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Ligand nature of coordinated NO_2^- in the oxidation reaction of Ru(II) complexes, $[Ru(NO_2)(OH_2)(py)_{4-2n}(bpy)_n]^+ (n=0, 1, 2)$, and their related complexes

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Abstract

Under the chemical conditions using NaClO, the title complexes undergo an oxidation which gives different products: $[Ru^{IV}(ONO)(O)(py)_4]^+$ (for $n=0$), $[Ru^{IV}(NO_2)(O)(py)_2(bpy)]^+$ (for $n=1$) and $[Ru_2^{III,III}O(NO_2)_2(bpy)_4]^{2+}$ (for $n=2$). All these complexes retain the original nitro nitrogen. However, the electrochemical oxidation proceeds along basically the same mechanistic pathway; each of the title complexes undergoes a one-electron oxidation to give the corresponding Ru(III) complexes; then the formation of a dimeric intermediate consisting of both nitro and nitrito complexes of Ru(III) results in the generation of a nitrosyl complex of Ru(II). This pathway suggests that a metal–nitrite bond breaking process is involved in the electrochemical oxidation. We also investigated the oxidation of the μ-oxo complex of Ru(III,III) with nitro ligand, $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$, which was isolated as the product species in the chemical oxidation of the complex with $n=2$. In this oxidation, an intramolecular electron transfer process is operating; a one-electron oxidized $(NO_2^-{-}Ru^{III}{-}O{-}Ru^{IV}{-}NO_2^-)^{3+}$ moiety first changes to $(NO_2^-{-}Ru^{III}{-}O{-}Ru^{III}{-}NO_2^0)^{3+}$; this change brings about the liberation of the non-charged NO_2, along with the formation of solvation species containing the $(NO_2^-{-}Ru^{III}{-}O{-}Ru^{III}{-}CH_3CN)^{3+}$ moiety.

Keywords: Electrochemistry; Oxidation reaction; Ruthenium complexes; Nitro complexes

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1. Introduction

Our research has concentrated on the study of chemical reactions of the coordinated nitro ligand, including that of the nitrosyl, which are accompanied by the redox reaction of the central metal site [1–6]. Special attention has been paid recently to the ruthenium(III) nitro complexes, because this class of compounds exhibited an unexpected chemical reaction which involves an intramolecular electron transfer process [5–9]. We have shown that the oxidation reaction of nitro complexes of Ru(II) depends on the spectator ligand; *trans*-$[Ru(NO_2)Cl(py)_4]$ is oxidized to give *trans*-$[Ru^{IV}(O)Cl(py)_4]^+$ by a 1.25-electron oxidation reaction [5,6], while *trans*-$[Ru(NO_2)(OH_2)(py)_4]^+$ generates *trans*-$[Ru^{IV}(ONO)(O)(py)_4]^+$, by a two-electron scheme, with retention of the original nitro nitrogen [6]. We have also reported that a three-electron oxidation process which gives complexes with the $(Ru^{IV}{=}O^{2-})$ moiety will exist in the oxidations of other *trans*-$[Ru(NO_2)X(py)_4]^n$ ($n=0$ for $X=NO_2^-$, $n=1+$ for $X=NH_3$) complexes [10]. Clearly, the conversion processes are affected by the spectator ligands. The present work deals with a series of title complexes ($[Ru(NO_2)(OH_2)(py)_4]^+$, $[Ru(NO_2)(OH_2)(py)_2(bpy)]^+$ and $[Ru(NO_2)(OH_2)(bpy)_2]^+$ [1], including their chemical oxidation products with nitro ligands. We investigated the ligand nature of coordinated NO_2^-

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[1] $[Ru(NO_2)(H_2O)(bpy)_2]ClO_4$ could be obtained as analytically pure material by the reaction of $[Ru(NO)(H_2O)(bpy)_2]^{3+}$ with NaOH in an aqueous media, but the isolation of the nitro complex of Ru(II) has been believed to be difficult. Actually, one cyclic voltammogram shows that the nitro complex is contaminated by small amounts of an unidentified material, probably $[Ru(NO_2)(OH)(bpy)_2]$. Complicated acid–base and redox properties have been investigated; results suggest that the nitro complex of Ru(II) exists in equilibrium with $[Ru(NO)(H_2O)(bpy)_2]^{3+}$, $[Ru(NO)(OH)(bpy)_2]^{2+}$ or $[Ru(NO_2)(OH)(bpy)_2]$, depending on the pH value of the solution: a private communication from Professor Thomas. J. Meyer of the University of North Carolina at Chapel Hill.

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under both chemical and electrochemical oxidation conditions.

2. Experimental

2.1. Material and electrochemical measurements

Tetraethylammonium perchloride (TEAP) was special polarographic grade (Nacalai Tesque Inc). The CH_3CN solvent was carefully purified, as described in a previous report [6]. *Trans*-$[Ru(NO_2)(H_2O)(py)_4]PF_6$, *trans*-$[Ru(ONO)(O)(py)_4]PF_6$, and *cis*-$[Ru(NO_2)Cl(bpy)_2]$ were prepared by the methods reported previously [6,8]. Other chemicals used were reagent grade.

All measurements were at a platinum disk electrode ($\phi = 1.6$ mm), with a counter or auxiliary electrode made of a spiral of platinum wire. Potentials were measured versus an Ag/0.01 mol dm^{-3} $AgNO_3$ in CH_3CN reference electrode (BAS Co. RE5). Cyclic and normal-pulse voltammetries and controlled-potential electrolysis were carried out by using a Huso polarograph, model 321, and Huso coulometer, model 343B.

2.2. Isolation of complexes

2.2.1. $[Ru(NO_2)(H_2O)(py)_2(bpy)]PF_6$

A mixture of $[Ru(NO_2)_2(py)_2(bpy)]$ (60 mg/H_2O 20 cm^3) and CF_3SO_3H (0.1 cm^3) was refluxed for 4–7 h to give a homogeneous purple solution [2]. The solution contains $[Ru(NO)(OH)(py)_2(bpy)]^{2+}$ species as the main product. An aqueous solution of NaOH was added to the solution, and the solution pH was adjusted to 11–12. A reddish brown solid was deposited when NH_4PF_6 (100 mg) was added to the solution. The solid was collected by filtration and washed with cold water, with ethanol, and then with ether. Yield 55 mg, 75%. *Anal.* Found: N, 11.05; C, 37.60; H, 2.73. Calc. for $[Ru(NO_2)(H_2O)(py)_2(bpy)]PF_6$: N, 10.90; C, 37.39; H, 3.14%. Instead of $[Ru(NO_2)(H_2O)(py)_2(bpy)]PF_6$, we measured the ^{13}C NMR of $[Ru(NO)(H_2O)(py)_2(bpy)](PF_6)_3$ (in CD_3CN). The nitrosyl complex has been reported to change reversibly to the present nitro complex, based on a nitro–nitrosyl acid–base reaction [11]; $\delta = 155.55$, 154.27, 152.43, 151.70, 149.66, 145.35, 143.81, 142.98, 131.71, 130.31, 128.33, 127.28, 126.11.

2.2.2. $[Ru(NO_2)(py)_3(bpy)]PF_6 \cdot 4H_2O$

The complex can be obtained from the corresponding nitrosyl, $[Ru(NO)(py)_3(bpy)](PF_6)_3$ [2], by the known reversible nitro–nitrosyl acid–base reaction [11]. Yield 90%. *Anal.* Found: N, 11.23; C, 39.91; H, 3.13. Calc. for $[Ru(NO_2)(py)_3(bpy)]PF_6 \cdot 4H_2O$: N, 11.09; C, 39.63; H, 3.06%.

