Successive Chemical Reactions Accompanying a One-Electron Oxidation of a $\{MNO\}^6$-Type Nitrosyl Complex, Pentachloro(nitrosyl)ruthenate(2−), and a Characterization of the Product Species

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A one-electron oxidation species of the title complex, $[Ru(NO)Cl_5]^-$ ($\{RuNO\}^5$-type nitrosyl complex), converted into *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ ($\{RuNO\}^6$-type nitrosyl complex) at low temperature (5 °C) in the dark. The product species could be isolated and characterized. An X-ray structure determination showed a remarkably short N–O bond distance of the Ru–NO moiety: ℓ(N–O)=0.998 Å, ℓ(Ru–N)=1.787(5) Å, ∠Ru–N–O=175.1(6)°. Under room light at 25 °C, the complex underwent a facile nitrosyl photoelimination to give *trans*-$[RuCl_4(CH_3CN)_2]^-$, the structure of which was also established. During the course of the reactions, two other unidentified species were confirmed to exist by cyclic voltammetry.

Although reactions which take place by the reduction of a coordinated nitrosyl in $\{MNO\}^6$-type complexes have been investigated by many researchers for a long time,[1,2] an example of a reaction which proceeds accompanied by oxidation is rare. Recently, the oxidation of $[M(NO)Cl_5]^{2-}$ (M=Os, Ru) has been achieved by several authors; in such cases the original $\{MNO\}^6$-type complex is changed to a $\{MNO\}^5$-type complex.[3] They reported that the generated one-electron oxidation species could be isolated as $(Et_4N)[Os(NO)Cl_5]$ in the osmium case,[3b,3c] while isolation of the corresponding ruthenium species was unsuccessful, due to a chemical instability.[3a] We have been interested in the type of reactivity observed in the one-electron oxidation species of $[Ru(NO)Cl_5]^{2-}$, pentachloro(nitrosyl)ruthenate(1−) ($[Ru(NO)Cl_5]^-$), because we have found in a separate study that an unexpected reaction occurred when $[Ru(NO)(py)_4(X)]^{2+}$ (X=Cl, OH) was oxidized.[4] In the present work, we investigated the reactivity in CH_3CN of $[Ru(NO)Cl_5]^-$ ($\{RuNO\}^5$-type complex): The reaction processes were monitored by cyclic voltammetry, UV-vis, and solution IR techniques. Authentic samples of the products species were also synthesized and their molecular structures were confirmed by an X-ray structure determination in order to establish the reaction paths. The chemical oxidation of $[Ru(NO)Cl_5]^{2-}$ using KIO_4 as the oxidizing agent has been reported, without any isolatable product.[5]

Experimental

Measurements. The IR spectra were recorded on a Perkin–Elmer FT-1650 IR Spectrophotometer using KBr (solid IR) or CH_3CN (solution IR). UV and visible absorption spectra were recorded with a Hitachi U-3210 spectrophotometer. Electrochemical measurements were carried out as described previously.[4] ESR spectra were obtained in frozen solutions at 123 K with quartz tubes in a JEOL-JES-RE3X spectrometer operating at the X-band frequency.

Materials. Tetrabutylammonium pentachloronitrosylruthenate(2−) was prepared according to a modified method of a reference,[6] using tetrabutylammonium chloride as a precipitant. The crude product obtained was purified by column chromatography (Al_2O_3–CH_3CN). Other reagents were purchased with the highest purity available and were used without purification. The following two materials were obtained as authentic samples of the products species in the conversion reaction of $[Ru(NO)Cl_5]^-$ ($\{RuNO\}^5$-type complex).

***cis*-$(Bu_4N)[Ru(NO)Cl_4(CH_3CN)]$.** All of the procedures were carried out in the dark, unless otherwise noted. To a CH_3CN solution of $(Bu_4N)_2[Ru(NO)Cl_5]$ (0.1 g/40 cm^3), which was cooled to 5 °C, were added PbO_2 (0.1 g) along with CF_3COOH (1 cm^3). The solution color changed immediately from purple to blue, due to the formation of $[Ru(NO)Cl_5]^-$.[3a] The unreacted PbO_2 was removed by a piece of filter paper under argon. The resultant solution was then allowed to stand at room temperature for one day. The color of the solution changed from blue to a pale brown during this time. After the solution had been allowed to stand for several more days, the solution volume was reduced to 5 cm^3 using a rotary evaporator. Adding ether to the solution precipitated a pale brown material. This was collected by filteration, washed with ether, and air dried. Yield; 83% (65 mg). Anal. Found: C, 27.06; N, 9.52; H, 5.25%. Calcd for $RuCl_4ON_3C_{18}H_{39}$: C, 27.03; N, 9.46; H, 5.23%.

