Electron self-exchange, oxidation, and reduction reactions of bis(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)copper(II/I) and bis(6,6′-dimethyl-2,2′-bipyridine)copper(II/I) couples in acetonitrile: gated ET for the reduction, oxidation, and self-exchange processes

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

Abstract: The electron self-exchange rate constant for the $Cu(dmbp)_2^{2+/+}$ couple (dmbp = 6,6′-dimethyl-2,2′-bipyridine) was measured in acetonitrile by the NMR method (k_{ex} = 5.5 × 10^3 kg mol^{-1} s^{-1}, ΔH^* = 35.0 ± 0.3 kJ mol^{-1} and ΔS^* = –56 ± 1 J mol^{-1} K^{-1}). Reduction reactions of $Cu(bcp)_2^{2+}$ (bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and $Cu(dmbp)_2^{2+}$ with $Co(bipy)_3^{2+}$ (bipy = 2,2′-bipyridine) and ferrocene ($Fe(Cp)_2$ = bis(cyclopentadienyl)iron(II)), and oxidation reactions of $Cu(bcp)_2^+$ and $Cu(dmbp)_2^+$ by $Ni(tacn)_2^{3+}$ (tacn = 1,4,7-triazacyclononane) and $Mn(bipyO_2)_3^{3+}$ ($bipyO_2$ = *N*,*N*′-dioxo-2,2′-bipyridine) were also studied in acetonitrile. The electron self-exchange rate constants, k_{ex}, estimated for the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples from the oxidation reactions of $Cu(bcp)_2^+$ and $Cu(dmbp)_2^+$ by $Ni(tacn)_2^{3+}$ and $Mn(bipyO_2)_3^{3+}$ were consistent with the directly measured values by NMR, while k_{ex} estimated from the reduction reactions of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ by $Co(bipy)_3^{2+}$ ($[Cu(bcp)_2^{2+}]_0$, $[Cu(dmbp)_2^{2+}]_0$ >> $[Co(bipy)_3^{2+}]_0$) were 10^3 times smaller than those directly measured by the NMR method. The pseudo-first-order rate constant for the reduction reaction of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ by $Fe(Cp)_2$ was not linear against the concentration of excess amounts of $Fe(Cp)_2$. Analyses of the reactions revealed that the reductions of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ involve slow paths related to the deformation of $Cu(II)N_4$ center from tetragonal to tetrahedral coordination. The energetic preference for the deformation of Cu(II) species rather than that of Cu(I) was discussed on the basis of the ligand field activation energy (LFAE).

Key words: electron transfer, copper(II) and copper(I) complexes, gated behavior.

Résumé : Opérant dans l’acétonitrile et faisant appel à la RMN, on a mesuré la constante de vitesse d’auto-échange électronique du couple $Cu(dmbp)_2^{2+/+}$ (dmbp = 6,6′-diméthyl-2,2′-bipyridine) (k_{ex} = 5,5 × 10^3 kg mol^{-1} s^{-1}, ΔH^* = 35,0 ± 0,3 kJ mol^{-1} et. ΔS^* = –56 ± 1 J mol^{-1} K^{-1}). Opérant dans l’acétonitrile, on a aussi étudié les réactions de réduction du $Cu(bcp)_2^{2+}$ (bcp = 2,9-diméthyl-4,7-diphényl-1,10-phénanthroline) et du $Cu(dmbp)_2^{2+}$ par le $Co(bipy)_3^{2+}$ (bipy = 2,2′-bipyridine) et le ferrocène ($Fe(Cp)_2$ = bis(cyclopentadiényl)fer(II)) et les réactions d’oxydation du $Cu(bpc)_2^+$ et du $Cu(dmbp)_2^+$ par le $Ni(tacn)_2^{3+}$ (tacn = 1,4,7-triazacyclononane) et le $Mn(bipyO_2)_3^{3+}$ ($bipyO_2$ = *N*,*N*′-dioxo-2,2′-bipyridine). Les constantes de vitesse d’auto-échange électronique, k_{ex}, évaluées pour les couples $Cu(bcp)_2^{2+/+}$ et $Cu(dmbp)_2^{2+/+}$ à partir des réactions d’oxydation du $Cu(bcp)_2^+$ et du $Cu(dmbp)_2^+$ par $Ni(tacn)_2^{3+}$ et $Mn(bipyO_2)_3^{3+}$, sont en accord avec les valeurs mesurées directement par RMN; par ailleurs, les valeurs de k_{ex} évaluées à partir des réactions de réduction du $Cu(bcp)_2^{2+}$ et du $Cu(dmbp)_2^{2+}$ par le $Co(bipy)_3^{2+}$ ($[Cu(bipy)_2^{2+}]_0$, $[Cu(dmbp)_2^{2+}]_0$ >> $[Co(bipy)_3^{2+}]_0$) sont 10^3 fois plus faibles que celles mesurées directement par la méthode de RMN. La constante de vitesse de pseudo-ordre un pour la réaction de réduction du $Cu(bcp)_2^{2+}$ et du $Cu(dmbp)_2^{2+}$ par le $Fe(Cp)_2$ n’est pas linéaire par rapports à la concentration de quantités excédentaires de $Fe(Cp)_2$. L’analyse des réactions révèle que les réductions du $Cu(bcp)_2^{2+}$ et du $Cu(dmbp)_2^{2+}$ impliquent des voies lentes reliées à la déformation du centre $Cu(II)N_4$ d’une coordination tétragonale à tétraédrique. On fait appel à l’énergie d’activation du champ de ligand pour discuter de la préférence énergétique pour la déformation de l’espèce Cu(II) par rapport à celle de l’espèce Cu(I).

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N. Koshino,[1] Y. Kuchiyama, S. Funahashi, and H.D. Takagi.[1] Inorganic and Analytical Chemistry Division, Department of Chemistry and Physics, Graduate School of Sciences, Nagoya University, Furocho, Chikusa, Nagoya 464-8602, Japan.

[1] Authors to whom correspondence may be addressed. Telephone and fax: +81-52-789-5473. e-mail: NK: nkoshino@chem4.chem.nagoya-u.ac.jp; HDT: htakagi@chem4.chem.nagoya-u.ac.jp

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Introduction

For ordinary outer-sphere electron transfer reactions, concerted inner- and outer-sphere reorganizations are assumed (1, 2). Therefore, the electron transfer reaction is slow for the reactions involving a large coordination geometry change during the course of the electron transfer process. Recent theoretical investigations by Hoffman and Ratner (3) and Brunschwig and Sutin (4) indicate that the "gated *intramolecular* process" with high-energy intermediates never competes with the direct outer-sphere process in the *normal* region. This indication, however, does not exclude the "gated electron transfer" phenomena postulated by Rorabacher et al. (5–9) in which large stereochemical changes take place *prior to* the ordinary outer-sphere electron transfer processes. Although such gated reactions cannot be treated as a simple outer-sphere process (i.e., the Ratner type cross relation has the possibility of failing to predict proper electron self-exchange rate constants for such reactions), the outer-sphere electron transfer reactions between the deformed species and the outer-sphere redox reagents may follow the norm of the Ratner type cross relation (10). Therefore, the classical "entatic state view," saying that the rate of the electron transfer is slow for the redox couple with large coordination geometry changes, seems still valid irrespective of the condition whether the reaction is gated or not (11, 12).