2.2.3. *Cis*-$[Ru(NO_2)(H_2O)(bpy)_2]ClO_4$

A mixture of a suspension of $[Ru(NO_2)_2(bpy)_2]$ (250 mg/50 cm^3) and $HClO_4$ (5 cm^3) was heated to give a homogeneous reddish brown solution; in this solution $[Ru(NO)(H_2O)(bpy)_2]^{3+}$ was generated. Some aqueous NaOH solution was added. When the pH was adjusted to 10–11, a pale brown material deposited. This precipitate was collected by filtration and washed with water, and then dried in vacuo (see footnote on p. 111). Yield 220 mg, 80%. *Anal.* Found: C, 42.17; N, 12.36; H, 2.78. Calc. for $[Ru(NO_2)(H_2O)(bpy)_2]ClO_4$: C, 41.67; N, 12.14; H, 3.17%.

2.2.4. *Cis*-$[Ru(NO_2)(CH_3CN)(bpy)_2]ClO_4$

$[Ru(NO_2)(H_2O)(bpy)_2]ClO_4$ (250 mg) dissolved in CH_3CN (50 cm^3) was set aside at room temperature for 24 days. The resultant solution was concentrated using a evaporator, and excess ether was added to give a brown precipitate. The collected product was purified by column chromatography (Al_2O_3; CH_3CN–EtOH). This purified green material was collected, washed with ether, and then dried in vacuo. Yield 155 mg, 60%. *Anal.* Found: N, 13.80; C, 43.75; H, 3.53. Calc. for $[Ru(NO_2)(CH_3CN)(bpy)_2]ClO_4$: N, 14.01; C, 44.04; H, 3.19%.

2.2.5. $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4](ClO_4)_2 \cdot 4H_2O$

The μ-oxo complex was prepared according to procedures (i) and (ii).

(i) $[Ru^{III,III}{}_2O(CH_3COO)(bpy)_4](ClO_4)_3 \cdot 7H_2O$ was first prepared as the starting material for $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$; $[Ru(CO_3)(bpy)_2] \cdot 2H_2O$ (200 mg/50 cm^3 H_2O), which was obtained by a modified procedure of the method Meyer and co-workers [12], was decomposed by $HClO_4$ (2 mol dm^3). This solution was first maintained at about pH 2, then it was heated at 60 °C for 10 min to give a dark brown solution. (We assume that the solution contains *cis*-$[Ru(H_2O)_2(bpy)_2]^{2+}$ as the main species.) After the solution was neutralized using aqueous NaOH (2 mol dm^{-3}), $CH_3COONa \cdot 3H_2O$ (2.5 g) was added, along with CH_3COOH (3 drops). The mixed solution was refluxed for 5 h; during this time, the color changed to blue. The solution volume was reduced to 25 cm^3 and then $NaClO_4$ (1.5 g) was added. The green crystalline material which was obtained was filtered off, washed with cold water, and then air-dried. Yield 200 mg, 75%. We tentatively formulated the product as

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[2] The starting material $[Ru(NO_2)_2(py)_2(bpy)]$ was synthesized via the isolation of $[RuCl_2(bpy)(DMSO)]$ and then $[RuCl_2(bpy)(py)_2]$. Other related complexes, with both pyridine and 2,2′-bipyridine ligands, can also be synthesized from $[RuCl_2(bpy)(py)_2]$ (see text).

$[Ru^{III,III}{}_2O(CH_3COO)(bpy)_4](ClO_4)_3 \cdot 7H_2O$. *Anal.* Found: N, 8.40; C, 37.92; H, 2.71. Calc.: N, 8.45; C, 38.03; H, 2.51%.

(ii) A mixed solution of $[Ru_2O(CH_3COO)(bpy)_4](ClO_4)_2 \cdot 7H_2O$ (200 mg/H_2O 50 cm^3) and $NaNO_2$ (150 mg) was heated on a hot plate for 2 h. The solution was cooled down to room temperature and then $NaClO_4$ (1 g) was added. The dark brown crystalline material which was obtained was filtered off, washed with cold water, and then air-dried. The crude product was purified by column chromatography (Al_2O_3; CH_3CN containing a small portion of water). Yield 90 mg, 50%. *Anal.* Found: N, 11.77; C, 40.45; H, 2.63. Calc. for $[Ru_2O(NO_2)_2(bpy)_4](ClO_4)_2 \cdot 4H_2O$: N, 11.60; C, 39.80; H, 3.02%.

2.2.6. $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4][Ce^{III}(NO_3)_6] \cdot 5H_2O$

An acetonitrile solution of $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4](ClO_4)_2 \cdot 4H_2O$ (50 mg/20 cm^3) was mixed with $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (25 mg, 1:1 mole ratio). The solution color changed gradually from blue via green to brown; from this, brown crystals deposited. The product was collected by filtration, washed with CH_3CN, and then air-dried. Yield 45 mg, 75%. *Anal.* Found: N, 14.16; C, 31.53; H, 2.14. Calc. for $[Ru_2O(NO_2)_2(bpy)_4][Ce^{III}(NO_3)_6] \cdot 5H_2O$: N, 14.58; C, 31.26; H, 2.75%.

2.2.7. $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4](ClO_4)_3 \cdot 2H_2O$

A solution containing $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$ was generated electrochemically at 25 °C by a one-electron oxidation of $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4](ClO_4)_2 \cdot 4H_2O$ (120 mg)/CH_3CN 40 cm^3); its volume was reduced using an evaporator. Ether was added to the resultant solution to give a green crude precipitate. The product was collected by filtration, and then purified by column chromatography (Al_2O_3; CH_3CN–H_2O(1%)). The purified green material was collected, washed with ether, and then dried in vacuo. Yield 60 mg, 50%. *Anal.* Found: N, 10.87; C, 39.95; H, 2.88. Calc. for $[Ru_2O(NO_2)(CH_3CN)(bpy)_4](ClO_4)_3 \cdot 2H_2O$: N, 11.08; C, 39.90; H, 2.80%.

2.2.8. $[Ru_2O(Br)_2(bpy)_4](ClO_4)_2$

To an aqueous solution of *cis*-$[RuCl_2(bpy)_2]$ (550 mg/15 cm^3) was added solid $AgNO_3$ (0.46 g). A white precipitate was separated by filtration, and the resultant solution was mixed with an aqueous solution of NaBr (1.5 g/50 cm^3), and then refluxed for 1 h. A precipitate was separated again, and the volume of the filtrate was reduced to 25 cm^3. A dark green solid which deposited was collected by filtration, washed with cold water, and dried in vacuo. Yield 325 mg, 50%. *Anal.* Found: N, 9.03; C, 38.66; H, 2.81. Calc. for $[Ru_2O(Br)_2(bpy)_4](ClO_4)_2$: N, 9.10; C, 38.82; H, 2.93%.

2.2.9. Reaction of $[Ru(NO_2)(H_2O)(bpy)_2]^+$ with NaClO: formation of $[Ru_2O(NO_2)_2(bpy)_4](ClO_4)_2 \cdot 4H_2O$

An aqueous solution of *cis*-$[Ru(NO)(H_2O)(bpy)_2](ClO_4)_3$ (250 mg/H_2O 15 cm^3) was mixed with NaClO (5%, 0.4 cm^3). The solution pH was kept at about 11 by adding an aqueous solution of NaOH (1 mol dm^{-3}, 0.8 cm^3). The brown solution was stirred for 0.5 h at room temperature to give a green intermediate solution, which was stored in a refrigerator for 1 h. Some powdered $NaClO_4$ (0.5 g) was added to this green solution. The green product which deposited was collected by filtration. The crude product was soaked in EtOH for 3 h, and then purified by column chromatography (Al_2O_3; CH_3CN–EtOH). The purified green material was collected, washed with ether, and then dried in vacuo. Yield 120 mg, 60%. *Anal.* Found: N, 11.61; C, 40.08; H, 2.83. Calc. for $[Ru_2O(NO_2)_2(bpy)_4](ClO_4)_2 \cdot 4H_2O$: N, 11.62; C, 39.84; H, 3.02%.

