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Chemical Behavior of an Oxygen Ligand in the Reaction between Oxo Complex of Ru^{IV} and Alcohols to Give Both Hydroxo and Alkoxo Complexes of Ru^{III}

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Under mild conditions, *trans*-$[RuCl(O)(py)_4]^+$ in alcohols changes to an alkoxo complex, *trans*-$[RuCl(OR)(py)_4]^+$. The hydroxo complex, *trans*-$[RuCl(OH)(py)_4]^+$, which retains the reactive oxygen of the oxo complex, was found to exist as a precursor in the formation of the alkoxo complex. The reaction progress was traced by spectrometrical and ^{18}O-labelling experiments.

There has been growing interest in high-valence ruthenium complexes with a reactive oxygen ligand ($Ru^{IV}=O^{2-}$). This interest centers mainly on the chemical and electrochemical generation of the oxo ligand,[1–5] on structural and spectrochemical characterization of the moiety,[6–8] and on its reactivity, in particular as an oxygen-transfer agent.[9–13] We have reported a new synthetic route for an oxo complex of Ru^{IV}, *trans*-$[RuCl(O)(py)_4]^+$, which was prepared by the oxidation of a nitrosyl complex of Ru^{II}.[5,6] As an extension of this study, the chemical behavior of the ($Ru^{IV}=O^{2-}$) unit in the oxo complex toward alcohols (MeOH, EtOH, and *n*- and *i*-PrOH) was investigated. Such a study has not yet been reported, although Meyer et al. investigated a reaction of *cis*-$[Ru(O)(bpy)(trpy)]^{2+}$ (trpy: 2,2′:6′,2″-terpyridine) with *i*-PrOH containing large amounts of water from kinetic and mechanistic viewpoints.[10] They concluded that the reaction is initiated by a formation of the corresponding hydroxo complex of Ru^{III}, as an intermediate, which is the one-electron reduced species of the oxo complex of Ru^{IV}. Here, we report on synthetic evidence which proves the existence of the hydroxo complex of Ru^{III} as a precursor in the reaction of the oxo complex of Ru^{IV} with alcohols. Also reported is evidence that the reactivity of the ($Ru^{IV}=O^{2-}$) unit, as an oxidant toward alcohols, depends on the property of the oxo complex used for the reaction. Five new complexes were isolated as the reaction products between *trans*-$[RuCl(O)(py)_4]^+$ and the alcohols. Among the alkoxo complexes obtained here, the methoxo complex of Ru^{III} has already been reported in part.[5]

Experimental

Instruments and Reagents. IR spectra were measured on a Hitachi EPI G2 spectrometer. UV-vis spectra were recorded on a Hitachi 200-20 spectrometer. Magnetic moments were measured by the Gouy method. Elemental analyses were performed by the Sophia University Analytical Facility. Cyclic voltammetry and normal pulse voltammetry were carried out by using a Fuso Polarograph Model 321 with a stationary platinum disk electrode. $RuCl_3 \cdot nH_2O$ was purchased from Nippon Engelhardt. MeOH(Spectrosol), used for both synthetic and spectrometric studies was purchased from Wako Chemical Co. The CH_3CN, used for the electrochemical experiment, was purified by a procedure described in the literature.[5] All other chemicals were obtained as reagent grade and used without further purification. $H_2{}^{18}O$ (99.0%) was purchased from the Japan Radioisotope Association. Oxo complexes, *trans*-$[RuX(O)(py)_4]Y$ (X=Cl, Br; Y=ClO_4, PF_6), were prepared as starting materials of the present reactions by procedures described elsewhere.[5,13]

Isolation of Reaction Products. Chloro(hydroxo)tetrakis(pyridine)ruthenium(III) Hexafluorophosphate, $[RuCl(OH)(py)_4]PF_6$ (1A): $[RuCl(O)(py)_4]PF_6$ (100 mg) was dissolved in the mixed solution of MeOH–H_2O (15–15 cm^3). It was refluxed for 15 min., until the color changed from green to yellow. The solution was kept standing for 1—2 d at room temperature. The yellow crystals which appeared were collected, washed with ether, and dried in vacuo. Yield 70%. Found: C, 38.8; N, 9.0; H, 3.4%. Calcd for $C_{20}H_{21}ON_4ClPF_6Ru$: C, 39.1; N, 9.1; H, 3.4%.

Chloro(hydroxo)tetrakis(pyridine)ruthenium(III) Perchlorate, $[RuCl(OH)(py)_4]ClO_4$ (1B): This was prepared by the same procedure, using the corresponding oxo complex of perchlorate salt. Yield 60%. Found: C, 42.1; N, 9.8; H, 3.7%. Calcd for $C_{20}H_{21}N_4O_5Cl_2Ru$: C, 42.2; N, 9.8; H, 3.7%.

Chloro(methoxo)tetrakis(pyridine)ruthenium(III) Hexafluorophosphate, $[RuCl(OMe)(py)_4]PF_6$ (2A): Oxo complex (PF_6 salt 50 mg) was dissolved in methanol (25 cm^3), using a Erlenmeyer flask, and kept at room temperature for 2 d in the dark, until the solution color changed to greenish yellow. The volume of the solution was reduced to 5 cm^3 using a rotary evaporator to produce a red crystalline material. The product was filtered out, washed with acetone and then ether, and dried in vacuo. Yield 60%. Found: C, 40.0; H, 3.6; N, 8.8%. Calcd for $C_{21}H_{23}N_4OClPF_6Ru$: C, 40.1; H, 3.7; N, 8.9%.

