Oxo and Oxofree Rhenium(V) Complexes with N,O-donor Schiff Bases

Irvin N. Booysen*, Muhammed Ismail†, Thomas I.A. Gerber‡, Matthew Akerman* and Benjamin Van Brecht#

*School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville, Pietermaritzburg, 3209, South Africa.
†Department of Chemistry, Nelson Mandela Metropolitan University, Port Elizabeth, 6031, South Africa.

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ABSTRACT

The reaction between cis-[ReO2(PPh3)4] and H2duo (N-(2-hydroxybenzimidazol-5-yl)methanol) led to the formation of the oxofree, imido compound, trans-[ReO2Hduo(PPh3)3]I (1) (H2ddd = 5,6-diamino-1,3-dimethyluracil). An oxo complex, cis-[ReO2Cl2(PPh3)2](2) [Hbcp = N-(2-hydroxybenzimidazol-2-yl)ethanesulphonamide] was isolated from the reaction of trans-[ReO2Cl2(PPh3)2] with Hbcp. The crystal structures of the compounds were determined by single crystal X-ray diffraction.

KEYWORDS

Rhenium(V), imido, oxo, crystal structure, spectral characterization.

The focus on the coordination chemistry of rhenium has been largely due to the potential application of the 186,188Re radionuclides in radiotherapy.1 Pivotal to the further advancement of rhenium radiotherapeutics is the coordination of biologically relevant ligand systems, which is essential for optimal biodistribution. For example, the 186Re radiolabelled Pittsburgh Compound B (PIB) has shown excellent diagnostic properties for amyloidal plaques of Alzheimer’s disease, and has led to an extensive search for novel Re-PIB analogues.2

Recently we reported the reaction of cis-[ReO2(PPh3)4] with H2ddd to afford the oxofree compound, cis-[ReOCl2(PPh3)2]I (1) (H2ddd = 5,6-diamino-1,3-dimethyluracil). The study was further extended to the derivatization of H2ddd to form the Schiff base N,N,N′,N′-tetraaminobenzimidazole-5-amino-1,3-dimethyl uracil (H2duo). The reaction of trans-[ReOCl2(PPh3)2] with H2duo in ethanol gave a mixed crystal structure which contains both the neutral oxorhenium(V) complex [ReOCl(Hduo)] and the imido rhenium(V) [Re(duo)Cl2(PPh3)] in an equimolar ratio in the asymmetric unit cell.4 The interest in the H2ddd ligand and derivatives arises from its antitumour activity and biological relevance with nucleotide bases.5

Herein, we communicate the coordination behaviour of the [ReO2]1+ core towards the Schiff base ligands, H2duo and Hbcp which afford the oxofree compound (1) and the oxo complex (2), respectively. The ligands, H2duo and Hbcp were synthesized by the condensation reactions of salicylaldehyde with H2ddd and 2-aminobenzothiazole, respectively (Scheme 1). These compounds were characterized via UV–Vis, IR, NMR spectroscopy, conductance, cyclic voltammetry and single crystal X-ray diffraction.

The oxofree ‘3+1’ complex cation, trans-[ReO2Hduo(PPh3)3]I was isolated as the iodide salt from a 1:2 molar ratio reaction between cis-[ReO2(PPh3)4] and H2duo. The ddd ligand is formed by hydrolysis. Reactions with the metal precursor cis-[ReO2(PPh3)4] have formed several cationic compounds with iodide as the counterion.6 For example, the rhenium(V) cationic salts [ReO(dien)(aa)]1+ with iodide as an anion, was isolated from diethylenetriamine (dien) and the respective amino acids glycine, alanine, valine (aa).7 An unusual dimeric compound, (µ-O)2[ReO2(btn)]I, was synthesized from (btn = bis(benzimidazole-2-ylethyl)sulphide) and cis-[ReO2I(PPh3)3].8 This dicationic compound exhibits an asymmetric (µ-O)2Re2 core and the two btn ligands act as neutral N,S chelators.5

The oxo complex, cis-[ReO2(bcp)OCl2(PPh3)2](2) was synthesized in good yield from the reaction of trans-[ReO2Cl2(PPh3)2] with Hbcp. The bcp ligand acts as a monoanionic bidentate moiety with coordination through the neutral imino nitrogen and the deprotonated phenolic oxygen. Although the complex can also be obtained from a 1:1 molar ratio, the best yield was obtained through a 1:3 molar ratio with respect to the rhenium precursor.

Both 1 and 2 are soluble in most polar solvents, except for 1 which is insoluble in chloroform. Compound 1 is a 1:1 electrolyte (Aion = 89 ohm−1 cm2 mol−1) in DMF whereas complex 2 was found to be a non-electrolyte in DMSO. The 1H NMR spectra showed shifts of the Schiff Base hydrogens for the respective compounds.

For 1, a downfield shift of the imine proton from δ10.05 ppm (in the free H2duo ligand) to δ9.44 ppm (in the complex) is observed. For 2, the Schiff base hydrogen, H5(5) resonates at δ8.42 ppm which is considerably lower than the free ligand, Hbcp (at δ10.66 ppm).