***trans*-$(Bu_4N)[RuCl_4(CH_3CN)_2]$.** According to the procedure which gave the authentic sample of *cis*-$(Bu_4N)[Ru(NO)Cl_4(CH_3CN)]$, a pale brown solution containing *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ was obtained. The solution was allowed to stand at 22—26 °C under room light for 5 d. A thus obtained yellow solution was purified by column chromatography (Al_2O_3–CH_3CN). The addition of ether to the purified solution gave a yellow product, which was collected by filtration, washed with ether, and dried in vacuo. Yield; 58% (46 mg). Anal. Found: C, 42.00; N, 7.35; H, 7.48%. Calcd for $RuCl_4N_3C_{20}H_{42}$: C, 42.32; N, 7.41; H, 7.47%. The complex has been prepared by an alternative procedure.[7)]

Monitoring the Progress of the Decomposition Reaction of $[Ru(NO)Cl_5]^-$. A CH_3CN solution containing $(Bu_4N)_2[Ru(NO)Cl_5]$ (1.0 mmol dm^{-3}) was electrolyzed to give a one-electron oxidation species, $[Ru(NO)Cl_5]^-$, under 5 °C in the dark, using a Huso coulometer (Model 343B). The decomposition reaction of the electrochemically-generated one-electron oxidation species was initiated when the solution was allowed to stand at 22—26 °C in the dark. The progress of the reactions was monitored by cyclic voltammetry. IR, UV-vis, and ESR spectra were also measured on aliquots of the solution containing the electrochemically-generated $[Ru(NO)Cl_5]^-$ under the same conditions.

X-Ray Crystallographic Studies. The crystallographic data of both *cis*-$(Et_4N)[Ru(NO)Cl_4(CH_3CN)]$ and *trans*-$(Et_4N)[RuCl_4(CH_3CN)_2]$ are summarized in Table 1. The reflections of an X-ray analysis were collected by the ω–2θ scan technique ($2\theta<59.9°$) on a Enraf–Nonius automated four-circle X-ray diffractometer with graphite monochromatized Mo $K\alpha$ radiation (0.71068 Å). All of the calculations were carried out on a Silicon graphics Indigo Computor system using the TEXSAN program. The structures of *cis*-$(Et_4N)[Ru(NO)Cl_4(CH_3CN)]$ were solved by a direct method, and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and induced in structure factor calculations. The final cycle of the full-matrix least-squares refinements was based on 2816 observed reflections ($|F|>3.00\sigma(|F|)$) and 172 variable parameters. The structures of *trans*-$(Et_4N)[RuCl_4(CH_3CN)_2]$ were solved by heavy-atom Patterson methods, and were expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and induced in structure factor calculations. The final cycle of full-matrix least-squares refinements was based on 2046 observed reflections ($|F|>3.00\sigma(|F|)$) and 179 variable parameters. The data were corrected for Lorentz and polarization factors. An empirical absorption correction using the program DIFABS[8)] was applied; this resulted in transmission factors ranging from 0.83 to 1.14 (for *cis*-$(Et_4N)[Ru(NO)Cl_4(CH_3CN)]$) and from 0.91 to 1.05 (for *trans*-$(Et_4N)[RuCl_4(CH_3CN)_2]$). The final atomic coordinates are listed in Tables 2 and 3.

Tables of the atomic coordinates, thermal parameters, bond lengths, and angles for the complexes have been deposited as Document No. 68050 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Schematic Description on Successive Conversion Reactions of a One-Electron Oxidation Species, $[Ru(NO)Cl_5]^-$. The scheme shown in

Table 1. Crystallographic Data for **3** and **4**

Parameter	*cis*-$(Et_4N)[Ru(NO)Cl_4(CH_3CN)]$ (**3**)	*trans*-$(Et_4N)[RuCl_4(CH_3CN)_2]$ (**4**)
Formula	$RuCl_4ON_3C_{10}H_{23}$	$RuCl_4N_3C_{12}H_{26}$
MW	444.19	455.24
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc
a/Å	15.595(2)	19.572(3)
b/Å	7.719(2)	7.6688(9)
c/Å	15.748(2)	14.115(2)
β/°	104.21(1)	111.16(1)
V/Å^3	1837.8(5)	1975.7(4)
Z	4	4
D_c/g cm^{-3}	1.605	1.530
μ(Mo $K\alpha$)/cm^{-1}	14.30	13.29
F(000)	896.00	924.00
Scan mode	ω–2θ($2\theta\leq60°$)	ω–2θ($2\theta\leq60°$)
Scan width	$0.95+0.35\tan\theta$	$0.80+0.35\tan\theta$
No. of reflections collected	5892	6325
No. of reflections with $\lvert F\rvert\geq3\sigma(\lvert F\rvert)$	2816	2046
R[a)]	0.042	0.027
R_w[b)]	0.037	0.027

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

Table 2. Atomic Coordinates and B_{iso}/B_{eq} for *cis*-$(Et_4N)[Ru(NO)Cl_4(CH_3CN)]$ (**3**)

