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Synthesis and Properties of Oxo Complex of Ruthenium(IV), *trans*-[RuCl(O)(py)$_4$]$^+$, which is Formed by the Oxidation of Nitrosyl Complex of Ruthenium(II), *trans*-[RuCl(NO)(py)$_4$]$^{2+}$

Kimitake Aoyagi, Yasuhiko Yukawa, Kunio Shimizu, Masao Mukaida*
Toshio Takeuchi, and Hidetake Kakihana
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho, Chiyoda-ku, Tokyo 102
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Oxidation of *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ with NaClO gives oxo complex of Ru^{IV}, *trans*-[RuCl(O)(py)$_4$]$^+$, with bond breaking of the metal-nitrosyl ligand. An X-ray structural study revealed that the complex has a much longer Ru–O bond distance (1.862(8) Å) than those of known mono-oxo complexes. A facile reactivity of the oxoruthenium(IV) complex was observed: with methanol methoxo complex, *trans*-[RuCl(OMe)(py)$_4$]$^+$, was formed. With PPh_3, a two-electron transfer process was indicated by the formation of Ph_3PO.

Considerable attention has been focused on the chemistry of high-valent ruthenium complexes with $Ru^{IV}=O^{2-}$ unit, in connection with their usefulness as an oxygen-transfer agent in the selective oxidation of oganic substrates.[1] Although several other oxoruthenium(IV) complexes have recently been prepared,[2,3] there was no structural information concerning the $Ru^{IV}=O^{2-}$ unit until a preliminary report of the present work and a work by Che et al. appeared.[4,5] Here we describe the syntheses, properties and structures of new mono-oxo complexes of ruthenium(IV), *trans*-[RuX(O)(py)$_4$]$^+$ (X=Cl, Br), which were prepared by the oxidation of the corresponding nitrosyl complex, *trans*-[RuX(NO)(py)$_4$]$^{2+}$, with sodium hypochlorite solution. The present work to afford the mono-oxo complex by the oxidation of the nitrosyl complex appears to be valuable as a synthetic route for the mono-oxo type of complexes.

The nitrosyl ligand coordinated to Ru^{II} atom is believed to be remarkably stable and to persist through a variety of substitution reactions. This is certainly true for most complexes with $Ru^{II}NO^+$ moiety studied so far. The nitrosyl ruthenium complex described above was nevertheless used as a starting material, in order to explore a possible oxidation reaction for the nitrosyl ligand. Recently, Meyer et al. have studied the oxidation of a nitrosyl complex of Ru^{II}, *cis*-[RuCl(NO)(bpy)$_2$]$^{2+}$ (bpy: 2,2′-bipyridine), which gives the corresponding nitrato complex via a reactive nitro complex of Ru^{III}.[6] Their work, however, was mainly a survey on the oxidation at acidic or neutral conditions. The oxidation reaction under a basic condition has not been reported.

Experimental

IR spectra were measured on a Hitachi EPI G2 spectrometer. UV-vis spectra were recorded on a Hitachi 200-20 spectrophotometer. Magnetic moments were measured by the Gouy method using mercury tetrakis(thiocyanato)cobaltate(II) as the calibrant. Elemental analyses were performed by both the Sophia University Analytical Facility and the Institute of Chemical and Physical Research, Wako, Saitama 351. The cyclic voltammetry and the normal pulse voltammetry were carried out by using a Fuso Polarograph Model 321 and a Fuso Potential Scanning unit Model 321 with a stationary platinum disk electrode(ϕ=1.99 mm). All the potentials were measured against a silver-silver ion electrode (Ag/0.1 mol dm^{-3} $AgClO_4$ in acetonitrile). The measurements were carried out at 25 °C. Deoxygenation of solution was carried out with argon gas, which had been passed through two wash bottles containing acetonitrile kept at 25 °C.[7]

Syntheses. Starting material in this work, *trans*-[RuX(NO)(py)$_4$]Y$_2$ (X=Cl, Br. Y=ClO_4, PF_6) were prepared according to the method reported previously.[8]