2.2.10. Reaction of $[Ru(NO_2)(H_2O)(py)_2(bpy)]PF_6$ with NaClO: formation of $[Ru(NO_2)(O)(py)_2(bpy)]PF_6$

To a suspension of $[Ru(NO_2)(H_2O)(py)_2(bpy)]PF_6$ (100 mg/H_2O 5 cm^3) was added NaClO (5%, 1 cm^3), along with NH_4PF_6 (0.2 g). The mixture was stirred for 2–3 h at room temperature during which time the brown suspended material became green. The green material was collected by filtration, washed with cold water, and then dried in vacuo. Yield 80 mg, 80%. *Anal.* Found: N, 11.12; C, 38.00; H, 2.82. Calc. for $[Ru(NO_2)(O)(py)_2(bpy)]PF_6 \cdot 0.5H_2O$: N, 11.09; H, 38.04; H, 2.87%.

2.2.11. Reaction of $[Ru(NO_2)(py)_3(bpy)]PF_6$ with NaClO: formation of $[Ru(O)(py)_3(bpy)](PF_6)_2$

The starting material, $[Ru(NO_2)(py)_3(bpy)]PF_6$, was treated by a procedure similar to that described for $[Ru(NO_2)(O)(py)_2(bpy)]PF_6$. Yield 90 mg, 80%. *Anal.* Found: N, 8.72; C, 37.35; H, 2.81. Calc. for $[Ru(O)(py)_3(bpy)](PF_6)_2$: N, 8.75; C, 37.51; H, 2.90%.

3. Results and discussion

The starting materials of the present chemical oxidations of $[Ru(NO_2)(H_2O)(py)_{4-2n}(bpy)_n]^+$ type complexes, and their product materials, are shown in Table 1. The newly prepared complexes are those with both pyridines and 2,2′-bipyridine ligands ($[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$, $[Ru(NO_2)(O)(py)_2(bpy)]^+$, and their related complexes). These can easily be identified based on the data that was reported previously [3,6]. Complexes with the formula $[Ru(NO_2)(X)(py)_2(bpy)]^+$ have four diastereoisomers, two of which have enantiomers. Under the preparative conditions, only the isomer depicted in Fig. 1(b) is present. The ^{13}C NMR spectrum

Table 1
Characterization data for chemical oxidation products and their related materials

	IR[a]					μ_{eff} (BM)	Ref.
	–NO_2		–ONO				
	ν_{as}	ν_s	ν(N–O)	ν(N=O)	ν(RuO)		
Oxidation products							
$[Ru^{IV}(ONO)(O)(py)_4]ClO_4$			976	1476	798	2.91	[6]
$[Ru^{IV}(NO_2)(O)(py)_2(bpy)]PF_6$	1394	1328			806	2.75	
$[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4](ClO_4)_2$	1368	1307				1.51	
Starting materials							
$[Ru^{II}(NO_2)(H_2O)(py)_4]PF_6$	1315	1280				dia	[6]
$[Ru^{II}(NO_2)(H_2O)(py)_2(bpy)]PF_6$[b]	1331	1273				dia	
$[Ru^{II}(NO_2)(H_2O)(bpy)_2]ClO_4$	1333	1271				dia	
Related complexes							
$[Ru^{II}(NO_2)(py)_3(bpy)]PF_6$	1330	1291				dia	
$[Ru^{IV}(O)(py)_3(bpy)](PF_6)_2$					806	2.57	
$[Ru^{IV}Cl(O)(py)_4]PF_6$					806	2.92	[6]

[a] In cm^{-1} (KBr).

[b] ^{13}C NMR data are also available for the complex (see Section 2).

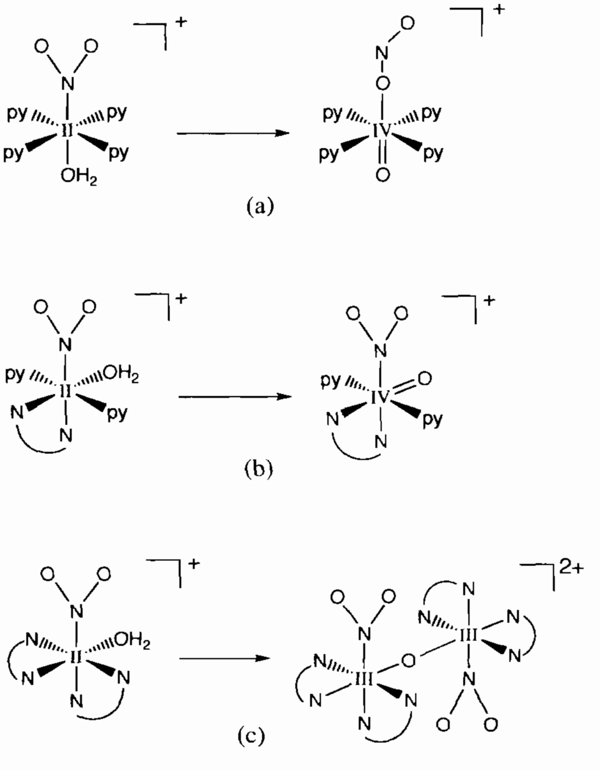

Fig. 1. Starting materials and their products in the chemical oxidation of $[Ru(NO_2)(CH_3CN)(py)_{4-2n}(bpy)_n]^+$ using NaClO: (a), $n=0$; (b) $n=1$; (c) $n=2$.

of $[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$ shows the presence of 13 magnetically inequivalent carbon atoms (see Section 2); 8 or 16 resonances would be seen in the ^{13}C NMR spectra of other isomers.

3.1. Chemical oxidation of $[Ru(NO_2)(OH_2)(py)_{4-2n}(bpy)_n]^m$ ($n=0$, 1, 2): product species depends on the number n

We investigated the ligand nature of coordinated NO_2^- in a series of $[Ru(NO_2)(OH_2)(py)_{4-2n}(bpy)_n]^+$ complexes ($n=0$–2). The oxidation reactions showed that the number n affected their reactivities strongly, as summarized in Fig. 1 and Table 1. Their electrochemical data are tabulated in Table 2.

As mentioned earlier, the nitro complex of Ru(II) (*trans*-$[Ru^{II}Cl(NO_2)(py)_4]$) can be converted to the monooxygen complex of Ru(IV) (*trans*-$[Ru^{IV}Cl(O)(py)_4]^+$) [2–6]. Mechanistic investigation had shown that such a reaction is initiated by the oxidation; it will give the corresponding nitro complex of Ru(III) (*trans*-$[RuCl(NO_2)(py)_4]^+$) (Eq. (1)). Then the following disproportionation occurs: the oxidized species undergoes a facile isomerization to give the nitrito complex of Ru(III) ($[RuCl(ONO)(py)_4]^+$) (Eq. (2)), which results in the formation of a transient dimeric intermediate species ($\{Cl(py)_4Ru\text{–}NO(O)\text{–}N(O)O\text{–}Ru(py)_4Cl\}^{2+}$) (Eq. (3)). Bonding rupture occurs in the intermediate to give three product species: (*trans*-$[RuCl(O)(py)_4]^+$, *trans*-$[RuCl(NO)(py)_4]^{2+}$ and *trans*-$[RuCl(OH)(py)_4]^+$) (Eq. (4)). A total of 1.25 electrons is required for the reaction [6]. When the oxidation is carried out using NaClO (in NaOH), the reaction progresses, in principle, until all of the *trans*-$[RuCl(NO_2)(py)_4]$ is converted into *trans*-$[RuCl(O)(py)_4]^+$, via the generation of the original nitro complex of Ru(II), based on the acid–base reaction of coordinated nitrosyl (Eq. (5)) [6,11], along with the oxidation of ($Cl\text{–}Ru^{III}\text{–}OH$) in Eq. (5).

