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Flipping of Coordinated Triazine Moiety in Cu(I)-L_2 and Small Electronic Factor, κ_{el}, for Direct Outer-Sphere Cross Reactions: Syntheses, Crystal Structures and Redox Behavior of Copper(II)/(I)-L_2 Complexes (L = 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine)

Atsutoshi Yamada, Takuya Mabe, Ryohei Yamane, Kyoko Noda, Yuko Wasada,[1] Masahiko Inamo, [2] Koji Ishihara,[3] Takayoshi Suzuki,*[4] and Hideo D. Takagi*

Research Center for Materials Science, Nagoya University, Nagoya 464-8602 Japan, [1]Department of Chemical Engineering, Nagoya Institute of Technology, Nagoya 466-8555 Japan, [2]Department of Chemistry, Aichi University of Education, Kariya 448-8542, Japan,[3] School of Science and Engineering, Waseda University, Tokyo 169-8555, Japan, [4] Department of Chemistry, Okayama University, Okayama, 700-8530 Japan

E-mail: suzuki@okayama-u.ac.jp, and h.d.takagi@nagoya-u.jp

(*Abstract*)

Six-coordinate $[Cu(pdt)_2(H_2O)_2]^{2+}$ and four-coordinate $[Cu(pdt)_2]^+$ complexes were synthesized and the cross redox reactions were studied in acetonitrile (pdt = 3-(2-pyridyl)-5,6-diphenyl-1,2,4- triazine). Single crystal analyses revealed that $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ was in the D_{2h} symmetry with two axial water molecules and two symmetrically coordinated equatorial pdt ligands, while the coordination structure of $[Cu(pdt)_2]BF_4$ was a squashed tetrahedron (dihedral angle = 54.87°) with an asymmetric coordination by two pdt ligands: one pdt ligand coordinated to Cu(I) through pyridine-N and triazine-N2 while another pdt through pyridine-N and triazine-N4, and a stacking interaction between the phenyl ring on one pdt and the triazine ring on another pdt caused the squashed structure and nonequivalent Cu-N bond lengths. The cyclic voltammograms for $[Cu(pdt)_2(H_2O)_2]^{2+}$ and $[Cu(pdt)_2]^+$ in acetonitrile were identical to each other and quasi-reversible. The reduction of $[Cu(pdt)_2(H_2O)_2]^{2+}$ by decamethylferrocene and oxidation of $[Cu(pdt)_2]^+$ by $[Co(2,2'\text{-bipyridine})_3]^{3+}$ in acetonitrile revealed that both cross reactions were sluggish through a gated process (structural change took place prior to the electron transfer) accompanied by slow direct electron transfer processes. It was found that the triazine ring of the coordinated pdt ligand rotates around the C-C bond between the triazine and pyridine rings with the kinetic parameters $k = 51 \pm 5\ \mathrm{s^{-1}}$ (297.8K), $\Delta H^{\ddagger} = 6.2 \pm 1.1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -192 \pm 4$ J mol^{-1} K^{-1}. The electron self-exchange process was directly measures by using the line-broadening method: $k_{ex} = (9.9 \pm 0.5) \times 10^4$ kg mol^{-1} s^{-1} (297.8K) with $\Delta H^{\ddagger} = 44 \pm 7$ kJ mol^{-1} and $\Delta S^{\ddagger} = 0.2 \pm 2.6$ J mol^{-1} K^{-1}. By comparing this rate constant with the self-exchange rate constants estimated from the cross reactions by using the Marcus cross relation, the non-adiabaticity (electronic) factors, κ_{el}, for the direct electron transfer process between $[\mathrm{Cu(pdt)_2}]^{+\ \mathrm{or}\ 2+}$ and non-copper metal ($\mathrm{Fe^{2+}}$ and $\mathrm{Co^{3+}}$) complexes were estimated as ca 10^{-7}, indicating that the electronic coupling between the d orbitals of copper and of non-copper metals are very small.

Introduction

It is well known that copper(II)/(I) couples exhibit a characteristic redox behavior: either the reduction or oxidation reaction is regulated by the coordination structural change that takes place prior to the electron transfer step. Such a mechanism of the electron transfer reactions has been known as the “gated” mechanism. The outer-sphere gated electron transfer process is important in biological reactions involving some metalloenzymes.[1-4] In such reaction systems, the reaction of thermodynamically unfavored direction is accelerated or the reaction of thermodynamically favored direction is slowed down so as to steadily control the concentration of metabolically important chemical species, by means of the conformational changes around the metal centers. As the gated behavior is generally observed for redox couples in which the coordination structures of the oxidized and reduced forms are largely different, it has been believed that the large energy barrier for the structural change (inner-sphere reorganization) is the essential factor that induces gated phenomena. With this respect, gated behavior has been reported only for the reactions involving Cu(II)/Cu(I) couples in which Cu(I) is in the tetrahedral structure while Cu(II) in the trigonal bipyramidal or square pyramidal structures in most cases.[5-14] On the other hand, we found that the electron transfer (cross) reactions between different copper complexes and the electron self-exchange reactions are not gated.[14] Such results led us to consider that the essential factor that causes the gated phenomena may be related to the adiabaticity of the cross reactions with non-copper metal complexes: the energy level of the d orbital of copper is the lowest compared with those for any other metal species, because of the large effective nuclear charge.[15] Such a large difference in the d-orbital energies between the oxidizing and reducing reagents may significantly reduce the orbital overlap upon the outer-sphere electron transfer process, and the electron transfer reaction will become significantly less adiabatic (i.e. slowed down with apparently large activation energies). On the other hand, a sequential electron transfer process through the ligand's occupied/vacant orbitals may provide a significantly lower-enegy pathway than such a non-adiabatic outer-sphere process when convenient mediating ligand's orbitals are available. It was also found that the non-gated reactions with other metal complexes are observed only for the copper complexes with strong low-energy LMCT /MLCT bands, and therefore we asserted that such CT interactions may provide a lower-energy pathway than the outer-sphere reaction with less-adiabatic *direct* metal-metal interactions.[16,17]

$$k = K_{\mathrm{os}}\kappa_{\mathrm{el}}\nu_{\mathrm{eff}}\Gamma\exp(-\Delta G^{*}/RT) \tag{1}$$

$$\kappa_{\mathrm{el}}\nu_{\mathrm{eff}} \approx \frac{2H_{\mathrm{PR}}^{2}}{h}\left(\frac{2\pi^{3}}{2E_{\mathrm{out}}RT + E_{\mathrm{in}}h\nu_{\mathrm{in}}\cosh(h\nu_{\mathrm{in}}/2k_{\mathrm{B}}T)}\right)^{1/2} \tag{2}$$

$$H_{\mathrm{PR}}^{\mathrm{eff}} = \sum_{j}\frac{H_{\mathrm{R,CT}_{j}}^{\mathrm{ii}}H_{\mathrm{CT}_{j},\mathrm{CT}_{j}}^{\mathrm{if}}H_{\mathrm{CT}_{j},\mathrm{P}}^{\mathrm{ff}}}{(\Delta E_{\mathrm{CT}_{j}}^{0})^{2}} \tag{3}$$

where ν_{in} and ν_{eff} are the inner- and effective- frequency terms and Γ is the nuclear tunneling factor (usually taken to be unity). The E_{in} and E_{out} are the inner- and outer-sphere contributions to the free-energy term and ΔE^{0} is the energy gap between the diabatic thermal activation energy and the corresponding CT energy level at the position of the thermal transition state on the reaction coordinate. H's are the coupling elements for the relevant MLCT and LMCT transitions, respectively, and can be expressed by the ordinary bra (<|) and ket (|>) notation with the electronic Hamiltonian as follows.

$$H_{lm} = \left\langle \Psi_{l} \middle| H_{el} \middle| \Psi_{m} \right\rangle$$

Therefore, when the energy level of the CT (MLCT or LMCT) band is sufficiently low (i.e. ΔE^0 is small), the increase in the electronic coupling is expected to become large and the apparent electronic factor (= transmission coefficient), κ_{el}, significantly increases.