Chloro(oxo)tetrakis(pyridine)ruthenium(IV) Perchlorate, [RuCl(O)(py)$_4$]ClO_4 1A: To a solution of *trans*-[RuCl(NO)(py)$_4$](ClO_4)$_2$ (0.5 g) in H_2O (15 cm^3), aqueous solution of NaClO (2 cm^3) was added.[9] A yellow precipitate, which formed immediately, became light green with stirring for 4 h at 23—26 °C. The crystalline product obtained was kept for 3 more hours, without stirring, and then filtrated out, washed with cold water, and dried in vacuo. Yield 90—95%. It should be noted that effective stirring of the mixed solution and keeping it warm (at 23—26 °C) are necessary for the synthesis in order to avoid contamination by the unoxidized material of the yellow precipitate described above. The mono-oxo complex is stable as a solid and remained unchanged for several months when stored in a desiccator. Found: C, 42.2; H, 3.4; N, 9.9%. Calcd for $C_{20}H_{20}O_5N_4Cl_2Ru$: C, 42.2; H, 3.5; N, 9.9%.

Chloro(oxo)tetrakis(pyridine)ruthenium(IV) Hexafluorophosphate, [RuCl(O)(py)$_4$]PF_6 1B, and Bromo(oxo)tetrakis(pyridine)ruthenium(IV) Perchlorate, [RuBr(O)(py)$_4$]-ClO_4 2, were prepared by the same procedure using the corresponding nitrosyl complexes. For **1B** yield 90%. Found: C, 39.0; H, 3.2; N, 9.2; PF_6, 23.5%. Calcd for $C_{20}H_{20}N_4OClPF_6Ru$: C, 39.1; H, 3.3; N, 9.1; PF_6, 23.6%. For **2** yield 90%. Found: C, 39.0; H, 3.2; N, 9.1%.

Calcd for $C_{20}H_{20}O_5N_4BrRu$: 39.2; H, 3.3; N, 9.1%.

Chloro(nitro)tetrakis(pyridine)ruthenium(II), [RuCl(NO_2)(py)$_4$] 3: As was described in the preparation of **1A**, addition of NaClO solution to aqueous solution of *trans*-[RuCl(NO)(py)$_4$](ClO_4)$_2$ gave immediately a yellow precipitate. The precipitate filtered out, washed with water and dried in vacuo. Found: C, 46.1; H, 4.0; N, 13.2%. Calcd for $C_{20}H_{22}N_5O_3ClRu$ (as monohydrate): C, 46.4; H, 4.3; N, 13.5%.

Chloro(methoxo)tetrakis(pyridine)ruthenium(III) Hexafluorophosphate, [RuCl(OMe)(py)$_4$]PF_6 4A: Complex **1B** (50 mg) was dissolved in methanol (25 cm^3), using a Erlenmeyer flask, and kept at room temperature for 2 d in 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 70%. 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 4B, was prepared by almost the same procedure using the corresponding mono-oxo complex **1A**. Found: C, 43.4; H, 4.0; N, 9.6%. Calcd for $C_{21}H_{23}N_4O_5ClPF_6Ru$: C, 43.2; H, 4.0; N, 9.6%.

Intensity Data Collection. A crystal with dimensions of 0.16×0.14×0.30 mm^3 was used for the measurement without shaping. The crystallographic data are: $RuC_{20}H_{20}N_4O_5Cl_2$, F. W. 568.4, tetragonal, space group *P4/ncc*, Z=16, a=25.781(5), c=14.130(4) Å, U=9391(4) Å^3, D_x=1.61, D_m=1.59 g cm^{-3}, μ(Mo $K\alpha$) 9.21 cm^{-1}. The reflections were collected by the ω scan technique ($2\theta<55°$) on a Rigaku AFC-6A automated four-circle diffractometer, with graphite monochromated Mo $K\alpha$ radiation (0.7107 Å). The 2122 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for the 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 on a HITAC M-200H computer at the Computer Center of the University of Tokyo, using the local version of UNICS.[10] The atomic scattering factors were taken from the table.[11]

Structure Determination. The structure was solved by a heavy-atom method. The position of ruthenium and chlorine atoms were obtained from a three-dimensional Patterson function, while the positions of all the non-hydrogen atoms were succesively located by Fourier syntheses. Since the positions of only a few hydrogen atoms were obtained by a difference-Fourier syntheses, all of the positions were calculated and fixed. Their isotropic temperature factors were assumed to be 5.0 Å^2.

