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The syntheses and structures of ‘3+2’ and ‘2+2+1’ oxorhenium mixed-ligand complexes employing 8-hydroxy-5-nitroquinoline as the bidentate N,O donor ligand

Xiaoyuan Chen^a, Frank J. Femia^a, John W. Babich^b, and Jon Zubieta^{a,*}

^a Department of Chemistry Syracuse University, Syracuse, NY 13244, USA

^b Biostream Inc., 160 Second Street Cambridge, MA 02142, USA

Abstract

The syntheses and structural characterizations of a series of novel ‘3+2’ and ‘2+2+1’ mixed-ligand complexes carrying 8-hydroxy-5-nitroquinoline (HL) as the bidentate N,O donor atom system are reported. Thus one-pot reactions of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with dianionic tridentate ligands H_2L^n (where $\text{H}_2\text{L}^1 = \text{HOC}_6\text{H}_4\text{-2-CH=NC}_6\text{H}_4\text{-2-OH}$; $\text{H}_2\text{L}^2 = \text{HOC}_6\text{H}_4\text{-2-CH=N-C}_6\text{H}_4\text{-2-SH}$; $\text{H}_2\text{L}^3 = \text{HOC}_6\text{H}_4\text{-2-CH=NN=C(NHC}_6\text{H}_5\text{)-SH}$; $\text{H}_2\text{L}^4 = 2\text{-CH}_2\text{OH-C}_5\text{H}_3\text{N-6-CH}_2\text{SH}$; and $\text{H}_2\text{L}^5 = 2\text{-CO}_2\text{H-C}_5\text{H}_3\text{N-6-CO}_2\text{H}$) and HL afforded a series of ‘3+2’ oxorhenium complexes of the type $[\text{ReO}(\text{H}_2\text{L}^n)(\text{L})]$ **2–6**, which exhibit distorted octahedral geometries. Crystals of **1** are monoclinic space group $C2/c$, $a=16.702(1)$, $b=14.275(1)$, $c=22.363(2)$ Å, $\beta=108.083(1)^\circ$, $V=5068.2(7)$ Å³ and $Z=8$; those of **2** are monoclinic space group $P2_1/n$, $a=8.5093(4)$, $b=38.518(2)$, $c=11.6092(5)$ Å, $\beta=97.708(1)^\circ$, $V=3770.7(3)$ Å³ and $Z=8$; those of **5** are triclinic, space group $P\bar{1}$, $a=7.5899(8)$, $b=10.322(1)$, $c=11.905(1)$ Å, $\alpha=78.636(2)^\circ$, $\beta=74.229(2)^\circ$, $\gamma=71.391(2)^\circ$, $V=844.3(2)$ Å³, and $Z=2$. Upon reaction of 2,6-pyridinedimethanol (H_2L^6) with the intermediate complex $[\text{ReOCl}_2(\text{L})(\text{PPh}_3)]$ (**1**), only one of the two methylene hydroxy group was deprotonated and a new ‘2+2+1’ complex $[\text{ReO}(\text{OCH}_3)(\text{HL}^6)(\text{L})]\cdot\text{CH}_3\text{OH}$ (**7**) was obtained. Crystal data for **7**: monoclinic $P2_1/n$, $a=12.0579(6)$, $b=11.0993(6)$, $c=14.9262(8)$ Å, $\beta=107.872(1)^\circ$, $V=1901.2(2)$ Å³, and $Z=8$. In the preparation of complex **3**, cleavage of the C=N bond of the Schiff base H_2L^2 was observed and the ‘2+2+1’ complex **8** $[\text{ReO}(\text{PPh}_3)(\eta^2\text{-NHC}_6\text{H}_4\text{-2-S})(\text{L})]\cdot\text{CH}_2\text{Cl}_2$ having 2-aminothiophenol as a dianionic bidentate ligand was isolated. Crystals of **8** are monoclinic space group $C2/c$, $a=25.627(2)$, $b=8.1305(6)$, $c=31.404(2)$ Å, $\beta=96.147(1)^\circ$, $V=6505.7(8)$ Å³, and $Z=8$. Reduction of HL to 8-hydroxy-5-aminoquinoline was realized during the formation of complex **6**, and a new complex **9** was thus isolated involving the coordination of two sets of N,O donor atoms from L and 8-hydroxy-5-aminoquinoline while a methoxy oxygen atom completes the octahedral coordination geometry. Crystals of **9** are monoclinic space group $P2_1/n$, $a=7.5330(6)$, $b=15.095(1)$, $c=16.394(1)$ Å, $\beta=99.690(2)^\circ$, $V=1837.7(3)$ Å³, and $Z=4$.

Keywords

Crystal structures; Rhenium complexes; Oxo complexes; N,O donor ligand complexes

1. Introduction

Medicinal inorganic chemistry is a rapidly developing field and it offers new possibilities in pharmaceutical industries which have been traditionally dominated by organic chemistry alone [1-3]. For example the peculiar magnetic properties of trivalent rare earth metal ions such as Gd^{3+} have been widely used as contrast agents (CA) in conjunction with magnetic resonance imaging (MRI) [4-6]; the use of luminescent Eu(III) and Tb(III) complexes has been developed in time resolved luminescent bioassays to replace radioimmunoassay [7,8]. Parallel to the active development of non-radioactive metal chelates for biomedical applications there is a massive worldwide research effort into developing radiopharmaceuticals — drugs containing a radionuclide — for the diagnosis and treatment of diseases [9-11].

Among the γ -emitting radionuclides, such as ^{51}Co , ^{51}Cr , ^{64}Cu , ^{67}Ga , ^{99m}Tc , ^{111}In , ^{117m}Sn , ^{169}Yb and ^{201}Tl [12], which are useful for diagnostic nuclear medicine, ^{99m}Tc -labeled radiopharmaceuticals have become the mainstay [13-17] by virtue of the optimal nuclear properties ($E_{max}=140$ KeV; $t_{1/2}=6.02$ h) and easy availability from ^{99}Mo – ^{99m}Tc generator. The radionuclides of rhenium, the Group VII cogener of Tc, are β -emitters whose properties make them suitable candidates for therapeutic applications (^{186}Re : $\beta_{max}=1.07$ MeV $t_{1/2}=90$ h; ^{188}Re : $\beta_{max}=2.12$ MeV, $t_{1/2}=17$ h) [10,18]. One successful strategy to the development of diagnostic imaging agents of Tc and potential therapeutic reagents based upon Re has exploited ligands to stabilize the oxometal $[MO]^{3+}$ core (where M=Tc and Re). A major class of technetium and rhenium complexes involve $N_xS_{(4-x)}$ tetradentate ligands and the oxometal core with square pyramidal geometry. These tetradentates include N_4 propylene amine oxime (PnAO) [19] N_3S triaminomonothiol [20], N_2S_2 diamidodithiols (DADS) [21] monoamidomonodithiols (MAMA) [22] and diaminodithiols (DADT) [23]. However, the inevitable formation of multiple isomers differing in their pharmacokinetic properties has hindered the widespread application of these systems [24,25].

