

The Oxidation of Rhenium(III) by Dioxygen in the Presence of Tri- and Tetradentate N,O-donor Ligands

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ABSTRACT

The oxidation of *trans*-[ReCl₃(MeCN)(PPh₃)₂] by dioxygen in the presence of the potentially tridentate N₂O-donor ligand 2-[(2-pyridinylmethyl)amino)methyl]phenol (Hham) in ethanol led to the formation of the hydrogen-bonded oxorhenium(V) dimer [ReOCl₂(ham)]₂. With the potentially tetradentate N₂O₂-chelate *N,N*-bis(2-hydroxybenzyl)-aminomethylpyridine (H₂hap), the '4 + 1' complex [ReOCl(hap)] was isolated. Both compounds were characterized by ¹H NMR and infrared spectroscopy, and X-ray crystallography.

KEYWORDS

Oxidation, oxorhenium(V), multidentate ligands, crystal structures.

1. Introduction

Interest in the chemistry of oxorhenium(V) complexes stems from their applications in catalysis and therapeutic nuclear medicine.¹ One successful approach to the development of potential therapeutic agents based on rhenium has been the exploitation of Schiff base ligands to stabilize the oxorhenium(V) core. Multidentate Schiff base ligands provide considerable versatility in their substituent groups, and the possibility thus exists for designing rhenium complexes with useful biological properties.² Oxorhenium(V) complexes with different tri- and tetra-dentate N,O-donor Schiff bases have been investigated extensively, but very few structurally characterized [ReO]³⁺ complexes with conformationally labile, reduced Schiff bases are known.^{3–5}

In this account the syntheses of the complexes [ReOCl₂(ham)]₂ and [ReOCl(hap)], derived from the oxidation reactions (by O₂) of *trans*-[ReCl₃(MeCN)(PPh₃)₂] with the tridentate N₂O-donor chelate 2-[(2-pyridinylmethyl)amino)methyl]phenol (Hham) and the N₂O₂-donor *N,N*-bis(2-hydroxybenzyl)-aminomethylpyridine (H₂hap, Fig. 1), respectively, are described. Oxorhenium(V) complexes are normally prepared by the substitution reactions of the monodentate ligands in the common starting complexes *trans*-[ReOCl₃(PPh₃)₂] and (*n*-Bu₄N)[ReOCl₄], usually with prolonged (>3 h) reaction periods.^{3,4} In this study it was found that the oxidation route to oxorhenium(V) species requires much shorter reaction times to obtain reasonable yields of products.

2. Experimental

2.1. Materials

All chemicals were of reagent grade, and solvents were purified by standard techniques and drying methods. *trans*-[ReCl₃(MeCN)(PPh₃)₂], Hham and H₂hap were prepared by literature methods.^{6,7}

2.2. Physical Measurements

¹H NMR spectra were recorded in DMSO-*d*₆ on a Bruker Avance (300 MHz) spectrometer (Johannesburg, South Africa) at

ambient temperatures, and values are reported relative to TMS. Infrared spectra were obtained with a Digilab FTS 3100 Excalibur HE spectrophotometer (SMM Instruments, Randburg, South Africa) with solid samples prepared as KBr disks. Microanalyses were obtained on a Carlo Erba EA 1108 elemental analyzer (Waltham, MA, USA). Melting points were determined using an Electrothermal 1A-9100 melting point apparatus (Chula Vista, CA, USA). Conductivity measurements were carried out in acetonitrile at 293 K on a Philips PW 9509 digital conductometer (PANalytical, Randburg, South Africa).

2.3. Syntheses of the Complexes

[ReOCl₂(ham)]₂ (1)

