

Multidentate Dipyriddy Derivatives as Chelates for Rhenium(V)

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Rhenium(V) complexes with the following multidentate dipyriddy ligands were prepared: 2,2'-dipyridylamine (DPA), 1,2-bis(2-pyridyl)ethylene (DPE) and di-(2-picolyl)amine (HDIPA). Reactions of a twofold molar excess of the potentially NN donor ligand DPA with *trans*-[ReO(OEt)Cl₂(PPh₃)₂] in ethanol led to isolation of a monomer [ReOCl₂(OEt)(DPA)] (1). Treatments of *trans*-[ReOCl₃(PPh₃)₂] with a tenfold molar excess of DPA in ethanol at reflux yielded [ReO₂(dpa)₂]Cl (2), but with a twofold molar excess a dimer (μ -O)[{ReOCl₂(dpa)}₂] (3a) was isolated. The latter reaction with (*n*-Bu₄N)[ReOCl₄] as starting material in ethanol at room temperature led to a dark green product, also with the formulation (μ -O)[{ReOCl₂(dpa)}₂] (3b). Reacting equimolar quantities of (*n*-Bu₄N)[ReOCl₄] and HDIPA in acetone led to [ReOCl(OH₂)(DIPA)]Cl (4) in which HDIPA acted as a monoanionic terdentate chelate. The reaction of *trans*-[ReOCl₃(PPh₃)₂] with DPE, in which DPE undergoes a metal-promoted nucleophilic attack by a water molecule, produces a complex with a general formula [ReO(DPE.OH)Cl₂] (5).

1. Introduction

Oxorhenium(V) complexes with terdentate dianionic ONX (X = O, S) donor Schiff base ligands have been well studied.^{1,2,3} It was found that the three donor atoms are bonded to the metal on the *cis* equatorial plane with respect to the Re = O linkage in complexes of the type [ReOCl(ONX)(MeOH)]. A study of oxorhenium(V) complexes with terdentate Schiff base ligands having the ONN donor-atom set has shown that it is the imino nitrogen that is bonded *trans* to the oxo oxygen in complexes of the type [ReOCl₂(ONN)].⁴ We have previously reported the products [ReOCl₂(ONN)] obtained from the reaction of *trans*-[ReOCl₃(PPh₃)₂] with terdentate ONN-donor ligands of the pyridylaminophenol type, which are similar to the terdentate Schiff base ligands, except that they contain an amino nitrogen in place of the imino nitrogen.⁵

We report here the synthesis of rhenium(V) complexes with the following multidentate dipyriddy ligands: 2,2'-dipyridylamine (DPA), di-(2-picolyl)amine (HDIPA) and 1,2-bis(2-pyridyl)ethylene (DPE).

2. Experimental

Materials. *Trans*-[ReOCl₃(PPh₃)₂],⁶ (*n*-Bu₄N)[ReOCl₄]⁷ and *trans*-[ReO₂(OEt)(PPh₃)₂]⁸ were synthesized by literature methods. 2,2'-Dipyridylamine (DPA), 1,2-bis(2-pyridyl)ethylene (DPE) and di-(2-picolyl)amine (HDIPA) were obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. Infrared spectra were obtained using KBr disks. The instrumentation used is the same as reported earlier.⁵

Synthesis of [ReOCl₂(OEt)(DPA)] (1). DPA (137 mg, 800 μ mol) was added to a stirred suspension of *trans*-[ReOCl₃(PPh₃)₂] (300 mg, 360 μ mol) in 10 cm³ ethanol, and the mixture was heated under reflux for 30 min. After about 10 min of heating the lime-green colour of the starting material changed to purple, and after heating was stopped and the solution cooled to room temperature, a purple solid was filtered off. Recrystallization

from dichloromethane/ethanol afforded dark blue crystals. Yield = 58%, mp 299–301 °C. IR (cm⁻¹): ν (Re = O) 954 s, ν (C = C) 1587 s, ν (C = N) 1630 s, ν (N-H) 3216 w, δ (OCH₂) 916 vs, ν (Re-N) 524 m, ν (Re-Cl) 318 m.

