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Reactivity toward Alcohols of ($Ru^{IV}=O^{2-}$) Unit in *trans*-$[RuCl(O)(py)_4]^+$

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The reactivity with alcohol of *trans*-$[RuCl(O)(py)_4]^+$ was investigated. In MeOH, *trans*-$[RuCl(OH)(py)_4]^+$ was confirmed to exist as a precursor in the formation of *trans*-$[RuCl(OMe)(py)_4]^+$. The reaction progress was traced by spectrometrical and ^{18}O-labelling experiments.

There has been growing interest in high-valence ruthenium complexes with reactive oxygen ligand ($Ru^{IV}=O^{2-}$). We have developed a new synthetic route for an oxo complex of Ru^{IV}, *trans*-$[RuCl(O)(py)_4]^+$,[1] and now, as an extension of the study, the chemical behavior of ($Ru^{IV}=O^{2-}$) unit in the oxo complex toward alcohols (MeOH, EtOH, and *n*- and *i*-PrOH) was investigated. Such a study has actually been not reported, although Meyer et al. investigated a reaction of *cis*-$[Ru(O)(trpy)(bpy)]^{2+}$ with *i*-PrOH containing excess water from kinetic and mechanistic viewpoints.[2,3] They have proposed 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 the first synthetic evidence for the existence of the intermediate complex, along with evidence that the reactivity of the unit as an oxidant toward alcohols depends on the conditions adopted for the reaction.

The reaction products, isolated by the procedures described below, were formulated as the hydroxo complex and the alkoxo complex of Ru^{III}, **1** and **2**-**5** (Table 1).

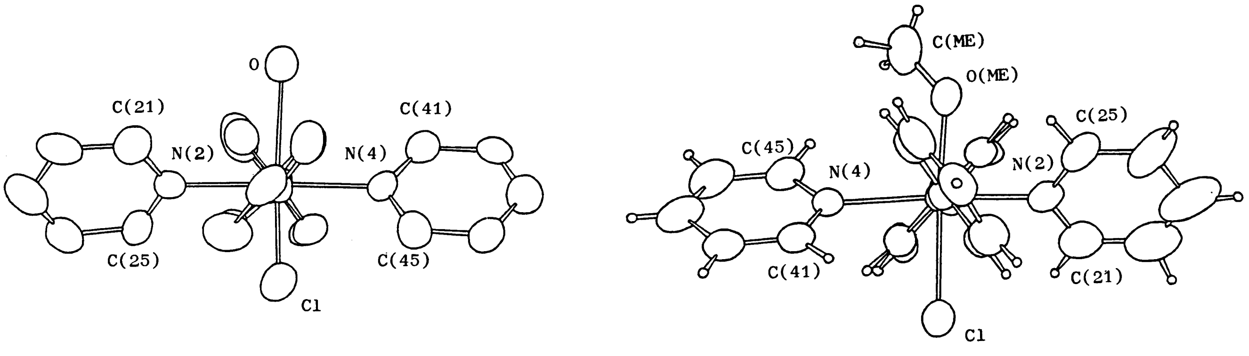
Table 1. Products and their properties

Complex		μ_{eff}/μ_B a)	$E_{1/2}/V$ b)	$\lambda(\varepsilon)$ c)
$[RuCl(OH)(py)_4]PF_6$	(**1**)	2.05	-0.68	297 (1.2×10^4) 262 (1.0×10^4)
$[RuCl(MeO)(py)_4]ClO_4$	(**2**)	2.15	-0.74	427 (2.3×10^3) 301 (1.2×10^4)
$[RuCl(EtO)(py)_4]PF_6$	(**3**)		-0.77	434 (2.2×10^3) 302 (1.1×10^4)
$[RuCl(n\text{-}PrO)(py)_4]PF_6$	(**4**)		-0.78	437 (2.1×10^3) 302 (1.0×10^4)
$[RuCl(i\text{-}PrO)(py)_4]PF_6$	(**5**)		-0.79	433 (2.2×10^3) 300 (1.0×10^4)