To [ReCl₃(MeCN)(PPh₃)₂] (116 mg, 135 μmol) in 5 mL of acetonitrile was added Hham (310 mg, 145 μmol) in 10 mL of acetonitrile. The resulting mixture was heated at reflux for 1 h. During this time the colour of the reaction mixture gradually changed to green, and upon cooling to room temperature a green precipitate was filtered off. The slow evaporation of the filtrate at room temperature deposited green needles which were suitable for X-ray diffraction studies. Yield = 64 %; m.p. >300 °C. Anal. calcd. for C₁₃H₁₃N₂O₂Cl₂Re: C, 32.10; H, 2.69; N, 5.76 %. Found: C, 32.21; H, 2.61; N, 5.88 %. Infrared: ν(Re=O) 964 (vs), ν(NH) 3156 (s), δ(py) 1613 (m), ν(C-O) 1273 cm⁻¹ (vs). ¹H NMR: 10.09 (br s, NH), 9.35 (d, 2H, H¹³, H²⁶); 7.93 (t, 2H, H¹¹, H²⁴); 7.75 (t, 2H, H¹², H²⁵); 7.59 (d, 2H, H¹⁰, H²³); 7.13 (d, 2H, H², H¹⁵); 6.83 (t, 2H, H³, H¹⁶); 6.69 (t, 2H, H⁴, H¹⁷); 5.96 (d, 1H, H², H¹⁵); 5.05 (d, 2H, H^{8a}, H^{21a}); 4.67 (dd, 2H, H^{8b}, H^{21a}); 4.39 (d, 2H, H^{7a}, H^{20a}); 4.09 ppm (dd, 2H, H^{7b}, H^{20a}). Conductivity (10⁻³ mol L⁻¹): 9 ohm⁻¹ cm² mol⁻¹.

[ReOCl(hap)] (2)

To a suspension of 79 mg of H₂hap (247 μmol) in 5 mL of acetonitrile was added 107 mg of [ReCl₃(MeCN)(PPh₃)₂] (125 μmol) dissolved in 7 mL of acetonitrile. The reaction mixture was heated at reflux for 1 h, after which the dark green solution was cooled and filtered. The slow evaporation of this solution yielded green crystals that were suitable for X-ray crystallo-

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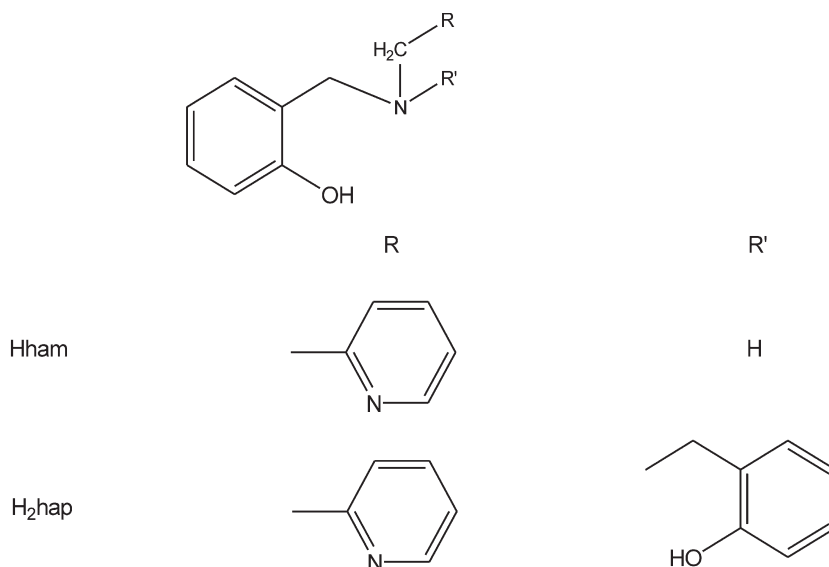


Figure 1 Structures of the ligands.

graphic studies. The crystals were collected by filtration and dried under vacuum. Yield = 67 %; m.p. 275 °C. Anal. calcd. for $C_{20}H_{18}N_2O_3ClRe$: C, 43.20; H, 3.26; N, 5.04 %. Found: C, 43.22; H, 3.23; N, 4.82 %. Infrared: $\nu(Re=O)$ 960 (vs), $\nu(C-O)$ 1248 (s), 1273 (s), $\nu(Re-N)$ 494 (m), 516(m), $\nu(Re-O)$ 468 cm^{-1} (w). 1H NMR: 8.97 (d, 1H, H^{20}); 7.89 (t, 1H, H^{18}); 7.69 (t, 1H, H^{19}); 7.59 (d, 1H, H^4); 7.44 (t, 1H, H^6); 7.34 (d, 1H, H^{11}); 7.16 (d, 1H, H^7); 7.05 (d, 1H, H^{14}); 6.92 (t, 1H, H^5); 6.85 (t, 1H, H^{12}); 6.56 (d, 1H, H^{17}); 6.06 (t, 1H, H^{13}); 5.89 (d, 2H, H^{15}); 5.14 (d, 2H, H^1); 4.86 ppm (d, 2H, H^8). Conductivity ($10^{-3} mol L^{-1}$): 18 $ohm^{-1} cm^2 mol^{-1}$.