Synthesis of *trans*-[ReO₂(DPA)₂]Cl (2). DPA (626 mg, 3.65 mmol) in ethanol (5 cm³) was added to a stirred suspension of *trans*-[ReOCl₃(PPh₃)₂] (331 mg, 400 μ mol) in the same solvent (10 cm³), and the resulting solution was heated under reflux for 30 min. During this time the solution changed colour from yellow-green to brown, and after 20 min a bright orange precipitate was formed. After cooling the mixture to room temperature the solid was filtered off, washed with ethanol (2 \times 2 cm³) and dried under vacuum. Crystals of the 3H₂O solvate, suitable for X-ray diffraction, were obtained by slow evaporation of the mother liquor from the synthetic solution. Yield = 72%, mp 229 °C. IR (cm⁻¹): ν (O = Re = O) 814 vs, ν (C = C) 1582 s, ν (C = N) 1637 s, ν (N-H) 3232 w, ν (Re-N) 540 m.

Synthesis of (μ -O)[{ReOCl₂(DPA)}₂] (3a). To an ethanol (10 cm³) suspension of *trans*-[ReOCl₃(PPh₃)₂] (300 mg, 400 μ mol) was added DPA (137 mg, 800 μ mol). The mixture was heated under reflux for 30 min, generating a brown solution from which a green solid precipitated. The mixture was cooled to room temperature and the green product was filtered off after standing overnight. It was then washed with cold ethanol and diethyl ether, and vacuum dried. Recrystallization was from acetonitrile. Yield = 76%, mp 274 °C. IR (cm⁻¹): ν (Re = O) 913 m, ν (Re-O-Re) 697 vs, ν (C = C) 1585 s, ν (C = N) 1632 s, ν (N-H) 3297 w, ν (Re-N) 529 m, ν (Re-Cl) 317 m, 322 m.

Synthesis of (μ -O)[{ReOCl₂(DPA)}₂] (3b). A solution of DPA (190 mg, 1110 μ mol) in ethanol (10 cm³) was added dropwise to a stirred suspension of 324 mg (552 μ mol) of (*n*-Bu₄N)[ReOCl₄] in 10 cm³ of ethanol. An intense purple solution was obtained in a few minutes, and after stirring for 30 min a dark green crystalline precipitate was filtered off, washed rapidly with water, acetone and diethyl ether, and dried under vacuum. Recrystallization was from DMSO/*n*-hexane. Yield = 74%, mp 246 °C. IR (cm⁻¹): ν (Re = O) 923 m, ν (Re-O-Re) 697 vs, ν (C = C) 1585 s, ν (C = N) 1628 s, ν (N-H) 3301 m, ν (Re-N) 534 m, ν (Re-Cl) 319 m.

Synthesis of [ReOCl(OH₂)(DIPA)] (4). HDIPA (0.0244 g, 123 μ mol) dissolved in 6 cm³ acetone was added to a light

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green, stirred solution of (*n*-Bu₄N)[ReOCl₄] (0.07191 g, 123 μmol) in the same solvent (6 cm³). A dark green solid immediately formed, and the suspension was stirred for further 4 h at room temperature. The solid was removed by filtration, washed with acetone (2 × 3 cm³), and dried under vacuum. Recrystallization from acetonitrile produced avocado-green crystals, suitable for X-ray diffraction studies. Yield = 65%, mp > 300 °C. IR (cm⁻¹): ν(Re = O) 957 vs, ν(C = N) 1613 s, ν(C = C) 1562 w, ν(Re-N_{py}) 590 m, ν(Re-N) 664 w, ν(Re-Cl) 309 m.

Synthesis of [ReOCl₂(DPE.OH)] (5). A solution of 43 mg (235 μmol) of DPE in 10 cm³ ethanol was added to a suspension of *trans*-[ReOCl₃(PPh₃)₂] (in 5 cm³ ethanol). The mixture was heated under reflux for 24 h. The colour of the solution gradually turned from green to blue, with the continuous precipitation of a blue compound. After cooling to room temperature, the blue precipitate was collected by filtration, washed with ethanol (2 × 2 cm³) and dried under vacuum. Yield = 90% (51 mg); mp 223 °C. IR (cm⁻¹): ν(Re = O) 940; ν(Re-N) 523, 511; ν(Re-O) 441; ν(Re-Cl) 322.