Chloro(methoxo)tetrakis(pyridine)ruthenium(III) Perchlorate $[RuCl(OMe)(py)_4]ClO_4$ (2B): This was prepared by almost the same procedure as in 2A, using the corresponding perchlorate salt of the oxo complex. Found: C, 43.4; H,

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4.0; N, 9.6%. Calcd for $C_{21}H_{23}N_4O_5ClRu$: C, 43.4; H, 4.0; N, 9.6%. The corresponding bromo complex, $[RuBr(OMe)(py)_4]PF_6$, was obtained by the same procedure, using the bromo complex as a starting material. Found: C, 40.1; H, 3.6; N, 8.9%. Calcd for $C_{21}H_{23}N_4OBrPF_6Ru$: C, 40.2; H, 3.7; N, 8.9%.

Chloro(ethoxo)tetrakis(pyridine)ruthenium(III) Hexafluorophosphate $[RuCl(OEt)(py)_4]PF_6$ (3A): Oxo complex (PF_6 salt, 80 mg) was dissolved in EtOH (100 cm^3), using a Erlenmeyer flask, and kept at room temperature for 5—6 d in the dark. When the solution color changed from green to pale yellow, the volume of the solution was quickly reduced using a rotary evaporator. A small amount of red crystals deposited. Excess ether was added to the solution (total volume 80—100 cm^3); this was then kept in a refrigerator overnight. The product was filtered out, washed with a mixed solvent (EtOH–ether) and then ether, and dried in vacuo. Yield 50%. Found: C, 40.8; H, 3.9; N, 8.5%. Calcd for $C_{22}H_{25}N_4OPF_6ClRu$: C, 41.1; H, 3.9; N, 8.7%. The corresponding bromo complex, $[RuBr(OEt)(py)_4]PF_6$, was obtained by the procedure described above, using $[RuBr(O)(py)_4]PF_6$. Found: C, 38.3; H, 3.7; N, 8.2%. Calcd for $C_{22}H_{25}ON_4BrPF_6Ru$: C, 38.4; H, 3.7; N, 8.2%.

Chloro(propoxo)tetrakis(pyridine)ruthenium(III) Hexafluorophosphate, $[RuCl(OPr^n)(py)_4]PF_6$ (4): Oxo complex (PF_6 salt, 35 mg) was suspended in *n*-PrOH (50 cm^3) using a Erlenmeyer flask (50 cm^3). The suspension was stirred for one week at room temperature in the dark, until a homogeneous pale yellow solution was obtained. After the solution was filtered out, the filtrate was concentrated using a rotary evaporator. When a small amount of red crystals deposited, ether was added to the solution (total volume 50 cm^3); this was then kept in a refrigerator overnight. The red crystals were collected, washed with ether–EtOH and then ether, and dried in vacuo. Found: C, 42.4; H, 4.3; N, 8.3%. Calcd for $C_{23}H_{27}ON_4ClPF_6Ru$: C, 42.0; H, 4.1; N, 8.5%. Yield 40%. The corresponding bromo complex, $[RuBr(OPr^n)(py)_4]PF_6$, could be obtained by the same procedure, using the PF_6 salt of the bromo oxo complex. Found: C, 39.2; H, 4.0; N, 7.9%. Calcd for $C_{23}H_{27}ON_4BrPF_6Ru$: C, 39.4; H, 3.9; N, 8.0%.

Chloro(isopropoxo)tetrakis(pyridine)ruthenium(III) Hexafluorophosphate, $[RuCl(OPr^i)(py)_4]PF_6$ (5): The complex was prepared by almost the same procedure as that for 4. Yield 40%. Found: C, 41.8; H, 4.1; N, 8.3%. Calcd for $C_{23}H_{27}ON_4ClPF_6Ru$: C, 42.0; H, 4.1; N, 8.5%. All the alkoxo complexes were stored under argon to avoid hydrolysis (described later).

^{18}O Labelling. Complex 4 (8 mg) was dissolved in $H_2{}^{18}O$ (1 cm^3) containing a small amount of HPF_6; the solution was heated until a pale green solid ($[RuCl(^{18}OH)(py)_4]PF_6$) deposited. After removal of the solid, $(NH_4)_2Ce(NO_3)_6$ was added to the mother liquor, and the solution was gently warmed until its color changed to green (2—3 min), and then cooled down to room temperature. NH_4PF_6 (6 mg) was added until a green product ($[RuCl(^{18}O)(py)_4]PF_6$) appeared. Both products were collected by sintered-glass filters and washed by a mixed solvent of EtOH and ether and then by ether. The ^{18}O incorporation was found to be achieved almost completely, based on the relative intensity of the $\nu(^{18}OH)$ and $\nu(^{16}OH)$ in the hydroxo complex.