Results of the early works on the reactions of $Cu(bpy)_2^{2+/+}$, $Cu(phen)_2^{2+/+}$, and its derivative $Cu(dmp)_2^{2+/+}$ (13–15) indicated the gated ET, as the self-exchange rate constants for these redox couples estimated by the Marcus cross relation from the *forward* and *backward* reactions were inconsistent with each other. In 1983, Lee and Anson (16) pointed out that steric interconversion may have an important role in the electron transfer processes of the $Cu(bpy)_2^{2+/+}$ and $Cu(phen)_2^{2+/+}$ couples. The studies of electron transfer reactions for $Cu(dmp)_2^{2+/+}$ with various reaction partners in aqueous solution were also reported (17–22). However, ambiguities in the coordination structures of these ions as well as the low solubility of these ions in water made it difficult to analyze the reactions more precisely. The studies of the reduction of water-soluble $Cu(dpsmp)_2^{2-}$ (dpsmp = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline) by Sykes and co-workers (23, 24) and Lappin and co-workers (25) indicated the involvement of such steric interconversion. There are some cases where electron exchange is extremely slow even for the near tetrahedral Cu(II/I) couples (26–28). Most recently, Stanbury and co-workers (29) reported a very slow electron exchange reaction of $Cu(bib)_2^{2+/+}$ (bib = 2,2′-bis(2-imidazoly)biphenyl). The estimated self-exchange rate constant of $Cu(bib)_2^{2+/+}$ is merely 0.16 kg mol^{-1} s^{-1}. Takagi and Swaddle (30, 31) have been studying Cu(II/I) electron self-exchange reactions by NMR where the coordination geometry of Cu(I) and Cu(II) are constrained to be similar, in which the kinetic behavior *was* expected to follow the context of the moderately fast electron transfer case, and no significant change in coordination number or coordination geometry *had been* expected in the electron transfer processes.

In the case of the gated ET reactions, a *slow* equilibrium corresponding to the deformation of one of the reactants precedes the outer-sphere ET process. For copper(II/I) couples, a tetragonal four or five coordination (D_{2d} symmetry) is expected for Cu(II), while tetrahedral geometry is expected for copper(I). When cyclic polythiaethers were used as ligands, Rorabacher et al. (5–9) showed that the oxidation reaction of Cu(I) is gated, which implies that the deformation of Cu(I) from tetrahedral to tetragonal conformation takes place prior to the ET process. In such a case, the principle of the microscopic reversibility requires that the deformation of Cu(II) is energetically less favored compared to that of Cu(I).

In this article, we examined electron transfer reactions of two $Cu(II/I)(N_2)_2$ couples and found that the electron transfer reactions for $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ are gated. When the normal coordination geometry (slightly twisted structure from the ordinary tetragonal 4 or 5 coordination preferred by the Cu(II) species) is in equilibrium with the deformed tetrahedral state, the electron transfer processes involving the deformed tetrahedral Cu(II) may be much faster than those involving the ground state Cu(II). The energetic origin of the gated ET is discussed on the basis of the ligand field activation energies (LFAE) corresponding to the Cu(II) deformation. A possibility of the mixing of the *gated* and *direct* ET was also examined for the electron self-exchange processes of $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples.[2]

Experimental section

Chemicals

Acetonitrile was obtained from Wako Pure Chemicals Inc. and purified by distillation from phosphorus pentoxide. The content of the residual water in thus purified acetonitrile was examined by a Mitsubishi Kasei CA01 Karl–Fisher apparatus by which the amount of residual water was determined to be less than 5 mmol kg^{-1}. Ferrocene (Wako) was purified by sublimation at ambient pressure. All other chemicals from Wako, Aldrich, and Fluka were used without further purification. Bis(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)-copper(II) and -(I) perchlorate were synthesized by the reported method (32, 33). Anal. calcd. for $CuC_{52}H_{40}N_4Cl_2O_8$: C 63.5, N 5.70, H 4.10; found: C 63.8, N 5.62, H 4.18. Anal. calcd. for $CuC_{52}H_{40}N_4ClO_4$: C 70.7, N 6.34, H 4.56; found: C 71.0, N 6.42, H 4.52. Bis(6,6′-dimethyl-2,2′-bipyridine)-copper(II) and -(I) perchlorate were synthesized by the reported method (32, 33). Anal. calcd. for $CuC_{24}H_{24}N_4Cl_2O_8$: C 45.7, N 8.88; found: C 44.7, N 8.72. Anal. calcd. for $CuC_{24}H_{24}N_4ClO_4$: C 54.2, N 10.5, H 4.55; found: C 54.4, N 9.98, H 4.60.

$[Co(bipy)_3](ClO_4)_2$, $[Ni(tacn)_2](ClO_4)_3$, and $[Mn(bipyO_2)_3](ClO_4)_2$ were synthesized by the literature method (34–36). Anal. calcd. for $CoC_{30}H_{24}N_6Cl_2O_8$: C 49.6, H 3.33, N 11.6; found:

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[2] Tables of rate constants (Tables SI to SV) have been deposited as supplementary material and may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada, K1A 0S2.

Table 1. Electron self-exchange rate constants and activation parameters for the reactions of $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ at 298 K in acetonitrile.[a]

Reaction	k_{12}/kg mol^{-1} s^{-1}	$k_{CuL_2^{2+/+}}$[b]/kg mol^{-1} s^{-1}	ΔH*/kJ mol^{-1}	ΔS*/J mol^{-1} K^{-1}
$Cu(bcp)_2^{2+}$ + $Cu(bcp)_2^{+}$	—	1.4×10^3	38.1 ± 2.4	–57 ± 8
$Cu(bcp)_2^{+}$ + $Ni(tacn)_2^{3+}$	5.20×10^5	2.0×10^3	21.9 ± 0.2	–61.9 ± 0.8
$Cu(bcp)_2^{2+}$ + $Co(bipy)_3^{2+}$	5.71×10^2	1.2	33 ± 2	–158 ± 0.6
$Cu(dmbp)_2^{2+}$ + $Cu(dmbp)_2^{+}$	—	5.5×10^3	35.0 ± 0.3	–56 ± 1
$Cu(dmbp)_2^{+}$ + $Ni(tacn)_2^{3+}$	9.3×10^4	6.7×10^2	24.9 ± 0.5	–66 ± 2
$Cu(dmbp)_2^{+}$ + $Mn(bipyO_2)_3^{3+}$	2.14×10^3	1.9×10^3	32 ± 1	–75 ± 4
$Cu(dmbp)_2^{2+}$ + $Co(bipy)_3^{2+}$	1.92×10^3	1.4	21.0 ± 0.4	–112 ± 1

[a] Ionic strength of the solutions was adjusted to 0.1 mol kg^{-1} by $(n\text{-}Bu_4N)ClO_4$ or $(Et_4N)BF_4$.

[b] Calculated by the redox potential (V vs. $Fc^{+/0}$), self-exchange rate constant (kg mol^{-1} s^{-1}), and ionic radii (pm): 0.275, 1.40×10^{3c}, 760 for $Cu(bcp)_2^{2+/+}$; 0.346, 5.5×10^3, 650 for $Cu(dmbp)_2^{2+/+}$; 0.555, 6.0×10^{3d}, 380 for $Ni(tacn)_2^{3+/2+}$; 0.435, 80^e, 400 for $Mn(bipyO_2)_3^{3+/2+}$; –0.081, 0.645^f, 700 for $Co(bipy)_3^{3+/2+}$.