Scheme 1

Structures of the ligands.
The IR spectrum of 1 contains a weak absorption at 1090 cm$^{-1}$, which is within the region (1000–1200 cm$^{-1}$) expected for the ν(Re=O) bond. An intense ν(Re=O) stretching frequency is observed at 970 cm$^{-1}$ (for 2) which is within the literature region [890–1020 cm$^{-1}$] found for other oxorhenium(V) compounds. The ν(C=N) of 1 occurs at a lower frequency compared to that of the free ligand H$_{2}$dudo (at 1608 cm$^{-1}$). The C=N vibrational frequencies of the Schiff base (1585 cm$^{-1}$) and heterocyclic (1603 cm$^{-1}$) bonds of 2 appeared at lower frequencies compared to that of the Hbcpf free ligand (1608 cm$^{-1}$) for ν(C=N)$_{schiff}$base and 1661 cm$^{-1}$ for ν(C=N)$_{heterocyclic}$. The UV/Vis spectrum of 1 exhibits a single electronic transition at 391 nm due to the intra-ligand π→π$^{*}$ transition which is at a longer wavelength compared to 2 (at 340 nm). No d-d transitions were observed for both complexes. Redox properties were probed via cyclic voltammetry in dry DMF, using a glassy carbon electrode. The sweep to negative potentials showed irreversible redox processes at E$^{p}$ = –0.961 V (for 1) and E$^{c}$ = –0.703 V (for 2). The sweep to positive potentials exhibited a single electronic transition which is at a lower frequency compared to that of the Hbcpf free ligand (1608 cm$^{-1}$) for ν(C=N)$_{schiff}$base and 1661 cm$^{-1}$ for ν(C=N)$_{heterocyclic}$. The Re-O(1) = 85.6(1)$^\circ$ compared to the five-membered chelate ring [N(5)-Re-N(6) = 73.2(1)$^\circ$]. Although the complex displays a distorted octahedral geometry, no displacement of the rhenium atom was observed out of the N(1)N(6)N(5)O(1) equatorial plane. The uracil moiety of the ddu ligand forms a dihedral angle of 4.06$^\circ$ with the N(1)N(6)N(5)O(1) equatorial plane.

Within the ddu ligand, a dihedral angle of 11.27$^\circ$ is observed between the planes of the uracil moiety and phenyl moiety. The C(14)-N(5)-C(13) = 119.0(3)$^\circ$ bond angle is close to 120$^\circ$ which confirms that the nitrogen is sp$^2$ hybridized. This bond angle concurs with the bond length N(5)-C(13) = 1.318(6) Å which is within the expected range found for Schiff base bond lengths.

The Re-N(6) = 2.094(3) Å falls just outside the expected range of 2.001(3)–2.051(3) Å. The Re-O(1) = 1.72(1)–1.74(1) Å for a triply bonded nitrogen to the metal centre. The same phenomenon was observed for [Re(ddd)(Hddd)(PPh$_3$)$_2$] (ReO$_4$) where the ddd ligand coordinated in the same manner. A similar pyridylidimido bond angle [168.8(5)$^\circ$] and Re=N length [1.779(5) Å] was observed.

The rhenium amido bond length, Re-N(6) = 2.094(3) Å falls just outside the expected range of 1.91(1)–2.05(1) Å. The Re-O(1) = 2.001(3) Å and Re-N(5) = 2.185(3) Å bond lengths agree well with those found in literature for Re=O phenolates and Re=O$_{chelate}$ bonds. Interactions via π-π stacking occur through the ddu ligand function and the respective triphenylphosphine [P(1)Ph$_3$ and P(2)Ph$_3$] groups. A centroid to centroid distance of 3.829 Å is observed between the C(7)-C(12) phenyl plane of the ddu ligand and the plane of the phenyl ring C(20)–C(25) of the triphenylphosphine moiety P(1), with the distance between the C(7)–C(12) and C(38)–C(43) planes being longer at 4.222 Å. These different interactions may be accounted to the shorter bond length of Re-P(2) [2.461(1) Å] compared to Re-P(1) [2.506(1) Å].

**Figure 1** Molecular diagram and atom numbering scheme of trans-[Re(ddd)Hduo(PPh$_3$)$_2$]$. ^{+}$ Thermal ellipsoids are drawn at 40 % probability, the iodide counterion and hydrogen atoms have been omitted for clarity.
Cis-[Re\textsuperscript{V}(bcp)OCl\textsubscript{2}(PPh\textsubscript{3})] (2)

Complex 2 is monomeric, neutral and exhibits a distorted octahedral geometry with the equatorial plane defined by the Cl(1)Cl(2)PN atoms (see Fig. 2). This octahedral imperfection is largely due to the bite angle N-Re-O (2) [82.8(2)\degree], which induces a non-linear axial bond angle O(1)-Re-O(2) [165.80\degree]. However, largely due to the bite angle N-Re-O(2) [82.8(2)\degree], which induces a non-linear axial bond angle O(1)-Re-O(2) [165.80\degree].

