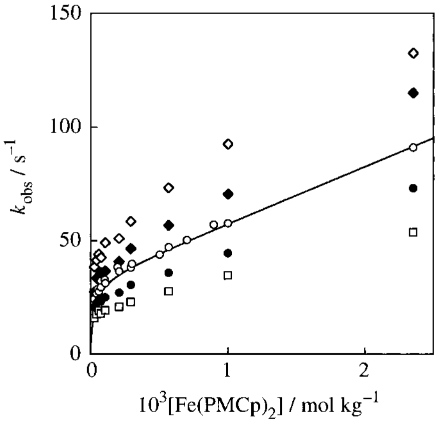


Figure 4. Dependence of k_{obs} on the concentration of $Fe(PMCp)_2$ for the reduction reaction of $Cu(dmp)_2^{2+}$. $[Cu(dmp)_2^{2+}] = 5.56 \times 10^{-6}-1.01 \times 10^{-5}$ mol kg^{-1}, $[dmp]_{free} = (0.53-2.0) \times 10^{-4}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). Symbols are as in Figure 3.

Reduction Reaction of $Cu(dmp)_2^{2+}$ by $Fe(PMCp)_2$. The reduction reaction of $Cu(dmp)_2^{2+}$ by $Fe(PMCp)_2$ also shows pseudo-first-order behavior up to 3 half-lives under conditions where $[Cu(dmp)_2^{2+}]_0 \ll [Fe(PMCp)_2]_0$. However, the plot of k_{obs} against the initial concentration of $Fe(PMCp)_2$ showed curvatures as shown in Figure 4. Such curvature was reported previously by Rorabacher et al., for the oxidation reaction of Cu^I-thioether complex.[5,7,8] The dependence in Figure 4 may be explained by the "mixing" of both path B and path A caused by the 500 mV more negative potential of $Fe(PMCp)_2^{+/0}$ as discussed later. In such case, k_{obs} is expressed by eq 8, using the rate constants in Scheme 1.

$$k_{obs} = \left(k_{A2} + \frac{k_{OQ}k_{B2}}{k_{B2}[A_{Red}] + k_{QO}}\right)[A_{Red}] \qquad (8)$$

The best-fit values of each rate constant estimated by the least-squares analysis (a curve fitting program, SIGMA PLOT) are listed in Table 2.

Discussion

Application of Square Scheme. Rorabacher et al. tried to explain the "gated" electron transfer for copper-cyclic thioether ions using the mechanisms described in Scheme 1.[4-8] They found that the reactions proceed mostly through path A for the copper-thioether complexes by comparing the electron exchange rate constants estimated from both the reduction and oxidation cross reactions.

In this study, the electron self-exchange rate constant for the $Cu(dmp)_2^{2+/+}$ couple was estimated from both the oxidation reactions of $Cu(dmp)_2^+$ by $Ni(tacn)_2^{3+}$ and $Mn(bpyO_2)_3^{3+}$ and the reduction reaction of $Cu(dmp)_2^{2+}$ by $Co(bpy)_3^{2+}$. By using the Marcus cross relation, the estimated self-exchange rate constants were 5.9×10^2 and 2.9×10^4 kg mol^{-1} s^{-1} from the results of the oxidation reactions, while the result for the reduction reaction gave merely 1.6 kg mol^{-1} s^{-1}. As the electron exchange rate constant directly measured by the NMR method is 5 × 10^{3} kg mol^{-1} s^{-1},[27] it is obvious that the reaction involving the $Cu(dmp)_2^{2+/+}$ couple is also "gated," and the preferred pathway for the redox reaction of this couple is path B in Scheme 1. The results for the reduction reaction of $Cu(dmp)_2^{2+}$ by $Fe(Cp)_2$ also strongly indicates that the reaction is "gated" and proceeds through path B in Scheme 1.

According to Scheme 1, Rorabacher et al. derived rate laws for oxidation and reduction reactions corresponding to path A and path B as follows, by assuming steady state for the concentrations of the intermediates, $Cu^{II}L(Q)$ and $Cu^{I}L(P)$.[4,5]

Reduction Reaction

$$-\frac{d[Cu^{II}L]}{dt} = \left(\frac{k_{A2}k_{PR}}{k_{2A}[A_{Ox}] + k_{PR}} + \frac{k_{B2}k_{OQ}}{k_{B2}[A_{Red}] + k_{QO}}\right) \times [Cu^{II}L(O)][A_{Red}] \quad (9)$$

