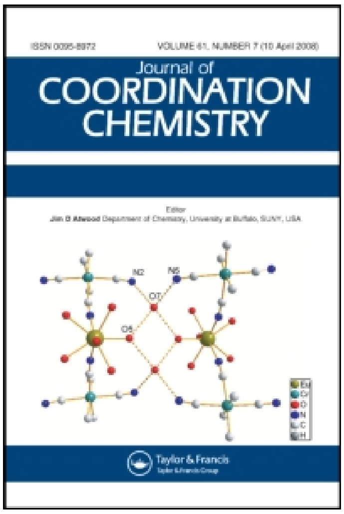

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Syntheses and crystal structures of neutral oxorhenium(V) complexes of N_2O_2-donor tripodal ligands

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SYNTHESES AND CRYSTAL STRUCTURES OF NEUTRAL OXORHENIUM(V) COMPLEXES OF N_2O_2-DONOR TRIPODAL LIGANDS

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The neutral distorted octahedral complexes [ReOCl(L)] {H_2L = *N*,*N*-bis(2-hydroxybenzyl)-2-(2-aminoethyl)-dimethylamine (H_2had); *N*,*N*-bis(2-hydroxybenzyl)-aminomethylpyridine (H_2hap); *N*,*N*-bis(2-hydroxybenzyl)-2-(2-aminoethyl)pyridine (H_2hae)} were prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a twofold molar excess of H_2L in ethanol. X-ray structure determinations of [ReOCl(had)] (**1**) and [ReOCl(hap)] (**2**) were performed, and the structures compared. In both complexes the choride is coordinated *trans* to the tripodal tertiary amino nitrogen, with a phenolate oxygen trans to the oxo oxygen.

Keywords: Oxorhenium(V); Tripodal ligands; Tetradentate N_2O_2; X-ray structures

INTRODUCTION

The immense current activity in the coordination chemistry of rhenium is mainly the result of its analogy to technetium chemistry, as well as its expanding application in therapeutic nuclear medicine [1]. The impetus for advances in the coordination and radiopharmaceutical chemistry of rhenium is the synthesis of novel compounds, which can explore the effect of pendant groups, geometry, molecular weight, size and charge of these complexes on their biodistribution.

One approach to the development of novel rhenium(V) complexes has been the "3 + 1" concept of ligand permutation, which provides a strategy for the consistent synthesis of complexes with the ReO^{3+} core [2,3]. This concept is based on the ligation of a dinegative tridentate chelate in combination with a monodentate uninegative thiolate in

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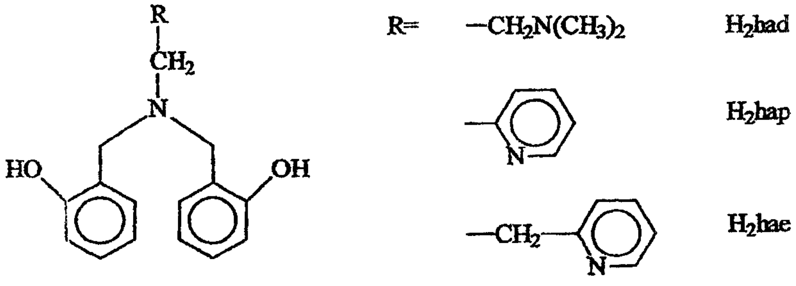
the square-pyramidal geometry of the rhenium(V) complex [4]. However, these "3 + 1" complexes were found to be relatively unstable *in vitro* and *in vitro* [5]. Kinetic stability was improved somewhat by "3 + 2" six-coordinated oxorhenium(V) complexes [6]. In addition, "2 + 2" ligand combinations have been exploited [7].

We have now extended this concept to "4 + 1" complexes by using dianionic tetradentate N_2O_2-donor chelates around the oxorhenium(V) core. Several Re(V) complexes with tetradentate ligands have been described [8–10]; however, most of these ligands were of the Schiff-base type.

