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SYNTHESIS OF A ‘4+1’ Re(V) COMPLEX FROM Re(III), AND ITS DISPROPORTIONATION TO Re(IV) AND Re(VII)

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ABSTRACT. The distorted octahedral oxorhenium(V) complex [ReOCl(had)] (**1**) (H_2had = N,N-*bis*(2-hydroxybenzyl)-2-(2-aminoethyl)dimethylamine) was prepared from the oxidation of [$ReCl_3(MeCN)(PPh_3)_2$] by dioxygen in the presence of H_2had in ethanol. This reaction was done under reflux conditions for a relatively short reaction time of an hour. However, increasing the reaction period to seven days led to the disproportionation of **1** to [$Re^{IV}Cl(had)(PPh_3)$]($Re^{VII}O_4$) (**2**). Both compounds were characterized by infra-red spectroscopy and X-ray crystallography.

KEY WORDS: Oxidation, Rhenium(III), Oxorhenium(V), Disproportionation, X-ray structures

INTRODUCTION

One approach to the consistent synthesis of oxorhenium(V) complexes is based on the ligation of dinegative tridentate chelates in combination with monodentate uninegative thiolates to give ‘3+1’ complexes with a square-pyramidal geometry [1-3]. However, these ‘3+1’ complexes are rather unstable [4]; the kinetic stability of ‘3+2’ six-coordinate oxorhenium(V) complexes is greater [5]. In addition, ‘2+2’ ligand combinations have also been exploited [6]. The syntheses of these ‘x+y’ oxorhenium(V) complexes have been achieved by the ligand substitution of the monodentate ligands in the common oxorhenium(V) starting materials like *trans*-[$ReOCl_3(PPh_3)_2$] and (n-Bu_4N)[$ReOCl_4$] by the multidentate chelates, and long reaction times up to 3 h were normally necessary to achieve acceptable yields.

In this report the concept of ligand permutation has been extended to ‘4+1’ complexes by using a dianionic, tetradentate N_2O_2-donor chelate around the oxorhenium(V) core. Several rhenium(V) complexes with tetradentate ligands have been described, with most of these ligands being of the Schiff base type [7-9]. However, we have synthesized the oxorhenium(V) complex [ReOCl(had)] by the reaction of the rhenium(III) starting material [$ReCl_3(MeCN)(PPh_3)_2$] with the tetradentate N_2O_2-donor ligand *N,N-bis*(2-hydroxybenzyl)-2-(2-aminoethyl)dimethyl-amine (H_2had) in the presence of oxygen with a relatively short reaction time of 30 min. However, if the reaction time is increased to 7 days, the rhenium(IV) complex salt [$ReCl(had)(PPh_3)$](ReO_4) was isolated.

EXPERIMENTAL

Materials

All chemicals were of reagent grade, and were purified by standard techniques. H_2had and *trans*-[$ReCl_3(MeCN)(PPh_3)_2$] were prepared by literature methods [10, 11].

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Physical measurements

^{1}H NMR spectra were recorded in DMSO-d_6 on a Bruker Avance (300 MHz) spectrometer at ambient temperatures, and values are reported relative to TMS. Infrared spectra were obtained with a Digilab FTS 3100 Excalibur HE spectrophotometer with solid samples prepared as KBr disks. Microanalyses were obtained on a Carlo Erba EA 1108 elemental analyser. Melting points were determined using an Electrothermal 1A9100 melting point apparatus. Conductivity measurements were carried out at 293 K on a Phillps PW 9509 digital conductometer.

Syntheses of the complexes

*[Re^{V}OCl(had)] (**1**)*

To a suspension of 144 mg of H$_2$had (479 μmol) in 5 mL of ethanol was added 204 mg of *trans*-[Re^{III}Cl$_3$(MeCN)(PPh$_3$)$_2$] (242 μmol) dissolved in 7 mL ethanol. The reaction mixture was heated under reflux in air for an hour, after which the dark green solution was cooled to room temperature and filtered. The slow evaporation of the filtrate in a desiccator over 2 days yielded green crystals that were suitable for X-ray crystallographic studies. The crystals were filtered off 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, 5.25. Found: C, 40.26; H, 4.43; N, 5.06. Infrared: ν(Re=O) 957(s); ν(C-O) 1257(s), 1276(s); ν(Re-O) 476(w), ν(Re-N) 501(m), ν(N-CH_3) 1290(s). ^{1}H NMR (DMSO-d_6, for numbering see Figure 1): 7.33 (m, 4H, H^4, H^6, H^{11}, H^{13}); 7.05 (d, 1H, H^7); 7.00 (t, 1H, H^5); 6.85 (t,1H, H^{12}); 6.76 (d, 1H, H^{14}); 5.23 (d, 1H, $H_A{}^1$); 4.38 (d, 1H, $H_B{}^1$); 4.18 (d, 1H, $H_A{}^8$); 3.96 (d, 1H, $H_B{}^8$); 3.49 (t, 2H, H^{15}); 3.30 (t, 2H, H^{16}); 3.06 (s, 3H, $^{17}CH_3$); 2.96 (s, 3H, $^{18}CH_3$). Electronic spectrum (λ_{max}, nm/ε, M^{-1}cm^{-1}): 603 (170), 333 (7900). Conductivity (10^{-3} M, CH$_3$CN): 17 ohm^{-1}cm^{2}mol^{-1}.