Table 2
Electrochemical data for the products and their related materials

	CV[a]						Ref.
	Oxidation			Reduction			
	E_{pa}	E_{pc}	$E_{1/2}$	E_{pc}	E_{pa}	$E_{1/2}$	
$[\mathrm{Ru^{IV}(ONO)(O)(py)_4}]\mathrm{ClO_4}$	1.12			−1.00			[6]
$[\mathrm{Ru^{IV}(NO_2)(O)(py)_2(bpy)}]\mathrm{PF_6}$				−0.74			
$[\mathrm{Ru^{III,III}{}_2O(NO_2)_2(bpy)_4}](\mathrm{ClO_4})_2$	0.59	0.53	0.56	−0.54	−0.50	−0.52	
$[\mathrm{Ru^{II}(NO_2)(CH_3CN)(py)_4}]\mathrm{PF_6}$	(0.88)						[10]
$[\mathrm{Ru^{II}(NO_2)(H_2O)(py)_2(bpy)}]\mathrm{PF_6}$	(0.98)	(0.84)	(0.95)[b]				
$[\mathrm{Ru^{II}(NO_2)(CH_3CN)(bpy)_2}]\mathrm{ClO_4}$	(0.89)	(0.81)	(0.85)				
$[\mathrm{Ru^{II}(NO_2)(py)_3(bpy)}]\mathrm{PF_6}$	0.70		0.68[b]				
$[\mathrm{Ru^{IV}(O)(py)_3(bpy)}](\mathrm{PF_6})_2$				−0.68			
$[\mathrm{Ru^{IV}Cl(O)(py)_4}]\mathrm{PF_6}$	1.39			−1.00			[6]

[a] In $\mathrm{CH_3CN}$; V vs. Ag|$\mathrm{AgClO_4}$ (numbers in parentheses: V vs. Ag|$\mathrm{AgNO_3}$).

[b] An analysis of normal pulse voltammograms showed the Nernstian electrochemical result.

$$2(\mathrm{Cl{-}Ru^{II}{-}NO_2}) \longrightarrow 2(\mathrm{Cl{-}Ru^{III}{-}NO_2}) + 2e^- \tag{1}$$

$$2(\mathrm{Cl{-}Ru^{III}{-}NO_2}) \longrightarrow (\mathrm{Cl{-}Ru^{III}{-}NO_2}) + (\mathrm{Cl{-}Ru^{III}{-}ONO}) \tag{2}$$

$$\longrightarrow \{\mathrm{Cl{-}Ru{-}NO(O){-}N(O)O{-}Ru{-}Cl}\}^{2+} \tag{3}$$

$$\begin{aligned} &\longrightarrow (\mathrm{Cl{-}Ru^{II}{-}NO^+}) + 1/2(\mathrm{Cl{-}Ru^{IV}{=}O}) \\ &\quad + 1/2(\mathrm{Cl{-}Ru^{III}{-}OH}) + \mathrm{NO_2}^- + 0.5e^- \end{aligned} \tag{4}$$

$$(\mathrm{Cl{-}Ru^{II}{-}NO^+}) + 2\mathrm{OH}^- \longrightarrow (\mathrm{Cl{-}Ru^{II}{-}NO_2}) + \mathrm{H_2O} \tag{5}$$

Another oxidation reaction is possible for the nitro complex of Ru(II), depending on the disintegration mode of the intermediate species:

$$\begin{aligned} &\{\mathrm{Cl{-}Ru{-}NO(O){-}N(O)O{-}Ru{-}Cl}\}^{2+} \longrightarrow \\ &\qquad (\mathrm{Cl{-}Ru^{II}{-}NO^+}) + (\mathrm{Cl{-}Ru^{II}{-}ONO_2}^-) \end{aligned} \tag{6}$$

$$(\mathrm{Cl{-}Ru^{II}{-}ONO_2}^-) \longrightarrow (\mathrm{Cl{-}Ru^{III}{-}ONO_2}^-) + e^-$$

This is the 1.5-electron oxidation scheme that has been reported by Meyer and co-workers [8]. Our recent work has shown that the reaction expressed by Eq. (6) sometimes proceeds further to give a solvation product, depending on the reaction conditions [10,13]:

$$\begin{aligned} &\{\mathrm{Cl{-}Ru{-}NO(O){-}N(O)O{-}Ru{-}Cl}\}^{2+} \longrightarrow \\ &\qquad (\mathrm{Cl{-}Ru^{II}{-}NO^+}) + (\mathrm{Cl{-}Ru^{II}{-}solv}) + \mathrm{ONO_2}^- \end{aligned} \tag{7}$$

We have also reported another example in which the reaction of the nitro complex of Ru(II) proceeds without involving the disproportionation of the nitro complex of Ru(III) [6]. When *trans*-$[\mathrm{Ru(NO_2)(OH_2)(py)_4}]^+$ (the complex of $n=0$) undergoes two-electron oxidation, *trans*-$[\mathrm{Ru(ONO)(O)(py)_4}]^+$ can be obtained, via the formation of *trans*-$[\mathrm{Ru(NO_2)(OH)(py)_4}]^+$:

$$\begin{aligned} &(\mathrm{H_2O{-}Ru^{II}{-}NO_2}) \longrightarrow \\ &\qquad (\mathrm{HO{-}Ru^{III}{-}NO_2}) + \mathrm{H}^+ + e^- \end{aligned} \tag{8}$$

$$\begin{aligned} &(\mathrm{HO{-}Ru^{III}{-}NO_2}) \longrightarrow \\ &\qquad (\mathrm{O{=}Ru^{IV}{-}ONO}) + \mathrm{H}^+ + e^- \end{aligned} \tag{9}$$

In contrast to the above chemical oxidation reactions, the present nitro complexes with 2,2′-bipyridine ligand(s) as the spectator ligand, $[\mathrm{Ru(NO_2)(OH_2)(py)_2(bpy)}]^+$ ($n=1$) and *cis*-$[\mathrm{Ru(NO_2)(OH_2)(bpy)_2}]^+$ ($n=2$), gave unexpected products: $[\mathrm{Ru^{IV}(O)(NO_2)(bpy)(py)_2}]^+$ and $[\mathrm{Ru_2{}^{III,III}O(NO_2)_2(bpy)_4}]^{2+}$, respectively, both having the nitro moiety.

Although the chemical reactivity of the title complexes differs depending on n, as summarized in Fig. 1, the formation processes of the products can be explained by basically the same mechanistic pathway as that reported for the oxidation of *trans*-$[\mathrm{Ru(NO_2)(H_2O)(py)_4}]^+$ ($n=0$) [6]: in the complex with either $n=1$ ($[\mathrm{Ru(NO_2)(OH_2)(py)_2(bpy)}]^+$) or $n=2$ (*cis*-$[\mathrm{Ru(NO_2)(OH_2)(bpy)_2}]^+$), the first step is a one-electron oxidation to give the corresponding hydroxo complexes of Ru(III) (Eq. (8)); this is followed by a further one-electron oxidation to give the ($\mathrm{Ru^{IV}{=}O}$) moiety (Eq. (9), for $n=1$), or a facile dimerization to afford the μ-oxo moiety (Eq. (10), for $n=2$).

$$\begin{aligned} &(\mathrm{HO{-}Ru^{III}{-}NO_2}) \longrightarrow \\ &\qquad 1/2(\mathrm{NO_2{-}Ru^{III}{-}O{-}Ru^{III}{-}NO_2}) + 1/2\mathrm{H_2O} \end{aligned} \tag{10}$$

We especially emphasize that the original nitro ligand is still retained in the product species of the complexes of $n=1$ and 2, without a nitro–nitrito isomerization. Neither the disproportionation which gives the ($\mathrm{Ru^{IV}{=}O}$) moiety (Eqs. (1)–(4)) nor the formation of the nitrato complex of Ru(III) (Eqs. (1)–(3), (6)) occurred in the chemical oxidation of the $[Ru(NO_2)(H_2O)(py)_{4-2n}(bpy)_n]^+$ complexes.

