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# An Important Role of the One-Electron Reduction Nitrosyl Coordinated to Ruthenium.
# A Redox-Induced Oxygen Atom Transfer Reaction between the Nitrosyl and Adjacent Nitrite Moieties of $\{\mathrm{RuNO}\}^7$-Type Nitrosyl Complex

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A facile redox-induced nitrito-to-nitro isomerization occurs in *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}$ ($\{\mathrm{RuNO}\}^6$-type nitrosyl, bpy = 2,2′-bipyridine). At room temperature, the one-electron reduction species (*cis*-$[\mathrm{Ru(NO\cdot)(ONO)(bpy)_2}]^+$($\{\mathrm{RuNO}\}^7$)) changes immediately to *cis*-$[\mathrm{Ru(NO\cdot)(NO_2)(bpy)_2}]^+$ ($\{\mathrm{RuNO}\}^7$), which can be converted to *cis*-$[\mathrm{Ru(NO)(NO_2)(bpy)_2}]^{2+}$ ($\{\mathrm{RuNO}\}^6$) by one-electron oxidation. The nitro species is an isomeric twin of the original nitrito species. A mechanistic investigation has established that, during the nitrito–nitro redox-induced rearrangement, an oxygen-atom transfer reaction proceeded between the nitrosyl and the adjacent nitrite ligands. Such a behavior could not be found in the thermally-induced nitrito–nitro rearrangement of the $\{\mathrm{RuNO}\}^6$-type nitrosyl complex mentioned above. The $\{\mathrm{RuNO}\}^7$-type nitrosyl complex appears to behave as a key intermediate species of the oxygen-atom transfer reaction.

Although a thermally-induced linkage isomerization of $\mathrm{NO_2^-}$ bound to a metal atom has been extensively investigated and reviewed,[1—5] little is known about redox-induced nitro–nitrito linkage isomerization. Meyer et al. have studied the oxidation of a nitro complex of ruthenium(II) (*cis*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$), which results in the formation of the corresponding nitrito complex of ruthenium(III) (*cis*-$[\mathrm{RuCl(ONO)(bpy)_2}]^+$).[6—8] A similar but somewhat expanded investigation has been reported by the present authors, using *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$.[9—14] The nitrito complexes of ruthenium(III) in both studies are capable of being returned to the original nitro complex of ruthenium(II), via a one-electron reduction process, under limited condition (−40 °C). The nitrito species generated are chemically very reactive, and they tend to convert rapidly to a nitrato complex of ruthenium(III) (*cis*-$[\mathrm{RuCl(NO_3)(bpy)_2}]^+$) or an oxo complex of ruthenium(IV) (*trans*-$[\mathrm{RuCl(O)(py)_4}]^+$), depending on the nitro complex of ruthenium(II) used as a starting material.[6—14] Consequently, these works, including that reported recently by Takeuchi and co-workers,[15] have opened no opportunity for any mechanistic study on the redox-induced nitro–nitrito linkage isomerization.

Very recently, we have reported nitro–nitrito isomeric pair complexes of ruthenium(II), which have nitrosyl as a spectator ligand, *cis*-$[\mathrm{Ru(NO)(X)(bpy)_2}]^{n+}$ and *cis*-$[\mathrm{Ru(NO)(X)(bpy)(py)_2}]^{n+}$ ($n = 2$ for $\mathrm{X = ONO}$ and $\mathrm{NO_2}$. $n = 3$ for X = py; pyridine).[16] Their behavior during thermally-induced nitro–nitrito isomerization has been investigated in some detail; we have delayed a study of a redox-induced linkage isomerization of *cis*-$[\mathrm{Ru(NO)(X)(bpy)_2}]^{2+}$, while that of *cis*-$[\mathrm{Ru(NO)(X)(bpy)(py)_2}]^{2+}$ was carried out to some extent.[16] The latter complex has been shown to give rise to a redox-induced linkage isomerization, from the nitrito isomer to the nitro; subsequently, it returns to the original nitrito isomer by thermally-induced linkage isomerization. The purpose of the present work was to investigate the mechanistic process of the redox-induced isomerization of *cis*-$[\mathrm{Ru(NO)(X)(bpy)_2}]^{2+}$ ($\{\mathrm{RuNO}\}^6$-type nitrosyl).[17] During the course of the redox-induced linkage isomerization, the complex exhibited an oxygen-atom transfer reaction at the *cis*-(NO)(ONO (or $\mathrm{NO_2}$))moieties, which was distinct from that observed previously in the thermally-induced isomerization.[16] Such behavior gave us a clue for understanding the mechanistic process of the redox-induced structural rearrangement. The study could establish an important role of the $\{\mathrm{RuNO}\}^7$-type nitrosyl, *cis*-$[\mathrm{Ru(NO\cdot)(X)(bpy)_2}]^+$, which acts as an isomeric intermediate species and also facilitates the oxygen transfer reaction. Oxygen-atom transfer reactions involving $\mathrm{NO}_x$ ($x = 1$—3) species, and also $\mathrm{CO}_x$ ($x = 1$ or 2) species, have been of fundamental importance, particularly to those interested in the effect of these species on the environment.[18] Part of the present work has been communicated briefly.[19]

## Experimental

**Materials.** The following complexes were prepared by literature methods: *cis*-$[\mathrm{Ru(NO)(H_2O)(bpy)_2}](\mathrm{ClO_4})_3$,[20] *cis*-$[\mathrm{Ru(NO)(NO_2)(bpy)_2}](\mathrm{PF_6})_2$,[16] *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)_2}](\mathrm{PF_6})_2$.[16] All $^{15}\mathrm{N}$ labeled complexes were obtained by procedures reported in the literature.[16]

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**Measurements.** Infrared spectra were recorded with a Perkin–Elmer FT-1650 spectrophotometer. Electrochemical measurements were carried out using a Huso polarograph Model 312; the current–potential waves were recorded with a Rikendenshi Instruments Model F-3F recorder. The experiments were performed in $CH_3CN$, with a supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate (TBAH) or tetraethylammonium perchlorate (TEAP)) concentration of 0.1 mol dm$^{-3}$. Three-electrode, one-compartment cells were used. They were equipped with a silver reference electrode (Ag|$AgNO_3$, 0.01 mol dm$^{-3}$). The coulometric experiments were performed in two-compartment cells using a platinum-gauze working electrode, with the auxiliary electrode in the second compartment separated by a glass frit. The number of Coulombs were measured by a Huso coulometer Model 343B digital coulometer.