In 1989, Brunschwig and Sutin theoretically predicted that no reaction pathway involving a reactant's excited state (R*) competes with the direct concerted mechanism in the normal region.[18] They also concluded that a gated reaction may not take place unless the electron transfer of R* is faster than the deactivation rate of R*. The latter conclusion may be achieved when the following two conditions are fulfilled: the **Condition (1)** when a direct concerted pathway is non-adiabatic and the **Condition (2)** when a MLCT/LMCT band of R* induces the very rapid CT-perturbed electron transfer that is faster than the deactivation process of R*. In relation to the condition (2), we reported that the transient species of the oxidation reaction of dimeric $[Cu_2(diphen)_2]^{2+}$ (diphen = 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane) having a terahedral coordination geometry exhibited a strong LMCT band in the visible region (the corresponding monomeric Cu(II) complex in the trigonal bipyramidal structure exhibits no CT band in the visible region).[13]

As for the experimental results, gated electron transfer reaction is originally defined for the redox process controlled *completely* by the rate of structural reorganization. However, any electron transfer reaction regulated by the coordination structural reorganization (separated from the succeeding electron transfer step) is regarded as *partly* gated reactions nowadays since the completely gated reaction is scarce.[14] In such *partly* gated reactions, we usually observe two types of kinetic behavior. In one case, a saturation kinetics is observed: the rate constant of the structural reorganization can be isolated from that of the succeeding electron transfer step in such a case. In another case, the observed rate constant depends linearly on the concentration of the major component in solution: judgment whether the reaction is gated or not can be made by comparing the two self-exchange rate constants (k_{ex}) estimated from the measured cross reduction and cross oxidation rate constants by using the Marcus cross relation. More than two orders of difference between thus estimated k_{ex}'s are obtained when one of the directions (corresponding to the smaller k_{ex}) is gated. Copper polypyridine (CuN_4) complexes and copper polythioether (CuS_4) complexes have been intensively studied to date, where the coordination structures are trigonal bipyramidal or square pyramidal for Cu(II) and deformed tetrahedral for Cu(I) in most cases.[6]

As for the reactions of six-coordinate Cu(II) / four coordinate Cu(I) couple, van Eldik and co-workers reported the redox behaviors of Cu(II)/(I)-ferrozine complexes (ferrozine = 3-(2-pyridyl)-5,6-bis(4-sulfonatophenyl)-1,2,4-triazine, see Fig. 1) in 2003.[19] Their primary objective was to know the specific interactions of this anionic metal complex with the cationic cytochrome-*c*. As the copper(II)/(I) complexes could not be isolated as crystals in their study, they prepared them in aqueous media *in situ*. In addition, they had to use the TRIS buffer to achieve metabolic pH conditions. Under such restrictions, they successfully carried out the experiments. Their computer simulations for the CV signal of the Cu(II)/(I)-ferrozine couple clearly indicated the involvement of the gated electron transfer: the redox potentials at ca -0.5 V and ca +0.10 V were assigned to the five-coordinate (C_{4v}) and four-coordinate (T_d) Cu(II)/(I) couples, respectively. However, such a large difference in the redox potentials has never been reported to date for five-coordinate Cu(II) / four-coordinate Cu(I) couples.

In this study, we succeeded in isolating the Cu(II)/(I) complexes with the uncharged pdt ligand (pdt = 3-(2-pyridyl)-5,6-diphenyl-1,2,4- triazine, see Fig. 1) and the crystal structures were obtained for the first time, especially for the Cu(I) complex. The redox reactions of $[Cu(pdt)_2]^{2+/+}$ were examined in acetonitrile. The non-adiabaticity factor (transmission coefficient) for the electron transfer processes, which is related to the condition (1) noted above,[18] were estimated for the first time, by comparing the self-exchange rate constant estimated from the rate constants for the direct (non-gated) cross reactions with that for the electron self-exchange reactions of the $[Cu(pdt)_2]^{2+/+}$ couple. The reactivity of R* (or CT-entatic state in this case) was also discussed in relation to the Condition (2) postulated by Brunschwig and Sutin.[18]

Results and Discussion

Crystal Structures Crystal data and the structures are shown in Table 1, and Figs 2 and 3 for $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ and $[Cu(pdt)_2]BF_4$, respectively. Selected bond lengths and angles for $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ and $[Cu(pdt)_2]BF_4$ are listed in Tables 2 and 3 together with the dihedral angles between each defined plane.

The coordination structure of the $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ complex was in the D_{2h}

symmetry: two equatorially-positioned pdt ligands symmetrically coordinated with the pyridine nitrogen atom (N32) and the N2-nitrogen atom (N2) on the triazine ring. The Cu-N distances are 2.034Å(N2) and 2.045Å(N32) while the Cu-O bond lengths are very long (2.413Å) as a result of the first-order Jahn-Teller effect. The structure of this $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ complex was very similar to that reported previously for $[Cu(pdt)_2(H_2O)_2](ClO_4)_2$.[20] As the diffuse reflectance spectrum of this compound was identical to that in acetonitrile solution, the solid state structure was retained in solution. As described in the experimental section, ^{1}H-NMR spectra of bulk water in the acetonitrile solution of $[Cu(pdt)_2(H_2O)_2]^{2+}$ broadened and shifted with increasing the concentration of $[Cu(pdt)_2(H_2O)_2]^{2+}$, strongly indicating that water molecules are in the coordination sphere of Cu(II). Therefore, $[Cu(pdt)_2]^{2+}$ in acetonitrile is certainly in the 6-coordinate form of either $[Cu(pdt)_2(H_2O)_2]^{2+}$ or $[Cu(pdt)_2(solvent)_2]^{2+}$, depending on the amount of water in the solvent.

On the other hand, $[Cu(pdt)_2]BF_4$ had the asymmetric coordination structure: one of the pdt ligands coordinated to Cu(I) with the pyridine nitrogen (N32) and triazine N2-nitrogen while another pdt ligand with the pyridine nitrogen (N132) and triazine N14-nitrogen. As a result, the complex was in the C_1 symmetry although coordinating four nitrogen atoms form the D_2 structure around the central copper ion (the dihedral angle between the two pdt ligands was 54.87°). In other metal-pdt compounds such as tetrahedral $[Zn(pdt)Cl_2]$, octahedral $[Sn(pdt)Et_2]Cl_2$ and $[Ru(pdt)(bpy)_2]^{2+}$, the pdt ligands coordinated to the metal centers with the pyridine nitrogen atom and the N2-nitrogen atom of the 1,2,4-triazine ring.[21-23] Therefore, $[Cu(pdt)_2]BF_4$ is the first example of an asymmetric coordination in which one of the pdt ligands coordinates with the N4-nitrogen atom. The extended Hückel calculation of a pdt molecule indicates that the HOMO level at -11.795 eV corresponds to the lone pair of N1, N2 and N4 while the LUMO level at -10.382 eV corresponds to the π^* level of N1, N2 and N4. Therefore, the calculation indicates that the HOMO and LUMO orbitals on the three nitrogen atoms of the triazine ring are essentially identical. In addition, the MP2 calculation indicates that the flattened geometry of the free ligand is more stabilized by 1 kcal mol^{-1} when the N4 and N3 nitrogen atoms are located in close vicinity.

The MP2 and CAM-B3LYP calculations of Cu(I) structures indicate that the coordination by N(2 or 12) and N(4 or 14) do not make much difference in energy, while the coordination structure observed in the crystal was certainly stabilized by 6 kJ mol^{-1} compared with the non-stacked coordination by N2 of both pdt ligands.

In the six-coordinate $[Sn(pdt)Et_2]Cl_2$ and $[Ru(pdt)(bpy)_2]^{2+}$ complexes, the distances between metal-N2 and metal-N(pyridine) are somewhat different (0.1 Å and 0.05 Å for Sn and Ru complexes, respectively). It was reported that these differences originates form the steric interaction between pdt and other coordinated ligands. In the $[Cu(pdt)_2]^+$ complex, all of the Cu-N distances are significantly different, although the HOMO and LUMO levels (basicity and acidity) of these nitrogen atoms are essentially the same. It should be noted that the two Zn-N distances are almost identical in the $[Zn(pdt)Cl_2]$ complex (the four-coordination ionic radius of Zn^{2+} is identical to that of Cu^+, 60 pm). As the triazine ring – phenyl ring distance is ca 3.39 Å it seems the π - π stacking interaction exists in the $[Cu(pdt)_2]^+$ complex. We may, therefore, conclude that (1) the π - π stacking interaction explains the coordination of one of the triazine ring through the N4(N14) nitrogen atom, and that (2) the differences in the Cu-N bond lengths, and somewhat flattened structure (the dihedral angle between the two pdt ligands is 54.87^{o}) resulted because of the stacking interaction.

As discussed later in the section on NMR observations, it was found that the triazine ring rotates around the C-C bonds between the triazine and pyridine rings in the Cu(I) complex. There was no indication of such a rotation in the free pdt ligand. Therefore, this type of rotation is allowed only for the coordinated pdt in the tetrahedral coordination environment: in the case of octahedral complexes, the triazine ring of the equatorially coordinating pdt ligands cannot rotate because of the steric congestion by the phenyl substituents.

Electrochemical studies Cyclic voltammograms of the $[Cu(pdt)_2]^+$ and $[Cu(pdt)_2(H_2O)]^{2+}$ solutions are shown in Figs. 4. The anodic peak for both $[Cu(pdt)_2(H_2O)_2]^{2+}$ and $[Cu(pdt)_2]^+$ appeared at -50 mV vs ferricinium / ferrocene couple, while the cathodic peaks were observed at -242 mV, and -244 mV for the $[Cu(pdt)_2(H_2O)_2]^{2+}$ and $[Cu(pdt)_2]^+$ solutions, respectively. As the difference in the two cathodic peaks for two solutions are taken to be within the experimental uncertainties, we concluded that the E^o value for the $[Cu(pdt)_2(H_2O)_2]^{2+}$ / $[Cu(pdt)_2]^+$ redox couple was determined as -147 ± 2 mV.