2.4. Crystallography

Crystals of complexes **1** and **2** were grown from the slow evaporation of the mother liquors of the synthetic solutions. Diffraction data were measured using an Enraf-Nonius Kappa CCD diffractometer (Cologne, Germany) (graphite-monochromated MoK_{α} radiation, $\lambda = 0.71073 \text{ \AA}$). Intensity data were processed using the DENZO-SMN package.⁸ The structures were solved using the direct-methods program SIR92,⁹ which located all the non-hydrogen atoms. Subsequent full-matrix least-squares refinements were carried out using the CRYSTALS program suite.¹⁰ Hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Details of the crystal data, measurement of intensities and data processing are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

3. Results and Discussion

3.1. Synthesis

The treatment of $[ReCl_3(MeCN)(PPh_3)_2]$ with Hham in a 1:2 molar ratio in ethanol led to the isolation of the hydrogen-bonded dinuclear '3+2' compound $[ReOCl_2(ham)]_2$ (**1**) in moderate yield. The same product was isolated with equimolar quantities of the reactants, albeit in a lower yield. With H_2hap as ligand in acetonitrile the neutral six-coordinate '4+1' monooxorhenium(V) complex $[ReOCl(hap)]$ (**2**) was produced. No oxidation to the perrhenate anion was observed in any of these reactions. Complex **1** is soluble in DMF, insoluble in acetone, dichloromethane, benzene, THF and chloroform, and partially soluble in acetonitrile and alcohols. Complex **2** is sparingly soluble, but stable in polar solvents like DMSO, DMF,

acetonitrile, acetone and chloroform. Both complexes are stable for months in the solid state and in solution, in which they maintain their original individual colours.

In previous work the reactions of $trans-[ReOCl_3(PPh_3)_2]$ with Hham and H_2hap led to the isolation of $[ReOCl_2(ham)(PPh_3)]$, with ham coordinated bidentately with a free pyridyl group, and $[ReOCl(hap)]$ respectively.¹¹

3.2. Spectral Characterization

The infrared spectra of both complexes prove that the multi-dentate ligands are coordinated, as evidenced by shifts in absorptions relative to those of the free ligands. The infrared spectrum of $[ReOCl_2(ham)]_2$ (**1**) is characterized by a very strong absorption at 964 cm^{-1} which is assigned to $\nu(Re=O)$. This frequency occurs in the range normally observed for neutral

Table 1 Crystallographic data for **1** and **2**.

	1	2
Chemical formula	$C_{13}H_{13}Cl_2N_2O_2Re$	$C_{20}H_{18}ClN_2O_3Re$
Formula mass/g mol ⁻¹	436.36	556.03
Crystal system	orthorhombic	triclinic
Space group	$Pna2_1$	$P-1$
$a/\text{\AA}$	18.7478(5)	11.5483(2)
$b/\text{\AA}$	7.3188(2)	12.0556(2)
$c/\text{\AA}$	22.0835(6)	3.8561(2)
$\alpha/^\circ$		90.013(1)
$\beta/^\circ$		103.8599(9)
$\gamma/^\circ$		91.957(1)
Volume/ \AA^3	3030.1(1)	1871.74(5)
Z	8	4
Density (calc.)/g cm ⁻³	2.132	1.973
$F(000)$	1840	1072
Crystal size/mm	0.14 × 0.28 × 0.31	0.04 × 0.09 × 0.11
θ range for data collection/ $^\circ$	3.9, 26.3	3.1, 27.5
Index ranges	-21 ≤ h ≤ 23 -9 ≤ k ≤ 9 -27 ≤ l ≤ 19	-14 ≤ h ≤ 14 -15 ≤ k ≤ 15 -17 ≤ l ≤ 17
Observed data [$I > 2\sigma(I)$]	4508	7094
Parameters	361	487
Goodness-of-fit on F^2	0.95	1.05
Final R indices: R	0.0238	0.0245
wR2	0.0446	0.0485
Largest diff. peak/hole/e \AA^{-3}	0.88/-0.96	1.10/-0.85

Table 2 Selected bond distances [Å] and angles [°] for **1**.