3.2. Electrochemical oxidation of $[Ru(NO_2)(H_2O)(py)_{4-2n}(bpy)_n]^+$ (n = 0, 1, 2) complexes in CH_3CN: basically the same EC reaction is proceeding

The title complexes show basically the same electrochemical behavior; they follow an oxidation process which involves a dimeric intermediate consisting of both nitro and nitrito complexes of Ru(III) (Eq. (3)) [6,8]. To avoid extra complexity due to a solvation problem, we investigated the solvation species, $[Ru(NO_2)(CH_3CN)(py)_{4-2n}(bpy)_n]^+$. The exception was the complex of $n=1$, whose solvation species was still too difficult to isolate. The cyclic voltammograms of the solvation species are shown in Fig. 2.

Fig. 3(A) shows the cyclic voltammograms of $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ measured at 25 °C (V versus $Ag/AgNO_3$). A single irreversible oxidation wave (i) was found at 0.89 V within the potential region expected for Ru(II)/Ru(III) oxidation. The electron transfer process is diffusion-controlled, with $i_p/v^{1/2}$ constant over the range of scan rate used, 50–200 mV s^{-1}. The current height of the coupled reduction is smaller than that of the oxidation wave. On the scan reversal, small waves (ii), (iii) and (iv) were observed at 0.68, 0.21 and −0.64 V, respectively, in addition to the coupled reduction wave found at 0.81 V ((iv) was omitted from Fig. 3). The data are summarized in Table 3. We can reasonably assign the (iii) and (iv) waves to $[Ru(NO)(CH_3CN)(bpy)_2]^{3+/2+/+}$, based on the observations described later.

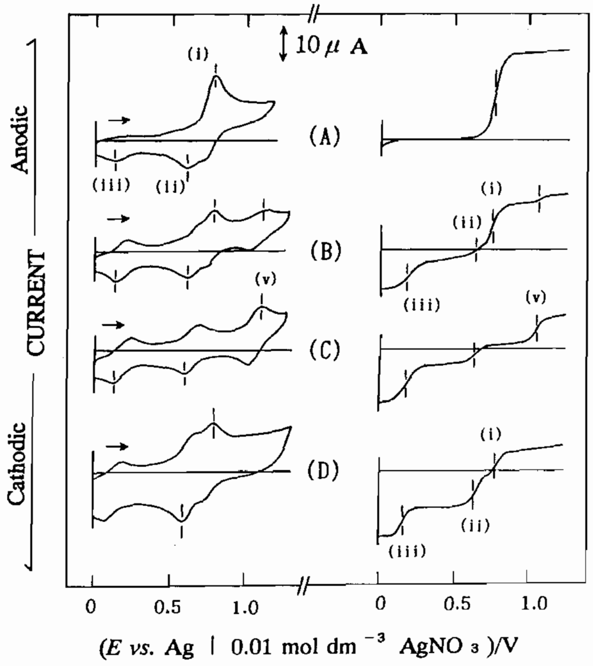

Fig. 3. CVs and hydrodynamic voltammograms (Pt disk electrode (1600 rpm)) monitoring the course of controlled-potential oxidation (0.95 V) of *cis*-$[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ (1.0 mmol dm^{-3}) in CH_3CN (0.1 mol dm^{-3} TEAP): (A) prior to electrolysis; (B) during electrolysis; (C) at the end of electrolysis ($n=1.03$) at 25 °C; (D) electrolyzed solution, measured just after the electrolysis was performed ($n=0.52$) at −30 °C.

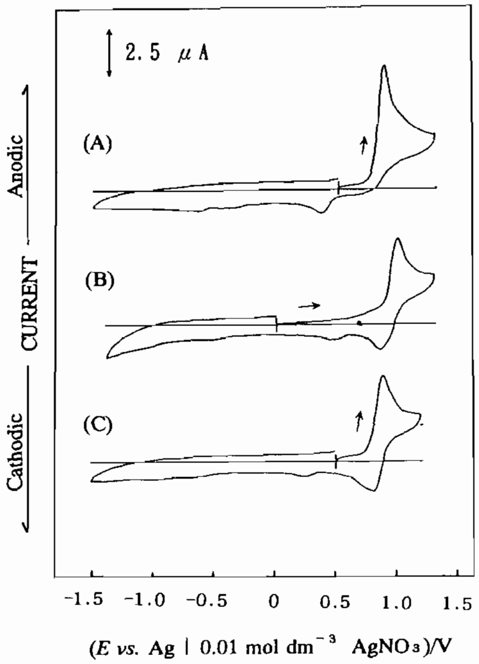

Fig. 2. Typical cyclic voltammograms of $[Ru(NO_2)(CH_3CN)(py)_{4-2n}(bpy)_n]^+$ ($n=0$, 1, 2): (A) $[Ru(NO_2)(CH_3CN)(py)_4]^+$; (B) $[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$; (C) $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ in CH_3CN at 25 °C (stationary Pt electrode, Et_4NClO_4 (0.1 mol dm^{-3})) (200 mV s^{-1}).

The changes of cyclic voltammograms during the oxidative exhaust electrolysis were followed at 25 °C; the shapes of the two waves (iii) and (iv), assigned to $[Ru(NO)(CH_3CN)(bpy)_2]^{3+/2+/+}$, developed as the electrolysis progressed (Fig. 3(B)). At the final stage of the electrolysis (Fig. 3(C)), the current height examination by hydrodynamic voltammetry showed that a quantity of nearly one mole of $[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$ was generated from 2 moles of $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$. The generation of the nitrosyl species (waves (iii) and (iv), $[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$) is informative for understanding how the electrochemical oxidation of $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ occurs through a process which involves a dimeric intermediate consisting of both nitro and nitrito complexes of Ru(III) (Eqs. (1)–(3)) [6].

The wave (ii) observed at 0.68 V, however, did not develop constantly during the period of electrolysis. A further new anodic wave (v) appeared at $E_{pa}=1.20$ V, and it developed in compensation for this wave (ii). We assigned the species (wave (ii)) as being due to $[Ru(ONO_2)(CH_3CN)(bpy)_2]^+$, based on Meyer's scheme (Eqs. (1)–(3), (6)). The generation of wave (v) is understood as showing that the nitrato complex of Ru(II) (wave (ii)) undergoes a facile decomposition to release the ONO_2^- ion, giving $[Ru(CH_3CN)_2(bpy)_2]^{2+}$ (Eq. (7)). The di-acetonitrile complex of Ru(II), $[Ru(CH_3CN)_2(bpy)_2]^{2+}$, has been reported to show its redox potential at a positive potential region that is comparable to the 1.20 V observed above [14][3].

Some evidence which supports the above assumption is available from the oxidative exhaust electrolysis at −30 °C. In this low temperature experiment, wave (ii) developed constantly along with waves (iii) and (iv), and the anodic wave (v) could not be detected by cyclic voltammetry (Fig. 3(D)). However, when an identical electrolyzed solution was allowed to stand at room temperature, wave (v) appeared. It developed gradually while wave (ii) diminished at the same time (similarly to Fig. 3(C)). The findings in the electrolysis of $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ were different from the result that was observed in the corresponding chloro complex, $[Ru(NO_2)Cl(bpy)_2]$, in which only two species, $[Ru(NO)Cl(bpy)_2]^{2+}$ and $[Ru(ONO_2)Cl(bpy)_2]^+$ (Eq. (6)), were generated. This was expected from Meyer's 1.5-electron oxidation scheme, which was confirmed to proceed under these conditions [7,8].

The assignments of the coupled waves (iii) and (iv) as due to $[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$ species were confirmed by the following observation: cyclic voltammograms of *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ in CH_3CN at 25 °C (Fig. 4) exhibited two one-electron reduction waves. This was the typical CV pattern expected for $\{RuNO\}^6$ type complexes [15,16], but the peak separation of the first reduction wave ($\Delta E = 0.15$ V ($E_{pa}(0.29$ V$) - E_{pc}(0.14)$) was too large.