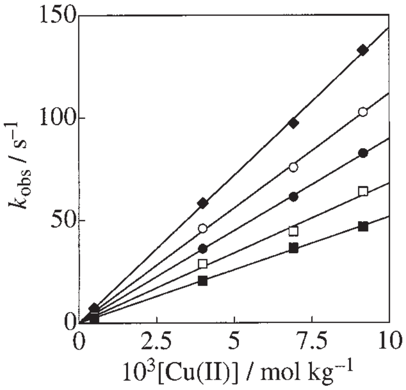
[c] Reference 33.

[d] Reference 56.

[e] Reference 57.

[f] Reference 58.

Fig. 1. Dependence of k_{obs} on the concentration of $Cu(dmbp)_2^{2+}$ for the electron self-exchange reaction of $Cu(dmbp)_2^{2+/+}$. $[Cu(dmbp)_2^{+}] = 7.90 \times 10^{-2}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). The symbols represent the data obtained at 319.1 (◆), 313.1 (○), 308.5 (●), 302.9 (□), and 297.8 (■) K.



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 by water and oxygen from the environment. 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 analyses. Under the conditions of [Cu(II)] << [L] (L = dmbp or bcp), no electroactive species other than $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ was observed within the redox window of acetonitrile (–2 ~ +2 V) by cyclic voltammetry, which indicates that either $Cu(bcp)^{2+}$, $Cu(dmbp)^{2+}$, or Cu^{2+} produced by the decomposition of $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ in solution does not oxidize ferrocene and $Co(bipy)_3^{2+}$ used in this study. The absorbance changes at 470 and 454 nm, corresponding to the absorption maxima of $Cu(bcp)_2^{+}$ and $Cu(dmbp)_2^{+}$, respectively, were monitored for the kinetic measurements.

Electrochemical measurements were carried out by a BAS 100BW electrochemical analyzer with a 1.5 mm ϕ platinum disk or glassy carbon disk 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 $Mn(bipyO_2)_3^{3+}$ was prepared electrochemically in acetonitrile, containing 0.10 mol kg^{-1} TBAP at carbon electrode (Hokuto Denko HX-201). The NMR measurements were carried out by a Bruker AMX-400WB spectrometer.

Results

Electron self-exchange rate constant for $Cu(dmbp)_2^{2+/+}$

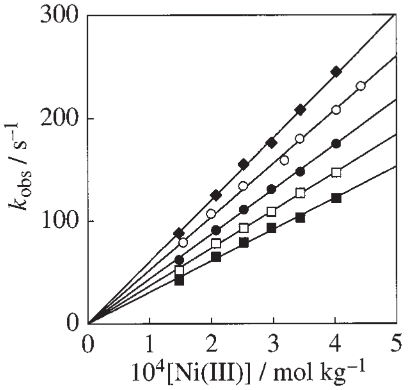
$$[1] \qquad Cu(dmbp)_2^{2+} + {}^*Cu(dmbp)_2^{+} \xrightarrow{k_{ex}} Cu(dmbp)_2^{+} + {}^*Cu(dmbp)_2^{2+}$$

The electron self-exchange rate constant, k_{ex}, of the $Cu(dmbp)_2^{2+/+}$ couple was measured by monitoring the broadening of the methyl proton signal on diamagnetic $Cu(dmbp)_2^{+}$ by the addition of $Cu(dmbp)_2^{2+}$.

$$[2] \qquad k_{obs} = \pi(\nu_{obs} - \nu_0) = k_{ex}[Cu(dmbp)_2^{2+}]$$

where ν_{obs} is the line width of the methyl proton signal at the half signal height in the presence of $Cu(dmbp)_2^{2+}$, while ν_0 is the line width at the half signal height in the absence of $Cu(dmbp)_2^{2+}$. The dependence of k_{obs} on the concentration of added $Cu(dmbp)_2^{2+}$ at constant ionic strength (0.10 mol kg^{-1} by TBAP) is shown in Fig. 1 at various temperatures. The estimated electron self-exchange rate constant at 298 K and the activation parameters are listed in Table 1.

Fig. 2. Dependence of k_{obs} on the concentration of $Ni(tacn)_2^{3+}$ for the oxidation reaction of $Cu(bcp)_2^+$. $[Cu(bcp)_2^+] = 1.50 \times 10^{-5}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). The symbols represent the data obtained at 303.0 (◆), 298.0 (○), 293.2 (●), 288.4 (□), and 283.2 (■) K.



Oxidation reactions of $Cu(bcp)_2^+$ and $Cu(dmbp)_2^+$ by $Ni(tacn)_2^{3+}$ and $Mn(bipyO)_3^{3+}$

The reaction of $Cu(bcp)_2^+$ with $Ni(tacn)_2^{3+}$ in acetonitrile was first order for up to three half-lives and was described by eq. [3] under the pseudo-first-order conditions of $[Cu(bcp)_2^+]_0 << [Ni(tacn)_2^{3+}]_0$.

$$[3] \qquad Cu(bcp)_2^+ + Ni(tacn)_2^{3+} \xrightarrow{k_{12}} Cu(bcp)_2^{2+} + Ni(tacn)_2^{2+}$$

$$[4] \qquad k_{obs} = k_{12}[Ni(tacn)_2^{3+}]_0$$

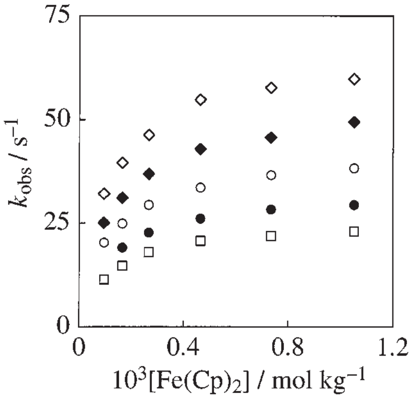
The dependence of k_{obs} on the concentration of $Ni(tacn)_2^{3+}$ at various temperatures is shown in Fig. 2 for the reaction of $Cu(bcp)_2^+$. The second-order rate constants thus estimated at 298 K, $I = 0.1$ mol kg^{-1} are listed in Table 1 for the reactions of $Cu(bcp)_2^+$ and $Cu(dmbp)_2^+$, together with the activation parameters of the reactions. The estimated electron self-exchange rate constants for the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples by the Marcus cross relation were 2.0×10^3 and 6.7×10^2 kg mol^{-1} s^{-1}, respectively, both of which were in fair agreement with the values (1.4×10^3 and 5.5×10^3 kg mol^{-1} s^{-1}, respectively) obtained from the NMR measurements (33) in view of the uncertainties inherent in the Marcus cross relation (37).

The oxidation reaction of $Cu(dmbp)_2^+$ by $Mn(bipyO)_3^{3+}$ was also carried out under the conditions of $[Cu(dmbp)_2^+]_0 >> [Mn(bipyO)_3^{3+}]_0$. The second-order rate constants as well as the activation parameters are also listed in Table 1. The electron self-exchange rate constants for $Cu(dmbp)_2^{2+/+}$ was estimated as 1.9×10^3 kg mol^{-1} s^{-1} by the Marcus cross relation.