Re(1)-Cl(1)	2.385(2)	Re(2)-Cl(3)	2.379(2)
Re(1)-Cl(2)	2.372(2)	Re(2)-Cl(4)	2.369(2)
Re(1)-O(1)	1.940(4)	Re(2)-O(3)	1.956(3)
Re(1)-O(2)	1.685(4)	Re(2)-O(4)	1.685(4)
Re(1)-N(1)	2.171(6)	Re(2)-N(3)	2.179(6)
Re(1)-N(2)	2.122(6)	Re(2)-N(4)	2.113(6)
O(1)-C(1)	1.357(7)	O(3)-C(14)	1.360(7)
N(1)-C(8)	1.494(8)	N(3)-C(21)	1.489(9)
O(1)-Re(1)-O(2)	166.8(2)	O(3)-Re(2)-O(4)	166.9(1)
O(1)-Re(1)-N(1)	82.8(2)	O(3)-Re(2)-N(3)	83.1(2)
O(2)-Re(1)-N(1)	85.3(2)	O(4)-Re(2)-N(3)	85.6(2)
O(2)-Re(1)-N(2)	91.0(2)	O(4)-Re(2)-N(4)	90.6(2)
O(2)-Re(1)-Cl(1)	96.8(2)	O(4)-Re(2)-Cl(3)	98.2(1)
O(2)-Re(1)-Cl(2)	100.8(2)	O(4)-Re(2)-Cl(4)	100.5(1)
Cl(1)-Re(1)-N(1)	94.1(2)	Cl(3)-Re(2)-N(3)	94.4(2)
Cl(1)-Re(1)-N(2)	169.9(2)	Cl(3)-Re(2)-N(4)	168.7(2)
Cl(1)-Re(1)-O(1)	89.8(2)	Cl(3)-Re(2)-O(3)	89.1(2)
Cl(2)-Re(1)-N(1)	172.5(2)	Cl(4)-Re(2)-N(3)	172.9(2)
Re(1)-O(1)-C(1)	136.3(4)	Re(2)-O(3)-C(14)	134.3(3)
N(1)-Re(1)-N(2)	80.0(2)	N(3)-Re(2)-N(4)	79.3(2)
Re(1)-N(1)-C(8)	108.6(4)	Re(2)-N(3)-C(21)	108.0(5)

six-coordinate monooxorhenium complexes.^{5,12–15} Mono-oxorhenium(V) complexes with an anionic oxygen atom in the position *trans* to the oxo group have the $\nu(\text{Re}=\text{O})$ typically¹⁶ in the range 950–968 cm^{-1} . The corresponding stretch for [ReOCl(hap)] (**2**) appears as a very strong absorption at 960 cm^{-1} . In complex **1** a strong absorption band at 3150 cm^{-1} has been assigned to $\nu(\text{N}-\text{H})$, proving that the amino nitrogen remains protonated upon complexation to the metal. In the free ligand this band appears at 3266 cm^{-1} . Deprotonation of the phenolic OH groups in both complexes is suggested by the absence of bands in the region 3200–3500 cm^{-1} , and coordination of the deprotonated phenolic oxygens to rhenium is reflected by $\nu(\text{C}-\text{O})$ at 1273 cm^{-1} (in **1**) and at 1248 and 1273 cm^{-1} (in **2**).

The ¹H NMR spectra of the compounds consist of easily identifiable singlets, doublets, triplets and multiplets. The lack of paramagnetic broadening in the ¹H NMR spectra of both complexes confirms their diamagnetic character. The broad singlet centred at δ 10.09 ppm in the spectrum of **1** is attributed to the amino

Table 3 Selected bond distances [Å] and angles [°] for **2**.

