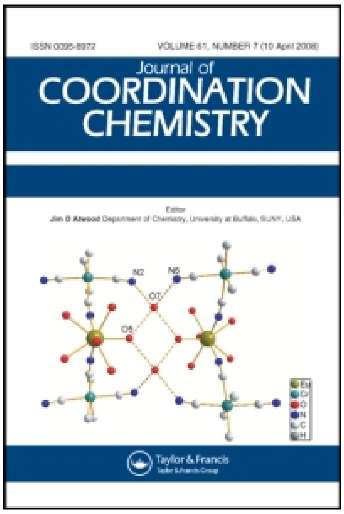

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Oxorhenium(V) complexes containing bidentate *N*,*O*-donor ligands of the pyridyl type

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The reaction of equimolar quantities of *trans*-[$ReOCl_3(PPh_3)_2$] and 8-hydroxyquinoline (Hhqn) in benzene led to the isolation of the six-coordinate complex [$ReOCl_2$(hqn)(PPh_3)] (**1**). With 2-pyridine-ethanol (Hhep) the compound [$ReOCl_2$(hep)(PPh_3)] (**2**) was obtained. Both hqn and hep ligands act as monoanionic bidentate *N*,*O*-donor chelates. Although the two complexes are very similar, there are some significant differences in certain bond distances and angles in them. Both complexes contain the nearly linear *trans* O=Re–O axis, with this angle equal to 160.9(2)° and 167.8(1)° in **1** and **2**, respectively.

Keywords: Rhenium(V)-oxo; Crystal structure; *N*,*O*-donor pyridyl ligands

1. Introduction

The chemistry of oxorhenium(V) complexes is receiving increasing attention because of the potential application of the isotopes ^{186}Re and ^{188}Re as radiotherapeutic agents against cancer [1], and because of its similar chemical behaviour to technetium, its second row congener, which has found major applications in diagnostic nuclear medicine [1]. We are currently interested in the coordination chemistry of oxorhenium(V) cores with *N*,*O*-donor ligands containing various types of donor atoms. This report focusses on monomeric oxorhenium(V) complexes formed with the *N*,*O*-donor ligands 8-hydroxyquinoline (Hqn) and 2-pyridine-ethanol (Hhep), with a pyridyl nitrogen and a phenolate or alcoholate oxygen as donor atoms. We have reported earlier on complexes of oxorhenium(V) with bidentate aromatic 2-amino-alcohols [2], and with bidentate *N*,*O*-donor imidazole derivatives [3]. However, the most extensive studies in this particular research area were done with Schiff base ligands. Bidentate aromatic *N*,*O*-donor Schiff bases, containing an imine nitrogen and phenolic

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oxygen, give complexes with the phenolate oxygen *trans* to the oxo group in a distorted octahedral geometry around the ReO^{3+} core [4]. The reaction of *trans*-[$ReOCl_3(PPh_3)_2$], for example, with *N*-methylsalicylideneimine (MesalH) yields the six-coordinate complexes [$ReOCl_2$(Mesal)(PPh_3)] and [ReOCl(Mesal)$_2$] under various conditions.

2. Experimental

Trans-[$ReOCl_3(PPh_3)_2$] was prepared by a literature procedure [5]. The ligands 8-hydroxyquinoline (Hhqn) and 2-pyridine-ethanol (Hhep) were obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. IR spectra were obtained using KBr disks and ^1H NMR spectra were run in d_6-DMSO at ambient temperatures. The instrumentation is the same as reported earlier [6].

2.1. *Synthesis of* cis-*[ReOCl₂(hqn)(PPh₃)] (1)*

A mixture of 0.100 g of *trans*-[$ReOCl_3(PPh_3)_2$] (120 µmol) and 0.019 g of Hhqn (131 µmol) in 20 cm^3 of benzene was heated under reflux for 90 min. After heating was stopped and the dark green solution cooled to room temperature, a green precipitate was removed by filtration. It was washed with benzene and diethylether, and dried under vacuum. Recrystallization from 2 : 1 CH_3CN/MeOH gave dark green crystals, which were suitable for X-ray crystallographic studies. Yield = 62%, m.p. 268°C. Anal. Calcd for $C_{27}H_{21}NO_2PCl_2Re$ (%): C, 47.72; H, 3.12; N, 2.06. Found: C, 48.11; H, 3.12; N, 2.42. IR (cm^{-1}): ν(Re=O) 976; ν(Re–N) 532; ν(Re–O) 420; ν(Re–Cl) 323, 331. ^1H NMR (δ, ppm): 9.14 (1H, d, *H*(1)), 9.07 (1H, d, *H*(7)), 8.78 (1H, t, *H*(8)), 8.24 (1H, t, H(2)), 7.85–7.28 (16H, m, P*Ph*$_3$, *H*(3)), 6.61 (1H, d, *H*(9)).