When the CVs were recorded at regular time intervals during the reductive electrolysis at 0.10 V, the reduction wave of the first coupled wave changed; the peak potential of E_{pc} was found to shift gradually to the positive side, while that of E_{pa} did not move. The cyclic voltammograms finally obtained had a well-shaped reversible wave ($\Delta E_p = 0.08$ V ($E_{pa}(0.29$ V$) - E_{pc}(0.21$ V$)$); they agreed well with that of $[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$ generated in the exhaust electrolysis of $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ mentioned above. The solvation of $[Ru(NO)(H_2O)(bpy)_2]^{3+}$ by CH_3CN is relatively slow, and it appears to be facilitated by the reduction of the $(RuNO)^{3+}$ moiety[4].

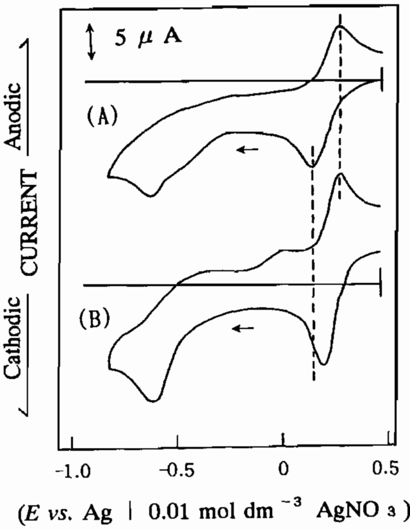

Fig. 4. Variation of cyclic voltammogram of *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ in CH_3CN at 25 °C: (A) prior to electrolysis (reduction) at 0.10 V; (B) at the end of the electrolysis ($n = 1.0$).

We obtained $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ by treatment of $[Ru(NO_2)(H_2O)(bpy)_2]^+$ (the complex of $n = 2$) with CH_3CN (see Section 2), but under the same conditions $[Ru(NO_2)(CH_3CN)(py)_2(bpy)]^+$ (the solvation complex of $n = 1$) could not be obtained as a solid. We therefore used $[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$ for the present electrochemical investigation. No evidence is yet available for $[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$ to show whether it underwent solvation or not. The aqua complex, $[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$, shows essentially the same EC reaction as that illustrated for *cis*-$[Ru(NO_2)(CH_3CN)(bpy)_2]^+$. In the cyclic voltammetry carried out at 25 °C, an anodic wave is found at around 0.98 V ($E_{pc} = 0.84$ V), together with the coupled cathodic wave on the reverse scan. The peak current ratio i_{pa}/i_{pc} was nearly unity, but the peak potential separation $\Delta E = 140$ mV at scan rate (50–200 mV s^{-1}) was near the value expected for a one-electron quasi-reversible couple. Plots of peak current versus the square root of the scan rate were almost linear, showing the oxidation to be diffusion-controlled.

Oxidative controlled potential electrolysis ($n = 1.2$–1.3) of the complex at 25 °C shows that new waves appeared at 0.51 ($E_{1/2}$), −0.52 (E_{pc}) and 0.90 (E_{pa}) V by repeated cyclic scanning. A further wave also appeared at 1.40 V, in the potential region positive to the original oxidation wave of $[Ru(NO_2)(H_2O)(py)_2(bpy)]^+$. These waves developed

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[3] The potential value reported by Walsh and Durham (1.44 V vs. SSCE) [14] corresponds to 1.20 V vs. Ag|AgNO₃ [14], which has been measured under our experimental conditions.

[4] When a CH_3CN solution containing *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ is allowed to stand for a long time, without reduction, an unidentified species forms, which has its $E_{1/2}$ value at −0.01 V. A reaction in which a nitrosyl moiety acts as an electrophile to the solvent molecules has been observed in *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ [16].

as the electrolysis progressed. If the coupled waves observed at 0.51 and −0.52 V are attributable to $[Ru(NO)(H_2O)(py)_2(bpy)]^{3+/2+/+}$ (or its solvation species) (note that $\{RuNO\}^6$ complexes usually have two one-electron reduction waves, as mentioned above), the waves at 0.90 and 1.40 V are expected to be due to $[Ru(ONO_2)(H_2O)(py)_2(bpy)]^+$ (or $[Ru(ONO_2)(CH_3CN)(py)_2(bpy)]^+$) and $[Ru(CH_3CN)(H_2O)(py)_2(bpy)]^+$ (or $[Ru(CH_3CN)_2(py)_2(bpy)]^+$), respectively, by the same reasoning that was used in the electrolysis of $[Ru(CH_3CN)_2(bpy)_2]^+$. Presently, authentic samples are not yet available for these complexes. Further study was therefore not carried out on the complex.

We also did not succeed in the isolation of the solvation complex of $n=0$, $[Ru(NO_2)(CH_3CN)(py)_4]^+$, as described earlier. Previous work has shown that the solvation of $[Ru(NO_2)(H_2O)(py)_4]^+$ occurs immediately when the aqua complex is dissolved in CH_3CN at 25 °C [10]. A nitro–nitrito isomerization of the complex has also been inferred by cyclic voltammetry [6], suggesting an oxidation pathway via a dimeric intermediate process (Eq. (7)). A controlled-potential electrolysis was unsuccessful; the oxidation wave (0.88 V) due to $Ru^{3+/2+}$ did not vanish, even when a large excess current flowed. No direct generation of the ($Ru^{IV}=O$) moiety could be confirmed.

3.3. *Further oxidation of the product species having a nitro moiety*

As described earlier, three species which retain the original nitro nitrogen can be isolated as the chemical oxidation products: $[Ru(NO_2)(O)(py)_2(bpy)]^+$ and $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$, including $[Ru(ONO)(O)(py)_4]^+$. There are problems involving why the nitro ligands of both $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$ and $[Ru^{IV}(NO_2)(O)(py)_2(bpy)]^+$ do not undergo a nitro–nitrito isomerization, even though these complexes contain the relatively high-valent form of ruthenium metal. Actually, the isomerization to give $[Ru(ONO)(O)(py)_4]^+$ has been found in $[Ru(NO_2)(OH_2)(py)_4]^+$ [6]. Further electrochemical oxidation was therefore attempted for both $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$ and $[Ru^{IV}(NO_2)(O)(py)_2(bpy)]^+$ to determine the specific details of their coordinated NO_2^- ligands.

3.3.1. *The NO_2^- ligand in $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$ is released by an intramolecular electron transfer process*

As summarized in Table 3, $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$ in CH_3CN undergoes both reversible one-electron oxidation and reduction (Fig. 5), each of which has accompanying chemical reactions which are illustrated below. Meyer and co-workers have reported detailed investigations on the electrochemical behavior of $[Ru_2O(Cl)_2(bpy)_4]^{2+}$ [17], but they have only briefly mentioned $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$. The ligand nature of the nitro moiety observed here has not been reported. The electron transfer mechanisms that are suggested for the oxidation reaction of $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$ are supported by the data given in Table 4 and Figs. 5 and 6.

At 25 °C, a one-electron oxidation transfer process is found at 0.59 V (E_{pa}) and at 0.53 V (E_{pc}) versus Ag/0.1 mol dm^{-3} $AgClO_4$. A one-electron reduction transfer process is also found at −0.54 V (E_{pc}) and at −0.50 V (E_{pa}). These were labeled waves 1 (wave 1a, oxidation; wave 1b, reduction) and 2 (wave 2a, reduction; wave 2b, oxidation) in Fig. 5. Wave 1 has reversible cyclic voltammetric behavior and is a diffusion-controlled one-electron transfer at 0.56 V ($E_{1/2}$). For wave 1, ΔE_p is 60 mV at a scan rate of 100 mV s^{-1}, and the ratio of peak currents is near unity. In addition, the ratio of the peak current to the square root of the scan rate ($i_p/v^{1/2}$) is a constant. Wave 2 also showed reversible cyclic voltammetric behavior. Bulk oxidative electrolysis performed at 25 °C gives values of $n=1.0$ (for wave 1, upon oxidation at 0.59 V). Almost the same electrochemical processes are found at low temperature (−30 °C).

