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Redox- and Thermally-Induced Nitro−Nitrito Linkage Isomerizations of Ruthenium(II) Complexes Having Nitrosyl as a Spectator Ligand

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Three new nitro−nitrito isomeric pairs are prepared and characterized as *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$, *cis*-$[Ru(NO)X(pyca)_2]$, and *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ (X = ONO, NO_2; 2,2′-bpy = 2,2′-bipyridine; pyca = pyridine-2-carboxylate; py = pyridine). Molecular structures of the isomers are established by X-ray structure studies, except for *cis*-$[Ru(NO)(ONO)(pyca)_2]$. Redox-induced linkage isomerization occurs in *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ (X = ONO, NO_2); the nitrito isomer is capable of being interchanged to the nitro isomer, via a one-electron redox process of the $(RuNO)^{3+}$ moiety. Thermally-induced isomerization also occurs, with different isomerization patterns, depending on the spectator ligands: *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ gave an equilibrium mixture of the nitro and the nitrito isomers; in *cis*-$[Ru(NO)X(pyca)_2]$, the nitrito isomer changed to the nitro isomer; contrastively, the nitro isomer of *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ converted to the nitrito isomer. Some mechanistic investigations about the isomerization reactions were carried out using various ^{15}N-substituted complexes; no oxygen exchange reaction between the nitrosyl and the nitro (nitrito) ligands was found.

Introduction

Investigation of linkage isomerizations which occur in complexes with an ambidentate ligand is becoming increasingly important in inorganic chemistry.[1] Because of its ability to function as such an ambidentate ligand, a nitrite ion has been of special interest both because of its coordination mode and because of the mechanistic process of the rearrangement between nitro and nitrito moieties. Various studies on thermally- and photochemically-induced rearrangements have been reported.[2] Previously, we have reported on the electrochemical behavior of a series of *trans*-$[RuX(NO_2)(py)_4]^n$ (py = pyridine) complexes, in which the redox-induced rearrangement of the nitro moiety was established.[3] However, the experimental conditions of the system were limited, and we were able to find the rearrangement experimentally only at a low temperature (−20 to −40 °C); consequently, the isomeric pair has never been isolated. A similar reaction has also been reported in *cis*-$[Ru(NO_2)X(2,2'\text{-bpy})_2]^n$ (X = Cl, py; 2,2′-bpy = 2,2′-bipyridine)[4] without any opportunity for isolating nitrito isomer.

We wish to report here new nitro−nitrito isomeric pair complexes of ruthenium, with nitrosyl as a spectator ligand; both nitro and nitrito isomers of this system are easily isolatable, and they are capable of being interchanged, via a one-electron redox process at the $(RuNO)^{3+}$ moiety. To our knowledge, the present report appears to be the first one in which a redox-induced nitro−nitrito rearrangement is proved definitely to occur, using authentic samples of both the nitro and the nitrito isomers.

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The present paper also explains that the system described here undergoes a thermally-induced linkage isomerization, with different isomerization patterns, depending on the spectator ligands: in *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ (X = NO_2, ONO), an equilibrium mixture of the nitro and nitrito isomers is formed. On the other hand, a thermodynamically stable species of *cis*-[Ru(NO)X(pyca)$_2$] pair (X = NO_2, ONO; pyca = pyridine-2-carboxylate) was the nitro isomer. Contrastively, the nitrito species of *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ (X = NO_2, ONO) is stable under the same conditions. Some mechanistic evidence is given for these thermally-induced linkage isomerizations, using various ^{15}N-isotopomers.

Experimental Section

Materials. The following complexes were prepared by the literature methods as raw materials for the present syntheses: *cis*-$[Ru(NO_2)_2(2,2'\text{-bpy})_2]\cdot H_2O$,[5] *cis*-$[Ru(NO)(H_2O)(2,2'\text{-bpy})_2](ClO_4)_3$,[6] *cis*-$[RuCl(NO)(pyca)_2]$,[7] *cis*-$[Ru(NO_2)_2(2,2'\text{-bpy})(py)_2]\cdot 2H_2O$,[8] *cis*-$[Ru(NO)(OH)(2,2'\text{-bpy})(py)_2](ClO_4)_2$.[8] Other complexes were prepared for comparative study of characteristics: *cis*-$[Ru(NO_2)(2,2'\text{-bpy})(py)_3]PF_6$ [8] and *cis*-$[Ru(NO_2)(py)(2,2'\text{-bpy})_2]PF_6$.[9]

Measurements. Elemental analyses were performed by the Sophia University Analytical Facility. Infrared spectra were recorded with a Perkin-Elmer FT-1650 spectrophotometer. UV−visible spectra were obtained with a Hitachi 200-20 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with JEOL GX-270 spectrophotometer. All NMR spectra were obtained in CD_3CN; Me_4Si was used as an internal reference in the measurements of both ^1H and ^{13}C NMR spectra. Electrochemical measurements used 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 concentration of 0.1 M (either tetraethylammonium perchlorate (TEAP) or tetra-*n*-butylammonium hexafluorophosphate). Three-electrode, one-compartment cells were used. They were equipped with a platinum working electrode (ϕ =1.6 mm), a platinum auxiliary electrode, and 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 was measured by a Huso coulometer Model 343B digital coulometer.

Syntheses. *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})_2](PF_6)_2$ (1). The complex was prepared by a modification of the literature procedure.[10] A suspension of *cis*-$[Ru(NO_2)_2(2,2'\text{-bpy})_2]\cdot H_2O$ (100 mg (0.19 mmol)) in water (5 cm^3) was dissolved by hydrochloric acid (5 cm^3) at room temperature, using an ice bath. To the homogeneous orange solution was added immediately an aqueous solution of NH_4PF_6 (50 mg/5 cm^3); *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})_2](PF_6)_2$ was precipitated. The yellow product was collected by filtration, washed with cold water, ethanol, and then ether, and air-dried; yield 130 mg, 87%. ^{13}C NMR (CD_3CN/TMS at −20 °C, ppm): δ 156.54, 155.34, 154.69, 154.26, 154.20, 153.21, 150.09, 145.90, 145.77, 144.92, 131.47, 131.17, 130.59, 130.03, 127.44, 126.60, 126.51. UV−vis (CH_3CN, nm (ϵ/(M^{-1} cm^{-1}))) 440 (1.5×10^2), 327 (9.7×10^3), 297 (1.8×10^4).

***cis*-$[Ru(NO)(ONO)(2,2'\text{-bpy})_2](PF_6)_2$ (2).** A 100 mg (0.13 mmol) of *cis*-$[Ru(NO)(H_2O)(2,2'\text{-bpy})_2](ClO_4)_3$ was dissolved in H_2O (20 cm^3), and the solution pH was adjusted to 2.0 using CF_3SO_3H (3 M). After the solution was cooled to 4 °C by ice, a 100 mg portion of powdered $NaNO_2$ (1.45 mmol) was added to the solution. The mixed solution was stirred at this temperature for 30 min to give a yellow solution. Brown crystalline material precipitated immediately when solid NH_4PF_6 (50 mg) was added to this yellow solution. The product was washed by cold water, ethanol, and then ether and dried in vacuo; yield 75 mg, 80%. Anal. Calcd for $C_{20}H_{16}N_6O_3P_2F_{12}Ru$: N, 10.78; C, 30.82; H, 2.07. Found: N, 10.72; C, 30.82; H, 2.13. ^{13}C NMR (CD_3CN/TMS at −20 °C, ppm): δ 156.57, 155.80, 154.88, 154.73, 154.45, 153.71, 152.85, 149.62, 145.81, 145.33, 144.80, 144.28, 130.82, 130.65, 130.60, 130.20, 127.41, 127.30, 126.78. UV−vis (CH_3CN, nm (ϵ/(M^{-1} cm^{-1}))): 445 (2.3×10^2), 323 (1.6×10^4), 293 (1.8×10^4).

***cis*-$[Ru(NO)(NO_2)(pyca)_2]$ (3).** An ethanol solution of *cis*-$[Ru(NO)Cl(pyca)_2]$ (200 mg (0.49 mmol)/45 cm^3) was mixed with H_2O (5 cm^3) containing $NaNO_2$ (350 mg). This solution was refluxed for 7 h; during this period the solution color changed from the original reddish-brown to yellow. The volume of the solution was reduced by heating, until it became near 10 cm^3, and then the solution was stored in a refrigerator overnight. The crystalline material thus formed was collected by filtration, washed with cold water, ethanol, and then ether, and air-dried; yield 140 mg, 68%. Anal. Calcd for $C_{12}N_4O_7H_8Ru$: N, 13.30; C, 34.21; H, 1.91. Found: N, 12.91; C, 34.44; H, 1.84. UV−vis (CH_3CN, nm (ϵ/(M^{-1} cm^{-1}))): 430 (1.0×10^2), 260 (1.2×10^4).