2.2. *Synthesis of* cis-*[ReOCl₂(hep)(PPh₃)] (2)*

Complex **2** was prepared with Hhep by the same method and reaction conditions as for **1**. Recrystallization from a 2 : 1 chloroform/ethanol mixture gave purple crystals with the formulation **2** · $CHCl_3$, which were suitable for X-ray studies. Yield = 73%, m.p. 239°C. Anal. Calcd for $C_{26}H_{24}NO_2PCl_5Re$ (%): C, 40.20; H, 3.11; N, 1.80. Found: C, 40.01; H, 2.77; N, 1.95. IR (cm^{-1}): ν(Re=O) 945; ν(Re–N) 528; ν(Re–O) 443; ν(Re–Cl) 328, 324. ^1H NMR (δ, ppm): 8.69 (1H, d, *H*(1)); 7.58–7.23 (17H, m, P*Ph*$_3$, *H*(3), *H*(4)), 7.03 (1H, t, *H*(2)), 4.24 (2H, t, *H*(7)), 3.21 (2H, t, *H*(6)).

2.3. *Crystallography*

Data collection was performed on a Nonius Kappa CCD diffractometer at 200 K with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods applying SIR97 [7] and refined by least-squares procedures using SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. The data were corrected by a numerical absorption correction [9] after optimising the crystal shape with XShape [10]. Crystal and structure refinement data are given in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystal data and structure refinement details for **1** and **2**.

	1	**2**
Chemical formula	$C_{27}H_{21}NO_2Cl_2PRe$	$C_{26}H_{23}NO_2Cl_2PRe \cdot CHCl_3$
Formula weight	679.55	776.92
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 7.6582(2)$	12.8310(2)
	$b = 8.0377(2)$	15.2502(3)
	$c = 19.7820(7)$	15.0293(3)
	$\alpha = 94.738(1)$	
	$\beta = 90.374(1)$	104.050(1)
	$\gamma = 94.493(1)$	
V (Å^3)	1209.67(6)	2852.89(9)
Z	2	4
Density (Calcd) (Mg m^{-3})	1.866	1.809
Absorption coefficient (mm^{-1})	5.336	4.809
F(000)	660	1512
Crystal size (mm^3)	$0.01 \times 0.05 \times 0.08$	$0.05 \times 0.10 \times 0.15$
θ range for data collection (°)	3.2–26.0	3.2–25.0
Index ranges		
	$-9 \leq h \leq 9$	$-15 \leq h \leq 14$
	$-9 \leq k \leq 9$	$-18 \leq k \leq 18$
	$-24 \leq l \leq 22$	$-17 \leq l \leq 17$
Reflections measured	15,144	26,179
Independent/observed reflections	4708/3882	5027/4314
Data/parameters	4708/307	5027/325
Goodness-of-fit on F^2	1.01	1.05
Final R indices [$I > 2.0\sigma(I)$]	0.0382 ($wR_2 = 0.0786$)	0.0244 ($wR_2 = 0.0497$)
Largest diff. peak/hole (e Å^{-3})	0.80/−1.41	0.95/−1.08

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

	1	**2**
Re–O(1)	1.683(4)	1.694(2)
Re–O(2)	1.997(4)	1.868(2)
Re–N	2.148(4)	2.200(2)
Re–Cl(1)	2.410(1)	2.4223(9)
Re–Cl(2)	2.338(2)	2.3812(8)
Re–P	2.454(2)	2.4737(9)
O(1)–Re–O(2)	160.9(2)	167.8(1)
O(1)–Re–N	87.0(2)	86.0(1)
O(1)–Re–P	92.8(1)	87.37(9)
O(1)–Re–Cl(1)	99.5(2)	94.65(9)
O(1)–Re–Cl(2)	103.6(2)	99.24(7)
Cl(1)–Re–Cl(2)	88.91(6)	88.56(3)
Cl(1)–Re–P	167.73(5)	177.96(3)
N–Re–O(2)	75.9(2)	83.38(9)
N–Re–Cl(2)	168.6(1)	173.89(7)

3. Results and discussion

3.1. *Synthesis*

The reactions of *trans*-[$ReOCl_3(PPh_3)_2$] with equimolar quantities of 8-hydroxyquinoline (Hhqn) and 2-pyridine-ethanol (Hhep) in benzene resulted in the complexes [$ReOCl_2(L)(PPh_3)$] (L = hqn, hep). Experimental evidence suggests that the ligands L are present in the complexes **1** and **2** as bidentate monoanionic chelates with coordination through the pyridyl nitrogen and deprotonated phenolic/alcoholate oxygen. The two complexes are non-electrolytes in DMF, and are weakly soluble in acetonitrile, chloroform, DMF and DMSO.