In this account, we report oxorhenium(V) complexes formed by the reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ with the tetradentate N_2O_2-donor ligands *N*,*N*-bis(2-hydroxybenzyl)-2-(2-aminoethyl)dimethylamine (H_2had), *N*,*N*-bis(2-hydroxybenzyl)-aminomethylpyridine (H_2hap) and *N*,*N*-bis(2-hydroxybenzyl)-2-(2-aminoethyl)pyridine (H_2hae).



EXPERIMENTAL

Materials

All chemicals were of reagent grade and were used as received from the suppliers. Solvents were purified and dried. *trans*-$[ReOCl_3(PPh_3)_2]$ [11] and (*n*-$Bu_4N)[ReOCl_4]$ [12] were synthesised according to literature procedures. The ligands H_2had, H_2hap [13] and H_2hae [14] were prepared by literature methods.

Instrumentation

Scientific instrumentation used is the same as reported elsewhere [15]. Infrared spectra were obtained using KBr discs and ^1H NMR spectra (ppm) were run in d_6-DMSO. Electronic spectra and conductivity measurements (in $cm^2\,ohm^{-1}\,mol^{-1}$) were obtained in acetonitrile, and spectroscopic data are given as λ_{max} with extinction coefficients (in $M^{-1}\,cm^{-1}$) in parentheses.

Synthesis of the Complexes

[*ReOCl*(*had*)] (*1*) To a suspension of 77 mg of H_2had (256 μmol) in 5 cm^3 of ethanol was added 104 mg of *trans*-$[ReOCl_3(PPh_3)_2]$ (125 μmol) dissolved in 7 cm^3 ethanol. The reaction mixture was heated under reflux for 30 min, after which the dark green solution was cooled to room temperature and filtered. Slow evaporation of this solution in a desiccator over three days yielded green crystals that were suitable for X-ray crystallographic studies. The crystals were collected by filtration, washed with water, toluene and diethylether, and dried under vacuum. Yield = 58%; m.p. 213°C. Anal. Calcd. for $C_{18}H_{22}N_2O_3ClRe$(%): C, 40.33; H, 4.14; N, 5.23. Found: C, 40.43; H, 3.97; N, 5.14. Infrared: ν(Re = O) 957(s); ν(Re–Cl) 327(m); ν(C–O) 1271(s), 1255(s); ν(Re–O) 458(w), 480(w); ν(Re–N) 501(m), 524(m); ν(N–CH_3) 1283(s). ^{1}H NMR: 7.33(m, 4H, H^2, H^4, H^9, H^{11}); 7.05(d, 1H, H^{12}, $J = 7.5$ Hz); 7.00(t, 1H, H^{10}); 6.85(t, 1H, H^3); 6.76(d, 1H, H^5); 5.02(d, 1H, H^{14}_A); 4.71(d, 1H, H^{14}_B); 4.48(d, 1H, H^7_A); 4.02(d, 1H, H^7_B); 3.49(t, 2H, H^{15}); 3.30(t, 2H, H^{16}); 3.06(s, 3H, $^{17}CH_3$); 2.96(s, 3H, $^{18}CH_3$). Conductivity = 17. Electronic spectrum: 626(1220), 374(26 400).

