Bull. Chem. Soc. Ethiop. **2008**, 22(2), 247-252.
Printed in Ethiopia
ISSN 1011-3924

A *CIS*-DIBROMORHENIUM(V) IMINOPHENOLATO COMPLEX

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(Received September 28, 2007; revised October 13, 2007)

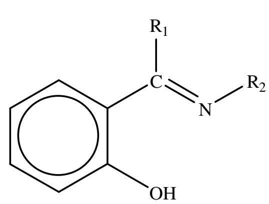
ABSTRACT. The complex *cis*-[$ReOBr_2$(msa)(PPh_3)](**1**) was prepared from *trans*-[$ReOBr_3(PPh_3)_2$] and 2-(1-iminoethyl)phenol (Hmsa) in acetonitrile. An X-ray crystallographic study shows that the two bromides are coordinated *cis* to each other in the equatorial plane *cis* to the oxo group. DFT calculations on **1** and its *trans* isomer show that the energy difference between the HOMO and LUMO in the *cis* isomer is smaller than that in the *trans*.

KEY WORDS: Rhenium(V), Iminophenol, *cis*-Dibromo, Crystal structure

INTRODUCTION

Interest in Schiff bases as ligands stems from the biological and pharmaceutical applications of their metal complexes, which show increased antibiotic activity after coordination of the ligands [1-3]. For example, Schiff base complexes of iron(III) have exhibited widespread antiviral activity in biological systems [4, 5].

The development of the coordination chemistry of rhenium is important, since some compounds of its $^{186/188}$Re radionuclides have been found to be useful in therapeutic nuclear medicine [6]. Rhenium(V) complexes with potentially uninegative bidentate *N*,*O*-donor Schiff base ligands (Hnor) are well studied, and produce complexes with the formulae [$ReOX_2$(nor)(PPh_3)] and [ReOX$(nor)_2$] (X = Cl, Br) [7-10]. Similar products were obtained with 8-hydroxyquinoline as ligand [9]. In the case of [$ReOX_2$(nor)(PPh_3)], some systems have been isolated as *cis* and *trans* isomers [7-12].



R_1	R_2	Hnor
CH_3	H	Hmsa

In this study the synthesis and crystal structure of [$ReOBr_2$(msa)(PPh_3)] (**1**) are reported. In **1** the two bromides are coordinated in *cis* positions relative to each other, although the starting complex [$ReOBr_3(PPh_3)_2$] has the *mer-trans* structure with the bromines *cis* to the oxo group *trans* to each other [10]. This study investigates this coordination behaviour.

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EXPERIMENTAL

Reactants and methods

Trans-[$ReOBr_3(PPh_3)_2$] was synthesized by a literature method [13]. Hmsa was synthesized as described earlier [14]. Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. All manipulations were done under nitrogen using standard Schlenk and cannula techniques. Infrared spectra were obtained using KBr discs and ^{1}H NMR spectra (300 MHz) were run at room temperature in d_6-DMSO. The instrumentation used is the same as reported earlier [15].

Synthesis

*cis-[$ReOBr_2(msa)(PPh_3)$] (**1**).* Hmsa (30 mg, 222 µmol) was added to a solution of *trans*-[$ReOBr_3(PPh_3)_2$] (100mg, 103 µmol) in 20 mL acetonitrile and the mixtures were heated under reflux for 90 min. The colour of the reaction mixture turned green, and after cooling to room temperature, the solution was filtered and left to evaporate slowly at room temperature. After two days a crystalline precipitate was collected by filtration, and washed with ethanol and diethyl ether. Recrystallization from a 2:1 v/v mixture of dichloromethane:ethanol gave green crystals suitable for X-ray crystallographic analysis. Yield 58 mg (74%), mp 247 °C. Anal.: found (%): C, 41.34; H, 3.08; N, 2.01. Calc.: C, 41.17; H, 3.06; N, 1.85. IR(cm^{-1}): ν(Re=O) 952 m; ν(C=N) 1592 vs; ν(Re-N) 522 m; ν(Re-O) 486 m; ν(Re-Br) 304 m, 288 m. ^{1}H NMR δ (ppm), see Figure 1 for numbering: 11.42 (br s, 1H, N*H*), 7.89 (d, 1H, *H5*), 7.42-7.68 (m, 15H, P*Ph*$_3$), 7.48 (t, 1H, *H7*), 7.18 (d, 1H, *H8*), 6.99 (t, 1H, *H6*), 2.68 (s, 3H, C*H*$_3$).

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 [16]. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [17]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were geometrically constrained. An ORTEP view of **1**, along with the numbering scheme, is given in Figure 1. A summary of the crystal data and refinement details is given in Table 1. Selected bond distances and angles are given in Table 2.

Computational study

The SPARTAN v1.03 program [18] was used in the calculations. The geometry optimization was done by the DFT method with the use of the B3LYP functional [19]. The calculations were performed with the 6-31G* basis set.

