Syntheses, structures, and properties of oxorhenium(V) complexes with 2-, 5-, and/or 7-substituted 8-quinolinolato ligands

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Abstract

Five mononuclear oxorhenium(V) complexes containing 8-quinolinolato derivatives, [ReOCl₂(2-X-5-Y-7-Z-8-Oqn)(PPh₃)] (qn = quinoline; PPh₃ = triphenylphosphine; X = Me, Y = Z = H, 1; X = Z = H, Y = Cl, 2; X = H, Y = Z = Cl, 3; X = H, Y = Cl, Z = I, 4; X = H, Y = Z = Br, 5), were newly synthesized by the reaction of [ReOCl₃(PPh₃)₂] with the corresponding 8-hydroxyquinoline ligands. From X-ray crystal structural analyses, all the obtained complexes have the same geometry; the Re-O bond occupies the trans position to the O atom of the deprotonated 8-hydroxyquinoline ligand. The complexes, which retain their structures in solution, were characterized on the basis of IR, UV–vis, ³¹P NMR spectra, and cyclic voltammetry. Depending on the existence of 2-Me substituent in the ligands, some stereochemical and electrochemical differences were observed. In contrast to the case of the corresponding 2-methylquinolin-8-ylamido complex [ReOCl₂(2-Me-8-HNqn)(PPh₃)], substitution reaction of PPh₃ to OPPh₃ (=triphenylphosphine oxide) or pyridine did not take place, reflecting the high stability of the present 8-quinolinolato complexes.

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Keywords: Re(V) complexes; Crystal structures; IR spectra; UV–vis spectra; ³¹P NMR spectra; Cyclic voltammetry

1. Introduction

Rhenium complexes are well known as technetium surrogate to design many types of coordination compounds because of the chemical similarities of these group seven elements. They have been of interest as radiopharmaceuticals [1]. Indeed, ⁹⁹m-technetium complexes are widely used for diagnostic imaging, whereas ¹⁸⁶/¹⁸⁸-rhenium complexes are used for nuclear medical therapy [2]. On the other hand, the chemistry of rhenium involves several oxidation states from -I to VII. In particular, the oxidation of Re(V) complexes to Re(VII) complexes is an essential step in the catalytic cycle by which such a pair catalyzes oxygen atom transfer (OAT) reaction [3]. For example, the OAT catalytic properties of mono and dinuclear methyloxorhenium(V) complexes have been energetically investigated [4]. When the design of rhenium complexes for medicine and engineering are considered, steric demand is always an important issue. Therefore, it is important to explore the stereoselective synthesis and reactivity of rhenium complexes.

Re(V/VII) redox system is isoelectronic to Mo(IV/VI) and W(IV/VI) ones, which are observed at the active sites of molybdenum and tungsten enzymes. There are many molybdenum and tungsten enzymes, such as xanthine oxidase, sulfite oxidase, and dimethyl sulfoxide reductase, in vivo, and they indicate an excellent OAT catalytic activity [5–7]. Although any enzymes containing rhenium ion have never discovered, it has been reported that the OAT catalytic activities of some Re complexes are superior to those of the corresponding Mo complexes [8]. Thus, studies on stereochemistry and reactivity of oxorhenium(V) complexes as model complexes also involve biological interest.

We have obtained the nitrogen-containing Re(V) complexes by using the asymmetrical didentate-N,N ligands (two types of the nitrogen atoms in heterocyclic ring and aromatic amine) 8-amino-2-methylquinoline (2-Me-8-H₂Nqn) and 8-aminoquinoline (8-H₂Nqn), such as [ReOCl₂(2-Me-8-HNqn)(PPh₃)] and [ReCl₃(8-Nqn)(PPh₃)]

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(PPh3=triphenylphosphine) [9,10]. The result gave the interest that the structures and properties of these complexes were different depending on 2-substituent group. Namely, the complex containing the ligand with 2-Me substituent retains the [ReO\(\text{V}\)]\(^{3+}\) core [9], whereas the complex containing the ligand without 2-Me was obtained as the imido complex, which has a Re=N bond [10]. Further, the complex with 2-Me-8-HNqn was unstable in solution and it easily reacts with a monodentate ligand such as triphenylphosphine oxide (OPPh\(_3\)) [9]. By the use of this property, the complex can be expected for the possibility as an OAT catalyst. Indeed, we have found quite recently that [ReOCl\(_2\)(2-Me-8-HNqn)(PPh\(_3\))] shows OAT catalytic property from pyridine oxide to PPh\(_3\) [11]. From such differences for structure and reactivity, it may be assumed that the existence of the substituent group affects the reactivity and stereochemistry.

