

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

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ABSTRACT

The reaction between *cis*-[Re^VO₂I(PPh₃)₂] and H₃duo (*N*-(2-hydroxybenzylidene)-5-amino-1,3-dimethyl uracil) led to the formation of the oxofree, imido compound, *trans*-[Re^V(ddd)(Hduo)(PPh₃)₂]I (1) (H₂ddd = 5,6-diamino-1,3-dimethyluracil). An oxo complex, *cis*-[Re^V(bcp)OCl₂(PPh₃)₂](2) [Hbcp = *N*-(2-hydroxybenzylidene)-benzothiazole] was isolated from the reaction of *trans*-[ReO^VCl₃(PPh₃)₂] with Hbcp. The crystal structures of the compounds were determined by single crystal X-ray diffraction.

KEYWORDS

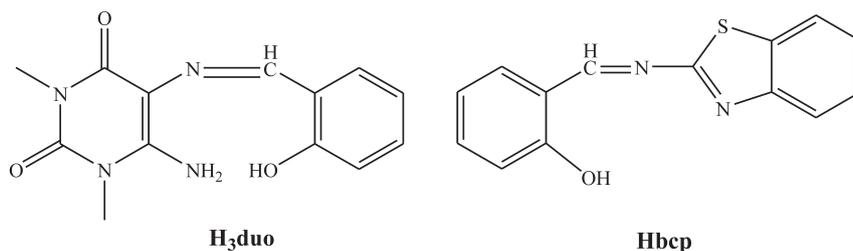
Rhenium(V), imido, oxo, crystal structure, spectral characterization.

The focus on the coordination chemistry of rhenium has been largely due to the potential application of the ^{186/188}Re radionuclides in radiotherapy.¹ Pivotal to the further advancement of rhenium radiopharmaceuticals is the coordination of biologically relevant ligand systems, which is essential for optimal biodistribution. For example, the ¹¹C radiolabelled Pittsburgh Compound B (PIB) has shown excellent diagnostic properties for amyloid 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*-[ReO₂I(PPh₃)₂] with H₂ddd to afford the product [Re(ddd)(Hddd)I(PPh₃)₂](ReO₄).³ The study was further extended to the derivatization of H₂ddd to form the Schiff base *N*-(2-aminobenzylidene)-5-amino-1,3-dimethyl uracil (H₃dua). The reaction of *trans*-[ReOCl₃(PPh₃)₂] with H₃dua in ethanol gave a mixed crystal structure which contains both the neutral oxorhenium(V) complex [ReOCl(Hdua)] and the imido rhenium(V) [Re(dua)Cl₂(PPh₃)₂] 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 [Re^{VO}]³⁺ core towards the Schiff base ligands, H₃duo and Hbcp which afford the oxofree compound (1) and the oxo complex (2), respectively. The ligands, H₃duo 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.

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Scheme 1
Structures of the ligands.

The oxofree '3+1' complex cation, *trans*-[Re^V(ddd)(Hduo)(PPh₃)₂]⁺ was isolated as the iodide salt from a 1:2 molar ratio reaction between *cis*-[Re^{VO}₂I(PPh₃)₂] and H₃duo. The ddd ligand is formed by hydrolysis. Reactions with the metal precursor *cis*-[ReO₂I(PPh₃)₂] have formed several cationic compounds with iodide as the counterion.⁶ For example, the rhenium(V) cationic salts [ReO(dien)(aa)]⁺ 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[Re₂O₂(btn)₂]I₂ was synthesized from (btn = bis(benzimidazole-2-ylethyl)sulfide) and *cis*-[ReO₂I(PPh₃)₂]. This dicationic compound exhibits an asymmetric (μ-O)₂Re₂ core and the two btn ligands act as neutral N₂S chelators.⁸

The oxo complex, *cis*-[Re^V(bcp)OCl₂(PPh₃)₂](2) was synthesized in good yield from the reaction of *trans*-[ReO^VCl₃(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 (Λ_m = 89 ohm⁻¹ cm² mol⁻¹) in DMF whereas complex 2 was found to be a non-electrolyte in DMF. 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 H₃duo ligand) to δ9.44 ppm (in the complex) is observed. For 2, the Schiff base hydrogen, H(5) resonates at δ8.42 ppm which is considerably lower than the free ligand, Hbcp (at δ10.66 ppm).