One way to avoid the existence of syn/anti stereoisomers that are often produced in the tetradentate oxorhenium and technetium complexes is to incorporate the oxometal core into an integrated '3+1' system, in which the neutral complexes with the $[MO]^{3+}$ core exhibit a mixed ligand set of a dianionic tridentate ligand carrying at least one sulfur donor group such as [SSS], [SOS], [SN(R)S], [SNN(R)], or [ONS] donor atoms (where R=various alkyl or aryl-substitute pendant groups) and a monodentate thiolate [26,27]. The advantage of this integrated system concept in the development of technetium and rhenium essential radiopharmaceuticals lies in the fact that extensive substituent modifications can be introduced at either the tridentate or the monodentate ligand or even at both sites [28,29]. The geometry of these five-coordinate complexes varies between square-pyramidal and trigonal bipyramidal: geometries highly dependent on small structural variations in the tridentate ligand and which can be quantitatively evaluated by trigonality index, τ , as defined by Addison et al. [30]. However, these '3+1' complexes are found to be relatively unstable in vitro and in vivo due to the metabolism and substitution of the labile monothiolate RS^- group through transchelation by physiological thiols such as cysteine and glutathione [31,32]. This metabolism leads to accumulation of the decomposed complexes in thiolate-rich organs such as the liver instead of localization in organs of interest. According to a simple valence electron count rule [33], '3+1' complexes usually take a maximum electron count (MEC) of 16, deficient from the ideal value of 18 [34]. The '3+1' complexes tend to further coordinate the incoming monodentate ligand with the donor group *trans* to the $Re=O$ core, or to replace the labile monothiol with competing bidentate ligands to satisfy a closed shell electron configuration. However, the observation that '3+1+1' complexes do not form from '3+1' species is attributed to the fact that thiol ligands are very unlikely to be added *trans* to the $M=O$ core. One of the very few examples exhibiting a thiolate

group *trans* to Re=O core is a '2+2+1' system [ReO(PPh₃)(η²-HOC₆H₄-2-CH₂NC₆H₄-2-S)(η²-SC₅H₄)] [35].

By replacing the monothiolate ligand with a bidentate N,O donor set such as 8-hydroxy-5-nitroquinoline, we were able to achieve a series of '3+2' six-coordinate oxorhenium complexes of the general formulation [ReO(Lⁿ)(L)] (where HL=8-OH-5-NO₂-C₉H₅N; H²L¹=HOC₆H₄-2-CH=NC₆H₄-2-OH (**2**); H²L²=HOC₆H₄-2-CH=N-C₆H₄-2-SH (**3**); H²L³=HOC₆H₄-2-CH=NN=C(NHC₆H₅)-SH (**4**); H²L⁴=2-CH₂OH-C₅H₃N-6-CH₂SH (**5**); H²L⁵=2-CO₂H-C₅H₃N-6-CO₂H (**6**)) (Scheme 1) by one-pot synthesis utilizing [ReOCl₃(PPh₃)₂] as the oxorhenium starting material. In contrast, under the same reaction condition, a '2+ 2+1' complex [ReO(HL⁶)(L)(OCH₃)] (**7**) rather than the '3+2' complex was obtained when a potentially tridentate ligand 2,6-pyridinedimethanol (H₂L⁶) was employed. In the case of H₂L², decomposition of the [ONS] Schiff base resulted in a new '2+2+1' complex [ReO(PPh₃)(η²-NHC₆H₄-2-S)(L)] (**8**) as side product which could be isolated from **3** through column separation. Furthermore, we also observed the reduction of HL to 8-hydroxy-5-aminoquinoline in attempts to synthesize the '3+2' complex **6**. A new '2+2+1' complex [ReO(OCH₃)(η²-8-O-5-NH₂-C₉H₅N)(L)] (**9**) involving the coordination of NO donors from both L and 8-hydroxy-5-aminoquinoline was isolated.

2. Experimental

2.1. General

All chemicals were of reagent grade and were used as such without further purification. All reactions were performed under a nitrogen atmosphere. Synthesis and purification of H₂L¹, HOC₆H₄-2-CH=NC₆H₄-2-OH [36], H₂L², HOC₆H₄-2-CH=N-C₆H₄-2-SH [37], H₂L³, HOC₆H₄-2-CH=NN=C(NHC₆H₅)-SH [38], 2-CH₂OH-C₅H₃N-6-CH₂SH [35] were performed according to published methods with minor modifications. Rhenium was purchased from Aldrich as NH₄ReO₄ and was converted to [ReOCl₃(PPh₃)₂] as described previously [39]. Chloroform and methylene chloride were distilled from CaH₂ prior to use. Triethylamine was dried by distillation from CaH₂ and stored over KOH pellets. Methanol was distilled from Mg/I₂ and stored over 3 Å molecular sieves. Reaction progress and flash chromatography were monitored by analytical thin-layer chromatography (TLC). Silica gel used in flash chromatography was 70–230 mesh. TLC was conducted on 0.25 mm silica gel aluminum-backed plates, and visualization of TLC plates was realized by using short-wave UV light (254 nm). IR spectra were recorded as KBr pellets with a Perkin–Elmer Series 1600 FT-IR spectrometer in the region of 500–4000 cm⁻¹ with polystyrene as reference. Elemental analyses for carbon, hydrogen and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. ¹H NMR spectra were recorded on a Bruker DPX 300 (¹H 300.10 MHz) spectrometer in CDCl₃ (δ 7.27 ppm).

2.2. Synthesis of [ReOCl₂(L)(PPh₃)], intermediate complex **1** (where HL=8-HO-5-NO₂-C₉H₅N)

To a refluxing solution of [ReOCl₃(PPh₃)₂] (100 mg, 0.12 mmol) in ethanol (50 ml) was added with stirring 8-hydroxy-5-nitroquinoline (HL) (23 mg, 0.12 mmol) in ethanol (10 ml). The olive green reaction mixture was refluxed for 1 h, while the color changed gradually to emerald green. The reaction mixture was left to cool down to ambient temperature and the emerald green solid was collected (68 mg, 78%) and was washed with ethanol (2×5 ml). X-ray quality crystals of **1** were grown by solution diffusion of pentane into a methylene chloride solution of the compound. *Anal.* Calc. (found) for C₂₇H₂₀Cl₂N₂O₄Pre: C, 44.76 (44.63); H, 2.78 (2.82); N, 3.87 (3.75)%. IR (KBr, n/cm⁻¹): 1505, 1306, 976 (Re=O str), 756. ¹H NMR (CDCl₃, ppm): 9.02 (dd, J₁=8.7 Hz, J₂=1.2 Hz, H₂), 8.4–8.5 (m, H₃ and H₅), 7.73 (dd, J₁=9.0 Hz, J₂=5.1 Hz, H₄), 7.22–7.42 (m, 15H, PPh₃), 6.64 (d, J=9.0 Hz, H₁).