To explore the effect on the substituent group and characteristic of Re(V) complexes, we selected the denticate-N,O ligands 8-hydroxyquinoline (8-HOqn) derivatives, which can be easily available and confirmed by systematic experiments. We attempted the synthesis of oxorhenium(V) complexes containing 8-quinolinolato derivatives by changing a substituent group at positions 2, 5, and/or 7. As a result, [ReO\(\text{V}\)]\(^{3+}\) core complexes [ReOCl\(_2\)(8-Oqn)(PPh\(_3\))] were obtained in all cases. Structures of these oxorhenium(V) complexes were determined by X-ray diffraction study and their spectrochemical properties are discussed in relation to their structures.

2. Experimental

2.1. Materials

Rhenium, PPh\(_3\), and OPPh\(_3\) were purchased from Soekawa Chemical Co., Ltd, Wako Pure Chemical Industries, Ltd, and Aldrich Chemical Co., Inc., respectively. 2-Methyl-8-hydroxyquinoline (2-Me-8-HOqn), 5-chloro-8-hydroxyquinoline (5-Cl-8-HOqn), 5,7-dichloro-8-hydroxyquinoline (5-Cl-7-Cl-8-HOqn), 5,7-dichloro-8-hydroxyquinoline (5-Cl-7-I-8-HOqn), and 5,7-dibromo-8-hydroxyquinoline (5-Br-7-Br-8-HOqn) were purchased from Tokyo Kasei Kogyo Co., Ltd. The other materials were purchased from Wako Pure Chemical Ind., Ltd. All the chemicals were used without further purification. The starting material [ReOCl\(_2\)(PPh\(_3\))]\(_2\) was prepared by the general procedure from rhenium, hydrogen peroxide, and PPh\(_3\) [12].

2.2. Preparation of complexes

2.2.1. [ReOCl\(_2\)(2-Me-8-HOqn)(PPh\(_3\))] (I)

To a suspension containing [ReOCl\(_2\)(PPh\(_3\))]\(_2\) (200 mg, 0.24 mmol) in C\(_6\)H\(_5\)CH\(_3\) (40 cm\(^3\)) was added a solution containing an equimolar 2-Me-8-HOqn (39 mg) in C\(_6\)H\(_5\)CH\(_3\) (20 cm\(^3\)). The mixture was heated and stirred for 3.5 h, whereupon the color of the mixture turned from light-green to dark-brown. After cooling to room temperature, the solution was concentrated to ca. 5 cm\(^3\) by vacuum line. The brownish green powder was collected by filtration and washed with Et\(_2\)O. The obtained complex was recrystallized from CH\(_2\)Cl\(_2\)/C\(_6\)H\(_5\)CH\(_3\) (5:1) to yield the brownish green crystals. A well-formed crystal of 1-C\(_6\)H\(_5\)CH\(_3\) was used for an X-ray structural analysis. Yield: 129 mg (78%). Anal. Found: C, 53.50; H, 3.98; N, 1.78%. Calcd for [ReOCl\(_2\)(2-Me-8-Oqn)(PPh\(_3\))] \cdot C\(_6\)H\(_5\)CH\(_3\): C\(_{25}\)H\(_{23}\)Cl\(_2\)NO\(_2\)PRe \cdot C\(_6\)H\(_5\)CH\(_3\): C, 53.26; H, 3.90; N, 1.75%.

