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Intra- and Intermolecular Electron-Transfer Reaction of Viologen-Linked Copper(II) Schiff Base Complexes

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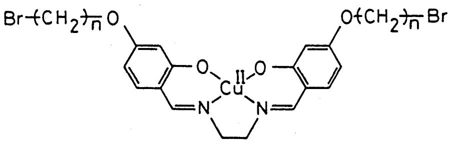
The copper(II) Schiff base complexes linked to viologen via number 3 and 4 of methylene groups were synthesized and characterized. The complexes are the binuclear type, the second Cu(II) of which binds with two iodide ions to the phenolate edge of *N,N'*-bis(salicylidene)ethylenediaminatocopper(II). A pulse radiolytic study in acetonitrile showed that the intramolecular electron transfer from the viologen radical to the $Cu(II)O_2I_2$ site occurred along with an intermolecular electron transfer between the viologen radical and the $Cu(II)O_2I_2$ site of the other complexes existing in excess; also, the number of the methylene groups (3 and 4) little affected the intra- and intermolecular electron-transfer rate. A trinuclear copper(II) Schiff base complex linked to viologen via number 5 of methylene groups was also synthesized and characterized.

The intramolecular electron-transfer type reaction has received considerable attention in both the fields of chemistry and biochemistry; particularly, studies of the role of the redox-site separation distance on the intramolecular electron transfer are significant for understanding electron transfer in biological systems.1) The viologens are diquaternary salts of 4,4'-bipyridine. They undergo reversible one-electron reduction to form colored radical cations the property of which is utilized in the catalytic photolysis of water to liberate hydrogen. Recently, viologen-linked metal complexes have been developed in order to improve such photo-catalytic systems.2) The Ni(II) Schiff base complex, linked to viologen via number six of the methylene groups, has also been prepared by us.3) A study of the intramolecular electron-transfer reaction by using model compounds has an important problem regarding whether the possibility of an intermolecular electron transfer between the radical intermediate and the reactant existing in excess can be excluded against an intramolecular electron transfer. We have recently reported that three decay modes of the radical cation intermediate have been observed after reacting pentaammine(1-methyl-4,4'-bipyridinium)cobalt(III) with the $CO_2^{\cdot-}$ radical anion: an intramolecular electron transfer from the coordinated viologen radical to the Co(III) center, an intermolecular electron transfer between the radical cation intermediate and the Co(III) complex in excess, and a disproportionation of the radical cation intermediate.4)

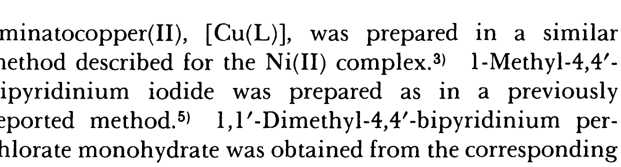
In the present work we synthesized viologen-linked Cu(II) Schiff base complexes (Fig. 1) and studied both the intra- and intermolecular electron transfer of the viologen radical cation intermediate produced in the reaction of the complexes with an acetonitrile radical anion by using a pulse radiolytic technique.

Experimental

Materials. *N,N'*-Bis(4-hydroxysalicylidene)ethylenediaminatocopper(II), [Cu(L)], was prepared in a similar method described for the Ni(II) complex.3) 1-Methyl-4,4'-bipyridinium iodide was prepared as in a previously reported method.5) 1,1'-Dimethyl-4,4'-bipyridinium perchlorate monohydrate was obtained from the corresponding chloride salts. All other chemicals used were of guaranteed grade.



[Cu(LC$_n$Br)] (n=3~6)



$[CuCu(LC_nMV)]^{2+}$ (n=3 and 4)

Fig. 1. Structure of the Cu(II) complexes.