***cis*-$[Ru(NO)(ONO)(pyca)_2]$ (4).** (i) $[Ru(NO)(H_2O)(pyca)_2]ClO_4$ was first prepared as follows. An aqueous solution of *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ (70 mg (0.17 mmol)/15 cm^3) containing $HClO_4$ (4 M, 0.3 cm^3) was heated at 80 °C for 3−4 h; during this period the color of the solution became yellow. The volume of the solution was reduced by heating, until it became near 5 cm^3, and then some solid $NaClO_4$ (300 mg) was added to the solution. The solution was stored in a refrigerator overnight. The yellow crystalline material thus formed was collected by filtration, washed with cold water, ethanol, and then ether, and air-dried; yield 50 mg, 59%. Anal. Calcd for $C_{12}N_3O_{11}H_{12}ClRu$: N, 8.23; C, 28.22; H, 2.37. Found: N, 8.33; C, 28.35; H, 2.03.

(ii) An aqueous solution of $[Ru(NO)(H_2O)(pyca)_2]ClO_4$ (100 mg (0.20 mmol)/15 cm^3) containing solid $NaNO_2$ (150 mg) was stirred using an ice bath for 30 min. Salmon color material precipitated soon from the reaction solution when it was stored in a refrigerator for 30 min. The precipitate was collected by filtration, washed with cold water, ethanol, and then ether, and air-dried; yield 70 mg, 50%. Anal. Calcd for $C_{12}N_4O_7H_8Ru$: N, 13.30; C, 34.21; H, 2.03. Found: N, 13.19; C, 33.97; H, 1.75. ^{13}C NMR (CD_3CN, ppm): δ 210.55, 172.40, 152.95, 151.63, 150.84, 150.46, 144.44, 143.11, 130.66, 130.47, 128.89, 128.81. UV−vis (CH_3CN, nm (ϵ/(M^{-1} cm^{-1}))): 445 (9.9×10), 266 (9.9×10^3).

Caution! While we have used perchloric acid or perchlorate without incident, these are potentially explosive. Care should be exercised in using a spatula or stirring rod to agitate any solid perchlorate mechanically.

***cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2](PF_6)_2$ (5).** Preparative work of the isomer has been reported briefly.[8] A suspension of *cis*-$[Ru(NO_2)_2(2,2'\text{-bpy})(py)_2]\cdot 2H_2O$ (100 mg (0.18 mmol)) in water (5 cm^3) was dissolved quickly using hydrochloric acid (0.5 cm^3) at room temperature, to give a pale orange solution. To the homogeneous orange solution was added immediately an aqueous solution of NH_4PF_6 (50 mg/5 cm^3); *cis*-$[Ru(NO)(NO_2)(bpy)(py)_2](PF_6)_2$ was precipitated. The product was stored, without filtering, in a refrigerator (4 °C) for 30 min. The product was then collected by filtration, washed with cold water, ethanol, and then ether, and air-dried. It was stored again in a refrigerator (−16 °C); yield 130 mg, 90%. Anal. Calcd for $C_{20}H_{18}N_6O_3P_2F_{12}Ru$: N, 10.75; C, 30.74; H, 2.32. Found: N, 10.77; C, 31.44; H, 2.24. ^{13}C NMR (CD_3CN/TMS at −20 °C, ppm): δ 155.69, 154.35 (both 2,2′-bpy), 154.20, 151.28 (both 6,6′-bpy), 152.84 (2,6-py), 146.33, 144.80 (both 4,4′-bpy), 143.68 (4-py), 131.88, 131.36 (both 5,5′-bpy), 129.01 (3,5-py), 127.69, 127.39 (both 3,3′-bpy). UV−vis (CH_3CN, nm (ϵ/(M^{-1} cm^{-1}))): 455 (1.0×10^2), 336 (4.8×10^3), 293 (1.1×10^4).

***cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2](CF_3SO_3)_2$.** In the procedure which gives *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2](PF_6)_2$ (**5**), CF_3SO_3Na (100 mg) was used as a precipitant, instead of NH_4PF_6; yield 90%. Anal. Calcd for $C_{22}H_{18}N_6O_9F_6S_2Ru$: N, 10.64; C, 33.46; H, 2.30. Found: N, 10.57; C, 33.29; H, 2.19.

***cis*-$[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2](PF_6)_2$ (6).** The complex was prepared by exactly the same procedure as that described in the preparation of *cis*-$[Ru(NO)(ONO)(2,2'\text{-bpy})_2](PF_6)_2$, using *cis*-$[Ru(NO)(OH)(2,2'\text{-bpy})(py)_2](ClO_4)_2$ as a starting material; yield 80 mg, 80%.

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Table 1. Crystallographic Data and Experimental Conditions for Intensity Collection of the Nitro Isomers

	cis-[Ru(NO)(NO_2)(2,2′-bpy)$_2$](PF_6)$_2$ (**1**)	*cis*-[Ru(NO)(NO_2)(pyca)$_2$] (**3**)	*cis*-[Ru(NO)(NO_2)(2,2′-bpy)(py)$_2$](PF_6)$_2$ (**5**)
chem formula	$RuP_2F_{12}O_3N_6C_{20}H_{16}$	$RuO_7N_4C_{12}H_8$	$RuP_2F_{12}O_3N_6C_{20}H_{18}$
fw	779.38	421.29	781.40
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	*P*bca (No. 61)	$P2_1/n$ (No. 14)
a, Å	13.276(2)	14.950(7)	9.292(2)
b, Å	16.888(4)	16.012(7)	16.703(2)
c, Å	12.526(5)	12.064(8)	17.712(1)
β, deg	95.37(2)		92.487(9)
V, Å^3	2796(1)	2887(2)	2746.4(5)
Z	4	8	4
T, °C	20	23	23
λ, Å	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.851	1.938	1.890
diffractometer	Enraf-Nonius CAD4	Rigaku AFC5S	Rigaku AFC5S
μ(Mo Kα), cm^{-1}	7.92	11.33	8.06
R^a	0.062	0.046	0.050
$R_w{}^b$	0.074	0.027	0.035

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Crystallographic Data and Experimental Conditions for Intensity Collection of the Nitrito Isomers

	cis-[Ru(NO)(ONO)(2,2′-bpy)$_2$](PF_6)$_2$ (**2**)	*cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$](PF_6)$_2$ (**6**)
chem formula	$RuP_2F_{12}O_3N_6C_{20}H_{16}$	$RuP_2F_{12}O_3N_6C_{20}H_{18}$
fw	779.38	781.40
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	14.207(3)	13.146(7)
b, Å	14.638(4)	19.315(6)
c, Å	13.106(3)	11.183(5)
β, deg	97.74(2)	93.48(4)
V, Å^3	2700(1)	2834(3)
Z	4	4
T, °C	20	23
λ, Å	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.917	1.831
diffractometer	Enraf-Nonius CAD4	Rigaku AFC5R
μ(Mo Kα), cm^{-1}	8.19	7.81
R^a	0.051	0.049
$R_w{}^b$	0.041	0.035

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Anal. Calcd for $C_{20}H_{18}N_6O_3P_2F_{12}Ru$: N, 10.76; C, 30.73; H, 2.32. Found: N, 10.40; C, 30.73; H, 2.32. ^{13}C NMR (CD_3CN/TMS at −20 °C, ppm): δ 155.92, 154.91 (both 2,2′-bpy), 153.49, 150.90 (both 6,6′-bpy), 151.81 (2,6-py), 146.23, 144.54 (both 4,4′-bpy), 143.29 (4-py), 132.41, 131.46 (both 5,5′-bpy), 128.87 (3,5-py), 127.84, 127.03 (both 3,3′-bpy). UV−vis (CH_3CN, nm (ϵ/M^{-1} cm^{-1}))): 492 (1.1 × 10^2), 327 (6.2 × 10^3), 292 (8.7 × 10^3).

***cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$](CF_3SO_3)$_2$·H_2O.** In the procedure which gives *cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$](PF_6)$_2$ (**6**), CF_3SO_3Na (100 mg) was used as a precipitant, instead of NH_4PF_6; yield 90%. Anal. Calcd for $C_{22}H_{19}N_6O_{10}F_6S_2Ru$: N, 10.41; C, 32.72; H, 2.25. Found: N, 10.21; C, 33.00; H, 2.16.

^{15}N-Labeled Complexes. Various ^{15}N-labeled complexes were prepared mainly for a mechanistic study of the nitro−nitrito linkage isomerization. Both *cis*-[Ru(^{15}NO)($^{15}NO_2$)(2,2′-bpy)$_2$]$^{2+}$ and *cis*-[Ru(^{15}NO)($^{15}NO_2$)(2,2′-bpy)(py)$_2$]$^{2+}$ were prepared by an acid decomposition of the corresponding ^{15}N-labeled dinitro complexes of Ru(II). The following nitrito complexes, *cis*-[Ru(^{15}NO)(ONO)(2,2′-bpy)$_2$]$^{2+}$, *cis*-[Ru(^{15}NO)(O^{15}NO)(2,2′-bpy)$_2$]$^{2+}$, and *cis*-[Ru(^{15}NO)(ONO)(pyca)$_2$], were prepared by the reactions of the corresponding ^{15}N labeled aqua(nitrosyl) complexes of Ru(II) with $NaNO_2$ or Na$^{15}NO_2$. In a similar way, *cis*-[Ru(NO)(O^{15}NO)(2,2′-bpy)$_2$]$^{2+}$, *cis*-[Ru(NO)(O^{15}NO)(pyca)$_2$], and *cis*-[Ru(NO)(O^{15}NO)(2,2′-bpy)(py)$_2$]$^{2+}$ were obtained by the reactions between the corresponding aqua(or hydroxo)(nitrosyl) complex of Ru(II) and Na$^{15}NO_2$. To obtain *cis*-[Ru(^{15}NO)($^{15}NO_2$)(pyca)$_2$], the corresponding chloronitrosyl complex, *cis*-[Ru(^{15}NO)Cl(pyca)$_2$], was prepared first from the reaction between K_2[Ru(^{15}NO)Cl_5] and pyca. Then chloro ligand substitution was attempted to give *cis*-[Ru(^{15}NO)($^{15}NO_2$)(pyca)$_2$] according to the procedure described earlier, using Na$^{15}NO_2$. Both *cis*-[Ru(^{15}NO)(NO_2)(pyca)$_2$] and *cis*-[Ru(NO)($^{15}NO_2$)(pyca)$_2$] were obtained by a thermal isomerization of *cis*-[Ru(^{15}NO)(ONO)(pyca)$_2$] and [Ru(NO)(O^{15}NO)(pyca)$_2$], respectively.

X-ray Structure Determination. The diffraction experiments were carried out on Enraf-Nonius CAD4 and Rigaku AFC5S or AFC5R diffractometers at room temperature (20−23 °C) with Mo Kα radiation (λ = 0.71069 Å); the resulting crystal data and details concerning data collection and refinement are given in Tables 1 and 2. All calculations were carried out on a Silicon Graphics Indigo Computer, using program TEXSAN. X-ray structural determination of *cis*-[Ru(NO)(ONO)(pyca)$_2$] (**4**) was not accomplished, since single crystals of the isomer are not available yet.

Results

(1) Syntheses and Characterization of the Nitro−Nitrito Isomeric Pairs.

Three new nitro−nitrito isomeric pairs were prepared and characterized as *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ (X = NO_2 (**1**), ONO (**2**)), *cis*-[Ru(NO)X(pyca)$_2$] (X = NO_2 (**3**), ONO (**4**)), and *cis*-[Ru(NO)X(2,2′-bpy)(py)$_2$]$^{2+}$ (X = NO_2 (**5**), ONO (**6**)). Among these compounds, *cis*-[Ru(NO)(NO_2)(2,2′-bpy)$_2$]$^{2+}$ (**1**) has been prepared by Godwin and Meyer[10] without detailed investigation about the linkage isomerization. The nitro isomers (**1**, **3**, and **5**) were prepared by two common procedures: (i) an acid decomposition of the corresponding dinitro complexes of Ru(II) (for **1** and **5**) and (ii) a chloro ligand substitution of *cis*-[Ru(NO)Cl(pyca)$_2$] by NO_2^- ion (for **3**). The procedure developed for the syntheses of nitrito (**2**, **4**, and **6**) isomers is also simple and gives the products in relatively high yields, but they are isolatable only when the experiment is

Table 3. Characteristic Data of Infrared Spectra (Both ^{14}N- and ^{15}N-Compounds) and Cyclic Voltammograms

	IR[b]					CV[c]	
complexes[a]	$\nu(NO)$	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	$\nu(N{=}O)$	$\nu(N{-}O)$	E_{pc1}	E_{pc2}
1							
$[Ru(NO)(NO_2)(2,2'\text{-bpy})_2]^{2+}$	1944	1426	1321			0.14	−0.70
$[Ru(^{15}NO)(^{15}NO_2)(2,2'\text{-bpy})_2]^{2+}$	1905	1400	1303				
2							
$[Ru(NO)(ONO)(2,2'\text{-bpy})_2]^{2+}$	1928			1478	988	−0.02	−0.75
$[Ru(NO)(O^{15}NO)(2,2'\text{-bpy})_2]^{2+}$	1929			1453	967		
$[Ru(^{15}NO)(ONO)(2,2'\text{-bpy})_2]^{2+}$	1891			1474	981		
$[Ru(^{15}NO)(O^{15}NO)(2,2'\text{-bpy})_2]^{2+}$	1891			1453	965		
3							
$[Ru(NO)(NO_2)(pyca)_2]$	1907	1422	1320			−0.42	−1.22
$[Ru(NO)(^{15}NO_2)(pyca)_2]$	1907	1391	1308				
$[Ru(^{15}NO)(NO_2)(pyca)_2]$	1869	1420	1322				
$[Ru(^{15}NO)(^{15}NO_2)(pyca)_2]$	1870	1396	1305				
4							
$[Ru(NO)(ONO)(pyca)_2]$	1896			1470	1006	−0.58	−1.24
	1862 sp			1454 sp			
$[Ru(NO)(O^{15}NO)(pyca)_2]$	1896			1445	989		
	1862 sp			1430 sp			
$[Ru(^{15}NO)(ONO)(pyca)_2]$	1859			1470	1008		
	1825 sp			1454 sp			
5							
$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2]^{2+}$	1942	1430	1326			0.22	−0.79
$[Ru(^{15}NO)(^{15}NO_2)(2,2'\text{-bpy})(py)_2]^{2+}$	1904	1403	1309				
6							
$[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{2+}$	1918			1500	952	0.00	−0.87
$[Ru(NO)(O^{15}NO)(2,2'\text{-bpy})(py)_2]^{2+}$	1918			1477	931		

[a] PF_6 salt except for **3** and **4**. [b] cm^{-1} (KBr disk). [c] V vs Ag|$AgNO_3$ (0.1 mol dm^{-3} TEAP−CH_3CN) at 25 °C.

carried out at low temperature (~4 °C), within a limited time range. Another factor which is essential for the successful isolation of the nitrito isomers is the starting materials; we used an aqua or hydroxo complex of Ru(II) with a nitrosyl as a spectator ligand (see Experimental Section). Similar procedures using aqua complexes of Ru(II) which lack a nitrosyl ligand, *cis*-$[Ru(H_2O)_2(2,2'\text{-bpy})_2]^{2+}$ and *trans*-$[RuCl(H_2O)(2,2'\text{-bpy})_2]^{+}$, always give the nitro complexes of Ru(II), *cis*-$[Ru(NO_2)_2(2,2'\text{-bpy})_2]$ and *trans*-$[RuCl(NO_2)(2,2'\text{-bpy})_2]$, respectively, under a similar preparative condition. No evidence for formation of nitrito species such as *cis*-$[Ru(ONO)(H_2O)(2,2'\text{-bpy})_2]^{+}$ and *trans*-$[RuCl(ONO)(2,2'\text{-bpy})_2]$ was obtained, although their generation could not be ruled out.

