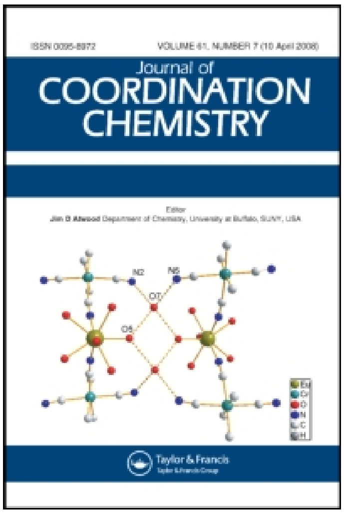

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Imidazolate coordination of 2,6-bis(2-benzimidazolyl) pyridine in a dimeric rhenium(V) complex

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The oxo-bridged dinuclear complex $[(\mu\text{-O})\{ReOCl_2(pimH)\}_2]\cdot 2H_2O\cdot 2DMF$ was prepared by reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ and 2,6-bis(2-benzimidazolyl)pyridine ($pimH_2$) in acetonitrile, with recrystallization from CH_2Cl_2/DMF. An X-ray crystallographic study shows that pimH is coordinated as a tridentate monoanionic chelate, with deprotonation of an imidazolyl N(1)H group. The axis of the molecule is formed by the O=Re–O–Re=O moiety, with the bridging oxygen lying on a crystallographic inversion center. The two O–Re=O angles are therefore equal [172.7(1)°].

Keywords: Oxo-bridge; Rhenium(V); Dimeric; Bis(benzimidazolyl)pyridine; Crystal structure

1. Introduction

In recent months our group has become interested in the coordination chemistry of rhenium(V) with multidentate ligands containing the imidazolyl group [1, 2]. We have now extended our studies to include the ligand 2,6-bis(2-benzimidazolyl)pyridine ($pimH_2$), which presents interesting possibilities as a chelate. It can act as a neutral tridentate or bidentate chelate, with the N–H bonds being involved in interesting hydrogen bond patterns. Deprotonation of one or both of the N–H moieties can lead to possible bi- or tridentate, mono- or dianionic chelation, respectively, or even to bridging between metal centers.

In this report, we describe the synthesis and structure of the linear oxo-bridged complex $(\mu\text{-O})[ReOCl(pimH)]_2$. Each ligand pimH acts as a tridentate monoanionic chelate, in which one N–H moiety is deprotonated to preserve the neutrality of the complex. Imidazolate coordination of imidazole has been observed previously for a large variety of metals in many oxidation states [3–6], although it has not been reported previously for rhenium.

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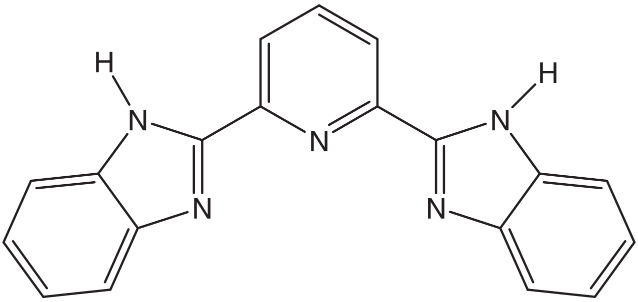

$pimH_2$

2. Experimental

Trans-[$ReOCl_3(PPh_3)_2$] was prepared by a literature method [7]. The ligand 2,6-bis(2-benzimidazolyl)pyridine ($pimH_2$) (97%) was obtained commercially from Aldrich and used without further purification. All chemicals were of reagent grade and used as received. Solvents were purified and dried before use. Scientific instrumentation used is the same as reported previously [8]. Infrared spectra were obtained using KBr disks and ^1H NMR spectra were run in d_6-DMSO.

