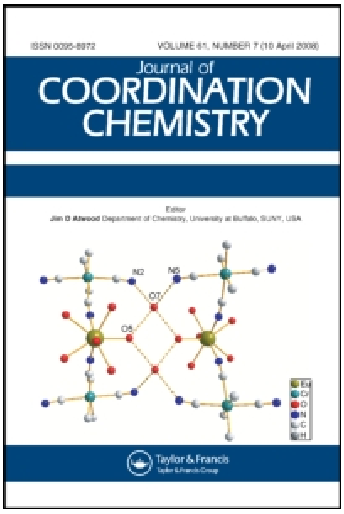

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Synthesis, characterization and structure of oxorhenium(V) complexes with 2-methylmercaptobenzamide

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The neutral, mononuclear complex [ReO(mta)$_2$Cl] (**1**) [Hmta = 2-(methylmercapto)aniline] was prepared by reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with a twofold molar excess of Hmta in methanol. The oxo-bridged dimer (μ-O)[ReO(mta)$_2$]$_2$ (**2**) was synthesized by reacting [ReOCl$_3$(PPh$_3$)$_2$] with a twofold excess of Hmta in a 9 : 1 acetone/water mixture. The compounds were characterized by spectroscopy and complex **1** also by X-ray crystallography. Complex **1** has a distorted octahedral geometry with the chloride coordinated *trans* to the oxo group, and with the chelating ligands in the equatorial plane in a *cis-N cis-S* configuration.

Keywords: Oxorhenium(V); Crystal structure; Thioether-amido coordination

1. Introduction

The design of rhenium complexes for possible therapeutic applications [1] is not only influenced by the nature of the ligands, but also by the positions of the donor atoms relative to each other in the coordination sphere. The coordination chemistry of rhenium(V) is dominated by the presence of the oxo (O^{2-}) group, which influences the nature of the donor atom in the coordination site *trans* to it because of its high *trans* influence. Although six-coordinate oxorhenium(V) complexes are most common, the square-pyramidal geometry (with the site *trans* to the oxo group vacant) has been found in many compounds [2–4].

The compound *trans*-[ReOCl$_3$(PPh$_3$)$_2$] has been used widely as a common starting material for the preparation of various oxorhenium(V) complexes [5–8]. One reason for its use is the easy substitution of the labile chloride *trans* to the oxo group. Thus there are few oxorhenium(V) complexes with chloride coordinated at this *trans* site. In fact, only certain types of donor atoms are preferred

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in the *trans* coordination position. Phenolate or alcoholate oxygens are by far the preferred donor atoms in this position, although aromatic and secondary amino nitrogens have also been found in a few examples [9–11]. This phenomenon is consistent with the principle of hard and soft acids and bases (HSAB) [12] as already applied to rhenium(V) complexes [13]. The repulsion exerted by the oxo oxygen on the equatorial ligands increases in the order $P < N(\text{imino}) < S^- < Cl^- < O^-$, an order which corresponds to that of increasing hardness of the ligand as a base. Increasing hardness of the base leads to increasing ionic character of its bond with the hard acid rhenium(V). This means that the affinity of the above groups to occupy the site *trans* to the oxo group in six-coordinate rhenium(V) complexes will be in the order $O^- > Cl^- > S^- > N > P$.

In this account we report the synthesis, characterization and X-ray crystal structure of the product obtained by the reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ and 2-(methylmercapto)aniline (Hmta). In the product, $[ReO(mta)_2Cl]$ (**1**), both mta ligands act as bidentate monoanionic chelates with coordination *via* the neutral sulfur atom and amido nitrogen in the equatorial plane *cis* to the oxo oxygen, with the chloride in the *trans* position. We have previously reacted *trans*-$[ReOCl_3(PPh_3)_2]$ with 2-aminothiophenol (H_2atp) to produce the oxo-free rhenium(V) complex $[ReCl(PPh_3)(atp)_2]$, in which atp is coordinated as a dianionic bidentate amidothiolate [5].

2. Experimental

Trans-$[ReOCl_3(PPh_3)_2]$ was prepared by a literature method [14]. The ligand 2-(methylmercapto)aniline (Hmta) was obtained commercially (Aldrich). Scientific instrumentation used is the same as reported previously [15]. IR spectra were obtained using KBr disks and ^1H NMR spectra were run in d_6-DMSO.

2.1. *Synthesis*

2.1.1. $[ReO(mta)_2Cl]$ (1). *Trans*-$[ReOCl_3(PPh_3)_2]$ (53 mg, 64 µmol) and 18 mg of Hmta (129 µmol) were dissolved in 15 cm^3 of a 1 M sodium acetate solution in methanol, and the mixture heated under reflux for 90 min. After heating was stopped, the solution was cooled to room temperature, and a brown precipitate was collected by filtration. The residue was washed with methanol and diethylether, and dried under vacuum. Slow evaporation of the mother liquor at room temperature overnight yielded a batch of brown crystals which were suitable for X-ray crystallographic studies. Yield = 25 mg (76%); m.p. 198°C. Anal. Calcd for $C_{14}H_{16}N_2S_2ClORe$ (%): C, 32.71; H, 3.14; N, 5.45. Found: C, 33.01; H, 2.96; N, 3.31. IR: ν(Re=O) 947(s); ν(N–H) 3059 (m); ν(Re–N) 522 (s); ν(Re–Cl) 303 (m). ^1H NMR (δ, ppm): 14.60 (br s, 1H, N*H*); 12.33 (br s, 1H, N*H*); 7.40 (d, 2H, *H*(3), *H*(10)); 7.18 (t, 2H, *H*(5), *H*(12)); 7.12 (d, 2H, *H*(6), *H*(13)); 7.01 (t, 2H, *H*(4), *H*(11)); 2.43 (s, 6H, *H*(7), *H*(14)).