2.2.2. [ReOCl\(_2\)(5-Cl-7-Z-8-Oqn)(PPh\(_3\))] (Z=H, 2; Cl, 3; I, 4) and [ReOCl\(_2\)(5-Br-7-8-Oqn)(PPh\(_3\))] (5)

To a suspension containing [ReOCl\(_2\)(PPh\(_3\))]\(_2\) (200 mg, 0.24 mmol) in CH\(_2\)Cl\(_2\) (60 cm\(^3\)) was added a solution containing an equimolar 5-Cl-7-X-8-HOqn (Y=H, 44 mg; Cl, 52 mg; I, 74 mg) or 5-Br-7-Br-8-HOqn (73 mg) in C\(_6\)H\(_5\)CH\(_3\) (10 cm\(^3\)). The mixture was stirred overnight, whereupon the color of the mixture turned from light-green to dark-brown. After filtration of insoluble materials, the filtrate was concentrated to ca. 8 cm\(^3\) by vacuum line. The solution was allowed to stand for 3 d at room temperature whereupon the dark-brown precipitate was deposited. The complexes were collected by filtration and washed with H\(_2\)O and Et\(_2\)O. Each complex was recrystallized from CH\(_2\)Cl\(_2\)/C\(_6\)H\(_5\)CH\(_3\) (6:1) to yield the dark-brown crystals. Well-formed crystals were used for an X-ray structural analysis. The samples for the elemental analysis were ground and dried before measurements. 2: Yield: 71 mg (41%). Anal. Found: C, 46.90; H, 3.15; N, 1.98%. Calcd for [ReOCl\(_2\)(5-Cl-7-H-8-Oqn)(PPh\(_3\))] \cdot 0.4C\(_6\)H\(_5\)CH\(_3\): C\(_{27}\)H\(_{19}\)Cl\(_2\)NO\(_2\)PRe \cdot 0.4C\(_6\)H\(_5\)CH\(_3\): C, 47.00; H, 3.13; N, 1.89%. 3: Yield: 148 mg (82%). Anal. Found: C, 43.27; H, 2.74; N, 1.85%. Calcd for [ReOCl\(_2\)(5-Cl-7-I-8-Oqn)(PPh\(_3\))] \cdot 0.4C\(_6\)H\(_5\)CH\(_3\): C\(_{27}\)I\(_2\)Cl\(_2\)NO\(_2\)PRe \cdot 0.4C\(_6\)H\(_5\)CH\(_3\): C, 43.33; H, 2.56; N, 1.87%. 4: Yield: 167 mg (83%). Anal. Found: C, 38.88; H, 2.50; N, 1.61%. Calcd for [ReOCl\(_2\)(5-Cl-7-I-8-Oqn)(PPh\(_3\))] \cdot C\(_2\)Cl\(_2\)NO\(_2\)PRe: C, 38.61; H, 2.28; N, 1.67%. 5: Yield: 145 mg (72%). Anal. Found: C, 42.03; H, 2.87; N, 1.53%. Calcd for [ReOCl\(_2\)(5-Br-7-8-Oqn)(PPh\(_3\))] \cdot C\(_2\)Cl\(_2\)NO\(_2\)PRe: C, 42.50; H, 2.90; N, 1.55%.

2.3. Measurements

Elemental analyses (C, H, N) were performed by the Research Facility Center for Science and Technology in the University of Tsukuba. IR spectra were recorded using KBr pellets in the range of 4600–400 cm\(^{-1}\) and using Nujol mull in the range of 650–50 cm\(^{-1}\) on a JASCO FT/IR-550 spectrometer. The UV–vis spectra in CH\(_2\)Cl\(_2\) were recorded with a JASCO V-560 spectrophotometer. The diffuse reflectance (DR) spectra were recorded using powder samples, which were diluted by MgO, on a JASCO V-570 spectrophotometer equipped with an integrating sphere.
apparatus (JASCO ISN-470). The $^{31}$P($^1$H) NMR spectra in CDCl$_3$ were obtained on a BRUKER AVANCE 600 spectrometer using PPh$_3$ as an external reference. Electrochemical experiments were performed by a CV-50W voltammetry analyzer (BAS, Inc.) using a platinum-working electrode (BAS, Pt). An acetonitrile Ag/AgCl/Bu$_4$NClO$_4$ (saturated; BAS, Pt) and a platinum wire were used as reference and auxiliary electrodes, respectively. The experiments were conducted by the complexes (0.001 mol dm$^{-3}$) in an acetonitrile solution of Bu$_4$NClO$_4$ (0.1 mol dm$^{-3}$) as a supporting electrolyte. Ferrocene (Fc) was used as an external reference. All the measurements were carried out at room temperature.