Analytical data of the complexes agreed with those of each expected chemical formula. All the complexes have diamagnetic properties and show well-defined IR spectra, which are assignable clearly to the nitro or nitrito moiety. As Table 3 shows, three characteristic IR absorption bands, due to $\nu(NO)$, $\nu_{as}(NO_2)$, and $\nu_s(NO_2)$, are found in all nitro isomers at the expected regions.[11] The bands due to the $\nu(NO)$, $\nu(N{=}O)$, and $\nu(N{-}O)$ are also found in the nitrito isomers.[11,12] In the ^{15}N labeling experiment, all these bands shifted to the lower frequency side. The shifted values are consistent with results of other labeling studies.[3c,12b,13]

In cyclic voltammograms, the two characteristic reduction waves appeared in all complexes, while the redox potentials differ depending on the type of linkage isomer (whether the nitro isomer or the nitrito isomer) and also depending on the spectator ligand(s). The cyclic voltammograms are typical for the $\{RuNO\}^6$-type nitrosyl complexes of Ru(II).[9,14]

^{13}C NMR spectra measurements indicated a *cis* configuration: 17 and 19 resonances were detected in **1** and **2**, respectively (see Experimental Section), where 20 resonances of *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ were expected; this disagreement in the number of resonance lines is due to their overlapping. Such disagreement about the spectral lines has also been found in ^{13}C NMR of *cis*-$[Ru(NO)(Cl)(2,2'\text{-bpy})_2]^{2+}$;[15] only 15 resonances were detected in that case, and some theoretical comment recently appeared about the observation.[16]

Nitrito isomer **4** of *cis*-$[Ru(NO)X(pyca)_2]$ gave the expected 12 resonance lines, but we could not examine the ^{13}C NMR measurement to **3**, owing to its low solubility in the common solvent used for NMR measurements.

We found 13 resonance lines in *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$. The complexes with the formula of $[Ru(NO)(X)(2,2'\text{-bpy})(py)_2]^{2+}$ (X = NO_2, ONO) have four diastereoisomers, two of which have enantiomers.[8] The ^{13}C NMR spectrum shows the presence of 13 magnetically inequivalent carbon atoms; this corresponds to the structure elucidated by X-ray structure determination (see later), for which 10 resonances from 2,2'-bipyridine and 3 from pyridine ligand are expected. Other isomers will show 8 resonances or 16 resonances in total.[8]

The molecular structures of the isomeric pairs are depicted in Figure 1, along with the selected bond lengths and angles. The cations of *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ (X = NO_2 (**1**), ONO (**2**)) and *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ (**3**) have the expected

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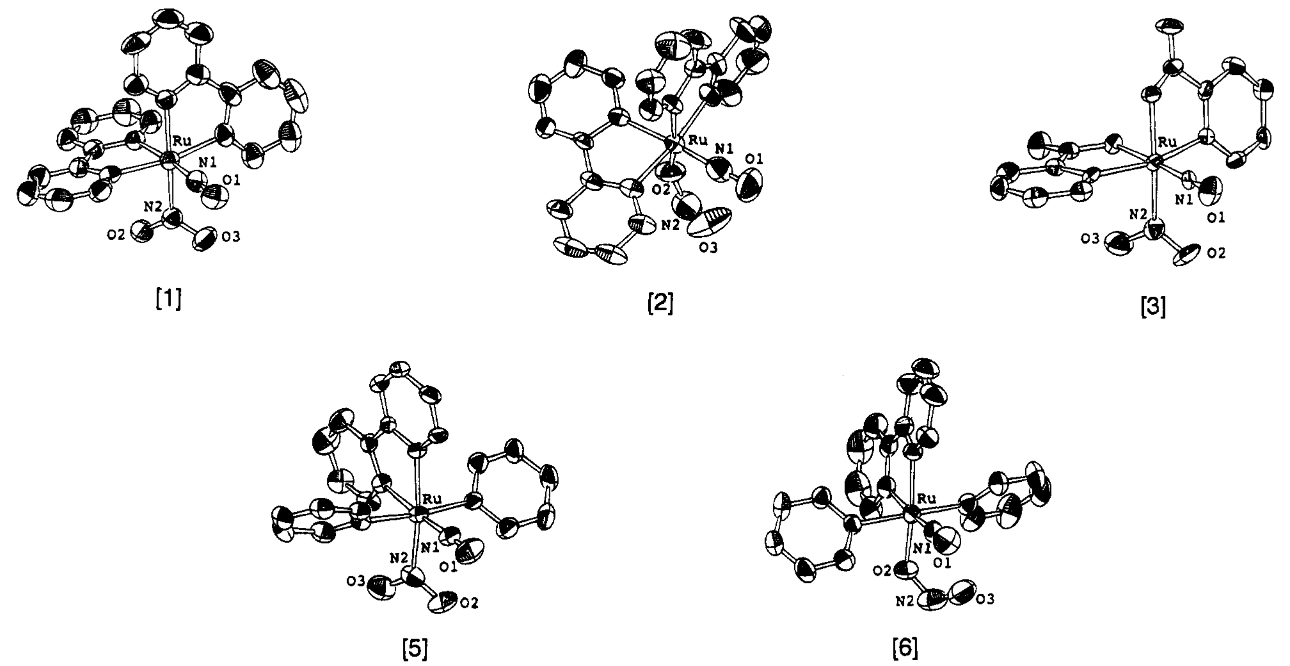

Figure 1. Molecular structures of the isomers (**1**–**3**, **5**, and **6**). Selected interatomic distances (Å) and angles (deg). For **1**: Ru–N1, 1.764(8); N1–O1, 1.116(9); N2–O2, 1.207(9); N2–O3, 1.231(9); Ru–N2, 2.090(8); Ru–N1–O1, 174.8(8); O2–N2–O3, 121.0(8). For **2**: Ru–N1, 1.713(10); N1–O1, 1.13(1); N2–O2, 1.24(1); N2–O3, 1.17(1); Ru–N2, 2.030(8); Ru–N1–O1, 178.1(9); O2–N2–O3, 118(1). For **3**: Ru–N1, 1.748(7); N1–O1, 1.148(8); N2–O2, 1.200(9); N2–O3, 1.247(10); Ru–N2, 2.053(8); Ru–N1–O1, 177.8(7); O2–N2–O3, 118.7(9). For **5**: Ru–N1, 1.754(7); N1–O1, 1.132(7); N2–O2, 1.240(8); N2–O3, 1.222(8); Ru–N2, 2.072(8); Ru–N1–O1, 178.6(7); O2–N2–O3, 119.8(9). For **6**: Ru–N1, 1.769(5); N1–O1, 1.126(5); N2–O2, 1.324(6); N2–O3, 1.227(7); Ru–N2, 2.033(4); Ru–N1–O1, 175.3(5); O2–N2–O3, 116.3(6).

octahedral coordination geometries: the two bidentate (2,2′-bipyridine or pyridine-2-carboxylate) rings are situated in a position *cis* to each other, and ligand X (X = NO_2, ONO) is also situated in a position *cis* to NO. The nitrite ion is linked by one oxygen atom (O2) to Ru with the O2–N2–O3 bond angle of 118(1) Å for **2**; N–O bond distances of 1.24(1) Å (O2–N2) and 1.17(1) Å (N2–O3) are within the range reported for other nitrito complexes.[12] The nitrite ions of both **1** and **3** show a common type of nitro coordination mode; the N–O bond distances and the O–N–O bond angles are also within the normal range for transition-metal nitro complexes.[17]

The molecular structures of *cis*-$[Ru(NO)(X)(2,2'\text{-bpy})(py)_2]^{2+}$ (X = NO_2 (**5**), ONO (**6**)) also support the present identification. In octahedral geometry, the X ligand exists at the *cis* position with respect to the NO ligand. The two pyridine ligands are situated in positions *trans* to each other, and they are also situated in positions *cis* to the NO ligand. Coordination modes of both nitro and nitrito ligands, including their structural parameters, are very similar to those observed in the other two types of isomeric pairs, *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ and *cis*-$[Ru(NO)X(pyca)_2]$. The structures of the nitrosyl moiety are essentially the same in all isomers: a linear coordination mode was confirmed. The structural parameters of this moiety were the typical values for the $\{RuNO\}^6$-type complexes.[18]

(2) Redox-Induced Nitro–Nitrito Isomerization. Of particular interest to the present study are the redox-induced nitro–nitrito isomerization observed in *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ (NO_2 (**5**), ONO (**6**)). Electrochemical investigation showed that the nitro and nitrito isomers are capable of being interchanged, via a one-electron redox process as described below.