Oxidation Reaction

$$-\frac{d[Cu^{I}L]}{dt} = \left(\frac{k_{2A}k_{RP}}{k_{2A}[A_{Ox}] + k_{PR}} + \frac{k_{2B}k_{QO}}{k_{B2}[A_{Red}] + k_{QO}}\right) \times [Cu^{I}L(R)][A_{Ox}] \quad (10)$$

where A_{Red} and A_{Ox} denote the reducing reagent and the oxidizing reagent, respectively. When the reactions proceed through path B, the rate laws are expressed by the second term of the right-hand side of eqs 9 and 10. As the reduction of $Cu(dmp)_2^{2+}$ is "gated" through path B, the rate law is expressed by eq 6. In the case where the reaction corresponding to k_{OQ} is slow, the reverse reaction for the conformational change in Cu(II) species, k_{QO}, may be very fast. The validity of this assumption is given later. When the concentration of A_{Red} is large enough, the two processes, $k_{B2}[A_{Red}]$ and k_{QO} start to compete. Therefore, the slope of the plot in Figure 3 corresponds to $k_{QO}/k_{OQ}k_{B2}$ ($=1/K_{OQ}k_{B2}$). On the other hand, when the concentration of A_{Red} is small compared with $[Cu^{II}L]$, i.e., $k_{B2}[A_{Red}] \ll k_{QO}$, the rate law is reduced to eq 11 and the dependence of the pseudo-first-order rate constant on the concentration of $Cu^{II}L$ is linear as seen for the reaction of $Cu(dmp)_2^{2+}$ with $Co(bpy)_3^{2+}$.

$$k_{obs} = \left(\frac{k_{OQ}k_{B2}}{k_{QO}}\right)[Cu^{II}L] \quad (11)$$

Similar results to those shown in Figure 3 were reported by Sykes et al. for the reaction of $Cu(dpsmp)_2^{2-}$.[20,21] The rate constant (k_{OQ}) for the conformational change of $Cu(dpsmp)_2^{2-}$ was reported as *ca*. 140 s^{-1}. The difference of k_{OQ} for the deformation of $Cu(dmp)_2^{2+}$ and $Cu(dpsmp)_2^{2-}$ may be attributed to the difference in the basicity of dmp and dpsmp^{2-} ligands: in the studies of $Cu(dmp)_2^{2+}$ and $Cu(dpsmp)_2^{2-}$ in water, a water molecule is coordinated to Cu(II) ion where the hydrolysis constants of $Cu(dmp)_2^{2+}$ and $Cu(dpsmp)_2^{2-}$ have been obtained 5.8 and 5.3.[22,37] For the reaction of $Cu(dmp)_2^{2+/+}$ in acetonitrile, it is also likely that a solvent molecule is coordinated to $Cu(dmp)_2^{2+}$.[27] However it has been reported that the rate constant for the water exchange in the Cu^{II}-2,2′,2″-triaminotriethylamine complex is very fast (2 × 10^{5} s^{-1}).[38] Therefore, the solvent dissociation process may not compete with the k_{OQ} process. The activation entropy for the k_{OQ} process was estimated as −110 ± 10 J mol^{-1} K^{-1}. Such large negative activation entropies were also reported for several racemization reactions through the "twist" mechanism in which similar a structural change to that for the k_{OQ} process is expected.[39] As the theoretical investigation for *intramolecular* ET reactions by Brunschwig and Sutin suggests that no gated process involving conformational change of *intramolecular* ET can compete with the direct electron transfer in the *normal* region,[30] the kinetic results obtained in this study strongly indicate that the reaction involves a conformational change *prior to* the outer-sphere electron transfer.

Calculation of the Ligand Field Activation Energy. With the d^9 configuration, Cu(II) ion prefers a tetragonal structure in general.[3] When the intermediate, $Cu^{II}L(Q)$, is the same for reduction reactions with any reductant, the Marcus type cross relation may be applicable to the k_{B2} process.[40] The deformation from ground-state Cu(II) ion to pseudo-tetrahedral Cu(II) ion lowers the crystal field stabilization energy of the Cu(II) ion and also raises the redox potential for the cross reaction to occur more rapidly. This situation is shown in Scheme 2 by assuming a tetragonal structure for O ($=Cu(dmp)_2^{2+}$) in the ground state and a pseudo-tetrahedral structure for Q ($=Cu(dmp)_2^{2+}*$).