X-Ray Data Collection. Crystals (**1A** and **2B**) were used for the measurements without shaping. Crystal data are as follows. For **1A**: tetragonal, with space group $P4/ncc$, $a=25.937(4)$ Å, $c=14.469(1)$ Å, $V=9733(2)$ Å^3, $\mu(\text{Mo}\,K\alpha)=8.78$ cm^{-1}, F.W.=614.9, $Z=16$, $D_m=1.67$ g cm^{-3}, $D_x=1.68$ g cm^{-3}. For **2B**: monoclinic, $P2_1/n$, $a=22.311(3)$ Å, $b=13.546(2)$ Å, $c=8.091(1)$ Å, $\beta=95.89°$, $V=2432.4(6)$ Å^3, $\mu=8.91$ cm^{-1}, F.W.=583.4, $Z=4$, $D_m=1.58$ g cm^{-3}, $D_x=1.59$ g cm^{-3}. The reflections were collected by ω-scan technique ($2\theta<55°$ for **1A**, $2\theta<50°$ for **2B**) on a Rigaku AFC-6A automated four-circle diffractometer, with graphite monochromated Mo $K\alpha$ radiation (0.7107 Å). The 3123 (for **1A**) and 6154 (for **2B**) independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for a structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for the absorption. All the calculations were carried out in a HITAC M-200H computer at the Computer Center of the University of Tokyo, using a local version of UNICS.[14] The atomic scattering factors were taken from the Tables.[15]

Structure Determination. The structures were solved by a heavy-atom method. The positions of Ru and Cl atoms were obtained from a three-dimensional Patterson function, while the positions of all the non-hydrogen atoms were successively located by Fourier syntheses. In case of **2B**, all hydrogen atoms of both pyridine and methoxyl groups were found at reasonable positions on the final difference Fourier map; they were then included in the calculation, while those of **1A** were calculated and fixed, since only a few positions of hydrogen atoms were obtained.

Positions and thermal parameters of all other atoms were refined by a repeated block-diagonal least-squares method. The weighting scheme was $W=1/[\{\sigma(|F_o|)\}^2+(0.02\times|F_o|)^2]$. In the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R values ($R=\sum||F_o|-|F_c||/\sum|F_o|$) were 0.083 for **1A** and 0.040 for **2B**. The F_o-F_c data and the anisotropic temperature parameters are deposited as Document No. 8752 at the Office of the Editor of the Bulletin of the Chemicai Society of Japan.

Results and Discussion

Spectral Change Observed for *trans*-$[RuCl(O)(py)_4]^+$ in MeOH. A green methanol solution of *trans*-$[RuCl(O)(py)_4]PF_6$ changes gradually to yellow-orange while standing at room temperature. The reaction which gave the hydroxo complex of Ru^{III} was monitored by spectrophotometry; its progress can be conveniently divided into three steps (in Fig. 1). A freshly prepared methanol solution of the oxo complex exhibits a strong absorption band at 265 nm and a weak band at 690 nm. In the first stage of the reaction ([A] in Fig. 1), the intensity of the band at 265 nm slowly decreased as a new band appeared at 285 nm. The intensity of this new band developed as it moved to 296 nm (this took about 50 h). The weak band at 690 nm also decreased in intensity and was replaced by a weak band at 640 nm, which remained without remarkable changes in either wave length or intensity until the solution color changed to yellow.

In the second stage ([B]), the band at 296 nm shifted slightly to 300 nm, while its intensity decreased (60—70 h). Later (dotted line in [B]), two new bands appeared near 245 and 375 nm, with further decreasing of the intensity of the two bands at 265 and 300 nm. The presence of an isosbestic point could not be observed in any stage. When the experiment was attempted in a preparative scale, using the PF_6 salt of the oxo complex, the solution obtained in the first stage of the reaction gave a yellow product when the solution volume is reduced, while that of the second step gives red crystals. The yellow crystalline product could be isolated when the intensities of the two absorption bands at 265 and 296 nm became almost the same.

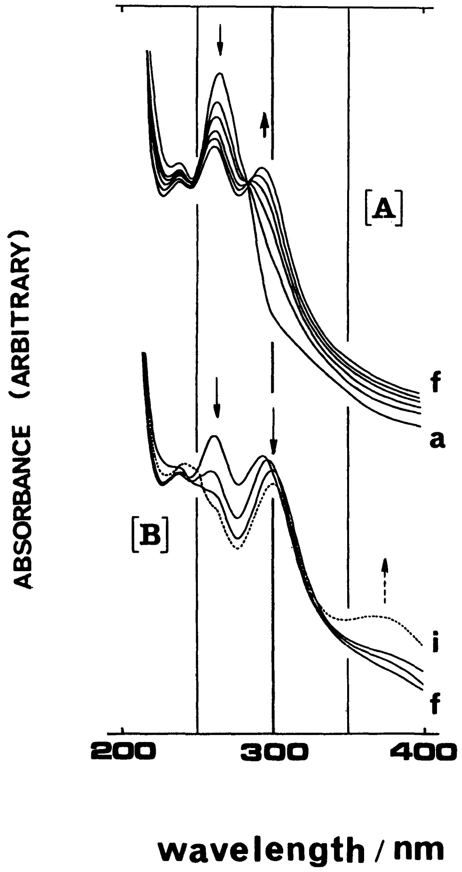

Fig. 1. UV spectral Change of $[RuCl(O)(py)_4]PF_6$ (6.5×10^{-5} mol dm^{-3}) in MeOH at room temperature (22 °C).
[A]: 1st step of the reaction, (a) immediately after, (b) 10 h, (c) 25 h, (d) 37 h, (e) 45 h, (f) 51 h. [B]: 2nd and 3rd (dotted line) steps, (f) 51 h, (g) 61 h, (h) 68 h, (i) 75 h. Arrows illustrate the direction of change of the peaks on subsequent scans.