The oxorhenium (V) complexes are stabilized by bond lengths of [1.68(1)–1.72(1) Å] found for this class of oxorhenium (V) complexes. The Re\textsuperscript{V}O\textsubscript{phenolates} [1.949(5) Å] and Re\textsuperscript{V}N\textsubscript{imines} [2.165(6) Å] bond lengths of 2 are comparable with those of compound 1. The similar compounds cis and trans-[ReO\textsubscript{X}(hpb)PPh\textsubscript{3}] (X = Cl, Br), (Hhp = 2-(2-hydroxyphenyl)-1H-benzimidazole) have comparative Re-O\textsubscript{phenolates} bond lengths.\textsuperscript{15} The oxorhenium(V) complex cis-[ReO\textsubscript{Br}(dhp)(PPh\textsubscript{3})] (Hdp = 2-(2-hydroxyphenyl)-1H-benzothiazole) has a Re-P [2.486(2) Å] bond length almost identical to 2 [Re-P = 2.481(2) Å].\textsuperscript{16} The different bond lengths for Re-Cl(1) [2.401(2) Å] and Re-Cl(2) [2.351(2) Å] bonds are ascribed to the stronger trans effect of the P atom. The complex is stabilized by \pi-\pi stacking between the C(16)-C(21) phenyl plane of the triphenylphosphine and the C(1)-C(6) phenyl plane of the bcp ligand. A centroid to centroid distance of 3.810 Å is observed between the two planes.

**Experimental**

**Synthesis of 1**

H\textsubscript{15}duo (0.063 g, 230 \mu mol) was added to a solution of cis-[Re\textsuperscript{IV}O\textsubscript{I}(PPh\textsubscript{3})\textsubscript{2}] (0.100 g, 115 \mu mol) in 20 cm\textsuperscript{3} acetonitrile and the mixture was heated for reflux for 1 h under a nitrogen atmosphere. Brown cubic crystals suitable for X-ray crystallographic analysis were grown from the mother liquor. Yield = 56 \% (0.088 g); m.p. > 350 \degree C; Conductivity (DMF, 10 \textsuperscript{-3} M) = 89.01 \text{cm}^{2}\text{ mol}^{-1} \text{ cm}^{-1}; IR (\nu_{\text{max}}/\text{cm}^{-1}): \nu(\text{N-H)} 3428, 3229 (w), \nu(C=O) 1679 (s), \nu(C=N) 1595 (s), \nu(\text{Re=O-N}) 1090 (w), \nu(P-C) 795 (vs); \textsuperscript{1}H NMR (d\textsubscript{6}-DMSO/ppm): 11.27 (s, 1H, N(6)-H), 10.23 (t, 2H, H2, H3), 9.81 (d, 2H, H1, H4), 9.44 (s, 1H, H5), 7.05–7.93 (m, 30H, 2xPPh\textsubscript{3}), 7.85 (s, 2H, N(4)-H), 3.49 (s, 6H, C(16)H\textsubscript{3}, C(18)H\textsubscript{3}), 3.01 (s, 6H, C(3)H\textsubscript{3}, C(5)H\textsubscript{3}); UV-Vis (DMF, \lambda_{\text{max}} (\varepsilon, M\textsuperscript{-1} cm\textsuperscript{-1}): 391 nm (4880).

**Synthesis of 2**

A mixture of Hbcp (0.137 g; 540 \mu mol) and trans-[ReO\textsubscript{Cl}(PPh\textsubscript{3})\textsubscript{2}] (0.150 g; 180 \mu mol) in acetonitrile (20 cm\textsuperscript{3}) was heated under reflux for three hours. The resultant dark green solution was allowed to cool to room temperature. Slow evaporation of the filtered solution yielded green, needle-like crystals. Yield = 56 \% (0.088 g); m.p. > 350 °C; Conductivity (DMF, 10 \textsuperscript{-3} M) = 16.54 ohm \textsuperscript{-1} cm\textsuperscript{2} mol\textsuperscript{-1}; IR (\nu_{\text{max}}/\text{cm}^{-1}): \nu(N-H) 3068 (w), \nu(C=N)\textsubscript{phenolate} 1603 (m), \nu(C=N)\textsubscript{imino} 1585 (m), \nu(\text{Re=O}) 970 (s), \nu(P-C) 747 (vs); \textsuperscript{1}H NMR (d\textsubscript{6}-DMSO/ppm): 8.42 (s, 1H, H5), 8.04 (t, 1H, H8), 7.40–7.71 (m, 15H, PPh\textsubscript{3}), 7.21 (d, 1H, H7), 6.90–7.06 (m, 5H, H1, H2, H3, H4, H6); UV-Vis (DMF, \lambda_{\text{max}} (\varepsilon, M\textsuperscript{-1} cm\textsuperscript{-1}): 340 nm (1720).

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**Supplementary Materials**

CCDC-885630 and 885631 contains crystallographic data for this article. 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]. Geometrical parameters, crystal and structure refinement data for both compounds can be obtained in the supplementary material.

**References**