X-ray Structure Determination. Data collection was performed at 200 K on a Nonius Kappa CCD using Mo Kα radiation. Nonhydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealized and fixed. Due to twinned crystals in **4** only the Re, Cl(1), Cl(2), O(1) and O(2) were refined anisotropically. Structural refinements were carried out by the full-matrix least-squares method on *F*² using the program SHELXL-97.⁹ The crystal data and details of the structure determinations are given in Table 1.

3. Results and Discussion

Structure of [ReOCl₂(OEt)(DPA)]. The rhenium atom (Figure 1) is at the centre of a distorted octahedral environment. The basal plane is defined by a N₂Cl₂ donor set. The ethoxide ion and the oxo group are in *trans* axial positions. Distortion from an ideal rhenium centred octahedron mainly result in a nonlinear O(1) = Re-O(2) axis of 169.6(2)°, accomplished by N(1)-Re-Cl(2) and N(3)-Re-Cl(1) angles of 175.6(2)° and 179.0(2)° respectively. The rhenium atom is lifted out of the mean equatorial plane by 0.0488(1) Å towards O(1), which is the result of the nonorthogonal angles O(1)-Re-N(1) = 87.9(3)°, O(1)-Re-N(3) = 85.7(2)°, O(1)-Re-Cl(1) = 95.1(2)° and O(1)-Re-Cl(2) = 96.0(2)°. The pyridine rings of DPA are “flapped”

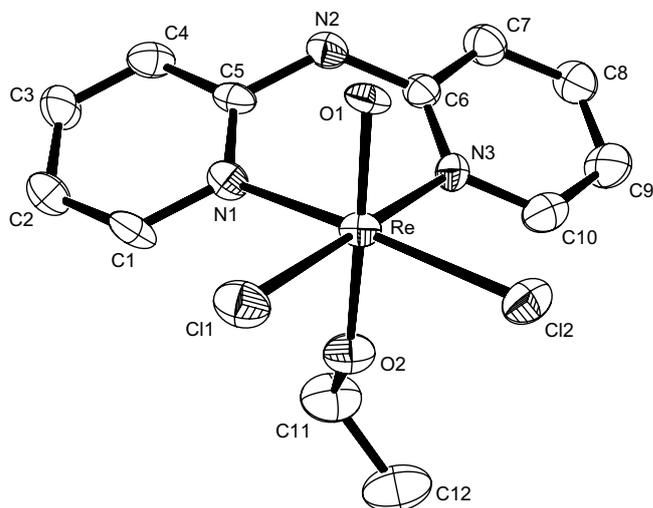


Figure 1. An ORTEP view of the structure of **1**, showing the atom labelling scheme and thermal ellipsoids drawn at the 40% probability level (Re-O(1) = 1.690(5), Re-O(2) = 1.866(5), Re-N(1) = 2.131(4), Re-N(3) = 2.156(7), Re-Cl(1) = 2.384(2), Re-Cl(2) = 2.408(2), O(2)-C(11) = 1.430(9); O(1)-Re-O(2) = 169.6(2), N(1)-Re-N(3) = 86.1(3), Cl(1)-Re-Cl(2) = 88.3(1), C(5)-N(2)-C(6) = 129.4(6)).

around N(2) away from O(1) towards O(2). The two rings make dihedral angles of 32.24° and 31.79° with the mean equatorial plane, and 30.25° with each other.