The experimental conditions for the isolation of the yellow crystals are rigid, since it appears to be short-lived relative to the red one. The experimental data (analyses, CV, UV-vis, and IR) observed for both yellow and red crystals are the same as those of **1A** and **2A** prepared as authentic samples. The spectrometric experiment showed that the addition of a small amount of water (1—3 cm^3) to the methanol solution served to slow down the progress of the reaction, where the same products can be observed to form. No spectral evidence which suggested the formation of the aqua complex of Ru^{II}, $[RuCl(H_2O)(py)_4]^+$, as the two-electron reduced species of the original oxo complex, could be observed. The aqua complex of Ru^{II} could only be formed when the oxo complex was reduced in an acidic aqueous solution by a strong reductant such as Zn–Hg amalgam.[16]

Characterization of Reaction Products between the Oxo Complex and Alcohols. The reaction products were formulated as the hydroxo and alkoxo complex of Ru^{III}, **1** and **2**—**5** (Table 1), based on analyses, magnetic measurements, cyclic voltammetry, IR spectra, and X-ray structure determination (for **1A** and **2B**). The effective magnetic moments for **1A** and **2B** were found to be 2.05 and 2.15 B.M., respectively. These values are almost the same as that observed for $[RuCl_2(py)_4]PF_6$ and are close to spin-only values for one-unpaired spin.[17]

The cyclic voltammograms of all these complexes in CH_3CN exhibit reversible reduction waves at −0.7—−0.8 V (vs. Ag|$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN) at 25 °C), which is a reasonable potential

Table 1. Products and Their Properties

Complex		μ_{eff}/μ_B a)	$E_{1/2}/V$ b)	$E_{pc(ox)}/V$	$\lambda(\varepsilon)$ c)
$[RuCl(OH)(py)_4]PF_6$	**1A**	2.05	−0.68	≈1.4	$297(1.2\times10^4)$ $262(1.0\times10^4)$
$[RuCl(MeO)(py)_4]ClO_4$	**2B**	2.15	−0.74	1.0, ≈1.4	$427(2.3\times10^3)$ $301(1.2\times10^4)$
$[RuCl(EtO)(py)_4]PF_6$	**3A**		−0.77	1.0, ≈1.4	$434(2.2\times10^3)$ $302(1.1\times10^4)$
$[RuCl(n\text{-}PrO)(py)_4]PF_6$	**4**		−0.78	1.0, ≈1.4	$437(2.1\times10^3)$ $302(1.0\times10^4)$
$[RuCl(i\text{-}PrO)(py)_4]PF_6$	**5**		−0.79	1.0	$433(2.2\times10^3)$ $300(1.0\times10^4)$

a) 22 °C. b) Ru^{II}/Ru^{III} couple (vs. Ag|$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN)) at 25 °C. c) nm(ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN.

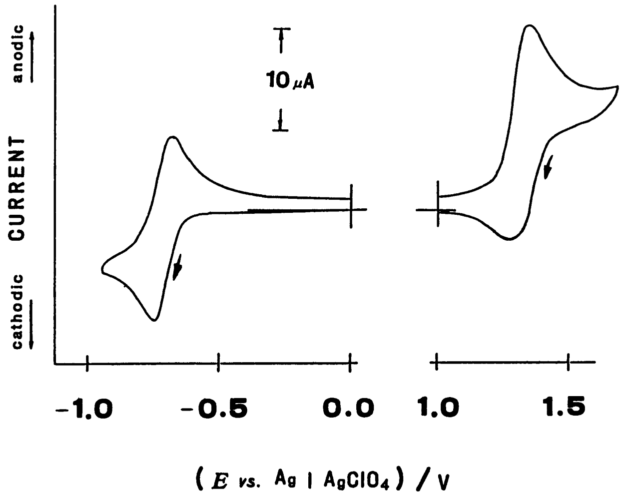

Fig. 2. Cyclic voltammograms of $[RuCl(OH)(py)_4]^+$ **1A** at a stationary platinum electrode in 0.1 mol dm^{-3} TEAP-CH_3CN at 25 °C (scan rate 200 mV s^{-1}).

region for Ru$^{III/II}$ reduction. A typical cyclic voltammogram of **1A** is shown in Fig. 2. The results are summarized in Table 1. The current heights, observed by the normal pulse voltammetry at the same experimental conditions, of the reduction waves of these complexes were almost the same as that of $[RuCl_2(py)_4]PF_6$, which has been well characterized in our laboratory.[17] At the oxidative scan the cyclic voltammogram of **1A** exhibits an irreversible one-electron oxidation wave at 1.39 V. The oxidation potential of **1A** appeared at almost the same potential region as that of $[RuCl_2(py)_4]PF_6$, which indicates a

Table 2. Infrared Spectra of **1A** and the Labelled (^{2}H and ^{18}O) Complexes

1A	^{2}H-**1A**$^{a)}$	^{18}O-**1A**$^{b)}$		Assignment
3544	2620	3530	s,sharp	ν(OH)
938	c)	936	m	δ(RuOH)
599	580	570	s	ν(RuO)

a) $[RuCl(OD)(py)_4]PF_6$. b) $[RuCl(^{18}OH)(py)_4]PF_6$. c) Overlapped with a band due to py ligand.