2.3. General procedure for the synthesis of the '3+2' complexes [ReO(Lⁿ)(L)]

To a refluxing solution of [ReOCl₃(PPh₃)₂] (83 mg, 0.1 mmol) in CHCl₃ (30 ml) was added HL (19 mg, 0.1 mmol) and 1 equiv. of dianionic tridentate ligand H₂Lⁿ. Upon addition of three drops of triethylamine (31 mg, 0.3 mmol), the reaction mixture changed from olive green to emerald green to red and then to dark brown immediately. The reaction mixture was refluxed for further 15 min. After cooling to room temperature, the reaction mixture was washed with water. The organic layer was separated from the mixture and dried over Na₂SO₄. The volume was reduced to 3 ml and then purified on silica gel column using gradient eluent (from 100% CHCl₃ to 90:10 CHCl₃/acetone).

2.3.1. [ReO(η³-OC₆H₄-2-CH=NC₆H₄-2-O)-(η²-8-O-5-NO₂-C₉H₅N)], [ReO(L¹)(L)] (2)

—Yield: 87%. *R*_f=0.82 (SiO₂, 90:10 CHCl₃/acetone). Slow evaporation of ether into complex **2** in minimum amount of CH₂Cl₂ afforded red plates suitable for X-ray analysis. *Anal.* Calc. (found) for C₂₂H₁₄N₃O₆Re: C, 43.81 (43.98); H, 2.32 (2.19); N, 6.97 (6.88)%. IR (KBr, ν/cm⁻¹): 1612, 1586, 1442, 1422, 1387, 1352, 1007, 962 (Re=O str), 939. ¹H NMR (CDCl₃, ppm): 9.14 (d, *J*=9.0 Hz, H₂), 8.99 (s, 1H, CH=N), 8.70 (d, *J*=9.0 Hz, H₃), 8.63 (d, *J*=5.1 Hz, H₅), 7.91 (dd, *J*₁=9.0 Hz, *J*₂=5.1 Hz, H₄), 7.8–6.8 (m, 9H, ArH), 6.67 (d, *J*=9.0 Hz, H₁).

2.3.2. [ReO(η³-OC₆H₄-2-CH=NC₆H₄-2-S)(η²-8-O-5-NO₂-C₉H₅N)], [ReO(L²)(L)] (3)

—Yield: 55%. *R*_f=0.43 (SiO₂, CHCl₃). *Anal.* Calc. (found) for C₂₂H₁₄N₃O₅ReS: C, 42.72 (42.54); H, 2.23 (2.31); N, 6.80 (6.73)%. IR (KBr, ν/cm⁻¹): 968 (Re=O str). ¹H NMR (CDCl₃, ppm): 9.42 (dd, *J*₁=8.7 Hz, *J*₂=1.5 Hz, H₂), 9.22 (s, 1H, CH=N), 8.75 (dd, *J*₁=5.1 Hz, *J*₂=1.2 Hz, H₃), 8.68 (d, *J*=8.7 Hz, H₅), 7.91 (dd, *J*₁=9.0 Hz, *J*₂=5.1 Hz, H₄), 7.7–6.7 (m, 9H, ArH), 6.65 (d, *J*=9.3 Hz, H₁).

2.3.3. [ReO(η³-OC₆H₄-2-CH=N=N=C(NHPh)-S)(η²-8-O-5-NO₂-C₉H₅N)], [ReO(L³)(L)] (4)

—Yield: 89%. *R*_f=0.91 (SiO₂, 90:10 CHCl₃/acetone). *Anal.* Calc. (found) for C₂₃H₁₆N₅O₅ReS: C, 41.82 (42.01); H, 2.42 (2.49); N, 10.61 (10.74)%. IR (KBr, ν/cm⁻¹): 1603, 1578, 1534, 1504, 1463, 1439, 1384, 1295, 1194, 1150, 1103, 1009, 975 (Re=O, str). ¹H NMR (CDCl₃, ppm): 9.49 (d, *J*=9.0 Hz, H₂), 9.22 (s, 1H, CH=N), 8.90 (d, *J*=4.8 Hz, H₃), 8.69 (d, *J*=9.0 Hz, H₅), 7.91 (dd, *J*₁=9.0 Hz, *J*₂=5.1 Hz, H₄), 7.7–6.7 (m, 9H, ArH), 6.70 (d, *J*=9.0 Hz, H₁), 5.12 (s br, 1H, -NHPh).

2.3.4. [ReO(η³-OCH₂C₅H₃NCH₂S)(η²-8-5-NO₂-C₉H₅N)], [ReO(L⁴)(L)] (5)

—Yield: 78%. *R*_f=0.85 (SiO₂, 90:10 CHCl₃/acetone). *Anal.* Calc. (found) for C₁₆H₁₂N₃O₅ReS: C, 35.26 (35.04); H, 2.20 (2.11); N, 7.71 (7.73)%. IR (KBr, ν/cm⁻¹): 1597, 1560, 1508, 1290, 1192, 1032, 957 (Re=O, str). ¹H NMR (CDCl₃, ppm): 9.23 (d, *J*=8.7 Hz, H₂), 8.65 (d, *J*=8.7 Hz, H₃), 8.57 (d, *J*=4.8 Hz, H₅), 8.15 (t, *J*=8.1 Hz, 1H, pyH), 7.97 (d, *J*=7.8 Hz, pyH), 7.75 (dd, *J*₁=8.7 Hz, *J*₂=5.1 Hz, H₄), 7.53 (d, *J*=7.2 Hz, pyH), 6.60 (d, *J*=9.3 Hz, H₁), 6.24 (d, *J*=18.9 Hz, 1H, -OCH₂ ax), 6.11 (d, *J*=18.9 Hz, 1H, -SCH₂ ax), 5.79 (d, *J*=18.3 Hz, 1H, -OCH₂ eq), 4.81 (d, *J*=18.3 Hz, 1H, -SCH₂ eq).

2.3.5. [ReO(η³-O₂CC₅H₃NCO₂)(η²-8-5-NO₂-C₉H₅N)], [ReO(L⁵)(L)] (6)

—Yield: 48%. *R*_f=0.95 (SiO₂, 80:20 CHCl₃/acetone). *Anal.* Calc. (found) for C₁₆H₈N₃O₈Re: C, 34.53 (34.61); H, 1.44 (1.37); N, 7.55 (7.48)%. IR (KBr, ν/cm⁻¹): 1600, 1561, 1505, 1453, 1416, 1297, 1190, 1138, 1113, 1034, 958 (Re=O, str), 819, 751. ¹H NMR (CDCl₃, ppm): 9.62 (d, *J*=8.7 Hz, H₂), 9.04 (d, *J*=9.0 Hz, H₃), 8.76 (d, *J*=5.1 Hz, H₅), 7.8–7.4 (m, 3H, pyH), 7.90 (dd, *J*₁=9.0 Hz, *J*₂=5.1 Hz, H₄), 6.45 (d, *J*=9.0 Hz, H₁).