3.2. *Spectroscopic characterization*

IR spectra of **1** and **2** display Re=O stretching frequencies as sharp strong bands at 976 and 945 cm^{-1}, respectively. These values imply that the Re=O bond in **1** is shorter (and stronger) than in **2**, which is also reflected in their bond lengths (see table 2). Re–N stretches appear at 532 and 528 cm^{-1} for **1** and **2**, respectively, again implying that this bond is stronger in **1**. The large difference in ν(Re–O) for **1** (at 420 cm^{-1}) and **2** (at 443 cm^{-1}) is also reflected in the Re–O bond distances (table 2) of the complexes. The two values for ν(Re–Cl) that are observed for both complexes imply the coordination of *cis* chlorides in the equatorial plane. ^{1}H NMR spectra are complicated somewhat by the overlap of some of the proton signals of the aromatic rings of the chelates with those of the PPh_3 ligands. The protons attached to C(1) in **1** and **2** appear furthest downfield as a doublet at δ 9.14 and 8.69 ppm, respectively. The ethanolate protons of hep in **2** are seen as two two-proton triplets at δ 4.24 and 3.21 ppm (δ 3.99 and 3.01 ppm in the spectrum of the free ligand).

3.3. *Description of the structure of [$ReOCl_2$(hqn)(PPh_3)] (1)*

The structure of **1** (figure 1) exhibits distorted octahedral geometry around the rhenium(V) centre. The basal plane is defined by the pyridyl nitrogen of the hqn ligand,

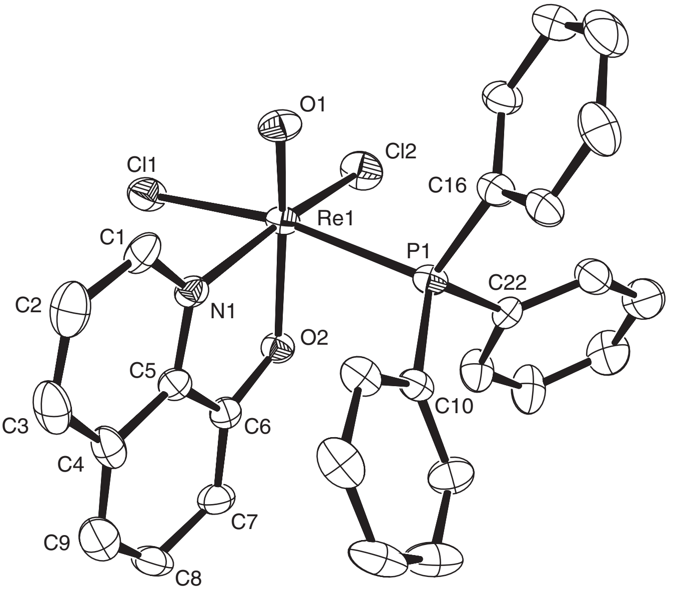

Figure 1. A view of the structure of [$ReOCl_2$(hqn)(PPh_3)] (**1**), showing the atom labelling scheme and 40% thermal ellipsoids.

two chlorides and the phosphorus atom of PPh_3, with the quinolate and oxo oxygens in *trans* axial positions. The two chlorides are coordinated *cis* to each other, with the Cl–Re–Cl angle practically orthogonal at 88.91(6)°. The distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(1)=Re–O(2) axis of 160.9(2)°, accomplished by P–Re–Cl(1) and N–Re–Cl(2) angles of 167.73(5)° and 168.6(1)°, respectively. The rhenium atom is lifted out of the mean equatorial Cl_2PN plane by 0.230 Å towards the oxo oxygen O(1), as the result of the non-orthogonal angles O(1)–Re–Cl(2) = 103.6(2)°, O(1)–Re–Cl(1) = 99.5(2)°, O(1)–Re–P = 92.8(1)° and O(1)–Re–N = 87.0(2)°. In the O_2Cl_2NP polyhedron the rhenium atom is 1.01 Å from the Cl(1)O(1)Cl(2) plane, and 1.39 Å from PO(2)N, with the dihedral angle being 11.79°.The Re–Cl(1) bond, *trans* to P, at 2.410(2) Å, is significantly longer than the chloride *trans* to the pyridyl N [2.338(2) Å], which confirms the higher *trans* influence of the phosphine group. The Re–O(2) distance of 1.997(4) Å is very similar to other Re(V)–O (phenolate) distances [2, 11], and the Re=O(1) bond distance [1.683(4) Å] is within the range observed for this kind of bond [12, 13]. Other bond distances and angles are normal (table 2).