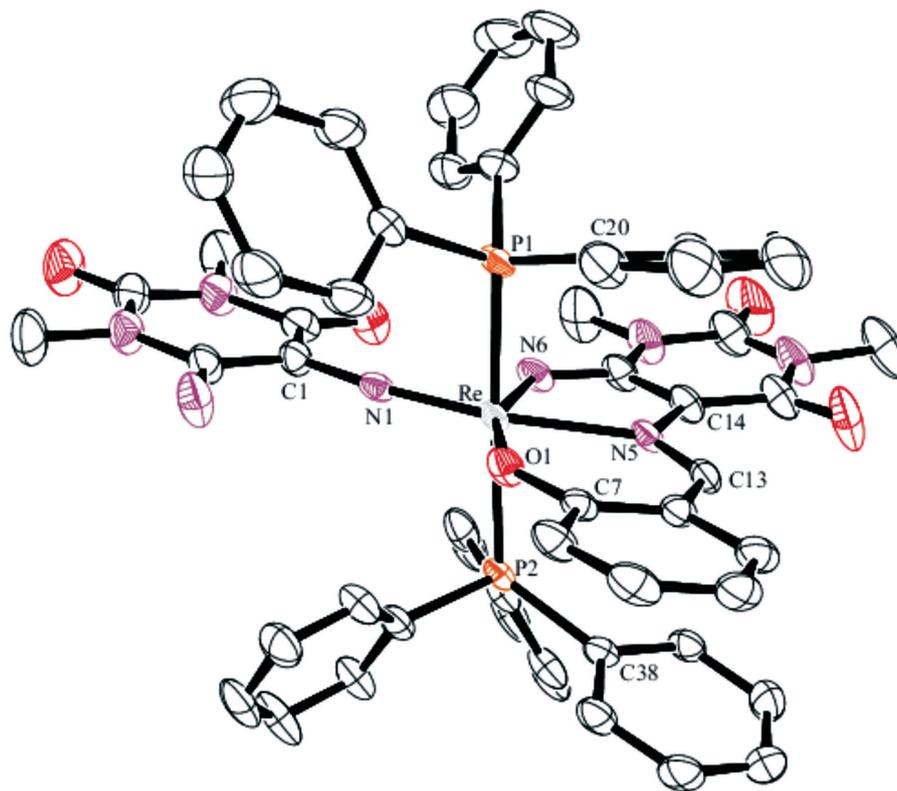


Figure 1 Molecular diagram and atom numbering scheme of *trans*-[Re(ddd)Hduo(PPh₃)₂]⁺. Thermal ellipsoids are drawn at 40 % probability, the iodide counterion and hydrogen atoms have been omitted for clarity.

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 $\nu(\text{Re}\equiv\text{N})$.⁹ An intense $\nu(\text{Re}=\text{O})$ 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.¹⁰ The $\nu(\text{C}=\text{N})$ of **1** occurs at a lower frequency compared to that of the free ligand H₃duo (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 $\nu(\text{C}=\text{N})_{\text{Schiff base}}$ and 1661 cm⁻¹ for $\nu(\text{C}=\text{N})_{\text{heterocyclic}}$).

The UV/Vis spectrum of **1** exhibits a single electronic transition at 391 nm due to the intra-ligand $\pi\rightarrow\pi^*$ 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 $E_p = -0.703$ (for **2**) *vs.* Ag|AgCl, which are due to the one electron reduction for the Re(IV)/Re(V) redox couple. Both redox processes exhibit diffusion controlled behaviour at various scan rates and have comparable oxidation potentials with other Re(V) compounds.¹¹

Trans-[Re(ddd)(Hduo)(PPh₃)₂]I (**1**)

The rhenium atom is at the centre of a distorted octahedron with the bond angles P(1)-Re-P(2) [169.45(4)°], N(1)-Re-N(5) [163.6(1)°] and N(6)-Re-O(1) [158.8(1)°] deviating substantially from linearity (see Fig. 1). Subsequently, the P(1)-Re-N(1) [85.6(1)°], P(1)-Re-N(5) [98.95(9)°], P(1)-Re-N(6) [102.94(9)°] and P(1)-Re-O(1) [78.61(9)°] bond angles emphasize the deviation from orthogonality. These deviations are ascribed to the constraints imposed by the coordinated tridentate Hduo ligand which affords a larger bite angle for the six-membered chelate ring [N(5)-Re-O(1) = 85.6(1)°] compared to the five membered

chelate ring [N(5)-Re-N(6) = 73.2(1)°]. 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 ddd ligand forms a dihedral angle of 4.06° with the N(1)N(6)N(5)O(1) equatorial plane.

Within the Hduo ligand, a dihedral angle of 11.27° is observed between the planes of the uracil moiety and phenyl moiety. The C(14)-N(5)-C(13) = 119.0(3)° bond angle is close to 120° which confirms that the nitrogen is sp² 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.¹² The linear pyridylimido core [Re-N(1)-C(1)] affords a bond angle of 168.6(3)° which deviates considerably from linearity. Indicative to the bond angle, the Re-N(1) has a bond length of 1.766(3) Å which is unexpected since it falls outside the range [1.72(1)–1.74(1) Å] for a triply bonded nitrogen to the metal centre.¹³ The same phenomenon was observed for [Re(ddd)(Hddd)I(PPh₃)₂](ReO₄) where the ddd ligand coordinated in the same manner. A similar pyridylimido bond angle [168.8(5)] and Re≡N length [1.779(5) Å] was observed.³

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.^{4,13} 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^V-O_{phenolate} and Re^V-N_{imino} bonds.¹⁴ Interactions *via* $\pi\text{-}\pi$ stacking occur through the Hduo phenyl group and the respective triphenylphosphine [P(1)Ph₃ and P(2)Ph₃] groups. A centroid to centroid distance of 3.829 Å is observed between the C(7)-C(12) phenyl plane of the Hduo 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].