*[Re^{IV}Cl(had)(PPh$_3$)](ReO$_4$) (**2**)*

A mixture of *trans*-[ReCl$_3$(MeCN)(PPh$_3$)$_2$] (200 mg, 237 μmol) and H$_2$had (142 mg, 472 μmol) in 15 mL of ethanol was heated under reflux in air for 7 days, with the solution gradually changing colour to dark red. The solution was cooled to room temperature and filtered to give a dark red solution. Standing at room temperature for 3 days gave red crystals, which were collected by filtration. Yield = 69%, based on Re; m.p. > 300 ˚C. Anal. calcd. for $C_{36}H_{37}N_2O_6PRe_2$ (%): C, 41.88; H, 3.61; N, 2.71. Found: C, 41.85; H, 3.70; N, 2.68. M.p. 308 °C. Infrared: ν(ReO$_4^-$) 910(s), ν(C-O) 1242(s), 1255(s); ν(Re-O) 496(w), 480(w); ν(Re-N) 509(m), 525(m); ν(N-CH$_3$) 1243(s). Conductivity (DMF, 10^{-3} M): 70 ohm^{-1}cm^{2}mol^{-1}.

Crystallography

Diffraction data for [ReOCl(had)] and [ReCl(had)PPh$_3$](ReO$_4$) were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package [12]. The structures were solved by the direct methods program SIR92, which located all non-hydrogen atoms [13]. Subsequent full-matrix least-squares refinements were carried out using the CRYSTALS program suite [14]. Crystallographic data for **1**: $C_{18}H_{22}ClN_2O_3Re$, orthorhombic, $P2_12_12_1$, a = 7.2113(4) Å, b = 10.3811(5) Å, c = 24.509(1) Å, V = 1834.8(2) Å^3, Z = 4, μ = 6.788 mm^{-1}, F(000) = 1040, R(F) = 0.0303, Rw = 0.0549. For **2**: $C_{36}H_{37}ClN_2O_2Re.ReO_4$, monoclinic, $P2_1/c$, a = 17.2270(5) Å, b = 9.6870(2) Å, c = 21.6113(5) Å, β = 100.440(1)˚, V = 3546.8(2) Å^3, Z = 4, μ = 6.988 mm^{-1}, F(000) = 1988. Selected bond lengths and angles for **1** are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Re-O(1)	1.942(5)		Re-O(2)	1.988(5)
Re-O(3)	1.674(5)		Re-N(1)	2.173(5)
Re-Cl	2.364(2)		Re-N(2)	2.230(6)
C(3)-O(1)	1.355(1)		C(10)-O(2)	1.350(9)
N(1)-C(1)	1.504(9)		C(18)-N(2)	1.487(7)
Cl-Re-N(1)	175.09(2)		O(1)-Re-O(3)	166.4(3)
Cl-Re-N(2)	96.60(2)		O(2)-Re-O(3)	96.5(2)
O(2)-Re-N(2)	175.9(3)		O(3)-Re-N(1)	85.4(3)
N(1)-Re-N(2)	82.9(2)		O(3)-Re-N(2)	86.1(2)
Re-N(1)-C(8)	106.6(4)		Re-O(1)-C(3)	140.6(5)

RESULTS AND DISCUSSION

Synthesis

The reaction of *trans*-[$ReCl_3(MeCN)(PPh_3)_2$] with a twofold molar excess of H_2had in ethanol under reflux in air for an hour gave the green, six-coordinate complex [Re^{V}OCl(had)]. However, if the heating time was increased to 7 days, the product [$Re^{IV}Cl(had)(PPh_3)](ReO_4$) was obtained. With an equimolar ratio of reactants none of the complexes could be isolated. This result illustrates that oxorhenium(V) complexes can easily be prepared from rhenium(III) precursors in the presence of ligands and dioxygen, and that short reaction times are necessary to form products in good yields. Usually, if oxorhenium(V) complexes are synthesized from the ligand substitution of oxorhenium(V) starting materials, much longer reaction times (> 3 h) are necessary for reasonable yields. The effect of extremely long reaction times under reflux conditions on the formation of oxorhenium(V) complexes is also illustrated by the disproportionation to perrhenate and rhenium(IV) species, e.g. by the isolation of [$Re^{IV}Cl(had)(PPh_3)](ReO_4$) in this study.

