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PREPARATION AND STRUCTURE OF THE RUTHENYL COMPLEX, *trans*-$[RuCl(O)(py)_4]^+$

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trans-$[RuCl(O)(py)_4]^+$ with Ru^{IV}=O (ruthenyl) unit was obtained by the reaction of *trans*-$[RuCl(NO)(py)_4]^{2+}$ with NaClO. The remarkably long bond distance of Ru-O (1.862(8) Å), compared with those of known mono-oxo complexes, is indicative of its facile reactivity as an oxygen transfer agent.

Considerable attention has been focused on the chemistry of high-valent ruthenium complexes with Ru^{IV}=O unit in connection with their usefulness as an oxygen transfer agent in the selective oxidation of organic substrates.[1] Though several ruthenyl complexes have recently been prepared,[1b,2] structural information concerning the ruthenyl unit has not been reported yet. Here we describe the structure of a new ruthenyl complex, *trans*-$[RuCl(O)(py)_4]ClO_4$, which was prepared by the reaction of *trans*-$[RuCl(NO)(py)_4]^{2+}$ with sodium hypochlorite solution.[3]

Addition of sodium hypochlorite solution[4] (2 cm^3) to the aqueous solution of *trans*-$[RuCl(NO)(py)_4](ClO_4)_2$,[5] (0.5 g/$H_2O$ 15 cm^3), gave immediately a yellow precipitate which became gradually light green with stirring for 3 h at room temperature. The crystalline product obtained was kept for 3 more hours without stirring and then filtered out, washed with cold water, and dried *in vacuo*.[6]

The crystals are tetragonal, with the space group P4/ncc, a=25.781(5) Å, c=14.130(4) Å, V=9391(4) $Å^3$, μ(Mo $K\alpha$)=9.21 cm^{-1}, $F.W.$=568.4, Z=16, D_m=1.59 g cm^{-3}, D_x=1.61 g cm^{-3}. The structure was solved by the heavy atom method, and refined to give an R value of 0.076 for the 2122 independent reflections with $|F_o|>3\sigma(|F_o|)$. The reflections were collected by ω scan technique ($2\theta<55°$) on a Rigaku AFS-6A automated four-circle diffractometer, using Mo $K\alpha$ radiation (λ=0.7107 Å). The per-

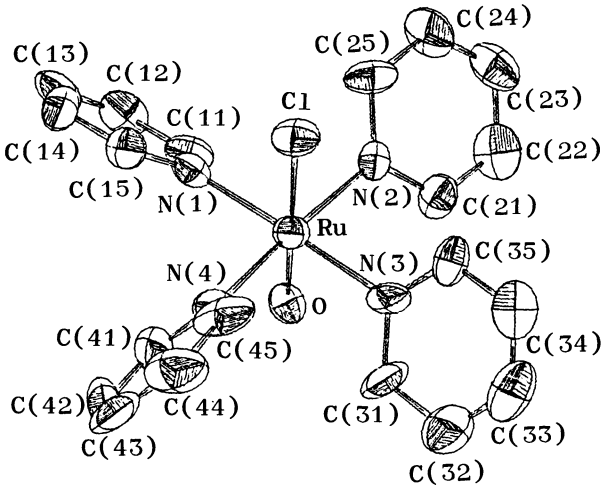

Fig. 1. The perspective drawing of $[RuCl(O)(py)_4]^+$ and the numbering scheme of non-hydrogen atoms.

spective drawing of the complex is shown in Fig. 1. Selected interatomic distances and angles are listed in Tables 1 and 2.

As shown in Fig. 1, the cation is an oxo ruthenium(IV) complex ion, with *trans* octahedral geometry; it has four equatorial pyridine ligands, while the oxo and the chloro ligands are coordinated in the axial direction. Similar to the original nitrosyl complex,

Table 1. Selected interatomic distances

	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(6)	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 2. Selected bond angles

			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(3)	177.6(4)
N(2)	-Ru-	N(4)	177.9(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)
C(15)-	N(1)-	C(11)	123(1)

trans-$[RuCl(NO)(py)_4]^{2+}$,[7] the oxo complex has a propeller-like structure. The oxo and chloro ligands are almost on the line including the ruthenium(IV); O-Ru-Cl, 178.2(3)°. It is worth noting that the Ru-O distance, 1.862(8) Å, is much longer than those of known mono-oxo complexes,[8] and is comparable to those of μ-oxo ruthenium(III) and -(IV) complexes.[9] The distance of Ru-Cl, 2.419(4) Å, is a little longer than those of ruthenium(IV) complexes.[10] The dihedral angles between the best plane of RuN_4 and those of the pyridine rings range from 44.1 – 54.1°. The angles between the two pyridine planes in *trans* positions are 80.6 – 82.7°, which are a 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 oxo 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 oxygens of ClO_4^- on the four- and two-fold rotation axis, and their positions could not be determined.