**Examination of an Oxygen-Atom Transfer Reaction: Isolations of the Products Which Were Generated by the Redox-Induced Nitro–Nitrito Rearrangement.** Voltammograms of the redox-induced rearrangement of nitrito-to-nitro (and also nitro-to-nitrito) were obtained as reported previously,[16)] after bulk electrolysis under argon flow conditions. In a typical experiment, a $CH_3CN$ solution containing *cis*-$[Ru(NO)(ONO)(bpy)_2](PF_6)_2$ (50 mg, $6.4\times10^{-2}$ mmol/40 cm$^3$) was cathodically electrolyzed at −40 °C (at −0.10 V vs. Ag|$AgNO_3$), in which a solution of *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ was generated. After completion of the electrolysis, the solution was allowed to stand at room temperature for 0.5 h to give *cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$, which was then anodically electrolyzed (at 0.10 V). The nitro species (*cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$) thus generated was isolated as a $PF_6$ salt, by a standard technique using a rotary evaporator.

Two similar experiments ((a) and (b)) were carried out separately to identify the isomerization processes (i)—(iii), which will be described in Section 2, Results and Discussion.

**(a) Isolation of *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ as the Redox-Induced Isomerization Product of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$.** At 25 °C, an exhaust reductive electrolysis was performed in a $CH_3CN$ solution (40 cm$^3$) containing *cis*-$[Ru(NO)(ONO)(bpy)_2](PF_6)_2$ (50 mg, $6.4\times10^{-2}$ mmol), where more than 95% of the nitrito isomer underwent a reduction to give *cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$, via the formation of *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$. The generated *cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$ was re-oxidized quickly to *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ by the exhaust electrolysis. The electrolyzed solution containing *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ was dried up using a rotary evaporator. The solid material thus obtained consists of mainly *cis*-$[Ru(NO)(NO_2)(bpy)_2](PF_6)_2$ and TBAH used as a supporting electrolyte. The solid material was treated by $CH_2Cl_2$ (20 cm$^3$) in order to remove TBAH, which was very soluble in this solvent. The nitrosyl–nitro complex which remained was collected by filtration, and washed with $CH_2Cl_2$ and then ether, and air-dried. Yield, 20—30 mg (40—60%). The identification was made by both infrared spectroscopy and cyclic voltammetry.

**(b) Isolation of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ Which Was Regenerated via the Redox Process Using *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ as a Starting Material.** At −40 °C, an exhaust reductive electrolysis was performed in a $CH_3CN$ solution (40 cm$^3$) containing *cis*-$[Ru(NO)(ONO)(bpy)_2](PF_6)_2$ (50 mg, $6.4\times10^{-2}$ mmol), where more than 95% of the nitrito isomer underwent a reduction to give *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$. The generated *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ was re-oxidized quickly by exhaust electrolysis to give *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ under the same experimental conditions. The electrolyzed solution was dried using a rotary evaporator. The solid material thus obtained was treated by $CH_2Cl_2$ (20 cm$^3$) for a purpose similar to that described in (a). The remaining nitrosyl–nitrito complex was collected by filtration, washed with $CH_2Cl_2$ and then ether, and air-dried. Yield, 20—25 mg (40—50%). Identification was based on the results obtained by infrared spectroscopy and cyclic voltammetry.

**Measuring the Rate of Nitrito-to-Nitro Isomerization in the $\{RuNO\}^7$-Type Nitrosyl Complexes at 25 °C. *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ and the Related Complex (*cis*-$[Ru(NO\cdot)(ONO)(bpy)(py)_2]^+$).** The rate constant on *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ was determined from individual CV's by the Nicholson–Shain method.[21,22)] For the rearrangement of this complex, the peak ratio of $i_{pa}/i_{pc}$ for the *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+/+}$ couple was measured for each scan rate. From the data of the switching potential and the working curve, the rate constant of the forward reaction was estimated ($k = 1.7(\pm0.1)\times10^{-2}$ s$^{-1}$. The rate data obtained was shown to be independent of the concentration of the complex.

The conversion rate on the analogous complex, *cis*-$[Ru(NO\cdot)(ONO)(bpy)(py)_2]^+$, was too slow to be determined by the Nicholson–Shain method under our experimental conditions. Consequently, the rate data were evaluated from the monitoring data by hydrodynamic voltammograms (HDV): *cis*-$[Ru(NO\cdot)(ONO)(bpy)(py)_2]^+$ was accumulated by an exhaust electrolysis of *cis*-$[Ru(NO)(ONO)(bpy)(py)_2]^{2+}$ at −40 °C. The $I_d$ of *cis*-$[Ru(NO\cdot)(NO_2)(bpy)(py)_2]^+$ appeared and developed at the expense of *cis*-$[Ru(NO\cdot)(ONO)(bpy)(py)_2]^+$. The rearrangement was found to be complete within about 60 min in the dark. A plot of ln $[I_0 - I_\infty / I_t - I_\infty]$ vs. *t* gave a straight line. The first-order rate constant was estimated to be $k = 1.1(\pm0.1)\times10^{-3}$ s$^{-1}$, where $I_0, I_t$, and $I_\infty$ are values of *I* observed initially, after the elapse of time *t*, and corresponding to 100% formation of *cis*-$[Ru(NO\cdot)(NO_2)(bpy)(py)_2]^+$. The values of $I_\infty$ were obtained by graphical extrapolation.