Atom	x	y	z	B_{eq}
Ru	0.55102(3)	0.23182(5)	0.31988(3)	2.914(8)
Cl1	0.58219(9)	0.1603(2)	0.18592(8)	4.17(3)
Cl2	0.69617(9)	0.1458(2)	0.39330(9)	3.94(3)
Cl3	0.41029(9)	0.3323(2)	0.24148(9)	4.10(3)
Cl4	0.4989(1)	−0.0472(2)	0.3299(1)	5.06(4)
O1	0.5103(3)	0.3072(7)	0.4783(3)	7.0(1)
N1	0.5265(3)	0.2865(7)	0.4216(3)	4.1(1)
N2	0.6010(3)	0.4715(5)	0.3027(3)	3.6(1)
N3	0.1978(3)	0.3436(5)	0.4286(3)	3.21(9)
C1	0.6322(4)	0.5929(7)	0.2858(3)	3.7(1)
C2	0.6737(4)	0.7479(7)	0.2624(4)	4.7(1)
C3	0.1884(4)	0.4524(7)	0.5055(3)	4.0(1)
C4	0.1129(4)	0.2470(8)	0.3889(3)	4.6(1)
C5	0.2748(3)	0.2227(8)	0.4629(4)	4.3(1)
C6	0.2154(4)	0.4559(7)	0.3550(3)	3.9(1)
C7	0.1177(4)	0.5893(8)	0.4843(4)	4.8(2)
C8	0.0832(4)	0.1213(9)	0.4511(4)	6.3(2)
C9	0.2943(4)	0.0956(8)	0.3977(4)	5.6(2)
C10	0.2936(4)	0.5764(8)	0.3819(4)	5.1(2)

Table 3. Atomic Coordinates and B_{iso}/B_{eq} for *trans*-$(Et_4N)[RuCl_4(CH_3CN)_2]$ (**4**)

Atom	x	y	z	B_{eq}
Ru	0.0016	0.2505(3)	0.0013	2.340(5)
Cl1	0.0951(1)	0.1176(4)	0.1410(2)	3.22(5)
Cl2	0.0923(1)	0.3824(4)	−0.0458(2)	3.64(5)
Cl3	−0.0899(1)	0.3779(4)	−0.1360(2)	3.52(5)
Cl4	−0.0901(1)	0.1213(4)	0.0505(2)	3.60(5)
N1	0.0034(4)	0.460(1)	0.0842(6)	3.3(2)
N2	0.0042(4)	0.038(1)	−0.0816(6)	2.7(1)
N3	0.7555(6)	0.1153(5)	0.2452(8)	2.36(8)
C1	0.0000(5)	0.574(2)	0.1250(7)	4.2(2)
C2	0.0052(4)	−0.0876(9)	−0.1280(5)	1.8(1)
C3	−0.0029(5)	0.747(1)	0.1866(6)	3.1(1)
C4	0.0061(6)	−0.228(2)	−0.1832(9)	5.6(3)
C5	0.6961(5)	0.006(1)	0.2660(7)	3.2(2)
C6	0.7911(6)	0.230(1)	0.3407(8)	3.7(2)
C7	0.8091(4)	0.003(1)	0.2241(7)	3.4(2)
C8	0.7080(6)	0.224(2)	0.1578(8)	4.4(2)
C9	0.7232(6)	−0.124(2)	0.3633(8)	4.4(2)
C10	0.7529(7)	0.352(2)	0.3856(9)	5.2(2)
C11	0.7768(6)	−0.125(2)	0.1508(7)	3.9(2)
C12	0.7617(6)	0.355(2)	0.1340(8)	4.7(2)

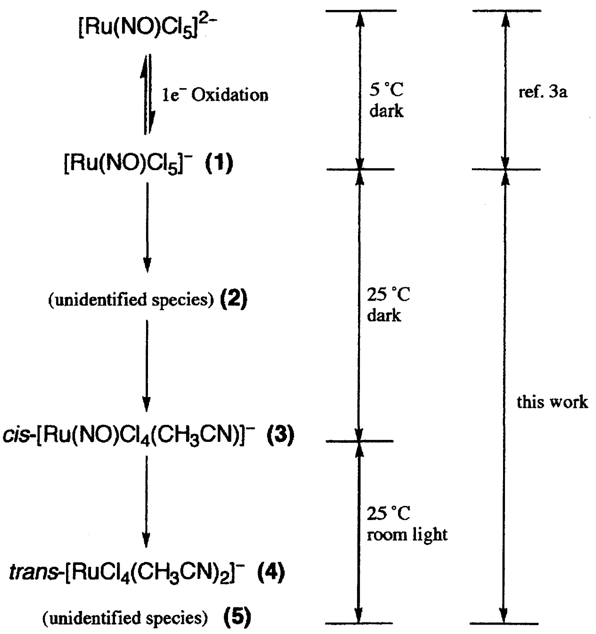


Fig. 1. Scheme for the conversion processes of electrochemically-generated $[Ru(NO)Cl_5]^-$ in CH_3CN.