A freshly prepared CH_3CN solution of **6** exhibits two one-electron waves at 0.04 V($E_{1/2}$) and −0.87 V(E_{pc}) [vs Ag|$AgNO_3$ (0.01 mol dm^{-3} in CH_3CN)] (Figure 2). No other wave is found in a measurable potential region. This is a typical electrochemical feature in the reductive process of $\{RuNO\}^6$-type nitrosylruthenium complex. The first wave can be explained as due to the reversible redox behavior of $[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{2+/+}$ couple (eq 1), and the irreversible second one is ascribed to $[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{+/0}$ couple (eq 2).

$$[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{2+} + e^- \rightleftharpoons [Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{+} \quad (1)$$

$$[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{+} + e^- \rightarrow [Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{0} \quad (2)$$

Although a reversible one-electron reduction occurred in **6** at 0.04 V($E_{1/2}$) (eq 1) on a cyclic voltammetry time scale, a controlled potential electrolysis carried out at 25 °C for the first

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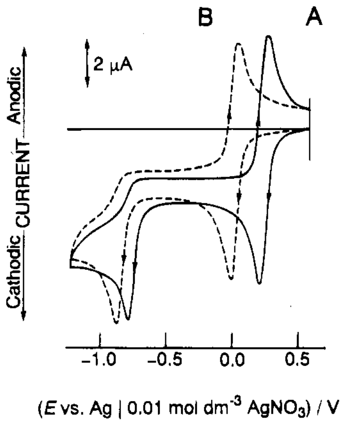

Figure 2. CVs of *cis*-[Ru(NO)X(2,2′-bpy)(py)$_2$]$^{2+}$ (X = NO$_2$ (**5**), ONO (**6**)) at a stationary Pt disk electrode in 0.1 mol dm^{-3} TEAP + AN (concentration of both isomers, 1.00 mmol dm^{-3}): (A) **5**, measured immediately after the solution was prepared; (B) **5**, measured for the solution that was allowed to stand for 7 days at room temperature in the dark, under argon (the CV is exactly the same as that measured for **6**).

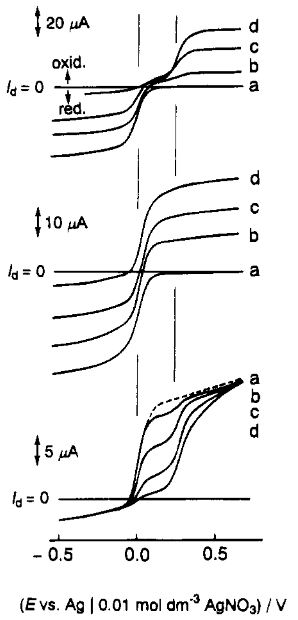

Figure 3. Hydrodynamic voltammograms (HDV) in monitoring the course of controlled potential reduction of **6** (1.49 mmol dm^{-3}) in AN (0.1 mol dm^{-3} TEAP) at 25 °C (for i) and at −20 °C (for ii): a, prior to electrolysis; b and c, during the electrolysis; d, at the end of the electrolysis (n = 0.95). iii shows variation of HDV of the electrochemically generated *cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$]$^+$ at −20 °C (dotted line; this corresponds to "d" in ii) when the species is allowed to stand at 25 °C (concentration of **6**, 0.86 mmol dm^{-3}): a, after 5 min; b, after 15 min; c, after 30 min; d, after 60 min (notice that "d" in iii corresponds to "d" in i).

reduction wave indicated that the one-electron reduction was followed by a rapid linkage isomerization to give *cis*-[Ru(NO)(NO$_2$)(2,2′-bpy)(py)$_2$]$^+$ (a one-electron reduction species of **5**); the one-electron reduction nitro species was identified using an authentic sample of **5**. The hydrodynamic voltammograms obtained by a rotating disk electrode show that the electrolysis proceeded by two different reactions: the reduction and the linkage isomerization. Before the electrolysis, a cathodic current (the reduction wave of **6**) is observed (a in Figure 3i). When the electrolysis was initiated, the cathodic current decreased and a coupled anodic current appeared, along with another anodic current (b in Figure 3i) whose $E_{1/2}$ is found at 0.26 V. The potential data of the latter anodic current agree well with those of the *cis*-[Ru(NO)(NO$_2$)(2,2′-bpy)(py)$_2$]$^{2+/+}$ couple (CV in Figure 2 (solid line)). A continuous electrolysis shows that the anodic current due to *cis*-[Ru(NO)(NO$_2$)(2,2′-bpy)(py)$_2$]$^+$ increased gradually (c and d in Figure 3i), while the anodic current of *cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$]$^+$ (a one-electron reduction species of **6**) does not develop constantly. In the final stage, the anodic wave of *cis*-[Ru(NO)(NO$_2$)(2,2′-bpy)(py)$_2$]$^+$ remained as a major wave, along with a small anodic wave of *cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$]$^+$ (n = 0.95 by Coulometry), but the cathodic current due to **6** almost disappeared.

The above electrochemical findings became simple and easy to understand when the exhaust reductive electrolysis was carried out at low temperature (−20 °C): hydrodynamic voltammograms show that only *cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$]$^+$ is generated during the electrolysis, without linkage isomerization occurring (n = 0.95 by Coulometry, Figure 3ii). When the electrolyzed solution containing *cis*-[Ru(NO)(ONO)(2,2′-bpy)(py)$_2$]$^+$ was warmed to 25 °C, as Figure 3iii shows, the species underwent a facile conversion to give the corresponding nitro isomer, *cis*-[Ru(NO)(NO$_2$)(2,2′-bpy)(py)$_2$]$^+$ (Figure 3iii, b → c → d).

The generated {RuNO}^{7}-type nitro complex, *cis*-[Ru(NO)(NO$_2$)(2,2′-bpy)(py)$_2$]$^+$, can be changed to the nitro isomer of {RuNO}^{6}-type, **5**, when an exhaust oxidative electrolysis is attempted for the electrolyzed solution at −20 °C (n = 0.95 by Coulometry). If the oxidative electrolysis is carried out at 25 °C, a small quantity of **6** is generated, in addition to **5**, owing to a spontaneous thermally-induced linkage isomerization (see the later description).

All of the electrochemical data are consistent with the following scheme that illustrates the electrochemical behavior of both **5** and **6** (both 2,2′-bpy and py ligands are omitted for clarity):

$$\begin{tikzcd}
\{\mathrm{Ru(ONO)(NO)}\}^{2+} + e^- \arrow[r, "-20\,^\circ\mathrm{C}\ (0.04\ \mathrm{V})"] & \{\mathrm{Ru(ONO)(NO\bullet)}\}^{+} \arrow[d, "25\,^\circ\mathrm{C}"] & (3) \\
\{\mathrm{Ru(NO_2)(NO)}\}^{2+} + e^- \arrow[u, "25\,^\circ\mathrm{C}*"] & \{\mathrm{Ru(NO_2)(NO\bullet)}\}^{+} \arrow[l, "-20\,^\circ\mathrm{C}\ (0.26\ \mathrm{V})"'] & (4)
\end{tikzcd}$$

* Spontaneous isomerization occurs at this temperature.

The site of the reductions in the {RuNO}^{6}-type nitrosyl complex has been regarded to be a nitrosyl moiety.[9] We note that only two isomers, **5** and **6** (and their reduction species), are detected by CV monitoring throughout the electrochemical experiments. This indicates that, except for the linkage isomerization, no structural rearrangement occurs in either the nitro or the nitrito isomers.

A redox-induced linkage isomerization, similar to that of *cis*-[Ru(NO)X(2,2′-bpy)(py)$_2$]$^{2+}$, occurred also in both *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ and *cis*-[Ru(NO)X(pyca)$_2$]. In practice, the redox-induced isomerization proceeded between the nitrito and nitro species, but an unexpected electrochemical behavior was found in these complexes, during an exhaust electrolysis, probably owing to the closeness of the redox potentials of the nitro and nitrito isomers. Further investigation of the electrochemical behavior is now under way; results will be reported separately.