The voltammograms of the solutions of these two complexes did not exhibit any other significant signal within the potential window of -0.8 V ~ +0.8 V vs. the ferrocene/ferricinium couple, and therefore we concluded that the $[Cu(pdt)_2(H_2O)_2]^{2+}$ and $[Cu(pdt)_2]^{+}$ are certainly the redox pair although the coordination mode of the pdt ligand is different in two different oxidation states of Cu (see the section on the crystal structures). On the other hand, two irreversible signals (-0.5 V and +0.1 V vs Ag^{+}/Ag^{0} electrode) coupled with chemical reactions were reported for the $[Cu(ferrozine)_2]^{2+/+}$ complexes in aqueous solution:[19] the redox signal at +0.1 V was assigned to the tetrahedral Cu(II)/(I), while the signal at -0.5 V was assigned to the square pyramidal Cu(II)/(I) couple by the authors. Note that ferrozine has the same structure with pdt except that ferrozine is water-soluble because of the sulfonate substituents (see Fig. 1). The voltammograms of Cu(II)/(I) couples with polypyridine ligands examined so far never exhibited such a different pair of CV signals in acetonitrile.[5,10-12] Two independent CV signals were observed only for the dimeric/monomeric pairs of Cu(II)/(I) couples with 1,2-bis(9-methyl-1,10-phenanthroline-2-yl)ethane ligand.[13] Rorabacher and co-workers studied the CV signals of various Cu(II)/(I)-S_4 complexes in aqueous solution, but no such separated CV signals like that for the $[Cu(ferrozine)_2]^{2+/+}$ complexes was reported to date.[4,6,8,9] It seems that the two irreversible redox signals for the Cu(II)/(I)-ferrozine complexes[19] was observed only for the aqueous solutions prepared *in situ* with the TRIS buffer reagent.[24] Such a difference in the electrochemical behavior of $[Cu(pdt)_2]^{2+/+}$ and $[Cu(ferrozine)_2]^{2-/3-}$ may be attributed to the relatively high solubility of the ferrozine ligand to water and the negative charges of the Cu(II)/(I)-ferrozine complexes.

Kinetic studies

Intra-molecular rotation of triazine ring in $[Cu(pdt)_2]^{+}$ and electron self-exchange reaction of $[Cu(pdt)_2]^{2+/+}$ couple

The NMR spectrum of $[Cu(pdt)_2]^{+}$ in acetonitrile-d_3 exhibited rather broad signals even without paramagnetic Cu(II) species (see supplementary materials). The homo-coupled ^{1}H signals for pyridine protons at 7.75 ~ 9.0 ppm were observed as singlet signals with line widths as broad as 20 Hz, indicating a site exchange process. These broad signals split into narrow doublets and triplets at -30°C (see supplementary materials) and enabled us to estimate the coupling constant as 7.0 Hz. Furthermore, the line width of these proton signals hardly changed by addition of the free pdt ligand to the $[Cu(pdt)_2]^+$ solution at room temperature. Therefore, the idea of a ligand(pdt) exchange between the coordinated and free pdt ligands was discarded (although the solubility of pdt ligand in acetonitrile is low the dissociation of coordinated pdt was possible): the site-exchange process observed for the $[Cu(pdt)_2]^+$ solution at room temperature was *intra*-molecular.

Addition of paramagnetic $[Cu(pdt)_2]^{2+}$ to a $[Cu(pdt)_2]^+$ solution further broadened these proton signals of coordinated pdt on $[Cu(pdt)_2]^+$, without changing their positions. This result indicates the electron self-exchange reaction between $[Cu(pdt)_2]^{2+}$ and $[Cu(pdt)_2]^+$ takes place in the slow-exchange region of the NMR time scale.[25,26] Assuming the homo-coupling constant is not affected by the chemical exchange process, the electron self-exchange rate constant for the $[Cu(pdt)_2]^{2+/=}$ couple was directly estimated from the extra broadening ($\Delta\nu$) caused by the addition of $[Cu(pdt)_2]^{2+}$: $k_{ex} = \pi\Delta\nu$ / $[Cu(pdt)_2{}^{2+}]$.[26] Results are summarized in supplementary Table S1. In supplementary Table S2, the rate constants of the *intra*-molecular process for the $[Cu(pdt)_2]^+$ complex at various temperatures are listed. For these measurements, we used a rather narrow temperature region in which the proton signals on the pyridine moiety were observed as broad singlet signals, and the kinetic analyses were carried out without complicated procedures using the density matrix treatment.[26,27] The temperature dependence of the rate constants for these processes are shown in Figs. 5 and 6. The self-exchange rate constant was estimated as $k_{ex} = (9.9 \pm 0.5) \times 10^4$ kg mol^{-1} s^{-1} at 297.8K with $\Delta H^‡ = 44 \pm 7$ kJ mol^{-1} and $\Delta S^‡ = 0.2 \pm 2.6$ J mol^{-1} K^{-1}, while the kinetic parameters for the *intra*-molecular site-exchange process in $[Cu(pdt)_2]^+$ were $k = 51 \pm 5$ s^{-1}, $\Delta H^‡ = 6.2 \pm 1.1$ kJ mol^{-1} and $\Delta S^‡ = -192 \pm 4$ J mol^{-1} K^{-1}.

The free-rotation of the coordinated triazine ring in $[Cu(pdt)_2]^+$ indicates that the structural change between Cu(I) and Cu(II) complexes is relatively rapid. On the other hand, such a rotation of the triazine ring may not be rapid in the $[Cu(ferrozine)_2]^{3-}$ complex because of the bulky sulfonate substituents and the strong hydrophilic interaction between $-SO_3^-$ and water.[19] The differences in the electrochemical behavior and the reaction mechanisms (discussed later) between the $[Cu(pdt)_2]^{2+/+}$ and $[Cu(ferrozine)_2]^{2-/3-}$ couples may be explained by these factors.

Cross Reactions The reduction reaction of $[Cu(pdt)_2(H_2O)_2]^{2+}$ by decamethylferrocene was observed under the conditions of [Cu(II)] << [Fe(II)]. The results are shown in Fig. 7. Although the plots appear to be linear, they are actually slightly bent and do not go through the origin when we assume straight lines. It has been known that the reduction reactions of trigonal bipyramidal Cu(II)-N_4 complexes are controlled by the slow structural change prior to the electron transfer step, and the slowness of such a structural change (k_{OQ} in Scheme 1) was explained by the multi-step, symmetry-allowed processes.[5,10,12,14] According to the Square Scheme (Scheme 1) proposed by Rorabacher and co-workers, the rate law for the reduction reactions of Cu(II) is given by Eq. 4.

$$-\frac{[\mathrm{Cu^{II}L}]}{\mathrm{d}t}=\left(\frac{k_{\mathrm{A2}}k_{\mathrm{PR}}}{k_{\mathrm{2A}}\left[\mathrm{A_{Ox}}\right]+k_{\mathrm{PR}}}+\frac{k_{\mathrm{B2}}k_{\mathrm{OQ}}}{k_{\mathrm{B2}}\left[\mathrm{A_{Red}}\right]+k_{\mathrm{QO}}}\right)[\mathrm{Cu^{II}L(O)}]\ [\mathrm{A_{Red}}] \qquad (4)$$

where $[\mathrm{A_{red}}]$ and $[\mathrm{Cu^{II}L(O)}]$ correspond to the concentrations of decamethylferrocene and $[\mathrm{Cu(pdt)_2(H_2O)_2}]^{2+}$, respectively, and the k's correspond to the rate constants shown in Scheme 1. The first term on the right hand side of the equation corresponds to Path A by the direct electron transfer through the product's excited state, while the second term corresponds to Path B via a sluggish structural reorganization. As the concentration $\mathrm{A_{red}}$ is low ($<1.5 \times 10^{-4}$ mol kg^{-1}) while the maximum value of k_{B2} is $\sim 10^{12}$ kg mol^{-1} s^{-1} (diffusion controlled rate), $k_{\mathrm{B2}}[\mathrm{A_{red}}]$ is assumed to be smaller than k_{QO}, since k_{QO} corresponds to the relaxation process from the high-energy constrained structure: k_{QO} was estimated as 7.7×10^7 s^{-1} for the $[\mathrm{Cu(2,9\text{-}dimethyl\text{-}1,10\text{-}phenanthroline)_2}]^{2+}$ complex.[10] Then Eq. 4 is simplified as Eq. 5 (Validity of this assumption was verified by the results of the curve-fit. See Table 4),

$$k_{\mathrm{obs}}=\left(k_{\mathrm{A2}}+\frac{k_{\mathrm{OQ}}}{\left[\mathrm{A_{Red}}\right]+k_{\mathrm{QO}}/k_{\mathrm{B2}}}\right)[\mathrm{Cu^{II}L(O)}]\ [\mathrm{A_{Red}}] \qquad (5)$$