Fig. 1 gives the main reaction sequences of the successive chemical reaction of a one-electron oxidation species of $[Ru(NO)Cl_5]^{2-}$. This scheme involves unidentified products, in addition to the characterized products species. Evidence for the reaction sequences is given by cyclic voltammetry, along with an X-ray structure determination of the authentic samples, which greatly aids in elucidating the reaction paths.

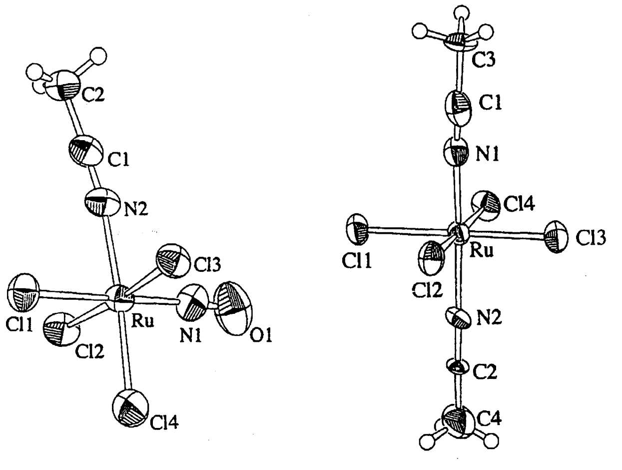
In the dark at 5 °C, $[Ru(NO)Cl_5]^{2-}$ in CH_3CN can be oxidized to give $[Ru(NO)Cl_5]^-$ (**1**), which belongs to an $\{RuNO\}^5$-type nitrosyl complex of Ru(III) with an NO^+ moiety.[3a)] We found that the one-electron oxidation species was chemically reactive, and gradually changed to form *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**), via the formation of an unidentified species **2**. The product species **3** is the same $\{RuNO\}^6$-type nitrosyl complex as the original nitrosyl complex, $[Ru(NO)Cl_5]^{2-}$, that has been formally characterized to contain the Ru(II) and NO^+ moieties.[1)] While **3** is the final product in the dark at 5 °C, further reactions occur when *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**) is exposed to room light at 25 °C, and at least two new species (**4** and **5**) were found to form. Although the **4** species was identified as *trans*-$[RuCl_4(CH_3CN)_2]^-$, the identity of the other decomposition species (**5**) is unclear.

Isolation and Identification of Authentic Samples of Products, 3 and 4. In addition to the electrochemically generated species **1**, authentic samples of the two species, **3** and **4**, could be obtained; however, the existence of two other species, **2** and **5**, were evidenced only be electrochemical measurements (by the cyclic voltammetry). Since the one-electron oxidation species, $[Ru(NO)Cl_5]^-$, has been investigated by V. T. Coombe et al,[3a)] without any description concerning the reactivity, our present attention was focused mainly on the conversion reaction of the oxidation species. Some characteristic data of *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**) and *trans*-$[RuCl_4(CH_3CN)_2]^-$ (**4**) used for the identification are summarized in Table 4. X-Ray structure studies definitely support the present characterization. ORTEP drawings are shown in Fig. 2. Some selected bond lengths and angles are listed in Tables 5 and 6. The *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**) anion has the *cis*-octahedral coordination geometry, with the N-bonded CH_3CN ligand and three Cl li-

Table 4. Data for Characterization.

Complexes	CV[d)]			IR[f)]			UV-vis[i)]	ESR[k)]
				νNO		νCN	ε[j)]	
	E_{pa}	E_{pc}	($E_{1/2}$)	Solid[g)]	Solution[h)]	Solid[g)]		
$[Ru(NO)Cl_5]^{2-}$ [a)]	1.22	1.16	1.19	1833 (s)	1850 (s)		520 (52)	
(**1**) $[Ru(NO)Cl_5]^-$	1.22	1.16	1.19		1926 (s)		652 391 290	2.12 2.10 2.06
($[Ru(NO)Cl_5]^-$)[b)]	1.53[e)]				1920 (s)		690 (sh) 655 (4300) 398 (2100) 294 (10900)	2.16 2.11 2.06
(**2**) (Unidentified)	0.80							2.02
(**3**) *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$	1.65				1870 (s)		480 264	
(**3**) Authentic sample[c)]	1.65			1894 (s)	1872 (s)	2331 (w)	480 (56.8)	
(**4**) *trans*-$[RuCl_4(CH_3CN)_2]^-$			1.13				475 410 397 (sh) 302	
(**4**) Authentic sample[c)]			1.10			2301 (w)	475 (810) 411 (5120) 302 (1560)	
(**5**) (Unidentified)			0.87					

a) Bu_4N salt. b) From Ref. 3b. c) Et_4N salt. d) V vs. Ag|$AgNO_3$ in CH_3CN. e) V vs. Ag|AgCl in CH_2Cl_2 at 293 K. f) cm^{-1}. (s): strong, (w): weak. g) KBr disk. h) In CH_3CN. i) nm in CH_3CN. j) $mol^{-1}\,dm^3cm^{-1}$. k) g value in CH_3CN at 123 K.