RESULTS AND DISCUSSION

Synthesis

The complex **1** was obtained in good yield from the reaction of *trans*-[$ReOBr_3(PPh_3)_2$] with a twofold molar excess of Hmsa in acetonitrile, according to the equation

$$ReOBr_3(PPh_3)_2 + Hmsa \rightarrow \mathbf{1} + PPh_3 + HBr$$

Pure products could not be isolated from the reaction of equimolar quantities. Also, a complex of the formula [ReOBr(msa)$_2$] could not be isolated, even with a five-fold molar excess of Hmsa in the presence of triethylamine. The complex is diamagnetic and a non-electrolyte in DMF, and it is soluble in a wide variety of polar solvents.

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

	1
Chemical formula	$C_{26}H_{23}NO_2PBr_2Re$
Formula weight	758.46
Crystal system	Triclinic
Space group	-
Unit cell dimensions (Å, °)	P1
	a = 10.5943(2)
	b = 11.1521(2)
	c = 12.9522(2)
	α = 83.470(1)
	β = 70.126(1)
Volume (Å^3)	γ = 62.554(1)
Z	1275.47(4)
Density (calc.) (Mg/m^3)	2
Absorption coefficient (mm^{-1})	1.975
F (000)	7.983
Crystal size (mm)	724
θ range for data collection (°)	0.06x0.07x0.09
Index ranges	3.2-27.5
	$-13 \leq h \leq 13$,
	$-14 \leq k \leq 14$,
Reflections measured	$-16 \leq \ell \leq 16$
Independent/observed reflections	28177
Data/parameters	5849/5296
Goodness-of-fit on F^2	5849/299
Final R indices [$I > 2\sigma(I)$]	1.09
Largest diff. peak and hole	0.0221 ($wR2$ = 0.0464)
(e/Å^3)	0.99, -0.89

Structure

A perspective view of the asymmetric unit of **1** is shown in Figure 1. The complex exhibits a distorted octahedral geometry about the central rhenium(V) ion. The basal plane is defined by the phosphorus atom of the PPh_3 group, the two bromides *cis* to each other, and the neutral imino nitrogen of msa. The oxo group and phenolate oxygen lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron results in a non-linear O(2)=Re-O(1) axis of 167.3(1)°, and Br(2)-Re-P and Br(1)-Re-N angles of 175.75(2)° and 169.10(7)°, respectively (Table 2). The metal is shifted out of the mean equatorial plane formed by Br_2PN by 0.132 Å towards O(2), with angles O(2)-Re-Br(1) = 100.01(8)°, O(2)-Re-Br(2) = 97.14(7)°, O(2)-Re-P = 87.09(7)° and O(2)-Re-N = 90.1(1)°. The Re=O(2) axis is inclined at 177.0° with respect to the equatorial plane.

The Re=O(2) bond length of 1.691(2) Å is within the range expected with a phenolate oxygen *trans* to the oxo group [18,21]. The Re-O(1) bond length of 1.940(2) Å is shorter than the usual length for a Re-O single bond [2.04 Å], which may be reflecting the delocalization of π-electron density from the oxo bond to the *trans* Re-O bond [22]. The Re-Br(2) bond length is significantly longer than the Re-Br(1) one, due to the larger *trans* effect of P compared to the imino N. The bite angle of the msa ligand is 80.5(1)°. C(2)-N is a double bond [1.288(4) Å], and the N-C(2)-C(3) bond angle of 120.9(3)° is indicative of the sp^2 hybridization of C(2). Intramolecular hydrogen-bonds exist between NH and O(2) [3.033(3) Å] and between C(16)H and O(1) [3.175(4) Å].

The dihedral angle between the least-squares planes through the phenyl ring C(3)-C(8) of msa and the C(9)-C(14) ring of PPh_3 is 15.34°, and the distance between their centroids is 4.129 Å.

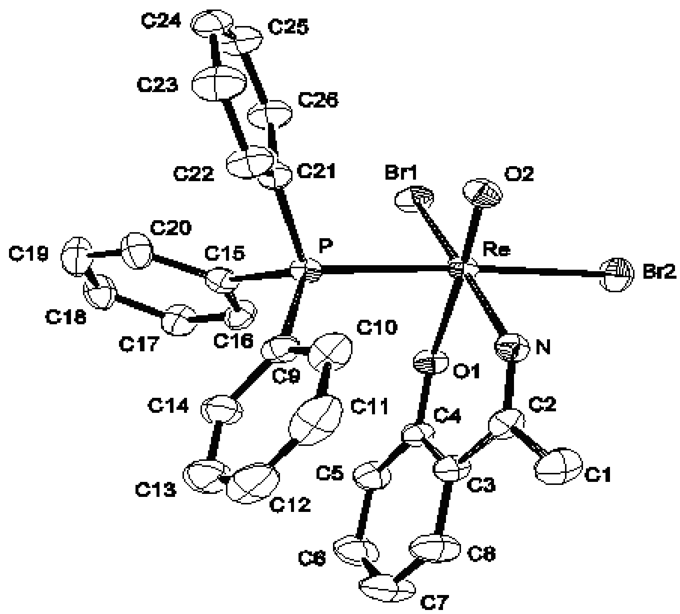

Figure 1. An ORTEP view of $[ReOBr_2(msa)(PPh_3)]$(**1**), showing the atom labelling scheme and thermal ellipsoids at the 40 % probability level.