A careful investigation of the oxidation process at 25 °C showed that while $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$ exhibited the reversible voltammetric nature as described above, this was not retained when a controlled-potential electrolysis was carried out. During the electrolysis, the cyclic voltammograms changed; before the electrolysis, only the anodic current due to the oxidation of the $(NO_2–Ru^{III}–O–Ru^{III}–NO_2)^{4+}$ moiety was observed at the positive potential region (1a in Fig. 6(A)). When the exhaust oxidative electrolysis progressed at 0.59 V, a new anodic current developed gradually at a slightly positive potential, 0.75 (E_{pa}) V (Fig. 6 (B)). In continuous electrolysis, the anodic current (1a) due to the oxidation of $(NO_2–Ru^{III}–O–Ru^{III}–NO_2)^{4+}$ almost disappeared, and further increases of both the new anodic and its coupled cathodic current were found by the oxidative CV scanning (dotted line in Fig. 6(A)). In the final stage, only the redox current, observed at 0.75 (E_{pa}) and 0.68 (E_{pc}) V, remained (Fig. 6(B)). The same trend can be seen in a hydrodynamic voltammogram, which was monitored using a Pt rotating disk electrode (1600 rpm) during the controlled-potential oxidation. Nearly 1 mole of electrons per mole of $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$ was released, as described earlier. The new species, generated by the electrolysis, could be identified as $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$ using an authentic sample. When the controlled-potential electrolysis was carried out at −20 °C, no new wave appeared in the cyclic voltammograms (Fig. 6(B)).

The observation described above leads us to conclude that, at 25 °C, the intramolecular electron transfer processes that are illustrated by Eqs. (11)–(13) exist;

Table 3
Electrochemical data for the species generated during the oxidative electrolysis of $[Ru(NO_2)(CH_3CN)(bpy)_2]^+$ at 25 °C[a]

	Oxidation			Reduction			n (e^-)
	E_{pa}	E_{pc}	$E_{1/2}$	E_{pc}	E_{pa}	$E_{1/2}$	
$[Ru(NO_2)(CH_3CN)(bpy)_2]^{2+/+}$ [b]	0.89	0.81	0.85				1.2–1.25
$[Ru(NO)(CH_3CN)(bpy)_2]^{3+/2+}$				0.21 −0.64	0.29	0.25	
$[Ru(ONO_2)(CH_3CN)(bpy)_2]^{2+/+}$ [c]				0.68	0.76	0.72	
$[Ru(CH_3CN)_2(bpy)_2]^{3+/2+}$	1.20	1.12	1.16				

[a] In CH_3CN; V vs. Ag|$AgClO_4$ (numbers in parentheses: V vs. Ag|$AgNO_3$).
[b] ClO_4 salt.
[c] Tentatively assigned.

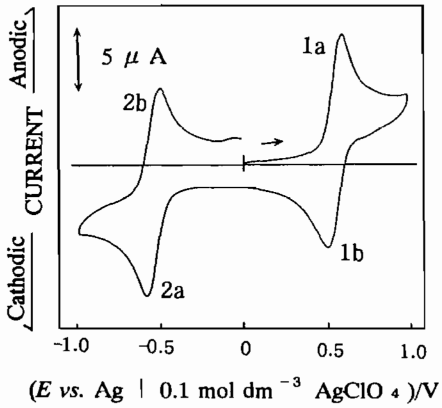

Fig. 5. Cyclic voltammograms of $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$ (1.0 mmol dm^{-3}) in 0.1 mol dm^{-3} TEAP–CH_3CN on Pt disk electrode (ϕ = 1.6 mm) at 25 °C (100 mV s^{-1}).

the generated transient species, $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$, is the reactive dimer which results in the liberation of the neutral NO_2 to leave $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$. The decrease with time in the current height at 0.59 V (E_{pa}), and the increase in that at 0.75 V (E_{pa}), are attributed to the formation of solvation species, as is shown in Eqs. (11) and (13), in the Ru(III)–Ru(III) dimer.

$$[Ru^{III,III}{}_2O(NO_2{}^-)_2(bpy)_4]^{2+}$$

$$\longrightarrow [Ru^{III,IV}{}_2O(NO_2{}^-)_2(bpy)_4]^{3+} + e^- \qquad (11)$$

$$\longrightarrow \{Ru^{III,III}{}_2O(NO_2{}^-)(NO_2{}^0)(bpy)_4\}^{3+} \qquad (12)$$

$$\longrightarrow [Ru^{III,III}{}_2O(NO_2{}^-)(CH_3CN)(bpy)_4]^{3+} + NO_2{}^0 \qquad (13)$$

The generated one-electron oxidation species in Eq. (11), $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$, can exist as a stable species at temperatures lower than −20 °C, while it decomposes to $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$, as described above, when the temperature of the solution is elevated. It should be emphasized that, during the decomposition process of $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$, only two species, $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$ and $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$, are detected by cyclic voltammetry. The process in which the coordinated $NO_2{}^-$ is liberated is of special interest in our research; whether the species containing the nitrito moiety, $[Ru^{III,IV}{}_2O(NO_2)(ONO)(bpy)_4]^{3+}$, was formed or not before the liberation of $NO_2{}^-$, is important for the present purpose, but no definite evidence for the isomerization has been obtained yet.

Cyclic voltammetry can follow the time course for the appearance of the solvation species, $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$, by the decomposition of $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$ at an elevated tem-

Table 4
Electrochemical data of the μ-oxo complexes at 25 °C[a]

	Oxidation			Reduction			n (e^-)
	E_{pa}	E_{pc}	$E_{1/2}$	E_{pc}	E_{pa}	$E_{1/2}$	
$[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$	0.59	0.53	0.56	−0.54	−0.50	−0.52	1.00
	(0.73)	(0.67)	(0.70)	(−0.40)	(−0.36)	(−0.38)	
$[Ru^{III,III}{}_2O(CH_3CN)(NO_2)(bpy)_4]^{3+}$	0.75	0.68	0.72	−0.40	−0.34	−0.37	
$[Ru^{III,III}{}_2O(Cl)_2(bpy)_4]^{2+}$	0.31	0.25	0.28	−0.75	−0.68	−0.72	0.97
$[Ru^{III,III}{}_2O(Br)_2(bpy)_4]^{2+}$	(0.50)	(0.44)	(0.47)	(−0.55)	(−0.48)	(−0.52)	(0.95)

[a] In CH_3CN; V vs. Ag|$AgClO_4$ (numbers in parentheses: V vs. Ag|$AgNO_3$).

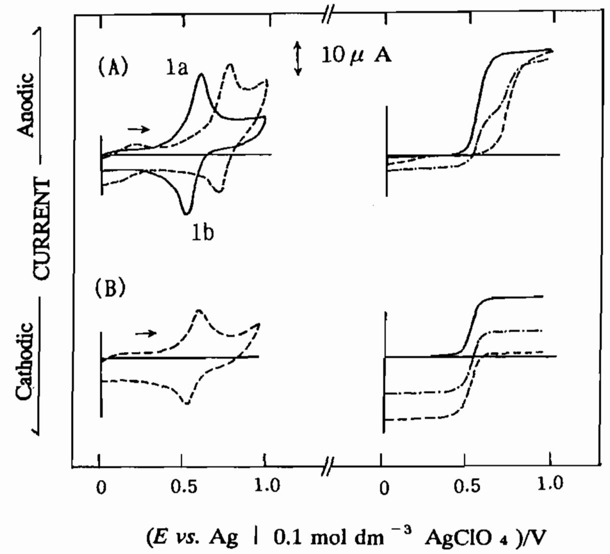

Fig. 6. Controlled-potential electrolysis of $[Ru_2O(NO_2)_2(bpy)_4]^{2+}$: (A) at 25 °C, (B) at −30 °C. ——, CVs and hydrodynamic voltammograms prior to electrolysis; –·– and – – –, CVs and hydrodynamic voltammograms of the solution electrolyzed at 0.60 V (for $n=0.6$ and 1.0, respectively).

perature, along with the time course for its disappearance at the exhaust electrolysis. Changes in $\ln(I_d/\mu A)$ with time at 25 °C were found to follow the first-order rate law. The rate constants (at 25 °C) estimated roughly for the decomposition of $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$ and that for the formation of $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$ were 5.18×10^{-4} and 4.80×10^{-4} s^{-1}, respectively ($E=1.55\times10^2$ and 1.65×10^2 KJ mol^{-1}, respectively).