In case of $Cu(dmp)_2^{2+}$, it has been reported that the ground state structure is originally strongly distorted from the normal tetragonal structure and the dihedral angle between the two $N-Cu^{II}-N$ planes are close to 60°.[37,41,42] Therefore $Cu(dmp)_2^{2+}$ exhibits D_{2d} symmetry. In this study, we tried to calculate the energy difference (ligand field activation energy, LFAE) between this largely deformed tetragonal ground state and the pseudo-tetrahedral state, by estimating the 10*Dq* value corresponding to the tetrahedral conformation of $Cu(dmp)_2^{2+}*$ ($4\Delta_o/9$) from the diffuse reflectance spectrum of $Cu(dmp)_2(ClO_4)_2$.[43] The observed band maxima (in cm^{-1}) for $Cu(dmp)_2(ClO_4)_2$ are listed in Table 3. For a Cu(II) species with the perfect D_{2d} symmetry, three *d*−*d* bands corresponding to the transition from $^2B_2$ to ^2E, $^2B_1$, and $^2A_1$ are predicted. Further distortion from D_{2d} to D_2 or C_s, and/or the spin−orbit coupling causes ^2E to split into Γ_6 and Γ_7.[44,45] As the strong distortion from the ordinary tetragonal structure lifts the degeneracy of all *d* orbitals,[46,47] four major absorptions corresponding to $^2B_2 \rightarrow \Gamma_7(^2E)$, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow \Gamma_6(^2E)$, and $^2B_2 \rightarrow {}^2A_1$ should appear in the visible and near-IR region. Each observed band maximum was assigned as shown in Table 3. It is assumed that the energy level for spherically symmetric CuN_4 geometry lies close to the difference in the weighted mean energy levels of *T* and *E* terms. Therefore, the tetrahedral 10*Dq* may be close to 6260 cm^{-1} for $Cu(dmp)_2^{2+}$. The octahedral 10*Dq* value for $Cu(en)_3^{2+}$ was reported as 1.64 × 10^{4} cm^{-1} by Orgel.[48] Therefore, the

---

[37] Tran, D.; Skelton, B. W.; White, A. H.; Laverman, L. E.; Ford, P. C. *Inorg. Chem.* **1998**, *37*, 2505.

[38] Rablen, D. P.; Dodgen, H. W.; Hunt, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1771.

[39] Lawrance, G. A.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 929.

[40] Ratner, M. A.; Levine, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 4898.

[41] Kuchiyama, Y.; Kobayashi, N.; Takagi, H. D. *Inorg. Chim. Acta* **1998**, *277*, 31.

[42] van Meerssche, M.; Germain, G.; Declercq, J. P. *Cryst. Struct. Commun.* **1981**, *10,* 47.

[43] Figgis, B. N. *Introduction to Ligand Fields*; John Wiley and Sons Inc.: New York, 1966.

[44] Lever, A. B. P *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984.

[45] Ferguson, J. *J. Chem. Phys.* **1964**, *40*, 3406.

[46] Gouge, E. M.; Geldard, J. F.; Sinn, E. *Inorg. Chem.* **1980**, *19*, 3356.

[47] Gouge, E. M.; Geldard, J. F. *Inorg. Chem.* **1978**, *17*, 270.

[48] Orgel, L. E. *An Introduction to Transition-Metal Chemistry*; Methuen: London, 1960.

Scheme 2. Free Energy Diagrams for the Species in the Reactions of $Cu(dmp)_2^{2+}$ with Ferrocene and Decamethylferrocene at 298 K

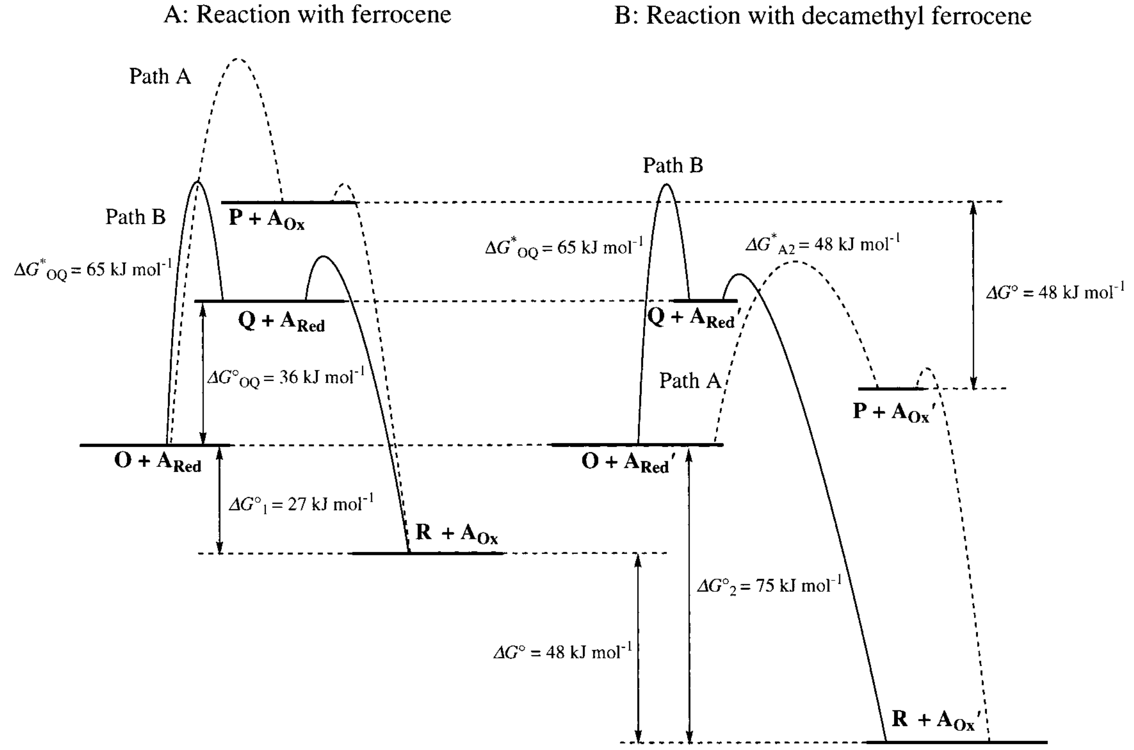
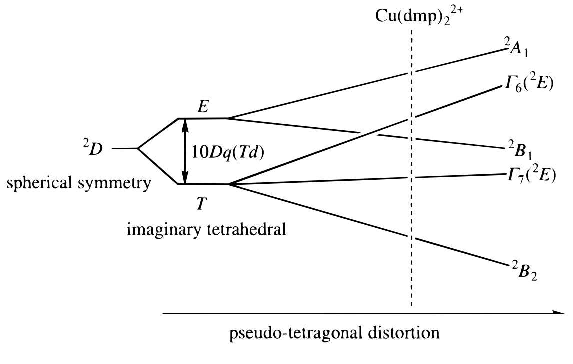