2.3.6. Synthesis of [ReO(OCH₃)(η²-OCH₂C₅H₃-NCH₂OH)(η²-8-O-5-NO₂-C₉H₅N)]·CH₃OH, [ReO(OCH₃)(HL⁶)(L)]·CH₃OH (7)

—To a refluxing solution of [ReOCl₂(L)]

(PPh₃)] (**1**) (37 mg, 0.05 mmol) in 1:1 CHCl₃/CH₃OH (30 ml) was added 2,6-pyridinedimethanol (8 mg, 0.06 mmol) with stirring. Five drops of triethylamine were then added and the solution was refluxed for additional 40 min, after which the color of the reaction mixture turned from emerald green to bloody red. The product was purified as mentioned above. Yield: 73%. $R_f=0.77$ (SiO₂, 90:10 CHCl₃/acetone). X-ray quality crystals were obtained by slow evaporation from a CH₂Cl₂/CH₃OH mixture. *Anal.* Calc. (found) for C₁₈H₂₀N₃O₈Re: C, 36.49 (36.28); H, 3.38 (3.19); N, 7.09 (6.98)%. IR (KBr, ν/cm^{-1}): 1601, 1561, 1506, 1298, 1019, 960 (Re=O, str), 801. ¹H NMR (CDCl₃, ppm): 8.90 (d, $J=9.0$ Hz, H₂), 8.79 (dd, $J_1=9.0$ Hz, $J_2=1.8$ Hz, H₃), 8.53 (d, $J=8.7$ Hz, H₅), 8.18 (t, $J=4.8$ Hz, 1H, pyH), 7.90 (d, $J=7.5$ Hz, 2H, pyH), 7.80 (dd, $J_1=9.0$ Hz, $J_2=5.1$ Hz, H₄), 6.54 (d, $J=9.0$ Hz, H₁), 6.22 (d, 1H, -CH₂O ax), 4.92 (s, 2H, -CH₂OH), 4.80 (d, $J=9.3$ Hz, 1H, -CH₂O eq), 4.78 (s, 1H, CH₃OH), 3.49 (s, 3H, CH₃OH).

2.4. '2+2+1' complex [ReO(PPh₃)(η^2 -HNC₆H₄-2-S)-(η^2 -8-O-5-NO₂-C₉H₅N)]·CH₂Cl₂, [ReO(PPh₃)(η^2 -HNC₆H₄-2-S)(L)]·CH₂Cl₂ (**8**)

Compound **8** was isolated as a side product in the preparation of **3**. Yield: 38%. $R_f=0.77$ (SiO₂, 90:10 CHCl₃/acetone). *Anal.* Calc. (found) for C₃₄H₂₇Cl₂N₃-O₄PreS: C, 47.38 (47.28); H, 3.13 (2.95); N, 4.87 (4.81)%. IR (KBr, ν/cm^{-1}): 1654, 1607, 1564, 1527, 1505, 1458, 1426, 1379, 1296, 1193, 1150, 1103, 1010, 967 (Re=O, str), 753. ¹H NMR (CDCl₃, ppm): 9.05 (d, $J=8.7$ Hz, 1H, H₂), 8.7–8.5 (m, 2H, H₃ and H₅), 7.88 (dd, $J_1=9.0$ Hz, $J_2=4.8$ Hz, H₄), 7.5–7.2 (m, 19H, PPh₃+ArH), 6.83 (d, $J=9.0$ Hz, H₁).

2.5. [ReO(OCH₃)(η^2 -O-5-NH₂-C₉H₅N)(η^2 -8-5-NO₂-C₉H₅N)], [ReO(OCH₃)(η^2 -O-5-NH₂-C₉H₅N)(L)] (**9**)

Complex **9** was isolated as a minor product in the preparation of **6**. Yield: 32%. $R_f=0.48$ (SiO₂, 80:20 CHCl₃/acetone). *Anal.* Calc. (found) for C₁₉H₁₅N₄O₆Re: C, 39.24 (39.41); H, 2.58 (2.53); N, 9.64 (9.52)%. IR (KBr, ν/cm^{-1}): 1599, 1580, 1561, 1507, 1468, 1430, 1374, 1295, 1229, 1187, 1148, 1095, 1041, 1009, 963 (Re=O str), 817, 773, 747, 670. ¹H NMR (CDCl₃, ppm): 8.96 (d, $J=8.7$ Hz, H₂), 8.86 (d, $J=5.1$ Hz, 1H), 8.56 (d, $J=9.3$ Hz, H₃), 8.43 (d, $J=9.0$ Hz, H₅), 8.03 (d, $J=4.8$ Hz, 1H), 7.91 (dd, $J_1=9.3$ Hz, $J_2=5.1$ Hz, H₄), 7.7–7.4 (m, 2H, pyH), 7.08 (d, $J=8.4$ Hz, 1H), 6.45 (d, $J=9.0$ Hz, H₁), 4.80 (s, 3H, CH₃).

2.6. X-ray crystal structure determinations of [ReOCl₂(PPh₃)(L)] intermediate **1**, the '3+2' [ReO(Lⁿ)(L)] complexes **2** and **4**, and the '2+2+1' complexes [ReO(OCH₃)(HL⁶)(L)]·CH₃OH (**7**), [ReO(PPh₃)(η^2 -HNC₆H₄-2-S)(L)]·CH₂Cl₂ (**8**) and [ReO(OCH₃)(η^2 -O-5-NH₂-C₉H₅N)(L)] (**9**)

Selected crystals of **1**, **2**, **4**, **7**, **8** and **9** were measured with a Siemens P4 diffractometer equipped with the SMART CCD system [40] and using graphite-monochromated Mo K α radiation ($\lambda=0.071073$ Å). The data collection was carried out at 89(5) K. The data were corrected for Lorentz and polarization effects, and absorption corrections were made using SADABS [41]. Neutral atom scattering factors were taken from Cromer and Waber [42] and anomalous dispersion corrections were taken from those of Creagh and McAuley [43]. All calculations were performed using SHELXL [44]. The structures were solved by direct methods [45] and all of the non-hydrogen atoms were located from the initial solution. After locating all the initial nonhydrogen atoms in each structure, the models were refined against F^2 , initially using isotropic and later anisotropic thermal displacement parameters until the final value of $\Delta/\sigma_{\text{max}}$ was less than 0.001. At this point the hydrogen atoms were located from the electron density difference map and a final cycle of refinements was performed, until the final value of $\Delta/\sigma_{\text{max}}$ was again less than 0.001. No anomalies were encountered in the refinement of any of the structures. The relevant parameters for crystal data, data collection, structure solution and refinement are summarized in Table 1, and important bond lengths and angles in Tables 2–7. A complete description of the details of the crystallographic methods is given in Section 5.