(3) Thermally-Induced Nitro–Nitrito Isomerization. The patterns of the thermally-induced linkage isomerization observed in the present isomeric pairs differ depending on the spectator ligand(s). IR measurements (KBr disk) show that, at room temperature, neither *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ nor *cis*-[Ru(NO)X(pyca)$_2$] underwent any rearrangement. On the other hand, **5** changed spontaneously to give **6**. Under heating conditions at 60 °C for 3 h, however, both *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ and *cis*-$[Ru(NO)X(pyca)_2]$ came to undergo an isomerization: in *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$, either **1** or **2** gave an equilibrium mixture of both nitro–nitrito isomers.[19] The nitrito-to-nitro isomerization occurred in **4** to give **3**, under the same heating conditions; this was confirmed by IR measurement. No IR band due to the nitrito moiety could be detected in the isomerization product of **4**. Noticeably, the rearrangement is the reverse in direction to that of *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$, in which the nitro isomer changes to the nitrito isomer. No thermally-induced linkage isomerization could be found in **3**.

These thermally-induced rearrangements could also be confirmed by cyclic voltammetry. However, we must mention two results which were not available from the IR measurements described above: (i) For the equilibrium mixture of *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$ of **1** and **2**, we could estimate roughly the relative amount of the two components to be 70:30 (percent ratio) based on the wave height of the normal pulse voltammogram (NPV). (ii) Although IR observation showed that **4** was converted completely to **3** at 60 °C, as a sole product, monitoring by both CV and NPV revealed that a very small amount of **4** remained (less than ~5% (estimated from the NPV)), without undergoing the nitrito-to-nitro isomerization. An equilibrium mixture appears to be formed in this system, similar to *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$.

The thermally-induced isomerization occurs also in **5**. This was confirmed by cyclic voltammetry; CV monitoring of the CH_3CN solution of **5**, which shows a spontaneous nitro-to-nitrito isomerization to give **6**, indicated that the variation of the voltammograms finished after a 7 day period.

Discussion

(1) Some Mechanistic Evidence for the Linkage Isomerization. (a) Rates of the Thermally-Induced Isomerization.

The thermally-induced linkage isomerization of *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2]^{2+}$ was monitored, at 60 ± 1 °C, using ^1H NMR spectroscopy. The bpy protons of the isomer give a diagnostic pattern of doublet–doublet, due to 6,6′-bpy,[20] with integrals 1:1 in the range of 9.1–9.8 ppm in CD_3CN solution; the signals are not found in *cis*-$[Ru(NO)(ONO)(2,2'\text{-bpy})(py)_2]^{2+}$, while an alternative doublet–doublet resonance exists in the nitrito isomer at 9.4–10.0 ppm. The ^1H NMR spectra of *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2]^{2+}$ changed quickly when the solution temperature of the isomer was elevated; two new signals appear at 10.0 and 9.4 ppm in a *ca.* 1:1 ratio. They then developed further at the expense of the two signals of *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})(py)_2]^{2+}$ observed at 9.8 and 9.1 ppm. The rearrangement was found to be complete after 150 min in the dark. A plot of $-\ln\{[\text{nitro}]_t/[\text{nitro}]_0\}$ vs *t* gave a straight line; the first-order rate constant was estimated to be 9.0×10^{-4} s^{-1}. Similar treatment of *cis*-$[Ru(NO)(ONO)(pyca)_2]$, using signals at 8.8 ppm, also gave a first-order rate constant of 9.0×10^{-5} s^{-1} (the corresponding signal of *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ appeared at 8.7 and 8.9 ppm).

Monitoring the thermal isomerization by a ^1H NMR spectral change was also possible in *cis*-$[Ru(NO)X(2,2'\text{-bpy})_2]^{2+}$, but additional treatment was necessary for obtaining the rate constant, since the isomerization gives an equilibrium mixture of the nitro and nitrito isomers. As Figure 4 (deposited as a Supporting Information) shows, ^1H NMR spectra patterns of the *cis*-$[Ru(2,2'\text{-bpy})_2]^{2+}$ fragment are sensitive to the coordination mode of the nitrite in both isomers. We found a spectral pattern of doublet–doublet resonances in *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})_2]^{2+}$, due to 6,6′-protons of the bpy ring, with relative intensity 1:1 in the range 9.1–9.2 ppm. The resonances disappeared in *cis*-$[Ru(NO)(ONO)(2,2'\text{-bpy})_2]^{2+}$, but a doublet was detected alternatively at the 9.1 ppm region.

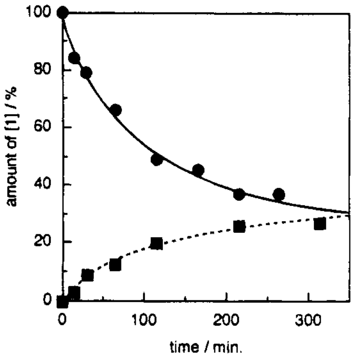

Figure 5. Variation of the amount of **1** with time when **1** (or **2**) was heated at 60 °C (amount of **1** (100[**1**]/[**1**] + [**2**]) was estimated from the peak intensity of the ^1H NMR spectra (Figure 4)): ●, started from nitro isomer **1**; ■, started from nitrito isomer **2**.

Figure 5 shows plots of the isomer ratio in the equilibrium mixture, which was estimated from variation of the peak heights mentioned above, using *cis*-$[Ru(NO)(NO_2)(2,2'\text{-bpy})_2]^{2+}$ as a starting material (the same was attempted for *cis*-$[Ru(NO)(ONO)(2,2'\text{-bpy})_2]^{2+}$); this suggests that the equilibrium mixture at 60 °C for 200 min of heating consists of 70% of the nitrito and 30% of the nitro isomers.

$$[Ru(NO_2)(NO)(2,2'\text{-bpy})_2]^{2+}\ (\mathbf{1}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(ONO)(NO)(2,2'\text{-bpy})_2]^{2+}\ (\mathbf{2}) \qquad (5)$$

The rate constant for the isomerization reaction of **1** to give **2** (eq 5) was evaluated from the intensity change of the 6,6′-position proton signal of the bipyridine ligand using the following equation (eq 6, where $[\mathbf{1}]_0$ = initial concentration of **1** and $[\mathbf{1}]$ = concentration of **1** at *t*); the calculation was made using the program *Delta Graph pro 3.0.4 for Macintosh* to obtain the best fit between the observed and calculated curves.[21]

The isomerization reaction, from **2** to **1**, was also investigated

$$d[\mathbf{1}]/dt = -k_1[\mathbf{1}] + k_{-1}([\mathbf{1}]_0 - [\mathbf{1}]) \qquad (6)$$

similarly, and we could obtain the following data: $k_1 = (1.0 \pm 0.3) \times 10^{-4}\ s^{-1}$; $k_{-1} = (4.6 \pm 0.8) \times 10^{-5}\ s^{-1}$.

(b) Oxygen Scrambling between Nitrosyl and Nitro (or Nitrito) Ligands. Ileperuma and Feltham have reported that an intramolecular oxygen exchange reaction occurs in the adjacent NO and NO_2 groups of *cis*-form nitrosyl complexes,[22] and it has actually been found in some other complexes,[23] while a complex which does not show the oxygen exchange reaction has also been reported.[24] The possibility of such oxygen

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[19] These were checked by solid samples prepared as follows: a CH_3CN solution containing each isomer was heated at 60 °C for 3 h in the dark. From this solution, we could obtained a solid material, by adding an excess ether.

[20] The assignment was established by the COSY technique.

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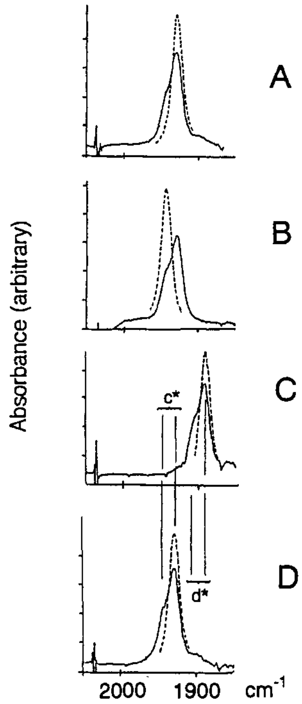

	Before Isomerization / cm^{-1} (Dotted line)		After Isomerization / cm^{-1} (Solid line)	
A	{^{14}NO–O^{14}NO}	1929	{^{14}NO–^{14}NO$_2$}	1944 (sh)
			{^{14}NO–O^{14}NO}	1928
B	{^{14}NO–^{14}NO$_2$}	1944	{^{14}NO–^{14}NO$_2$}	1944 (sh)
			{^{14}NO–O^{14}NO}	1928
C	{^{15}NO–O^{14}NO}	1891	{^{15}NO–^{14}NO$_2$}	1904 (sh)
			{^{15}NO–O^{14}NO}	1891
D	{^{14}NO–O^{15}NO}	1929	{^{14}NO–^{15}NO$_2$}	1944 (sh)
			{^{14}NO–O^{15}NO}	1929