Complex **1** could also be prepared from the rhenium(V) precursor *trans*-[$ReOCl_3(PPh_3)_2$] with a twofold molar excess of H_2had in ethanol, albeit with a longer reaction time of three hours, from the reaction of (*n*-$Bu_4N)[ReOCl_4$] with a twofold molar excess of H_2had in ethanol, or with equimolar quantities in the presence of triethylamine [15].

Repeated attempts to obtain crystals of **2** suitable for X-ray analysis were unsuccessful.

Complex **1** is diamagnetic (formally d^2) and is a non-electrolyte in acetonitrile. The conductivity of complex **2** in DMF confirms that it is a 1:1 electrolyte in solution. The complexes are weakly soluble, but stable, in polar solvents like DMSO, DMF, acetonitrile, acetone and chloroform. Both complexes are stable for months in the solid state and for days in solution without undergoing any decomposition or oxidation.

Spectral characterisation

In the infrared spectrum of **1** the asymmetric Re=O stretching frequency of 957 cm^{-1} appears as a sharp, strong band which falls in the region of 951-966 cm^{-1} that is normally observed for complexes with a phenoxy donor atom *trans* to the Re=O moiety [10, 16, 17]. The infrared spectrum of **2** provides evidence for the presence of the perrhenate anion, with the characteristic strong absorption band at 910 cm^{-1} ascribed to ν(Re=O) of ReO_4^-. 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) peaks at 1257 and 1276 cm^{-1}.

The ^{1}H NMR spectrum of **1** presents a pattern characteristic of diamagnetic species in solution and supports the arrangement of the tetradentate ligand around the rhenium(V) centre, with the signals of all the protons shifted downfield with respect to those of the free ligand. The paramagnetic nature of **2** (d^3) led to broad peaks in its spectrum, which made assignment of the signals impossible.

*Description of the structures. [ReOCl(had)] (**1**)*

The X-ray crystal structure of **1** (Figure 1) consists of a discrete, monomeric and neutral oxorhenium complex unit packed with no intermolecular contacts shorter than the sum of the Van der Waals radii. The coordination geometry around the rhenium is highly distorted octahedral. The two nitrogen atoms N(1) and N(2) from the tetradentate dinegative ligand lie on the equatorial plane, along with the chloride and phenolate O(2) atoms, with the phenolate O(1) *trans* to the O(3) oxo atom in axial positions. The chloride is coordinated *trans* to the tripodal N(1) atom. The O(1)-Re-O(3) axis is non-linear at 166.4(3)° and the rhenium atom is displaced from the mean equatorial plane by 0.0728(1) towards the oxo oxygen atom. For example, as a measure of the octahedral distortion in the ClN_2O_3 polyhedron, the Re atom is -1.23 Å from the N(2)N(1)O(3) plane and +1.20 Å from the Cl(1)O(2)O(1) one, the angle between the two triangular faces being 7.54°. The interligand angles in the equatorial planes depart considerably from the ideal of 90°, and vary from 82.9(2)° [N(1)-Re-N(2)] to 99.4(2)° [Cl-Re-O(3)].

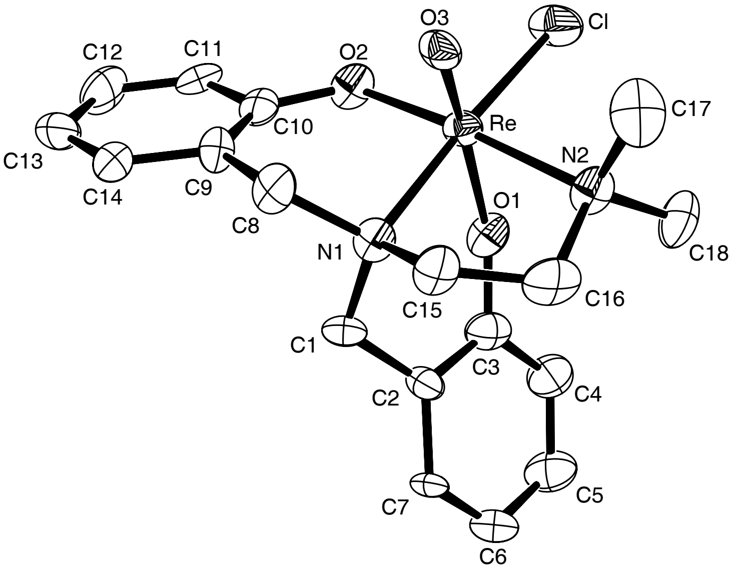

Figure 1. ORTEP view of complex **1**, showing the atom labelling. Hydrogen atoms have been omitted for clarity.