All other positions and thermal parameter were refined by a repeated block-diagonal least-squares method. The weighting scheme was $W=1/[\{\sigma(|F_o|)\}^2+(0.04\times|F_o|)^2]$. 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 value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was 0.076. The F_o—F_c data and the anisotropic temperature parameter are deposited as Document No. 8627 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

Results and Discussion

Syntheses. The reaction of *trans*-[RuX(NO)(py)$_4$]$^{2+}$ (X=Cl, Br) in a basic aqueous solution containing NaClO as an oxidant gave the mono-oxo complex, *trans*-[RuX(O)(py)$_4$]Y (**1A**; for X=Cl, Y=ClO_4. **1B**; for X=Cl, Y=PF_6. **2**; for X=Br, Y=ClO_4), in high yield. In the initial step of the reaction, nitro complex, [RuCl(NO_2)(py)$_4$] **3**, was formed by the known nitrosyl-nitro conversion reaction (Eq. 1)[12]

$$[Ru^{II}Cl(NO)(py)_4]^{2+} \xrightarrow{OH^-} [Ru^{II}Cl(NO_2)(py)_4] \quad (1)$$

The nitro complex **3** was isolable and its identity was confirmed by a direct comparison with an authentic sample reported previously.[8] The next step of the reaction appears to be an oxidation of the nitro complex of Ru^{II} to Ru^{III} which is followed by a Ru^{III}–NO_2^- bonding rupture, resulting in the corresponding hydroxo complex (Eqs. 2 and 3):

$$[Ru^{II}Cl(NO_2)(py)_4] \xrightarrow{-e^-} [Ru^{III}Cl(NO_2)(py)_4]^+ \quad (2)$$

$$\xrightarrow{-NO_2^-} [Ru^{III}Cl(OH)(py)_4]^+ \quad (3)$$

The oxidation was also attempted for the corresponding hydroxo nitrosyl complex, *trans*-[Ru(OH)(NO)(py)$_4$]$^{2+}$, which has been known as a poor electrophile compared to *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ used as the starting material of the present reaction.[8] In this case, however, the nitrosyl–nitro conversion reaction did not occur under the conditions, and the isolated product, by adding PF_6^-, was *trans*-[Ru(OH)(NO)(py)$_4$]$^{2+}$.[13]

Nitro complex of Ru^{III} has been found to be chemically unstable.[6] In the electrochemical experiment, in fact, a facile reaction due to a decomposition of the nitro complex of Ru^{III} was observed when **3** in CH_3CN undergoes a one-electron oxidation. As is shown in cyclic voltammogram (Fig. 1), **3** in CH_3CN displays a one-electron oxidation wave (E_{pa}=0.28 V vs. Ag/$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN)) in the potential region expected for the Ru^{II}/Ru^{III} couple. On scan reversal, a small reduction wave appeared at −0.12 V with decreasing of a cathodic responce, corresponding to a pair of oxidation wave observed at 0.28 V.[14] The next cycle showed a new oxidation peak at −0.07 V, not present in the original anodic cyclic voltammogram, which is presumed to be the couple with the small reduction wave at −0.12 V. The lack of the cathodic responce and the appearance of the new couple are evidently due to a rapid decomposition of the oxidized species [Ru^{III}Cl(NO_2)(py)$_4$]$^+$, although more study with coulometric experiments is needed to clarify the electrochemical

behavior in the oxidation reaction of **3**. The cyclic voltammogram observed here is similar to that of *cis*-$[RuCl(NO_2)(bpy)_2]$, where nitro-nitrito isomerization has been known to occur by the oxidation of the Ru^{II}-NO_2^- moiety.[6] The fate of the NO_2^- ligand released (Eq. 3) could not be elucidated; it is probably changed into NO_3^-.

The final step to generate $Ru^{IV}=O^{2-}$ moiety from the hydroxo complex (Eq. 4) is the same reaction as found in *cis*-$[RuCl(O)(bpy)_2]^+$ [1b]:

$$[Ru^{III}Cl(OH)(py)_4]^+ \xrightarrow{-e^-} [Ru^{IV}Cl(O)(py)_4]^+ \quad (4)$$

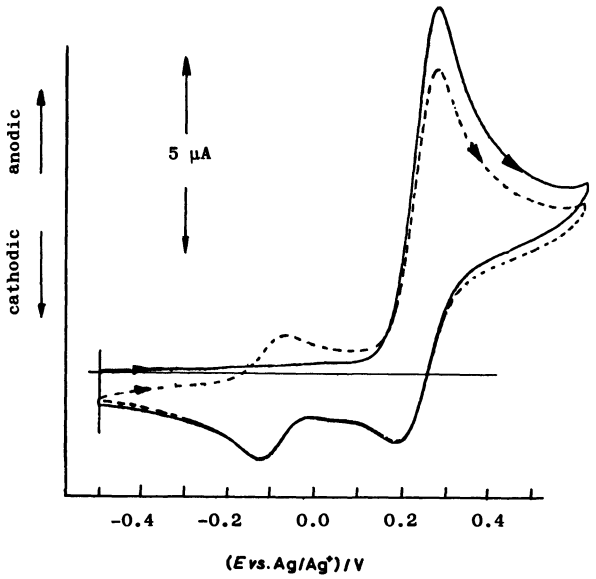

Fig. 1. The cyclic voltammogram of $[RuCl(NO_2)(py)_4]$ **3** (1.00 mol dm^{-3}) at a stationary platinum electrode (50 mV S^{-1}) in 0.1 mol dm^{-3} TEAP+AN at 25 °C. Initial potential: −0.5 V. The dashed curve shows the result of the second scan.

In the solid state, the complexes **1A**, **1B**, and **2** are stable indefinitely at room temperature. It was found, however, that the magnetic susceptibility of the complexes decreased markedly when the complexes were washed with organic solvents such as alcohols or acetone. Therefore, further purification by recrystallization was not attempted.

IR Spectra. The IR absorption band ascribed to Ru-O stretching vibration in **1A**, **1B**, and **2** was observed at the same frequency region, 800 cm^{-1} (Table 1). As reported previously, the absorption band due to the stretching vibration of the terminal oxo ligand occurs in 800—900 cm^{-1} for a variety of oxidation states of metal complexes.[15] This IR region, however, is almost the same as those for an antisymmetric stretching vibration (ν_3) of μ-oxo ruthenium complexes.[16] The absorption band due to ν_3 mode of a linear or quasi-linear M-O-M system has usually been regarded as a diagnostic for identifying the μ-oxo complexes.[16] Thus, the overlapping of these regions characteristic for both terminal- and bridging-oxo ruthenium complexes did not provide further information for identifying the present complex, and the choice in the correct formula between the mono-oxo complex, $[RuX(O)(py)_4]^+$, and the μ-oxo complex, $[Ru_2O(X)_2(py)_8]^{2+}$, could only be established by an X-ray structural determination.

Structure. The final atomic parameters are listed in Table 2, the interatomic distances in Table 3, and the bond angles in Table 4. The perspective drawing of the complex **1A** and the numbering scheme of the atoms are in Fig. 2. The cation is an oxo ruthenium(IV) complex ion, with trans octahedral geometry; it has four equatorial pyridine ligands, while the oxo and chloro ligands are coordinated in the axial direction. The oxo complex has a propeller-like

Table 1. Ru-O Distances and Stretching Frequencies in Selected Terminal- and Bridging-Oxo Ruthenium Complexes

Complex	Ru-O/Å	νRu-O/cm^{-1}	μ_{eff}/B.M.[c]	Refs.
Ru=O system				
$[RuCl(O)(py)_4]ClO_4$ **1A**	1.862(8)	805	2.94	this work
$[RuCl(O)(py)_4]PF_6$ **1B**		805	2.92	this work
$[RuBr(O)(py)_4]ClO_4$ **2**		805	2.93	this work
$[Ru(O)(tmc)(MeCN)](PF_6)_2$	1.765(5)		2.93	5
$[Ru(O)(bpy)(trpy)](ClO_4)_2$		792 (752)[a]	2.92	1
Ru-O-Ru system				
$[\{RuCl_5\}_2O]^{4-}$	1.801(2)	886[b]		18
$[\{Ru(NO_2)(bpy)_2\}_2O]^{2-}$	1.883(6)			19
$[\{Ru(TPP)(p\text{-}OC_6H_4CH_3)\}_2O]$	1.789(11)			20
$[\{Ru(OEP)(OH)\}_2O]$	1.847(13)			21
$[(NH_3)_5RuORu(en)_2ORu(NH_3)_5]^{6+}$	1.87			22

a) $\nu Ru\text{-}^{18}O$. b) Raman spectra. c) 1 B.M. = 9.274078(36) 10^{-24} J T^{-1}. Abbreviations: tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; TPP, 5,10,15,20-tetraphenylporphine; OEP, 2,3,7,8,12,13,17,18-octaethylporphine; trpy, 2,2′ : 6′,2″-terpyridine.