[ReOCl(hap)] (*2*) The synthesis was carried out in exactly the same way as for complex **1**. Green diamond-shaped crystals with the formulation **2** · 0.25MeOH were grown from a methanol solution of **2**. Yield = 67%; m.p. 275°C. Anal. Calcd. for $C_{20}H_{18}N_2O_3ClRe$(%): C, 43.20; H, 3.26; N, 5.04. Found: C, 43.22; H, 3.23; N, 4.82. Infrared: ν(Re=O) 961 (vs); ν(Re–Cl) 322(m); ν(C–O) 1252(s), 1274(s); ν(Re–N) 496(m), 518(m); ν(Re–O) 458(w), 471(w). ^{1}H NMR: 8.97(d, 1H, H^{13}, $J = 5.1$ Hz); 7.89(t, 1H, H^{11}, $J = 7.5$ Hz); 7.69(t, 1H, H^{12}); 7.59(d, 1H, H^{17}), $J = 7.7$ Hz); 7.44 (t, 1H, H^{19}, $J = 7.5$ Hz); 7.34 (d, 1H, H^4, $J = 7.2$ Hz); 7.16 (d, 1H, H^{20}, $J = 8.0$ Hz); 7.05(d, 1H, H^7); 6.92(t, 1H, H^{18}); 6.85(t, 1H, H^5); 6.56(d, 1H, H^{10}); 6.06(t, 1H, H^6); 5.89(d, 2H, H^8); 5.14(d, 2H, H^{14}); 4.86(d, 2H, H^1). Conductivity = 18. Electronic spectrum: 595(760), 379(21 000).

[ReOCl(hae)] (*3*) The method of preparation was the same as for **1**. Yield = 67%; m.p. 311°C. Anal. Calcd. for $C_{21}H_{20}N_2O_3ClRe$(%): C, 44.24; H, 3.54; N, 4.91. Found: C, 44.36; H, 3.67; N, 4.99. Infrared: ν(Re=O) 957 (vs); ν(Re–Cl) 324(m); ν(C–O) 1259(s), 1270(s); ν(Re–N) 494(m), 514(m); ν(Re–O) 451(m), 465(m). ^{1}H NMR: 9.23(d, 1H, $J = 5.4$ Hz); 7.82(t, 1H); 7.73(t, 1H); 7.56(d, 1H); 7.33(t, 1H); 7.16(d, 1H); 7.08(d, 1H); 7.00(m, 2H); 6.80(t, 1H); 6.67(t, 1H); 6.39(d, 1H); 4.95 (m, 4H); 4.32(d, 2H); 4.09(d, 2H). Conductivity = 16. Electronic spectrum: 590(850), 395(23 400).

Crystallography

Crystals of complex **1** were grown by slow evaporation of the mother liquor of the synthetic solution, and those of **2** · 0.25MeOH from a methanol solution. Diffraction data were measured using an Enraf-Nonius Kappa CCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package [16]. The structures were solved using the direct-methods program SIR92 [17], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinements were carried out using the CRYSTALS program suite [18]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms, except for C and O of MeOH in **2**, were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Refinements for **1** and **2** converged satisfactorily to give $R = 0.0252$, $wR = 0.0287$ and $R = 0.0256$, $wR = 0.0646$, respectively. Thermal ellipsoid plots (ORTEP-3 [19]) at 40% probability are given in Figs. 1 and 2, respectively, for the structures of **1** and **2**.