Re(1)-O(1)	1.964(2)	Re(1)-O(2)	1.985(2)
Re(2)-O(4)	1.964(2)	Re(2)-O(5)	1.987(2)
Re(1)-Cl(1)	2.3972(8)	Re(1)-O(3)	1.689(2)
Re(2)-Cl(2)	2.384(1)	Re(2)-O(6)	1.688(2)
Re(1)-N(2)	2.134(2)	Re(1)-N(1)	2.155(3)
Re(2)-N(4)	2.135(3)	Re(2)-N(3)	2.161(3)
C(3)-O(1)	1.362(5)	C(10)-O(2)	1.361(4)
C(23)-O(4)	1.361(4)	C(30)-O(5)	1.352(4)
N(1)-C(8)	1.510(4)	N(1)-C(15)	1.503(4)
N(3)-C(28)	1.508(4)	N(3)-C(35)	1.510(4)
Cl(1)-Re(1)-O(1)	89.32(7)	O(1)-Re(1)-O(2)	92.6(1)
Cl(2)-Re(2)-O(4)	89.61(7)	O(4)-Re(2)-O(5)	92.6(1)
Cl(1)-Re(1)-O(2)	87.11(7)	O(1)-Re(1)-O(3)	166.1(1)
Cl(2)-Re(2)-O(5)	87.81(7)	O(4)-Re(2)-O(6)	165.8(1)
Cl(1)-Re(1)-O(3)	98.56(8)	O(2)-Re(1)-N(1)	94.50(9)
Cl(2)-Re(2)-O(6)	98.62(8)	O(5)-Re(2)-N(3)	94.19(9)
Cl(1)-Re(1)-N(1)	173.54(7)	O(3)-Re(1)-N(1)	87.4(1)
Cl(2)-Re(2)-N(3)	173.83(7)	O(6)-Re(2)-N(3)	86.8(1)
O(2)-Re(1)-N(2)	171.1(1)	O(3)-Re(1)-N(2)	87.3(1)
O(5)-Re(2)-N(4)	171.1(1)	O(6)-Re(2)-N(4)	87.4(1)
N(1)-Re(1)-N(2)	79.2(1)	Re(1)-O(1)-C(3)	131.3(2)
N(3)-Re(2)-N(4)	80.1(1)	Re(2)-O(4)-C(23)	131.1(2)

proton of ham (at δ 7.28 ppm in the free ligand). The appearance of this signal so far downfield indicates the existence of the dimer, stabilized by hydrogen bonding, also in solution. The corresponding protons in the two complexes forming the dimer are magnetically equivalent, and this discussion is limited to the complex of Re(1). The doublet at δ 9.35 ppm is assigned to the proton adjacent to the pyridinic nitrogen (H^{13}), a downfield shift of δ 0.83 ppm from the free ligand. The aromatic region of the spectrum consists of two triplets centred at δ 7.93 and 7.75 ppm (H^{11} , H^{12}), and two doublets at δ 7.59 and 7.13 ppm (H^{10} , H^2). The lower region of the spectrum exhibits a doublet at δ 5.05 ppm (H^{8a}) and a doublet of doublets centred at δ 4.67 ppm (H^{8b}). Again, a similar pattern is also observed for protons H^{7a} and H^{7b} . The upfield shift in the protons of these methylene groups (H^7 , H^8) indicates the non-equivalence of the methylene protons of each chelated ligand in solution. This is in contrast with the free ligand, where each of these methylene protons resonates as singlets at the same chemical shift. The absence of the O-H phenolic proton signals supports the phenolate coordination. The resonance of the NH proton as a broad singlet farthest downfield (δ 9.35 ppm) suggests that ham acts as a tridentate monoanionic chelate.

The ¹H NMR spectrum of **2** supports the arrangement of H₂hap around the rhenium(V) centre, with all the aromatic protons in different chemical environments. In the aromatic region there are 12 separate signals (six doublets and six triplets) for the 12 aromatic protons. Furthermore, the signals of all the protons are shifted downfield with respect to those of the free ligand.