Table 3. Final Positional Parameters (×10^4 for Non-Hydrogen Atoms Except for the Atoms of PF_6 Anion; ×10^3 for Hydrogen Atoms and for PF_6 Anion) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2) for $[RuCl(OH)(py)_4]^+$ **1A**

Atom	*X*	*Y*	*Z*	B_{eq}/Å^2	Atom	*X*	*Y*	*Z*	B_{iso}/Å^2
Ru	52.5(3)	1827.5(3)	1333.0(6)	2.79	P (7)	−250	250	500	4.30(1)
Cl	5(1)	2429(1)	96(2)	3.98	F (51)	−71(1)	448(1)	188(1)	15.00
O	113(3)	1370(3)	2404(5)	4.31	F (52)	−22(1)	496(1)	153(1)	15.00
N (1)	587(3)	1377(3)	597(7)	3.63	F (53)	12(1)	435(1)	221(1)	15.00
N (2)	643(4)	2256(3)	1930(6)	3.20	F (61)	250	250	367(1)	5.13(3)
N (3)	−491(3)	2253(3)	2070(7)	3.35	F (62)	250	250	587(1)	5.15(3)
N (4)	−527(3)	1378(3)	752(6)	3.29	F (63)	206(0)	208(0)	473(1)	9.54(3)
C (11)	975(5)	1151(5)	1024(10)	4.76	F (71)	−250	250	389(2)	16.66(7)
C (12)	1317(5)	837(6)	548(13)	6.82	F (72)	−311(0)	246(0)	494(1)	8.31(2)
C (13)	1263(6)	774(6)	−370(12)	6.69	H (11)	102	121	176	7.00
C (14)	871(6)	1009(5)	−817(11)	6.37	H (12)	163	64	94	7.00
C (15)	537(5)	1309(5)	−330(9)	4.29	H (13)	153	53	−75	7.00
C (21)	641(5)	2343(5)	2851(8)	4.12	H (14)	82	96	−158	7.00
C (22)	1032(5)	2629(5)	3299(9)	4.41	H (15)	21	151	−70	7.00
C (23)	1418(5)	2806(5)	2785(8)	4.50	H (21)	33	218	326	7.00
C (24)	1427(4)	2724(5)	1884(10)	4.78	H (22)	101	271	405	7.00
C (25)	1048(4)	2439(4)	1451(8)	3.69	H (23)	173	302	312	7.00
C (31)	−875(5)	2015(5)	2538(9)	4.77	H (24)	174	289	147	7.00
C (32)	−1240(5)	2269(6)	3020(10)	6.17	H (25)	106	236	70	7.00
C (33)	−1236(6)	2826(5)	2998(11)	5.90	H (31)	−89	159	252	7.00
C (34)	−871(6)	3054(5)	2525(11)	5.74	H (32)	−154	205	342	7.00
C (35)	−488(5)	2775(4)	2090(9)	4.14	H (33)	−153	305	337	7.00
C (41)	−490(5)	870(4)	769(10)	4.60	H (34)	−87	348	247	7.00
C (42)	−878(5)	537(5)	457(12)	6.10	H (35)	−17	298	174	7.00
C (43)	−1313(6)	742(6)	100(13)	6.88	H (41)	−13	70	104	7.00
C (44)	−1351(5)	1264(6)	64(11)	5.70	H (42)	−83	11	52	7.00
C (45)	−958(5)	1581(5)	417(9)	4.49	H (43)	−163	50	−17	7.00
				B_{iso}/Å^2	H (44)	−170	145	−24	7.00
P (5)	−30(0)	470	250	6.61(1)	H (45)	−101	201	40	7.00
P (6)	250	250	474(0)	4.10(1)					

reversible couple of $Ru^{III/IV}$.[17] The smallness of the cathodic response in **1A** indicates that the facile deprotonation occurs in ($Ru^{III}-OH^-$) group to give ($Ru^{IV}=O^{2-}$).[5] In the methoxo complex **2B**, two irreversible oxidation waves were observed at 1.0 and 1.4 V regions. A ligand oxidation reaction in MeO ligand is expected to occur in these potential regions.

The IR spectra of **1A** are essentially the same as those of $[RuCl_2(py)_4]PF_6$, except for the absorption bands observed at 3544, 938, and 599 cm^{-1}, which are assignable to ν(OH), δ(RuOH), and ν(RuO) respectively, as are shown in Table 2. ^2H- and ^{18}O- labelling experiments using $[RuCl(OD)(py)_4]^+$ and $[RuCl(^{18}OH)(py)_4]^+$ support these assignments. The IR spectra of **2** could also be reasonably assigned by a comparison with those for its deuterated complex, $[RuCl(OCD_3)(py)_4]^+$. Several IR studies on the assignment of the methoxyl ligand have been reported.[18] Upon the deuteration, the methoxyl CH stretching vibration bands at 2860 and 2786 cm^{-1} shifted to 2172 and 2040 cm^{-1}, respectively. The methoxyl CH bending vibration band at 1422 cm^{-1} disappeared; it is thought to have shifted over to near the 1100 cm^{-1} region, where a strong absorption band due to ClO_4^- was observed. The band at 1035 cm^{-1} which is believed to be due to methoxyl CO stretching vibration, shifted to 1004 cm^{-1}. The Ru–O stretching vibration at 549 cm^{-1} shifted to 526 cm^{-1} in its deuterated complex. These shifts found in C–O and Ru–O stretching vibrations are regarded as being reasonable for the deuteration of a methoxyl group coordinated to metals.[18]

The structure of both **1A** and **2B** were determined to confirm the above characterization. The final atomic parameters are listed in Tables 3 and 4. The perspective drawings of **1A** and **2B**, and the numbering schemes of the atoms are given in Figs. 3 and 4. Selected interatomic distances and angles are given in Tables 5 and 6. The cations are a hydroxo complex ion and a methoxo complex ion of Ru^{III}. They have the expected trans octahedral geometry, with pyridine nitrogen atoms approximately in a plane containing the ruthenium atom. As can be seen in Figs. 3 and 4, **1A** and **2B** have a propeller-like structure similar to those of both oxo and nitrosyl complexes,[5,19] used as starting material for the present reaction. No remarkable difference between the