Structure of *trans*-[ReO₂(DPA)₂]Cl·3H₂O. The rhenium atom is at the centre of an octahedron with the equatorial plane formed by a N₄ pyridinic donor set (Figure 2). The two oxo groups are in *trans* positions relative to each other with the O(1)-Re-O(2) bond angle close to linearity at 179.2(1)°. The Re = O distances (1.762(3) Å average) and the Re-N distances (from 2.137(4) to 2.150(4) Å) lie in the range usually found in other *trans*-dioxo [ReO₂L₄]⁺ cations (where L = py¹⁰ or imidazole¹¹). The rhenium atom is coplanar with the four nitrogen donor atoms (it is 0.0086 Å out of the mean equatorial N₄ plane towards O(1)), with the result that the four O(1)-Re-N angles are all orthogonal (from 90.08(13)° to 90.45(13)°). The average bite angle of the two DPA ligands equals 83.80(15)° [N(1)-Re-N(3) = 83.95(15)°; N(4)-Re-N(6) = 83.64(15)°], which is larger than that of 2,2'-bipyridine (BIPY) in rhenium(V) complexes (~75°).¹²

Structures of (μ-O)[{ReOCl₂(DPA)}₂] (3a) and (μ-O)[{ReOCl₂(DPA)}₂]·2DMSO (3b·2DMSO). Complexes **3a**

TABLE 1: Crystal Data and Structure Refinement Details for 1, 2, 3a, 3b, 4 and 5

	1	2·3H₂O	3a	3b·2DMSO	4·Cl	5
Empirical Formula	C ₁₂ H ₁₄ N ₃ O ₂ Cl ₂ Re	C ₂₀ H ₂₄ ClN ₆ O ₃ Re	C ₂₀ H ₁₈ Cl ₄ N ₆ O ₃ Re ₂	C ₂₄ H ₃₀ Cl ₄ N ₆ O ₅ S ₂ Re ₂	C ₁₂ H ₁₄ N ₃ Cl ₂ O ₂ Re	C ₁₂ H ₁₁ N ₂ O ₂ Cl ₂ Re
Formula Weight	489.37	650.1	904.6	1060.9	489.37	472.34
Temperature (K)	200	200	200	200	200	200
Crystal System	Orthorhombic	Triclinic	Tetragonal	Triclinic	Monoclinic	Orthorhombic
Space group	<i>Pna</i> 2 ₁	<i>P</i>	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
Unit cell dimensions						
a (Å)	14.8212(4)	7.3141(3)	13.8640(6)	9.0089(11)	8.2765(4)	11.3582(9)
b (Å)	7.6036(2)	11.2706(4)	13.8640(6)	9.2570(11)	12.1139(9)	14.9274(12)
c (Å)	13.1638(4)	13.8906(6)	25.5319(17)	10.9635(14)	14.6718(8)	16.1135(13)
Volume (Å ³)	1483.5(1)	1112.7(1)	4907.5(4)	800.6(2)	1467.90(15)	2732.0(4)
Z	4	2	8	1	4	8
Density (calcd., Mg/m ⁻³)	2.191	1.940	2.449	2.200	2.214	2.297
Absorption coefficient (mm ⁻¹)	8.555	5.626	10.330	8.063	8.645	9.284
F(000)	928	636	3376	506	928	1776
Crystal Size (mm)	0.18 × 0.03 × 0.02	0.07 × 0.10 × 0.12	0.07 × 0.13 × 0.20	0.05 × 0.10 × 0.14	0.03 × 0.05 × 0.12	0.03 × 0.18 × 0.26
Theta min-max	3.15–25.01	3.2–27.4	2.6–28.0	2.0–28.1	2.2–24.0	2.5–24.0
R, wR2	0.0251, 0.0509	0.0367, 0.0756	0.0181, 0.0403	0.0272, 0.0591	0.0475, 0.1107	0.0285, 0.05