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

The structures of both **1** and **2** were determined to confirm the above characterization. Crystal data are as follows. For **1**; tetragonal, with space group $P4/ncc$, a=25.937(4) Å, c=14.469(1) Å, V=9733(2) Å^3, μ(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 **2**; monoclinic, $P2_1/n$, a=22.311(3) Å, b=13.546(2) Å, c=8.091(1) Å, β=95.89°, V=2432.4(6) Å^3, μ=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 structures were solved by the heavy atom method, and refined to give an R value of 0.083 for 3123 independent reflections with $|F_o|>3\sigma(|F_o|)$ for **1**, and of 0.040 for 6154 independent reflections with $|F_o|>3\sigma(|F_o|)$ for **2**. The reflections were collected by ω scan technique (2θ<55° for **1**, <50° for **2**) on a Rigaku AFC-6A automated four-circle diffractometer, using Mo $K\alpha$ radiation (λ=0.7107 Å). The perspective drawings of the complexes are shown in Fig. 1. Selected interatomic distances and angles are listed in Tables 2 and 3. The cations are a hydroxo complex ion and a methoxo complex ion of Ru^{III}, with trans octahedral geometry: they have four equatorial pyridine ligands. No remarkable difference between the structure of **1** and that of **2** could be observed, except CH_3 group in **2**; CH_3 group of the methoxo ligand was directed to bisect the N(1)-Ru-N(4) angle, with Ru-O-C angle of 127.1(2)°.[4)]

Fig. 1. Perspective drawing of $[RuCl(OH)(py)_4]^+$ **1** and $[RuCl(MeO)(py)_4]^+$ **2**, and their numbering scheme.



Complex **1**

Complex **2**

Table 2. Selected interatomic distances and bond angles for **1**

	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 3. Selected interatomic distances and bond angles for **2**

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

The reaction of the oxo complex with MeOH(Spectrosol) was monitored by spectrophotometry; the mixed solution must be allowed to stand at least 5 days when the experiment is attempted in a preparative scale. The reaction progress can be divided conveniently into three steps (Fig. 2). A freshly prepared MeOH 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]), the intensity of the band at 265 nm decreased slowly 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 and was replaced by a weak band at 640 nm, which remained hereafter without remarkable changes in either wave length or intensity. 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 at 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.$^{5)}$ It was found that the addition of a small amounts of water (1-3 cm^3) to the MeOH solution served to slow down the progress of the reaction.

The solution obtained in the first stage of the reaction gave a yellow product by reducing the solution volume,$^{6)}$ while that of the second step gave 2 as red crystals. The experimental conditions for the isolation of the yellow crystals are rigid, since it appears to be a short-lived species relative to 2. The experimental data (Anal, CV, UV, IR) observed for the yellow product are the same as those of 1 prepared as an authentic sample.

Above observations could clarify the existence of the hydroxo complex of Ru^{III} as a precursor in the stage before the formation of the alkoxo complex. The present work also indicates that the reactivity of ($Ru^{IV}{=}O^{2-}$) unit depends on the reaction conditions; although the first product which was confirmed to be the hydroxo complex of Ru^{III} was the same as that proposed by Meyer et al.,$^{4)}$ the second product in their work studied in *i*-PrOH containing water was an aqua complex of Ru^{II}, while that clarified by the present work was the alkoxo complex of Ru^{III}, even in the reaction with *i*-PrOH.$^{7)}$

The alkoxo complexes 3-5 undergo a facile hydrolysis to give 1, while that of 2 is extremely slow. Treatment of the hydrolyzed solution with Ce^{4+} used as oxidant gave the original oxo complex quantitatively. By the same procedure