Table 4. Final Positional Parameters ($\times 10^4$ for Non-Hydrogen Atoms; $\times 10^3$ for Hydrogen Atoms) and Equivalent Isotropic Temperature Factors ($B_{eq}/Å^2$) for $[RuCl(OMe)(py)_4]^+$ **2B**

Atom	X	Y	Z	$B_{eq}/Å^2$	Atom	X	Y	Z	$B_{eq}/Å^2$
Ru	1145.1(1)	−1781.4(2)	88.5(4)	2.40	O (51)	3856(3)	−90(3)	1911(6)	9.63
Cl(1)	527.2(5)	−813.7(8)	−1855.6(16)	3.72	O (52)	3451(3)	−1465(4)	474(6)	9.24
O (1)	1685(1)	−2597(2)	1529(4)	3.49	O (53)	3451(2)	−1392(4)	3271(6)	7.86
N (1)	1439(2)	−502(3)	1360(5)	2.95	O (54)	4327(2)	−1610(4)	2044(9)	10.39
N (2)	1855(2)	−1649(3)	−1388(5)	3.40					$B_{iso}/Å^2$
N (3)	892(2)	−3082(2)	−1213(5)	2.91	H (11)	228(2)	−94(3)	167(6)	3.58(10)
N (4)	399(2)	−1901(2)	1474(5)	2.81	H (12)	264(2)	47(3)	293(5)	3.11(9)
C (11)	1066(2)	240(3)	1638(6)	3.45	H (13)	207(2)	168(4)	349(7)	6.97(14)
C (12)	1265(2)	1096(4)	2419(7)	4.46	H (14)	97(3)	144(5)	263(7)	7.44(15)
C (13)	1870(3)	1201(4)	2956(7)	4.78	H (15)	62(2)	16(4)	134(6)	4.78(12)
C (14)	2254(2)	445(4)	2681(7)	4.26	H (21)	171(2)	−20(3)	−197(6)	4.61(10)
C (15)	2030(2)	−391(3)	1895(6)	3.37	H (22)	245(3)	−3(5)	−374(8)	8.81(18)
C (21)	1968(2)	−800(4)	−2142(7)	4.96	H (23)	302(3)	−125(6)	−399(10)	11.06(25)
C (22)	2426(3)	−720(6)	−3162(8)	6.62	H (24)	295(2)	−275(4)	−285(7)	7.22(15)
C (23)	2765(3)	−1521(7)	−3463(8)	7.35	H (25)	215(2)	−302(3)	−98(5)	3.18(9)
C (24)	2648(3)	−2408(6)	−2673(8)	6.48	H (31)	86(2)	−255(4)	−352(6)	5.11(12)
C (25)	2197(2)	−2438(4)	−1646(7)	4.40	H (32)	73(3)	−408(5)	−483(8)	9.33(19)
C (31)	820(2)	−3108(3)	−2884(6)	3.61	H (33)	43(3)	−523(5)	−334(7)	8.02(16)
C (32)	699(3)	−3971(4)	−3752(7)	4.68	H (34)	72(2)	−536(4)	−58(6)	5.27(13)
C (33)	654(3)	−4830(4)	−2916(7)	5.23	H (35)	93(2)	−386(3)	73(6)	4.13(10)
C (34)	713(3)	−4816(4)	−1206(7)	5.10	H (41)	−9(2)	−239(3)	−34(6)	4.11(11)
C (35)	840(2)	−3927(3)	−404(6)	3.74	H (42)	−99(2)	−267(4)	91(7)	6.35(14)
C (41)	−119(2)	−2262(4)	732(6)	3.55	H (43)	−94(3)	−217(4)	363(7)	6.06(15)
C (42)	−632(2)	−2355(4)	1520(7)	4.33	H (44)	−2(2)	−147(4)	493(7)	6.02(12)
C (43)	−622(2)	−2072(5)	3151(7)	5.07	H (45)	76(2)	−130(3)	360(6)	4.01(10)
C (44)	−100(2)	−1677(4)	3921(7)	4.61	H (61)	195(2)	−305(3)	365(6)	5.39(12)
C (45)	399(2)	−1600(4)	3057(6)	3.47	H (62)	152(3)	−270(5)	361(7)	9.39(16)
C (Me)	1738(3)	−2625(4)	3224(7)	5.01	H (63)	163(2)	−188(4)	379(7)	6.14(14)
Cl(50)	3762(1)	−1110(1)	1923(2)	3.71					

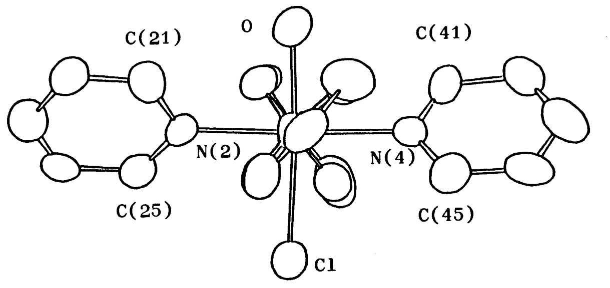

Fig. 3. Perspective drawing of [RuCl(OH)(py)$_4$]$^+$ **1A** and the numbering scheme.