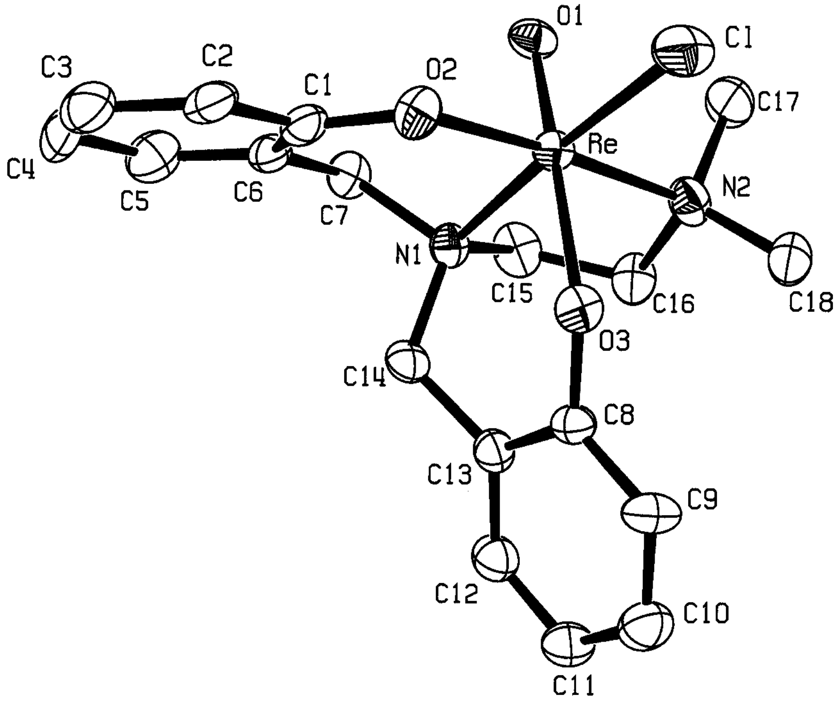


FIGURE 1 An ORTEP view of [ReOCl(had)] (**1**) showing the atom labelling scheme and 40% probability ellipsoids.

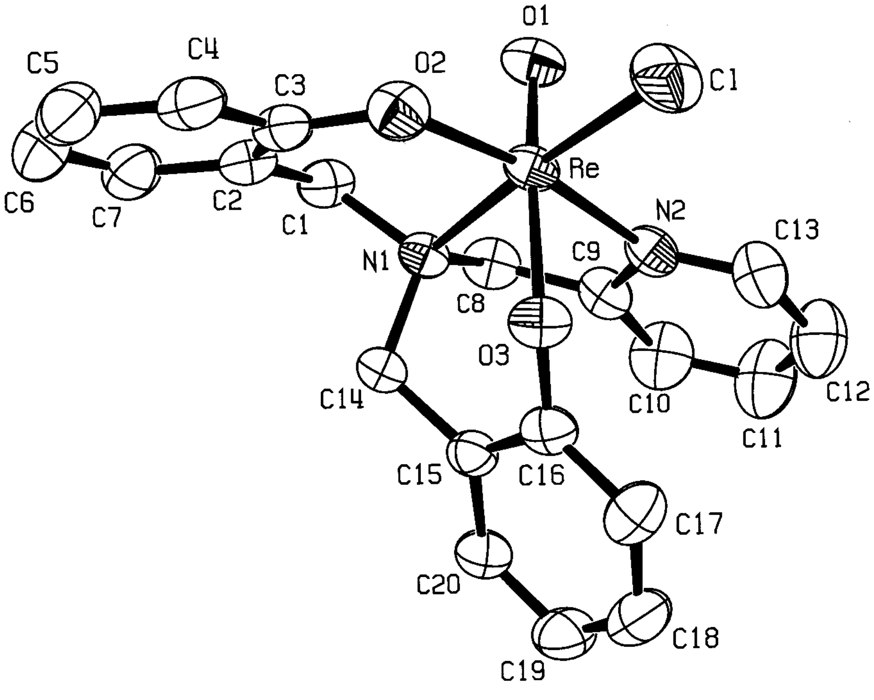


FIGURE 2 ORTEP view (at 40% probability) of [ReOCl(hap)] (**2**).

Details of the crystal data, measurement of intensities and data processing are summarised in Table I. Selected bond lengths and angles for **1** and **2** are listed in Tables II and III, respectively.

Tables giving the final atomic coordinates and equivalent isotropic thermal parameters of all atoms, complete crystallographic experimental details, bond distances and angles and anisotropic thermal parameters are available from the authors.

TABLE I Crystal data and structure refinement details for [ReOCl(had)] (**1**) and [ReOCl(hap)] (**2**)