Reduction reactions of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ by $Co(bipy)_3^{2+}$

The reactions were observed under the conditions of $[Cu(bcp)_2^{2+}]_0$, $[Cu(dmbp)_2^{2+}]_0 >> [Co(bipy)_3^{2+}]_0$. The kinetic traces were first order for up to three half lives. The dependence of the pseudo-first-order rate constant on the concentration of $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ was linear at various temperatures. The second-order rate constants at 298 K and the corresponding activation parameters for these reactions are listed in Table 1. The application of the Marcus cross relation to these reactions yielded 1.2 and 1.4 kg mol^{-1} s^{-1}, respectively, as the electron self-exchange rate constant, which are some 10^3 times smaller than those directly estimated by the NMR method.

Fig. 3. Dependence of k_{obs} on the concentration of $Fe(Cp)_2$ for the reduction reaction of $Cu(bcp)_2^{2+}$. $[Cu(bcp)_2^{2+}] = 8.47 \times 10^{-6}$ mol kg^{-1}, $[bcp]_{free} = 1.01 \times 10^{-4}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP). The symbols represent the data obtained at 308.2 (◇), 303.2 (◆), 298.2 (○), 293.2 (●), and 288.2 (□) K.



Reduction reaction of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ by $Fe(Cp)_2$

The kinetic traces were excellently first-order for Cu(II) up to three half lives.

$$[5] \qquad -\frac{d[Cu(II)]}{dt} = k_{obs}[Cu(II)] \qquad [Fe(Cp)_2]_0 >> [Cu(II)]_0$$

However, the dependence of the pseudo-first-order rate constants on the concentration of $Fe(Cp)_2$ was not linear as shown in Fig. 3. The curvature in Fig. 3 may be explained by the following two-step mechanism involving a conformational change of Cu(II) *prior to* the fast electron transfer reaction (Path B in Scheme 1 proposed by Rorabacher et al. (5–9)).

$$[6] \qquad Cu(II) \underset{k_{QO}}{\overset{k_{OQ}}{\rightleftharpoons}} Cu(II)^* \qquad Cu(II)^* + A_{Red} \xrightarrow{k_{B2}} Cu(I) + A_{Ox}$$

where Cu(II), Cu(II)*, A_{Red}, and A_{Ox} represent $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ in the ground state, deformed $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$, $Fe(Cp)_2$ and $Fe(Cp)_2^+$, respectively. When the conformational change (k_{OQ}) is slower than the electron transfer process (k_{B2}), the pseudo-first-order rate constant is expressed by eq. [7] by using the terms in Scheme 1.

$$[7] \qquad \text{Rate} = \frac{k_{B2}k_{OQ}}{k_{B2}[A_{Red}] + k_{QO}}[A_{Red}][Cu^{II}L]$$

Scheme 1.

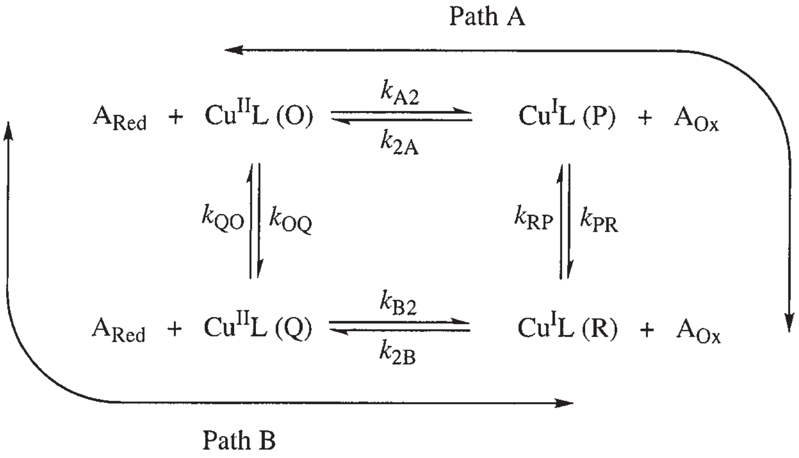


Table 2. Estimated rate constants for the reactions of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ at 298 K.[a]

Reaction			ΔH^{*b}	ΔS^{*c}
$Cu(bcp)_2^{2+} + Fe(Cp)_2$	k_{OQ}	$40\ s^{-1}$	32.0 ± 0.3	-107 ± 1
	k_{QO}	$6.5 \times 10^6\ s^{-1}$		
	$k_{OQ}/k_{QO} = K_{OQ}$	6.2×10^{-6}		
	$k_{B2}{}^d$	$6.6 \times 10^{10}\ kg\ mol^{-1}\ s^{-1}$		
$Cu(dmbp)_2^{2+} + Fe(Cp)_2$	k_{OQ}	$50\ s^{-1}$	30.5 ± 1.3	-110 ± 4
	k_{QO}	$1.7 \times 10^7\ s^{-1}$		
	$k_{OQ}/k_{QO} = K_{OQ}$	3.0×10^{-6}		
	$k_{B2}{}^d$	$9.1 \times 10^{10}\ kg\ mol^{-1}\ s^{-1}$		

[a] Ionic strength of the solutions was adjusted to 0.1 mol kg^{-1} by $(n\text{-}Bu_4N)ClO_4$.

[b] kJ mol^{-1}.

[c] J $mol^{-1}\ K^{-1}$.

[d] Using the estimated values of the electron self-exchange rate constant for $Cu(bcp)_2^{2+*/+}$ (3.8×10^{10} kg mol^{-1} s^{-1}) or $Cu(dmbp)_2^{2+*/+}$ (1.3×10^{10} kg mol^{-1} s^{-1}) and the self-exchange rate constant for $Fe(Cp)_2^{+/0}$ (9×10^6 dm^3 mol^{-1} s^{-1}). Ionic radii for $Fe(Cp)_2^{+/0}$ = 600 pm.

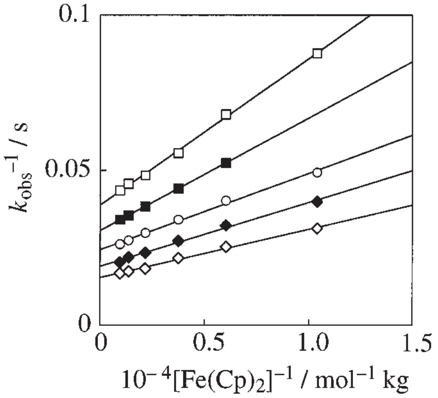
$$[8] \qquad k_{obs} = \frac{k_{OQ}k_{B2}}{k_{B2}[A_{Red}] + k_{QO}}\,[A_{Red}]\,([A_{Red}] >> [Cu^{II}L])$$

Therefore, the plots of the reciprocal value of k_{obs} against $[A_{Red}]^{-1}$ should be linear with an intercept when $[A_{Red}]_0 >> [Cu^{II}L]_0$. Such plots are shown in Fig. 4.

$$[9] \qquad \frac{1}{k_{obs}} = \frac{k_{QO}}{k_{OQ}k_{B2}[A_{Red}]} + \frac{1}{k_{OQ}}$$

The values of the rate constant, k_{OQ}, and the corresponding activation parameters are also listed in Table 2. It is clear that the estimation of k_{QO} and K_{OQ} is possible once the k_{B2} value is known.

