

SYNTHESIS AND CHARACTERIZATION OF AN OXO-BRIDGED RHENIUM(V) COMPLEX WITH AN AMINE-PHENOL TETRADENTATE LIGAND

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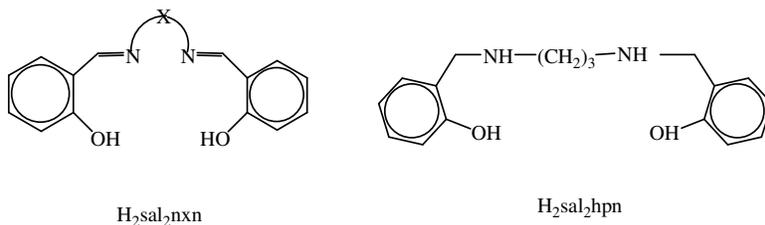
(Received March 15, 2006; revised May 4, 2006)

ABSTRACT. The oxo-bridged dinuclear complex $[(\mu\text{-O})\{\text{ReO}(\text{sal}_2\text{hpn})\}_2]\cdot\text{EtOH}$ was prepared by the reaction of *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with *N,N'*-propylenebis(salicylideneamine) ($\text{H}_2\text{sal}_2\text{hpn}$) in ethanol. An X-ray crystallographic study showed that each sal_2hpn is coordinated as a tetradentate dianionic chelate. The axis of the molecule is formed by the $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$ moiety, with the average $\text{O}=\text{Re}-\text{O}$ and $\text{Re}-\text{O}-\text{Re}$ bond angles equal to $165.2(2)^\circ$ and $164.8(2)^\circ$ respectively. The average $\text{Re}=\text{O}$ bond equals $1.697(5) \text{ \AA}$, and the $\text{Re}-\text{O}$ bonds have an average length of $1.928(4) \text{ \AA}$. The structure has a monoclinic space group *Cc* with $a = 13.7747(2) \text{ \AA}$, $b = 26.8715(4) \text{ \AA}$, $c = 9.6478(1) \text{ \AA}$, $\beta = 92.4202(9)^\circ$, $V = 3567.92(8) \text{ \AA}^3$ and $Z = 4$.

KEY WORDS: Oxo-bridge, Rhenium(V), Dimeric, Crystal structure

INTRODUCTION

Rhenium(V) complexes of tetradentate ligands have been well studied over the last 25 years, and these ligands were mainly Schiff bases of the imine-phenol type ($\text{H}_2\text{sal}_2\text{nxn}$) [1-5]. It was shown that complexes of the general formula



$[\text{MOCl}(\text{sal}_2\text{nxn})]$ [$M = \text{Re}, \text{Tc}$; $x = (\text{CH}_2)_2, (\text{CH}_2)_3$] are readily obtained from the reactions of *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ or $(n\text{-Bu}_4\text{N})[\text{ReOCl}_4]$ with $\text{H}_2\text{sal}_2\text{nxn}$ if air and moisture are excluded from the reaction mixtures [2, 4]. It was shown by X-ray and spectroscopic studies [2-4] that these complexes exhibit a distorted octahedral coordination geometry, with a *trans* oxo-chlorometallate(V) core. Another study, however, has shown that complexes of the $[\text{ReOCl}(\text{sal}_2\text{nxn})]$ type may also have the *cis* oxo-chlororhenate arrangement if the bridging unit X contains three carbon atoms [5]. However, if the reactions are done in air and wet solvents, so that some water is always present, complexes of the type $[\text{Re}_2\text{O}_3(\text{sal}_2\text{nxn})_2]$ are formed, with a linear $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$ grouping [1, 4].

In this account the reaction of the ligand $\text{H}_2\text{sal}_2\text{hpn}$ with *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ in air is reported. The oxo-bridged dimer $(\mu\text{-O})[\text{ReO}(\text{sal}_2\text{hpn})]_2$ was isolated as only product.

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EXPERIMENTAL

Trans-[ReOCl₃(PPh₃)₂] was prepared by a literature method [6]. The ligand H₂sal₂hpn (*N,N'*-propylenebis(salicylideneamine)) was prepared by the condensation reaction of salicylaldehyde and 1,3-diaminopropane in a 2:1 molar ratio in ethanol/benzene, followed by the reduction of the –CH=N bond with sodium borohydride at room temperature. All chemicals were of reagent grade and were used as received. Solvents were purified and dried before use. The scientific instrumentation used is the same as that reported previously [7]. Infrared spectra were obtained using KBr discs and ¹H NMR spectra were run in DMSO-*d*₆.