2.4. X-ray crystallography

Single crystal X-ray data collections were performed on a Rigaku Mercury CCD area detector for 1·C$_6$H$_5$CH$_3$ and a Rigaku AFC-7S four-circle diffractometer for 3, 4, and 5 with a graphite-monochromatized Mo K$_\alpha$ (0.71069 Å) radiation. The intensity data were collected up to 55° at 296 K. The crystal data and experimental parameters are listed in Table 1. The positions of most non-hydrogen atoms were determined by direct method (SIR 97 for 1·C$_6$H$_5$CH$_3$ and SIR 92 for 3, 4, and 5) [13,14] and some remaining atom positions were found by successive difference Fourier techniques (DIRDIF-99 for 1·C$_6$H$_5$CH$_3$ and DIRDIF-94 for 3, 4, and 5) [15,16]. The structures were refined by full-matrix least-square techniques using anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were included in the refinement but restrained to ride on the atoms (C–H = 0.95 Å, U(H) = 1.2U(C)). The calculations were performed using the CrystalStructure crystallographic software package for 1·C$_6$H$_5$CH$_3$ and the teXsan crystallographic software package for 3, 4, and 5 [17,18].

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 258402–258405. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. Formation and crystal structures

The complexes 1–5 were obtained by the reaction of the [Re$^{V}$]$_3^{3+}$ precursor [ReOCl$_3$(PPh$_3$)$_2$] with an equimolecular 8-hydroxyquinoline ligand in the mixed solvent which involved CH$_2$Cl$_2$ and C$_6$H$_5$CH$_3$ (Fig. 1). The substitution of a chloride ion and a PPh$_3$ for an oxygen atom and a nitrogen atom of ligand takes place in the course of the reaction. When using CH$_2$Cl$_2$/C$_6$H$_5$CH$_3$ with EtOH for recrystallization, the complexes were obtained more readily. In all cases, the similar cis(Cl)–[ReOCl$_3$(8-Oqn)(PPh$_3$)]-type complexes were obtained. Consequently, no significant influence of substituent groups was confirmed in 1–5 regarding the chemical reactivity and stability. Although a kinetically stable trans(Cl) isomer as well as a thermodynamically stable cis(Cl) isomer are observed for the 8-quinolinolato complex without any substituents [19], the corresponding trans(Cl) isomer could not be isolated in the present system.

The single crystal X-ray structural analyses for 1, 3, 4, and 5 revealed the presence of a discrete mononuclear complex molecule. The perspective views of the representative

| Table 1 Crystal data and experimental parameters for [ReOCl$_3$(2-Me-8-Oqn)(PPh$_3$)]; C$_6$H$_5$CH$_3$ (1·C$_6$H$_5$CH$_3$), [ReOCl$_3$(5-Cl-7-Cl-8-Oqn)(PPh$_3$)] (3), [ReOCl$_3$(5-Cl-7-I-8-Oqn)(PPh$_3$)] (4), and [ReOCl$_3$(5-Br-7-Br-8-Oqn)(PPh$_3$)] (5) |
|---|---|---|---|---|
| 1·C$_6$H$_5$CH$_3$ | 3 | 4 | 5 |
| Formula | C$_2$H$_7$I$_3$NO$_3$Re | C$_2$H$_7$I$_3$NO$_3$Re | C$_2$I$_3$Cl$_3$NO$_3$Re | C$_2$I$_3$Br$_2$ClNO$_3$Re |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| a/Å | 9.8021(4) | 18.370(2) | 18.424(2) | 18.421(5) |
| b/Å | 14.7217(5) | 10.1443(9) | 10.241(2) | 10.273(3) |
| c/Å | 22.8506(10) | 17.168(3) | 17.089(4) | 16.653(7) |
| β (°) | 102.1519(5) | 97.78(1) | 97.14(2) | 109.22(3) |
| V/Å$^3$ | 3223.5(2) | 3169.8(7) | 3199(1) | 2975(1) |
| Z | 4 | 4 | 4 | 4 |
| D$_{calcd}$/g cm$^{-3}$ | 1.619 | 1.568 | 1.744 | 1.869 |
| μ (Mo K$_\alpha$/cm$^{-1}$) | 40.18 | 42.45 | 50.88 | 70.36 |
| Reflections collected | 50978 | 8054 | 8251 | 7615 |
| Unique reflections | 7618 | 7275 | 7358 | 6889 |
| D(A>3σ(I)) | 5562 | 5893 | 5564 | 3249 |
| Variable parameters | 410 | 325 | 325 | 325 |
| Final R$(I^2)$ | 0.032 | 0.060 | 0.062 | 0.077 |
| Final R$_e$ $(I^2)$ | 0.083 | 0.187 | 0.200 | 0.200 |
| Goodness-of-fit | 1.01 | 1.17 | 1.22 | 1.11 |
complexes 1 and 4 are shown in Figs. 2 and 3, respectively. The selected bond distances, bond angles, and dihedral angles of 1, 3, 4, and 5 are listed in Table 2. The geometrical structures of four complexes are substantially the same as each other. In each complex, rhenium ion is coordinated by an oxygen atom with a double bond character, two chloride ions, a phosphorus atom from the PPh₃, an oxygen atom and a nitrogen atom from the deprotonated chelating didentate 8-Oqn ligand, to form a distorted octahedral geometry. The oxygen atom of 8-Oqn ligand lies in trans to oxo ligand along the axial direction, whereas the heterocyclic nitrogen atom, which is the other moiety of 8-Oqn ligand, phosphorus atom and two cis chloride ions occupy the equatorial plane. The similar coordination geometry was observed for the corresponding Re(V) complex [ReOCl₂(2-Me-8-Oqn)(PPh₃)] with N donor atom instead of O donor atom [9].