Fig. 4. Plots of $k_{obs}{}^{-1}$ vs. $[Fe(Cp)_2]^{-1}$ for the reduction reaction of $Cu(bcp)_2^{2+}$ by $Fe(Cp)_2$. The symbols are the same in Fig. 3.



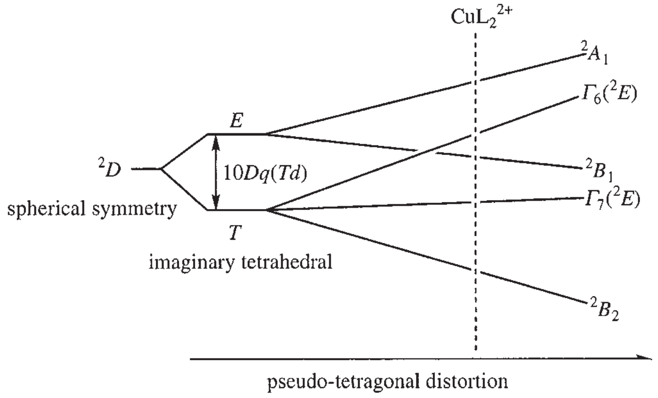
Discussion

General

Rorabacher et al. (5–9) explained the “gated” electron transfer for copper – cyclic thioether ions using the mechanism described by Scheme 1. The reactions proceeded mostly through Path A for the copper–thioether complexes by comparing the electron self-exchange rate constants estimated from both the reduction and oxidation cross reactions.

In this study, the electron self-exchange rate constants for the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples were estimated from both the oxidation and reduction reactions by using the Marcus cross relation, which were then compared with the values measured directly by the NMR method. The estimated self-exchange rate constants from the cross reactions were 2.0×10^3 and $(0.67–1.9) \times 10^3$ kg mol^{-1} s^{-1} from the oxidation reactions of $Cu(bcp)_2^{+}$ and $Cu(dmbp)_2^{+}$, respectively, while the estimated self-exchange rate constants from the reduction cross reactions were merely 1.2 and 1.4 kg mol^{-1} s^{-1}. As the electron self-exchange rate constants mea-

Table 3. Absorption band maxima for $Cu(bcp)_2(ClO_4)_2$ and $Cu(dmbp)_2(ClO_4)_2$ observed by the diffuse reflectance spectrophotometry.[a]



Assignment	$Cu(bcp)_2(ClO_4)_2$[b]	$Cu(dmbp)_2(ClO_4)_2$[b]
Charge transfer	23697	27027
$^2B_2 \rightarrow {}^2A_1$	14064	13698
$^2B_2 \rightarrow \Gamma_6(^2E)$	9891 (broad)	9900 (broad)
$^2B_2 \rightarrow {}^2B_1$	8658 (shoulder)	8620 (shoulder)
$^2B_2 \rightarrow \Gamma_7(^2E)$	5984	6042

[a] The 10*Dq* value for the imaginary tetrahedral field was estimated as 6.4×10^3 cm^{-1} for $Cu(bcp)_2^{2+}$ and 6.2×10^3 cm^{-1} for $Cu(dmbp)_2^{2+}$ 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).

[b] Band maximum/cm^{-1}.

sured by the NMR method are 1.4×10^3 and 5.5×10^3 kg mol^{-1} s^{-1} for the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples, respectively, the reactions involving the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples may also be gated, and the preferred pathway for the redox reactions of these couples seems Path B in Scheme 1, rather than Path A observed for the reactions of copper – macrocyclic thioether complexes.

According to Scheme 1, Rorabacher and co-workers (5, 6) 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 $Cu^{I}L(P)$.

Reduction reaction:

$$[10]\quad -\frac{d[Cu^{II}L]}{dt} = \left(\frac{k_{A2}k_{PR}}{k_{2A}[A_{Ox}]+k_{PR}} + \frac{k_{B2}k_{OQ}}{k_{B2}[A_{Red}]+k_{QO}}\right)[Cu^{II}L(O)][A_{Red}]$$

Oxidation reaction:

$$[11]\quad -\frac{d[Cu^{I}L]}{dt} = \left(\frac{k_{2A}k_{RP}}{k_{2A}[A_{Ox}]+k_{PR}} + \frac{k_{2B}k_{QO}}{k_{B2}[A_{Red}]+k_{QO}}\right)[Cu^{I}L(R)][A_{Ox}]$$

$Cu^{II}L(O)$ and $Cu^{I}L(R)$ represent the Cu(II) and Cu(I) species in the ground state: i.e., $Cu^{II}L(O)$ = $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ in the D_{2d} symmetry, and $Cu^{I}L(R)$ = $Cu(bcp)_2^{+}$ or $Cu(dmbp)_2^{+}$ in the T_d symmetry. As the reduction reactions of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ take place through Path B, the rate law is expressed by eq. [7]. When $k_{B2}[A_{Red}] << k_{QO}$, eq. [7] is reduced to eq. [12], and the dependence of the pseudo-first-order rate constant on the concentration of $Cu^{II}L$ becomes linear as seen for the reduction reactions of $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ by $Co(bipy)_3^{2+}$.

$$[12]\quad k_{obs} = \frac{k_{OQ}k_{B2}}{k_{QO}}[Cu^{II}L] \qquad ([A_{Red}]_0 << [Cu^{II}L]_0)$$

On the other hand, when $[A_{Red}] >> [Cu^{II}L]$, the dependence of k_{obs} on $[A_{Red}]_0$ deviates from a straight line as seen in Fig. 3. The slopes of the plots in Fig. 4 are given by $k_{QO}/k_{B2}k_{OQ}$ (= $1/K_{OQ}k_{B2}$).

As the theoretical investigation for intramolecular ET reactions by Brunschwig and Sutin (4) suggests that no reaction path with high-λ intermediate compete with the direct electron transfer in the *normal* region, the kinetic results obtained in this study strongly indicate the *intermolecular* gated electron transfer after a conformational change.

With a d^9 configuration, Cu(II) ion prefers tetragonal structure in general. In the case of $Cu(bcp)_2^{2+}$, it has been reported that the ground state structure is already largely distorted from the normal tetragonal structure, and the dihedral angle between the two phenanthroline planes is close to 60° (33), while the dihedral angle for $Cu(dmbp)_2^{2+}$ is merely 35° from the ESR measurements (33).[3] However, the similar values of the electron self-exchange rate constants for the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples indicate that either the coordination geometry or the ligand field in $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ is similar to each other. The similarity of the absorption spectra of these ions (Table 3) also indicates that the ligand fields by the bcp and dmbp ligands are similar to each other. From the crystal structures, these Cu(II) species may be the five coordination in solution (39, 40). However, the water exchange rate constant of five coordinated Cu(II)-2,2′,2″-triaminotriethylamine complex is 2×10^5 s^{-1} (41), which is much larger than the conformational change process, k_{OQ}. Therefore, such a fast solvent exchange for the fifth coordinated solvent molecule on Cu(II) may not affect the very slow conformational change from $Cu^{II}L(O)$ to $Cu^{II}L(Q)$.