(3) **(4)**

Fig. 2. ORTEPs of *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**) and *trans*-$[RuCl_4(CH_3CN)_2]^-$ (**4**).

Table 5. Selected Bond Distances (Å) and Angles (°) for *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**)

Bond distances			
Ru–N1	1.787(5)	Ru–Cl4	2.321(2)
Ru–N2	2.051(4)	N1–O1	0.998(5)
Ru–Cl1	2.344(1)	N2–C1	1.118(6)
Ru–Cl2	2.370(1)	C1–C2	1.450(7)
Ru–Cl3	2.369(1)		
Bond angles			
Cl1–Ru–Cl2	89.36(5)	Ru–N2–C1	171.5(5)
Cl1–Ru–Cl4	89.78(6)	Cl1–Ru–Cl3	88.76(5)
Cl1–Ru–N2	85.7(1)	Cl2–Ru–N1	91.0(1)
Cl2–Ru–Cl4	90.90(5)	Cl3–Ru–Cl4	92.51(6)
Cl2–Ru–N2	88.2(1)	Cl3–Ru–N2	88.2(1)
Cl3–Ru–N1	90.9(1)	Ru–N1–O1	175.1(6)
N1–Ru–N2	94.4(2)	N2–C1–C2	178.6(6)
N1–Ru–N2	94.4(2)	N2–C1–C2	178.6(6)

gands in equatorial positions and with both Cl and NO in axial positions. Various structural investigations have been made for the $\{RuNO\}^6$-type nitrosylruthenium complexes,[9)] in which an important feature has been found in the Ru–N–O moiety. The following are the data reported for the $\{RuNO\}^6$-type nitrosyl complex, $[Ru(NO)Cl_5]^{2-}$,[9a)] which was selected here as a representative of the related complexes: 1.112(7) Å for ℓ(N–O), 1.747(6) Å for ℓ(Ru–N), 176.8(9)° for ∠Ru–N–O, 2.359(2) Å for ℓ(Ru–*trans*-Cl), 2.372 Å for ℓ(Ru–*cis*-Cl (average of four values)). The N–O bond distance observed for *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**) was 0.998(5) Å; this is abnormally short: it appears to be the shortest one reported so far for the $\{RuNO\}^6$-type nitrosyl ruthenium complexes,[9a)] while a rather long Ru–N(nitrosyl) distance (1.787(5) Å) is found. The

Table 6. Selected Bond Distances (Å) and Angles (°) for *trans*-$[RuCl_4(CH_3CN)_2]^-$ (**4**)

Bond distances			
Ru–Cl1	2.382(3)	Ru–Cl2	2.338(3)
Ru–Cl3	2.327(3)	Ru–Cl4	2.364(3)
Ru–N1	1.979(10)	Ru–N2	2.020(9)
N1–C1	1.06(1)	N2–C2	1.17(1)
C1–C3	1.60(2)	C2–C4	1.33(1)
Bond angles			
Cl1–Ru–Cl2	89.16(9)	Cl1–Ru–N1	90.8(2)
Cl1–Ru–Cl4	90.9(1)	Cl2–Ru–Cl3	90.9(1)
Cl1–Ru–N2	87.8(2)	Cl2–Ru–N1	87.9(3)
Cl2–Ru–N2	90.3(3)	Cl3–Ru–Cl4	89.03(9)
Cl3–Ru–N1	89.8(2)	Cl3–Ru–N2	91.7(2)
Cl4–Ru–N1	91.1(3)	Cl4–Ru–N2	90.7(3)
Ru–N2–C2	178.5(8)	Ru–N1–C1	175.5(9)
N2–C2–C4	178(1)	N1–C1–C3	178(1)

sum of N–O and Ru–N lengths was 2.785 Å). The RuNO angle is approximately linear, 175.1(6)°; this is a typical feature for the $\{MNO\}^6$-type nitrosyl complexes.[9)]

The Ru–Cl(1) distance (2.344(1) Å) is also shorter than either the Ru–Cl(3) distance (2.369 Å) or the Ru–Cl(2) (2.370 Å) distance. When a nitrosyl acts as a strong π-acceptor ligand to a metal ion, a considerable shortening of the bond between the metal and Cl atom trans to the nitrosyl has been observed;[9a)] such a trans-strengthening effect appears to be operating on the Ru–Cl(1) atom. Another short bond distance was found in Ru–Cl(4) (2.321 Å); this is shorter than the Ru–Cl(1) distance (2.344 Å), which exists at the trans position of the nitrosyl. The unusual data can be explained if we assume that some trans-shortening effect due to the coordinated CH_3CN is operating. The nitrogen bound CH_3CN has been reported to act effectively as a π acid ligand,[10)] which may affect the Ru–Cl(4) bonding to bring about such a trans-strengthening effect.