Solid / broken lines in Fig. 7 describe the best-fit results calculated by a computer. The estimated rate constants for each process in Scheme 1 are listed in Table 4. The reliability of the $k_{\mathrm{QO}}/k_{\mathrm{B2}}$ value is low, because of the accumulated errors inherent in this type of curve-fitting algorithm in which digits of the parameters are largely different. However, it is clear that the ratio of $k_{\mathrm{QO}}/k_{\mathrm{B2}} < 1$, which certainly satisfies the condition postulated by Brunschwig and Sutin.[18]

The k_{OQ} values, that correspond to the structural change prior to the electron transfer step, are only slightly smaller than those reported for the reduction reactions of Cu(II) complexes with bidentate polypyridine ligands (trigonal bipyramidal structure with a solvent molecule at the fifth coordination site).[6] The necessity of the release of one or two solvent molecules form $[Cu(pdt)_2(H_2O)_2]^{2+}$ and twisting seems to have caused the somewhat smaller k_{OQ}, compared with the similar process observed for Cu(II)-polypyridine complexes, since the flipping of the triazine ring is relatively fast. We may conclude that the emergence of the direct electron transfer process (k_{A2}) is caused by the multi-step deformation of 6-coordinate $[Cu(pdt)_2]^{2+}$ to the pseudo-D_{2d} structure including the flipping process of the triazine ring.

The electron self-exchange rate constant estimated from k_{A2} by using the Marcus Cross Relation[30] was only 7 x 10^{-3} kg mol^{-1} s^{-1}, which is some 10^6 times smaller than the that directly measured for the Cu(II)/(I)-polypyridine complexes[5,10-12] or than that estimated from the cross reactions between copper (II) and (I) complexes bearing different ligands.[14] The electronic factor (or the transmission coefficient) of electron transfer process can be estimated by comparing the electron self-exchange rate constants for particular reactions through adiabatic and non-adiabatic pathways.[31] Since the direct self-exchange reactions as well as the pseudo-exchange reactions with other Cu complexes are taken to be adiabatic, the adiabatic self-exchange rate constants for the Cu(II)/Cu(I) couples are known to be in the range of $10^3 \sim 10^5$ kg mol^{-1} s^{-1}.[6,13,14] Therefore, we may safely conclude that the adiabaticity of this direct k_{A2} process is very low and κ_{el} = ca $10^{-5} \sim 10^{-7}$. Note that the adiabatic range of κ_{el} value is generally taken to be $10^{-3} \sim 1$ for the medium overlap case.

The oxidation reaction of $[Cu(pdt)_2]^+$ by $[Co(2,2'\text{-bipy})_3]^{3+}$ clearly exhibited the saturation kinetics (Fig. 8) under the conditions of $[Cu(pdt)_2]^+ << [Co(bipy)_3]^{3+}$. Results of the previous studies indicate that the redox reactions of copper species with strong CT bands were not sluggish because of the CT-perturbed sequential electron transfer mechanism.[6,10-14] As the $[Cu(pdt)_2]^+$ complex exhibits CT bands at $\lambda > 500$ nm, the sluggish behavior observed in this study (Fig. 8) was not expected for the oxidation reaction of $[Cu(pdt)_2]^+$. It seems that the π–π stacking interaction and the resulting non-equivalent Cu-N bond lengths in this complex is the reason of this result:

the molar extinction coefficient of the CT bands of $[\mathrm{Cu(pdt)_2}]^+$ was as small as one fifth (ca 1000 kg mol^{-1} cm^{-1}) of those reported for the other Cu(I) complexes with polypyridine ligands (ca 5000 ~6000 kg mol^{-1} cm^{-1}). [10-14]

The kinetic results were analyzed by using the following equation derived for the Square Scheme by Rorabacher and co-workers.[6,7]

$$-\frac{[\mathrm{Cu^IL}]}{\mathrm{d}t}=\left(\frac{k_{2\mathrm{A}}k_{\mathrm{RP}}}{k_{2\mathrm{A}}\left[\mathrm{A_{Ox}}\right]+k_{\mathrm{PR}}}+\frac{k_{2\mathrm{B}}k_{\mathrm{QO}}}{k_{\mathrm{B2}}\left[\mathrm{A_{Red}}\right]+k_{\mathrm{QO}}}\right)[\mathrm{Cu^IL(R)}]\,[\mathrm{A_{Ox}}] \qquad (6)$$

The first term on the right hand side of the equation corresponds to Path A via a product-excited state, while the second term corresponds to Path B by the sluggish electron transfer process with the reactant's excited state (gated). As the concentration $\mathrm{A_{red}}$ is low (<1.5 x 10^{-4} mol kg^{-1}) while the maximum value of k_{B2} is ~10^{12} kg mol^{-1} s^{-1}, $k_{\mathrm{B2}}[\mathrm{A_{red}}]$ is assumed to be sufficiently smaller than k_{QO}, since k_{QO} corresponds to the relaxation process from the high-energy constrained structure: k_{QO} was estimated as 7.7 x 10^7 s^{-1} for the $[\mathrm{Cu(2,9\text{-}dimethyl\text{-}1,10\text{-}phenanthroline)_2}]^{2+}$ complex.[10] Then Eq. 6 is simplified to Eq. 7 (Validity of this assumption was verified by the results of the curve-fit. See Table 5), and the rate constants were estimated using a computer.

$$k_{\mathrm{obs}}=\left(k_{2\mathrm{B}}+\frac{k_{\mathrm{RP}}}{\left[\mathrm{A_{Ox}}\right]+k_{\mathrm{PR}}/k_{2\mathrm{A}}}\right)[\mathrm{Cu^IL(R)}]\,[\mathrm{A_{ox}}] \qquad (7)$$

The best-fit results are shown by the solid and broken lines in Fig. 8, and the obtained rate constants are summarized in Table 5. The quality of the calculated results is low because of somewhat scattered experimental data and the number of the parameters to fit, although all rate constants obtained in this study are the average of minimum 10 runs. However, it is clear that the k_{RP} value is in the order of 10^{-1} s^{-1} and the ratio of $k_{\mathrm{PR}}/k_{2\mathrm{A}}$ is as small as 10^{-3} or less. Therefore, the Condition (2) given by Brunschwig and Sutin is certainly fulfilled for the observation of the gated electron transfer process. The $k_{2\mathrm{B}}$ value which corresponds to the direct electron transfer process was ca 4.9 x 10^{-1} kg mol^{-1} s^{-1} (298.2 K), although the accumulated error is relatively large. The electron self-exchange rate constant estimated from this value is 1 x 10^{-2} kg $mol^{-1}s^{-1}$: this estimates $\kappa_{el} \sim 10^{-7}$. This value is comparable to that estimated from the rate constant k_{A2} obtained from the reduction cross reaction, $\kappa_{el} \sim 10^{-5\sim-7}$. Therefore, we may safely conclude that the *direct* cross reactions (through the product excited state) of Cu(II)/(I)$(pdt)_2$ couple with *non-copper* metal complexes are non-adiabatic with κ_{el} being as small as 10^{-7}.

The results of electrochemical measurements that the observed CV signal for this couple was only one and quasi-reversible implies that the $[Cu(pdt)_2(H_2O)_2]^{2+}$ and $[Cu(pdt)_2]^+$ are certainly the redox pair at the electrode, although structures of these Cu(II) and Cu(I) complexes are largely different. This indicates that the overlap (coupling) between the orbital on the electrode and the d-orbitals on $[Cu(pdt)_2(H_2O)_2]^{2+}$ and $[Cu(pdt)_2]^+$ are sufficient and the electron transfer reactions in both directions are adiabatic for both homogeneous and heterogeneous processes. The electron self-exchange process at the equilibrium potential (at electrodes) is taken to require a half of the total reorganization energies necessary for the corresponding homogeneous self-exchange process.[32]

For the cross reactions of the Cu(II)/(I)-pdt couple in solution, the counter reagent (Co(III)-bipyridine or decamethylferrocene) should also activate symmetrically along the reaction coordinate and the activation process (structural change) of the counter reagent within the encounter complex (in the solvent cage) should also be identical to those for each self-exchange reaction of counter reagents, as far as the cross relation is applicable.[33] The concerted deformation (inner-sphere reorganization) process for the Cu species may also improve the CT-perturbation (especially when the twisting of the pdt ligands is involved).[12,13,14] We may therefore safely conclude that the non-adiabaticity factors, κ_{el}, estimated for both reduction reactions of $[Cu(pdt)_2(H_2O)_2]^{2+}$ and oxidation reactions of $[Cu(pdt)_2]^+$ in this study may be taken to be the upper limit for the *direct* electron transfer reactions for the concerted process, and the result certainly shows that the **Condition (1)** given by Brunschwig and Sutin is important for the intervention of the gated mechanism.