## Results and Discussion

**1. Redox-Induced Nitrito-to-Nitro Rearrangement in *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$ (X = ONO, $NO_2$).** A $CH_3CN$ solution of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ [**1**] exhibits two one-electron reduction waves on a cyclic voltammetry time scale (Fig. 1-a); a reversible wave was found at −0.02 ($E_{pc1}$) and an irreversible wave at −0.75 ($E_{pc2}$) V [vs. Ag|$AgNO_3$ (0.01 mol dm$^{-3}$ in $CH_3CN$)]. Such CV observation is common for the reductive process of $\{MNO\}^6$-type nitrosyl complexes,[5)] in which a ligand-based (NO) reduction proceeds.[23)]

Although cyclic voltammetry of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ [**1**] ($\{MNO\}^6$) exhibited a reversible behavior in the first reduction wave ($E_{pc1}$), a controlled potential electrolysis carried out at 25 °C indicated that a rapid structural change occurred. Similar to the analogous complex reported previously, *cis*-$[Ru(NO)(ONO)(bpy)(py)_2]^{2+}$,[16)] a one-electron reduction nitro species (*cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$ [**2′**] ($\{RuNO\}^7$)) was obtained, via the generation of a one-electron reduction nitrito species (*cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ [**1′**] ($\{RuNO\}^7$) ($n = 0.99$ by coulometry). When the reductive exhaust electrolysis of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ [**1**] was carried out at −40 °C, *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ [**1′**] was accumulated without a redox-induced linkage isomerization, while [**1′**] was followed by a rapid rearrangement to give the corresponding nitro species [**2′**] if the temperature was elevated (Fig. 1-b and c). The *cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$ [**2′**] thus generated could be converted to *cis*-$[Ru(NO)(NO_2)$-

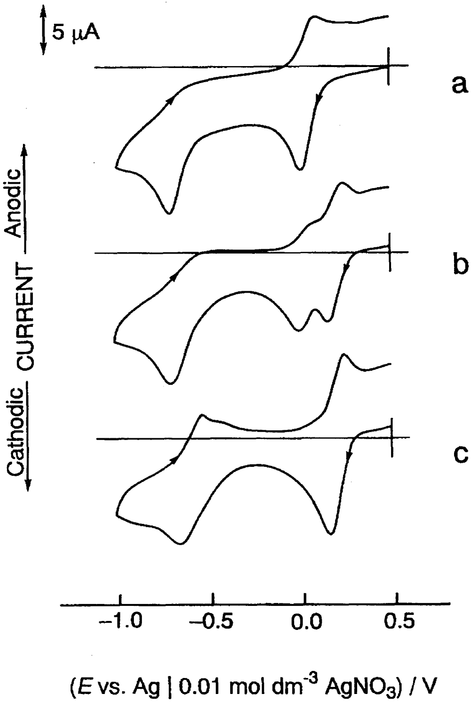

Fig. 1. CVs monitoring the course of controlled-potential reduction of *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}$. (a) prior to electrolysis; (b) during electrolysis; (c) at the end of the electrolysis. Stationary Pt disk electrode in 0.1 mol dm$^{-3}$ TEAP+AN. At 25 °C. 200 mV s$^{-1}$.

$\mathrm{(bpy)_2]^{2+}}$ [**2**] ($\{\mathrm{MNO}\}^6$) by an exhaust oxidative electrolysis ($n = 0.99$). These redox-induced conversion processes could be checked by measuring both the cyclic and hydrodynamic voltammograms. The data of the nitrito complex, along with those of the corresponding nitro complex, are summarized in Table 1.

In combination with the previous result of the thermally-induced isomerization of *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}$ [**1**] and *cis*-$[\mathrm{Ru(NO)(NO_2)(bpy)_2}]^{2+}$ [**2**],[16] the above observation can be represented by the following Eqs. 1, 2, 3, and 4:

$$\underset{[\mathbf{1}]}{[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}} + e^- \rightarrow \underset{[\mathbf{1'}]}{[\mathrm{Ru(NO\cdot)(ONO)(bpy)_2}]^{+}} \qquad (1)$$

$$\underset{[\mathbf{1'}]}{[\mathrm{Ru(NO\cdot)(ONO)(bpy)_2}]^{+}} \rightarrow \underset{[\mathbf{2'}]}{[\mathrm{Ru(NO\cdot)(NO_2)(bpy)_2}]^{+}}\ (25^\circ\mathrm{C}) \qquad (2)$$

$$\underset{[\mathbf{2'}]}{[\mathrm{Ru(NO\cdot)(NO_2)(bpy)_2}]^{+}} \rightarrow \underset{[\mathbf{2}]}{[\mathrm{Ru(NO)(NO_2)(bpy)_2}]^{2+}} + e^- \qquad (3)$$

$$\underset{[\mathbf{2}]}{[\mathrm{Ru(NO)(NO_2)(bpy)_2}]^{2+}} \rightleftharpoons \underset{[\mathbf{1}]}{[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}}(60\ ^\circ\mathrm{C}) \qquad (4)^{16)}$$

The participation of some species other than [**1**] and [**2**] (and their reduction species) in the redox processes could not be detected during the redox-induced isomerization. The rearrangement process described above is essentially the same as that observed previously in the analogous *cis*-$[\mathrm{Ru(NO)(X)(bpy)(py)_2}]^{2+}$, except that Eq. 4 has been described in Eq. 5.[16] As illustrated in Eq. 4, although an equilibrium mixture of the nitrito [**1**] and the nitro [**2**] is formed in the thermally-induced isomerization of *cis*-$[\mathrm{Ru(NO)(X)(bpy)_2}]^{2+}$, *cis*-$[\mathrm{Ru(NO)(X)(bpy)(py)_2}]^{2+}$ has been shown to undergo a facile one-way rearrangement, from the nitro species to the nitrito, under the same conditions (Eq. 5). No formation of such an equilibrium mixture could be found:[16]

Table 1. Electrochemical Data of *cis*-$[\mathrm{Ru(NO)(X)(bpy)_2}]^{2+}$ and Related Complexes

| Complex | $E$ (V)$^{a)}$ | | | |
|---|---|---|---|---|
| | $E_{\mathrm{p1/2}}$ | $\Delta E_{\mathrm{p}}$ | $E_{\mathrm{pc2}}$ | $n$ (e$^-$) |
| *cis*-$[\mathrm{Ru(NO)(NO_2)(bpy)_2}]^{2+}$ | 0.18 | 0.070 | −0.70 | 0.98 |
| *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}$ | 0.02 | 0.070 | −0.75 | 0.99 |
| *cis*-$[\mathrm{Ru(NO)(NO_2)(bpy)(py)_2}]^{2+\,b)}$ | 0.26 | 0.070 | −0.79 | 0.95 |
| *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)(py)_2}]^{2+\,b)}$ | 0.04 | 0.070 | −0.87 | 0.95 |

a) V vs. Ag|AgNO$_3$ (0.1 mol dm$^{-3}$ TEAP in CH$_3$CN) at 25 °C.
b) Ref. 16.