3.4. *Description of the structure of [$ReOCl_2(hep)(PPh_3)$] (2)*

The molecular structure of **2** (figure 2) shows that the rhenium atom is at the centre of a distorted octahedral environment. One of the features of the structure is that the O(1)–Re–O(2) axis is closer to linearity at 167.8(1)° than in **1**. The effect is that the Re–O(2) bond is considerably shorter (1.868(2) Å) than in **1**, since better overlap is achieved between the π orbitals of the alkoxide O(2) and the empty d_{xz} and d_{yz} orbitals

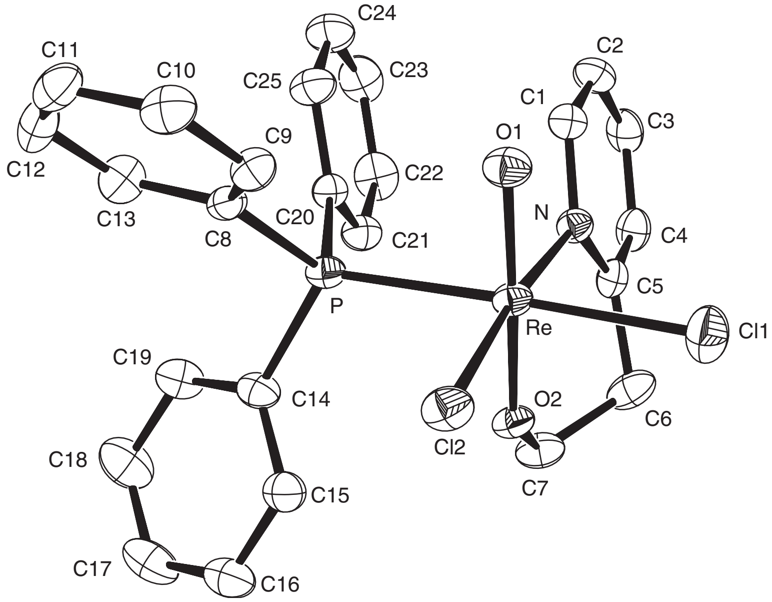

Figure 2. An ORTEP view of [$ReOCl_2(hep)(PPh_3)$] (**2**). Atomic displacement ellipsoids are drawn at the 40% probability level.

of rhenium. Distances of 2.04, 1.86 and 1.75 Å have been proposed [14] for typical single, double and triple bonds respectively, implying significant double-bond character for the Re–O(2) bond. Another indication of its double-bond character is that the Re–O(2)–C(7) angle is splayed to 141.2(2)°, when no apparent intramolecular nonbonding contacts exist. The shorter Re–O(2) bond leads to a slightly longer Re–O(1) bond [1.694(2) Å] than in **1**. A further effect is that the rhenium atom is lifted out of the mean equatorial plane, formed by the pyridyl nitrogen, two chlorides and phosphorus atom, by only 0.072 Å towards the oxo oxygen O(1). A longer Re–O(1) and shorter Re–O(2) bond mean that the O(1)–Re–N [86.0(1)°], O(1)–Re–P [87.37(9)°], O(1)–Re–Cl(1) [94.65(9)°] and O(1)–Re–Cl(2) [99.24(7)°] bond angles are all smaller than in complex **1**, with the effect that the bonds between rhenium and the equatorial donor atoms are all longer than in **1**. The pyridyl ring is parallel to the C(20)–C(25) phenyl ring of the phosphine with a dihedral angle of 8.78° between their least squares planes, and their centroids are 3.34 Å apart. As in complex **1**, the only hydrogen bond of note is C(1)–H(1) $\cdots$ O(1) = 2.772(4) Å.

Supplementary material

CCDC-281307 (for **1**) and CCDC-281308 (for **2**) contain crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

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