3.3. Description of the Structures

[ReOCl₂(hap)]₂ (**1**)

The complex exists as a centrosymmetric hydrogen-bonded dimer (Fig. 2). Each rhenium ion is in a distorted octahedral geometry. The basal plane is defined by the pyridyl nitrogen, two *cis* chlorides, and the amino nitrogen of ham. The oxo group and phenolate oxygen of ham lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron results in a non-linear O(1)=Re(1)-O(2) axis of 166.8(2)° accomplished by Cl(1)-Re(1)-N(2) = 169.9(2)° and Cl(2)-Re(1)-N(1) = 172.5(2)°. The corresponding angles for the second complex in the dimer are O(4)=Re(2)-O(3) = 166.9(1)°; Cl(3)-Re(2)-N(4) = 168.7(2)° and Cl(4)-Re(2)-N(3) = 172.9(2)°. The metal is shifted out of the mean equatorial Cl₂N₂ plane by 0.145 Å towards O(2) [for Re(1)] and by 0.157 Å towards O(4) [for Re(2)], with angles O(2)-Re(1)-Cl(1) = 96.8(2)° [O(4)-Re(2)-Cl(3) = 98.2(1)°], O(2)-Re(1)-Cl(2) = 100.8(2)° [O(4)-Re(2)-Cl(4) = 100.5(1)°], O(2)-Re(1)-N(1) = 85.3(2)° [O(4)-Re(2)-N(3) = 85.6(2)°] and O(2)-Re(1)-N(2) = 91.0(2)° [O(4)-Re(2)-N(4) = 90.6(2)°].

The Re=O bond lengths [average = 1.685 Å] are within the range expected with a phenolate oxygen *trans* to the oxo group.¹⁷ There is a significant difference in bond length between Re(1)-O(1) [1.940(4) Å] and Re(2)-O(3) [1.956(3) Å], which is also reflected in the difference between the Re(1)-O(1)-C(1) [136.3(4)°] and Re(2)-O(3)-C(14) [134.3(8)°] bond angles. These bond lengths are substantially shorter than 2.04 Å, which is representative of a Re(V)-O single bond.¹⁸ The Re-Cl bond distances [average = 2.379(2) Å] are within the expected range of other rhenium(V) complexes. The Re-N_{py} distances [average = 2.118(6) Å] are shorter than the bonds from the amino nitrogen to the metal [average = 2.175(6) Å].

These bond lengths are within the range expected from a comparison of other six-coordinate monooxorhenium(V) complexes