2.1. *Synthesis of (μ-O)[ReOCl(pimH)]$_2\cdot 2H_2O\cdot 2DMF$ (1)*

To 0.20 mmol of *trans*-[$ReOCl_3(PPh_3)_2$] (170 mg) in 10 cm^3 of acetonitrile was added a twofold molar excess of $pimH_2$ (125 mg) dissolved in 10 cm^3 of acetonitrile. The resulting mixture was heated under reflux for 60 min, giving a dark green solution. After cooling to room temperature, the green precipitate was removed by filtration, and washed with acetonitrile and diethylether. Recrystallization from CH_2Cl_2/DMF gave green crystals that were suitable for X-ray crystallography. Yield 77% (based on Re), m.p. 293°C. Anal. Calcd (%): C, 40.90; H, 3.12; N, 13.01. Found: C, 40.83; H, 3.16; N, 12.98. IR: ν(N–H) 3059; ν(C=N) 1620, 1605; ν(Re=O) 910; ν(Re–O–Re) 721; ν(Re–N) 467, 436, 421; ν(Re–Cl) 301 cm^{-1}. ^1H NMR (295 K), ppm: 8.68 (2H, d, *H*(9), *H*(11)), 8.48 (1H, t, *H*(10)), 7.88 (4H, m), 7.55 (4H, m).

2.2. *X-ray crystallography*

Intensity data for **1** were collected at 200(2) K on a Nonius Kappa CCD single-crystal diffractometer, using Mo Kα radiation. Unit cell and space group determinations were carried out in the usual manner [9]. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-96 [10]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were geometrically constrained. An ORTEP view of **1** along with the atom numbering scheme is given in figure 1. A summary of crystal data and refinement details is given in table 1. Selected bond distances and angles are given in table 2.

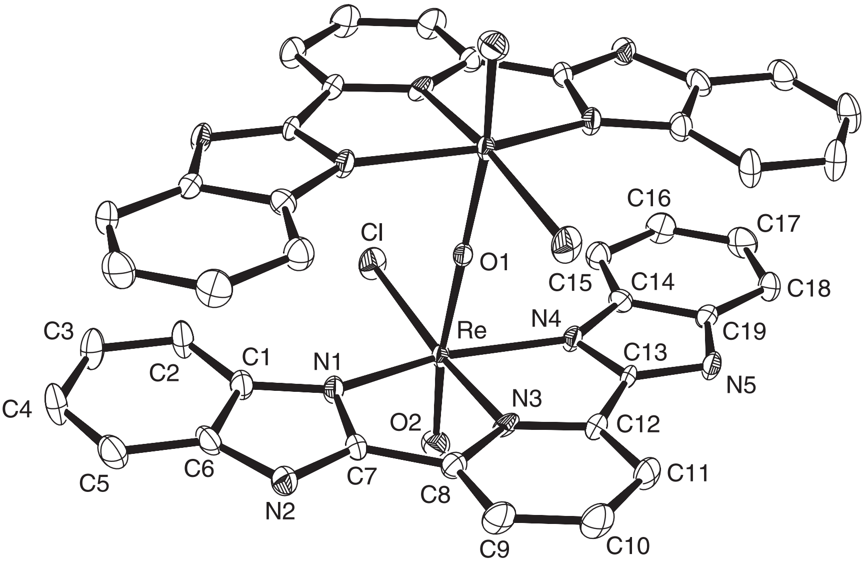

Figure 1. An ORTEP view of (μ-O)[ReOCl(pimH)]$_2$, showing the atom labeling scheme and 50% probability ellipsoids.

Table 1. Crystal data for (μ-O)[ReOCl(pimH)]$_2 \cdot 2H_2O \cdot 2DMF$ (**1**).

Formula	$C_{44}H_{40}Cl_2N_{12}O_7Re_2$
Formula weight	1292.19
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.7803(5)
b (Å)	11.3165(9)
c (Å)	20.1155(12)
β (°)	91.283(7)
Volume (Å^3)	2225.8(2)
Z	2
D_{calc} (g cm^{-3})	1.928
μ (mm^{-1})	5.620
F(000)	1256
Crystal size (mm)	0.06 × 0.09 × 0.26
T (K)	200(2)
Radiation (Å)	Mo Kα (0.71073)
θ range for data collection (°)	2.0–28.0
Index ranges	$-11 \le h \le 12$
	$-14 \le k \le 14$
	$-26 \le l \le 24$
Reflections collected/unique	19077/5029 [R(int) = 0.074]
Observed data [$I > 2.0\sigma(I)$]/parameters	3921/316
Goodness-of-fit on F^2	0.91
Final R indices [$I > 2\sigma(I)$]	$R = 0.0284$, $wR2 = 0.0607$
Largest diff. peak and hole (e Å^{-3})	1.06 and −2.05