When a direct self-exchange reaction proceeds through the concerted mechanism, the structural change within the encounter complex (in the solvent cage) involves the twisting of the coordinated pdt ligands and the rotation / flipping of the triazine ring as shown in Scheme 2, since the self-exchange reaction should proceed along the symmetric reaction coordinate. The bond lengths between Cu(II) and axial water / solvent molecules in the $[Cu(pdt)_2(H_2O)_2]^{2+}$ complex are originally long because of the first-order Jahn-Teller effect, and Cu(II) complexes tend to form square-pyramidal structure (pseudo-C_{4v}). The d^9 configuration of the Cu(II) species in the square-pyramidal structure induces further deformation to trigonal-bipyramidal structure (pseudo-D_{3h}) because of the second-order Jahn-Teller effect (Figure 9). As the d^9 configuration in the trigonal-bypyramidal structure also induces the structural deformation back to the square-pyramidal structure, the $[Cu(pdt)_2(H_2O)_2]^{2+}$ complex is in equilibrium with the pseudo-C_{4v} and pseudo-D_{3h} forms in solution. It is clear that flipping / rotation of the triazine ring of the coordinated pdt ligand is possible only in the pseudo-D_{3h} form or in the D_2 form because of the steric congestion of the phenyl substituents. Therefore, we may safely conclude that the concerted electron-transfer process is allowed only through the pseudo-D_{3h} form of $[Cu(pdt)_2(H_2O)]^{2+}$, as the flipping / rotation of the triazine ring within the encounter complex is necessary for this process (Scheme 2).

Conclusion

In this study, $[Cu(pdt)_2]^{2+/+}$ complexes were synthesized and the crystal structure of $[Cu(pdt)_2]^+$ was reported for the first time. The structure was unique (C_1) with asymmetric coordination of two pdt ligands, and the squashed coordination structure was caused by the stacking interaction between the phenyl group on one pdt ligand and the triazine ring on another pdt ligand. The NMR study of free pdt and coordinated pdt on $[Cu(pdt)_2]^+$ in acetonitrile-d_3 revealed that the triazine moiety in the pdt ligands on $[Cu(pdt)_2]^+$ flips with rate constant $k = 51 \pm 5\ s^{-1}$ at 297.8K.

The oxidation cross reaction by $[Co(bipy)_3]^{3+}$ and the reduction cross reaction by decamethylferrocene was examined in acetonitrile. For oxidation and reduction cross reactions, both gated and direct electron transfer processes were observed. The direct electron self-exchange reaction between $[Cu(pdt)_2]^{2+}$ and $[Cu(pdt)_2]^+$ were also observed and the rate constant $k_{ex} = (9.9 \pm 0.5) \times 10^4$ kg mol^{-1} s^{-1} (297.8K) was obtained. Comaprison of this value with the self-exchange rate constants estimated for the direct processes of the reduction and oxidation cross reactions revealed that the electronic coupling between copper complexes and non-copper complexes are very small, κ_{el} ~ $10^{-5\sim-7}$. These results indicate that the following two conditions are required for the emergence of the Gated process: (1) the direct concerted pathway is non-adiabatic and (2) when a MLCT/LMCT band of the reactant's excited state (R*) induces the very rapid CT-perturbed electron transfer that is faster than the deactivation process of R*, which is consistent with the predictions by Brunschwig and Sutin.[18]

In this study we could not observe CT-perturbed acceleration of the cross reactions, chiefly because of the relatively low HOMO/LUMO levels of the pdt ligand and relatively small transition dipole moment for these complexes: the H_{CT} terms in Eq (3) were not enhanced in these reactions. We could not obtain any information about the structures of Q and P in Scheme 1, since the gated pathways were slow and no or only limited improvement of the electronic coupling was achieved by such a structural change. On the other hand, a concerted self-exchange mechanism was proposed in Scheme 2, where the principle of microscopic reversibility and possible deformation of each species was considered on the basis of the Jahn-Teller theorem.

It was found that the electrochemical results as well as the redox reaction mechanisms were very different for the $[Cu(pdt)_2]^{2+/+}$ couple in acetonitrile and $[Cu(ferrozine)_2]^{3-/2-}$ couple in water.[19] Such a difference may be attributed to the difference in the stric bulk of the coordinated ligand and to the difference in the specific ligand - solvent interaction. It was shown that we can alter the redox reaction mechanism and rate, by varying the substituents on the ligand and the type of solvents.

Experimental

General Acetonitrile obtained from Wako Pure Chemicals Inc. was treated with dried molecular sieves 4A for several days followed by distillation under argon atmosphere. The concentration of water was determined by the Mitsubishi Kasei Carl-Fisher apparatus. This treatment reduced the content of water to less than 1 mmol kg^{-1}. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and tetrabutylammonium tetrafluoroborate ($TBABF_4$) from Aldrich were recrystallized twice from ethyl acetate – hexane mixture and dried under reduced pressure. Decamethylferrocene was sublimed at 90 °C before use.

Syntheses

$[Co(bpy)_3](PF_6)_3$ $[Co(bpy)_3](PF_6)_3$ was synthesized by a literature method.[34] The crude compound was recrystallized from the acetonitrile – diethyl ether mixture. Anal. Calcd for $C_{30}H_{24}N_6P_3CoF_{18}$: C, 37.4 ; H, 2.51 ; N, 8.73%, found: C, 37.5 ; H, 2.70 ; N, 9.03%

$[Cu(pdt)_2(H_2O)_2](BF_4)_2$ $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ was synthesized following the literature method.[20] To a 50 mL of 1:1 methanol / 1,4-dioxane mixed solvent containing 0.631 g (2.03 mmol) of pdt (pdt = 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine from Aldrich) was added a methanol solution (20 mL) of $Cu(BF_4)_2 \cdot 4H_2O$ (0.310 g, 1.00 mmol). The solvent was evaporated to 10 mL under reduced pressure, and the resulting green compound was collected. The crude compound was dissolved in a 1:1 mixture of acetonitrile / methanol and filtered. The solvent of the filtrate was evaporated and the resulting green granular crystals were collected, washed with diethyl ether and dried in a desiccator. The crystals were suitable for the X-ray analysis (yield 0.499 g, 55.8 %). Anal. calcd for $C_{40}H_{32}N_8B_2CuF_8O_2$: C, 53.74 ; H, 3.62 ; N, 12.54%. Found: C, 54.13; H, 3.60 ; N, 12.56%. NMR measurements were carried out at 298K in acetonitrile-d_3 containing 0.041 ± 0.009 mol kg^{-1} of H_2O. With increasing the concentration of $[Cu(pdt)_2(H_2O)_2]^{2+}$ ($0< [Cu(pdt)_2(H_2O)_2]^{2+} < 0.010$ mol kg^{-1}), the ^1H signal of H_2O in the bulk broadened and shifted toward the lower magnetic field, indicating rapid exchange of coordinated water molecules with those in the bulk.[35]

$[Cu(pdt)_2]BF_4$ $[Cu(pdt)_2]BF_4$ was synthesized by the following method. To an acetonitrile solution (10 mL) cotaining 0.401 g (1.28 mmol) of pdt, was added 20 mL of acetonitrile solution of $[Cu(acetonitrile)_4]BF_4$ (0.195 g) and the mixture was refluxed for 2 h. After removing the solvent to ca 10 mL under the reduced pressure, diethyl ether dried under argon was added with vigorous stirring. After the black oily substances were removed by filtration, the filtrate was stored for more than 2 days in a fridge. Resulting black needle-shaped crystals were collected and dried. The crystals were suitable for the X-ray analysis (yield 0.067 g, 13.3%). Anal. calcd for $C_{40}H_{28}N_8BCuF_4$: C, 62.31 ; H, 3.66 ; N, 14.53%. Found: C, 62.61 ; H, 3.64 ; N, 14.43%. ^{1}H-NMR(CD_3CN, 400MHz , 298K , ppm) : 8.90 (br,), 8.65 (br), 8.25 (br), 7.77 (br), 7.1-7.5 (m, br, Ar-H).

Measurements The electrochemical measurements were carried out in acetonitrile by a BAS 100B/W electrochemical analyzer at 25 ˚C. A 3 mmϕ glassy carbon was used as the working electrode, while a platinum wire and Ag^+ (0.010 mol kg^{-1})/Ag in acetonitrile containing 0.10 mol kg^{-1} $TBAPF_6$ were used as the counter and reference electrodes, respectively. All measurements were carried out under the argon atmosphere. An addition of water up to 10 mmol/kg did not alter the observed CV signals. Although the voltammograms were examined with scan rates from 100 mV/s to 500 mV/s, no splitting of cathodic / anodic signals were observed.