3. Results

3.1. Synthesis

The intermediate complex $[\text{ReOCl}_2(\text{L})(\text{PPh}_3)]$ (**1**) was readily synthesized by mixing the labile precursor $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and the monoanionic bidentate ligand 8-hydroxy-5-nitroquinoline (HL) in refluxing ethanol without the necessity of base. The '3+2' complexes $[\text{ReO}(\text{L}^n)(\text{L})]$ **2–6** were prepared using a one-pot synthesis by adding equimolar amounts of the labile precursor $[\text{ReOCl}_3(\text{PPh}_3)_2]$, HL and the dianionic tridentate ligand H_2L^n in the presence of triethylamine to neutralize HCl produced in situ. The '3+2' chemistry could still be accomplished but much longer reaction time was required for all the [ONS] tridentate ligands **2–5**. Attempts to produce a '3+2' complex employing 2,6-pyridinedimethanol as a dianionic tridentate ligand by a one-pot synthesis gave a mixture which was impossible to purify by column chromatography. Instead, the reaction of $[\text{ReOCl}_2(\text{L})(\text{PPh}_3)]$ (**1**) with 2,6-pyridinedimethanol (H_2L^6) in a mixture of CHCl_3 and CH_3OH afforded a '2+2+1' complex $[\text{ReO}(\text{OCH}_3)(\text{HL})(\text{L})]$ (**7**) as the major product. Partial decomposition of the Schiff base salicylaldehyde-2-mercaptoanil was observed during the production of **3**. A new complex **8** in 38% yield was thus isolated via column chromatography by applying 90:10 CHCl_3 /acetone as eluent. It was unexpected that partial reduction of 8-hydroxy-5-nitroquinoline (HL) to 8-hydroxy-5-aminoquinoline would occur to produce the unusual coordination environment of complex **9** in addition to the conventional '3+2' geometry of complex **6**.

3.2. Characterization

Elemental analyses, as given in Section 2, were in good agreement with the proposed formulations. The IR spectra exhibit the characteristic $\text{Re}=\text{O}$ stretching vibration in the 960–970 cm^{-1} range [46]. For the '3+2' complexes **2–4** containing [ONS] Schiff bases, the infrared spectra were dominated by $\nu(\text{C}=\text{C})$ stretching between 1400 and 1600 cm^{-1} and $\nu(\text{C}=\text{N})$ stretching in the range 1600–1615 cm^{-1} [47]. It is noteworthy that the shift of equilibrium from the thione tautomer in the free ligand salicylaldehyde *N*(4)-phenylthiosemicarbazone (H_2L^3) to the thiol tautomer occurs upon coordination with $\text{ReO}(\text{V})$ core in complex **4**. The deprotonation of the phenolic hydroxy group and SH group of the thiol tautomer is apparent from the disappearance of its $\nu(\text{O}-\text{H})$ (3380 cm^{-1}). The ONS mode of metal complexation, i.e. through phenolic oxygen, azomethine nitrogen and thiol sulfur atoms is ascertained from the red shift (22 cm^{-1}) of the $\nu(\text{C}=\text{N})$ and the blue shift (37 cm^{-1}) of the $\nu(\text{C}-\text{O})$ vibrations [48] of the parent ligand H_2L^3 . The tendency of the Schiff base to shift the equilibrium from the thione form to the thiol form may be attributed to stabilization arising from the conjugation of $-\text{C}=\text{N}-\text{N}=\text{C}$ group upon coordination with the $\text{ReO}(\text{V})$ core [49]. The IR spectrum of complex **9** displays two weak absorption bands at near 3500 and 3400 cm^{-1} , representing the 'free' asymmetrical and symmetrical N–H stretching modes. This confirms that the reduction of HL occurred and that 8-hydroxy-5-aminoquinoline was involved in the coordination in complex **9**.

Proton chemical shifts for complexes **1–9** are given in Section 2 and the numbering of the atoms of bidentate ligand HL used in the study is shown in Chart 1. Comparing the ^1H NMR of the free bidentate ligand HL and the intermediate complex **1** showed a significant upfield shift for all the proton resonances except H_4 , which is meta to the pyridine nitrogen ($\Delta\delta=0.57$ ppm for H_1 , 0.33 ppm for H_2 , 0.45 ppm for H_3 and 0.2 ppm for H_5). However, a downfield shift is always encountered in the '3+2' and '2+2+1' complexes **2–9**. Due to the symmetry of complex **5**, geminal protons at the same methylene carbon of the tridentate [ONS] backbone were distinguished as endo (protons pointing toward the $\text{Re}=\text{O}$ oxygen) and exo (protons pointing away from the $\text{Re}=\text{O}$ oxygen) [35,50,51]. Thus two doublets observed at 4.81 and 6.11 ppm were assigned to the endo and exo protons on the methylene thiolate backbone of the [ONS]/[NO] '3+2' complex **5**. Similarly, two doublets at 5.79 and 6.24 ppm were attributed

to the endo and exo protons on the hydroxymethyl pyridine methylene carbon. The explicit splitting pattern of these two protons excluded the rapid rotational scrambling of these protons that is generally found in [ONS]/[S] '3+1' complexes [35]. The presence of one coordinated methylene hydroxy group to the ReO core and one pendant methylene hydroxy group is evident from the ^1H NMR spectrum of complex **7**. A sharp singlet at $\delta=4.90$ ppm, and two doublets at $\delta=4.80$ and 6.22 ppm are attributed to the two identical protons of the pendant methylene hydroxy carbon backbone, endo and exo protons on the carbon backbone of the bound methylene hydroxy group, respectively.

3.3. Description of the structures

ORTEP diagrams of complexes **1**, **2**, **5**, **7**, **8** and **9** are given in Figs. 1-6, respectively, and selected bond distances and angles are collected in Tables 2-7, respectively. These structures are of discrete mononuclear complexes without significant intermolecular interactions.

Complex **1** exhibits overall distorted octahedral geometry about the central rhenium atom defined by the terminal oxo-group, two chlorine atoms, the phosphorus of the PPh_3 group, and the bidentate N,O donors of the ligand HL. The metal atom is located 0.22 Å above the equatorial plane formed by the two chlorine, one phosphorus and one quinoline nitrogen atoms and the $\text{Re}=\text{O}$ axis is inclined at 84.9° with respect to the equatorial plane. The $\text{Re}=\text{O}$ bond length is 1.683(2) Å, typical for rhenium(V) monooxo complexes [52]. The $\text{Re}-\text{Cl}(1)$ bond length *cis* to the PPh_3 phosphorus atom is slightly shorter than that of $\text{Re}-\text{Cl}(2)$ *cis* to quinoline nitrogen. The phenolate oxygen atom is *trans* to the $\text{Re}=\text{O}$ bond. The $\text{Re}-\text{O}(2)$ bond length of 2.015(2) Å is consistent with the *trans* influence of the $\text{Re}=\text{O}$ linkage on an oxygen from an axially bound ligand. The $\text{O}(2)-\text{Re}-\text{O}(1)$ angle of $161.1(1)^\circ$ deviates from the ideal of 180° for an octahedral complex. The $\text{Re}=\text{O}$ linkage significantly expands the angles to the equatorial chlorine atoms ($\text{Cl}(1)-\text{Re}-\text{O}(1)=106.4(1)^\circ$, and $\text{Cl}(2)-\text{Re}-\text{O}(1)=99.1(1)^\circ$), but not those to the equatorial nitrogen and phosphorus atoms ($\text{N}(1)-\text{Re}-\text{O}(1)=87.3(1)^\circ$, and $\text{P}(1)-\text{Re}-\text{O}(1)=89.2(1)^\circ$).