All of the bond distances, except the C5–Y and C7–Z bonds, and angles in 3–5 are nearly the same as each other (Table 2). The C7–Z distances (1.741(8) Å in 3, 2.06(1) Å in 4, and 1.90(2) Å in 5) seem to depend on the ionic radius of halogenide ion. On the other hand, somewhat differences of the bond distances and angles were observed between [ReOCl₂(2-Me-8-Oqn)(PPh₃)] (1) and [ReOCl₂(5-Y-7-Z-8-Oqn)(PPh₃)] (3–5) (Table 2). For example, the Re1–O2 distance (1.969(3) Å) in 1 is shorter than those (2.010(7)–2.036(5) Å) in 3–5. The phenolato oxygen atom (02) is trans to the Re V=O bond, and is consistent with the trans influence of Re V=O linkage on an oxygen from an axially bound ligand [20]. The Re1–O1 distances (1.674(5)–1.69(1) Å) are typical for the oxorhenium(V) complexes and the Re1–N1 distances (2.149(7)–2.175(4) Å) are within the normal Re–N single bond for the oxorhenium(V) complexes (2.11–2.18 Å) [20]. The Re1–Cl1 bond trans to the PPh₃ phosphorus is slightly longer than the Re1–Cl2 bond trans to the quinoline nitrogen. This seems to be due to the trans influence of phosphorus, as observed in the corresponding quinolinylamido complex [9]. In addition, the rhenium ion is located at ca. 0.2 Å (0.1929(9) Å in 1, 0.234(2) Å in 3, 0.226(2) Å in 4, and 0.227(4) Å in 5) above the equatorial plane in the direction of the Re V=O bond.

The O1–Re1–O2 angles (159.8(4)–162.3(2)°) deviate from 180° for an ideal octahedral structure. The Re V=O linkage significantly expands the angles to the equatorial chloride ions; the Cl2–Re1–O1 and Cl1–Re1–O1 angles are significantly deviated from 90°. Unlike these bond angles, obvious differences between 1 and 3–5 were observed in the P1–Re1–O1 and C11–Re1–O1 angles. Namely, the P1–Re1–O1 angle (84.9(1)°) in 1 is smaller than those (91.5(1°)–91.4(3)°) in 3–5, whereas the O1–Re1–N1 angle (93.0(1)°) in 1 is larger than those (85.8(4)–87.4(3)°) in 3–5. The facts may arise from an intramolecular interaction. The dihedral angles between the quinoline rings and one of the phenyl
Table 2
Selected geometric parameters for [ReOCl2(2-Me-8-Oqn)(PPh3)] (1), [ReOCl2(5-Cl-7-Cl-8-Oqn)(PPh3)] (2), [ReOCl2(5-Cl-7-1-8-Oqn)(PPh3)] (3), [ReOCl2(5-Br-7-Br-8-Oqn)(PPh3)] (4), and [ReOCl2(5-Br-7-Br-8-Oqn)(PPh3)] (5)