Spectral characterization

The infrared spectrum of **1** displays the Re=O stretching frequency at 952 cm^{-1}, which falls in the observed region of 945-968 cm^{-1} for neutral six-coordinate monooxorhenium(V) complexes having an anionic phenolate oxygen atom coordinated *trans* to the oxo group [23, 24]. The Re-N and Re-O stretches appear at 522 and 486 cm^{-1}, respectively. The spectrum also displays two distinct peaks at 304 and 288 cm^{-1}, which are typical for ν(Re-Br), and suggesting that the two bromides are in *cis* positions to the oxo group, and in *cis* sites to each other. In the ^{1}H NMR spectrum of the complex the broad singlet far downfield around 11.42 ppm is attributed to the imino proton. A fifteen proton multiplet in the range 7.4-7.7 ppm illustrates the presence of PPh_3. The four aromatic protons of msa give rise to a set of doublet-triplet-doublet-triplet signals in the range 7.89-6.99 ppm.

Bromide analogues of complex **1** are scarce in the literature. It was found, however, that the bromides in the complex $[ReOBr_2(Hdhp)(PPh_3)]$ (H_2dhp = 2,3-dihydroxypyridine), which was also synthesized from *trans*-$[ReOBr_3(PPh_3)_2]$, are also arranged in equatorial *cis* positions [25].

Optimized geometry

The geometry of **1** was optimized in a singlet state by using the DFT method with the B3LYP functional. The optimized geometric parameters are given in Table 2. The calculated bond lengths and angles of the *cis* isomer of **1** are in agreement with the values obtained by the X-ray crystal structure data. The largest difference is found for the Re-P bond distance, which is 0.105 Å longer than the experimental length. The differences in the calculated and experimental lengths for the Re-Br bonds are remarkably small [0.042 and 0.018 Å] when compared with other complexes with Re-Br bonds, where differences of up to 0.08 Å were observed [26]. The optimized Re-N distance is 0.036 Å longer than the experimental value. The computed Re=O(2) bond length [1.698 Å] is almost the same as the experimental value [1.691(2) Å], while the experimental Re-O(1) value [1.940(2) Å] is 0.033 Å shorter than the calculated one. The largest differences in the bond angles are for O(1)-Re-O(2), where the experimental value is 3.68° greater than the calculated one, and for O(2)-Re-Br(1), where the experimental value is 3.52° smaller than the computed one.

Table 2. Experimental and optimized bond lengths [Å] and angles [°] for **1**.

	Exp	*Calc*
Re-O(2)	1.691(2)	1.698
Re-O(1)	1.940(2)	1.973
Re-Br(1)	2.5178(4)	2.560
Re-Br(2)	2.5646(3)	2.583
Re-N	2.090(3)	2.126
Re-P	2.471(1)	2.576
C(4)-O(1)	1.343(4)	1.325
N-C(2)	1.288(4)	1.297
C(2)-C(3)	1.470(4)	1.461
O(1)-Re-O(2)	167.3(1)	163.6
Br(2)-Re-O(2)	97.14(7)	98.96
Br(1)-Re-O(2)	100.01(8)	103.53
N-Re-O(2)	90.1(1)	86.63
P-Re-O(2)	87.09(7)	85.59
Br(1)-Re-Br(2)	88.94(1)	90.28
Br(2)-Re-P	175.75(2)	175.36
Br(1)-Re-N	169.10(7)	169.41
O(1)-Re-N	80.5(1)	79.41
Re-O(1)-C(4)	137.6(2)	139.8
Re-N-C(2)	135.1(2)	135.5
N-C(2)-C(3)	120.9(3)	121.8

The atomic charges were obtained from the Natural Population Analysis (NPA). The calculated charge on the rhenium atom [+1.443] is considerably lower than the formal charge of +5, which is the result of significant charge donation by the bromides, oxo and imino nitrogen donor atoms. The terminal oxo group O(2) [-0.563] is also less negative than the phenoxy O(1) [-0.698], indicating that O(2) is donating more electron density to the rhenium atom by virtue of its stronger π-donor ability, which is also reflected in these respective bond lengths.

The rhenium ion possesses the d^2 configuration. The HOMO in both isomers is of the d_{xz} type with antibonding contributions from the p_π bromide orbitals. The remaining four d orbitals of rhenium are found amongst the unoccupied molecular orbitals. The HOMO-LUMO gap for the *cis* isomer equals 2.77 eV, and it is 2.86 eV for the *trans* one. Although the energy of the

LUMO orbital is about the same in the two isomers (-2.53 eV for *cis*; -2.54 eV for *trans*), the energy of the HOMO is significantly different in the two isomers [-5.30 eV for *cis*; -5.40 eV for *trans*]. This smaller energy difference may favour the formation and stability of the *cis* isomer of **1**.

Supplementary data

CCDC-647645 contains the crystallographic data for this paper. 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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