Table 2. Positional Parameters ($\times 10^4$ for Non-Hydrogen Atoms Except to the Atoms of Perchlorate Anions; $\times 10^3$ for others) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2), with the Estimated Standard Deviations

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Ru	41.5(4)	1836.8(4)	1462.2(8)	3.06	O(51)	−73(2)	445(2)	182(2)	15.77(13)
Cl	−22(2)	2446(1)	164(2)	4.17	O(52)	16	454	226	10.00
O(1)	102(3)	1385(3)	2488(6)	3.47	O(53)	−10	482(1)	337(2)	13.90(11)
N(1)	567(4)	1385(4)	673(8)	4.36	O(54)	−89(1)	483(1)	267(2)	12.58(10)
N(2)	649(4)	2278(4)	2033(7)	3.21	O(61)	250	250	370(2)	7.86(6)
N(3)	−580(4)	2267(4)	2206(7)	3.03	O(62)	213	210	494	9.20
N(4)	−544(4)	1374(4)	896(7)	3.75	O(63)	234	299	513	9.20
C(11)	954(6)	1138(6)	1126(12)	6.45	O(64)	300	237	513	9.20
C(12)	1297(6)	825(7)	598(16)	7.98	O(71)	−249(1)	205(1)	444(1)	11.07(4)
C(13)	1233(7)	753(7)	−342(17)	8.67					
C(14)	825(7)	996(6)	−773(12)	7.21	H(11)	100	118	192	7.14
C(15)	496(6)	1313(6)	−255(11)	5.20	H(12)	162	62	97	7.99
C(21)	654(5)	2397(5)	2969(9)	3.99	H(13)	150	51	−77	8.39
C(22)	1046(6)	2670(5)	3361(9)	4.54	H(14)	77	95	−153	7.21
C(23)	1446(5)	2843(5)	2820(11)	4.66	H(15)	17	151	−63	5.38
C(24)	1453(5)	2725(5)	1887(10)	4.33	H(21)	34	227	342	4.22
C(25)	1045(5)	2442(5)	1492(9)	3.81	H(22)	105	275	413	4.66
C(31)	−903(5)	2014(5)	2635(11)	4.44	H(23)	177	307	313	4.75
C(32)	−1288(6)	2268(6)	3094(11)	5.49	H(24)	177	285	144	4.34
C(33)	−1305(6)	2808(6)	3094(11)	5.69	H(25)	105	236	73	3.93
C(34)	−909(6)	3061(5)	2663(11)	5.31	H(31)	−91	159	263	4.10
C(35)	−522(6)	2794(5)	2205(10)	4.16	H(32)	−159	204	346	5.46
C(41)	−498(6)	857(5)	989(12)	5.29	H(33)	−163	302	345	5.67
C(42)	−873(6)	529(6)	612(14)	6.53	H(34)	−90	349	268	5.28
C(43)	−1278(7)	717(7)	131(13)	7.14	H(35)	−21	301	184	4.31
C(44)	−1329(6)	1270(7)	58(11)	5.48	H(41)	−16	70	139	5.55
C(45)	−954(6)	1568(6)	447(10)	4.65	H(42)	−85	11	70	6.20
					H(43)	−157	47	−23	6.48
Cl(5)	−38(1)	468	250	11.68(3)	H(44)	−167	141	−31	5.35
Cl(6)	250	250	471(1)	8.76(3)	H(45)	−100	200	39	4.59
Cl(7)	−250	250	500	6.02(2)					

Table 3. Selected Interatomic Distances with the Estimated Standard Deviations in Parentheses

	l/Å		l/Å
Ru-Cl	2.419(4)	N(1)-C(11)	1.38(2)
Ru-O	1.862(8)	C(11)-C(12)	1.46(2)
Ru-N(1)	2.107(11)	C(12)-C(13)	1.41(3)
Ru-N(2)	2.096(9)	C(13)-C(14)	1.38(2)
Ru-N(3)	2.089(9)	C(14)-C(15)	1.39(2)
Ru-N(4)	2.094(10)	C(15)-N(1)	1.38(2)
Cl-C(15)	3.25(2)	C(11)-C(25)	3.41(2)
Cl-C(25)	3.33(1)	C(21)-C(35)	3.36(2)
Cl-C(35)	3.27(2)	C(31)-C(45)	3.32(2)
Cl-C(45)	3.30(1)	C(41)-C(15)	3.33(2)
O-C(11)	2.95(2)	O-C(21)	3.04(2)
O-C(31)	3.06(2)	O-C(41)	2.91(2)