Table 3. Absorption Band Maximum for $Cu(dmp)_2(ClO_4)_2$ Observed by the Diffuse Reflectance Spectrophotometry[a]

band maximum/cm^{-1}	assignment
24390	charge transfer
13260	$^2B_2 \rightarrow {}^2A_1$
9765 (broad)	$^2B_2 \rightarrow \Gamma_6(^2E)$
9033 (shoulder)	$^2B_2 \rightarrow {}^2B_1$
5981	$^2B_2 \rightarrow \Gamma_7(^2E)$

[a] The 10*Dq* value for the imaginary tetrahedral field was estimated as 6260 cm^{-1} from the difference between the average value of the $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ transition and the average value of the energy levels of $^2B_2$, $\Gamma_7(^2E)$, and $\Gamma_6(^2E)$ (see text).



10*Dq* value for the corresponding tetrahedral CuN_4 system is 7 × 10^3 cm^{-1}. Thus the value of 6.26 × 10^3 cm^{-1} estimated for $Cu(dmp)_2^{2+}$ seems reasonable.

By using this value, the ligand field stabilization energies (LFSE) for the imaginary tetrahedral geometry and the ground-state geometry of d^9 $Cu(dmp)_2^{2+}$ are calculated as −2500 and −7600 cm^{-1} relative to the spherically symmetric geometry. Therefore, the largely distorted tetragonal structure of $Cu(dmp)_2^{2+}$ in the ground state is still ca. 61 kJ mol^{-1} more stabilized compared with perfectly tetrahedral $Cu(dmp)_2^{2+}*$, and this value can be taken as the upper limit of the enthalpy difference between $Cu(dmp)_2^{2+}$ in the ground state and the tetrahedral $Cu(dmp)_2^{2+}*$: the deformation from sterically constrained $Cu(dmp)_2^{2+}$ to $Cu(dmp)_2^{2+}*$. As the relaxation from the steric interaction between the bulky methyl groups on different dmp ligands takes place, it is concluded that the free energy difference between $Cu(dmp)_2^{2+}$ and $Cu(dmp)_2^{2+}*$ is somewhat smaller than 60 kJ mol^{-1}.

From the fact that the reduction of $Cu(dmp)_2^{2+}$ takes place through path B in Scheme 1, microscopic reversibility requires that the oxidation reaction of $Cu(dmp)_2^{+}$ (the reverse process) should also take place through path B. Therefore, it is required that $Cu^IL(P)$ [= $Cu(dmp)_2^{+}*$] is less stable compared with $Cu^{II}L(Q)$ [= $Cu(dmp)_2^{2+}*$] (cf. Schemes 1 and 2). In $Cu(dmp)_2^{+}$ with d^{10} electronic configuration, no change in the LFSE is expected for the change in the coordination geometry. Therefore, the free-energy difference between $Cu(dmp)_2^{+}$ in the ground state (tetrahedral) and $Cu(dmp)_2^{+}*$ (distorted tetragonal) should be attributed to the nature of Cu(I) with a strong thermodynamic preference to form the tetrahedral geometry.[3] It is known that the energy gap between the filled 3*d* orbital and the vacant 4*s* orbital is small in Cu(I), and that the combination of 3*d*−4*s* hybrid orbitals with the p_z orbital forms a stable linear conformation of d^{10} metal complexes.[49,50] In the same manner, many copper(I) species achieve the stable tetrahedral geometry.[51] It is a very difficult task to estimate the electronic energy levels of tetrahedral and tetragonal forms of Cu^IN_4 system. However, the free energy difference between tetrahedral and tetragonally distorted Cu^IN_4 geometries in solution may be roughly estimated by using the stability constant of tetrahedral $Cu(dmp)_2^{+}$ because the stability constant includes not only the contribution of geometric change but also the contribution of solvation free-energy changes accompanying the particular geometric change.