Syntheses of Complexes. *N,N'*-Bis[4-(ω-bromoalkoxy)-salicylidene]ethylenediaminatocopper(II), [Cu(LC$_n$Br)] (*n*=3—6). The complex [Cu(L)] (2.8 mmol) and *α,ω*-dibromoalkane (2.8 mmol) were dissolved in 200 ml of *N,N*-dimethylformamide (DMF) in the presence of K_2CO_3 (28 mmol). The mixture was stirred at room temperature for 3 days. After the suspension was filtered off, the filtrate was evaporated to a small volume. To this solution was added chloroform; the mixture was then filtered off to remove KBr. Then, the filtrate was loaded on a silica-gel column which had previously been equilibrated with chloroform. The first fraction eluted with chloroform was evaporated to a small volume and added to a mixture of hexane and benzene (1:1). A blue precipitate was collected. [Cu(LC$_3$Br)] Yield: 15%. Found: C, 47.64; H, 4.31; N, 4.29%. Calcd for $CuC_{22}H_{24}N_2O_4Br_2\cdot 0.5C_6H_{12}$: C, 46.49; H, 4.68; N, 4.34%. [Cu(LC$_4$Br)] Yield: 57%. Found: C, 45.46; H, 4.78; N, 3.87%. Calcd for $CuC_{24}H_{28}N_2O_4Br_2$: C, 45.62; H, 4.47; N, 4.43%. [Cu(LC$_5$Br)] Yield: 52%. Found: C, 47.15; H, 5.36; N, 3.91%. Calcd for $\mathrm{CuC_{26}H_{32}N_2O_4Br_2}$: C, 47.32; H, 4.89; N, 4.25%. [Cu(LC$_6$Br)] Yield: 22%. Found: C, 49.68; H, 4.56; N, 4.35%. Calcd for $\mathrm{CuC_{28}H_{36}N_2O_4Br_2}$: C, 48.89; H, 5.27; N, 4.07%.

[CuCu(LC$_n$MV)]I$_2$ (n=3 and 4). A mixture of [Cu(LC$_n$Br)] (0.32 mmol) and 1-methyl-4,4′-bipyridinium iodide (1.6 mmol) was dissolved in 150 ml of ethanol and refluxed for 3—4 days. The precipitate was collected and washed with warm water. Recrystallization was carried out by adding chloroform to a DMF solution. [CuCu(LC$_3$MV)]I$_2$ Yield: 10%. Found: C, 31.11; H, 2.99; N, 4.53; Cu, 10.97%. Calcd for $\mathrm{Cu_2C_{33}H_{35}N_4O_4BrI_4}$: C, 31.30; H, 2.79; N, 4.42; Cu, 10.04%. [CuCu(LC$_4$MV)]I$_2$ Yield: 14%. Found: C, 32.47; H, 3.06; N, 4.56; Cu, 9.92%. Calcd for $\mathrm{Cu_2C_{35}H_{39}N_4O_4BrI_4}$: C, 32.47; H, 3.04; N, 4.33; Cu, 9.82%.

[Cu$_2$Cu(LC$_5$MV)]Br$_2$. The same procedure as described for [CuCu(LC$_n$MV)]I$_2$ was employed. Yield: 13%. Found: C, 29.64; H, 3.08; N, 4.46; Cu, 11.87%. Calcd for $\mathrm{Cu_3C_{37}H_{43}N_4O_4Br_3I_4 \cdot C_3H_7NO}$: C, 29.68; H, 3.11; N, 4.33; Cu, 11.78%.

Measurements. Electronic absorption, infrared, and ^{1}H NMR spectra were recorded on Hitachi 200-20, Hitachi 260-50, and JEOL GX-270 spectrometers, respectively.

Cyclic voltammetry was carried out in a nitrogen atmosphere in DMF containing a 0.05 M (1 M=1 mol dm^{-3}) tetrabutylammonium perchlorate ([Bu$_4$N]ClO$_4$) with a Yanaco Model P-900 instrument. A three-electrode system was used with a Pt auxiliary electrode and a glassy carbon working electrode against an Ag/AgCl (0.1 M KCl) reference electrode.

The magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of tris(ethylenediamine)nickel(II) thiosulfate.

In pulse-radiolysis experiments a CN Van de Graaff electron accelerator at the Center for Fast Kinetics Research, The University of Texas, Austin in U.S.A., was used as an electron source. Pulses of 100-ns duration were delivered to samples in a quartz cell (1-cm optical path length) in a nitrogen atmosphere at 23 °C; the absorptions of species were monitored by using a tungsten lamp, a monochrometer, and a photomultiplier. The signals were digitized by a Biomation 8100 transient recorder and analyzed by the use of an on-line PDP 11/70 minicomputer. The radiolysis of acetonitrile by ionizing radiation produced the monomeric and/or dimeric acetonitrile anion radical ($\mathrm{CH_3CN}^{\dot{-}}$) with a *G* value (the number of product molecules formed by the absorption of 100 eV in solution) of 1.03.[6] The concentrations of the generated reducing radical were (1—5)$\times10^{-6}$ M and were determined using methyl viologen radical ($\mathrm{MV}^{\dot{+}}$) production in separate experiments ($\varepsilon_{600}=1.4\times10^4$ M^{-1} cm^{-1}).[7] The decay of the radical intermediate produced in the reaction of [CuCu(L$_n$MV)]$^{2+}$ (n=3 and 4) and [Cu$_2$Cu(LC$_5$MV)]$^{2+}$ with $\mathrm{CH_3CN}^{\dot{-}}$ was followed at 600 and 400 nm. The observed rate constant was an average of three to five runs.