3. Results and discussion

The complex (μ-O)[ReOCl(pimH)]$_2 \cdot 2H_2O \cdot 2DMF$ (**1**) was synthesized by the reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with a twofold molar excess of pimH$_2$ in acetonitrile, with recrystallization of the raw product from CH_2Cl_2/DMF in a system that was open

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

Re–O(2)	1.704(4)	Re–O(1)	1.9075(2)
Re–N(1)	2.072(4)	Re–Cl	2.414(1)
Re–N(3)	2.059(4)	C(1)–N(1)	1.371(6)
Re–N(4)	2.138(4)	C(7)–N(1)	1.381(5)
N(4)–C(13)	1.340(6)	C(7)–C(8)	1.454(6)
N(4)–C(14)	1.377(5)	C(7)–N(2)	1.330(5)
N(3)–C(12)	1.341(6)	C(6)–N(2)	1.385(6)
O(3)–C(20)	1.233(7)	C(20)–N(6)	1.335(7)
Re–O(1)–Re	180.0(0)	O(2)–Re–Cl	95.6(1)
O(1)–Re–O(2)	172.7(1)	O(2)–Re–N(3)	92.5(1)
O(2)–Re–N(1)	96.2(2)	Cl–Re–N(3)	171.9(1)
O(2)–Re–N(4)	90.3(2)	N(1)–Re–N(3)	79.2(2)
N(1)–Re–N(4)	156.4(2)	N(3)–Re–N(4)	77.9(1)
N(1)–Re–Cl	100.3(1)	Re–N(1)–C(7)	112.3(3)
N(4)–Re–Cl	101.6(1)	Re–N(4)–C(14)	142.4(3)
N(1)–C(7)–C(8)	126.6(3)	N(4)–C(14)–C(15)	131.5(4)
N(3)–C(12)–C(13)	111.4(3)		

to the atmosphere. Not surprisingly, the source of the bridging oxo group is atmospheric water. The reaction is given by the following equation:

$$2[\mathrm{ReOCl_3(PPh_3)_2}] + 2\mathrm{pimH_2} + \mathrm{H_2O} \rightarrow [\mathrm{Re_2O_3Cl_2(pimH)_2}] + 4\mathrm{HCl} + 4\mathrm{PPh_3}$$

Compound **1** is air stable and a nonelectrolyte in DMF, and is insoluble in most organic solvents, except DMF and DMSO.

The dominant feature in the IR spectrum of **1** is the presence of a strong absorption band at 721 $\mathrm{cm^{-1}}$ ascribed to the asymmetric Re–O–Re stretching mode [11, 12] and a weak peak at 910 $\mathrm{cm^{-1}}$ assigned to ν(Re=O). Weak or medium absorption corresponding to ν(Re=O) has been observed for dimeric species containing the imidazole ligand [11]. The medium intensity peak at 3059 $\mathrm{cm^{-1}}$ is assigned to ν(N–H). Its low frequency is explained by a strong hydrogen bond between this hydrogen and the oxygen of the DMF molecule [N(5)–H $\cdots$ O(3), 2.642 Å, see discussion on crystal structure]. Coordination of the benzimidazolyl and pyridyl rings is indicated by the shift in ν(C=N) from around 1670 to 1620 and 1605 $\mathrm{cm^{-1}}$, respectively. The coordination of the three nitrogen donor atoms of pimH is clearly illustrated by three medium intensity peaks at 467, 436 and 421 $\mathrm{cm^{-1}}$ [ν(Re–N)].