The crystal structures of the Cu(I) species have been reported: the dihedral angles between the two ligands for $Cu(bcp)_2^{+}$ and $Cu(dmbp)_2^{+}$ are 87.5° and 80.9°, respectively (32, 42). By considering the flexibility along the C—C bond

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[3] ESR parameters, $g_{//}$ and $A_{//}$, were estimated for $Cu(dmbp)_2^{2+}$ as 2.22 and 127 G, respectively, in glassy methanol at 77 K in this study. According to the relation of the dihedral angle and $g_{//}$ postulated by Yokoi and Addison (38), an apparent dihedral angle was estimated as 35°. However, the flexible bipyridine ligands such as dmbp may not follow the norm postulated by Yokoi and Addison.

of the dmbp ligand, the coordination structures of Cu(I) species examined in this study may be considered to be close to T_d in solution, as the strong preference of the tetrahedral structure by Cu(I) is well established (43).

It is possible to estimate the energy difference (LFAE) between the tetragonal $Cu^{II}L(O)$ ground state and the hypothetical tetrahedral $Cu^{II}L(Q)$ state, by calculating the $10Dq$ value corresponding to the hypothetical tetrahedral conformation of $Cu^{II}L(Q)$ ($4\Delta_o/9$) from the diffuse reflectance spectra of $Cu(bcp)_2(ClO_4)_2$ and $Cu(dmbp)_2(ClO_4)_2$ species (44). The absorption band maxima were observed as shown in Table 3. As the distortion from the ordinary tetragonal structure lifts the degeneracy of all d orbitals (45, 46), four major absorptions corresponding to ${}^2B_2 \rightarrow {}^2\Gamma_7({}^2E)$, ${}^2B_2 \rightarrow {}^2B_1$, ${}^2B_2 \rightarrow {}^2\Gamma_6({}^2E)$, ${}^2B_2 \rightarrow {}^2A_1$ should appear in the visible and near IR regions (the notation for the D_{2d} symmetry is used). The observed band maxima were assigned to these transitions. Following the method of Gouge et al. (45), the $10Dq$ values for the hypothetically tetrahedral $Cu(bcp)_2^{2+*}$ and $Cu(dmbp)_2^{2+*}$ (= $Cu^{II}L(Q)$) were estimated as shown in Table 3. It is assumed that the original energy level for the spherically symmetrical CuN_4 geometry lies close to the difference in the weighted mean energy levels of T and E terms.[4] By using the $10Dq$ values of hypothetical $Cu^{II}L(Q)$, the ligand field stabilization energies (LFSE) for the imaginary tetrahedral geometry and the ground state geometry of d^9 $Cu(bcp)_2^{2+}$ were calculated as –2560 and –7720 cm^{-1} relative to the energy of the spherically symmetric CuN_4^{2+} (–2500 and –7650 cm^{-1} were calculated for $Cu(dmbp)_2^{2+}$). The largely distorted tetragonal structures of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ in the ground state are, therefore, still ca. 62 kJ mol^{-1} more stabilized compared with perfectly tetrahedral geometry for both of the bcp and dmbp complexes, and this value may be taken as the upper limit of the free energy difference between $Cu(bcp)_2^{2+}$ or $Cu(dmbp)_2^{2+}$ (= $Cu^{II}L(O)$) in the ground state and hypothetical $Cu(bcp)_2^{2+*}$ or $Cu(dmbp)_2^{2+*}$ (= $Cu^{II}L(Q)$) in the tetrahedral configuration. It should be noted that the LFAE calculation above does not include the entropic contribution to the free energy.

As it is clear that the reduction reactions of $Cu^{II}L(O)$ (= $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ complexes) take place through Path B in Scheme 1, microscopic reversibility requires that the oxidation reaction of $Cu^{I}L(R)$ should also take place through Path B. Therefore, $Cu^{I}L(P)$ is necessarily less stable than $Cu^{II}L(Q)$. Cu(I) with d^{10} electronic configuration is well known to be stabilized as its tetrahedral form. The less stability of $Cu^{I}L(P)$ (distorted tetragonal form) may, therefore, be attributed to the nature of Cu(I) with a strong thermodynamic preference to form the tetrahedral geometry. Such tendency is explained by the possible hybridization of the 3d, 4s, and 4p orbitals and by the covalent character of the bonding. The tetrahedral $Cu(I)(N_2)_2$ is some 100 kJ mol^{-1} more stable than the hydrated Cu(I) ions, from the stability constant of Cu(I) species.[5] Therefore, the deformation of Cu(II) species seems preferred compared with the deformation of Cu(I) for the cases of $Cu(N_2)_2^{2+/+}$ couples. The preference of Path A in the case of Cu – macrocyclic thioether complexes (5–9) may be attributed to the less stable structures of $Cu^{I}L(R)$ species in solution: water or solvent coordination to the fourth position of Cu(I) is suggested for the [12]aneS_4, [13]aneS_4, [14]aneS_4 complexes, while corresponding Cu(II) complexes hold relatively planar coordination geometry suitable for the stabilization of $Cu^{II}L(O)$.

Estimation of K_{OQ} and k_{B2}

The value of the k_{B2} process 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, k_{B2} may be very fast: the deformation of $Cu(bcp)_2^{2+}$ to $Cu(bcp)_2^{2+*}$ raises the redox potential of the $Cu(bcp)_2^{2+*}/Cu(bcp)_2^{+}$ couple as much as the structural deformation of $Cu(bcp)_2^{2+}$ to $Cu(bcp)_2^{2+*}$ before the electron transfer process, and the electron transfer (k_{B2}) with minimal internal rearrangement for Cu(II) species must be very fast. The rise of the redox potential, which is equivalent to the LFAE, is estimated by using the Nernst equation.

$$[13] \qquad E^{\circ}_{Cu^{2+*/+}} = E^{\circ}_{Cu^{2+/+}} - \frac{RT}{F} \ln K_{OQ}$$

where $E^{\circ}_{Cu^{2+*/+}}$, $E^{\circ}_{Cu^{2+/+}}$, and F are the standard redox potentials of the $Cu(bcp)_2^{2+*/+}$ and $Cu(bcp)_2^{2+/+}$ couples and the Faraday constant, respectively. In this study, we obtained 0.275 V as $E^{\circ}_{Cu^{2+/+}}$ with reference to ferricinium/ferrocene couple. As the value of K_{OQ} (= k_{OQ}/k_{QO}) is expected to be small (no significant spectral change corresponding to the existence of such intermediate was observed throughout the study), $E^{\circ}_{Cu^{2+*/+}}$ may be large.