The Re=O(3) distance of 1.674(5) Å (Table 1) is similar to those reported previously [10,16,17]. The Re-O(1) bond length *trans* to the oxo oxygen O(3) is shorter than the equatorial Re-O(2) bond length [1.942(5) *vs* 1.988(5) Å]. This is in contrast with the complex [ReOCl(sal$_2$en)] (sal$_2$en = 1,3-*N,N'*-bis-(3,5-salicylideneimine)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 [10]. The Re-N(2) bond [2.230(6) Å] is significantly longer than the Re-N(1) bond [2.173(5) Å]. The bond angles around N(1) and N(2) are typical for sp^3 hybridized nitrogen atoms and are within the range expected from a comparison of other six-coordinate monooxorhenium(V) complexes containing the ClN_2O_3 donor set [10, 16, 17].

With the Schiff base ligands H_2salpd and H_2sal$_2$en (H_2L) complexes of the type [ReOCl(L)] were isolated, with a phenoxy oxygen coordinated *trans* to the oxo group [9, 10].

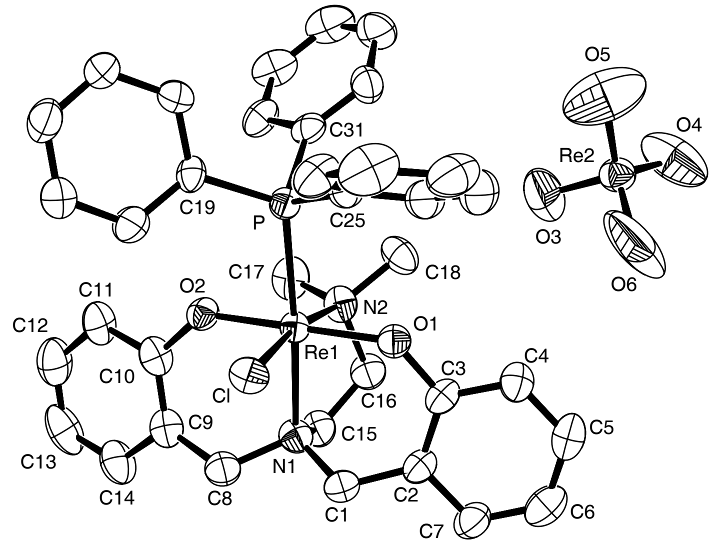

Figure 2. Molecular structure of compound **2**.

*[ReCl(had)(PPh$_3$)](ReO$_4$) (**2**)*

A perspective view of the asymmetric unit of $[ReCl(had)(PPh_3)]^+$ is shown in Figure 2. Refinement of the structure was compromised due to the poor crystal quality and high thermal motion. However, an acceptable data set could be obtained, and the connectivity and other general features of the structure were confidently determined, and the molecular positional parameters of the atoms in the “inner” core are well defined. The crystal structure consists of a mononuclear $[ReCl(had)(PPh_3)]^+$ cation and a perrhenate ion. The rhenium(IV) ion is in a distorted octahedral geometry. The basal plane is defined by the two phenolate oxygens of had [O(2) and O(1)], the chloride ion and the nitrogen N(2). The phosphorus atom of the PPh_3 group and the tertiary nitrogen N(1) are in *trans* axial positions. Distortion of an ideal rhenium-centred octahedron results in a non-linear O(1)-Re(1)-O(2) axis of 174.4° [175.9° for P-Re(1)-N(1) and Cl(1)-Re(1)-N(2) = 170.3°].

The Re-Cl distance of 2.37 Å deviates a little from previously observed bond distances in other rhenium(IV) complexes [18]. Distances of 2.308-2.356 Å have been reported in the literature for rhenium(V) complexes. Surprisingly, the Re(1)-N(1) distance is the same as the Re(1)-N(2) distance, despite the larger *trans* effect of the triphenylphosphine group. However, this may be an artefact, since the distances are derived from X-ray data of poor quality, so no definitive conclusions can be drawn.

The $[ReO_4]^-$ anion has a regular tetrahedral geometry, and it exhibits large thermal motions as shown by large thermal parameters of its oxygen atoms.

SUPPLEMENTARY DATA

CCDC 765690 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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