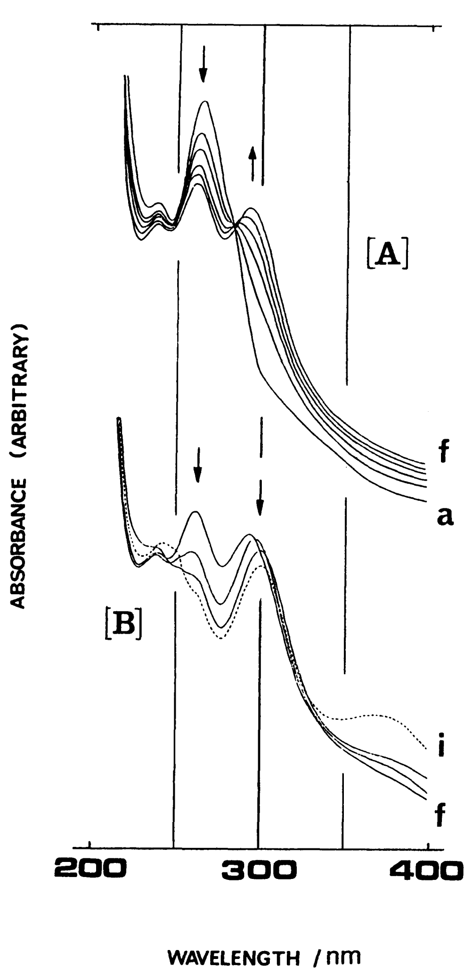


Fig. 2. UV spectral change of $[RuCl(O)(py)_4]PF_6$ (6.5×10^{-5} mol dm^{-3}) in MeOH at room temperature (22 °C). [A]: 1st step of the reaction, (a) immediately after, (b) 10 h, (c) 25 h, (d) 37 h, (e) 45 h, (f) 51 h. [B]: 2nd and 3rd (dotted line) steps, (f) 51 h, (g) 61 h, (h) 68 h, (i) 75 h.

using $H_2{}^{18}O$(99.1%), $[RuCl(^{18}O)(py)_4]PF_6$ could be obtained from the alkoxo complex **4**.[8] These results can be illustrated by the following scheme:

$$(Ru^{III}\text{-}OR) + H\text{-}\overset{*}{O}\text{-}H \longrightarrow (Ru^{III}\text{-}\overset{*}{O}H) \longrightarrow (Ru^{IV}{=}\overset{*}{O}) + e^-$$

The reverse reaction of the scheme may be indicative of the behavior of the ($Ru^{IV}{=}O^{2-}$) unit toward alcohol; the alkoxo complex does not retain the oxygen atom in the unit, whereas the hydroxo complex is considered to retain it.

Typical procedures for the isolation of the products are as follows. *trans*-$[RuCl(OH)(py)_4]PF_6$ **1**: $[RuCl(O)(py)_4]PF_6$ (300 mg) was dissolved in the mixed solution of MeOH-H_2O (50-50 cm^3), and it was refluxed for 15 min, until the color changed from green to yellow. The solution was kept at room temperature for 1 day. Yellow crystals which deposited were collected and washed with ether, then dried in vacuo. Yield 70-80%. Found: C, 38.9; N,9.0; H,3.4%. Calcd for $C_{20}H_{21}N_4OClPF_6Ru$: C, 39.1; N, 9.1; H, 3.5%. *trans*-$[RuCl(MeO)(py)_4]ClO_4$ **2**: The oxo complex (ClO_4 salt) (50 mg) was dissolved in MeOH (25 cm^3) and kept at room temperature for 5 days. Red crystals appeared by reducing the solution volume, and they were collected, washed with ether, and dried in vacuo. Yield 70-80%. Found: C, 43.2; N, 9.6; H, 3.9%. Calcd for $C_{21}H_{23}N_4O_5Cl_2Ru$: C, 43.4; N, 9.6; H, 4.0%. Other alkoxo complexes, **3**-**5**, were obtained by a similar procedure to that of **2**. Satisfactory analyses were observed.

References

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4) In case of **2**, all hydrogen atoms of both the pyridine rings and the methoxy group were found at reasonable positions on the final difference Fourier map; then they were included in the calculation, while those of **1** were calculated and fixed, since only a few hydrogen atoms were obtained.

5) UV spectra with isosbestic points were observed on further standing of the solution. It appears to form the one-electron reduced species of **2**, although its isolation was not possible.

6) The yellow crystalline product should be isolated when both absorption bands at 265 and 296 nm come to have almost the same intensity.

7) An additional difference between Meyer's and the present reactions was observed by UV spectral monitoring of the reaction. They found isosbestic points, which indicate the formation of first the hydroxo complex of Ru^{III} and then the aqua complex of Ru^{II}; the present reaction does not exhibit these points.

8) The IR absorption band due to $\nu(RuO)$, observed at 804 cm^{-1} for the original oxo complex,[1] disappeared upon ^{18}O substitution. This finding suggests the existence of ^{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 due to the pyridine moiety.

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