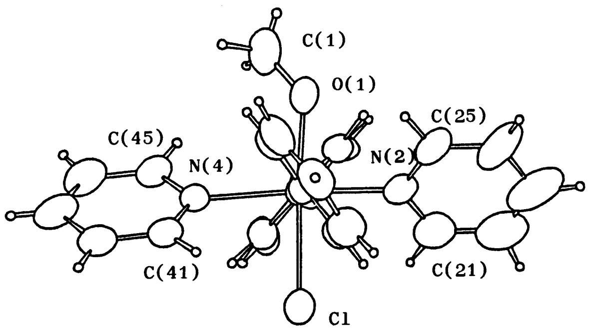

Fig. 4. Perspective drawing of [RuCl(OMe)(py)$_4$]$^+$ **2B** and the numbering scheme.

Table 5. Selected Interatomic Distances and Bond Angles for [RuCl(OH)(py)$_4$]$^+$ **1A**

	l/Å		l/Å
Ru-Cl	2.377(3)	N(1)-C(11)	1.32(2)
Ru-O	1.957(9)	C(11)-C(12)	1.38(2)
Ru-N(1)	2.100(10)	C(12)-C(13)	1.35(3)
Ru-N(2)	2.086(9)	C(13)-C(14)	1.35(2)
Ru-N(3)	2.081(9)	C(14)-C(15)	1.37(2)
Ru-N(4)	2.086(9)	C(15)-N(1)	1.36(2)
	ϕ/°		ϕ/°
Cl-Ru-O	176.0(3)	N(1)-Ru-N(3)	178.1(4)
Cl-Ru-N(1)	91.0(3)	N(2)-Ru-N(4)	178.2(4)
Cl-Ru-N(2)	90.0(3)		
Cl-Ru-N(3)	90.2(3)		
Cl-Ru-N(4)	91.5(3)		

Table 6. Selected Interatomic Distances and Bond Angles for [RuCl(OMe)(py)$_4$]$^+$ **2B**

	l/Å		l/Å
Ru-Cl	2.376(1)	O(1)-C(1)	1.365(5)
Ru-O(1)	1.937(2)	N(1)-C(11)	1.353(5)
Ru-N(1)	2.086(2)	C(11)-C(12)	1.375(5)
Ru-N(2)	2.087(3)	C(12)-C(13)	1.357(5)
Ru-N(3)	2.099(2)	C(13)-C(14)	1.368(5)
Ru-N(4)	2.104(2)	C(14)-C(15)	1.368(5)
		C(15)-N(1)	1.337(4)
	ϕ/°		ϕ/°
Cl-Ru-O	175.45(6)	Ru-O(1)-C(1)	127.1(2)
Cl-Ru-N(1)	89.93(7)	N(1)-Ru-N(3)	177.27(9)
Cl-Ru-N(2)	89.80(8)	N(2)-Ru-N(3)	177.17(10)
Cl-Ru-N(3)	91.33(6)		
Cl-Ru-N(4)	87.65(7)		

structures of **1A** and of **2B** could be observed, except that the CH$_3$ group of the methoxyl ligand was directed to bisect the N(1)-Ru-N(4) angle, with Ru-O-C angle of 127.1.(2)°. A similar structure of the CH$_3$O moiety has been found in [Mn^{IV}(TPP)-(OCH$_3$)$_2$].[18] The hydroxyl or the methoxyl oxygen and the chlorine atoms are almost on the line including the Ru atom: 175°. The Ru-O bond distances, 1.957(9) Å (for **1A**) and 1.937(2) Å (for **2B**) are shorter than the sum of the single bond radii for Ru^{III}-O^{2-} 2.03 Å), [20] but they are significantly longer than the value of 1.862(8) Å observed for the oxo complex, the starting material. Its bond length is consistent with the bond order of two. The Ru-Cl distances, trans to the oxygen atom, are 2.377(3) Å (for **1A**) and 2.376(1) Å (for **2B**). These distances are comparable to the values reported for various Ru^{III} complexes, and they are considerably longer than those of the original nitrosyl or the oxo complexes, where the shortening of the Ru-Cl distance trans to NO$^+$ or O^{2-} has been expected due to their ability to act as strong acceptor ligands.[2,21] The Ru-N distances vary from 2.081(9) Å to 2.104(2) Å. These values are almost the same as those of the original oxo complex, though less shortening was observed than in the cases of [RuCl(NO)(py)$_4$]$^{2+}$ or [Ru(py)$_6$]$^{2+}$.[19,22] The crystal data of **1A**, as well as its crystal packing, are almost the same as those of the original oxo complex.[5,23] The existence of the hydrogen atom in the OH moiety appears to be an unimportant factor in determining their crystal structures.

Reactivity of (Ru^{IV}=O^{2-}) Unit. Under mild conditions, *trans*-[RuCl(O)(py)$_4$]$^+$ in neat MeOH gave two complexes: The hydroxo and the methoxo complex. A formulation of the latter as a complex which involves a methanol molecule as a ligand or a solvent of crystallization can be ruled out. The spectral and synthetic investigations mentioned earlier proved that the hydroxo complex was a precursor in the formation of the methoxo complex. This appears to be the first example to be synthetically confirmed. It had also become apparent that the reactivity of the (Ru^{IV}=O^{2-}) unit depends on the oxo complex used for the reaction. As described above, the hydroxo complex of Ru^{III}, *trans*-[RuCl(OH)(py)$_4$]$^+$, and the methoxo complex of Ru^{III}, *trans*-[RuCl-(OMe)(py)$_4$]$^+$, were confirmed to be the first and the second products obtained. Although the first product of the present reaction was the same as that reported by Meyer et al. in the mechanistic study of *cis*-$[Ru(O)(bpy)(trpy)]^{2+}$ in 2-propanol containing water,[10] the second product was different; the second product in their work was an aqua complex of Ru^{II}, while that found in the present work was the alkoxo complex of Ru^{III}. Their reaction progress where 2-propanol is oxidized to acetone has been reported as follows (Eqs. 1—4):[10]

$$2(Ru^{IV}{=}O^{2-})^{2+} + (CH_3)_2CHOH \longrightarrow 2(Ru^{III}\text{-}OH^-)^{2+} + (CH_3)_2CO\cdot \qquad (1)$$