$$[\mathrm{Ru(NO)(NO_2)(bpy)(py)_2}]^{2+} \rightarrow [\mathrm{Ru(NO)(ONO)(bpy)(py)_2}]^{2+} \qquad (5)$$

**2. Evidence for the Redox-Induced Oxygen Atom Transfer Reaction.** Other researchers have shown that an intramolecular oxygen-atom transfer occurs in the nitrosyl and adjacent nitrite moieties at the *cis* position during a thermally-induced nitro–nitrito isomerization.[24—27] Numerous investigations have also addressed intramolecular oxygen-atom transfer from a $\mathrm{NO_2}$ ligand to an adjacent CO ligand, leading to a spontaneous $\mathrm{CO_2}$ loss and the formation of nitrosyl complexes.[28—41] In both *cis*-$[\mathrm{Ru(NO)(ONO)(bpy)_2}]^{2+}$ [**1**] and *cis*-$[\mathrm{Ru(NO)(NO_2)(bpy)_2}]^{2+}$ [**2**], however, such an oxygen transfer reaction did not occur,[16] although the complexes underwent thermally-induced linkage isomerization.[16] We could observe in the present work that an oxygen-atom transfer reaction actually proceeded when the redox-induced rearrangement occurred in these complexes. No such redox-prompted oxygen transfer reaction has yet been reported.

Some evidence which supports the presence of the oxygen-atom transfer reaction was established in the present complexes by the following synthetic experiments, which were carried out based on the reaction sequences described in Eqs. 1, 2, 3, and 4 above:

(i) Using *cis*-$[\mathrm{Ru(^{15}NO)(ONO)(bpy)_2}]^{2+}$ as [**1**] in Eq. 1, we carried out the isolation of the redox product [**2**] in Eq. 3 by the following procedure: the nitrosyl–nitrito isomer [**1**] ($\{\mathrm{RuNO}\}^6$) was reduced electrochemically at 25 °C to give the one-electron reduction nitrosyl–nitro isomer [**2′**] ($\{\mathrm{RuNO}\}^7$), via the one-electron reduction nitrosyl–nitrito isomer [**1′**] ($\{\mathrm{RuNO}\}^7$). A subsequent oxidation of [**2′**] species in Eq. 3 gave the nitrosyl–nitro isomer [**2**] ($\{\mathrm{RuNO}\}^6$) as an isolable species. If we assume that the reactions proceed without an oxygen-atom transfer, *cis*-$[\mathrm{Ru(^{15}NO)(ONO)(bpy)_2}]^{2+}$ used as [**1**] should give *cis*-$[\mathrm{Ru(^{15}NO)(NO_2)(bpy)_2}]^{2+}$ alone, as the redox-induced isomerization product [**2**]. IR studies, however, identified the isolated material as being a mixture composed of nearly equimolar amounts of *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ and *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ (Table 2 and Fig. 2). The result that *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ [**1**] generates equimolar amounts of the two kinds of isotopomers, *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ and *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$, is suggestive of the reaction progress depicted in Fig. 3(a) and/or (b) (see the later description).

(ii) An experiment similar to that described in (i) was carried out on Eq. 1, in order to check whether the oxygen-atom transfer occurred at the redox process between *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ [**1**] and *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^{+}$ [**1′**] or not. Since the isolation of [**1′**] is difficult, because the one-electron reduction species is very unstable in air, we tried to isolate the re-oxidation species of [**1′**] using *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ as [**1**]. The material recovered by this experiment was confirmed to be *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ (Fig. 4). The experiment using another isotopomer, *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$, as [**1**], also gave a similar result: *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ alone was obtained under the same conditions. The possibility of an oxygen-atom transfer

Table 2. IR Data[a] of *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$ and Their $^{15}N$ Isotopomers Which Were Recovered by the Redox Experiments (i) and (ii) (see also Fig. 2)

| Exp.[b] | Starting material[c] | Recovered material[c] | $\nu$(NO) | $\nu$(N=O) | $\nu$(N–O) | $\nu_{as}(NO_2)$ | $\nu_s(NO_2)$ |
|---|---|---|---|---|---|---|---|
| (i) | $[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ [**1**] | | 1929 | 1453 | 965 | | |
| | | $[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ [**2**] | 1945 | | | 1401 | 1304 |
| | | $[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ [**2**] | 1907 | | | 1431 | 1324 |
| | $[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ [**1**] | | 1890 | 1474 | 991 | | |
| | | $[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ [**2**] | 1944 | | | 1400 | 1304 |
| | | $[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ [**2**] | 1906 | | | 1425 | 1323 |
| (ii) | $[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ [**1**] | | 1929 | 1453 | 965 | | |
| | | $[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ [**1**] | 1929 | 1453 | 964 | | |
| | $[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ [**1**] | | 1890 | 1473 | 991 | | |
| | | $[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ [**1**] | 1894 | 1475 | 987 | | |

a) $cm^{-1}$ (KBr disk). b) See the text (Section 2 in Results and Discussion). c) All the complexes were isolated as $PF_6$ salt.