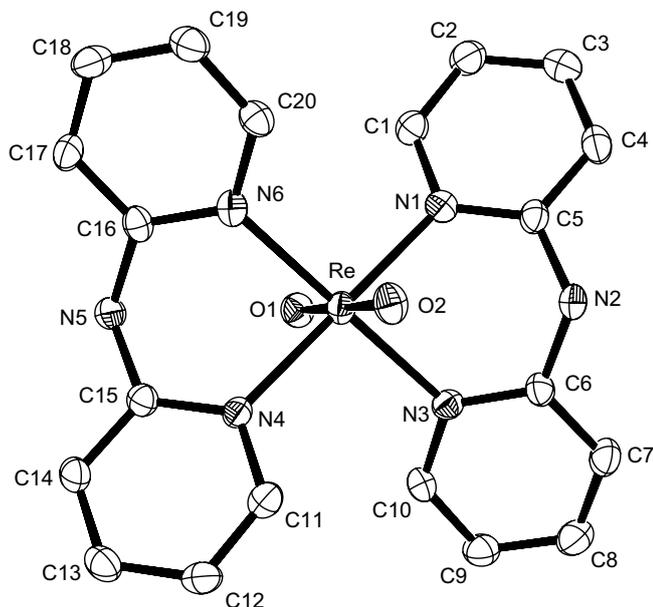


Figure 2. Molecular structure of **2** (Re-O(1) = 1.764(3), Re-O(2) = 1.760(3), Re-N(1) = 2.140(4), Re-N(3) = 2.150(4), Re-N(4) = 2.137(4), Re-N(6) = 2.137(4); O(1)-Re-O(2) = 179.2(1), O(1)-Re-N(1) = 90.1(1), O(1)-Re-N(6) = 90.5(1), C(5)-N(2)-C(6) = 126(1)).

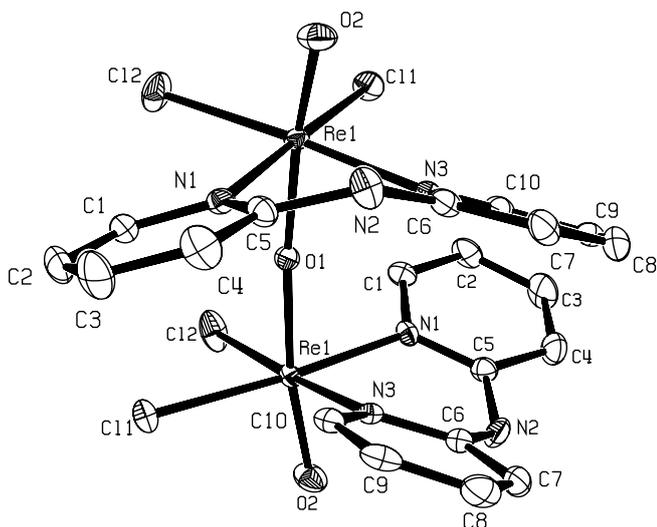


Figure 3. ORTEP view of the crystal structure of **3a** (Re-O(2) = 1.692(3), Re-O(1) = 1.9151(3), Re-Cl(1) = 2.398(1), Re-Cl(2) = 2.375(1), Re-N(1) = 2.127(3), Re-N(3) = 2.147(3); Re-O(1)-Re = 172.3(2), O(1)-Re-O(2) = 169.5(1), N(1)-Re-N(3) = 87.6(1)).

(Figure 3) and **3b**(Figure 4) each consists of two independent [ReOCl₂(DPA)] units bridged by an oxygen atom. In **3a**, the O = Re-O-Re = O backbone shows considerable deviation from linearity [O(2)-Re-O(1) = 169.5(1)°; Re-O(1)-Re = 172.3(2)°], with bending of the Re₂O₃ axis towards the two π -stacked pyridine rings coordinated *via* N(3). In **3b**, the bridging O(2) lies on a crystallographic inversion centre, making the Re-O-Re angle exactly 180°. The two O(1) = Re-O(2) angles are also equal at 171.1(1)°.

Each rhenium is centred in a distorted octahedron with the equatorial plane formed by a N₂Cl₂ donor set. The **3a** molecule adopts a conformation in which the ReN₂Cl₂ planes are mutually rotated by 61.42° about the Re₂O₃ axis, which, together with the bond along the Re-O-Re axis, allows the symmetry-related pyridine rings coordinated through N(3) on opposite sides of the molecule to interact at an average contact distance of 3.27 Å. The dihedral angle between the least-squares planes through these two stacked pyridine rings is 6.24°. In **3b** the ReN₂Cl₂ planes are mutually rotated by 180.0°, so that the chlorines of one ReON₂Cl₂ unit almost eclipse the nitrogen atoms of the other part of the molecule. The distances of the chlorine