Synthesis of (μ-O)[ReO(sal₂hpn)]₂.EtOH (1.EtOH)

To 100 mg of *trans*-[ReOCl₃(PPh₃)₂] (118 μmol) in 20 cm³ ethanol was added a twofold molar excess of H₂sal₂hpn (68 mg). The resulting mixture was heated under reflux for 24 h, giving a dark green solution. After cooling to room temperature, a green precipitate was removed by filtration. The product was washed with ethanol and diethyl ether, and dried under vacuum. The slow evaporation of the mother liquor over 2 days at room temperature gave another batch of green crystals, which were suitable for X-ray diffraction studies. Yield = 74 % (based on Re), m.p. = 238 °C. Anal. calcd. (%): C, 41.77; H, 4.48; N, 5.41. Found: C, 41.83; H, 4.61; N, 5.48. IR: ν(N-H) 3225; ν(C-O) 1263; ν(Re=O) 953; ν(Re-O-Re) 696; ν(Re-N) 522; ν(Re-O) 459 cm⁻¹. ¹H NMR (295 K), ppm: 10.72 (2H, s, NH), 10.21 (2H, s, NH), 7.66 (4H, d, H(2), H(16), H(19), H(33), *J* = 8.2 Hz), 7.52 (4H, t, H(4), H(14), H(20), H(31), *J* = 7.6 Hz), 6.98 (4H, t, H(3), H(15), H(20), H(32), *J* = 8.2 Hz), 6.90 (4H, d, H(5), H(13), H(22), H(30), *J* = 7.6 Hz), 3.35 (8H, m, C(8)H₂, C(10)H₂, C(25)H₂, C(27)H₂), 2.51 (8H, s, C(7)H₂, C(24)H₂, C(11)H₂, C(28)H₂), 1.06 (4H, t, C(9)H₂, C(26)H₂, *J* = 7 Hz). Electronic spectrum (CH₃CN, nm (ε M⁻¹cm⁻¹)): 368 (2200), 490 (150), 608 (300). Conductivity (10⁻³ M, CH₃CN) = 16 μS.cm⁻¹.

X-ray determination of crystal structure

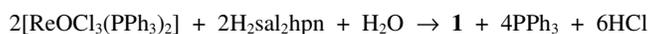
Intensity data for 1.EtOH were collected at 200(2) K on a Nonius Kappa CCD single-crystal diffractometer, using Mo K_α radiation. Unit cell and space group determinations were carried out in the usual manner [8]. The structure was solved by direct methods and refined by full matrix least-squares procedures using SHELXL-96 [9]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were geometrically constrained. The Flack parameter equals -0.02(8). 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.

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

Chemical formula	C ₃₆ H ₄₆ N ₄ O ₈ Re ₂
Formula weight	1035.19
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions (Å, °)	<i>a</i> = 13.7747(2) <i>b</i> = 26.8715(4) <i>c</i> = 9.6478(1) β = 92.4202(9)
Volume (Å ³)	3567.92(8)
Z	4
Density (calc.; Mgm ⁻³)	1.927
Absorption coefficient (mm ⁻¹)	6.837
F(000)	2016
Crystal size (mm)	0.03 x 0.06 x 0.21
Radiation (Å)	0.71073
θ range for data collection (°)	3.3-27.5
Index ranges	-17 ≤ <i>h</i> ≤ 17; -34 ≤ <i>k</i> ≤ 34; -11 ≤ <i>l</i> ≤ 12
Reflections measured	23596
Independent/observed reflections	7909/7712
Data/parameters	7909/441
Goodness-of-fit on F ²	1.04
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0279, <i>wR</i> 2 = 0.0648
Flack <i>x</i>	-0.02(8)
Largest diff. peak and hole (eÅ ⁻³)	0.77 -1.43

RESULTS AND DISCUSSION

The complex (μ -O)[ReO(sal₂hpn)]₂ (**1**) was synthesized by the reaction of *trans*-[ReOCl₃(PPh₃)₂] with a twofold molar excess of H₂sal₂hpn in ethanol in a system that was open to the atmosphere. Not surprisingly, the possible source of the bridging oxo group is atmospheric water, as was reported earlier [1-4]. The reaction is given by the equation:



Compound **1** is air-stable and a non-electrolyte in acetonitrile, and is insoluble in water and most organic solvents, except DMSO, DMF and acetonitrile.