The reaction of [Cu(LC$_3$Br)] with $\mathrm{MV}^{\dot{+}}$ and dithionite reductions of the Cu(II) complexes were also studied in an aqueous 70% acetonitrile solution (0.03 M Tris/HCl buffer at pH 8). The reaction was followed at 600 nm by a Gibson-Dionex stopped-flow apparatus interfaced with an OLIS data-collecting system. The $\mathrm{MV}^{\dot{+}}$ was prepared by adding of 0.95 eq of sodium dithionite to the MV^{2+} solution.

Results and Discussion

Characterization of Complexes. The electronic absorption spectra of [Cu(LC$_n$Br)] (n=3—6) in DMF (Fig. 2 and Table 1) show the characteristic of square planar Cu(II) Schiff base complexes.[8] The chain length of the methylene groups linked to the 4- and 4′-position little affected the absorption band. The infrared absorption spectra showed the presence of methylene groups at 2800—2900 cm^{-1}, the vibration of which can be assigned to C-H stretching. The ligand-field absorption bands (564—567 nm) of [CuCu(LC$_n$MV)]$^{2+}$ ions are very similar to those of the [Cu(LC$_n$Br)] ions. The dithionite reduction of [CuCu(LC$_3$MV)]$^{2+}$ in aqueous 70% of acetonitrile containing a 0.03 M Tris/HCl buffer at pH 8 generates a typical spectrum of methyl viologen radical (Fig. 2). The differences in the molar absorption coefficients between the radical and [CuCu(LC$_3$MV)]$^{2+}$ are 9.6$\times10^3$ M^{-1}cm^{-1} at 604 nm and 3.5$\times10^4$ M^{-1}cm^{-1} at 396 nm. These values are very similar to those of

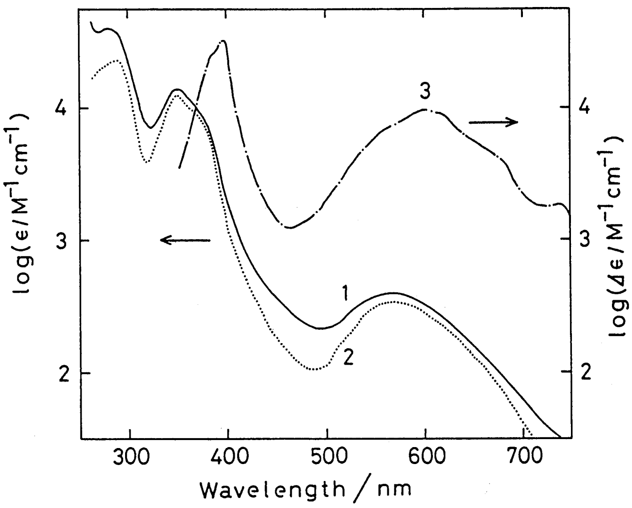


Fig. 2. Electronic absorption spectra of the Cu(II) Schiff base complexes. (1) ——: [CuCu(LC$_3$MV)]$^{2+}$ in DMF, (2) ······: [Cu(LC$_3$Br)] in DMF, and (3) —·—: a difference spectrum between [CuCu(LC$_3$MV$^{\dot{+}}$)] and [CuCu(LC$_3$MV)]$^{2+}$ in an aqueous 70% acetonitrile solution (0.03 M Tris/HCl buffer at pH 8) produced by a dithionite reduction under an argon gas.

Table 1. Absorption Spectral Data for Complexes in DMF

Complex		$\lambda_{\max}$/nm (log (ε/M^{-1}cm^{-1}))		
[CuCu(LC$_n$MV)]$^{2+}$	n=3	567 (2.60)	350 (4.14)	280 (4.60)
	n=4	565 (2.56)	350 (4.13)	283 (4.63)
[Cu$_2$Cu(LC$_5$MV)]$^{2+}$		564 (2.55)	349 (4.08)	280sh[a] (4.65)
[Cu(LC$_n$Br)]	n=3	571 (2.53)	348 (4.10)	287 (4.38)
	n=4	569 (2.57)	349 (4.15)	288 (4.43)
	n=5	570 (2.62)	349 (4.21)	289 (4.47)
	n=6	568 (2.57)	348 (4.14)	288 (4.42)

a) sh=shoulder.