	1	*2*
Empirical formula	$C_{18}H_{22}ClN_2O_3Re$	$C_{20}H_{18}ClN_2O_3Re.0.25CH_4O$
Formula weight	534.0	564.0
Temperature (K)	150	200
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 7.2072(1)$	12.3858(2)
	b=10.4014(2)	13.9446(2)
	$c = 24.3819(4)$	12.3117(1)
		$\beta = 112.456(1)$
Volume (Å^3)	1827.8	1965.2
Z	4	4
Density (calc.) (Mg m^{-3})	1.948	1.906
Crystal size (mm)	0.06 × 0.06 × 0.20	0.05 × 0.21 × 0.27
Absorption coefficient μ (mm^{-1})	6.814	6.344
F(000)	1034.5	1089
θ (min–max)	5.0–27.5°	3.3–27.5°
Limiting indices	$-9 \leq h \leq 9$	$-16 \leq h \leq 14$
	$0 \leq k \leq 13$	$-18 \leq k \leq 17$
	$0 \leq l \leq 31$	$-15 \leq l \leq 15$
Reflections collected/unique	17 773/4187	33 262/4473
Observed data	3480[$I > 3.0\sigma(I)$]	3918[$I > 2.0\sigma(I)$]
Nref, Npar	4187, 227	4473, 250
R, wR, S	0.0252/0.0287/1.01	0.0256/0.0646/1.08
Min and max resd. dens. (e Å^{-3})	−1.37, 1.07	−1.26, 1.29

TABLE II Selected bondlengths (Å) and angles (°) for [ReOCl(had)] (**1**)

Re–O(1)	1.676(4)	Re–O(2)	1.973(4)
Re–Cl	2.362(2)	Re–N(1)	2.174(4)
Re–N(2)	2.235(5)	Re–O(3)	1.950(4)
C(1)–O(2)	1.336(7)	C(8)–O(3)	1.363(7)
N(1)–C(15)	1.506(7)	N(1)–C(14)	1.497(7)
C(17)–N(2)	1.493(8)	C(18)–N(2)	1.479(8)
Cl–Re–O(1)	98.97(16)	O(1)–Re–O(2)	96.49(19)
Cl–Re–O(2)	86.60(14)	O(1)–Re–O(3)	167.28(19)
Cl–Re–O(3)	91.26(12)	O(2)–Re–O(3)	91.62(18)
Cl–Re–N(1)	175.23(13)	O(1)–Re–N(1)	85.7(2)
Cl–Re–N(2)	96.12(16)	O(2)–Re–N(1)	93.65(18)
O(1)–Re–N(2)	86.0(2)	O(3)–Re–N(1)	83.97(17)
O(2)–Re–N(2)	176.0(2)	O(3)–Re–N(2)	85.4(2)
N(1)–Re–N(2)	83.40(19)	Re–O(2)–C(1)	124.6(4)
Re–N(1)–C(7)	106.9(3)	Re–O(3)–C(8)	138.0(4)
C(7)–N(1)–C(14)	106.3(4)	C(7)–N(1)–C(15)	109.1(5)
C(16)–N(2)–C(17)	109.8(5)	O(3)–C(8)–C(9)	120.4(5)

TABLE III Selected bondlengths (Å) and angles (°) for [ReOCl(hap)] (**2**)

Re–O(1)	1.681(2)	Re–O(2)	1.980(3)
Re–Cl	2.389(1)	Re–N(1)	2.157(3)
Re–N(2)	2.149(4)	Re–O(3)	1.959(2)
C(3)–O(2)	1.352(5)	C(16)–O(3)	1.354(5)
N(1)–C(8)	1.511(5)	N(1)–C(14)	1.506(4)
Cl–Re–O(1)	98.42(10)	O(1)–Re–O(2)	99.70(14)
Cl–Re–O(2)	85.87(8)	O(1)–Re–O(3)	166.04(13)
Cl–Re–O(3)	90.00(8)	O(2)–Re–O(3)	91.96(10)
Cl–Re–N(1)	174.60(7)	O(1)–Re–N(1)	86.74(11)
Cl–Re–N(2)	99.30(9)	O(2)–Re–N(1)	94.87(12)
O(1)–Re–N(2)	87.34(15)	O(3)–Re–N(1)	84.62(10)
O(2)–Re–N(2)	170.63(11)	O(3)–Re–N(2)	80.29(12)
N(1)–Re–N(2)	79.25(13)	Re–O(2)–C(3)	123.6(2)
Re–N(1)–C(1)	107.5(2)	Re–O(3)–C(16)	130.2(2)
C(1)–N(1)–C(14)	107.5(3)	C(1)–N(1)–C(8)	110.3(2)
C(9)–N(2)–C(13)	119.2(4)	O(3)–C(16)–C(17)	121.6(3)