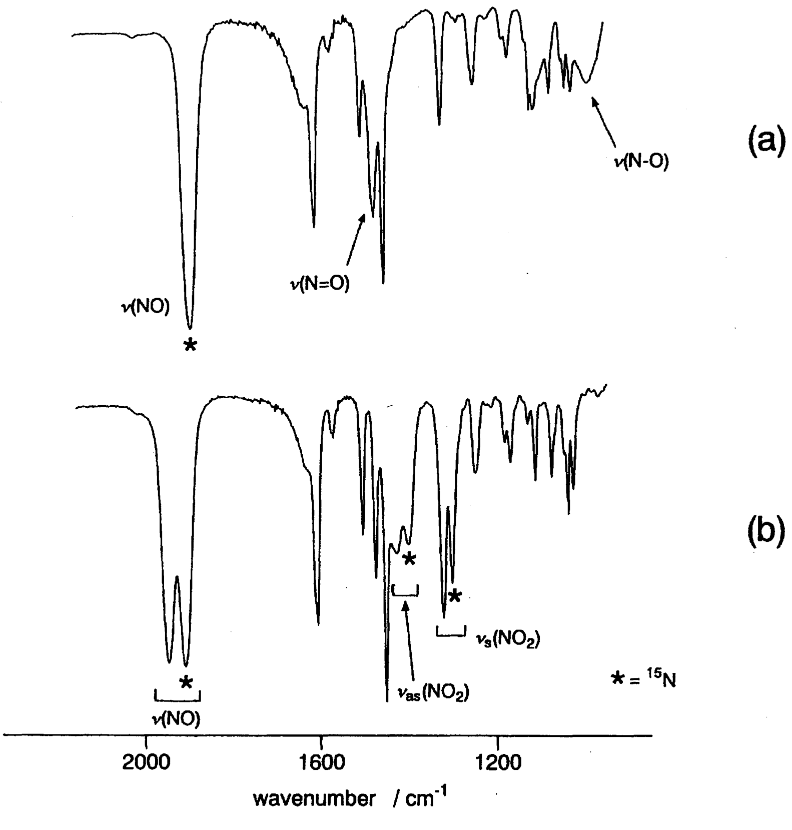

Fig. 2. IR spectra. (a) *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ used as a starting material of the redox reaction. (b) The recovered material in the redox reaction of (i); spectra due to both *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ and *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ are observed.

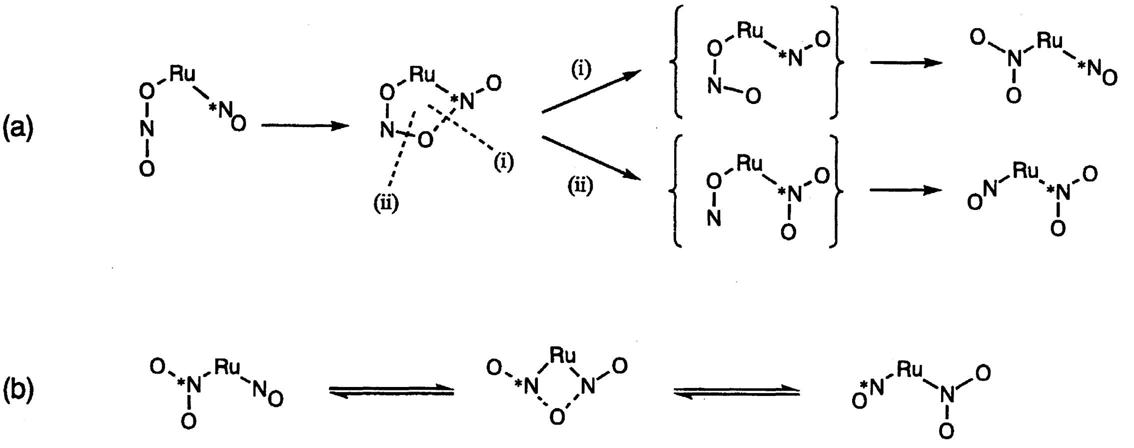

Fig. 3. Two possible scheme for the oxygen atom transfer reaction involving $\{RuNO\}^7$-type nitrosyl complexes ($^*N = ^{15}N$). (a): *cis*-$[Ru(^{15}NO\cdot)(ONO)(bpy)_2]^+$ gives *cis*-$[Ru(NO\cdot)(^{15}NO_2)(bpy)_2]^+$, along with *cis*-$[Ru(^{15}NO\cdot)(NO_2)(bpy)_2]^+$. (b): an interconversion process of *cis*-$[Ru(NO\cdot)(^{15}NO_2)(bpy)_2]^+$.

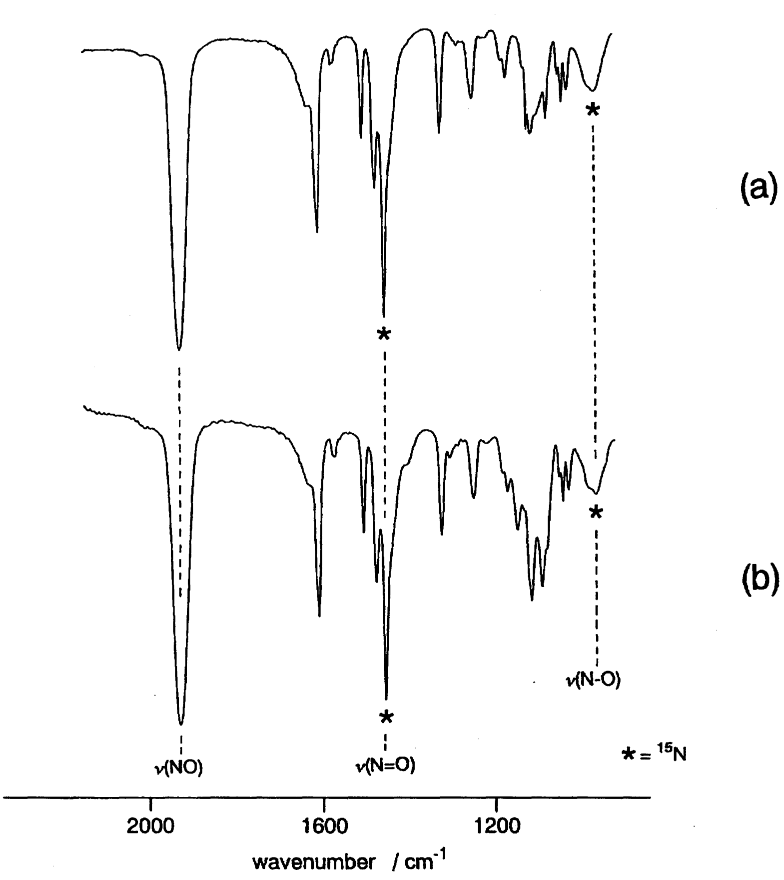

Fig. 4. IR spectra. (a) *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ used as a starting material of the redox reaction. (b) The recovered material in the redox reaction of (ii); the spectra due to *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ are observed.

occurring in Eq. 1 could thus be ruled out.

(iii) We could not carry out a survey of the process described in Eq. 3, due to the following reason: Although the isotopomer of nitrosyl–nitro species, *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ or *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$, is necessary to clarify the presence of an oxygen-atom transfer reaction between [**2**] and [**2′**], all efforts to prepare these isotopomers have so far been unsuccessful. Although *cis*-$[Ru(^{15}NO)(^{15}NO_2)(bpy)_2]^{2+}$ is available by a known procedure,[16] this isotopomer is useless for the present purpose.