The NMR spectra were observed by a Bruker AMX-400WB and JEOL A-400 spectrometers. Absorption spectra of solution samples were recorded by a JASCO V-570 spectrophotometer at 25 ^{o}C. Diffuse reflectance spectra were recorded at room temperature by a Hitachi U-3400 spectrophotometer equipped with an integration sphere. Kinetic measurements were carried out by using a Unisoku RSP-1000 stopped-flow apparatus. Temperatures of the sample solutions were controlled to ± 0.2^{o}C by using a Neslab RTE-111 temperature controller. Parameters such as the ionic radius and redox potentials used for the calculations on the basis of the Marcus cross relation are listed elsewhere.[6,10-13,36]

For the X-ray analyses, the intensity data were measured at 23 °C on an automated Rigaku AFC-5R four-circle diffractometer equipped with a graphite-monochromated Mo K_a radiation (λ = 0.71073 Å). Absorption corrections were applied by an empirical method based on three sets of Ψ-scan data.[37] The structures were solved by the direct method using the SIR 92[38] or SHELXS97[39] program, and refined on F^2 with all independent reflections using the SHELXL97 program.[39] All non-hydrogen atoms were refined anisotropically, and H atoms were treated by riding models. All calculations were carried out using a TeXsan software package.[40]

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Table 1 Crystallographic data for $[Cu(pdt)_2(H_2O)_2](BF_4)_2$ and $[Cu(pdt)_2]BF_4$

Compound	$[Cu(pdt)_2(H_2O)_2](BF_4)_2$	$[Cu(pdt)_2]BF_4$
Formula	$C_{40}H_{32}B_2CuF_8N_8O_2$	$C_{40}H_{28}BCuF_4N_8$
FW	893.90	771.05
T / K	200(2)	200(2)
Color, shape	Green, Block	Dark red, Block
Crystal dimension / mm	0.25 x 0.20 x 0.18	0.20 x 0.20 x 0.20
Crystal system	Monoclinic	Triclinic
Space grope	$C2/c$	P-1
Z	4	2
a / Å	11.870(4)	10.912(3)
b / Å	11.255(3)	12.707(3)
c / Å	29.713(13)	14.428(3)
α / deg.		68.615(4)
β / deg.	93.50(3)	68.335(4)
γ / deg.		75.403(4)
V / Å^3	3962(2)	1715.2(7)
D_x / Mg m^{-3}	1.499	1.493
$F(000)$	1820	788
μ(Mo K$_\alpha$) / mm^{-1}	0.637	0.703
T_{min}, T_{max}	0.700, 0.880	0.601, 0.869
Refln / param ratio	4560/286	7668/488
$R1$ [$F_o^3 > 2\sigma(F_o^3)$]	0.058	0.052
$wR2$ (all refln)	0.182	0.161
GoF	1.040	1.117

Table 2 Selected bond lengths, angles and dihedral angles between least-square planes for $[Cu(pdt)_2(H_2O)_2](BF_4)_2$

	$[Cu(pdt)_2(H_2O)_2](BF_4)_2$
Bond lengths	
Cu-N2	2.034(3)
Cu-N32	2.045(2)
Cu-O1	2.413(3)
Angles	
N2-Cu-N32	79.64(10)
Cu-N2-C3	114.66(19)
Cu-N32-C31	114.81(19)
Dihedral angles	
pl.[Cu, N2, C3, C31, N32] vs. pl.triazine[a]	2.82(7)
pl.[Cu, N2, C3, C31, N32] vs. pl.prydine[b]	1.5(1)
pl.triazine[a] vs. pl.pyridine[b]	1.9(1)
pl.triazine[a] vs. pl.phenyl(5)[c]	53.0(1)
pl.triazine[a] vs. pl.phenyl(6)[d]	37.9(1)

[a] Defined by N1, N2, C3, N4, C5 and C6. [b] Defined by C31, N32, C33, C34, C35 and C36. [c] Defined by C51, C52, C53, C54, C55 and C56. [d] Defined by C61, C62, C63, C64, C65 and C66.

Table 3 Selected bond lengths, angles and dihedral angles between least-square planes for [Cu(pdt)$_2$]BF$_4$

Bond length(Å)	
Cu–N132	1.995
Cu–N2	2.005
Cu–N32	2.025
Cu-N14	2.056
Bond angle(deg.)	
N132–Cu–N2	142.94
N132–Cu–N32	116.12
N132–Cu–N14	82.62
N2-Cu-N32	81.83
N2-Cu-N14	110.70
N32-Cu-N14	131.09
Dihedral angle(°)	
pl.(Cu1,N14,N132) vs.pl.(Cu1,N2,N32)	54.87

Table 4 Observed rate constants for the reduction reaction of $[Cu(pdt)_2(H_2O)_2]^{2+}$ by decamethylferrocene in acetonitrile

T/K	k_{A2}/kg mol^{-1} s^{-1}	k_{OQ} / s^{-1}	(k_{QO}/k_{B2})/mol kg^{-1}
278.2	$(3.40 \pm 0.11) \times 10^{5}$	1.24 ± 3.78	$(2.39 \pm 18.6) \times 10^{-5}$
283.2	$(4.15 \pm 0.20) \times 10^{5}$	9.70 ± 8.64	$(7.49 \pm 8.71) \times 10^{-5}$
288.2	$(5.29 \pm 0.18) \times 10^{5}$	13.4 ± 7.5	$(5.48 \pm 4.79) \times 10^{-5}$

Table 5. Estimated rate constants for the oxidation reaction of $[Cu(pdt)_2]^{+}$ by $[Co(2,2'\text{-bipyridine})_3]^{3+}$ in acetonitrile

T/K	k_{2B}/kg mol^{-1} s^{-1}	k_{RP} / s^{-1}	(k_{PR}/k_{2A})/mol kg^{-1}
288.2	$(6.1 \pm 27.5) \times 10^{-2*}$	$(2.78 \pm 1.95) \times 10^{-3}$	$(1.62 \pm 1.21) \times 10^{-3}$
293.2	$(5.26 \pm 1.16) \times 10^{-1}$	$(1.22 \pm 0.48) \times 10^{-3}$	$(4.55 \pm 3.53) \times 10^{-4}$
298.2	$(4.84 \pm 3.38) \times 10^{-1}$	$(2.45 \pm 1.93) \times 10^{-3}$	$(1.00 \pm 1.06) \times 10^{-3}$

* Calculated value is not sufficiently reliable because of the accumulated errors.

Figure Captions

Figure 1. Structure of ferrozine and pdt ligands.

Figure 2. Ortep (50% probability level) of cationic part of $[Cu(pdt)_2(H_2O)_2](BF_4)_2$.

Figure 3. Ortep (50% probability level) of cationic part of $[Cu(pdt)_2]BF_4$.

Figure 4. Cyclic voltammogram of $[Cu(pdt)_2]^+$ (4a) and $[Cu(pdt)_2]^{2+}$ (4b) in acetonitrile at $T = 298.2$K. [Cu] = 1 mmol kg^{-1} and scan rate = 100 mV s^{-1}.

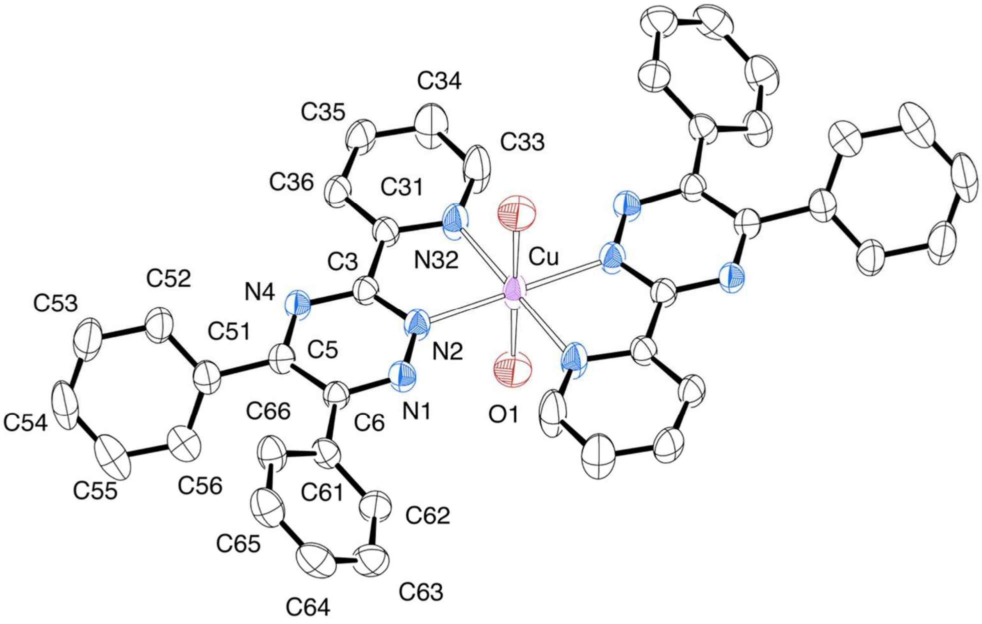
Figure 5. Temperature dependence of the electron self-exchange rate constant for the $[Cu(pdt)_2]^{2+/+}$ couple. $[Cu(pdt)_2{}^+]$ = 9.10 mmol/kg. $[Cu(pdt)_2{}^{2+}]$ = 0.25 mmol/kg. $I = 0.20$ mol / kg ($TBABF_4$).