RESULTS AND DISCUSSION

Synthesis

The simple reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a twofold molar excess of the ligands H_2had, H_2hap and H_2hae (H_2haa) in ethanol under reflux gave the green complexes [ReOCl(haa)] (**1**–**3**) as products. With an equimolar ratio of reactants none of the complexes **1**–**3** could be isolated, and only [$ReOCl_2(OEt)(PPh_3)_2$] was obtained. This indicates the following equation for the formation reactions of the complexes [ReOCl(haa)].

$$[\mathrm{ReOCl_3(PPh_3)_2}] + 2\mathrm{H_2haa} \rightarrow [\mathrm{ReOCl(haa)}] + [\mathrm{H_4haa}]\mathrm{Cl_2} + 2\mathrm{PPh_3}$$

One equivalent of H_2haa serves as a ligand, and the other as a base to deprotonate the phenolic hydroxy functions and to remove the two equivalents of HCl that are formed in the substitution reaction.

Complexes **1**–**3** could also be prepared by the reaction of (n-Bu_4N)[$ReOCl_4$] with a twofold molar excess of H_2haa in ethanol, or with equimolar quantities in the presence of triethylamine.

$$(n\text{-}\mathrm{Bu_4N})[\mathrm{ReOCl_4}] + \mathrm{H_2haa} + 2\mathrm{Et_3N} \rightarrow [\mathrm{ReOCl(haa)}] + 2[\mathrm{Et_3NH}]\mathrm{Cl} + n\text{-}\mathrm{Bu_4NCl}$$

All complexes are diamagnetic (formally d^2), and are non-electrolytes in acetonitrile. They are weakly soluble, but stable, in polar solvents such as DMSO, DMF, acetonitrile, acetone and chloroform.

Spectroscopic Chracterisation

In the infrared spectra, asymmetric Re=O stretching frequencies appear as sharp strong bands in the narrow range 957–961 cm^{-1}, which falls in the typical region of

951–966 cm^{-1} that is normally observed for complexes with a relatively hard phenoxy donor atom *trans* to the Re=O moiety [9,20,21]. Deprotonation of both phenolic OH groups in each complex is supported by the absence of a band in the 3200–3500 cm^{-1} region and the coordination of the deprotonated phenolate oxygens to rhenium is reflected by two ν(C–O) around 1255 and 1270 cm^{-1} in the spectrum of each complex. A single frequency at about 324 cm^{-1} is ascribed to the Re–Cl stretch, with the chloride coordinated *cis* to the oxo group in all three complexes.

^{1}H NMR spectra support the arrangement of the tetradentate ligands around the rhenium(V) centre, with all the aromatic protons in different chemical environments. In the aromatic region of the spectrum of [ReOCl(hap)], for example, there are twelve (six doublets and six triplets) separate signals for the twelve aromatic protons. A similar phenomenon is observed for complexes **1** and **3**. Furthermore, the signals of all protons are shifted downfield with respect to those of the free ligands.

Description of the Structures

The structures (see Figs. 1 and 2) of **1** and **2** (MeOH omitted for clarity) consist of discrete, monomeric and neutral oxorhenium complexes packed with no intermolecular contacts shorter than the Van der Waals radii sum. The coordination geometry around the rhenium is highly distorted octahedral; two nitrogen atoms N(1) and N(2) from the tetradentate dinegative ligands lie on the equatorial plane, along with the chloride and phenolate O(2) atoms, with the phenolate O(3) *trans* to the O(1) oxo atom. The chloride is coordinated *trans* to the tripodal N(1) atoms. In the coordination spheres of both complexes the six-membered metallocycle rings adopt the twist-boat conformation, dihedral angles between the two aromatic rings being 69.15° (in **1**) and 60.42° (in **2**).