The asymmetric unit of **2** contains two crystallographically independent oxorhenium complexes and one methanol solvent molecule. The overall geometry about the central rhenium atom is best described as distorted octahedral with the tridentate [ONO] ligand bound in a *fac*-coordination. In common with the intermediate complex **1**, the fourth position of the equatorial plane is taken by the nitrogen atom of the hydroxyquinoline bidentate ligand and the axial positions are occupied by the oxo ligand and the oxygen atom of the HL ligand. The $\text{Re}=\text{O}$, $\text{Re}-\text{O}_{\text{phenolate}}$ and $\text{Re}-\text{N}$ bond lengths are in the ranges observed for analogous compounds. The $\text{Re}-\text{O}(4)$ bond distance of 2.052(7) Å is longer than those of $\text{Re}-\text{O}(2)$ (2.013(8) Å) and $\text{Re}-\text{O}(3)$ (1.990(8) Å) on the distal plane, showing that the structural *trans* influence [53] of the oxo group is transmitted to the hydroxy oxygen atom. The rhenium atom lies 0.27 Å out of the equatorial plane toward the oxo ligand.

The overall geometry about the central rhenium of the '3+2' [ONS]/[NO] complex **5** is best described as distorted octahedral with the [ONS] donor atom set of the tridentate ligand L^4 and the nitrogen of the HL ligand defining the equatorial plane while the axial positions are occupied by the oxo ligand and the oxygen atom of the HL ligand. The ligand donor atoms *cis* to the $\text{Re}=\text{O}$ bond are bent away from the oxygen atom: the angles are $103.1(3)$, $103.1(3)$, $85.3(3)$ and $104.2(4)$ for $\text{N}(1)$, $\text{S}(1)$, $\text{N}(2)$ and $\text{O}(2)$, respectively. The $\text{Re}-\text{O}(3)$ bond length of 2.119(7) Å reflects the *trans* influence of the strong σ - and π -donor oxo ligand.

The most striking feature of the crystal structure of **7** is the bidentate binding of the potentially tridentate [ONO] ligand with one pendant $-\text{CH}_2\text{OH}$ group tilting away from the coordination sphere. This is clearly seen from the difference of the dihedral angles between $\text{N}(1)-\text{C}(2)-\text{C}(1)-\text{O}(2)$ of 9.9° and $\text{N}(1)-\text{C}(6)-\text{C}(7)-\text{O}(3)$ of 162.1° . Rhenium is displaced 0.239 Å from the

mean equatorial plane. The axial O(1)–Re–O(4) angle of $158.7(1)^\circ$ deviates considerably from 180° for an ideal octahedral complex. The principal distortions are the results of the bite angles of the bidentate ligands. The O(2)–Re–N(1) bite angle of the equatorially coordinated ligand is $79.9(1)^\circ$, while the O(4)–Re–N(2) bite angle for the axial ligand is $75.2(1)^\circ$. The Re=O group is almost perpendicular to the equatorial atoms (O(1)–Re–N(1) = $90.7(1)^\circ$, O(1)–Re–N(2) = $87.2(1)^\circ$, and O(1)–Re–O(5) = $91.0(1)^\circ$) except for O(2) (O(1)–Re–O(2) = $108.9(2)^\circ$).

In the '2+2+1' complex **8**, isolated as a side product in the formation of the anticipated '3+2' complex **3**, the retention of one triphenylphosphine in the equatorial plane confirms the dianionic nature of 2-aminophenol bidentate ligand, a cleavage product from the decomposition of the tridentate Schiff base H_2L^2 . It is noteworthy that a similar cleavage of a Schiff base ligand has been reported for the oxotechnetium(V)/ Schiff base system [54]. The Re–N(2) bond distance ($1.968(7) \text{ \AA}$) is about $0.2 \text{ \AA}$ shorter than Re–N(1) ($2.169(7) \text{ \AA}$), a characteristic observation for the deprotonation of a primary amine upon coordination with oxorhenium(V) core [55]. The rhenium is located $0.25 \text{ \AA}$ above the equatorial plane defined by N(1), N(2), P(1) and S(1), toward the oxo group. Again, a severe deviation of the axial O(1)–Re–O(2) angle ($157.9(2)^\circ$) from the linear idealized geometry is observed. The principle distortions are the results of the steric effect of the bulky triphenyl phosphine ligand and the bite angles of the bidentate ligands, N(1)–Re–O(2) $73.1(2)^\circ$ and N(2)–Re–S(1) $83.5(2)^\circ$. In the equatorial plane, the sulfur donor is *trans* to quinoline nitrogen N(1), while the phosphorus donor is *trans* to amino nitrogen N(2). The Re–S distance ($2.293(2) \text{ \AA}$) is slightly shorter and the Re–P distance ($2.504(2) \text{ \AA}$) is slightly longer than typical for oxorhenium(V) complexes.

The structure of **9** consists of distorted octahedral having both the bidentate ligand L and the reduced form of L (8-hydroxy-5-aminoquinoline) and a methoxy oxygen atom about the metal-oxo center. The rhenium is located $0.325 \text{ \AA}$ above the equatorial plane formed by the two nitrogens, one oxygen from HL and the methoxy oxygen atoms. The Re=O bond distance is $1.682(6) \text{ \AA}$, typical for rhenium(V) monooxo complexes and shorter than that usually assigned to a Re–O single bond or a Re=O double bond in $\{O=Re^V=O\}$ complexes ($1.74\text{--}1.79 \text{ \AA}$) [56]. This implies some triple bond character in the rhenium–oxygen bond. Because of the electron-donating resonance effect [57] of the amino group bonded at the *para*-site of the phenol ring, the bond lengths for C(5)–N(2) ($1.46(1) \text{ \AA}$) and C(17)–O(5) ($1.375(9) \text{ \AA}$) are significantly longer than those in the *para*-nitro substituted HL ligand (C(14)–N(4) $1.396(9) \text{ \AA}$ and C(8)–O(2) $1.323(9) \text{ \AA}$, respectively). The ligand donor atoms *cis* to the multiply bonded oxo ligand are bent away from the oxygen atom: the angles are $88.3(2)^\circ$, $95.3(2)^\circ$, $104.2(2)^\circ$ and $109.9(2)^\circ$ for N(1), N(3), O(6) and O(5), respectively. The two small bite angles (N(1)–Re–O(2) $75.0(2)^\circ$ and N(3)–Re–O(5) $80.1(2)^\circ$) account for the distortion of the configuration (O(1)–Re–O(2) = $161.5(2)^\circ$) from the ideal octahedral limits.

4. Discussion

The synthesis of neutral six-coordinate '3+2' complexes in this study involves the addition of dianionic tridentate ligands (H_2L^n) and 8-hydroxy-5-nitroquinoline (HL) to $[ReOCl_3(PPh_3)_2]$ in the presence of triethylamine to neutralize 3 equiv. of HCl produced in situ. In all cases the phenolic oxygen atom occupies a site *trans* to the strong σ - and π -donor oxo ligand rather than the quinolino nitrogen. Due to the weak acidity of the hydroxy protons in the 2,6-pyridinemethanol (H_2L^6), it is not possible to deprotonate both hydrogen atoms of the potentially tridentate [ONO] ligand during the complexation reaction. As a result, HL^6 functions as a bidentate ligand and the remaining coordination site in the equatorial plane is occupied by a methoxy oxygen.