This reaction (Eq. 1) has been believed to occur via the following reactions (Eqs. 2 and 3):

$$(Ru^{IV}{=}O^{2-})^{2+} + (CH_3)_2CHOH \longrightarrow (Ru^{II}\text{-}OH_2)^{2+} + (CH_3)_2CO \qquad (2)$$

$$(Ru^{IV}{=}O^{2-})^{2+} + (Ru^{II}\text{-}OH_2)^{2+} \longrightarrow 2(Ru^{III}\text{-}OH^-)^{2+}. \qquad (3)$$

In the final step, the hydroxo complex produced in Eq. 1 undergoes a further reduction to an aqua complex of Ru^{II}:

$$2(Ru^{III}\text{-}OH^-)^{2+} + (CH_3)_2CHOH \longrightarrow 2(Ru^{II}\text{-}OH_2)^{2+} + (CH_3)_2CO\cdot \qquad (4)$$

It should be emphasized that, under our experimental conditions, no evidence indicating any formation of the aqua complex of Ru^{II}($[RuCl(OH_2)(Py)_4]^+$), which corresponds to the final product in Eq. 4, could be observed by spectral monitoring.

The origin of the hydroxyl hydrogen atom in **1** could no be clarified. Meyer et al., have stated that the reduction of *cis*-$[Ru(O)(bpy)(trpy)]^{2+}$ to the corresponding hydroxo complex (Eq. 1) is initiated by a hydride transfer from the α-C-H bond of the 2-propanol to ($Ru^{IV}=O^{2-}$) unit.[10] A direct application of their mechanism to the present reaction appears to be difficult, owing to a disagreement in the spectral observations. They found isosbestic points due to the formation of first the hydroxo complex of Ru^{III} (Eq. 1) and then the aqua complex of Ru^{II} (Eq. 4), whereas the present reaction does not exhibit those points. Although a hydride-transfer mechanism can be acceptable if the aqua complex of Ru^{II} is confirmed to exist before the hydroxo complex formation occurs (Eq. 2), such an aqua complex as the intermediate species is not detectable, because it appears that the intermediate species is not built up to appreciable concentrations or is too short-lived to be seen spectrophotometrically.[10]

The alkoxo complex **3**—**5** undergo a facile hydrolysis to give the hydroxo complex, while the hydrolysis of **2** is extremely slow. Treatment of the hydrolysis solution with Ce^{4+}, used as an oxidant in acidic conditions, gave the original oxo complex quantitatively. By the same procedure using $H_2{}^{18}O$ (99%) $[RuCl(^{18}O)(py)_4]PF_6$ could be obtained from the alkoxo complex **4**. Upon ^{18}O substitution, the IR absorption band due to $\nu(RuO)$, observed at 804 cm^{-1} for the original oxo complex, disappeared. This finding suggests the existence of an ^{18}O atom in the product, although the IR absorption band ($\nu(Ru^{18}O)$) could not be confirmed, since the region where this would be expected (780—760 cm^{-1}) was hidden by the strong absorption band from the pyridine moiety. $[RuCl(^{18}OH)(py)_4]PF_6$ could also be isolated in this stage before the formation of the ^{18}O-labelled oxo complex occurs, without addition of any oxidant. The labelling experiment can be illustrated by the following scheme:

$$[Ru^{III}Cl(\boxed{OR})(py)_4]^+ + \boxed{H}\text{-}\overset{*}{O}\text{-}H \longrightarrow [Ru^{III}Cl(\overset{*}{O}H)(py)_4]^+ + ROH \qquad (5)$$

$$[Ru^{III}Cl(\overset{*}{O}H)(py)_4]^+ \longrightarrow [Ru^{IV}Cl(\overset{*}{O})(py)_4]^+ + e^- + H^+. \qquad (6)$$

If we assume that the alkoxo complex formation occurs by a water-condensation reaction between alcohol and the hydroxo complex, the reverse reaction of the schemes (Eqs. 5 and 6) may be indicative of the behavior of the ($Ru^{IV}=O^{2-}$) unit in *trans*-$[RuCl(O)(py)_4]^+$ toward alcohols; the alkoxo complex does not retain the oxygen atom in the ($Ru^{IV}=O^{2-}$) unit, whereas the hydroxo complex can be considered to retain it.

At room temperature, *trans*-$[RuCl(OMe)(py)_4]^+$ **2B** dissolved in methanol changed from yellow-orange to red after long standing. The absorption spectra of the solution was scanned repeatedly between 230—500 nm for 20 d. As shown in the dotted line of [B] (Fig. 1), decreasing of intensities of the bands at 265 and 300 nm and developing of the bands at 245 and 375 nm were observed, with isosbestic points forming at 237, 255, and 327 nm. A methoxo complex of Ru^{II}, $[RuCl(OMe)(py)_4]$, appears to from at this stage of the reaction. The electrochemical experiment described above showed that the methoxo complex **2** underwent a reversible one-electron reduction. Attempts to isolate the species were unsuccesful. In place of the methoxo complex of Ru^{II}, small amounts of red crystals, which could easily be identified as $[RuCl_2(py)_4]$,[25] deposited after further standing of the solution.

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