Complex **1** shows sharp peaks in its ^{1}H NMR spectrum, with no detectable paramagnetic shifts or line broadening of the signals. The signals of the three pyridyl protons are clearly distinguishable as a two-proton doublet the furthest downfield at δ 8.68 ppm, and a one-proton triplet at δ 8.48 ppm. The eight C–H protons of the two phenyl rings of each pimH ligand appear as two four-proton multiplets around δ 7.88 and 7.55 ppm. Although the N–H protons in free pimH$_2$ appear as a singlet at δ 13.02 ppm, its presence in the spectrum of the complex could not be detected.

Spectroscopic and crystallographic results show that each pimH ligand in **1** acts as a tridentate monoanionic chelate, with deprotonation of the imidazolyl nitrogen N(1) (see figure 1) to form a coordinated benzimidazolate. The lone pair of electrons on N(2) is only involved in hydrogen bonding to a water molecule of crystallization.

Coordination of the second benzimidazolyl moiety to rhenium(V) occurs through the lone pair of electrons on the neutral donor atom N(4).

Green crystals with the formulation $(\mu\text{-O})[\text{ReOCl(pimH)}]_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{DMF}$ were obtained by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{DMF}$ solution. The axis of the molecule is formed by the O=Re–O–Re=O moiety, with the bridging O(1) atom lying on a crystallographic inversion center. Therefore, the Re–O–Re angle is exactly 180°, and the two O–Re=O angles are equal [172.7(1)°], showing significant deviation from linearity.

Each rhenium atom is centered in an octahedron with the equatorial plane formed by an N_3Cl donor set. The octahedra are appreciably distorted, with the four equatorial donor atoms being displaced away from the Re=O bonds. The effect is small for the neutral donor atoms N(3) and N(4) [92.5(1) and 90.3(2)°, respectively], but significant for the anionic atoms Cl and N(1) [O(2)–Re–Cl = 95.6(1); O(2)–Re–N(1) = 96.2(2)°]. The result of this repulsion is that the rhenium atoms are displaced by 0.1455 Å from the mean equatorial plane towards O(2). The two bite angles of pimH, N(1)–Re–N(3) = 79.2(2)° and N(3)–Re–N(4) = 77.9(1)°, are different, again emphasizing the different donor properties of the neutral N(4) and anionic N(1) atoms. These small bite angles introduce little strain in the pimH molecule, with the N(1)–C(7)–C(8) and N(4)–C(13)–C(12) angles [118.1(3) and 120.2(4)°, respectively] being close to the ideal value of 120°.

There is a significant difference in the two Re–N (imidazole) bonds. As expected, the coordination of the neutral N(4) leads to a longer bond length [Re–N(4) = 2.138(4) Å] than the bonding of the deprotonated N(1) to Re(V) [Re–N(1) = 2.072(4) Å]. In addition, the Re–N(3) bond length [2.059(4) Å] is considerably shorter than Re–N(4), thereby reflecting the weaker π acidity of the neutral imidazole group compared to the pyridine group. The presence of the negatively charged N(1) has little effect on the intramolecular bond parameters of the pimH ligand. The average C–C bond length (1.393 Å) in the C(1)–C(6) phenyl ring is identical to that of the C(14)–C(19) ring. In the imidazole rings, the N(2)–C(7) [1.330(5) Å] and N(1)–C(7) [1.381(5) Å] bonds are localized double and single bonds, respectively. The corresponding bond lengths in the neutral imidazole ring [N(4)–C(13) = 1.340(6) Å, N(5)–C(13) = 1.341(6) Å] indicate delocalization over these two bonds. The inequivalence of the bonding character of N(1) and N(4) is also reflected in the difference in the torsion angles Re–N(1)–C(7)–N(2) = −174.4(3)° and Re–N(4)–C(13)–N(5) = −179.0(3)°, and in N(1)–C(7)–C(8)–N(3) = − 3.8(6)° and N(3)–C(12)–C(13)–N(4) = 0.3(6)°. Other minor differences in the respective angles of the two halves of pimH are N(1)–C(7)–N(2) = 115.3(4)° and N(4)–C(13)–N(5) = 112.9(4)°; C(7)–C(8)–N(3) = 113.1(3)° and N(3)–C(12)–C(13) = 111.4(3)°.