The dominant feature in the IR spectrum of **1** is the presence of a strong absorption band at 696 cm⁻¹, ascribed to the asymmetric Re-O-Re stretching mode [10, 11], and a medium-intensity peak at 953 cm⁻¹, assigned to $\nu(\text{Re}=\text{O})$. Weak or medium absorptions corresponding to $\nu(\text{Re}=\text{O})$ have been observed previously for dimeric species [10]. The medium intensity peak at 3225 cm⁻¹ is assigned to $\nu(\text{N-H})$, and this value intimates that this entity is not involved in hydrogen-bonding. The coordination of the four chemically equivalent nitrogen donor atoms is clearly illustrated by the single medium intensity peak at 522 cm⁻¹ [$\nu(\text{Re-N})$].

Complex **1** shows sharp peaks in its ¹H NMR spectrum, with no detectable paramagnetic shifts or line broadening of the signals. The signals of the aromatic protons are clearly distinguishable, and lead to a four-proton doublet (at 7.66 ppm), triplet (7.52 ppm), triplet (6.98 ppm) and doublet (6.90 ppm) pattern, which illustrates the chemical and magnetic equivalence of the four phenyl rings in **1**. The four NH protons surprisingly give rise to two two-proton singlets far downfield at 10.72 and 10.21 ppm. The obvious explanation for this phenomenon is

the existence of hydrogen-bonds involving the NH protons. The X-ray crystal structure determination shows that hydrogen-bonds exist in the solid state between N(1)H(1) and O(3)[3.331(7) Å], and between N(2)H(2) and O(4)[3.078(6) Å]. Similar hydrogen-bonds are not operative for the N(3) and N(4) protons.

The spectral and crystallographic results show that each sal₂hpn ligand in **1** acts as a tetradentate dianionic chelate, with deprotonation of the two phenolic oxygens of each ligand.

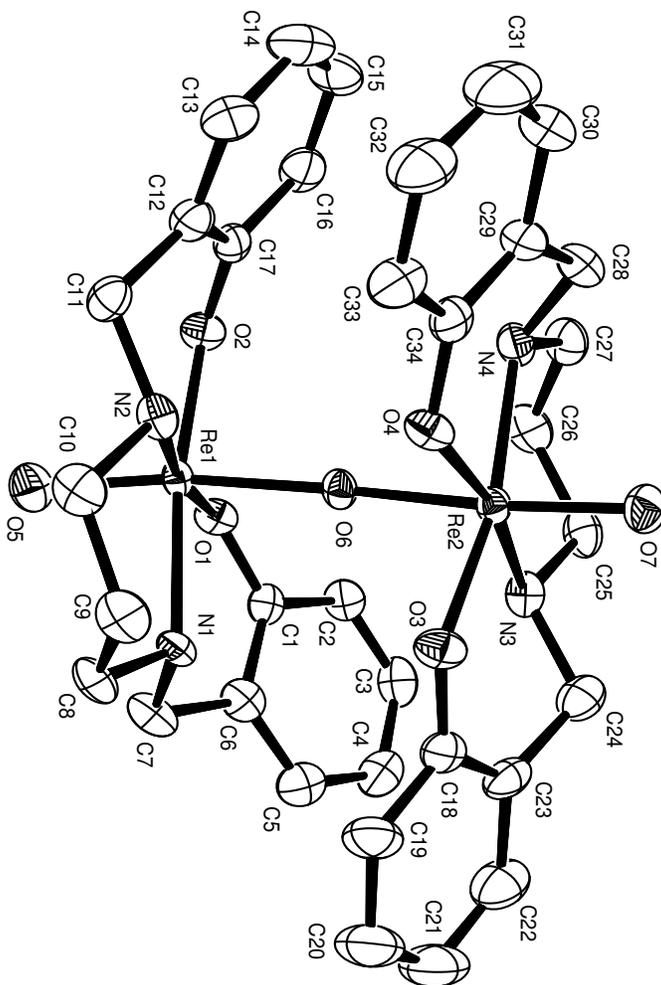


Figure 1. The molecular structure of $(\mu\text{-O})[\text{ReO}(\text{sal}_2\text{hpn})]_2$ (**1**), showing the atom numbering scheme and thermal ellipsoids drawn at the 40 % probability level.