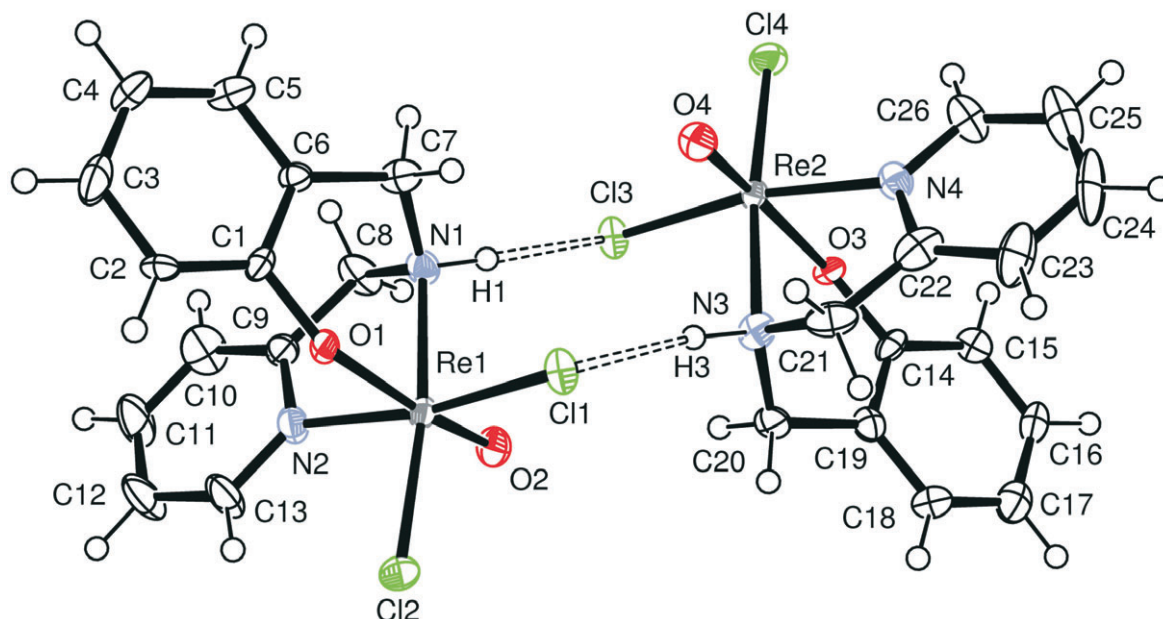


Figure 2 ORTEP representation of the hydrogen-bonded dimer $[\text{ReOCl}_2(\text{ham})]_2$ (1).

containing the ClN_2O donor set.^{15,19} The complex exists as a hydrogen-bonded dimer with both $\text{H}(1)\cdots\text{Cl}(3)$ and $\text{H}(3)\cdots\text{Cl}(1)$ bond distances equal to 2.310 Å, which render a high stability to the compound.

$[\text{ReOCl}(\text{hap})]$ (2)

The X-ray crystal structure of 2 reveals that the structure consists of two independent molecules of the complex, which

are almost identical to each other, in the asymmetric unit. The structure (see Fig. 3) consists of discrete, monomeric and neutral oxorhenium complexes packed with no intermolecular contacts shorter than the sum of the van der Waals radii. The coordination geometry around the rhenium is highly distorted octahedral; the two nitrogen atoms N(1) and N(2) from the tetradentate dinegative ligands lie on the equatorial plane, along with the chloride and phenolate O(2) atoms, with the phenolate O(1)

