

## Dichlorooxo(quinoline-8-thiolato- $\kappa^2N,S$ )(triphenylphosphine oxide- $\kappa O$ )rhenium(V) acetone solvate

Yoshitaro Miyashita,\* Tetuya Ohashi, Akiomi Imai,  
Nagina Amir, Kiyoshi Fujisawa and Ken-ichi Okamoto

Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba  
305-8571, Japan

Correspondence e-mail: ymiya@chem.tsukuba.ac.jp

Received 22 June 2005

Accepted 5 September 2005

Online 22 October 2005

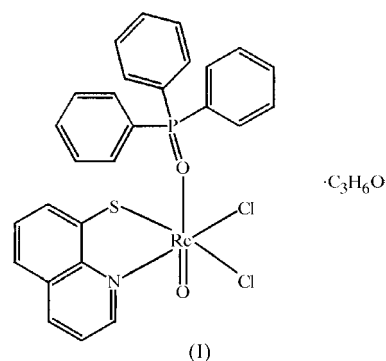
The complex molecule in the title compound,  $[\text{Re}(\text{C}_9\text{H}_6\text{NS})\text{Cl}_2\text{O}(\text{C}_{18}\text{H}_{15}\text{OP})]\cdot\text{C}_3\text{H}_6\text{O}$ , has distorted octahedral geometry. The  $\text{Re}=\text{O}$  bond occupies the position *trans* to the triphenylphosphine oxide O atom. The  $\text{Re}-\text{Cl}$  bond *trans* to the thiolate S atom is longer than that *trans* to the quinoline N atom, implying a stronger *trans* influence of the S atom. Intra- and intermolecular  $\pi-\pi$  interactions are also observed between the  $\pi$  rings in the complex.

### Comment

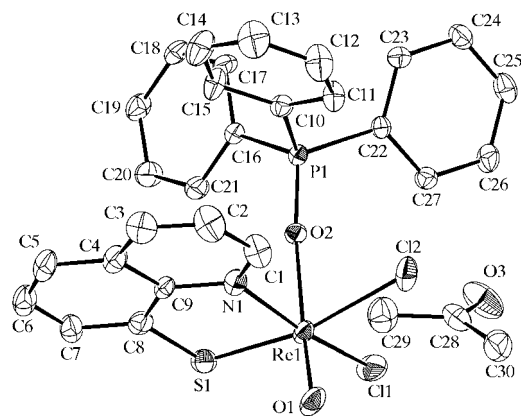
Oxorhenium(V) complexes are of interest because of their characteristic stereochemistry and reactivity as radiopharmaceuticals and O-atom transfer catalysts. We have synthesized oxorhenium(V) complexes using 8-substituted quinoline ligands as asymmetrical bidentate ligands to investigate stereoselectivity. For complexes containing *N,N*-bidentate ligands, the 8-aminoquinoline (8- $\text{H}_2\text{Nqn}$ ) complex  $[\text{ReCl}_3(8\text{-Nqn})(\text{PPh}_3)]$  ( $\text{PPh}_3$  is triphenylphosphine) lost the  $\text{Re}=\text{O}$  group and the metal atom formed a double bond with the N atom of the quinoline ligand (Miyashita *et al.*, 2001), whereas the 8-amino-2-methylquinoline (2-Me-8- $\text{H}_2\text{Nqn}$ ) complex  $[\text{ReOX}_2(2\text{-Me-8-HNqn})(\text{PPh}_3)]$  ( $X = \text{Cl}$  and  $\text{Br}$ ) retained the  $\text{Re}=\text{O}$  group (Ohashi *et al.*, 2003). Moreover, the complexes were unstable in solution and substitution of  $\text{OPPh}_3$  can occur. On the other hand, the corresponding oxorhenium(V) complexes  $[\text{ReOCl}_2(2\text{-X-5-Y-7-Z-8-Oqn})(\text{PPh}_3)]$  using the *N,O*-bidentate ligands 2-, 5- and/or 7-substituted 8-hydroxyquinoline (2-*X*-5-*Y*-7-*Z*-8- $\text{HOqn}$ ;  $X = \text{H}$  and  $\text{Me}$ ,  $Y = \text{H}$ ,  $\text{Cl}$  and  $\text{Br}$ , and  $Z = \text{H}$ ,  $\text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ) exhibit no  $\text{OPPh}_3$  substitution (Miyashita *et al.*, 2005). To elucidate the dependence of the stereochemistry and reactivity on the coordinating atom, we attempted to synthesize new oxorhenium(V) complexes using the *N,S*-bidentate ligand 8-mer-

captoquinoline (8- $\text{HSqn}$ ). We report here the crystal structure of the complex obtained, (I).