However, the chelation mode is not restricted exclusively to the well-documented '3+2' modes as anticipated. This is manifest in attempts to prepare complexes **3** and **6**. The mechanism for

the cleavage of C=N double of the tridentate Schiff base salicylade-hyde-2-mercaptoanil during the formation of the regular '3+2' complex **3** is unknown to the best of our knowledge. Even more surprisingly, the reduction of 8-hydroxy-5-nitroquinoline to 8-hydroxy-5-amino-quinoline during the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with HL and 2,6-pyridinedicarboxylic acid in the presence of triethylamine was observed. We recently reported the cleavage of the ligand N–OH bond during the reaction of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with salicylaldehyde in an attempt to make a N,O bidentate intermediate complex [58]. Instead of the formation of a complex such as $[\text{ReOCl}_2(\text{PPh}_3)(\eta^2\text{-OC}_6\text{H}_4\text{-C=NOH})]$, $[\text{ReOCl}_2(\text{PPh}_3)(\eta^2\text{-OC}_6\text{H}_4\text{-C=NH})]$ was isolated. Along with this unusual oxorhenium(V) complex, a Re(IV) species, $[\text{ReCl}_2(\text{OPPh}_3)_2]$ was also isolated, which could not be explained by the conventional oxygen atom transfer model [59]. These new phenomena may reflect the fact that the seemingly routine oxorhenium chemistry may be very complicated under certain circumstances. They also show that the structural evidence is of vital importance in guiding the development of small molecule rhenium and/or technetium radiopharmaceuticals. The in vitro and in vivo stability of this series of '3+2' complexes is now in progress and will be reported elsewhere.

5. Supplementary material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Scheme 1.

Fig. 1.
ORTEP diagram of [ReOCl₂(PPh₃)(L)] (1) showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Fig. 2. ORTEP diagram of $[\text{ReO}(\text{L}^1)(\text{L})]$ (**2**) showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Chart 1.

Fig. 3.
ORTEP diagram of [ReO(L⁴)(L)] (5) showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Fig. 4.
ORTEP diagram of [ReO(OCH₃)(HL⁶)(L)] (7) showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Fig. 5. ORTEP diagram of [ReO(PPh₃)(η²-NHC₆H₄-2-S)(L)] (**8**) showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Fig. 6. ORTEP diagram of $[\text{ReO}(\text{OCH}_3)(\eta^2\text{-O-5-NH}_2\text{-C}_6\text{H}_5\text{N})(\text{L})]$ (**9**) showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Table 1

Crystallographic data for [ReOCl₂(PPh₃)(L)] (1), [ReO(L¹)(L)] (2), [ReO(L⁴)(L)] (5), [ReO(OCH₃)(HL⁶)(L)]·CH₃OH (7), [ReO(PPh₃)(η²-NHC₆H₄-2-S)(L)]·CH₂Cl₂ (8) and [ReO(OCH₃)(η²-8-O-5-NH₂-C₉H₅N)(L)] (9)

	1	2	5	7	8	9
<i>Crystal data</i>						
Empirical formula	C ₂₇ H ₂₀ Cl ₂ N ₂ O ₄ P Re	C ₂₂ H ₂₄ N ₃ O ₆ Re	C ₁₆ H ₁₂ N ₃ O ₅ ReS	C ₁₇ H ₁₆ N ₃ O ₇ Re· CH ₃ OH	C ₃₂ H ₂₅ N ₃ O ₄ PReS· CH ₂ Cl ₂	C ₁₉ H ₁₅ N ₄ O ₆ Re
Formula weight	724.52	602.56	544.55	592.57	860.71	581.55
Crystal size (mm)	01.7×0.13×0.1	0.3×0.3×0.2	0.2×0.2×0.05	0.3×0.2×0.15	0.3×0.2×0.2	0.2×0.2×0.1
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n	$\bar{P}1$	P2 ₁ /n	C2/c	P2 ₁ /n
<i>a</i> (Å)	16.7018(13)	8.5093(4)	7.5899(8)	12.0579(6)	25.6266(17)	7.5330(6)
<i>b</i> (Å)	14.2747(11)	38.5184(18)	10.3215(10)	11.0993(6)	8.1305(6)	15.0954(13)
<i>c</i> (Å)	22.3626(17)	11.6092(5)	11.9047(12)	14.9262(8)	31.404(2)	16.3944(13)
<i>α</i> (°)			78.636(2)			
<i>β</i> (°)			74.229(2)			
<i>γ</i> (°)			71.391(2)			
<i>V</i> (Å ³)	5068.2(7)	3770.7(3)	844.33(15)	1901.24(17)	6505.7(8)	1837.7(3)
<i>Z</i>	8	8	2	4	8	4
<i>D</i> _{calc} (g cm ⁻³)	1.899	2.213	2.142	2.070	1.758	2.102
<i>F</i> (000)	2816	2320	520	1152	3384	1120
<i>λ</i> (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>μ</i> (mm ⁻¹)	5.108	6.495	7.354	6.446	4.057	6.661
<i>Data collection</i>						
<i>θ</i> Range (°)	1.92–23.25	1.06–28.28	1.79–28.31	1.91–28.28	1.30–28.28	1.85–28.30
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	–15/18, –13/15, –24/24	–11/11, –51/37, –15/14	–9/10, –6/13, –15/15	–15/7, –14/14, –19/19	–26/34, –10/10, –41/32	–9/9, –15/20, –15/21
Number of reflections	11392	25113	5665	12123	21296	12040
Number of unique data	3635	9084	3866	4534	7860	4424
<i>R</i> _{int} (%)	2.70	6.17	3.72	3.01	9.89	7.04
<i>Structure solution and refinement</i>						

	1	2	5	7	8	9
Parameters refined	334	577	235	274	415	271
Final indices (2σ data), R_1 (wR_2) ^a	0.0192 (0.0443)	0.0732 (0.1319)	0.0536 (0.1381)	0.0298 (0.0757)	0.0578 (0.1094)	0.0496 (0.0926)
All data, R_1 (wR_2)	0.0207 (0.0448)	0.1012 (0.1400)	0.0688 (0.1462)	0.0355 (0.0788)	0.1155 (0.1333)	0.0893 (0.1025)
Goodness-of-fit, S (F^2)	1.083	1.150	1.049	1.039	1.008	1.007

$$^a R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}, \quad wR_2 = \left\{ \frac{\sum \left[w(F_o^2 - F_c^2)^2 \right]}{\sum \left[w(F_o^2)^2 \right]} \right\}^{1/2}.$$

Table 2Selected interatomic distances (Å) and angles for complex [ReOCl₂(PPh₃)(L)] (**1**)