Figure 6. Solution IR (ν(NO)) of isotopomers of *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ (X = NO$_2$ (**1**), ONO (**2**)) and their equilibrium mixtures (in every case, dotted lines indicate IR (νNO) of the isotopomers before they undergo isomerization, and solid lines indicate IR ν(NO) of the equilibrium mixtures. Shoulders in the solid lines are due to the nitro isomers: A, [Ru(^{14}NO)(O^{14}NO)(2,2′-bpy)$_2$]$^{2+}$ (abbreviated as {^{14}NO–O^{14}NO}); B, [Ru(^{14}NO)(^{14}NO$_2$)(2,2′-bpy)$_2$]$^{2+}$ (abbreviated as {^{14}NO–^{14}NO$_2$}); C, [Ru(^{15}NO)(O^{14}NO)(2,2′-bpy)$_2$]$^{2+}$ (abbreviated as {^{15}NO–O^{14}NO}); and D, [Ru(^{14}NO)(O^{15}NO)(2,2′-bpy)$_2$]$^{2+}$ (abbreviated as {^{14}NO–O^{15}NO}). In C, the notation c* indicates that, if an oxygen transfer mechanism is operating for the linkage isomerization, two more peaks due to both nitro and nitrito isomers with ^{14}NO ligand will appear at this frequency region. (Similarly, both nitro and nitrito isomers with ^{15}NO ligands will appear in D at the frequency region d*). Both shoulders, due to {^{15}NO–^{14}NO$_2$} in C and {^{14}NO–^{15}NO$_2$} in D, were assigned without authentic isotopomers.

scrambling could be ruled out in the present complex; this was conformed by the IR measurements using various ^{15}N-isotopomers (see Table 3).

We compared the solution IR (CH$_3$CN, 2100–1850 cm^{-1} region) of ν(NO) in *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ (X = ONO, NO$_2$) and their ^{15}N-labeled complexes. All the isotopomers exhibited the single absorption band due to ν(NO) at a characteristic region (see Table 3). The isotopomers with ^{14}NO ligand are easily distingushable from those with ^{15}NO ligand, in both the nitro isomer and the nitrito isomer.

In the solution IR of the equilibrium mixtures (Figure 6A–D), we are able to find two absorption bands due to ν(NO), which indicate the existence of both nitro and nitrito isomers at their characteristic regions. The ν(NO) band of the nitro isomer always appears as a shoulder at the higher frequency region (by ~15 cm^{-1}) than the absorption peak of the corresponding nitrito isomer. If we assume that an oxygen transfer occurs from the nitrito (or nitro) to nitrosyl moiety during the isomerization, *cis*-[Ru(^{14}NO)(O^{15}NO)(2,2′-bpy)$_2$]$^{2+}$ will give the following four species in its equilibrium mixture: two species with the ^{15}NO ligand (*cis*-[Ru(^{15}NO)(O^{14}NO)(2,2′-bpy)$_2$]$^{2+}$ and *cis*-[Ru(^{15}NO)(^{14}NO$_2$)(2,2′-bpy)$_2$]$^{2+}$) and two more species with the ^{14}NO ligand (*cis*-[Ru(^{14}NO)(O^{15}NO)(2,2′-bpy)$_2$]$^{2+}$ and *cis*-[Ru(^{14}NO)(^{15}NO$_2$)(2,2′-bpy)$_2$]$^{2+}$). On the contrary, we found only the latter two species with the ^{14}NO moiety at the expected frequency regions (Figure 6C).

The IR experiment using another isotopomer, *cis*-[Ru(^{15}NO)(O^{14}NO)(2,2′-bpy)$_2$]$^{2+}$, also gave a similar result (Figure 6D); *cis*-[Ru(^{15}NO)(O^{14}NO)(2,2′-bpy)$_2$]$^{2+}$ and *cis*-[Ru(^{15}NO)(^{14}NO$_2$)(2,2′-bpy)$_2$]$^{2+}$ were found to exist in the equilibrium mixtures, but we could not detect IR bands due to either *cis*-[Ru(^{14}NO)(O^{15}NO)(2,2′-bpy)$_2$]$^{2+}$ or *cis*-[Ru(^{14}NO)(^{15}NO$_2$)(2,2′-bpy)$_2$]$^{2+}$. Such IR evidence suggests that, at least in *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ (X = ONO, NO$_2$), the linkage isomerization is proceeding without the oxygen transfer process proposed by Ileperuma and Feltham.[22]

A comment should be added to this IR study: the measurement of the ν(NO) region, using a KBr disk, did not give any useful information, at least about the proceeding of the rearrangement. As mentioned earlier, the isomers showed their characteristic ν(NO) frequency bands at 1929 cm^{-1} (for the nitrito isomer) and 1944 cm^{-1} (for the nitro isomer) when each isomer was measured separately as a single compound (KBr disk). Despite the mixture of the nitro and nitrito isomers, the equilibrium product shows only a single, but broadened, IR band due to ν(NO) at the region between 1929 and 1944 cm^{-1}, instead of the expected two ν(NO) bands of nitro and nitrito isomers. The peak position was less sensitive to the existence of the two isomers, and the IR band shifted depending on the component ratio of the isomers: attempts to monitor the thermally-induced linkage isomerization by IR study using the KBr disk method thus failed. We could overcome this difficulty by a solution IR technique, as described above.

More evidence which supports the above mechanistic assumption is available in the IR study (KBr disk) of *cis*-[Ru(NO)X(pyca)$_2$]: we found that nitrito isomer **4** gave the corresponding nitro isomer **3** as an isomerization product, without scrambling the nitrogen atom of the NO moiety. A CH$_3$CN solution of *cis*-[Ru(^{14}NO)(O^{15}NO)(pyca)$_2$] was heated at 60 °C for 3 h in the dark. We could isolate *cis*-[Ru(^{14}NO)(^{15}NO$_2$)(pyca)$_2$] from the solution (yield, higher than 90%). IR investigation of the product at the 900–1500 cm^{-1} region showed that the [^{15}N]nitrito nitrogen of *cis*-[Ru(^{14}NO)(O^{15}NO)(pyca)$_2$] remains intact in the isomerization species, as the ^{15}NO$_2$ moiety: no evidence for the formation of *cis*-[Ru(^{15}NO)(^{14}NO$_2$)(pyca)$_2$] was obtained (Figure 7). A similar result was found

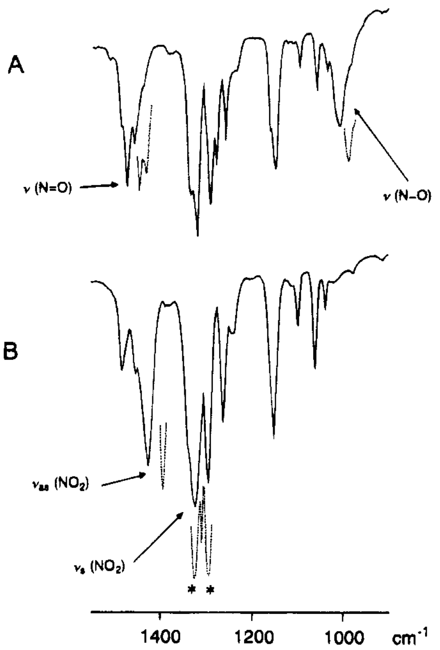

Figure 7. IR spectra (KBr disk) of **4** before (A) and after isomerization (B): solid line, ^{14}N-isomer; dotted line, ^{15}N-isomer. No ^{15}N substitution effect was observed in the ν(NO) band (this band does not appear in this figure). The two bands with asterisks did not undergo a ^{15}N-substitution effect.

in the thermal treatment of another isotopomer, *cis*-[Ru(^{15}NO)(O^{14}NO)(pyca)$_2$], which gave *cis*-[Ru(^{15}NO)(^{14}NO$_2$)(pyca)$_2$]; again *cis*-[Ru(^{14}NO)(^{15}NO$_2$)(pyca)$_2$] was not generated. The observation indicates clearly that no ^{15}N scrambling occurs in these isotopomers.