In conformity with the structure determination, the following properties were observed. An infrared absorption band assignable to Ru=O stretching vibration appeared around 800 cm^{-1} region,[11] in addition to those due to py and ClO_4^-. Magnetic measurement at room temperature gave μ_{eff} of 2.94 B.M. This is slightly higher than the spin-only value for two unpaired spins and is consistent with the presence of a d^4, paramagnetic Ru^{IV} ion. Cyclic and normal pulse voltammetries with platinum microdisk electrode (ϕ=1.99 mm) revealed that the complex in CH_3CN underwent a single two-electron reduction at -0.99 V *vs.* $Ag|AgClO_4$ (0.1 mol dm^{-3}). The reduction species having the oxo ligand decomposed with a fairly fast rate. The ruthenyl complex was reactive toward organic substrates such as PPh_3, MeOH, and acetone. The reaction with PPh_3 can be explained in terms of the oxygen transfer process to give Ph_3PO.[1a,12] In the reaction with MeOH, a ruthenium(III) complex which could tentatively be formulated as $[RuCl(OMe)(py)_4]^+$ was isolated in good yield. An X-ray structure determination of the product is currently under way.

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d) S. Goswami, A. R. Chakravarty, and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1982, 1288.

2) Chi-Ming Che, Tin-Wu Tang, and Chung-Kwong Poon, *J. Chem. Soc., Chem. Commun.*, 1984, 641.

3) One conceivable reaction scheme to give the oxo complex is as follows:

$$Ru^{II}\text{-}NO^{+} \xrightarrow{2OH^{-}} Ru^{II}\text{-}NO_2^{-} \xrightarrow{-e^{-}} Ru^{III}\text{-}NO_2^{-}$$

$$\xrightarrow{OH^{-}} (Ru^{III}\text{-}OH^{-} + NO_2^{-}) \xrightarrow{-e^{-},\ -H^{+}} Ru^{IV}{=}O^{2-}$$

The $Ru^{II}\text{-}NO_2^{-}$ species in the first stage was isolated and characterized as $[RuCl(NO_2)(py)_4]$.

4) Wako Co., available chlorine 10%.

5) F. Bottomley and M. Mukaida, *J. Chem. Soc., Dalton Trans.*, 1982, 1933.

6) Elemental analysis. Found: C, 42.2; H, 3.4; N, 9.9%. Calcd for $[RuCl(O)(py)_4]ClO_4$: C, 42.2; H, 3.5; N, 9.9%. Yield, 90%.

7) T. Kimura, T. Sakurai, M. Shima, T. Togano, M. Mukaida, and T. Nomura, *Inorg. Chim. Acta*, 69, 135 (1983).

8) a) 1.56 Å for V-O distance in $[VO(acac)_2]$: R. D. Dodge, O. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, 35, 55 (1961); b) 1.60 Å for V-O distance in $[VO(H_2O)(pmida)]$: S. Ooi, M. Nishikawa, K. Matsumoto, H. Kuroya, and K. Saito, *Bull. Chem. Soc. Jpn.*, 52, 452 (1979).

9) 1.883 Å (Ave.) in $[Ru_2O(NO_2)_2(bpy)_4](ClO_4)_2\cdot 2H_2O$: D. W. Phelps, E. M. Hahn, and D. J. Hodgson, *Inorg. Chem.*, 14, 2486 (1975); 1.80 Å in $K_4[Ru_2OCl_{10}]$: N. C. Baenziger, J. Wyart, J. M. Robestson, *Structure Reports, Bd.*, 16, 1952, *s.* 194.

10) 2.364 Å (Ave.) in $K_3[Ru_2NCl_8(H_2O)_2]$: M. Ciechanowicz and A. C. Skapski, *Chem. Commun.*, 1969, 574; 2.34 Å in $K_4[Ru_2OCl_{10}]$: Ref. 8b.

11) The corresponding band has been observed in this region for all known ruthenyl complexes which was reported in Refs. 1 and 2.

12) The product showed an IR band at 2240 cm^{-1}, which is the region expected for $\nu(C{\equiv}N)$, and $\nu(Ru{=}O)$ at 804 cm^{-1} disappeared in turn. Another product, Ph_3PO ($\nu(P{=}O)$, 1180 cm^{-1}), could also be obtained from the filtrate of the product, $[RuCl(CH_3CN)(py)_4]^{+}$.

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