| Bond distances (Å) | 1     | 2     | 3     | 4     | 5     |
|--------------------|-------|-------|-------|-------|-------|
| Re1–Cl1            | 2.380(1) | 2.371(2) | 2.372(3) | 2.381(5) |
| Re1–Cl2            | 2.341(1) | 2.327(2) | 2.328(3) | 2.333(5) |
| Re1–P1             | 2.486(1) | 2.470(2) | 2.474(3) | 2.465(5) |
| Re1–O1             | 1.678(3) | 1.674(5) | 1.677(7) | 1.691(9) |
| Re1–O2             | 1.969(3) | 2.036(5) | 2.017(7) | 2.02(1) |
| Re1–N1             | 2.175(4) | 2.149(7) | 2.163(9) | 2.16(2) |

Bond angles (°)

| Bond angles (°) | 1     | 2     | 3     | 4     | 5     |
|----------------|-------|-------|-------|-------|-------|
| O2–Re1–P1–C10  | 86.1(2) | 84.9(2) | 84.8(2) | 85.3(4) |
| O1–Re1–O2–P1   | 93.0(1) | 87.6(2) | 87.7(2) | 87.1(4) |
| P1–Re1–O2–P1   | 90.4(1) | 95.1(2) | 94.4(2) | 93.2(4) |
| Cl2–Re1–O1–N1  | 165.6(1) | 167.5(2) | 167.8(2) | 168.0(4) |
| Cl2–Re1–O1–O2  | 101.1(1) | 104.5(2) | 105.6(3) | 105.0(6) |
| Cl1–Re1–N1–C10 | 84.9(1) | 91.3(2) | 91.4(3) | 91.1(5) |
| Cl1–Re1–P1–C10 | 171.54(5) | 168.78(7) | 169.24(9) | 169.2(2) |
| Cl1–Re1–Cl2–P1 | 87.50(5) | 89.22(8) | 89.3(1) | 89.5(2) |

This difference can be attributed to the presence of a substitution group. Consequently, it is suggested that intramolecular π–π and/or CH–π stacking interactions exist between these two planes [21]. Although the corresponding 2-Me-8-HNqn complex also indicates the intramolecular stacking interactions (dihedral angle = 22.7(2)° and inter-ring average distances are 3.67(1) Å) [9], the interactions seem to weaker than those in the present complexes. From these results, the 2-substituent of the 8-quinolinolato affects the structure, although the 7-substituent hardly affects the structure.

Before the present work, the oxorhenium(V) complex [ReOCl2(5-NO2-8-Oqn)(PPh3)] using 5-nitro-8-hydroxyquinoline (5-NO2-8-HOqn), which is an only one example of stereochemically characterized Re(V) complex with quinolinolato derivatives, has been reported [20]. Its geometrical structure, which includes bond distances and angles, and spectrochemical character are similar to those of 3–5. In addition, the structure of [ReOCl2(5-Cl-8-Oqn)(PPh3)] (2) was also determined by single crystal X-ray analyses in this work. Although the space groups (P1) for 2 were different from those for 3–5, the presence of a complex molecule was revealed. The crystal was low-quality but the structure and geometry are identical with 3–5. Accordingly, the 5-substituent of the 8-quinolinolato does not affect the structure and the complexation.

3.2. Characterization and reactivity

Table 3 shows IR, far-IR, UV–vis absorption, DR, and 31P NMR spectral data for the present quinolinolato complexes 1–5. All the complexes showed similar IR and far-IR spectra to each other. The strong IR band of the Re\(^{V}\)=O bond was observed at ca. 980 cm\(^{-1}\) which are in the normal region (1000–940 cm\(^{-1}\)) for the analogous oxorhenium(V) complexes including [ReOCl2(8-Oqn)(PPh3)] (977 cm\(^{-1}\)) [22]. On the other hand, the value of the Re\(^{V}\)=O bond of the complex with 2-Me-8-HNqn, in which the amido exists \textit{trans} to the oxygen atom, is 908 cm\(^{-1}\) [9]. This low wavenumber shift corresponds to the usually long Re\(^{V}\)=O bond, which is due to the contribution of the \textit{trans} influence. The far-IR bands of the Re–Cl bonds were observed as two strong bands at ca. 340 cm\(^{-1}\) and ca.