(2) Function of the Nitrosyl as a Spectator Ligand. The present investigation shows that the characteristics of the nitro–nitrito isomers are affected strongly by the spectator ligands. A thermally-induced isomerization does not occur in nitro complexes of Ru(II), *cis*-[Ru(NO$_2$)X(2,2′-bpy)$_2$]$^+$ (X = py) and *cis*-[Ru(NO$_2$)X(2,2′-bpy)(py)$_2$]$^+$ (X = py), even at heating conditions; both complexes contain the X =py ligand, in place of the nitrosyl in **1** and **5**. In addition, although the electrochemical investigations have shown that the nitro complexes of Ru(II), which lack a nitrosyl ligand, undergo a redox-induced linkage isomerization when the metal atom is oxidized to Ru(III),[3,4] the generated nitrito species is very chemically reactive and results in the formation of an oxo complex of Ru(IV) or a nitrato complex of Ru(III);[3,4] this opened no opportunity for the study of isomeric characteristics of the nitro complexes of Ru(II).

The nitrosyl complex with O-bound nitrite has previously been isolated in a case where it exists *trans* to nitrosyl.[25] A similar *trans* type nitrito isomer with a monooxygen ligand, instead of the nitrosyl, has been reported in *trans*-[Ru(O)(ONO)(py)$_4$]$^+$.[3c] However, neither thermally-induced isomerization nor redox-induced isomerization has been reported in these complexes.[26] We could not observe any rearrangement in *cis*-[Ru(CO)(NO$_2$)(2,2′-bpy)$_2$]$^+$, analogous to **1**.[27]

Clearly, the present investigation shows that the nitrosyl ligand plays an important role in determining the coordination modes of the nitrite ion. As the redox experiment shows, the (RuNO)$^{2+}$ moiety (of the {RuNO}^{7}-type complex) prefers the nitro coordination mode to nitrite, but the nitrito bonding is a stable form when the (RuNO)$^{3+}$ moiety (of the {RuNO}^{6}-type complex) exists. It is well-known that a nitrosyl has a strong electronic interaction to the ligand that is placed at the *trans* position, through the dπ electron orbital of its central metal atom.[28] On the other hand, some *cis* interaction has also been reported in *cis*-[Ru(NO)X(2,2′-bpy)$_2$]^n, in which nitrosyl characteristics are affected strongly by the *cis* ligand X.[9]

The redox-induced isomeric behavior observed here can be understood, if we assume that the nitrosyl has an electronic interaction through the metal to the *cis* nitro (nitrito) ligand. Since NO$^+$ is a strong π-acid, it withdraws electron density from the metal through dπ–pπ (M → L) back-bonding, thereby reducing the relative tendency for the nitrogen atom on NO$_2^-$ to participate in π-bonding. As a consequence, when a nitrite is coordinated to the metal atom in a (RuNO)$^{3+}$ moiety, an oxygen bound nitrito mode is formed preferentially. The opposite is true for the complex having a (RuNO)$^{2+}$ moiety, in which the nitrosyl exists as a formally neutral molecule (NO$^\bullet$) and does not behave any more as a "strong" π-acid.

In this context, an acid–base (nitrosyl–nitro conversion) reaction observed here exhibits some interesting effects on the nitrosyl as a spectator ligand. Similar to other {RuNO}^{6}-type nitrosyl complexes,[10,15,29] either **1** or **5** underwent the acid–base reaction to give the corresponding dinitro complex of Ru(II), *cis*-[Ru(NO$_2$)$_2$(2,2′-bpy)$_2$], or *cis*-[Ru(NO$_2$)$_2$(2,2′-bpy)(py)$_2$] (eq 7). Under the same conditions, the nitrito isomers produced

$$\{\mathrm{Ru(NO_2)(NO)}\}^{2+} + 2\mathrm{OH}^- \rightarrow \{\mathrm{Ru(NO_2)_2}\} + \mathrm{H_2O} \quad (7)$$

also the dinitro complexes of Ru(II) (eq 8), instead of the

$$\{\mathrm{Ru(ONO)(NO)}\}^{2+} + 2\mathrm{OH}^- \rightarrow \{\mathrm{Ru(NO_2)_2}\} + \mathrm{H_2O} \quad (8)$$

expected nitro–nitrito complexes of Ru(II), *cis*-[Ru(NO$_2$)(ONO)(2,2′-bpy)$_2$], or *cis*-[Ru(NO$_2$)(ONO)(2,2′-bpy)(py)$_2$]; this suggests that the O-bound nitrito ligand of this system can exist only when the nitrosyl is present as the {RuNO}^{6}-type.

Base-catalyzed nitrito-to-nitro linkage isomerization,[30] which involves a conjugate base dissociation process, is unlikely to occur in the present complexes.

In the present isomeric pairs, all of the nitrito isomers with a (RuNO)$^{3+}$ moiety undergo a facile nitrito-to-nitro rearrangement in their redox-induced isomerization. In the thermally-induced isomerization, on the other hand, the isomeric pairs can be divided into two groups on the basis of their isomerization patterns: (i) *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ and *cis*-[Ru(NO)X(pyca)$_2$] give an equilibrium mixture, while the equilibrium of *cis*-[Ru(NO)X(pyca)$_2$] lies much closer to the nitro isomer; (ii) such an equilibrium is not found in *cis*-[Ru(NO)X(2,2′-bpy)(py)$_2$]$^{2+}$. The rate of thermally-induced isomerization also differs, depending on this group classification. It appears that although the complexes in both groups have the same *cis* configuration, their complex cores ("Ru(LL)$_2$" (LL = 2,2′-bpy, pyca) in group i and "Ru(2,2′-bpy)(py)$_2$" in group ii) differ in both steric configuration and spectator ligands. In "Ru(NO)X(2,2′-bpy)(py)$_2$", 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, inclu-

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luding the Ru atom. The other two residual pyridine ligands exist in positions above and below this plane. Such planarity does not exist in "Ru(NO)X(2,2′-bpy)$_2$"; only one donor nitrogen atom of each 2,2′-bipyridine occupies one of the corners of the equatorial plane, and the other nitrogen donor atom of each 2,2′-bipyridine is directed to the axial position to form the chelate ring. The "core effect", which might affect the electronic interaction between the nitrosyl and the nitro (or nitrito) ligands, is a problem for further study.

Conclusion

Three isomeric pairs of nitrosylruthenium(II) are investigated, focusing mainly on their redox-induced and thermally-induced linkage isomerizations. Some mechanistic evidence could be obtained in the thermally-induced linkage isomerization; the oxygen transfer process which has been reported to occur in the complexes with both nitrosyl and nitro (nitrito) moieties at *cis* positions was ruled out.[22] Another intramolecular process, which has been proposed by Basolo and Hammaker and also by Murmann and Taube, is likely to be operating.[31] We could not obtain any information about the intermediate species; three possible forms have been reported by Sargeson et al. on their isomerization process.[32]

The present work revealed also that the spectator ligand(s) had an important role in the nitro–nitrito linkage isomerization. In most of the complexes reported so far, the nitrito isomer is thermodynamically unstable, so it changes to the more stable nitro form.[2] Such a general trend was found in our isomeric pair of *cis*-[Ru(NO)X(pyca)$_2$]. Some different isomeric behavior was observed in *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$; despite having the same core fragment as that of *cis*-[Ru(NO)X(pyca)$_2$], the nitrito isomer of *cis*-[Ru(NO)X(2,2′-bpy)$_2$]$^{2+}$ was found to be the rather favorable species. A noticeable effect which stems mainly from both the spectator ligand and the core fragment can be found in *cis*-[Ru(NO)X(2,2′-bpy)(py)$_2$]$^{2+}$; the nitro isomer is an unstable species, so it changes spontaneously to the corresponding nitrito isomer, even at room temperature. It has been recognized that the manner of the bonding is influenced both by the electronic structure of the metal ion[2d] and by the extent of interligand repulsions within a complex.[33] We demonstrated here another factor: The spectator ligand(s) affected the nature of the coordinate nitrite moiety.

Acknowledgment. This work was supported by the Joint Studies Program (1993, No. 5-655, and 1994, No. 6-258) of the Institute for Molecular Science.

Supporting Information Available: Complete structure information of **1**–**3**, **5**, and **6**, including tables of crystal data, intensity measurements giving ORTEP structures and anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates, and intramolecular distances and angles and figures; Figure 4 showing the ^{1}H NMR spectra observed at the 8.9–9.4 ppm region of **1**, **2**, and the equilibrium mixture (57 pages). Ordering information is given on any current masthead page.

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