$MV^{+\cdot}$ ($\varepsilon_{607}=1.4\times10^4$ $M^{-1}cm^{-1}$ and $\varepsilon_{397}=4.2\times10^4$ $M^{-1}cm^{-1}$),[7] suggesting that the $[CuCu(LC_3MV)]^{2+}$ ion contains one viologen unit. The presence of the viologen unit was also confirmed by the ^1H NMR spectrum in dimethyl-d_6 sulfoxide; $\delta=4.3$—4.4 ppm (CH_3) and 8.6—9.2 ppm (bipyridinium ring). The other signals, due to the protons of Schiff base and methylene groups, were broadened. The infrared absorption spectrum showed the presence of the methyl group of the viologen at 3050 cm^{-1}, which can be assigned to the frequency of the C-H stretching vibration. Analyses of copper in the $[CuCu(LC_nMV)]I_2$ complexes ($n=3$ and 4) showed that two copper atoms are contained. Moreover, the maxima of the ligand-field bands of the $[CuCu(LC_nMV)]^{2+}$ ions shift to shorter wavelengths than those of the mononuclear $[Cu(LC_nBr)]$ complexes (see Table 1). These observations suggest that the second Cu(II) ion binds through phenolate oxygen bridges to the Schiff base complex. Cyclic voltammetry of the complexes showed the presence of the second Cu(II) sites (vide infra). The formation of the binuclear adducts is promoted in alcohol in the presence of copper(II) halides.[8] Therefore, $[CuCu(LC_nMV)]I_2$ might be formed by the reaction of the Cu(II) Schiff base complex with free copper ions, the latter being formed by a decomposition of the copper(II) complexes.

An attempt to prepare compounds $[CuCu(LC_5MV)]I_2$ and $[CuCu(LC_6MV)]I_2$ was unsuccessful, though a trinuclear-type compound $[Cu_2Cu(LC_5MV)]Br_2\cdot C_3H_7NO$ was obtained. The absorption spectrum of $[Cu_2Cu(LC_5MV)]^{2+}$ was similar to that of $[CuCu(LC_nMV)]^{2+}$ ($n=3$ or 4). An analysis of the copper ions showed the presence of three copper ions in the $[Cu_2Cu(LC_5MV)]^{2+}$ ion. The temperature dependence of the magnetic susceptibility of this complex is well explained by the susceptibility equation (Eq. 1) for a linear trinuclear system[9,10] with $J=-120$

$$\chi_A=\frac{Ng^2\beta^2}{12kT}\times\frac{1+\exp(2J/kT)+10\exp(3J/kT)}{1+\exp(2J/kT)+2\exp(3J/kT)}+N\alpha \quad (1)$$

cm^{-1} ($1\ cm^{-1}=1.986\times10^{-23}\ J$), $g=2.20$, and $N\alpha=0$ (Fig. 3). Here, J is the mean value for the exchange integrals between the adjacent copper ions, the other symbols have their conventional meanings. Moreover, the ^1H NMR spectrum of the $[Cu_2Cu(LC_5MV)]^{2+}$ ion in dimethyl-d_6 sulfoxide showed the presence of DMF as a crystal solvent. From these results, the $[Cu_2Cu(LC_5MV)]^{2+}$ ion might have the trinuclear structure, as is shown in Fig. 4.

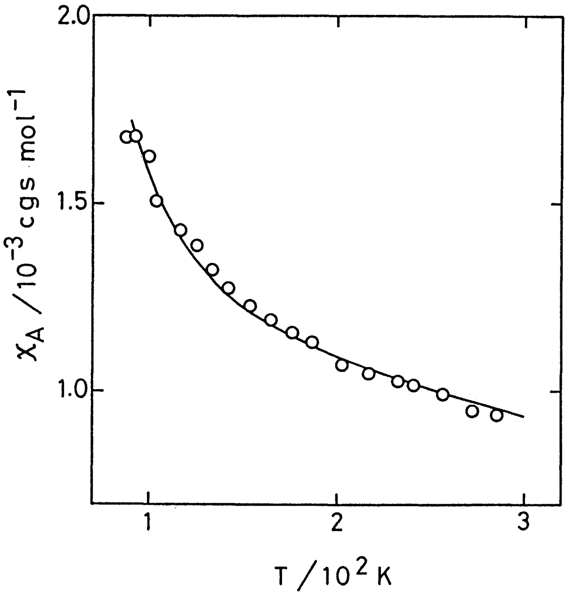


Fig. 3. Temperature dependence of magnetic susceptibility of $[Cu_2Cu(LC_5MV)]Br_2\cdot C_3H_7NO$. Solid curve is drawn on the basis of Eq. 1 using the parameters, $J=-120\ cm^{-1}$, $g=2.20$, and $N\alpha=0$.