Figure 6. Temperature dependence of the *intra*-molecular rotation of the triazine moiety of the coordinated pdt ligand on $[Cu(pdt)_2]^+$. $[Cu(pdt)_2{}^+]$ = 9.10 mmol/kg. $I = 0.20$ mol / kg ($TBABF_4$).

Figure 7. Plots of k_{obs} vs $[Fe(cp^*)_2]^+$. $[Cu(pdt)_2{}^{2+}] = 1.0 \times 10^{-5}$ mol kg^{-1}, $I =$ 0.1 mol kg^{-1} ($TBABF_4$).

Figure 8. Plots of k_{obs} vs $[Co(bipy)_3]^{3+}$. $[Cu(pdt)_2{}^+] = 1.0 \times 10^{-4}$ mol kg^{-1}, $I =$ 0.1 mol kg^{-1} ($TBAPF_6$).

Figure 9. The E' normal mode vibration for pseudo-D_{3h} and B_1 normal mode vibration for pseudo-C_{4v} induce inter-conversion between these two structures with d^9 electronic configurations.



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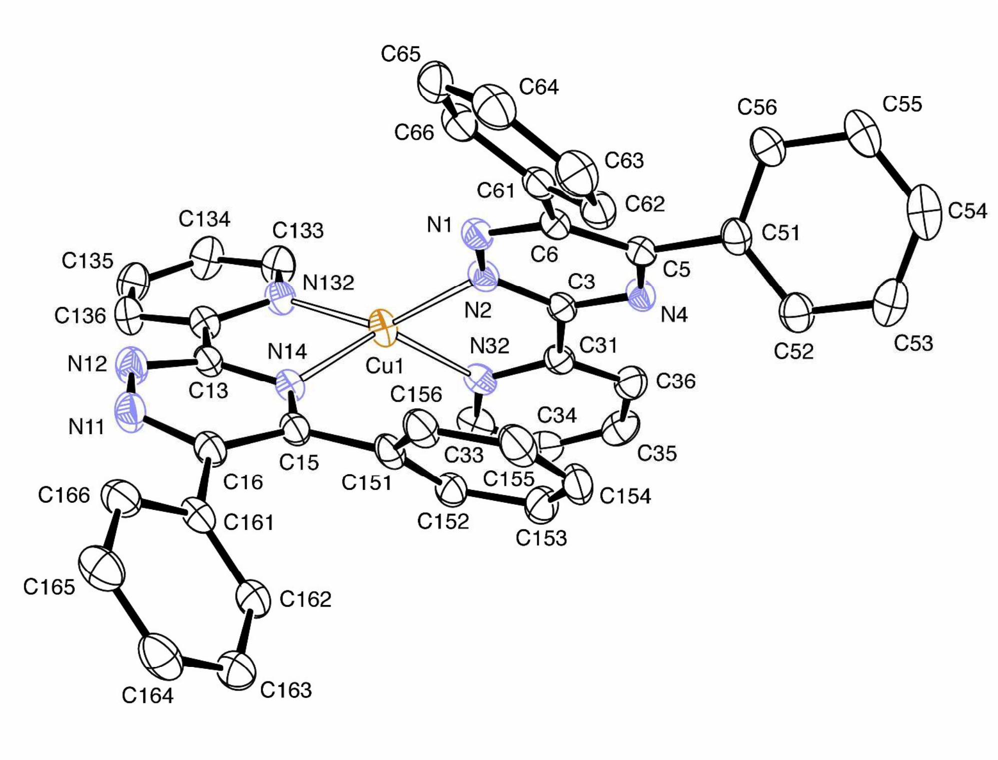

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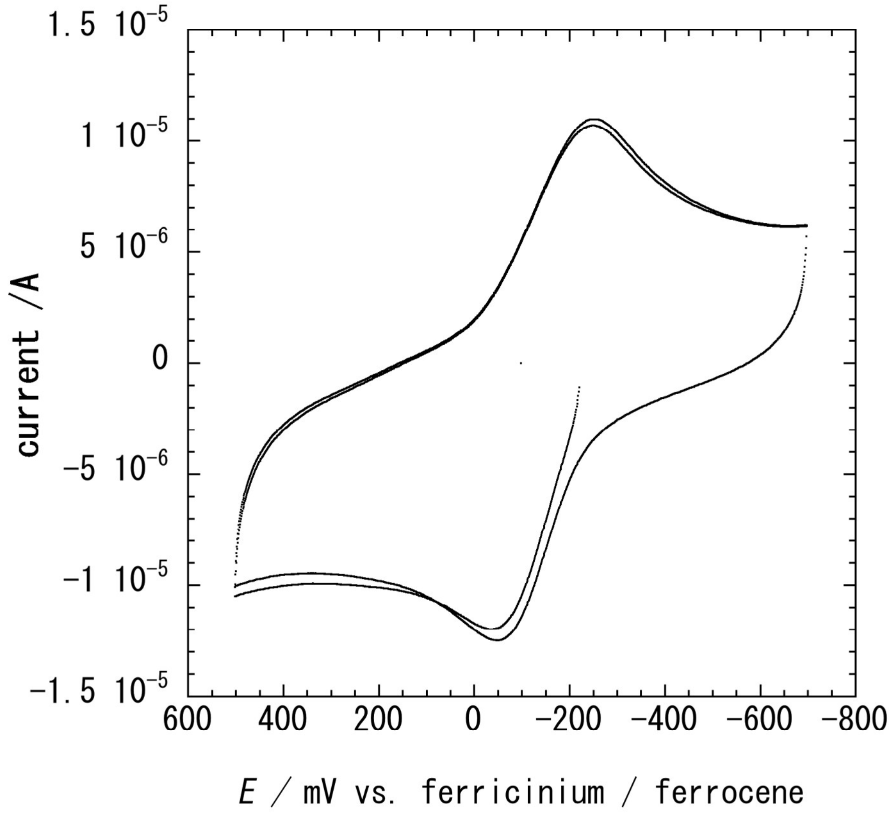