The **4** anion also has a trans-octahedral coordination geometry, with four Cl ligands in equatorial positions and with two CH_3CN in axial positions.

Successive Chemical Reactions of $[Ru(NO)Cl_5]^-$ ($\{RuNO\}^5$-Type Complex). i) Electrochemical Behavior of $(Bu_4N)_2[Ru(NO)Cl_5]$ ($\{RuNO\}^6$-Type Complex). Although the electrochemical behavior of $[Ru(NO)Cl_5]^{2-}$ has been reported,[3a)] we investigated it again by both cyclic voltammetry and coulometry under our conditions. As Fig. 3 shows, a cyclic voltammogram (CV) of the original $[Ru(NO)Cl_5]^{2-}$ at 25 °C in the dark exhibits a well-defined anodic wave, together with the coupled cathodic wave on the reverse scan ($E_{1/2}$=1.19 V vs. Ag|AgNO$_3$. E_{pa}=1.22 V, E_{pc}=1.16 V), within the potential region expected for $Ru^{2+/3+}$. The electron transfer process is diffusion-controlled, with $ip/v^{1/2}$ being constant over the range of the scan rate used. The peak current ratio is nearly unity, and the potential separation, $\Delta E = E_{pa} - E_{pc}$=60 mV, of the anodic and cathodic waves at all scannings measured corresponds to the expected value for a one-electron reversible electrochemical couple. A one-electron transfer sequence of the wave was also indicated by analyzing a normal pulse voltammogram. Such electrochemical features are essentially the same as those reported by Coombe et al.[3a)] In addition to the anodic wave, an irreversible cathodic wave appeared at −1.44 V in the reductive scanning. The wave is understood to be due to a $[Ru(NO)Cl_5]^{2-/3-}$ redox couple; the site of the reduction of the $\{RuNO\}^6$-type complex is attributable to the nitrosyl moiety.[11)]

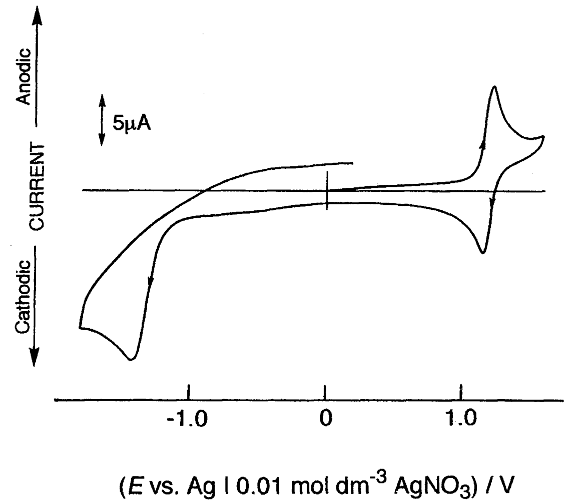


Fig. 3. Typical cyclic voltammogram of $(Bu_4N)_2[Ru(NO)Cl_5]$ (1.0×10^{-3} mol dm^{-3}) in CH_3CN at 25 °C (stationary Pt electrode, Et_4NClO_4 (0.1 mol dm^{-3})).

Although the above CV experiment exhibited a reversible anodic wave, an oxidative controlled-potential electrolysis carried out at 25 °C under "room light" gave a complicated result: the one-electron oxidation is followed by several rapid chemical reactions; the reaction progress was still unexplainable. However, the same electrolysis carried out under low temperature (5 °C) in the "dark" exhibited simple cyclic voltammograms; the electrochemically generated one-electron oxidation species, $[Ru(NO)Cl_5]^-$ (**1**), could be retained without any change in the cyclic voltammograms, for at least 10 h. Such findings enable us to trace the thermally-induced decomposition of $[Ru(NO)Cl_5]^-$ (**1**) at 25 °C in the "dark", using the solution electrolysed at 5 °C in the "dark".

ii) Monitoring the Decomposition Process of the Electrochemically Generated $[Ru(NO)Cl_5]^-$. Figure 4 shows the CV monitoring at 25 °C in the dark. The one-electron oxidation species, $[Ru(NO)Cl_5]^-$ (**1**), was found to convert into two species (**2** and **3**). This was indicated by the appearance of two new waves at 0.80 V (E_{pa}) for **2** and 1.65 V (E_{pa}) for **3**. The latter species (**3**) could be identified as *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ using the authentic sample. Both waves, **2** and **3**, developed at the expense of the original