Table 4. Selected Bond Angles with the Estimated Standard Deviations in Parentheses

	ϕ/°
Cl -Ru-O	178.2(3)
Cl -Ru-N(1)	90.4(3)
Cl -Ru-N(2)	89.2(3)
Cl -Ru-N(3)	89.2(3)
Cl -Ru-N(4)	91.6(3)
N(1)-Ru-N(4)	176.6(4)
N(1) -C(11)-C(12)	116(2)
C(11)-C(12)-C(13)	120(2)
C(12)-C(13)-C(14)	118(2)
C(13)-C(14)-C(15)	122(2)
C(14)-C(15)-N(1)	119(1)

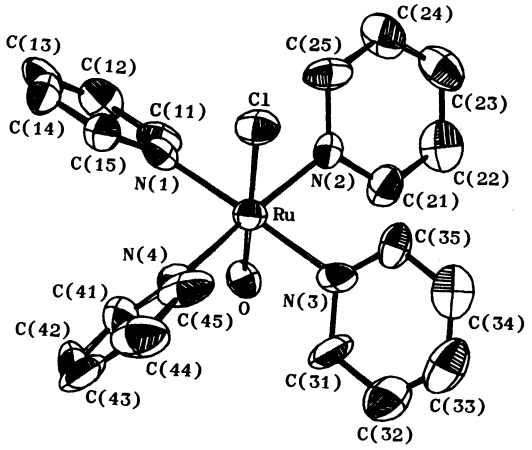

Fig. 2. The perspective drawing of $[RuCl(O)(py)_4]$-ClO_4 **1A** and the numbering scheme of non-hydrogen atoms.

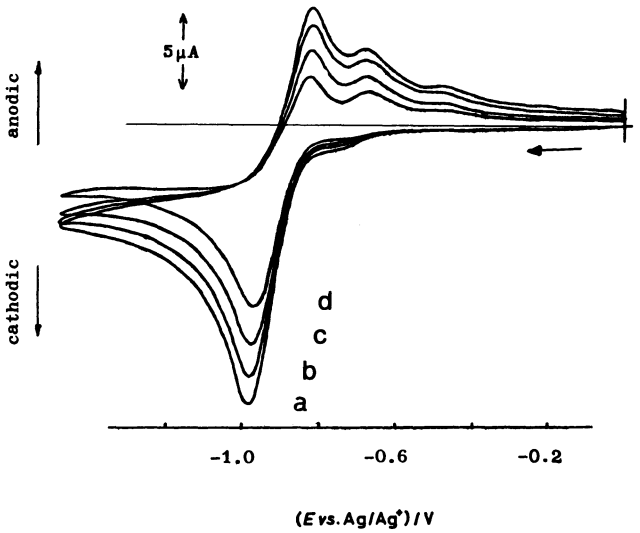

Fig. 3. The cyclic voltammograms of $[RuCl(O)(py)_4]$-ClO_4 **1A** (1.07 mol dm^{-3}) at a stationary platinum disk electrode (scan rate/mV S^{-1}): (a) 100; (b) 80; (c) 60; (d) 40 in 0.1 mol dm^{-3} TEAP+AN at 25 °C.

structure similar to that of the nitrosyl complex, *trans*-$[RuCl(NO)(py)_4]^{2+}$, used as starting material for the present oxidation reaction.[17] The oxo and chloro ligands are almost on the line including the ruthenium: O-Ru-Cl, 178.2(3)°. The Ru-O bond distance, 1.862(8) Å, is considerably shorter than the sum of the single bond radii for Ru^{IV}-O^{2-} (1.97 Å) and it is significantly longer than the value 1.756 Å reported recently for similar mono-oxo complex, *trans*-$[Ru(O)(tmc)(MeCN)]^{2+}$, of which the bond length is consistent with the expected bond order of two.[5] The remarkably long bond distance of the Ru-O observed here may be important factor to the reactivity of the mono-oxo moiety in **1A**. It is worth noting that the observed Ru-O distance is comparable with values reported for both μ-oxo complexes of Ru^{III} and Ru^{IV}, as shown in Table 1.[18-22]