Table 3 shows IR, far-IR, UV–vis absorption, DR, and 31P NMR spectral data for the present quinolinolato complexes 1–5. All the complexes showed similar IR and far-IR spectra to each other. The strong IR band of the Re\(^{V}\)=O bond was observed at ca. 980 cm\(^{-1}\) which are in the normal region (1000–940 cm\(^{-1}\)) for the analogous oxorhenium(V) complexes including [ReOCl2(8-Oqn)(PPh3)] (977 cm\(^{-1}\)) [22]. On the other hand, the value of the Re\(^{V}\)=O bond of the complex with 2-Me-8-HNqn, in which the amido exists \textit{trans} to the oxygen atom, is 908 cm\(^{-1}\) [9]. This low wavenumber shift corresponds to the usually long Re\(^{V}\)=O bond, which is due to the contribution of the \textit{trans} influence. The far-IR bands of the Re–Cl bonds were observed as two strong bands at ca. 340 cm\(^{-1}\) and ca. rings (13.2(2)° in 1, 13.7(3)° in 3, 13.0(4)° in 4, and 11.8(7)° in 5) means that the quinoline plates are nearly parallel to the phenyl, which are made of C11–C16 (1) or C10–C15 (3–5). The distances between two planes are 3.473(9) Å in 1, 3.38(1) Å in 3, 3.34(2) Å in 4, and 3.33(3) Å in 5. However, the O2–Re1–P1–C11 (86.1(2)°) and N1–Re1–P1–C11 (10.0(2)°) torsion angles in 1 are significantly different from the corresponding O2–Re1–P1–C10 (59.1(4)° to 60.3(8)°) and N1–Re1–P1–C10 (14.5(4)°) torsion angles in 3–5. This means that the C11–C16 phenyl ring position in 1 is not just above the quinoline ring, but it is over between the methyl group C10 and the edge of the quinoline ring C1. Contrarily, the C10–C15 phenyl ring position in 3–5 is just above the quinoline ring.
300 \text{ cm}^{-1}. Similar bands are also observed in \([\text{ReOCl}_2(8-\text{Oqn})(\text{PPh}_3)]\) (345 and 290 \text{ cm}^{-1}) \([22]\). The lower value is indicative of the Cl in the position trans to quinoline nitrogen atom. These values seem to correspond well to the bond distances, i.e. the bands of the 2-\text{Me}-8-\text{Oqn} complex 1 having relatively long Re–Cl bonds were observed in lower energy region than the other complexes.

The UV–vis spectra in CH$_2$Cl$_2$ solution of the complexes 1–5 were quite similar to each other all over the range (Table 3). This suggests that their skeletal structures are similar to each other. These results also indicate that these complexes do not depend upon the concentration, regardless of the complexes containing 2-\text{Me}-8-\text{HNqn} depend on the concentration \([9]\). It is suggested that these complexes form a distorted six-coordinated octahedral geometry, which can be observed in crystals. Each of the bands around 15\times10^3 \text{ cm}^{-1} in 1–5 are assigned to d–d transition and 25\times10^3 \text{ cm}^{-1} are ligand-to-metal charge transfer (LMCT) transition. The bands, which are broadened around 27–30\times10^3 \text{ cm}^{-1} are the peaks derived from quinoline ring and beyond 35\times10^3 \text{ cm}^{-1} are dependent on PPh$_3$. The DR spectra of all complexes are also similar to each other over the whole region. The bands around 25\times10^3 \text{ cm}^{-1} in 1–5 are due to LMCT. Furthermore, the DR bands in solid state were observed in approximately the same region as absorption bands in aqueous solution. It also suggests that the complexes retain the structures in solution as in solid state.

The $^{31}$P NMR spectra in CDCl$_3$ solution for all the complexes indicated only one sharp signal (Table 3). The chemical shift values differ from that of free PPh$_3$. Further, the absorption spectra showed no significant changes with time for at least a few hours. These facts indicate that the structures in solution of the complexes are retained at room temperature as in solid state. These results are different from the fact that the complex containing 2-\text{Me}-8-\text{HNqn}, which indicates quite similar $^{31}$P chemical shifts (δ −0.18 ppm from PPh$_3$) to free PPh$_3$ is unsuitable and dissociate in solution \([9]\). On the other hand, the $^{31}$P chemical shift (δ 28.41 ppm) for 1 is significantly different from those (δ 20.97–21.40 ppm) for 2–5. This means that the electronic condition on P atom is influenced by the 2-\text{Me} substituent.