The asymmetric unit of (I) contains a mononuclear complex molecule and an acetone solvent molecule. A perspective view of (I) is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. In the complex molecule, the Re atom is coordinated by two O atoms, one establishing a double bond to the metal atom and the other from the  $\text{OPPh}_3$  ligand, by two Cl atoms, and by a deprotonated S atom and an N atom from the 8- $\text{Sqn}$  ligand, forming a distorted octahedral geometry. The O atom of the  $\text{OPPh}_3$  group lies *trans* to the  $\text{Re}=\text{O}$  bond, along the axial direction, as observed in previously reported oxorhenium(V) complexes (Battistuzzi *et al.*, 2001; Hansen *et al.*, 1995), whereas the S atom, the heterocyclic N atom and the two *cis* Cl atoms occupy the equatorial plane. Similar coordination geometry was observed for the oxorhenium(V) complex  $[\text{ReOCl}_2(2\text{-Me-8-HNqn})(\text{OPPh}_3)]$  (Ohashi *et al.*, 2003).



The  $\text{Re1}-\text{N1}$  [2.120 (6) Å] and  $\text{Re1}=\text{O1}$  [1.649 (6) Å] distances in (I) are within the normal ranges for  $\text{Re}-\text{N}$  single-bond and  $\text{Re}=\text{O}$  multiple-bond distances found in oxorhenium(V) complexes. The  $\text{Re1}-\text{Cl2}$  bond *trans* to the S atom [2.448 (2) Å] is significantly longer than the  $\text{Re1}-\text{Cl1}$  bond *trans* to the quinoline N atom [2.353 (2) Å]. This difference appears to be a result of a stronger *trans* influence of the S atom. Indeed, the  $\text{Re1}-\text{S1}$  distance [2.298 (2) Å] in (I) is shorter than the  $\text{Re}-\text{S}$  distances [2.447 (3) and 2.313 (3) Å] in



**Figure 1**

A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 20% probability level and H atoms have been omitted for clarity.

[MeReO(8-Sqn)<sub>2</sub>] (Shan *et al.*, 2002), in which two S atoms occupy *trans* positions with respect to each other. The Re1—O2 distance, which is *trans* to the Re=O bond, is 2.117 (4) Å in (I). This value is consistent with the *trans* influence of the Re=O linkage on an O atom of an axially bound ligand (Ohashi *et al.*, 2003). In addition, in (I), the Re atom is located 0.277 (2) Å above the equatorial plane, in the direction of the Re=O bond.

The Re=O linkage significantly expands the angles to the equatorial Cl and P atoms [Cl1—Re1—O1 = 99.7 (2)° and S1—Re1—O1 = 100.7 (3)°], but not those to the equatorial N atom and the other Cl atom [O1—Re1—N1 = 92.6 (3)° and Cl2—Re1—O1 = 93.1 (3)°]. The O1—Re1—O2 angle is 170.9 (3)° in (I), which deviates from the value of 180° expected for an ideal octahedral structure. The Re1—O2—P1 angle [159.9 (3)°] is slightly smaller than that in [ReOCl<sub>3</sub>-(PPh<sub>3</sub>)(OPPh<sub>3</sub>)] [165.1 (3)°], which has a crowded structure (Bryan *et al.*, 1998). These configurations may arise from either the relatively less hindered structure or an intramolecular interaction. The dihedral angle between the N1/C1—C4/C9 ring of the quinoline system and the C10—C15 benzene ring is 11.8 (3)°. The distance between the two planes is 3.43 (2) Å.

In the crystal packing of (I), the C4—C9 rings of the quinoline systems of adjacent molecules overlap in the axial direction, and the complex molecules form a dimeric structure. The interplanar distance [3.53 (1) Å] between the planes at (x, y, z) and (−x, 1 − y, −z) are within the range of intermolecular π—π stacking; the centroid—centroid distance is 3.58 Å. Although the acetone solvent molecule is also incorporated into the crystal packing, it does not participate in significant intermolecular interactions. The O3···C17<sup>i</sup> contact distance is 3.33 (1) Å [symmetry code: (i) 1 − x, y − ½, ½ − z].