To the outer-sphere electron transfer reaction corresponding to the k_{B2} process, the Marcus cross relation is applicable. Coulombic work terms may be ignored for the reactions of $Cu(bcp)_2^{2+*}$ with ferrocene (29, 37).

$$[14] \qquad k_{B2} = \sqrt{k_{Cu^{2+*/+}} k_{Fe^{+/0}} K_{Cu^{2+*}/Fe} f W}$$

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

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

$$[17] \qquad w_{ij} = \frac{37.9 z_i z_j}{a(1 + 0.481 a \sqrt{\mu})} \quad (\text{kJ mol}^{-1})$$

where a, z, and μ are the interatomic distances (Å) between the reacting species, charge on complex ions, and the ionic

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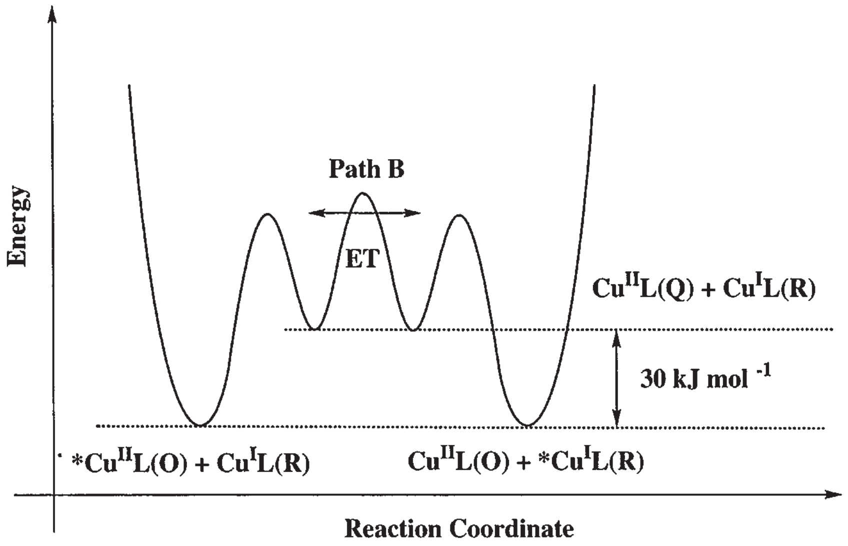
[4] The octahedral $10Dq$ value for $Cu(en)_3^{2+}$ was reported as 1.64×10^4 cm^{-1} by Orgel (47). The 4/9 of this value, 7.2×10^3 cm^{-1}, may be taken as the $10Dq$ for the tetrahedral coordination. Therefore, the values of 6.4×10^3 and 6.2×10^3 cm^{-1} obtained here seem reasonable as hypothetical $10Dq$ for the bcp and dmbp complexes.

[5] The stability constant for $Cu(dmp)_2^{+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) is reported as $10^{19.1}$ in water (48). With a naive assumption that the chemical potential of the distorted tetragonal form of Cu(I) is close to that for solvated Cu(I), the free energy difference between the solvated Cu_{aq}^{+} and $Cu(dmp)_2^{+}$ in water is estimated as 109 kJ mol^{-1} at 298 K. This value may be regarded as the upper limit for the energy difference between $Cu^{I}L(R)$ and $Cu^{I}L(P)$.

Scheme 2.



strength of the solution, respectively. By using the slope of the plot in Fig. 4, eq. [14] is rearranged to eq. [18].

$$[18] \qquad k_{B2} = 4.6 \times 10^4\, k_{Cu^{2+*/+}} k_{Fe^{+/0}}\, Sf$$

where S denotes the slope obtained from the plot in Fig. 4, and 4.6 × 10^4 represents the equilibrium constant for the overall reaction of $Cu(bcp)_2^{2+}$ with ferrocene ($\Delta E° = 0.275$ V).

The value of $k_{Cu^{2+*/+}}$ may be estimated as the limiting electron transfer rate constant by using Marcus theory (1), assuming this process is essentially controlled by the outer-sphere reorganization free energy and the electrostatic terms: 12 kJ mol^{-1} for ΔG^*_{os} and 0.5 kJ mol^{-1} for $\Delta G^*_{coul} + \Delta G^*_{DH}$, respectively, by setting the ionic radii of both $Cu(bcp)_2^{2+/+}$ to 760 pm in acetonitrile at 298 K (33). Using the value of ΔG^*_{os}, $k_{Cu^{2+*/+}}$ can be calculated as 3.8 × 10^{10} kg mol^{-1} s^{-1}. This result was obtained under the assumption that the reactions (each self-exchange reaction and the cross reaction) are adiabatic with the transmission coefficient, κ, is unity. As the driving force of the cross reaction is very large, the f factor in the Marcus cross relation becomes significantly smaller than 1. As a result, the calculated self-exchange rate constant for the $Cu^{2+*/+}$ couple becomes very large. Therefore, the value of 3.8 × 10^{10} kg mol^{-1} s^{-1} estimated here indicates that the electron self-exchange rate constant for the $Cu^{2+*/+}$ couple is taken to be close to the diffusion limit in acetonitrile. A similar explanation is possible for the value of k_{B2} estimated below. With 3.8 × 10^{10} kg mol^{-1} s^{-1} thus estimated for $k_{Cu^{2+*/+}}$, a value of 6.6 × 10^{10} kg mol^{-1} s^{-1} was obtained for k_{B2} by using the reported value of $k_{Fe^{+/0}}$, the electron self-exchange rate constant for the ferricinium/ferrocene couple (49). Therefore, $K_{OQ} = 6.2 \times 10^{-6}$, and $k_{QO} = 6.5 \times 10^6$ s^{-1}. The free energy difference between $Cu(bcp)_2^{2+}$ and $Cu(bcp)_2^{2+*}$ is ca. 31 kJ mol^{-1}, which is rather small compared with the estimated value, 62 kJ mol^{-1} from the LFAE calculation. These results indicate that the structure of $Cu^{II}L(Q)$ is either not perfectly tetrahedral as assumed for the above LFAE calculation, or the contribution of the entropy or the steric repulsion between four methyl groups on the ligands to the free energy is close to 31 kJ mol^{-1}. Similar results were obtained for the reaction of $Cu(dmbp)_2^{2+}$ with ferrocene. The kinetic parameters estimated for the reactions of $Cu(bcp)_2^{2+}$ and $Cu(dmbp)_2^{2+}$ are summarized in Table 2. The large negative activation entropies for the k_{OQ} process may be explained by the similar effect observed for several racemization reactions through the “twist” mechanism (50). The estimated pre-equilibrium constant for Path A (K_{RP}) by Villeneuve et al. (51) is in the order of 1 × 10^{-3} to 1 × 10^{-6} for Cu^+ – macrocyclic polythiaether complex. The value for K_{OQ} estimated in this study for CuN_4^{2+} ($\approx 10^{-6}$) is close to the lowest limit of the estimated value for Cu^+ – macrocyclic polythiaether complexes, which indicates that the deformation in the Cu(I)-S species is the more preferable to that in the Cu(II)-S species (intermediate P is the more stable compared with Q).

Apparent electron self-exchange rate constant directly measured by NMR for the gated reactions

It is possible that Path B is also the more preferred for the electron self-exchange reactions of the $Cu(bcp)_2^{2+/+}$ and $Cu(dmbp)_2^{2+/+}$ couples. As the free energy profile for the electron self-exchange reaction is symmetric along the reaction coordinate (Scheme 2), the rate law of the electron self-exchange reaction is described by eq. [19], assuming steady state for $Cu^{II}L(Q)$.

