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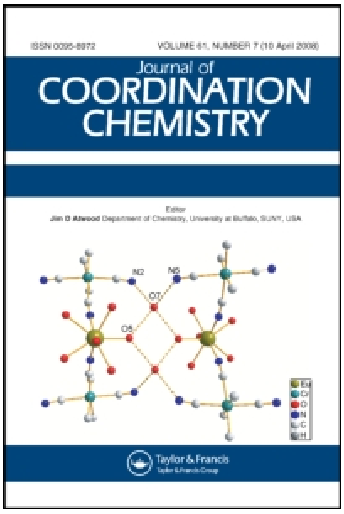

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Reaction of equimolar quantities of bis((pyridin-2-yl)methyl)amine (HBPA) with (n-Bu_4N)[$ReOCl_4$] in acetone at room temperature led to the six-coordinate rhenium(V) complex [$ReOCl(H_2O)(BPA)$]Cl (**1**). IR, NMR and X-ray crystallographic results indicate that BPA is coordinated as a terdentate uninegative chelate, with deprotonation of the amine nitrogen. The water molecule is coordinated *trans* to the oxo group, with Re=O and Re–OH_2 bond distances equal to 1.663(9) and 2.21(1) Å, respectively.

Keywords: Rhenium(V); Di-(2-pyridylmethyl)amine; Crystal structure

1. Introduction

The promise of ^{186}Re as a possible radionuclide for incorporation into therapeutic agents has rekindled the interest in the coordination chemistry of rhenium [1]. Our interest centres around rhenium(V), especially its interaction with terdentate ligands. During the last few years oxorhenium(V) complexes with dianionic terdentate ONX (X = O,S) donor Schiff base ligands have been well studied [2–4]. It was found that the three donor atoms are bonded to the metal on the *cis* equatorial plane with respect to the Re=O linkage in complexes of the type [ReOCl(ONX)(MeOH)]. A study of oxorhenium(V) complexes with terdentate Schiff base ligands having the ONN donor atom set has shown that it is the imino nitrogen that is coordinated *trans* to the oxo oxygen in complexes of the type [$ReOCl_2$(ONN)] [5]. We have previously reported the products [$ReOCl_2$(ONN)] obtained from the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with terdentate ONN-donor ligands of the pyridylaminophenol type, which are similar to the

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terdentate Schiff base ligands, except that they contain an amino nitrogen in place of the imino nitrogen [6].

This report focusses on the reaction between (n-Bu_4N)[$ReOCl_4$] and the terdentate NNN-donor ligand bis((pyridin-2-yl)methyl)amine (HBPA), which yields [$ReOCl(H_2O)(BPA)$]Cl (**1**). In this complex the amine nitrogen is deprotonated, with BPA acting as a terdentate uninegative chelate. Complex **1** is unusual since rhenium(V) complexes containing water as a ligand are rare and deprotonation of a secondary amino nitrogen is surprising in ligands of this type. In addition, the *trans* $O{=}Re{-}OH_2$ moiety is an example of the first step in the formation of the *trans* $O{=}Re{=}O$ group and the expected products would have been the neutral species [$ReOCl_2(BPA)$] or the cation [$ReOCl_2(HBPA)$]$^+$.

2. Experimental

2.1. *Reagents and instrumentation*

(n-Bu_4N)[$ReOCl_4$] was prepared using a literature procedure [7]. HBPA was obtained commercially (Aldrich), and all other chemicals were of reagent grade and used as received from commercial sources. Solvents were purified and dried by standard methods. Scientific instrumentation used is the same as reported elsewhere [8]. Infrared spectra were obtained using KBr discs and ^1H NMR spectra were run in d_6-DMSO.