---

(49) Orgel, L. E. *J. Chem. Soc.* **1958**, 4186.
(50) Fisher, K. J.; Drago, R. S. *Inorg. Chem.* **1975**, *14*, 2804.
(51) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991.

The equilibrium constant for the following reaction is reported as $10^{19.1}$ in water.[52]

$$\mathrm{Cu^+ + 2dmp \rightleftharpoons Cu(dmp)_2{}^+} \qquad (12)$$

By making a naïve assumption that the chemical potential of the distorted tetragonal form of Cu(I) is close to that for solvated Cu(I) (although it is known that Cu(I) in acetonitrile is tetrahedrally coordinated and stabilized), we estimate the free-energy difference between the solvated $\mathrm{Cu_{aq}{}^+}$ and $\mathrm{Cu(dmp)_2{}^+}$ in water to be 109 kJ $\mathrm{mol^{-1}}$ at 298 K. The transfer free-energy from water to acetonitrile is less than 10 kJ $\mathrm{mol^{-1}}$ for singly charged cations such as Cu(I).[53,54] Therefore, the free energy change for the equilibrium expressed by eq 12 in acetonitrile may be close to 100 kJ $\mathrm{mol^{-1}}$.

Estimation of the Conformational Equilibrium Constant (K_{OQ}). In the square scheme, k_{A2}, k_{2A}, k_{B2}, and k_{2B} represent the rate constants of electron-transfer reactions. Once these values are estimated, the conformational equilibrium constant can be obtained. The value of k_{B2} depends on the nature of the reaction partner, as this process includes the effect of the inner-sphere free energy change and the redox potential of the reductant. However, we have a good reason to assume that k_{B2} is very fast: the deformation of $\mathrm{Cu(dmp)_2{}^{2+}}$ to $\mathrm{Cu(dmp)_2{}^{2+*}}$ pushes up the redox potential of the $\mathrm{Cu(dmp)_2{}^{2+*/+}}$ couple significantly, as the stability of $\mathrm{Cu(dmp)_2{}^{2+*}}$ is reduced as much as the potential gap between $\mathrm{Cu(dmp)_2{}^{2+}}$ and $\mathrm{Cu(dmp)_2{}^{2+*}}$ *prior to* the outer-sphere electron-transfer process. The rise of the redox potential, which is equivalent to the LFAE, is estimated by using the Nernst equation.

$$E°_{\mathrm{Cu^{2+*/+}}} = E°_{\mathrm{Cu^{2+/+}}} - \frac{RT}{F}\ln K_{OQ} \qquad (13)$$

where $E°_{\mathrm{Cu^{2+*/+}}}$, $E°_{\mathrm{Cu^{2+/+}}}$, and F are the standard redox potentials of the $\mathrm{Cu(dmp)_2{}^{2+*/+}}$ and $\mathrm{Cu(dmp)_2{}^{2+/+}}$ couples and the Faraday constant, respectively. In this study, we obtained 0.280 V as $E°_{\mathrm{Cu^{2+/+}}}$ with reference to the ferricinium/ferrocene couple. As it is expected that the value of K_{OQ} ($= k_{OQ}/k_{QO}$) is small, $E°_{\mathrm{Cu^{2+*/+}}}$ may be large. As a result, the k_{B2} process is accelerated by a large driving force ($\Delta G° = -FE°_{\mathrm{Cu^{2+*/+}}}$) to achieve a very rapid electron transfer. Such a situation may be demonstrated on the basis of the Marcus cross relation. For the cross reaction of $\mathrm{Cu(dmp)_2{}^{2+*}}$ and ferrocene, the coulombic work terms are relatively small and may be ignored (w_{11} for the Cu(II)/(I) self-exchange reaction is merely 1 kJ $\mathrm{mol^{-1}}$ and W is close to unity).[35,36]

$$k_{B2} = \sqrt{k_{\mathrm{Cu^{2+*/+}}}k_{\mathrm{Fe^{+/0}}}K_{\mathrm{Cu^{2+*}/Fe}}f}\,W \qquad (14)$$

$$\ln f = \frac{[\ln K_{\mathrm{Cu^{2+}/Fe}} + (w_{\mathrm{Cu^{2+*}/Fe}} - w_{\mathrm{Cu^+/Fe^+}})/RT]^2}{4[\ln k_{\mathrm{Cu^{2+*/+}}}k_{\mathrm{Fe^{+/0}}}/Z^2 + (w_{\mathrm{Cu^{2+*/+}}} - w_{\mathrm{Fe^{+/0}}})/RT]} \qquad (15)$$