$$Cu^{II}L(O) \underset{k_{QO}}{\overset{k_{OQ}}{\rightleftharpoons}} Cu^{II}L(Q)$$

$$Cu^{II}L(Q) + *Cu^{I}L(R) \xrightarrow{k_{ET}} Cu^{I}L(R) + *Cu^{II}L(Q)$$

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

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

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

where $[\mathrm{Cu(I)}]_T$ and $[\mathrm{Cu(II)}]_T$ denote the total concentrations of Cu(I) and Cu(II) species, respectively. When k_{OQ} is small compared with k_{QO}

$$[22] \qquad k_{ex} = k_{ET}k_{OQ}/k_{QO}$$

The values of k_{QO} and k_{OQ} are 6.5×10^6 s^{-1} and 40 s^{-1} for the deformation of $\mathrm{Cu(bcp)_2}^{2+}$ while k_{ET} (ET rate constant for the $\mathrm{Cu^{II}L(Q)/Cu^{I}L(R)}$ couple without structural change, $k_{Cu^{2+*/+}}$) is 3.8×10^{10} kg mol^{-1} s^{-1} as estimated above. Therefore, k_{ex} for the $\mathrm{Cu(bcp)_2}^{2+/+}$ couple is calculated as 2.4×10^5 kg mol^{-1} s^{-1}, which may be compared with the directly measured value by NMR (1.4×10^3 kg mol^{-1} s^{-1}). For the electron self-exchange of $\mathrm{Cu(dmbp)_2}^{2+/+}$, a value of 3.9×10^4 kg mol^{-1} s^{-1} was calculated from eq. [22], while k_{ex} estimated by the NMR method was 5.5×10^3 kg mol^{-1} s^{-1}. Such differences may be attributed to the error introduced by the rough nature of the estimation of $k_{Cu^{2+*/+}}$. The activation free energy for the *gated* exchange reaction is, therefore, close to 50 ± 10 kJ mol^{-1}.

Direct (concerted) ET and Gated ET

The activation free energies obtained for the cross reactions examined in this study may be compared with those expected for the *direct* (concerted) electron transfer processes. The reorganization parameter for the cross reaction, λ_{rp}^{cross}, is generally described by eq. [23] (1, 2, 4).

$$[23] \qquad \lambda_{rp}^{cross} = \frac{\lambda_{rp}^{Cu} + \lambda_{rp}^{Fe}}{2}$$

where λ_{rp}^{Cu} and λ_{rp}^{Fe} represent the reorganization parameters of the imaginary *direct* self-exchange reactions for $\mathrm{Cu(dmbp)_2}^{2+/+}$ and $\mathrm{Fe(Cp)_2}^{+/0}$. The experimental results indicate that the reduction reaction of $\mathrm{Cu(dmbp)_2}^{2+}$ by ferrocene is gated. As the free energy difference for the reaction of $\mathrm{Cu(dmbp)_2}^{2+}$ with ferrocene, $\Delta G°$, is 32 kJ mol^{-1}, the following relation should be satisfied to achieve the observed *gated* ET

$$[24] \qquad \frac{(\lambda_{rp}^{cross} - \Delta G°)^2}{4\lambda_{rp}^{cross}} >> \Delta G^*_{gated}$$

where ΔG^*_{gated} is the activation free energy observed for the cross reaction of $\mathrm{Cu(dmbp)_2}^{2+}$ and ferrocene, ca. 50 kJ mol^{-1} ($k_{12} = K_{OQ}k_{B2}$). Therefore, λ_{rp}^{Cu} >> 388 kJ mol^{-1} by solving inequality [24] as $\lambda_{rp}^{Fe}/4$ is 33 kJ mol^{-1} ($k_{Fe^{+/0}} = 9 \times 10^6$ dm^3 mol^{-1} s^{-1}). A similar result was obtained for the reactions of $\mathrm{Cu(bcp)_2}^{2+/+}$. The expected activation free energy, ΔG^*, for the direct exchange reaction of the $\mathrm{Cu(L)_2}^{2+/+}$ couple (L = bcp or dmbp) should then be larger than 100 kJ mol^{-1}. The reorganization parameter for an electron self-exchange reaction is defined as the sum of the free energy of the products at the equilibrium nuclear configuration of the product's state (1, 4). The estimated very large reorganization parameter, >>400 kJ mol^{-1}, for the direct self-exchange reaction of $\mathrm{Cu(L)_2}^{2+/+}$ indicates that the inner-sphere and outer-sphere contribution to the reorganization parameter is significantly larger than the sum of the estimated values: 31 kJ mol^{-1} for the deformation of $\mathrm{Cu^{II}L(O)}$ to $\mathrm{Cu^{II}L(Q)}$ and 100 kJ mol^{-1} for the deformation of $\mathrm{Cu^{I}L(R)}$ to $\mathrm{Cu^{I}L(P)}$. Therefore, either (*i*) the free energy change for the deformation of $\mathrm{Cu^{I}L(R)}$ to $\mathrm{Cu^{I}L(P)}$ may be underestimated; or (*ii*) the relation of eq. [23] is not applicable to the cross reactions with very large reorganization parameters (1, 2), probably through the anharmonic nature of the potential surface; or (*iii*) the direct ET is nonadiabatic. In either case, the self-exchange, oxidation, and reduction cross reactions involving $\mathrm{Cu(bcp)_2}^{2+/+}$ and $\mathrm{Cu(dmbp)_2}^{2+/+}$ are all *gated*, as the gated process is energetically preferred. It is known that anharmonicity of the potential surface increases the value of transition probability (52), and quantum mechanical correction also increases the ET rate (53). Moreover, it is not probable that the reorganization energy required for the structural change from $\mathrm{Cu^{I}L(R)}$ to $\mathrm{Cu^{I}L(P)}$ is as large as 350 kJ mol^{-1}. Therefore, it may be concluded that the very slow *direct* (concerted) electron exchange between $\mathrm{Cu^{II}L(O)}$ and $\mathrm{Cu^{I}L(R)}$ is attributed to the nonadiabaticity of the reaction: a poor electronic coupling between $\mathrm{Cu^{I}L(R)}$ and $\mathrm{Cu^{II}L(O)}$ may originate from the ion pairing, the extensive solvation of these species in acetonitrile, and (or) the delocalization of the metal *d* electrons on the central Cu(II)/(I) ions because of the weak orbital interactions between Cu(II)/(I) and ligands in the deformed geometry (49, 54, 55). Nonadiabaticity of the direct ET process was also suggested for a certain *directional* (or intramolecular gated) reaction by Brunschwig and Sutin [4].

Conclusions

Reduction and oxidation reactions of the $\mathrm{Cu(bcp)_2}^{2+/+}$ and $\mathrm{Cu(dmbp)_2}^{2+/+}$ couples were examined in acetonitrile. It was found that the reduction reactions of $\mathrm{Cu(bcp)_2}^{2+}$ and $\mathrm{Cu(dmbp)_2}^{2+}$ were regulated by the slow conformational change, and the reactions proceeded through Path B in Scheme 1. The conformational change in Cu(II) species was attributed to the large LFAE from tetragonal $\mathrm{Cu^{II}L(O)}$ to the pseudo-tetrahedral $\mathrm{Cu^{II}L(Q)}$.

The apparent self-electron exchange rate constants for the $\mathrm{Cu(bcp)_2}^{2+/+}$ and $\mathrm{Cu(dmbp)_2}^{2+/+}$ couples were examined on the basis of the gated mechanism through Path B, and the calculated electron self-exchange rate constants using k_{OQ} and k_{QO} estimated from the results of the cross reactions were in fair agreement with the directly measured k_{ex} by the NMR method. Theoretical calculations of the activation free energies for the *direct* exchange reaction indicate that all the reactions, including the self-exchange reactions, examined in this study are *gated* through Path B in Scheme 1. Nonadiabaticity was suggested for the explanation of the very large free energy barrier of the *direct* exchange between $\mathrm{Cu^{II}L(O)}$ and $\mathrm{Cu^{I}L(R)}$.

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