A further electrochemical oxidation, which would generate $[Ru^{III,IV}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$, was also possible in $[Ru^{III,III}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$ at 0.75 V, but the exact n value was difficult to obtain, since the potential applied for the electrolysis was near the end of the potential window. We expect that $[Ru^{III,IV}{}_2O(NO_2)(CH_3CN)(bpy)_4]^{3+}$ will generate $[Ru^{III,III}{}_2O(CH_3CN)_2(bpy)_4]^{4+}$ again via an electron transfer process similar to that described in Eqs. (11)–(13).

For comparison, the corresponding μ-oxo complex with the Cl ligand, $[Ru^{III,III}{}_2OCl_2(bpy)_4]^{2+}$, was investigated under the same conditions. The reversible nature observed in the μ-oxo complex is the same as that reported by Meyer and co-workers [17]; reversible waves are found at 0.28 ($E_{1/2}$) and −0.71 ($E_{1/2}$) V, and no chemical reaction accompanying a one-electron oxidation could be found in the exhaust electrolysis at 0.31 V.

The results found in both $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$ and $[Ru^{III,III}{}_2OCl_2(bpy)_4]^{2+}$ lead to the following assumptions. If the observed electrochemical difference between them is ascribed simply to the difference in the standard oxidation potentials between NO_2^- and Cl^- (1.00 and 1.36 V [18], respectively), then the Br_2-releasing reaction which would accompany the electrochemical oxidation will occur in $[Ru^{III,III}{}_2OBr_2(bpy)_4]^{2+}$, at least on a qualitative scale, because both NO_2^- and Br^- have almost the same standard potential values (Br^-: 1.06 V [18]). The observed typical reversible nature of $[Ru^{III,III}{}_2OBr_2(bpy)_4]^{2+}$, however, suggests that no reaction which releases a coordinated Br^- ligand such as Br_2 occurs.

Additionally, a one-electron reduction process of $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$ was studied. Some interesting electrochemical behavior can be observed. The μ-oxo complex in CH_3CN exhibited reversible behavior in the cyclic voltammetry at −0.52 V ($E_{1/2}$), but exhaust reductive electrolysis showed that the generated species, $[Ru^{II,III}{}_2O(NO_2)_2(bpy)_4]^+$, was reactive again, and the species gave the original μ-oxo complex of Ru(III)–Ru(III) (nearly 0.5 mole), along with some unidentified material; a disproportionation reaction appears to occur for $[Ru^{II,III}{}_2O(NO_2)_2(bpy)_4]^+$. Further study on this reductive species is now in progress and will be reported elsewhere.

3.3.2. Cyclic voltammograms of both $[Ru(NO_2)(O)(py)_2(bpy)]^+$ and trans-$[Ru(ONO)(O)(py)_4]^+$

Both *trans*-$[Ru(ONO)(O)(py)_4]^+$ and $[Ru(NO_2)(O)(py)_2(bpy)]^+$ in CH_3CN showed essentially the same cyclic voltammograms as that of *trans*-$[Ru(O)Cl(py)_4]^+$ (Table 1), which has been investigated in both aqueous and non-aqueous solvents [19]. Based on this investigation, the electrochemical behavior of the present complexes can be illustrated as a two-electron acceptor; a two-electron reduction species containing the $(Ru^{II}–O^{2-})^0$ moiety is generated transiently by cyclic voltammetry. The exhaust reductive electrolysis, however, shows an unexplainable cyclic voltammogram, because the two-electron reduction of the $(Ru^{IV}=O)^{2+}$ moiety seems to be followed by rapid chemical reactions.

CVs of the complexes showed an oxidation wave at 1.12 V. Analysis of normal pulse voltammograms showed that the oxidation process observed in *trans*-$[RuCl(O)(py)_4]^+$ is a Nernstian one-electron process. The potential values of the present complexes are found at comparable potentials to that of *trans*-$[RuCl(O)(py)_4]^+$, but they are too high for us to investigate their electrochemical behavior further. We therefore did not attempt a controlled-potential electrolysis for $[Ru(NO_2)(O)(py)_2(bpy)]^+$. No information could be obtained about the nitro and nitrito moieties of either complex.

3.4. Ligand nature of the coordinated NO_2^- under the oxidation conditions

The present investigation shows one role of the spectator ligands in the oxidation reaction of

$[Ru(NO_2)X(py)_{4-2n}(bpy)_n]^m$ type complexes ($m=0$ for X=Cl, $m=1+$ for $X=H_2O$), though the sterical differences of the complexes should also be considered. In the chemical oxidation, $[Ru(NO_2)(OH_2)(py)_{4-2n}(bpy)_n]$ gave three products, which have the terminal or bridging oxo ligand, depending on *n*. In any case, however, rupturing the (Ru–nitrite) bond does not occur.

On the contrary, in the electrochemical oxidation, all the complexes react via a process which involves rupturing the ($Ru-NO_2$) bond by a dimeric intermediate mechanism (Eqs. (1)–(3), (7)). Electrochemical investigations so far reported have suggested that *trans*-$[Ru(NO_2)Cl(py)_4]$ ($n=0$ in $[Ru(NO_2)Cl(py)_{4-2n}(bpy)_n]$) is the only complex which generates directly the complex with the ($Ru^{IV}=O$) moiety, through the 1.25-electron oxidation scheme (Eqs. (1)–(4)) [5,6]. While the chemical oxidation of $[Ru(NO_2)(py)(py)_2(bpy)]^+$, a complex analogous to $[Ru(NO_2)(OH_2)(py)_2(bpy)]$ ($n=1$), occurs to give $[Ru(O)(py)(py)_2(bpy)]^{2+}$ (Table 1), probably via. Eqs. (1)–(4), no clear evidence for the generation of the complex with the ($Ru^{IV}=O$) moiety could be obtained in the electrochemical oxidation. Various efforts at the electrochemical generation of the ($Ru^{IV}=O$) moiety in the complex of $n=2$, *cis*-$[Ru(NO_2)X(bpy)_2]^r$ (X=Cl, py) were also unsuccessful.

Differences between the chemical and electrochemical observations primarily come from the ligand nature of the aqua moiety as a spectator ligand; under the chemical conditions (a basic aqueous media), releasing a proton of the aqua ligand is facilitated to give the hydroxo moiety [20,21]. The process then results in the formation of the $(Ru^{IV}=O)^{2-}$ or $(Ru^{III}-O-Ru^{III})^{4+}$ moiety (Eq. (9) or (10)), prior to the isomerization of the nitro ligand. Such a reaction cannot be anticipated in the electrochemical oxidation using CH_3CN solvent. The formation of the chemical oxidation species which still have the nitro ligand, $[Ru^{IV}(O)(NO_2)(py)_2(bpy)]^+$ and $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$, suggests that the existence of 2,2′-bipyridine as the spectator ligand acts to stabilize the bonding mode of nitro coordination. We assume that, once the O^{2-} moiety is formed, it may act to prevent isomerization from occurring, but no evidence is available yet.

Further electrochemical one-electron oxidation is feasible for $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$ [17]. Actually, we could also isolate the one-electron oxidation species, $[Ru^{III,IV}{}_2O(NO_2)_2(bpy)_4]^{3+}$, using Ce^{4+} as an oxidant (see Section 2). A nitro bonding, rather than a nitrito one, was retained in the μ-oxo complex of Ru(III)–Ru(IV), according to IR spectral measurements [22]. More chemical oxidation was possible in an aqueous solution of $[Ru^{III,III}{}_2O(NO_2)_2(bpy)_4]^{2+}$ using Ce^{4+} by heating, but the nitro ligands were liberated to give a product which was tentatively identified as $[Ru^{VI}(O)_2(bpy)_2]^{2+}$ [23].

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