$$W = \exp\left(\frac{-(w_{\mathrm{Cu^{2+*}/Fe}} + w_{\mathrm{Cu^+/Fe^+}} - w_{\mathrm{Cu^{2+*/+}}} - w_{\mathrm{Fe^{+/0}}})}{2RT}\right) \qquad (16)$$

$$w_{ij} = \frac{9.05z_iz_j}{a(1 + 0.481a\sqrt{\mu})}\ (\mathrm{kcal\ mol^{-1}}) \qquad (17)$$

where z is the charge on complex ions, a is the sum of the ionic radii of each reacting species (Å), μ is the ionic strength of the solution.[26] The slope of the plot of eq 7 gives $1/K_{OQ}k_{B2}$. Therefore, eq 14 is rearranged to eq 18.

$$k_{B2} = 5.4 \times 10^4 k_{\mathrm{Cu^{2+*/+}}}k_{\mathrm{Fe^{+/0}}}Sf \qquad (18)$$

where S denotes the slope obtained from the plot in Figure 3, and 5.4×10^4 is the equilibrium constant for the reaction of $\mathrm{Cu(dmp)_2{}^{2+}}$ and ferrocene.

The value of $k_{\mathrm{Cu^{2+*/+}}}$ may be estimated by Marcus theory,[1] because this process is essentially controlled by the outer-sphere reorganization free energy and the electrostatic terms: 14.0 kJ $\mathrm{mol^{-1}}$ for ΔG^*_{os} and -2 kJ $\mathrm{mol^{-1}}$ for $\Delta G^*_{coul} + \Delta G^*_{DH}$, respectively by setting the ionic radii of both Cu species at 650 pm in acetonitrile at 298 K.[27] With 4.8×10^{10} kg $\mathrm{mol^{-1}\ s^{-1}}$ thus estimated for $k_{\mathrm{Cu^{2+*/+}}}$, a value of 3.0×10^{11} kg $\mathrm{mol^{-1}\ s^{-1}}$ was obtained for k_{B2} by using the reported value of $k_{\mathrm{Fe^{+/0}}}$, the electron self-exchange rate constant for the ferricinium/ferrocene couple (9×10^6 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, ionic radii = 600 pm).[55] Therefore, $K_{OQ} = 4.3 \times 10^{-7}$, and a value of 7.7×10^7 $\mathrm{s^{-1}}$ was estimated for k_{QO}. The free energy difference between $\mathrm{Cu(dmp)_2{}^{2+}}$ and $\mathrm{Cu(dmp)_2{}^{2+*}}$ is, therefore, ca. 36 kJ $\mathrm{mol^{-1}}$, which is rather small compared with the estimated value, 60 kJ $\mathrm{mol^{-1}}$, from the LFAE calculation. In the LFAE calculation, it is assumed that the bond lengths between Cu(II) and nitrogen donor atoms do not change while the dihedral angle varies from ca. 60 to 90°. Therefore, a rather small energy difference between $\mathrm{Cu(dmp)_2{}^{2+}}$ and $\mathrm{Cu(dmp)_2{}^{2+*}}$ may indicate the existence of a metastable form of $\mathrm{Cu(dmp)_2{}^{2+*}}$ with different $\mathrm{Cu^{II}{-}N}$ lengths from those for ground-state $\mathrm{Cu(dmp)_2{}^{2+}}$. Such a structure may be possible as the steric repulsion between methyl groups is large in the ground-state $\mathrm{Cu(dmp)_2{}^{2+}}$: the Cu–N bond length in $\mathrm{Cu(dmp)_2{}^{2+}}$ complex is 206 pm, which is almost identical to that for the typical $\mathrm{Cu^{I}{-}N}$ bond length,[41,42] while a value of 199 pm is reported for the Cu(II)-N bond length for pseudo tetrahedral $\mathrm{Cu(2,9\text{-}diphenyl\text{-}1,10\text{-}phenanthroline)_2{}^{2+}}$.[56] The measured second-order rate constant for the reaction of $\mathrm{Cu(dmp)_2{}^{2+}}$ with $\mathrm{Co(bpy)_3{}^{2+}}$, 7.0×10^2 kg $\mathrm{mol^{-1}\ s^{-1}}$ at 298K, corresponds to $k_{B2}k_{OQ}/k_{QO}$. As K_{OQ} is independent of the nature of the reducing reagent, k_{B2} value for the reaction of $\mathrm{Cu(dmp)_2{}^{2+}}$ with $\mathrm{Co(bpy)_3{}^{2+}}$ was calculated as 1.6×10^9 kg $\mathrm{mol^{-1}\ s^{-1}}$, which seems reasonably smaller than k_{B2} for the reaction of $\mathrm{Cu(dmp)_2{}^{2+}}$ with ferrocene as the electron self-exchange rate constant for the $\mathrm{Co(bpy)_3{}^{3+/2+}}$ couple is small.[57,58]