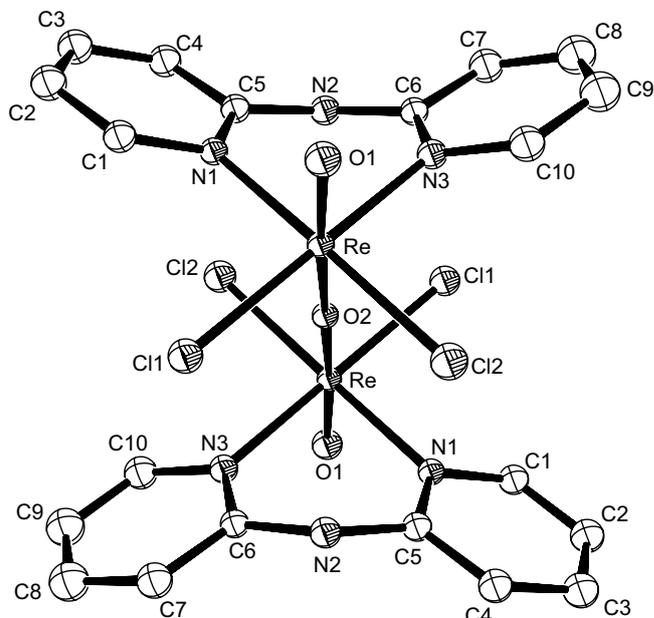


Figure 4. ORTEP plot of **3b** (Re-O(1) = 1.695(5), Re-O(2) = 1.9258(4) Re-N(1) = 2.127(4), Re-N(3) = 2.132(5), Re-Cl(1) = 2.380(2), Re-Cl(2) = 2.405(2); O(1)-Re-O(2) = 171.1(1), Re-O(2)-Re = 180.00, N(1)-Re-N(3) = 86.7(2)).

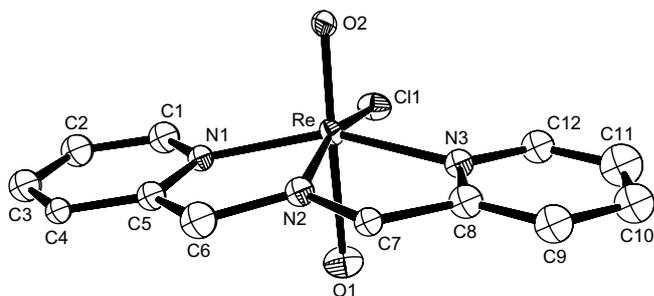


Figure 5. X-ray structure of **4** (Re-O(1) = 2.21(1), Re-O(2) = 1.663(9), Re-N(1) = 2.08(1), Re-N(2) = 1.89(1), Re-N(3) = 2.08(1), Re-Cl(1) = 2.462(3); O(1)-Re-O(2) = 167.2(4), N(1)-Re-N(3) = 153.9(4), O(2)-Re-N(1) = 99.0(5), C(6)-N(2)-Re = 118.3(9)).

atoms of one unit to the pyridine planes in the other unit are on average 3.080 Å, that is, about equal to the sum of the van der Waals radii.

In **3a**, the pyridine rings of each DPA ligand are “flapped” towards the bridging oxygen O(1). In contrast, the pyridine rings in **3b** are “flapped” towards the terminal oxo groups.