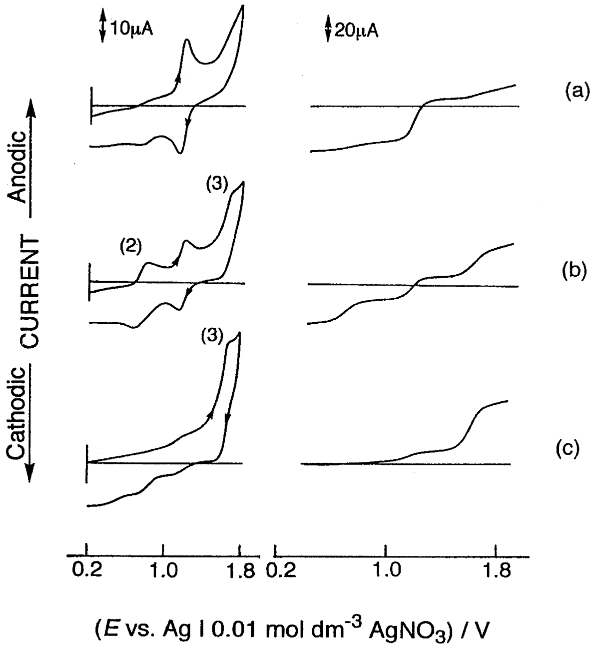


Fig. 4. Changes in both cyclic and hydrodynamic voltammograms of electrochemically-generated $[Ru(NO)Cl_5]^-$ (**1**), when the species is allowed to stand at 25 °C in the dark: (a) just after $[Ru(NO)Cl_5]^-$ (**1**) was generated electrochemically at 5 °C in the dark; (b) after 3 h; (c) after 15 h.

redox wave (1.19 V ($E_{1/2}$)) until about 3 h later, when the test solution containing $[Ru(NO)Cl_5]^-$ (**1**) was allowed to stand. The wave due to **2** (0.80 V (E_{pa})), however, gradually diminished when the solution was kept longer under the same conditions, while wave **3** developed continuously. In the final stage, 15 h later, only the wave due to **3** remained.

The **2** species did not give any evidence for the characterization, though the paramagnetic property (g=2.02) of the species was indicated by ESR measurements. The paramagnetic nature of $[Ru(NO)Cl_5]^-$ (g_1=2.12, g_2=2.10, g_3=2.06) was also confirmed. All $\{RuNO\}^6$-type nitrosyl complexes, including both $[Ru(NO)Cl_5]^{2-}$ and *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**), are silent species in ESR spectroscopy. Presently, we could not obtain any proof to assign species **2** as *trans*-$[Ru(NO)Cl_4(CH_3CN)]^-$, however it is the most probable precursor species of *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**); the assignment is difficult because of a relatively large difference in the redox potential data of the complexes (see Table 4).

The present work shows that a chloro ligand loss occurs in $[Ru(NO)Cl_5]^-$ (**1**) to give *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**). This was a rather unexpected reaction in the steric configuration of the product. Several kinetic studies concerning the chloro substitution of $[Ru(NO)Cl_5]^{2-}$ have been reported,[12] though no definitive work has yet appeared.[13] In general, a chloro ligand trans to the nitrosyl in the $\{RuNO\}^6$-type nitrosyl complexes has been believed to be labile; thus, *trans*-$[Ru(NO)Cl_4(solv)]^-$ was expected to form as a chloro ligand dissociation product. Recently, *cis*-$Ag_2[Ru(NO)Cl_4(OH)]$ has been isolated by Ishimori et al. from a component of the hydrolysis mixture of $[Ru(NO)Cl_5]^{2-}$;[14] the hydrolysis mixture also contained *trans*-$[Ru(NO)Cl_4(H_2O)]^-$ and $[Ru(NO)Cl_3(H_2O)_2]$. We assume that a direct comparison between the observation on the present chloro substitution and those of the reported study is difficult, since our result, which gives *cis*-$[Ru(NO)Cl_4(solv)]^-$, is initiated by participating in one-electron oxidation.

iii) Photochemical Influence on the Conversion Reaction of $[Ru(NO)Cl_5]^-$. Although **3** species, *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ in CH_3CN, was stable indefinitely under room temperature in the dark, decomposition occurred when the species was exposed to room light at 25 °C. As Fig. 5 shows, monitoring the cyclic voltammograms of *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**) under the conditions showed that two new waves (due to **4** and **5**) appeared at 1.10 V ($E_{1/2}$, for **4**) and 0.87 V ($E_{1/2}$, for **5**), and then they developed at the expense of the wave at 1.65 V, due to **3**. The two waves (due to **4** and **5**) were found to exist for at least several hours without any further change. We could identify species **4** as being *trans*-$[RuCl_4(CH_3CN)_2]^-$ by an X-ray structure determination using a authentic sample (see Fig. 2).