**3. Mechanistic Explanation for the Oxygen-Atom Transfer Reaction.** Two mechanistic illustrations are possible for the present oxygen-atom transfer reaction using Fig. 3-(a) and -(b): Fig. 3-(a) shows the nitrito-to-nitro rearrangement of *cis*-$[Ru(NO\cdot)(O^{15}NO)(bpy)_2]^+$, which occurs via the formation of an assumed cyclic intermediate. The assumed cyclic intermediate disintegrates in two ways (both (i) and (ii) in Fig. 3-(a)) to give either *cis*-[Ru(NO·)-

$(^{15}NO_2)(bpy)_2]^+$ or *cis*-$[Ru(^{15}NO\cdot)(NO_2)(bpy)_2]^+$. Bond breaking at (i) affords a species having the $\{Ru(^{15}NO\cdot)(ONO)\}^+$ moiety, which can undergo a facile rearrangement to give *cis*-$[Ru(^{15}NO\cdot)(NO_2)(bpy)_2]^+$ ([**2′**]), without any oxygen-atom transfer reaction occurring. The disintegration at (ii) gives *cis*-$[Ru(NO\cdot)(^{15}NO_2)(bpy)_2]^+$ ([**2′**]), via the formation process of a transient species having the *O*-bound nitrosyl moiety.[27] Such a rearrangement, from the *O*-bound nitrosyl moiety to the *N*-bound nitrosyl, has been reported to occur.[27] We also tried an experiment using *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ as [**1**], instead of the *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$ (described in (i)): it gave either *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ or *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$, as a mixture composed of nearly equimolar amounts of the isotopomers.

Another possible explanation is shown in Fig. 3-(b), which involves an equilibrium process between the nitro and the nitrosyl ligands. In this case, the oxygen-atom transfer occurs in the isomerized nitro species, *cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$, in Eq. 2 and/or Eq. 3, when Feltham's mechanism, as illustrated in Fig. 3-(b), is operating.[24,25] Unfortunately, the participations of such an oxygen-atom transfer processes in the equilibrium system can not be clarified experimentally, since neither *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ nor *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$ is obtainable, as mentioned in (iii) of the previous section (See also the illustration on the next Section 4). Although no clear evidence is yet available concerning the oxygen transfer reaction, process (a) is likely to proceed dominantly.[27]

The question that is raised by the proposed mechanism (Fig. 3-(a) and/or (b)) is why does the oxygen-atom transfer proceed so effectively in a $\{RuNO\}^7$-type nitrosyl complex. Although this is a problem for further study, at least the following results can be noted. The NO group will undergo a nucleophilic attack by an adjacent *cis*-ONO ligand intramolecularly to lead to Ru–ONON(O)–Ru bonding (see Fig. 3-(a); the disintegration of this moiety results in the oxygen-atom transfer reaction). The reactivity of such a ligand reaction should decrease in a $\{RuNO\}^7$-type nitrosyl more than that in a $\{RuNO\}^6$-type nitrosyl, because the electrophilicity of the $\{RuNO\}^7$-type nitrosyl is inferior to that of the $\{RuNO\}^6$-type nitrosyl. According to acid-base theory, however, we can expect that the NO moiety of the $\{RuNO\}^7$-type nitrosyl becomes more basic than of $\{RuNO\}^6$-type nitrosyl. This may allow the assumption that the one-electron reduction of the $\{RuNO\}^6$-type nitrosyl enables the nitrosyl and nitrito moieties to combine to form the Ru–ONON(O)–Ru bonding. In a steric sense, such bonding formation may also occur favorably in the $\{RuNO\}^7$-type nitrosyl; a bent Ru–N–O structure of the $\{RuNO\}^7$-type nitrosyl complex appears to facilitate this bonding formation. More investigation is needed for obtaining a complete answer to this question.

**4. Monitoring Study of the Interaction between *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ and $NO_2^-$ in an Non-aqueous Solvent: An Experimental Proof for the Synthetic Difficulty of $^{15}$N-Labeled Nitro Isotopomer.** As mentioned above, *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ (or *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$) is the essential $^{15}$N isotopomer for clarifying the mechanistic process of the redox-induced rearrangement, whether the oxygen-atom transfer process is involved in Eq. 3 or not. In this connection, we investigated the interaction reaction between *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ and $NO_2^-$, with the hope to obtain a proof for the possibility to synthesize *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ and/or *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$. Although such attempts were all unsuccessful, as described earlier, the result provides some profile to the nitrito bonding formation in *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$.

Figure 5 shows the CV monitoring the interaction reaction between *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ and $NO_2^-$ at 25 °C in $CH_3CN$ solvent. The aqua complex used as a starting material shows a quasi-reversible reduction wave at 0.24 V.[42] The addition of an aliquot of mother liquor of $(Et_4N)NO_2$ ($6.36\times10^{-1}$ mol dm$^{-3}$) to a non-aqueous solution ($CH_3CN$) containing *cis*-$[Ru(NO)(H_2O)(bpy)_2](PF_6)_3$ (1.0 mmol dm$^{-3}$) gave a new reduction wave at around −0.02 V within a brief moment; this wave corresponds to $E_{pc1}$ of the authentic *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$. Another irreversible oxidation wave with $E_{pa}=0.28$ V also appeared. We could