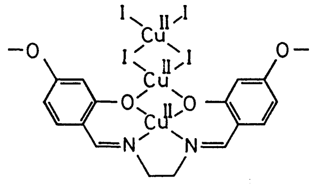


Fig. 4. Proposed structure of $[Cu_2Cu(LC_5MV)]^{2+}$.

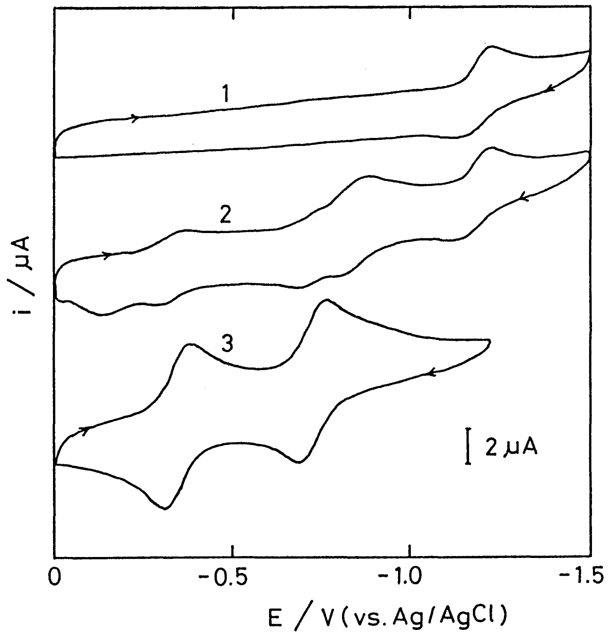


Fig. 5. Cyclic voltammograms of $[CuCu(LC_3MV)]^{2+}$ and $[Cu(LC_3Br)]$ along with MV^{2+} in DMF containing a 0.05 M $[Bu_4N]ClO_4$ with a scan rate of 5 $mV\,s^{-1}$. (1) $[Cu(LC_3Br)]$, (2) $[CuCu(LC_3MV)]^{2+}$, and (3) MV^{2+}.

Cyclic Voltammetry. Cyclic voltammograms of the $[CuCu(LC_nMV)]^{2+}$ and $[Cu(LC_nBr)]$ ions were measured in DMF. Figure 5 shows cyclic voltammograms of the Cu(II) complexes for $n=3$, along with methyl viologen. Though methyl viologen showed reversible waves, the complexes $[CuCu(LC_nMV)]^{2+}$ and $[Cu(LC_nBr)]$ ($n=3$ and 4) did not show wellresolved waves; especially, the waves of the Cu(II) sites were irreversible. Therefore, the half-wave potentials were obtained at a slow scan of 5 mV s^{-1}. The redox potential at −1.20 V for $[CuCu(LC_nMV)]^{2+}$ (n=3 or 4) can be assigned to that for the $Cu^{II}N_2O_2$ site, since the cyclic voltammogram for the corresponding mononuclear $[Cu(LC_nBr)]^{2+}$ complex shows only one redox wave at −1.20 V. The redox waves at −0.34 and at −0.74 V can be assigned to those for the $MV^{2+/+\cdot}$ and $MV^{+\cdot/0}$ couples, being comparable to those for methyl viologen. Therefore, the redox waves at −0.24 and at −0.87 V can be assigned to those for the $Cu^{2+/+}$ and the $Cu^{+/0}$ couples at the $Cu^{II}O_2I_2$ site. The $Cu^{II}O_2I_2$ site is more easily reduced than the $Cu^{II}N_2O_2$ site. This can be explained by the fact that the former has a distorted tetrahedral geometry and that the latter has a square-planar geometry similar to that for $[Cu(LC_nBr)]$. An X-ray crystallographic study of dichloro[*N*,*N′*-bis(salicylidene)ethylenediaminato-copper(II)]copper(II) has shown the tetrahedral geometry around the $Cu^{II}O_2Cl_2$ site.[11] Distorted-tetrahedral Cu(II) is more easily reduced to the Cu(I) state than is the square-planar Cu(II).[12]