Interpretation of the Mixing of two Paths. The free energy difference between the ground-state $\mathrm{Cu(dmp)_2{}^{2+}}$ and distorted $\mathrm{Cu(dmp)_2{}^{2+*}}$ is not affected by changing reducing reagent, as the change in the reaction partner merely influences the free energy gap, $\Delta G°_{OQ}$, as shown in Scheme 2A and 2B. When a more powerful reducing reagent is employed for the reduction of $\mathrm{Cu(dmp)_2{}^{2+}}$, it is clear from Scheme 2 that the mixing of path B and path A is expected to occur. Such case was observed for the reaction of $\mathrm{Cu(dmp)_2{}^{2+}}$ with $\mathrm{Fe(PMCp)_2}$ in this study. This phenomenon strongly indicates that the interchange in the activation process may take place for the gated electron-transfer

---

(52) Sillen, L. G., Martell, A. E., Eds. *Stability Constants of Metal-Ion Complexes*; Alden Press: Oxford, 1971.

(53) Cox, B. G.; Parker, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 3674.

(54) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477.

(55) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

(56) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *Inorg. Chem.* **1998**, *37*, 2285.

(57) Lappin, A. G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: Chichester, U.K., 1994.

(58) Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 1954.

reactions when the potential gap between the reactants and products are very large. The 500 mV larger potential difference for the reaction of $Cu(dmp)_2^{2+}$ with $Fe(PMCp)_2$ lowers the difference in the free energy levels between $[Q + A_{Red}']$ and $[P + A_{Ox}']$ as shown in Scheme 2B, and the effective mixing of path A and path B takes place. A computer calculation for eq 8 gave a best-fit value of $(2.5 \pm 0.1) \times 10^4$ and 3.2×10^{12} kg mol^{-1} s^{-1} for k_{A2} and k_{B2} by setting k_{OQ} and k_{QO} to 33 and 7.7×10^7 s^{-1}, respectively. The activation free energy corresponding to the k_{A2} process is 48 kJ mol^{-1}, which implies that the mixing of paths A and B takes place effectively and that the energy level of the $[P + A_{Ox}']$ state in Scheme 2B is somewhat smaller than this value. Therefore, the upper limit of the original energy gap between $[P + A_{Ox}']$ and $[R + A_{Ox}']$ states in Scheme 2B is ca. 123 kJ mol^{-1} ($\Delta G^\circ_2 + \Delta G^*_{A2}$), while the lower limit is 63 kJ mol^{-1} (the energy level of $[Q + A_{Red}]$ relative to $[R + A_{Ox}]$: $\Delta G^\circ_1 + \Delta G_{OQ}$. Thus, the free-energy difference between $Cu(dmp)_2^{+}$ and $Cu(dmp)_2^{+*}$ estimated from the stability constant for reaction 12 (109 kJ mol^{-1}) seems acceptable.

A direct electron-exchange rate constant between $Cu^{II}L(O)$ and $Cu^{I}L(P)$ without any structural change, which corresponds to path A, can be calculated by using k_{A2} and the self-exchange rate constant for the $Fe(PMCp)_2^{+/0}$ couple as 5×10^{-11} kg mol^{-1} s^{-1} ($\Delta G^* = 118$ kJ mol^{-1}) from the Marcus cross relation. Therefore, it is shown that the direct electron exchange (path A) does not compete with the electron exchange reaction through path B.

Electron Self-Exchange Reaction. The electron exchange reaction proceeds through the pathway with lower activation energy. Therefore, the electron self-exchange reaction for the $Cu(dmp)_2^{2+/+}$ couple proceeds also through path B. As the free energy profile for the electron self-exchange reaction is symmetric along the reaction coordinate, it may be described as shown in Scheme 3. According to Scheme 3, the rate law of the electron-exchange reaction is described by eq 19, assuming steady state for $Cu(dmp)_2^{2+*}$.

$$Cu(dmp)_2^{2+} \underset{k_{QO}}{\overset{k_{OQ}}{\rightleftharpoons}} Cu(dmp)_2^{2+*}$$

$$Cu(dmp)_2^{2+*} + Cu(dmp)_2^{+} \xrightarrow{k_{ET}}$$

$$rate = \frac{k_{ET}k_{OQ}/k_{QO}}{1 + k_{OQ}/k_{QO}}[Cu(I)]_T[Cu(II)]_T \qquad (19)$$