| Complex | Re$^{\text{VI/V}}$ | Re$^{\text{V/IV}}$ |
|---------|----------------|----------------|
|         | $E^\text{pa}$ | $E^\text{pc}$ | $E^\text{pa}$ | $E^\text{pc}$ | $E^\text{pa}$ |
| 1       | +1.06         | −1.36         |               |               |               |
| 2       | +1.11         | −1.20         | −1.24         | −1.15         | −1.11         |
| 3       | +1.10         | +1.14         | +1.06         | −1.15         | −1.18         | −1.11         |
| 4       | +1.08         | +1.12         | +1.03         | −1.15         | −1.18         | −1.11         |
| 5       | +1.10         | +1.14         | +1.06         | −1.15         | −1.18         | −1.11         |

The cyclic voltammetry experiment using CH$_3$CN solution showed two redox waves at ca. +1 and ca. −1 V (vs Fc/Fc$^+$) for each of complexes 1–5. Their redox potentials with scan rate 200 mV s$^{-1}$ are summarized in Table 4. The redox potentials with scan rate 100 mV s$^{-1}$ were almost the same values. Each of the peaks at ca. +1 V are assigned to the redox process of Re$^{\text{VI/V}}$, whereas each of the peaks at ca. −1 V are assigned to the redox process of Re$^{\text{V/IV}}$ \([23]\). The redox process of Re$^{\text{VI/V}}$ indicated slightly larger peak–peak separation. The almost reversible processes were observed for 2–5, although only 2 indicates quasi-reversible process. This suggests that their skeletal structures are similar to each other. On the other hand, the redox processes of 1 are irreversible even with scan rate 500 mV s$^{-1}$. Moreover, the waves of 1 were observed in relatively negative region (ca. 0.15 V) in comparison with those of 2–5. As observed in $^{31}$P NMR spectra, the redox potentials of Re seems to be also influenced by the 2-\text{Me} substituent.

Since the oxorhenium(V) complex containing 2-\text{Me}-8-\text{HNqn} indicated the geometrical change on reactions with OPPh$_3$ or pyridine \([9,11]\), the corresponding reactions were attempted for the present complexes. However, the complexes synthesized in this work do not react absolutely. On account of the coordination of O trans to Re$^{\text{V}}$=O, the structure may reflect to the high stability. As a general rule, moreover, oxygen atom tends to locate trans to Re$^{\text{V}}$=O \([20,24,25]\). For example, although several substitution reactions were carried out for \([\text{ReOCl}_2(5-\text{NO}_2-8-\text{Oqn})(\text{PPh}_3)]\), the trans position of Re$^{\text{V}}$=O is occupied by O atom of the chelate ligand for all obtained complexes \([20]\). The complex containing quinolinylamido and the complexes containing quinolinolato derivatives have a similar coordination geometry, but the atoms that coordinated trans to Re$^{\text{V}}$=O are different. Accordingly, it can be understood that the complexes, which have the phenoxo oxygen atom trans to the Re$^{\text{V}}$=O bond, are inactive and extremely stable. Since such complexes do not release PPh$_3$ in solution, it seems to be difficult to use the quinolinolato complexes as OAT catalysts.

### 4. Conclusion

The reactions of \([\text{ReOCl}_2(\text{PPh}_3)_2]\) with 8-hydroxyquinoline derivatives as the didentate-N,O ligand gave the oxorhenium(V) \([\text{ReOX}_2(8-\text{Oqn})(\text{PPh}_3)]\)-type complexes. The geometrical structures of these complexes are similar to each other. The complexes indicate the high stability in solution owing to UV–vis and NMR spectral data. Moreover, the substitution reactions of PPh$_3$ with OPPh$_3$ or pyridine do not completely proceed. These results differ from the complexes containing 2-\text{Me}-8-\text{HNqn}. This difference seems to be due to the atoms trans to Re$^{\text{V}}$=O bond, that is, the present complexes having a phenoxo oxygen atom trans to Re$^{\text{V}}$=O bond cannot be used as OAT catalysts. By the present work, it was also elucidated that
the influence of the 5- and/or 7-substituent groups on the ligand was not apparent, but that of the 2-substituent groups on the ligand was observed.

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