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2.2. *[$ReOCl(H_2O)(BPA)$]Cl (1)*

The ligand HBPA (0.0244 g, 123 µmol), dissolved in 6 cm^3 of acetone, was added to a stirred solution of 0.07191 g (123 µmol) of (n-Bu_4N)[$ReOCl_4$] in 6 cm^3 of acetone. A dark green precipitate immediately formed, and the suspension was stirred for a further 4 h at room temperature. The solid was removed by filtration, washed with acetone (2 × 3 cm^3), and dried under vacuum. Recrystallization from acetonitrile gave avocado green crystals suitable for X-ray diffraction studies. Yield = 39 mg (65%), m.p. > 300°C. Anal. Calcd (%): C, 29.45; H, 2.87; N, 8.59. Found: C, 29.51; H, 2.37; N, 8.63. IR (cm^{-1}): ν(Re=O) 957; ν(C=N) 1613; ν(C=C) 1562; $\nu(Re{-}N_{py})$ 590; ν(Re–N) 664; ν(Re–Cl) 309. ^1H NMR (ppm): 9.60 (d, 2H, *H*(1), *H*(12), $J = 6.1$ Hz), 8.39 (t, 2H, *H*(3), *H*(10), $J = 7.9$ Hz), 8.17 (d, 2H, *H*(4), *H*(9), $J = 7.9$ Hz), 8.03 (t, 2H, *H*(2), *H*(11), $J = 6.1$ Hz), 6.78 (d, 2H, C(7)*H*(2)), 5.00 (d, 2H, C(6)*H*(2)), 2.50(s, 2H, O(1)*H*(2)).

2.3 *X-ray structure*

Data collection was performed at 200 K on a Nonius Kappa CCD using Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [9]. Due to twinning crystals only Re, Cl(1), Cl(2), O(1) and O(2) were refined anisotropically. An ORTEP view of **1** along with the atom numbering scheme is given in figure 1. Relevant crystallographic data are given in table 1, with selected bond lengths and angles shown in table 2.

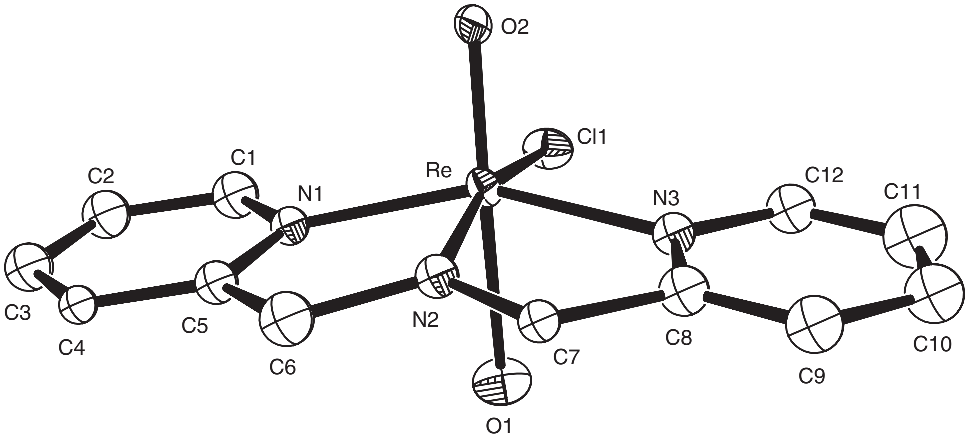

Figure 1. The molecular structure of $[ReOCl(H_2O)(BPA)]^+$ showing the atom numbering scheme with 40% displacement ellipsoids.

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

Empirical formula	$C_{12}H_{14}N_3Cl_2O_2Re$
Formula weight	489.37
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	$a = 8.2765(4)$ $b = 12.1139(9)$ $c = 14.6718(8)$ $\beta = 93.721(6)$
Volume ($Å^3$)	1467.9(2)
Z	4
Density (calc.) ($g\,cm^{-3}$)	2.214
Crystal size (mm^3)	$0.03 \times 0.05 \times 0.12$
Absorption coefficient (mm^{-1})	8.645
$F(000)$	928
θ range (°)	2.2–24.0
Index range	$-8 \le h \le 9$ $-13 \le k \le 13$ $-16 \le l \le 16$
Reflections collected/unique	6210/2236
Data/restraints/parameters	2236/0/112
Goodness-of-fit on F^2	0.86
Final R indices	$R = 0.0475$, $wR_2 = 0.1107$
Largest diff. peak and hole ($e\,Å^{-3}$)	2.29 and −1.98