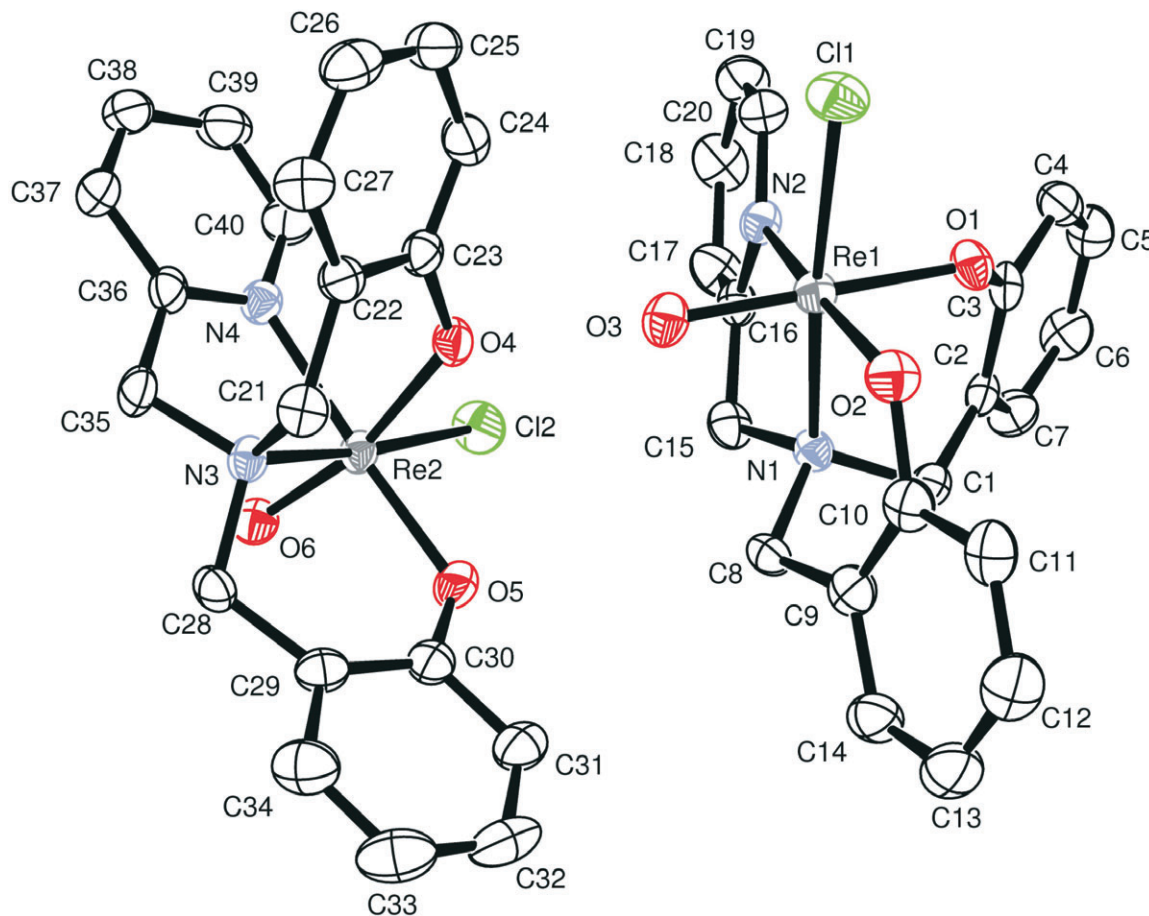


Figure 3 Crystal structure of the contents of the asymmetric unit of $[\text{ReOCl}(\text{hap})]$ (2).

trans to the O(3) oxo atom. The chloride is coordinated *trans* to the tripodal N(1) atom. In the coordination sphere of the complex the two six-membered metallocycles adopt the twist-boat conformation, the dihedral angles between the two aromatic rings being 60.42°.

The O(1)-Re(1)-O(3) axis is non-linear [166.1(1)°] and the rhenium atom is displaced from the mean equatorial plane by 0.124(1) Å towards the oxo oxygen atom. This is a result of the *cis* angles O(3)-Re(1)-N(1) = 87.4(1)°, O(3)-Re(1)-N(2) = 87.3(1)°, O(3)-Re(1)-Cl(1) = 98.56(8)° and O(3)-Re(1)-O(2) = 99.3(1)°. As a measure of the octahedral distortion in the ClN₂O₃ polyhedron, the Re atom is -1.23 Å from the N(2)N(1)O(3) plane and +1.22 Å from the Cl(1)O(2)O(1) plane, the angle between the two triangular faces being 7.62°. The interligand angles in the equatorial planes depart considerably from the ideal 90°, mainly due to the bite angles N(1)-Re(1)-N(2) = 79.7(1)° and N(1)-Re(1)-O(2) = 94.50(9)°.

The Re(1)=O(3) distance of 1.689(2) Å compares favourably with those reported previously.^{13–15} Surprisingly, the Re(1)-O(1) bond lengths *trans* to the oxo oxygen O(3) are significantly shorter than the equatorial Re(1)-O(2) bond lengths [*e.g.* 1.964(2) vs 1.985(2) Å]. This is in contrast with the complex [ReOCl(sal₂en)] (sal₂en = 1,3-*N,N'*-bis-(3,5-salicylideneimine) diamino-2,2-dimethylpropyl), where the *trans* Re-O bond length [1.994(5) Å] is significantly longer than the *cis* Re-O(phenoxy) bond length of 1.976(5) Å.¹³ The Re(1)-N(2) bond [2.134(2) Å] is significantly shorter than the Re(1)-N(1) bond [2.155(3) Å], which can be attributed to the *sp*³ character of N(1). The Re-Cl bond length agrees well with those reported in the literature and, furthermore, these bond lengths are within the range expected from a comparison of other six-coordinate monooxorhenium(V) complexes containing the ClN₂O₃ donor set.^{13–15}

4. Conclusion

The reactions of the rhenium(III) starting material *trans*-[ReCl₃(MeCN)(PPh₃)₂] with the tri- and tetradentate N₂O-donor 2-(((2-pyridinylmethyl)amino)methyl)phenol (Hham) and N₂O₂-donor *N,N*-bis(2-hydroxybenzyl)-aminomethylpyridine (H₂hap) ligands respectively in dioxygen were studied. In both cases the rhenium(V) oxidation products were isolated and characterized, i.e. the '3+2' complex [ReOCl₂(ham)]₂ as a hydrogen-bonded dimer, and the '4+1' complex [ReOCl(hap)].

5. Supplementary data

CCDC 765239 and 765240 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be

obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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