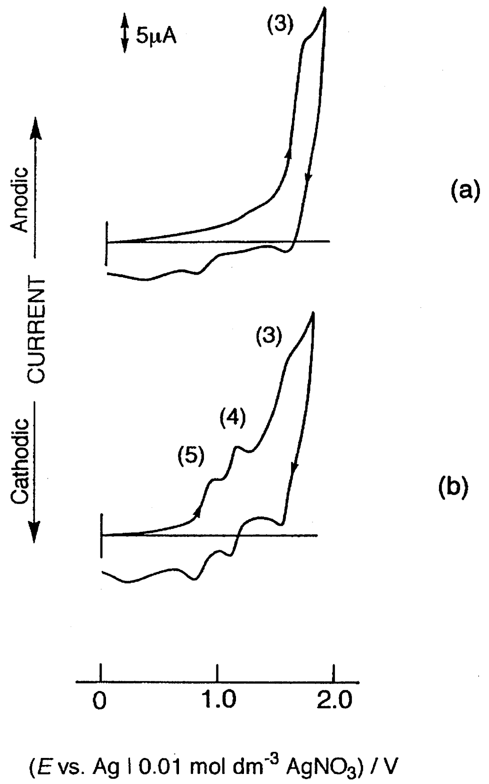


Fig. 5. Changes in the cyclic voltammograms of *cis*-$[Ru(NO)Cl_4(CH_3CN)]^-$ (**3**), when the species is allowed to stand at 25 °C under room light: (a) corresponds to (c) in Fig. 4; (b) after 7 d.

The formation of *trans*-$[\mathrm{RuCl_4(CH_3CN)_2}]^-$ (**4**) under the conditions suggests that the nitrosyl moiety in *cis*-$[\mathrm{Ru(NO)Cl_4(CH_3CN)}]^-$ (**3**) is eliminated more easily than that of $[\mathrm{Ru(NO)X_5}]^{2-}$ (X=Cl, Br, I):[15] a photochemical investigation of $[\mathrm{Ru(NO)X_5}]^{2-}$, which generates $[\mathrm{RuX_5(solv)}]^{3-}$, showed that a relatively higher energy irradiation is required for the elimination. A steric rearrangement, from cis to trans, also occurs in this stage to give *trans*-$[\mathrm{RuCl_4(CH_3CN)_2}]^-$. Attempts to identify species **5** were unsuccessful. The fate of the released NO ligand is also presently unknown.

iv) Monitoring by Solution IR and UV-vis Spectrometries. Monitoring the solution IR of the one-electron oxidation species, $[\mathrm{Ru(NO)Cl_5}]^-$ (**1**), gave some evidence for the formation process of *cis*-$[\mathrm{Ru(NO)Cl_4(CH_3CN)}]^-$ (**3**), but did not give anything for species **2**. At a stage before $[\mathrm{Ru(NO)Cl_5}]^{2-}$ underwent oxidation, the species showed a strong IR band, due to ν(NO), at 1850 $\mathrm{cm^{-1}}$. When $[\mathrm{Ru(NO)Cl_5}]^{2-}$ underwent electrochemical oxidation at 5 °C in the dark, the resultant species, $[\mathrm{Ru(NO)Cl_5}]^-$ (**1**), showed a strong absorption band at 1926 $\mathrm{cm^{-1}}$, in addition to a small band at 1870 $\mathrm{cm^{-1}}$. We assigned the former band as being due to ν(NO) of $[\mathrm{Ru(NO)Cl_5}]^-$ (**1**), and the latter to that of **3** (see below). The intensities of both bands gradually changed when a solution containing $[\mathrm{Ru(NO)Cl_5}]^-$ (**1**) was allowed to stand under the conditions described in Fig. 1: the band at 1870 $\mathrm{cm^{-1}}$ increased as the band at 1926 $\mathrm{cm^{-1}}$ decreased. Finally (nearly 30 min later), only the band at 1870 $\mathrm{cm^{-1}}$ remained. This is the identical energy region to the ν(NO) band that is observed in an authentic sample of **3**.

We also traced the UV-vis spectral change of the decomposition reaction. The electrochemically-generated green $\mathrm{CH_3CN}$ solution of $[\mathrm{Ru(NO)Cl_5}]^-$ (**1**) shows three medium intensity bands at 652, 391, and 290 nm. The intensities of all of three bands decreased during the course of the decomposition; two new bands appeared at around 470—480 nm and 260 nm, instead of the bands at 652, 391, and 290 nm, and new bands developed later. At the stage when the decomposition reaction had completed (5 h), the resultant solution showed bands at 480 and 264 nm, which were the same spectra as that found in the authentic sample of **3**. No spectral evidence for **2** could be obtained.

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1) The notation $\{\mathrm{MNO}\}^6$ was introduced by J. H. Enemark and R. D. Feltham (*Coord. Chem. Rev.*, **13**, 339 (1974)). If the NO group is assumed to be bound as $\mathrm{NO^+}$ ion, then *n* corresponds to the number of d electrons on the metal. Thus the $\{\mathrm{RuNO}\}^6$-type nitrosyl complex contains a $(\mathrm{Ru^{II}NO^+})^{3+}$ moiety.

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