The molecule adopts a staggered conformation in which the ReN_3Cl planes are mutually rotated by 180.0° about the O=Re–O–Re=O axis, so that the chlorines of one unit almost eclipse the N(3) nitrogen atom of the other part of the molecule (distance of Cl to the pyridyl mean plane = 3.397 Å). The dihedral angle between the least-squares planes through the two imidazole rings of each pimH ligand is 5.46°. Ring N(1)–C(1) makes a dihedral angle of 1.46° and ring N(4)–C(15) one of 6.43° with the mean equatorial N(1)N(3)N(4)Cl plane. In fact, each pimH molecule coordinates in a very planar fashion, with the least-squares plane through all its atoms showing deviations that only vary between −0.090 [for N(4)] and 0.128 [for C(2)].

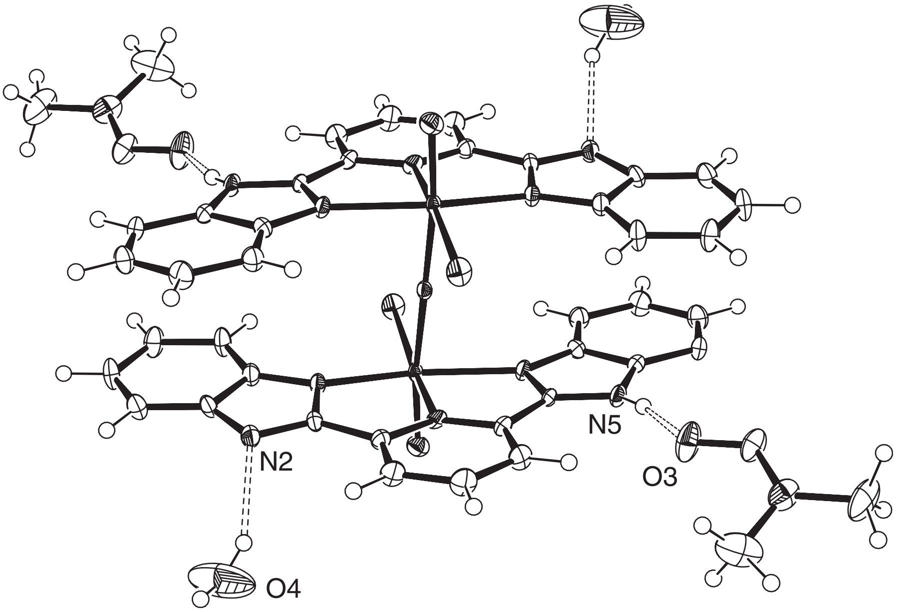

Figure 2. Thermal ellipsoid diagram of **1**, showing hydrogen bonds as broken lines.

The bond length of the Re=O cores is 1.704(4) Å, which falls close to the upper limit of the range [1.688(5)–1.706(7) Å] normally observed for nitrogen-coordinated dimers of the type $Re_2O_3^{4+}$ [13]. The bridging Re–O distance of 1.9075(2) Å is similar to that observed earlier in (μ-O)[ReOCl$_2$(biim)]$_2$ [1.905(1) Å] and in (μ-O)[ReOCl$_2$(py)$_2$]$_2$ [1.912(5) Å] [11, 12].

The packing of the complex is complemented by several hydrogen bonds (figure 2). The lone pair of electrons on N(2) leads to strong hydrogen bonding with a hydrogen of a water molecule [N(2) $\cdots$ H–O(4) = 2.867(7) Å]. Another strong bond exists between N(5)H and O(3) of the DMF solvent of crystallization [2.642(5) Å], in addition to the hydrogen bonds Cl $\cdots$ H–O(4) = 3.303(6), C(11)–H $\cdots$ O(3) = 3.159(6) and C(21)–H $\cdots$ O(4) = 3.352(9) Å.

Supplementary data

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 240409). Copies of this 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 http:// www.ccdc.ac.uk/conts/retrieving.html).

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