Dithionite Reduction of $[CuCu(LC_3MV)]^{2+}$. The $[CuCu(LC_3MV)]^{2+}$ ion ((1.00—3.00)×10^{-5} M) was reduced by dithionite ions ((0.20—1.00)×10^{-3} M) to generate the viologen radical $[CuCu(LC_3MV^{+\cdot})]$ in an aqueous 70% acetonitrile solution (a 0.03 M Tris/HCl buffer at pH 8). There were two reactions: fast (within 50 ms) and slow (over 10^3 s) at 5.0×10^{-4} M dithionite ions. The observed first-order rate constant for the first stage obtained by following at 600 nm was (5±2)×10^2 s^{-1} at 25 °C. The second-order rate constant for $SO_2^{-\cdot}$ reduction was estimated to be (7±3)×10^7 $M^{-1}s^{-1}$ by using the value of 10^{-7} M for the dissociation constant of dithionite to $SO_2^{-\cdot}$ radical anions in aqueous acetonitrile solutions.[13] The second-order rate constant for the $SO_2^{-\cdot}$ reduction of MV^{2+} under the same experimental conditions was obtained to be (1.1±0.4)×10^8 $M^{-1}s^{-1}$. The first stage, therefore, corresponds to the reduction of the viologen unit in the $[CuCu(LC_3MV)]^{2+}$ ion, being followed by intra- and/or intermolecular electron transfer reactions from the viologen radical to $Cu^{II}O_2I_2$ site (vide infra). The slow reaction might represent the reduction of the Cu(II) Schiff base site, $Cu^{II}N_2O_2$, since the rate of the reduction was similar to that for the $[Cu(LC_3Br)]$ ion ((1—2)×10^2 $M^{-1}s^{-1}$).

Intra- and Intermolecular Electron-Transfer Reaction of $[CuCu(LC_nMV^{+\cdot})]$. It is known that the solvated acetonitrile anion radical forms in pulse radiolysis in acetonitrile.[6] After irradiation of methyl viologen in acetonitrile the $MV^{+\cdot}$ radical cation was produced. Small amounts of $MV^{+\cdot}$ (<10%) were consumed within 4 ms, which may be attributed to a reaction with residual O_2. Most of the viologen radical was very stable during the measurements.

$$MV^{2+} + CH_3CN^{-\cdot} \longrightarrow MV^{+\cdot} + CH_3CN \qquad (2)$$

The reaction of $[CuCu(LC_nMV)]^{2+}$ ((1.25—5.00)×10^{-5} M) with $CH_3CN^{-\cdot}$ ((1.4—4.8)×10^{-6} M) was came to completion within 30 μs, and decay had barely commenced. The spectrum of the transient is very similar to that of $MV^{+\cdot}$, though the absorption band shifted slightly to a shorter wavelength (λ_{max} 590±10 nm). From the initial increase in the absorbance at 600 nm, the amounts of the viologen radical intermediate can be estimated (Table 2). About 70% of $CH_3CN^{-\cdot}$ reacted with the viologen unit to generate a radical cation intermediate $[CuCu(LC_nMV^{+\cdot})]$ (n=3 and 4); the remaining $CH_3CN^{-\cdot}$ attacked the Cu(II) site. The intermediate $[CuCu(LC_nMV^{+\cdot})]$ decayed within times ranging from 0.1—0.4 s, depending on the concentrations of the complexes pulsed. The decay was first order in the concentrations of the radical intermediate. The observed first-order rate constants were dependent on the concentrations of $[CuCu(LC_nMV)]^{2+}$ (n=3 and 4) remaining in excess, as is shown in Fig. 6. Therefore, the decay of the intermediate obeys the following rate law:

$$-d[[CuCu(LC_nMV^{+\cdot})]]/dt = k_{obsd}[[CuCu(LC_nMV^{+\cdot})]], \qquad (3)$$

where

$$k_{obsd} = k_{intra} + k_{inter}[[CuCu(LC_nMV)]^{2+}]. \qquad (4)$$

Table 2. Observed First-Order Rate Constants for the Decay of the Radical Cation Intermediates in Acetonitrile at 23 °C