The Ru^{IV}-Cl distance, trans to the oxygen atom, is 2.419(4) Å. The distance is longer than Ru^{IV}-Cl distances, 2.317—2.364 Å reported in the complexes, $[Ru_2OCl_{10}]^{4-}$ and $[Ru_2NCl_8(H_2O)_2]^{3-}$.[23] An elongation of metal-Cl distance trans to nitrido ligand (N^{3-}), which has a multiple bonding order, has been reported in $[Os^{IV}NCl_5]^{2-}$;[24] the Os-Cl bond distance trans to the nitrido is 2.61 Å and that to cis is 2.36 Å, whereas such a lengthening has not been found for the Ru^{IV}-Cl distance, trans to bridging oxo ligand in $[Ru_2OCl_{10}]^{4-}$ (Ru-Cl(*trans*), 2.317(7) Å; Ru-Cl(*cis*), 2.362(2) Å.[18b] The Ru-N distance vary from 2.089(6) to 2.107(11) Å. These Ru-N distances are slightly shorter than those previously reported for *trans*-$[RuCl(NO)(py)_4]^{2+}$ (2.103—2.118 Å), $[Ru(py)_6]^{2+}$ (2.10—2.14 Å) and $[(py)_4Ru(ox)Ru(py)_4]^{2+}$ (2.096—2.113 Å).[17,25,26] The dihedral angles between the best plane of RuN_4 and those of the pyridine rings range from 44.1—54.1°. The angle between the two pyridine planes in trans position are 80.6—82.7°, which are little larger than those of *trans*-$[RuCl(NO)(py)_4]^{2+}$. The distances between adjacent pyridine carbons and those between pyridine carbon and axial chloro ligand are slightly longer than the corresponding distances in the nitrosyl complex. On the other hand, the distances between pyridine carbon and the chloro ligand are shorter.

One counter anion, ClO_4^-, is on the four-fold rotatory inversion axis, the second is on the four-fold rotation axis, and the third is on the two-fold rotation axis. A statistical distribution was observed at the oxygen of ClO_4^- on the four- and two-fold rotation axis, and their positions could not be determined.

The effective magnetic moments were found to be 2.92—2.94 B.M., as shown in Table 1. These are almost the same as those observed in the known oxoruthenium(IV) complexes and are close to spin-only value for two unpaired spins. The observation of two unpaired electrons is consistent with the orbital splitting scheme proposed by Meyer et al.,[1b] in which the existence of the half filled $d\pi^*$ orbitals results in an extensive stabilization of the Ru-O bonding through a $p\pi(O^{2-})$-$d\pi(Ru)$ interaction.

Electrochemical Behavior. A cyclic voltammogram of **1A** in acetonitrile is shown in Fig. 3.[27] The reductive sweep shows a single wave at a much more negative potential than those of the known Ru^{IV}/Ru^{III} couple (E_{pc}=−0.99 V vs. $Ag/AgClO_4$(0.1 mol

dm^{-3} in CH_3CN)). The cyclic voltammogram also shows an indistinct reduction wave observable near −0.85 V. The origin of the dim reduction wave is not clear, but it is thought to be caused by a partial decomposition of **1A** in the organic solvent. In the back sweeping, a small oxidation wave, which is the pair to the reduction wave at −0.99 V, appeared at −0.92 V with two additional oxidation waves. We compared the current heights, observed by the normal pulse voltammetry at the same experimental conditions, of the reduction wave at −0.99 V with those of other Ru^{IV}/Ru^{III};[28] the reduction wave appeared to be a metal-centered two-electron transfer comprising the Ru^{IV} and Ru^{II} oxidation states

$$[Ru^{IV}Cl(O)(py)_4]^+ + 2e^- \longrightarrow [Ru^{II}Cl(O)(py)_4]^- \quad (5)$$