3. Results and discussion

Reaction of equimolar quantities of bis((pyridin-2-yl)methyl) amine (HBPA) with $(n\text{-}Bu_4N)[ReOCl_4]$ in acetone at room temperature led to the six-coordinate rhenium(V) complex $[ReOCl(H_2O)(BPA)]Cl$ (**1**). The green compound is air stable, diamagnetic and a 1 : 1 electrolyte in acetonitrile. IR spectra are characterized by a very strong absorption at 957 cm^{-1} assigned to $\nu(Re{=}O)$. The expected range for this vibration is 945–965 cm^{-1} [6]. There is no band in the range 3000–3300 cm^{-1} that can be ascribed

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

Re–O(1)	2.21(1)	Re–O(2)	1.663(9)
Re–N(1)	2.08(1)	Re–N(2)	1.89(1)
Re–N(3)	2.08(1)	Re–Cl(1)	2.462(3)
N(2)–C(6)	1.50(2)	N(2)–C(7)	1.41(2)
C(5)–C(6)	1.44(2)	C(7)–C(8)	1.53(2)
C(1)–N(1)	1.35(2)	C(1)–C(2)	1.41(2)
N(1)–C(5)	1.36(2)	C(2)–C(3)	1.37(2)
O(1)–Re–O(2)	167.2(4)	N(1)–Re–N(3)	153.9(4)
Cl(1)–Re–N(2)	162.9(4)	N(1)–Re–N(2)	81.1(5)
N(2)–Re–N(3)	78.9(5)	O(2)–Re–Cl(1)	90.6(4)
O(2)–Re–N(1)	99.0(5)	O(2)–Re–N(2)	106.4(5)
O(2)–Re–N(3)	102.5(5)	C(6)–N(2)–C(7)	119(1)
C(6)–N(2)–Re	118.3(9)	Re–N(2)–C(7)	122.6(9)
N(2)–C(6)–C(5)	110(1)	N(2)–C(7)–C(8)	108(1)
Re–N(1)–C(1)	125.5(9)	Re–N(3)–C(12)	126.9(9)

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to ν(N–H). The Re–Cl stretch appears as a medium intensity band at 309 cm^{-1}. The absence of an NH proton signal in ^1H NMR is in line with deprotonation of the secondary amine nitrogen N(2). Corresponding protons of the two pyridine rings of BPA are magnetically equivalent. Surprisingly, the two methylene groups are not magnetically equivalent, giving two-proton doublets at δ 6.78 and 5.00 ppm. The presence of water is indicated by a two-proton singlet at δ 2.50 ppm.

An ORTEP view of the asymmetric unit of **1** is shown in figure 1. The rhenium ion lies at the centre of a distorted octahedron. The basal plane is defined by the two pyridyl nitrogen atoms N(1) and N(3), the deprotonated secondary amine nitrogen N(2) and the chloride Cl(1). The oxo group O(2), and O(1) of the coordinated water molecule are in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(1)-Re-O(2) axis of 167.2(4)°, accomplished by N(1)–Re–N(3) and Cl(1)–Re–N(2) angles of 153.9(4)° and 162.9(4)°, respectively. Rhenium is displaced from the mean equatorial N_3Cl plane by 0.34 Å towards O(2) as a result of the non-orthogonal angles O(2)–Re–N(1) = 99.0(5)°, O(2)–Re–N(2) = 106.4(5)°, O(2)–Re–N(3)=102.5(5)° and O(2)–Re–Cl(1) = 90.6(4)°. The two bite angles of BPA are different, N(1)–Re–N(2) = 81.1(5)°, N(2)–Re–N(3) = 78.9(5)°. In the N_3O_2Cl polyhedron the rhenium atom lies 1.03 Å from the O(2)–N(1)–Cl(1) plane and 1.33 Å from O(1)–N(2)–N(3), the dihedral angle between these two planes being 16.0°. Edge distances span a rather large range (from 2.52 Å for N(2) ··· N(3) to 3.42 Å for Cl(1) ··· N(1)), and interligand angles in the equatorial plane range from 72.68° to 104.87°. These structural properties are a common feature for six-coordinate octahedral monooxo complexes of Re(V) [3–6].