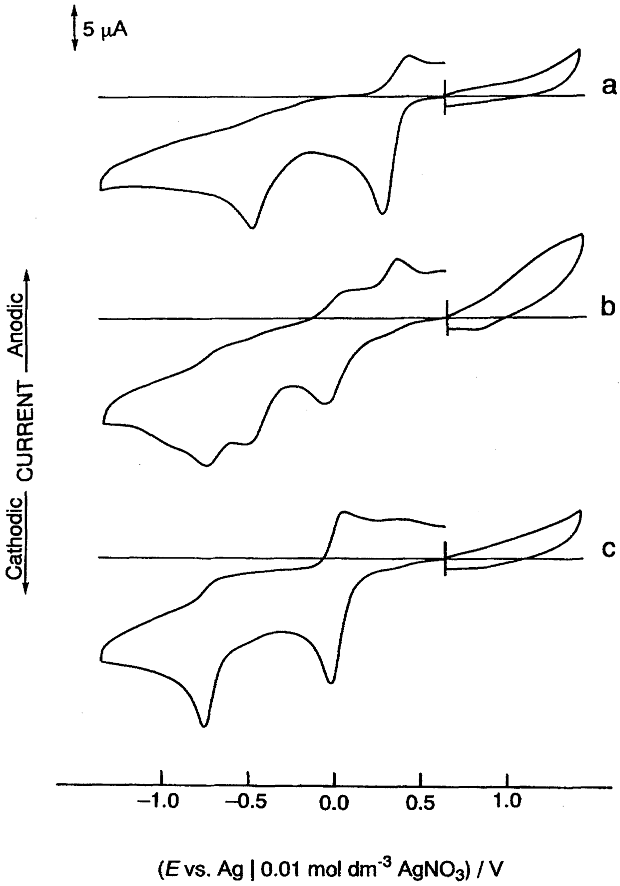

Fig. 5. CV monitoring of the reaction between $NO_2^-$ and *cis*- $[Ru(NO)(H_2O)(bpy)_2]^{3+}$ ($NO_2^-$/*cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}=1.0$) in $CH_3CN$ at 25 °C. (a) before the reaction. (b) after 3 min; (c) after 30 min (The CV corresponds to that of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$).

ascribe the oxidation wave to a free $NO_2^-$ used as a reagent. The oxidation wave decreased when the solution was allowed to stand (0.5 h), while the reduction wave due to *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ increased soon. The cyclic voltammograms measured after 60 min were almost identical with those of *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ reported previously.[16] Essentially the same result was found in experiments in which the molar ratio of $NO_2^-/[Ru(NO)(H_2O)(bpy)_2]^{3+}$ was varied from 0.4 to 1.2. Again, no evidence for the formation of *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ could be obtained. When an excess amount of $NO_2^-$ was added ($NO_2^-/[Ru(NO)(H_2O)(bpy)_2]^{3+}=3$—10), both waves of *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ and *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ appeared during an early stage of the reaction, but disappeared completely to form an unidentified species. We also tried the experiment on a synthetic scale. The same result as that described above was obtained; no *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ was available as a single compound.

The above observations conclusively show that the direct reaction between *cis*-$[Ru(^{15}NO)(H_2O)(bpy)_2]^{3+}$ and $NO_2^-$ (or *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ and $^{15}NO_2^-$) does not give the nitro species, either *cis*-$[Ru(^{15}NO)(NO_2)(bpy)_2]^{2+}$ or *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$, even under the non-aqueous solvent conditions. If the reaction is carried out under aqueous conditions, the $^{15}N$ labeled nitrito species is produced as *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ (or *cis*-$[Ru(NO)(O^{15}NO)(bpy)_2]^{2+}$),[16] without giving the corresponding nitro complexes.

It is worth noting that the nitrite ($NO_2^-$) reaction toward the nitrosyl complex depends strongly on the solvent ligand of *cis*-$[Ru(NO)(solv)(bpy)_2]^{3+}$ (solv=$H_2O$, $CH_3CN$). Under the same conditions using $CH_3CN$ as a solvent, *cis*-$[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$ gave both *cis*-$[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ and an unidentified species,[43] instead of the expected nitrosyl complex, *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ and/or *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$.[16] These reactions are still being studied, and further detailed results will be reported separately.

Although the nitro complex (*cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$) has often been prepared by an acid-decomposition of *cis*-$[Ru(NO_2)_2(bpy)_2]$ under aqueous conditions,[44] this preparative method is useless in the preparation of *cis*-$[Ru(NO)(^{15}NO_2)(bpy)_2]^{2+}$, because *cis*-$[Ru(^{15}NO_2)_2(bpy)_2]$ gives *cis*-$[Ru(^{15}NO)(^{15}NO_2)(bpy)_2]^{2+}$. Although we also tried the reaction of *cis*-$[Ru(^{15}NO_2)(solv)(bpy)_2]^+$ with NO (gas) or $NOBF_4$, the reaction gave an unsuccessful result again; the former generated a green solution, probably due to the formation of $[Ru_2(^{15}NO_2)_2O(solv)_2(bpy)_4]^{2+}$,[14] and the latter produced an unisolatable material.

**5. Other Features Observed in the Redox-Induced Linkage Isomerization.** Some different results between *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$ and *cis*-$[Ru(NO)(X)(bpy)(py)_2]^{2+}$ (reported previously) are described for a comparison. Although the complexes have the same *cis*-configuration, the core fragments ("Ru(bpy)$_2$" in the former and "Ru(bpy)(py)$_2$" in the latter) differ in both the steric configuration and the ligand.[16] In *cis*-$[Ru(NO)(X)(bpy)(py)_2]^{2+}$, an equatorial plane of octahedral configuration has been constituted by two nitrogen atoms of one chelating 2,2′-bipyridine, the nitrosyl nitrogen, and the X ligand, including the Ru atom. The two other residual pyridine ligands exist at positions above and below in this plane. Such planarity does not exist in *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$, since only one donor nitrogen atom of each 2,2′-bipyridine occupies one of the corners of the equatorial plane, and other nitrogen donor atom of each 2,2′-bipyridine is directed to the axial position to form a chelate ring. The differences noted above lead to some different features concerning their isomeric behavior: As Eq. 5 shows, the previous *cis*-$[Ru(NO)(NO_2)(bpy)(py)_2]^{2+}$ undergoes a one-way thermally-induced rearrangement, from the nitro to the nitrito, even at room temperature. Instead of such a rearrangement, the present *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ underwent an isomerization to produce an equilibrium mixture of the nitro and nitrito species at elevated temperature.[16] In both cases of the thermally-induced nitro–nitrito isomerization, no oxygen atom transfer reaction occurred.