$$\tau^{-1}_{ex} = k_{ex}[Cu(II)]_T \qquad (20)$$

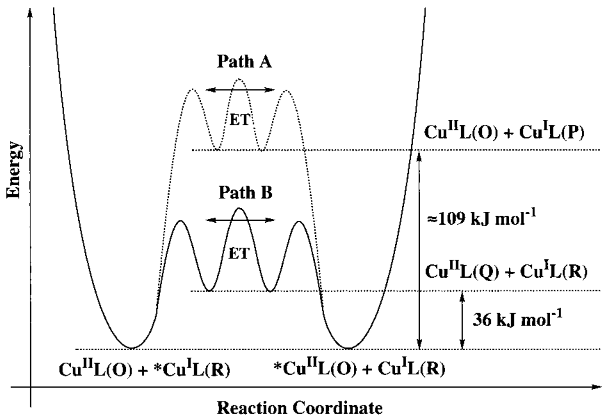
$$k_{ex} = \frac{k_{ET}k_{OQ}/k_{QO}}{1 + k_{OQ}/k_{QO}} \qquad (21)$$

where $[Cu(I)]_T$ and $[Cu(II)]_T$ denote the total concentrations of Cu(I) and Cu(II) species, respectively. When k_{OQ} is small compared with k_{QO}, which is the case observed for the reaction of the $Cu(dmp)_2^{2+/+}$ couple, eq 21 is reduced to eq 22.

$$k_{ex} = k_{ET}k_{OQ}/k_{QO} \qquad (22)$$

The values of k_{QO} and k_{OQ} are 7.7×10^7 s^{-1} and 33 s^{-1}, respectively, while k_{ET} (ET rate constant within the precursor complex without structural change, $k_{Cu^{2+*/+}}$) is 4.8×10^{10} kg mol^{-1} s^{-1} as estimated above. Therefore, k_{ex} is calculated as 2×10^4 kg mol^{-1} s^{-1}, which may be compared with the directly measured value by NMR (5×10^3 kg mol^{-1} s^{-1}).[27] Similar calculations were reported by Rorabacher et al.[59] The above discussion implies that any outer-sphere electron exchange process, gated or not, causes extra line broadening which depends on the concentration of the paramagnetic species, [Cu(II)] (eq 20). Recently, Stanbury et al. reported a [Cu(II)]-independent rate constant for the $Cu(bite)^{2+/+}$ electron exchange reaction (bite = biphenyldiiminodithioether).[25] They suggested that the traditional entatic state view which attributes rapid electron transfer at the blue copper sites to small structural differences between the Cu(I) and Cu(II) states[60,61] may be incorrect. However, the results in this study indicate that the classical entatic state view seems still valid, and the results observed for the $Cu(bite)^{2+/+}$ couple seems to be an exception compared with the other reported results including the $Cu(dmp)_2^{2+/+}$ couple.

Scheme 3



Conclusion

A complete analysis of the electron-transfer reactions involving the $Cu(dmp)_2^{2+/+}$ couple in acetonitrile was carried out in this study. It was shown that the reduction reaction of $Cu(dmp)_2^{2+}$ was "gated" because of the relatively slow conformational change in $Cu(dmp)_2^{2+}$. The slow conformational change in Cu(II) ion was attributed to the large LFAE from ground-state $Cu(dmp)_2^{2+}$ (the dihedral angle between two dmp planes is close to 60°) to the pseudo-tetrahedral $Cu(dmp)_2^{2+*}$. The mixing of path A (direct electron transfer) and path B (involving slow conformational change *prior to* the outer-sphere ET process) was observed for the reduction reaction of $Cu(dmp)_2^{2+}$ by $Fe(PMCp)_2$. The preference of path B for the $Cu(dmp)_2^{2+/+}$ couple was explained by the relative instability of $Cu(dmp)_2^{+*}$ compared to $Cu(dmp)_2^{2+*}$. The direct electron exchange rate constant for path A was estimated as 5×10^{-11} kg mol^{-1} s^{-1} from the results obtained for the cross reaction of $Cu(dmp)_2^{2+}$ with $Fe(PMCp)_2$. Although we cannot observe the minor intermediate, $Cu(dmp)_2^{2+*}$, the existence of such species was suggested as the *kinetic* evidence. Whether the $Cu(dmp)_2^{2+*}$ species has a distinct tetrahedral structure or not is an open question. The LFAE calculation may not lead to a certain potential minimum for the suitable structure of the intermediate, as discussed above. However, the reported Cu(II)−N distance in $Cu(dmp)_2^{2+}$ is rather long because of the repulsion between

---

(59) Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. *Inorg. Chem.* **1993**, *32*, 3957.
(60) Williams, R. J. P. *Eur. J. Biochem.* **1995**, *234*, 363.
(61) Kaim, W.; Schwederski, B. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*; Wiley: Chichester, U.K., 1994.

four methyl groups.[41] Therefore, the existence of a certain high-energy metastable $Cu(dmp)_2^{2+*}$ with a shorter Cu−N bond length may be possible.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research (Grant No. 10440193) from the Ministry of Education, Science, Culture and Sports of Japan. The authors express their thanks to the kind and stimulating suggestions and thoughtful instructions of the reviewers.

Supporting Information Available: Tables of the rate constants corresponding to the plots in Figures 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9810687