Fig. 3 also illustrates that the electrochemically produced $[RuCl(O)(py)_4]^-$ is not stable and probably undergoes a facile solvolysis to give $[RuCl(CH_3CN)(py)_4]^+$, which is responsible for the appearance of the oxidation waves at −0.84 V. A one-electron reduced species involving Ru^{III}–O^{2-} moiety was unobtainable by the electrochemical reduction in the aprotic solvent, while a succesive reduction of $Ru^{IV}=O^{2-}$ to give Ru^{III}–OH^- and Ru^{II}–OH_2 moieties has been observed in aqueous solvent for certain oxoruthenium(IV) complexes.[1b] As was described above, **1A** exhibited the two-electron reduction wave at a surprisingly negative potential region, where the Ru^{III}/Ru^{II} redox potential is generally observed. The very negative potential in **1A**, compared to those of known Ru^{IV}/Ru^{III} couples, could be understood as showing that the presence of the oxo ligand leads to extensive stabilization of Ru^{IV} state.[1b]

Reactivity. The oxoruthenium(IV) complex in CH_3CN reacts easily with PPh_3. Such a reaction, which produces Ph_3PO with a reducing of the oxidation state of the metal atom, is characteristic for the complexes containing a reactive oxygen ligand. When **1A** in CH_3CN was mixed with PPh_3 (mole ratio 1:1.5) at room temperature, the mixed solution changed immediately from green to yellow. A brown material could be obtained by adding an excess amounts of ether to the yellow solution. The composition of the brown material agreed well with that of $[RuCl(CH_3CN)(py)_4]PF_6$. IR spectra of this material exhibited a sharp absorption band at 2245 cm^{-1}; this is assignable to ν(CN) of the coordinated CH_3CN. Another product, Ph_3PO, could also be obtained as a white precipitate from the filtrate of $[RuCl(CH_3CN)(py)_4]PF_6$ by adding ether (ν(P=O), 1182 cm^{-1}). While a stoichiometric study of the reaction could not be achieved, the above results giving both $[RuCl(CH_3CN)(py)_4]^+$ and Ph_3PO can be understood by the following equation:

$$[RuCl(O)(py)_4]^+ + PPh_3 \longrightarrow [RuCl(S)(py)_4]^+ + Ph_3PO \quad (S=CH_3CN) \quad (6)$$

The oxoruthenium(IV) complex **1A** is reactive even for organic solvents, such as alcohols and acetone. Upon recrystallization with methanol, the effective magnetic moment decreased from 2.94 to near 2.5 B.M. (calculated for the same formula as the mono-oxo complex), as was described above. Although the oxo ligand in ($Ru^{IV}=O^{2-}$) unit has been known to act as an oxygen-transfer agent toward organic substrates, there was no example where a product was isolated from these reactions, except for the case of the Ph_3PO. Attempt to isolate the solvolysis product from methanol, in the present case, yielded a red crystalline product. The experimental data obtained so far for the product as follows. Satisfactory elemental analyses were obtained, from which *trans*-$[RuCl(OMe)(py)_4]^+$ **4** could be confirmed.[29] The effective magnetic moment (2.32 B.M.), which was measured by the Gouy method, is in the range expected for Ru^{III} complexes. IR spectra show new bands at 2860, 2786, 1422, 1038, and 549 cm^{-1}, with disappearance of the ν(Ru=O) band characteristic of the oxo complexes. The assignment of the methoxo bands was verified by a comparison of those for the deuterated complex, $[RuCl(OCD_3)(py)_4]^+$, with the results reported by Hill et al.[30] 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, and it is thought to shifted to near 1100 cm^{-1} region, where a strong absorption band due to ClO_4^- was observed. The band at 1038 cm^{-1}, which is believed to be methoxy CO stretching vibration, shifted to 1004 cm^{-1}. The Ru–O stretching vibration at 549 cm^{-1} is also shifted to 526 cm^{-1} in its deuterated complex. These shifts found in C–O and Ru–O stretching vibrations are regarded to be reasonable for the deuteration of a methoxo ligand coordinated to metal.[30]

Although further investigation is now in progress on the oxoruthenium(IV) complex, which acts as an oxidant toward organic substrates, we assume that the methoxo formation reaction involves a water condensation reaction between methanol and a hydroxo complex of Ru^{III}, $[RuCl(OH)(py)_4]^+$, which is formed by a one-electron reduction of **1A** (reverse of Eq. 4) with interaction of another methanol molecule

$$[RuCl(OH)(py)_4]^+ + MeOH \longrightarrow [RuCl(OMe)(py)_4]^+ + H_2O \quad (7)$$

The existence of the hydroxo complex could be presumed before the methoxo formation reaction occured.[31]

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