Despite such a difference, the redox-induced oxygen transfer reaction occurred either in *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$ or in *cis*-$[Ru(NO)(X)(bpy)(py)_2]^{2+}$; this was demonstrated using *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$, as described earlier, and also by an experiment using *cis*-$[Ru(^{15}NO)(ONO)(bpy)(py)_2]^{2+}$, which gave the same result. A mixture of nearly equimolar amounts of *cis*-$[Ru(^{15}NO)(NO_2)(bpy)(py)_2]^{2+}$ and *cis*-$[Ru(NO)(^{15}NO_2)(bpy)(py)_2]^{2+}$ was recovered as the products of the overall reaction, Eqs. 1, 2, 3, and 5, via Eq. 2 and then Eq. 3. The rate constants estimated for the isomerization process expressed by Eq. 2 (from the one-electron reduced nitrito species-to-the corresponding nitro species) differ in the following order: $k=1.7(\pm 0.1)\times 10^{-2}$ s$^{-1}$ for *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ and $k=1.1(\pm 0.1)\times 10^{-3}$ s$^{-1}$ for *cis*-$[Ru(NO\cdot)(ONO)(bpy)(py)_2]^+$ (both at 25 °C).

The present study demonstrated an important role of the one-electron reduction nitrosyl (NO•) existing as a spectator ligand. Such a ligand nature of the NO• has not yet been reported. In this context, it is significant to compare the nitro–nitrito isomeric observations between the present work and the previous one that has been described in the nitro complexes of Ru(II) (*trans*-$[RuCl(NO_2)(py)_4]$ and *cis*-$[RuCl(NO_2)(bpy)_2]$), which lack a nitrosyl ligand:[7,9—15] As Fig. 6 shows, the nitrito-to-nitro isomerization occurs in the nitrosyl complex when it undergoes a one-electron *reduction*, but the complex lacking nitrosyl exhibits nitro-to-nitrito isomerization by a one-electron *oxidation*. Despite these differences, we can describe the isomeric behavior of both previous and present complexes by essentially the same cyclic scheme (Fig. 6), as long as the experiment is carried out at low temperature (−40 °C); the low temperature experiment prevents the chemical reactions of *trans*-$[RuCl(NO_2)(py)_4]^+$ and *cis*-$[RuCl(NO_2)(bpy)_2]^+$, which gave *trans*-$[Ru(O)Cl(py)_4]^+$ and *cis*-$[RuCl(ONO_2)(bpy)_2]^+$, respectively, under room temperature conditions.[7—15] In both *trans*-$[RuCl(NO_2)(py)_4]$ and *cis*-$[RuCl(NO_2)(bpy)_2]$, the higher oxidation state of Ru atom ($d^5$) prefers the nitrito bonding formation, owing to a decrease in the d$\pi$ electron density compared to that of the

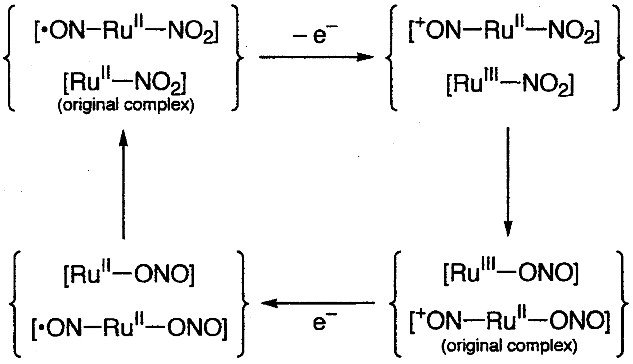

Fig. 6. Schematic explanations of the redox-induced nitro–nitrito linkage isomerizations of both *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ and *trans*-$[RuCl(NO_2)(py)_4]$.[12)]

lower oxidation state of Ru atom ($d^6$). A similar tendency is found in the present complex having nitrosyl ligand: Since the $NO^+$ is a strong π-acid, the ligand nature which withdraws an electron density from the metal dπ–pπ (M→L) back-bonding is expected in the $\{RuNO\}^6$-type nitrosyl complexes: This results in reducing the relative tendency for the nitrogen atom on nitrite to participate in π-bonding, if we assume that an electronic interaction through the metal to the *cis* nitro (or nitrito) ligand is possible for the nitrosyl. As a consequence, an oxygen bound nitrito mode is preferentially formed when a nitrite is coordinated to metal atom in a $(Ru^{II}NO^+)^{3+}$ moiety. One can assume the opposite for a complex having the $(Ru^{II}NO\cdot)^{2+}$ moiety.

**6. Summary.** The present work established that the redox-induced rearrangement was followed by an oxygen-atom transfer reaction between the nitrosyl and adjacent nitrite groups in the pathways illustrated by Eqs. 1, 2, 3, and 4. However, we need to carry out further study in order to describe a valid reaction process, though it is reasonable to assume that the rearrangement process of the $\{RuNO\}^7$-type nitrosyl complexes, expressed by Eq. 2 (from *cis*-$[Ru(NO\cdot)(ONO)(bpy)_2]^+$ [**1′**] to *cis*-$[Ru(NO\cdot)(NO_2)(bpy)_2]^+$ [**2′**]), is a very likely candidate for the transfer of an oxygen atom, since we have found that it does not occur in the thermally-induced rearrangement of the nitro–nitrito isomeric pair, either in *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ or *cis*-$[Ru(NO)(NO_2)(bpy)_2]^{2+}$ (both $\{RuNO\}^6$-type nitrosyl).[16)] The important role of the $\{RuNO\}^7$-type nitrosyl, which behaves as a key intermediate of the oxygen-atom transfer reaction, was thus demonstrated. Such a function of the $\{RuNO\}^7$-type nitrosyl, which significantly accelerates the oxygen-atom transfer reaction, has not yet been reported.

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42) A CV monitoring showed that the solvation of *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ ($\{RuNO\}^6$) in $CH_3CN$ was unexpectedly slow, while *cis*-$[Ru(NO\cdot)(H_2O)(bpy)_2]^{2+}$ ($\{RuNO\}^7$) underwent a facile solvation.[14] In a synthetic scale, it requires 3—4 d standing at room temperature for the completion of the solvation. Probably this results in a different reactivity between the complex of $X=CH_3CN$ and $H_2O$.

43) The product was tentatively identified as *cis*-$[Ru(NO)(CH_3C(O)NH)(bpy)_2]^{2+}$, based on the data of analysis, IR, $^1H$ and $^{13}C$ NMR spectra, mass spectra, and cyclic voltammetry. However, single crystals suitable for X-ray structure determination is not available yet. Such a reaction of $CH_3CN$ which gives $CH_3C(O)NH$ moiety has been reviewed recently.[45] Another reaction product, *cis*-$[Ru(NO_2)(CH_3CN)(bpy)_2]^+$, could be identified using an authentic sample.

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