The reactions of the starting materials [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] with 8-HSqn produced a dark-brown powder. When the powder was recrystallized from acetone, compound (I), containing OPPh<sub>3</sub> instead of PPh<sub>3</sub>, was obtained. It appears that PPh<sub>3</sub> was oxidized during the recrystallization process. The strong IR bands of the Re=O and P=O bonds in (I) were observed at 989 and 1143 cm<sup>−1</sup>, respectively. In the far-IR spectra, the Re—Cl stretching bands were observed as two strong bands (325 and 280 cm<sup>−1</sup>). These values for the Re=O and Re—Cl bonds reflect well the corresponding bond distances (Miyashita *et al.*, 2005).

## Experimental

To a suspension of [ReCl<sub>3</sub>O(PPh<sub>3</sub>)<sub>2</sub>] (200 mg, 0.24 mmol) (Johnson *et al.*, 1967) in CH<sub>2</sub>Cl<sub>2</sub> (60 ml) was added a solution of 8-HSqn·HCl (47 mg, 0.24 mmol) in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (10 ml). The mixture was stirred overnight at room temperature, whereupon the color of the mixture turned from light green to dark brown. After insoluble materials had been filtered off, the filtrate was dried using a vacuum line. The resulting dark-brown powder was washed with Et<sub>2</sub>O. Recrystallization in a refrigerator from acetone gave dark-brown block-shaped crystals (yield 83 mg, 45%). Analysis found: C 46.82, H 3.66, N 1.87%; calculated for C<sub>27</sub>H<sub>21</sub>Cl<sub>2</sub>NO<sub>2</sub>PREs·C<sub>3</sub>H<sub>6</sub>O: C 46.81, H 3.54, N 1.82%.

## Crystal data

[Re(C<sub>9</sub>H<sub>6</sub>NS)Cl<sub>2</sub>O(C<sub>18</sub>H<sub>15</sub>OP)]·  
C<sub>3</sub>H<sub>6</sub>O  
*M<sub>r</sub>* = 769.70  
Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 11.569 (3) Å  
*b* = 15.152 (7) Å  
*c* = 17.660 (8) Å  
β = 103.90 (3)°  
*V* = 3005 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.701 Mg m<sup>−3</sup>

Mo *K*α radiation  
Cell parameters from 25  
reflections  
θ = 14.5–14.9°  
μ = 4.38 mm<sup>−1</sup>  
*T* = 296.2 K  
Block, dark brown  
0.63 × 0.53 × 0.40 mm

## Data collection

Rigaku AFC-7S diffractometer  
ω-2θ scans  
Absorption correction: ψ scan  
(North *et al.*, 1968)  
*T*<sub>min</sub> = 0.148, *T*<sub>max</sub> = 0.174  
7600 measured reflections  
6887 independent reflections  
4608 reflections with *F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)

*R*<sub>int</sub> = 0.025  
θ<sub>max</sub> = 27.5°  
*h* = −15 → 4  
*k* = −19 → 0  
*l* = −22 → 22  
3 standard reflections  
every 150 reflections  
intensity decay: 0.2%

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045  
*wR*(*F*<sup>2</sup>) = 0.149  
*S* = 1.12  
6887 reflections  
352 parameters

H-atom parameters not refined  
*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + {0.08[Max(*F*<sub>o</sub><sup>2</sup>),  
+ 2*F*<sub>o</sub><sup>2</sup>]/3}]<sup>2</sup>  
(Δ/σ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 1.07 e Å<sup>−3</sup>  
Δρ<sub>min</sub> = −1.86 e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Re1—Cl1	2.353 (2)	Re1—O1	1.649 (6)
Re1—Cl2	2.448 (2)	Re1—O2	2.117 (4)
Re1—S1	2.298 (2)	Re1—N1	2.120 (6)
Cl1—Re1—Cl2	88.46 (9)	Cl2—Re1—N1	93.3 (2)
Cl1—Re1—S1	91.00 (9)	S1—Re1—O1	100.7 (3)
Cl1—Re1—O1	99.7 (2)	S1—Re1—O2	85.8 (1)
Cl1—Re1—O2	86.5 (1)	S1—Re1—N1	84.4 (2)
Cl1—Re1—N1	167.5 (2)	O1—Re1—O2	170.9 (3)
Cl2—Re1—S1	166.11 (8)	O1—Re1—N1	92.6 (3)
Cl2—Re1—O1	93.1 (3)	O2—Re1—N1	81.7 (2)
Cl2—Re1—O2	80.3 (1)	Re1—O2—P1	159.9 (3)

After their presence had been checked in a difference map, all H atoms were positioned geometrically and allowed to ride on their attached atoms [C—H = 0.95 or 0.97 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)].

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP II* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

This work has been supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science, the 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology, and University of Tsukuba Research Projects.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1252). Services for accessing these data are described at the back of the journal.

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