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

Re(1)-O(1)	2.018(4)	Re(2)-O(4)	2.012(4)
Re(1)-O(2)	2.015(4)	Re(2)-O(3)	1.998(4)
Re(1)-O(5)	1.694(5)	Re(2)-O(7)	1.700(5)
Re(1)-O(6)	1.912(4)	Re(2)-O(6)	1.943(4)
Re(1)-N(1)	2.178(5)	Re(2)-N(4)	2.168(5)
Re(1)-N(2)	2.168(5)	Re(2)-N(3)	2.167(5)
N(1)-C(7)	1.488(9)	N(4)-C(28)	1.470(9)
N(2)-C(11)	1.488(9)	N(3)-C(24)	1.470(8)
C(1)-O(1)	1.354(7)	N(2)-C(10)	1.492(8)
O(5)-Re(1)-O(6)	165.3(2)	O(7)-Re(2)-O(6)	165.0(2)
Re(1)-O(6)-Re(2)	164.8(2)	O(3)-Re(2)-O(4)	83.9(2)
O(1)-Re(1)-O(2)	82.8(2)	O(3)-Re(2)-N(4)	168.7(2)
O(1)-Re(1)-N(2)	171.2(2)	O(3)-Re(2)-N(3)	89.1(2)
N(1)-Re(1)-N(2)	93.3(2)	C(24)-N(3)-C(25)	111.8(5)
O(1)-Re(1)-N(1)	91.5(2)	C(27)-N(4)-C(28)	109.2(5)
O(2)-Re(1)-N(2)	91.6(2)	O(7)-Re(2)-O(3)	100.9(2)
C(7)-N(1)-C(8)	111.2(5)	O(7)-Re(2)-O(4)	101.7(2)
C(17)-O(2)-Re(1)	124.7(3)	O(7)-Re(2)-N(3)	87.9(2)
C(8)-C(9)-C(10)	115.2(5)	O(7)-Re(2)-N(4)	88.3(2)

The molecular structure of **1** is illustrated in Figure 1 and selected bond lengths and angles are listed in Table 2. The axis of the molecule is formed by the O=Re-O-Re=O moiety, with the Re-O(6)-Re angle being equal to 164.8(2)°. Each rhenium atom is centred in an octahedron with the equatorial plane formed by a N₂O₂ donor set. The octahedra are severely distorted, with the equatorial oxygen donor atoms O(1), O(2), O(3) and O(4) being displaced away from the Re=O bonds with the mean O=Re-O angle 101.0(2)°. The average O=Re-N angle is 87.5(2)°. The result of these distortions is non-linear O(5)-Re(1)-O(6) and O(6)-Re(2)-O(7) bond angles of 165.3(2)° and 165.0(2)°, respectively, with the Re atoms out of the mean equatorial plane by ~0.14 Å towards the O(5) and O(7) oxo atoms. The axial Re=O [1.697(5) Å average], the equatorial Re-O [2.011(4) Å average] and bridging Re-O [1.928(4) Å average] bond lengths are within the ranges found for these bonds in similar complexes [1-4, 11-13]. The average Re-N distance of 2.170(5) Å is similar to Re-N(amine) bonds found in other rhenium(V) complexes [3-5], and is significantly longer than the average of 2.00(3) Å for Re^V-N(amide) bonds [12, 13]. The molecule adopts a staggered conformation in which the equatorial ReN₂O₂ planes are mutually rotated by 169.3° about the O=Re-O-Re=O axis. The two phenyl rings of each NO-half of the sal₂hpn ligand bonded to Re(2) are nearly coplanar with a dihedral angle of 13.25°. However, the sal₂hpn ligand bonded to Re(1) is much more folded towards O(6), with the dihedral angle between the two phenyl rings equal to 47.06°. The dihedral angles between the C(1)-C(6) and C(18)-C(23) and C(12)-C(17) and C(29)-C(34) rings are 24.52° and 11.18°, respectively.

The intraligand bond distances illustrate π -delocalization in the phenyl rings [average C-C distance = 1.39(1) Å]. The N(1)-C(7) and N(2)-C(11) bond lengths are identical at 1.488(9) Å, as are the N(3)-C(24) and N(4)-C(28) lengths at 1.470(9) Å, illustrating their single bond nature. The angles around the four nitrogen donor atoms [110.3(5)° average] show the sp³-hybridization of the amine nitrogen's.

Previous studies with the potentially tetradentate dianionic Schiff base ligand H₂sal₂en [*N,N'*-ethylenebis(salicylideneimine)] have led to the Schiff base-bridged species (μ -sal₂en)[ReOCl₂(PPh₃)₂]₂, [μ -sal₂en]{ReOCl₃}₂²⁻ and [μ -H₂sal₂en]{ReOCl₄}₂²⁻, as well as the mononuclear complex [ReOCl(sal₂en)] [14-16].

Supplementary material

Crystallographic data for **1**.EtOH have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 299048). Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.ac.uk/conts/retrieving.html>).

ACKNOWLEDGEMENT

A.A. is grateful to the National Research Foundation for financial support.

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