Structure of [ReOCl(OH₂)(DIPA)](4). The rhenium atom is at the centre of a distorted octahedron (Figure 5). The basal plane is defined by the two pyridyl nitrogen atoms N(1) and N(3), the deprotonated secondary amine nitrogen N(2) and the chloride Cl(1). The oxo group O(2) and the O(1) of the coordinated water molecule are in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a nonlinear O(1)-Re-O(2) axis of 167.2(4)°, accomplished by N(1)-Re-N(3) and Cl(1)-Re-N(2) angles of 153.9(4)° and 162.9(4)° respectively. The rhenium atom is lifted out of the mean equatorial N₂Cl plane by 0.34 Å towards O(2), which is the result of the nonorthogonal angles O(2)-Re-N(1) = 99.0(5)°, O(2)-Re-N(2) = 106.4(5)°, O(2)-Re-N(3) = 102.5(5)° and O(2)-Re-Cl(1) = 90.6(4)°. The Re-O(1) distance of 2.21(1) Å is within of the value of 2.23(2) Å found for water molecules bound *trans* to the oxo atom in [ReOCl₂(tu)(H₂O)]Cl and [ReOCl₃(tu)(H₂O)].^{13, 14} The short Re-N(2) bond length of 1.89(1) Å is considerably shorter than the average Re-NH lengths of 2.21(2) Å found in complexes containing ligands of the pyridylaminophenol type,⁵ and illustrates a significant multiple bond character.

Structure of [ReO(DPE.OH)Cl₂](5). The structure contains discrete, monomeric, neutral monooxorhenium(V) com-

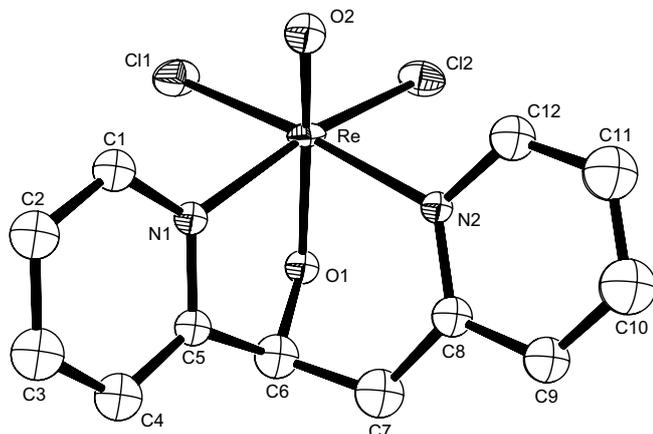


Figure 6. Molecular structure of **5** (Re-O(1) = 1.916(5), Re-O(2) = 1.694(5), Re-Cl(1) = 2.363(2), Re-Cl(2) = 2.351(2), Re-N(1) = 2.147(7), Re-N(2) = 2.168(6), O(1)-C(6) = 1.454(9); O(1)-Re-O(2) = 160.1(2), O(2)-Re-Cl(1) = 98.7(2), N(1)-Re-Cl(1) = 90.5(2), N(1)-Re-N(2) = 88.5(2), Cl(1)-Re-Cl(2) = 89.88(8), Re-O(1)-C(6) = 117.1(4)).

plex units, and the crystal packing is governed by van der Waals contacts. No intermolecular hydrogen bonds exist, and weak intramolecular hydrogen bonds are observed between C(1)H(1)⋯O(2) (2.947(9)Å) and C(12)H(12)⋯O(2) (2.85(1)Å). The DPE.OH moiety acts as a uninegative, terdentate NON donor ligand. Severe distortions from the ideal Re-centered octahedral configuration are as follows; (i) the Re atom lies out of the equatorial mean plane by 0.15 Å toward the oxo ligand; (ii) the nonlinear O(1)-Re-O(2) axis of 160.1(2)° is accomplished by Cl(1)-Re-N(2) and Cl(2)-Re-N(1) angles of 174.4(2)° and 170.0(2)°, respectively; (iii) the edge distances are observed in a rather narrow range (from 3.01 Å for N(1)⋯N(2) to 3.33 Å for Cl(1)⋯Cl(2)), and the interligand angles in the equatorial plane depart from the ideal 90° (from 86.5 to 93.4°); (iv) in the X₂N₂O₂ coordination polyhedron the Re atom is +1.02 Å away from the Cl(1)Cl(2)O(2) plane, and -1.35 Å from the N(1)N(2)O(1) one, the angle between the two triangles being 12.1°.

Bond lengths and angles in the complex show no unusual features, being within the range expected from the comparison of other six-coordinate monooxo complexes of Re(V).^{2, 3, 8-12}

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Supplementary Material. Full lists of crystallographic data are available from the authors upon request.

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