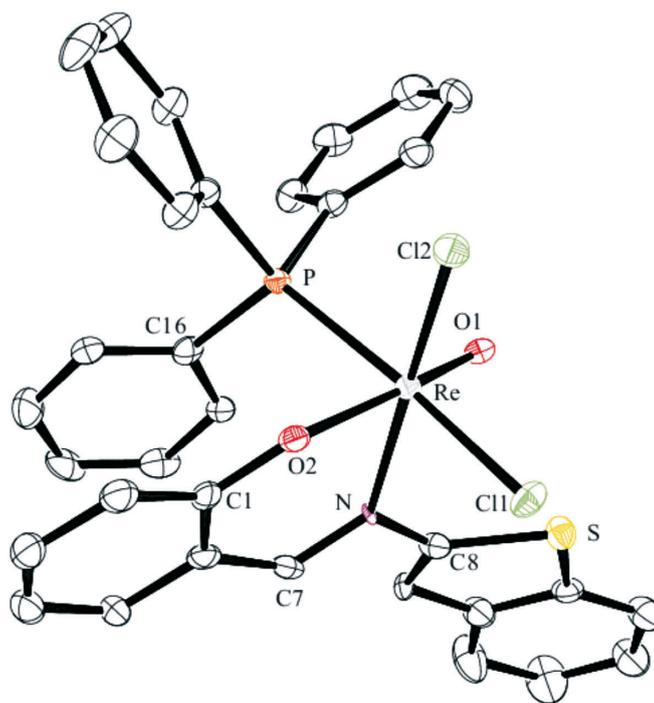


Figure 2 Molecular diagram and atom numbering scheme of *cis*-[Re(bcp)OCl₂(PPh₃)]. Thermal ellipsoids are drawn at 40 % probability and hydrogen atoms have been omitted for clarity.

Cis-[Re^V(bcp)OCl₂(PPh₃)] (**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)°], which induces a non-linear axial bond angle O(1)-Re-O(2) [165.80°]. However the Cl(1)-Re-Cl(2) = 88.14(7)°, P-Re-N = 94.14(2)°, P-Re-Cl(2) = 90.03(7)° and Cl(1)-Re-N = 87.1(2)° bond angles are relatively close to orthogonality.

The Re=O(1) bond length of 1.688(5) Å is within the range [1.68(1)–1.72(1) Å] found for this class of oxorhenium (V) complexes.¹⁵ The Re^V-O_{phenolate} [1.949(5) Å] and Re^V-N_{imino} [2.165(6) Å] bond lengths of **2** are comparable with those of compound **1**. The similar compounds *cis* and *trans*-[ReOX₂(hpb)PPh₃]₂ (X = Cl, Br), (Hhpb = 2-(2-hydroxyphenyl)-1H-benzimidazole) have comparative Re-O_{phenolate} bond lengths.¹⁶ The oxorhenium(V) complex *cis*-[ReOBr₂(dhp)(PPh₃)] (Hdhp = 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].¹⁷ 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 π - π 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**

H₃duo (0.063 g, 230 μ mol) was added to a solution of *cis*-[ReVO₂I(PPh₃)₂] (0.100 g, 115 μ mol) in 20 cm³ acetonitrile and the mixture was heated at 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 °C; Conductivity (DMF, 10⁻³ M) = 89.01 ohm⁻¹ cm² mol⁻¹; IR (ν_{\max} /cm⁻¹): ν (N-H) 3428, 3229 (w), ν (C=O) 1679 (s), ν (C=N) 1595 (s), ν (Re=N) 1090 (w), ν (P-C) 795

(vs); ¹H NMR (*d*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, 2*x*PPh₃), 7.85 (s, 2H, N(4)-H₂), 3.49 (s, 6H, C(16)H₃, C(18)H₃), 3.01 (s, 6H, C(3)H₃, C(5)H₃); UV-Vis (DMF, λ_{\max} (ϵ , M⁻¹ cm⁻¹)): 391 nm (4880).

Synthesis of **2**

A mixture of Hbcp (0.137 g; 540 μ mol) and *trans*-[ReOCl₃(PPh₃)₂] (0.150 g; 180 μ mol) in acetonitrile (20 cm³) 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 = 84 % (0.2480 g); m.p. 243–248 °C; Conductivity (DMF, 10⁻³ M) = 16.54 ohm⁻¹ cm² mol⁻¹; IR (ν_{\max} /cm⁻¹): ν (N-H) 3068 (w), ν (C=N)_{Schiff base} 1603 (m), ν (C=N)_{heterocyclic} 1585 (m), ν (Re=O) 970 (s), ν (P-C) 747 (vs); ¹H NMR (*d*⁶-DMSO/ppm): 8.42 (s, 1H, H5), 8.04 (t, 1H, H8), 7.40–7.71 (m, 15H, PPh₃), 7.36 (t, 1H, H5), 7.21 (d, 1H, H7), 6.90–7.06 (m, 5H, H1, H2, H3, H4, H6); UV-Vis (DMF, λ_{\max} (ϵ , M⁻¹ cm⁻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.

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