$[Cu(II)]_0$	$[radical]_T$	$[intermediate]_0$	$[Cu(II)]_{remained}$	k_{obsd}
10^{-6} M	10^{-6} M	10^{-6} M	10^{-6} M	s^{-1}
$[CuCu(LC_3MV)]^{2+}$				
12.5	1.4	1.0	11	18.8
25.0	3.2	2.3	22	28.8
50.0	4.8	3.4	45	48.0
$[CuCu(LC_4MV)]^{2+}$				
12.5	1.4	1.0	11	17.5
50.0	4.8	3.4	45	44.0
$[Cu_2Cu(LC_5MV)]^{2+}$				
11.1	1.4	1.0	10	10.0
22.3	3.0	2.1	19	13.0
41.0	3.0	2.1	38	21.4

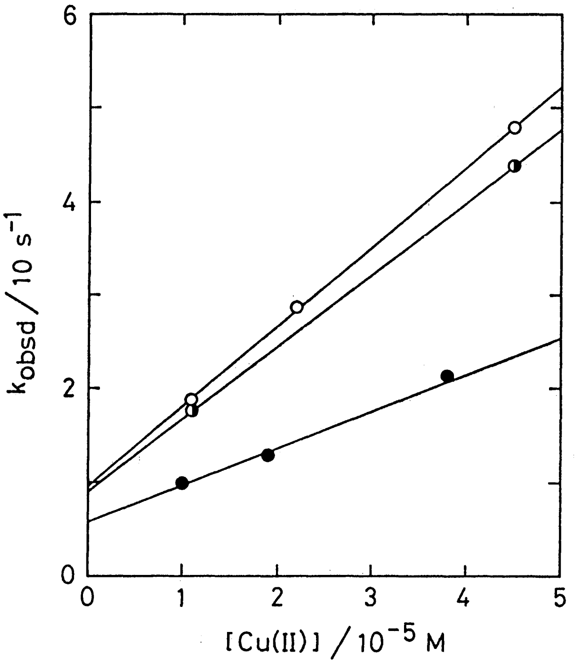


Fig. 6. Plots of k_{obsd} vs. the concentrations of $[\mathrm{CuCu(LC}_n\mathrm{MV)}]^{2+}$ (n=3 and 4) and $[\mathrm{Cu_2Cu(LC_5MV)}]^{2+}$ for the decay of the radical cation intermediates. ○: $[\mathrm{CuCu(LC_3MV)}]^{2+}$, ◑: $[\mathrm{CuCu(LC_4MV)}]^{2+}$, and ●: $[\mathrm{Cu_2Cu(LC_5MV)}]^{2+}$.

Table 3. Rate Constants for Intra- and Intermolecular Electron-Transfer Reaction of $[\mathrm{CuCu(LC}_n\mathrm{MV}^{+\cdot}]$ and $[\mathrm{Cu_2Cu(LC_5MV}^{+\cdot})]$ in Acetonitrile at 23 °C

Complex	$k_{\mathrm{intra}}/\mathrm{s}^{-1}$	$k_{\mathrm{inter}}/10^5\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$
$[\mathrm{CuCu(LC_3MV}^{+\cdot})]$	9.6±0.8	8.6±0.7
$[\mathrm{CuCu(LC_4MV}^{+\cdot})]$	8.9±0.7	7.8±0.6
$[\mathrm{Cu_2Cu(LC_5MV}^{+\cdot})]$	5.6±0.5	4.1±0.3

The path, being independent of the concentrations of the Cu(II) complex, should be the intramolecular electron transfer from the $\mathrm{MV}^{+\cdot}$ part to the $\mathrm{Cu^{II}O_2I_2}$ site, since the redox potential of the latter is higher than that of the former. The reaction scheme is presented as follows:

$$[\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV)}]^{2+} + \mathrm{CH_3CN}^{-\cdot} \longrightarrow [\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV}^{+\cdot})] \quad (\text{and } [\mathrm{Cu^{I}Cu^{II}(LC}_n\mathrm{MV)}]^{+}), \tag{5}$$

$$[\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV}^{+\cdot})] \xrightarrow{k_{\mathrm{intra}}} [\mathrm{Cu^{I}Cu^{II}(LC}_n\mathrm{MV)}]^{+}, \tag{6}$$

$$[\mathrm{Cu^{I}Cu^{II}(LC}_n\mathrm{MV)}]^{+} \not\rightleftarrows [\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV}^{+\cdot})] \quad \text{no reaction}, \tag{7}$$

and

$$[\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV}^{+\cdot})] + [\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV)}]^{2+} \xrightarrow{k_{\mathrm{inter}}} [\mathrm{Cu^{II}Cu^{II}(LC}_n\mathrm{MV)}]^{2+} + [\mathrm{Cu^{I}Cu^{II}(LC}_n\mathrm{MV)}]^{+}. \tag{8}$$

The rate constants for the intra- and intermolecular electron-transfer, k_{intra} and k_{inter}, respectively, are listed in Table 3. Both the intra- and intermolecular electron-transfer reactions are little affected by the chain length of the methylene groups of 3 and 4. This is probably because the two redox sites linked by the methylene groups can associate with each other due to the flexibility of the methylene chain.