The Re=O(2) distance of 1.663(9) Å implies some triple bond character and is typical of cationic complexes of this kind [6]. The Re–O(1) distance of 2.21(1) Å is close to the value 2.23(2) Å found for water molecules bound *trans* to the oxo atom in $[ReOCl_2(tu)(H_2O)]Cl$ and $[ReOCl_3(tu)(H_2O)]$ [10, 11]. Re–N_{py} distances of 2.08(1) Å are significantly shorter than the range 2.13(2)–2.15(2) Å found in monooxorhenium(V) complexes containing terdentate dipyridyl ligands [6, 12]. The Re–N(2) bond length of 1.89(1) Å is considerably shorter than the average Re–NH length 2.21(2) Å found in complexes containing terdentate ligands of the pyridylaminophenol type [6], and illustrates significant multiple bond character.

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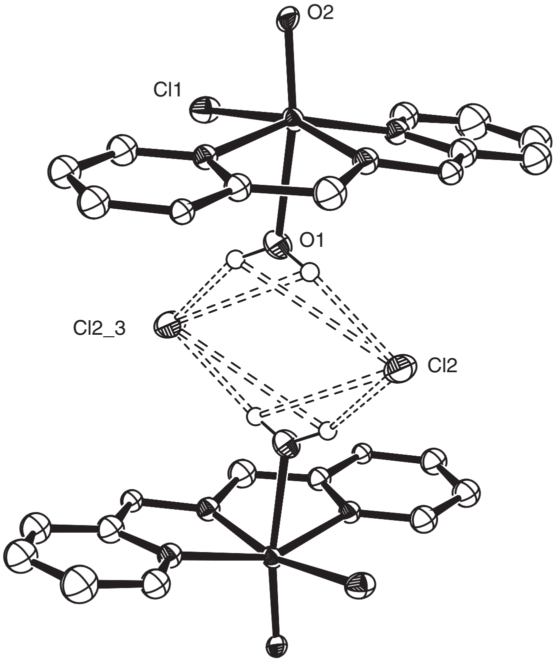

Figure 2. Hydrogen bond formation (dashed lines) between chloride counterion and the coordinated water molecule in **1**.

Deprotonation of N(2) is also manifested in the bond angles it makes. The C(6)–N(2)–C(7) angle of 119(1)° intimates sp^2 hybridization of N(2), and the N(1)–C(5)–C(6)–N(2)–C(7)–C(8)–N(3) chain is nearly perfectly planar, with torsion angles N(1)–C(5)–C(6)–N(2) = 1(2)° and N(2)–C(7)–C(8)–N(3) = 0(2)°. In fact, the whole BPA molecule is very planar, with the largest deviation from the mean plane involving N(2) (0.22 Å). The chloride counterions Cl(2) form weak hydrogen bonds (2.96(1) and 3.06(1) Å) with hydrogen atoms of the coordinated water in two complex units, as shown in figure 2. Although examples of water acting as a ligand in oxorhenium(V) complexes are few, the *trans* oxo-aquo moiety has been observed in distorted octahedral complexes of the type [ReO(H_2O)L]Cl, where L is a dianionic tetradentate ligand [13, 14].

Supplementary material

The file CCDC-264913 contains crystallographic data for the complex. 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 CB21EZ, UK; Fax: +44(0) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

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