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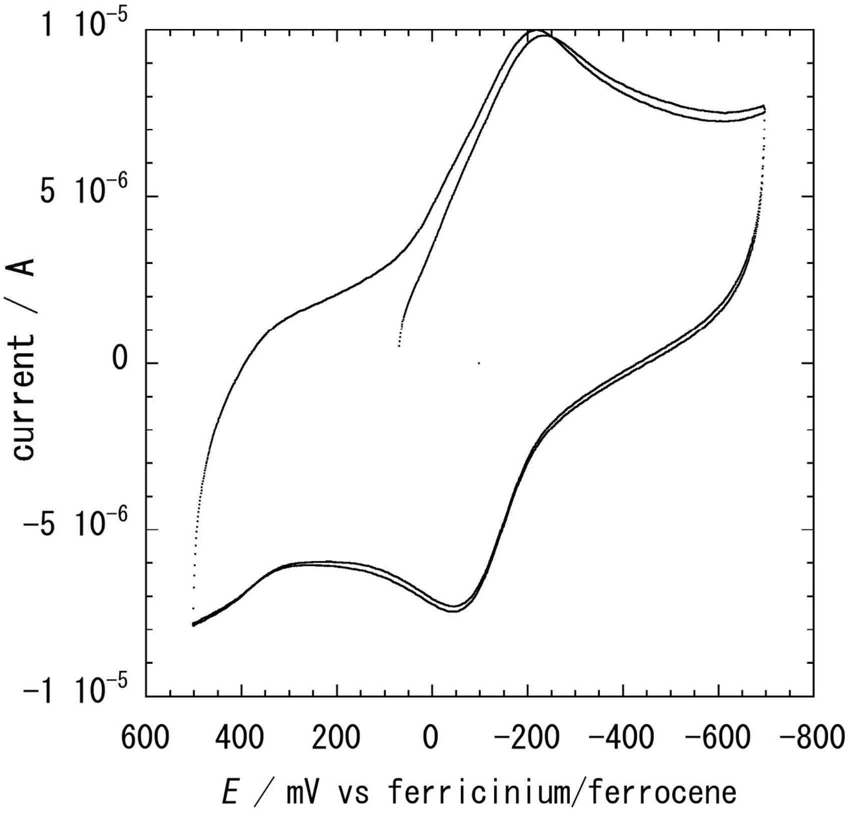
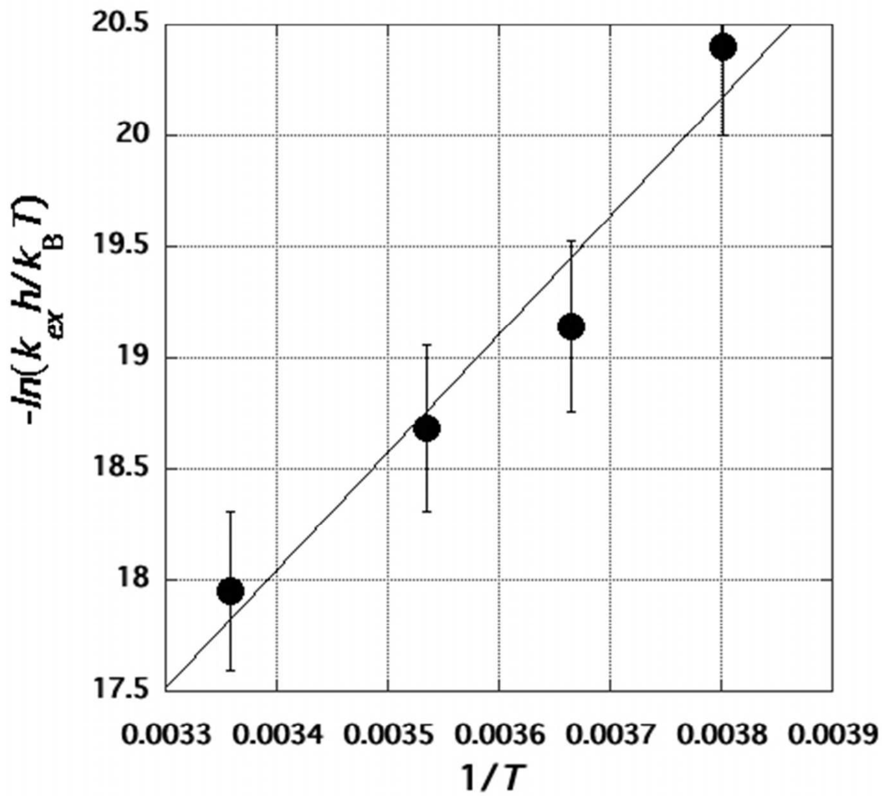
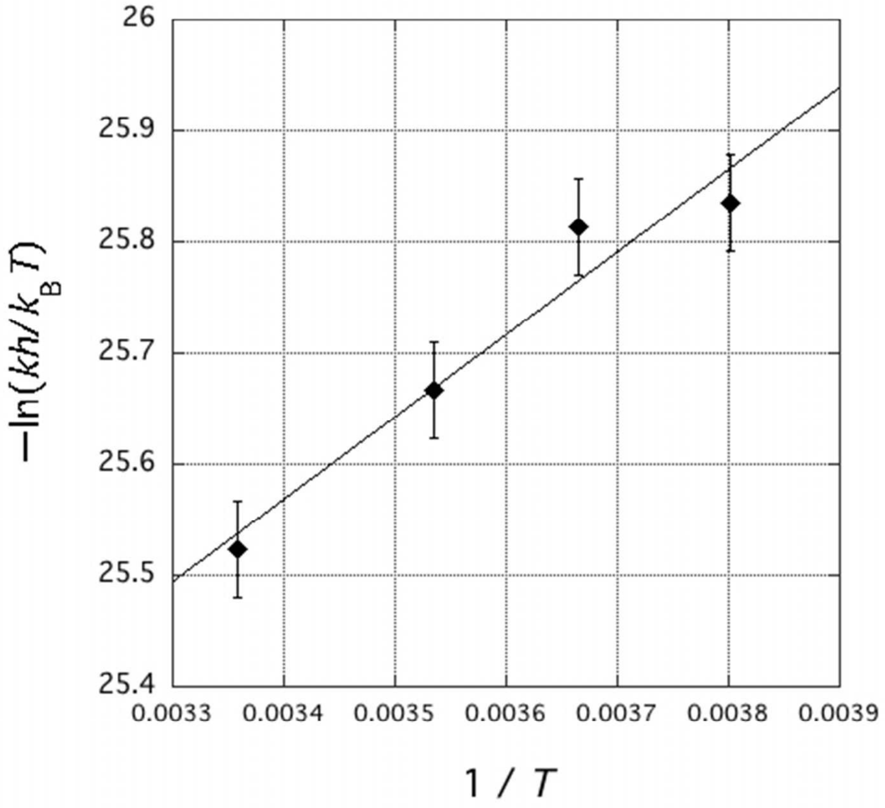


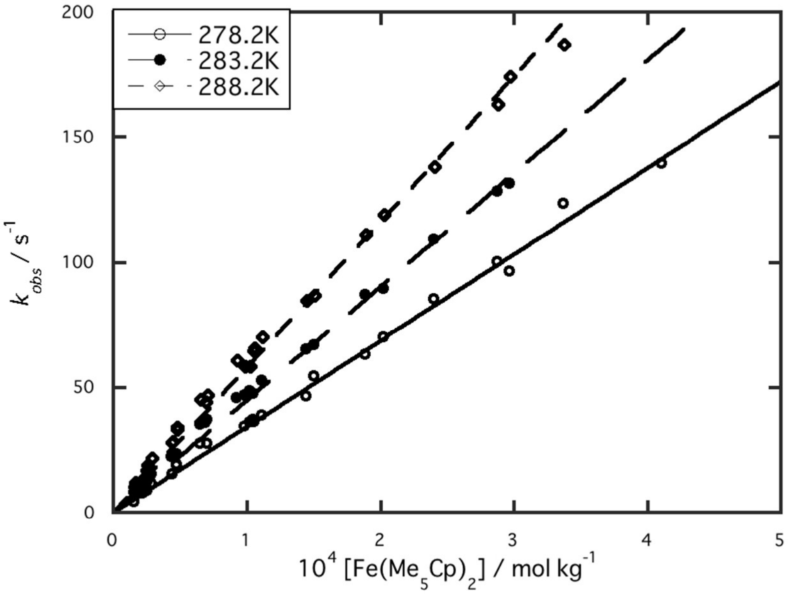
190x190mm (288 x 288 DPI)



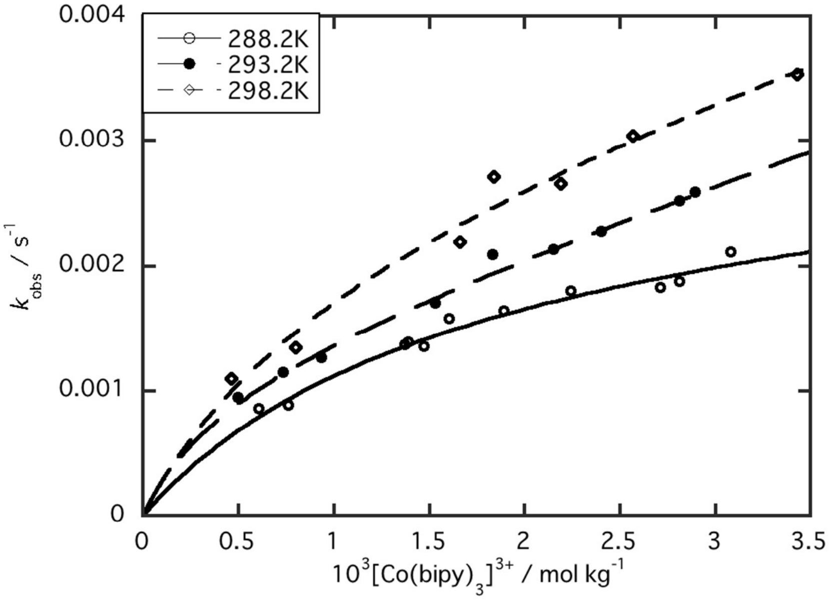
190x190mm (72 x 72 DPI)



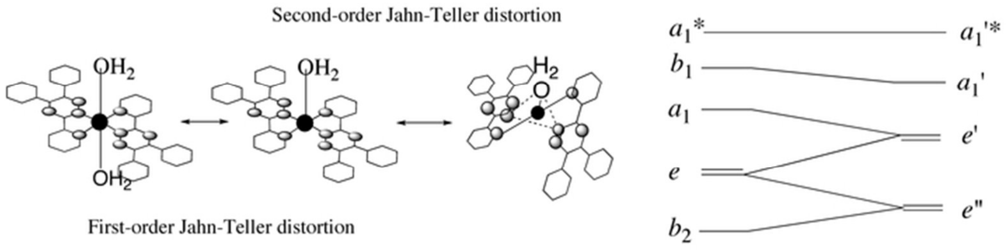
190x190mm (72 x 72 DPI)



101x76mm (288 x 288 DPI)



101x76mm (288 x 288 DPI)



60x14mm (300 x 300 DPI)

Redox reactions of $[Cu(pdt)_2(H_2O)_2]^{2+}$/ $[Cu(pdt)_2]^{+}$ couple in acetonitrile involved flipping of triazine ring of coordinated pdt ligand, and the non-adiabaticity factor, κ_{el}, for cross reactions was estimated as ca 10^{-7}.