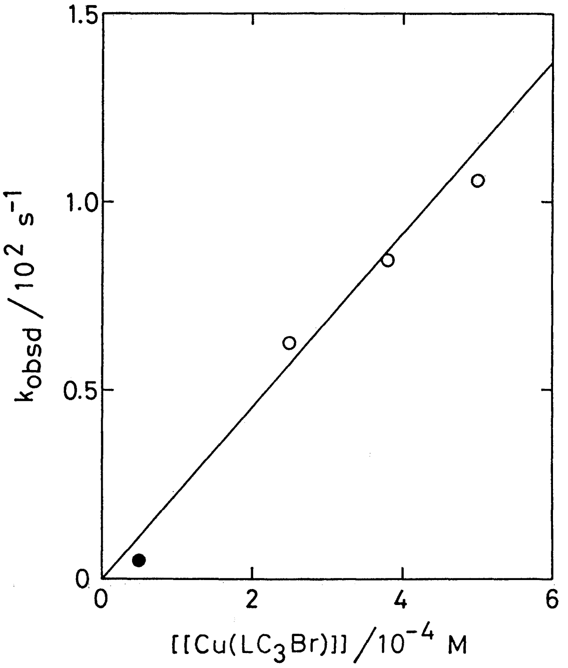


Fig. 7. Plots of k_{obsd} vs. $[[\mathrm{Cu(LC_3Br)}]]$ for the reaction of $\mathrm{MV}^{+\cdot}$ with $[\mathrm{Cu(LC_3Br)}]$ in an aqueous 70% acetonitrile solution. The concentrations of $\mathrm{MV}^{+\cdot}$ was (2—5)×10^{-6} M. ○: a stopped-flow method and ●: a pulse-radiolysis method described in the text.

We also examined the reduction of the trinuclear complex, $[\mathrm{Cu_2Cu(LC_5MV)}]^{2+}$, with $\mathrm{CH_3CN}^{-\cdot}$. The formation and decay of the radical intermediate, $[\mathrm{Cu_2Cu(LC_5MV}^{+\cdot})]$, was also observed and the rate constants, k_{intra} and k_{inter}, were obtained from the plots of k_{obsd} vs. the concentrations of $[\mathrm{Cu_2Cu(LC_5MV)}]^{2+}$. In this case the electron-transfer reaction might be very complicated, since there are two reducible Cu(II) sites ($\mathrm{Cu^{II}O_2I_2}$ and $\mathrm{Cu^{II}I_2I_2}$) by the viologen radical.

The presence of free iodide ions did not affect the rate of the reaction, since the reaction of $\mathrm{MV}^{+\cdot}$ with $\mathrm{I_2}^{-\cdot}$ produced by the irradiation of the I^- solution was very slow. The observed first-order rate constant for this reaction was 5 s^{-1} in the presence of 1.3×10^{-4}M KI.

It may be possible that the bromopropyl group of the Cu(II) complex reacts with the methyl viologen radical;[14] therefore, we also examined the reaction of $[\mathrm{Cu(LC_3Br)}]$ with $\mathrm{MV}^{+\cdot}$ by both stopped-flow and pulse-radiolysis methods. The decay of $\mathrm{MV}^{+\cdot}$ was first order in the concentrations of $\mathrm{MV}^{+\cdot}$ in the presence of $[\mathrm{Cu(L_3Br)}]$ in large excess. The reaction was also first order in the concentrations of the Cu(II) complex (Fig. 7). This reaction corresponds to the following reaction:

$$[\mathrm{Cu(LC_3Br)}] + \mathrm{MV}^{+\cdot} \longrightarrow [\mathrm{Cu(LCH_2CH_2CH_2\cdot)}] + \mathrm{Br}^- + \mathrm{MV}^{2+} \tag{9}$$

The second-order rate constant was $(2.3\pm0.2)\times10^5\,M^{-1}\,s^{-1}$, indicating that the reaction between the viologen-radical part of $[CuCu(LC_nMV^{\dotplus})]$ and the bromopropyl group of the complex is slower than reactions 6 and 8.

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