Re(1)–O(1)	1.683(2)	Re(1)–Cl(1)	2.3318(9)
Re(1)–O(2)	2.015(2)	Re(1)–Cl(2)	2.3959(8)
Re(1)–N(1)	2.141(3)	Re(1)–P(1)	2.4800(9)
O(1)–Re(1)–O(2)	161.06(10)	N(1)–Re(1)–Cl(2)	85.39(8)
O(1)–Re(1)–N(1)	87.29(11)	Cl(1)–Re(1)–Cl(2)	89.42(3)
O(2)–Re(1)–N(1)	75.71(9)	O(1)–Re(1)–P(1)	89.22(8)
O(1)–Re(1)–Cl(1)	106.36(8)	O(2)–Re(1)–P(1)	83.32(7)
O(2)–Re(1)–Cl(1)	91.17(7)	N(1)–Re(1)–P(1)	92.44(8)
N(1)–Re(1)–Cl(1)	166.03(8)	Cl(1)–Re(1)–P(1)	90.75(3)
O(1)–Re(1)–Cl(2)	99.08(8)	Cl(2)–Re(1)–P(1)	171.29(3)
O(2)–Re(1)–Cl(2)	87.97(7)		

Table 3Selected interatomic distances (Å) and angles for complex [ReO(L¹)(L)] (2)

Re(1)–O(1)	1.678(7)	Re(1)–O(4)	2.052(7)
Re(1)–O(3)	1.990(8)	Re(1)–N(1)	2.079(11)
Re(1)–O(2)	2.013(8)	Re(1)–N(2)	2.160(8)
O(1)–Re(1)–O(3)	101.4(3)	O(3)–Re(1)–N(1)	78.5(4)
O(1)–Re(1)–O(2)	98.8(4)	O(2)–Re(1)–N(1)	92.7(4)
O(3)–Re(1)–O(2)	159.4(3)	O(4)–Re(1)–N(1)	94.3(3)
O(1)–Re(1)–O(4)	160.8(3)	O(1)–Re(1)–N(2)	86.6(3)
O(3)–Re(1)–O(4)	81.0(3)	O(3)–Re(1)–N(2)	97.3(3)
O(2)–Re(1)–O(4)	81.2(3)	O(2)–Re(1)–N(2)	87.5(3)
O(1)–Re(1)–N(1)	104.9(4)	O(4)–Re(1)–N(2)	74.2(3)

Table 4Selected interatomic distances (Å) and angles for complex [ReO(L⁴)(L)] (**5**)

Re(1)–O(1)	1.683(8)	Re(1)–O(3)	2.119(7)
Re(1)–O(2)	1.981(7)	Re(1)–N(2)	2.183(8)
Re(1)–N(1)	2.057(8)	Re(1)–S(1)	2.323(3)
O(1)–Re(1)–O(2)	104.2(4)	O(2)–Re(1)–O(3)	77.2(3)
O(1)–Re(1)–N(1)	103.1(3)	N(1)–Re(1)–O(3)	98.0(3)
O(2)–Re(1)–N(1)	77.8(3)	O(1)–Re(1)–N(2)	85.3(3)
O(1)–Re(1)–O(3)	158.7(3)	O(2)–Re(1)–N(2)	95.8(3)

Table 5Selected interatomic distances (Å) and angles for complex [ReO(OCH₃)(HL⁶)(L)]·CH₃OH (**7**)

Re(1)–O(1)	1.691(3)	Re(1)–O(4)	2.067(3)
Re(1)–O(2)	1.915(3)	Re(1)–N(2)	2.131(4)
Re(1)–O(5)	1.964(3)	Re(1)–N(1)	2.177(4)
O(1)–Re(1)–O(2)	108.86(15)	O(5)–Re(1)–N(2)	81.57(12)
O(1)–Re(1)–O(5)	102.03(14)	O(4)–Re(1)–N(2)	75.17(12)
O(2)–Re(1)–O(5)	90.98(13)	O(1)–Re(1)–N(1)	90.71(14)
O(1)–Re(1)–O(4)	158.67(13)	O(2)–Re(1)–N(1)	79.93(13)
O(2)–Re(1)–O(4)	89.86(13)	O(5)–Re(1)–N(1)	166.27(13)
O(5)–Re(1)–O(4)	87.36(13)	O(4)–Re(1)–N(1)	82.39(13)
O(1)–Re(1)–N(2)	87.18(14)	N(2)–Re(1)–N(1)	104.43(13)
O(2)–Re(1)–N(2)	163.49(15)		

Table 6Selected interatomic distances (Å) and angles for complex [ReO(PPh₃)(η²-NHC₆H₄-2-S)(L)]·CH₂Cl₂ (**8**)

Re(1)–O(1)	1.710(5)	Re(1)–N(1)	2.169(7)
Re(1)–N(2)	1.968(7)	Re(1)–S(1)	2.293(2)
Re(1)–O(2)	2.097(5)	Re(1)–P(1)	2.504(2)
O(1)–Re(1)–N(2)	104.0(3)	O(2)–Re(1)–S(1)	94.85(16)
O(1)–Re(1)–O(2)	157.9(2)	N(1)–Re(1)–S(1)	165.38(18)
N(2)–Re(1)–O(2)	88.8(2)	O(1)–Re(1)–P(1)	88.8(2)
O(1)–Re(1)–N(1)	89.2(3)	N(2)–Re(1)–P(1)	167.2(2)
N(2)–Re(1)–N(1)	87.9(3)	O(2)–Re(1)–P(1)	79.25(17)
O(2)–Re(1)–N(1)	73.1(2)	N(1)–Re(1)–P(1)	92.87(19)
O(1)–Re(1)–S(1)	104.39(19)	S(1)–Re(1)–P(1)	92.85(8)
N(2)–Re(1)–S(1)	83.5(2)		

Table 7Selected interatomic distances (Å) and angles for complex [ReO(OCH₃)(η^2 -8-*O*-5-NH₂-C₉H₅N)(L)] (**9**)

Re(1)–O(1)	1.682(6)	Re(1)–O(2)	2.077(6)
Re(1)–O(6)	1.937(5)	Re(1)–N(3)	2.113(6)
Re(1)–O(5)	1.975(5)	Re(1)–N(1)	2.131(6)
O(1)–Re(1)–O(6)	104.2(2)	O(5)–Re(1)–N(3)	80.1(2)
O(1)–Re(1)–O(5)	109.9(2)	O(2)–Re(1)–N(3)	79.6(2)
O(6)–Re(1)–O(5)	91.2(2)	O(1)–Re(1)–N(1)	88.3(2)
O(1)–Re(1)–O(2)	161.5(2)	O(6)–Re(1)–N(1)	84.8(2)
O(6)–Re(1)–O(2)	82.5(2)	O(5)–Re(1)–N(1)	161.9(2)
O(5)–Re(1)–O(2)	86.9(2)	O(2)–Re(1)–N(1)	75.0(2)
O(1)–Re(1)–N(3)	95.3(2)	N(3)–Re(1)–N(1)	98.1(2)
O(6)–Re(1)–N(3)	160.4(2)		