In the two complexes the O(1)–Re–O(3) axis is non-linear (167.3° and 166.0° in **1** and **2**, respectively), and the rhenium atom is displaced from the mean equatorial plane by 0.0728(1) and 0.1203(1) Å in **1** and **2**, respectively, towards the oxo oxygen atom. For example, as a measure of the octahedral distortion in the ClN_2O_3 polyhedron in **1**, the Re atom is −1.23 Å from the N(2)N(1)O(1) plane and +1.20 Å from the Cl(1)O(2)O(3) one, the angle between the two triangular faces being 7.54° (−1.22 Å, +1.21 Å, 7.61°, respectively, for **2**). The interligand angles in the equatorial planes depart considerably from 90° (from 83.40 to 96.12° in **1** and from 79.25 to 99.30° in **2**).

Re=O(1) distances of 1.676(4) Å (in **1**) and 1.681(2) Å (in **2**) compare favourably with those reported previously [9,20,21]. Surprisingly, the Re–O(3) bondlengths, *trans* to the oxo oxygen O(1) are significantly shorter than the equatorial Re–O(2) bond lengths [e.g., 1.950 *vs* 1.973 Å in **1**; 1.959 *vs* 1.980(3) Å in **2**]. This is in contrast with the complex [ReOCl(sal_2en)] [sal_2en = 1,3-*N*,*N′*-bis-(3,5-dichlorosalicylidene)-diamino-2,2-dimethylpropyl], where the *trans* Re–O bond length [1.994(5) Å] is significantly longer than the *cis* Re–O(phenoxy) bond length of 1.976(5) Å [9]. In the complex [ReOCl{(2-$OC_6H_4CH{=}N(CH_2)_3OCH_2)_2$}] there is no significant difference between the two Re–O (phenoxy) distances [1.977(5) for *trans* and 1.983(6) Å for the *cis* bond] [20].

In complex **1**, the Re–N(2) bond [2.235(5) Å] is significantly longer than the Re–N(1) bond [2.174(4) Å], but in **2** the opposite is true [Re–N(2) = 2.149(4), Re–N(1) = 2.157(3) Å]. Bond angles around N(1) and N(2) in **1** are typical for trigonal planar nitrogen atoms. Also, the Re–Cl bond distance in **1** [2.362(2) Å] is considerably shorter than the equivalent bond in **2** [2.389(1) Å]. These bond lengths are within the range expected from the comparison of other six-coordinate monooxorhenium(V) complexes containing the ClN_2O_3 donor set [9,20,21].

If the structural data of **1** and **2** are compared, the main differences concern the Re–O(3)–C(8)–C(13) and C(8)–C(13)–C(14)–N(1) torsion angles in **1** (31.18 and −51.1°) compared with the equivalent Re–O(3)–C(16)–C(15) and C(16)–C(15)–C(14)–N(1) angles in **2** (50.1 and −58.0°), the dihedral angles between the mean equatorial plane and the six-membered ReO(3)C(8)C(13)C(14)N(1) ring in **1** and ReO(3)C(16) C(15)C(14)N(1) in **2** (79.9° in **1** and 71.2° in **2**), the Re–N(2)–C(16)–C(15) and N(2)–C(16)–C(15)–N(1) torsion angles in **1** (−33.7 and 54.9°, respectively) compared with Re–N(2)–C(9)–C(8) and N(2)–C(9)–C(8)–N(1) in **2** (−10.2 and 35.8°, respectively), and the Re–O(3)–C(8) bond angle (138.0° in **1**) decreasing to 130.2 in **2**.

Complexes of rhenium(V) with tetradentate N_2O_2-donor ligands have been reasonably well studied. With the Schiff-base ligands H_2sal_2en [9] and H_2salpd [8] (H_2L) complexes of the type [ReOCl(L)] were isolated, with a phenoxy oxygen coordinated trans to the oxo group.

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