2.1.2. (μ-O)$[ReO(mta)_2]_2$ (2). Some 27 mg of Hmta (190 µmol), dissolved in 5 cm^3 of acetone, was added to 78 mg (94 µmol) of *trans*-$[ReOCl_3(PPh_3)_2]$ in 10 cm^3 of a 9 : 1 acetone/water mixture. The mixture was heated under reflux for 2 h, during which time the green solution changed to blue. The solution was cooled to room temperature and the blue precipitate that formed collected by vacuum filtration. The product was washed with water and acetone, and dried under vacuum. Recrystallization was effected from a CH_3CN/acetone (1 : 1) mixture. Yield = 61% (based on Re), m.p. > 360°C. Anal. Calcd for $C_{28}H_{32}N_4S_4O_3Re_2$ (%): C, 34.56; H, 3.31; N, 5.76. Found: C, 34.29; H, 3.18; N, 5.53. IR: ν(NH) 3151 (m); ν(Re=O) 939 (m); ν(Re–O–Re) 708 (s); ν(Re–N) 529 (m). ^{1}H NMR (δ, ppm): 14.64 (br s, 1H, N*H*); 12.38 (br s, 1H, N*H*); 7.48 (d, 2H, *H*(3), *H*(10)); 7.24 (t, 2H, *H*(5), *H*(12)); 7.15 (d, 2H, *H*(6), *H*(13)); 6.98 (t, 2H, *H*(4), *H*(11)); 2.47 (s, 6H, *H*(7), *H*(14)).

2.2. *X-ray crystallography*

X-ray diffraction studies on crystals of **1** were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Further details are given in table 1, with selected bond lengths and angles in table 2. The structure was solved by direct methods [16]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Structural refinement was made by full-matrix least-squares methods on F^2 using SHELXL97 [17].

Table 1. Crystal data and structure refinement details for **1**.

Empirical formula	$C_{14}H_{16}N_2S_2ClORe$
Formula weight	514.08
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	$a = 6.7124(1)$ $b = 11.0819(2)$ $c = 22.1217(3)$
Volume (Å^3)	1645.55(4)
Z	4
Density (Calcd) (Mg m^{-3})	2.075
Absorption coefficient (mm^{-1})	7.799
$F(000)$	984
Crystal size (mm^3)	0.02 × 0.04 × 0.15
θ range (°)	3.2–27.5
Limiting indices	$-8 \le h \le 8$, $-13 \le k \le 14$, $-28 \le l \le 28$
Reflections collected/unique	20624/3751 [R(int) = 0.070]
Observed data [$I > 2\sigma(I)$]	3655
Data/parameters	3751/198
Goodness-of-fit on F^2	1.04
Final R indices	0.0241 ($wR_2 = 0.0541$)
Largest diff. peak/hole (e Å^{-3})	0.68/−1.15

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**.

Re–O	1.711(4)	Re–Cl	2.473(1)
Re–S(1)	2.503(1)	Re–S(2)	2.497(1)
Re–N(1)	1.949(4)	Re–N(2)	1.954(4)
S(1)–C(1)	1.780(5)	N(1)–C(2)	1.390(6)
S(1)–C(7)	1.818(6)	S(2)–C(14)	1.814(5)
O–Re–Cl	158.4(1)	O–Re–N(1)	105.6(2)
O–Re–S(1)	89.5(1)	O–Re–N(2)	105.2(2)
O–Re–S(2)	91.1(1)	N(1)–Re–S(1)	81.1(1)
C(7)–S(1)–C(1)	100.5(2)	N(2)–Re–S(2)	81.4(1)
S(1)–Re–N(2)	164.5(1)	N(1)–Re–S(2)	162.7(1)

3. Results and discussion

3.1. *Synthesis*

Treatment of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with Hmta in the presence of sodium acetate in methanol gave a red-brown solution, from which a brown powder was first precipitated. Slow evaporation of the mother liquor gave another batch of brown crystals. Elemental analysis, spectroscopic and X-ray crystallographic data identified the product as the oxorhenium complex [ReO(mta)$_2$Cl] (**1**), whose formation is given by the following equation:

$$\left[\mathrm{ReOCl_3(PPh_3)_2}\right] + 2\mathrm{Hmta} \rightarrow \mathbf{1} + 2\mathrm{PPh_3} + 2\mathrm{HCl}$$

The complex (μ-O)[ReO(mta)$_2$]$_2$ (**2**) was synthesized by reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_3$] with a two-fold molar excess of Hmta in acetone containing water,

$$2\left[\mathrm{ReOCl_3(PPh_3)_2}\right] + 4\mathrm{Hmta} + \mathrm{H_2O} \rightarrow \mathbf{2} + 4\mathrm{PPh_3} + 6\mathrm{HCl}$$

Complex **1** can be converted to **2** by the addition of a few drops of a 1 M aqueous ammonia solution to a suspension of **1** in water. Complex **2** can be converted to **1** by adding a few drops of a 1 M aqueous hydrochloric acid solution to a suspension of **2** in ethanol. Both complexes are diamagnetic (formally d^2) and are non-electrolytes in DMF. They are weakly soluble, but stable, in polar solvents such as chloroform, DMF, acetonitrile and DMSO.

3.2. *Spectroscopic characterization*

In the IR spectrum of **1** there is a strong absorption at 947 cm^{-1}, assigned to the Re=O stretch. This is supported by the observation that monooxorhenium(V) complexes with a chloride *trans* to the oxo group have ν(Re=O) in the range 940–960 cm^{-1} [18]. The dominant feature of the spectrum of **2** is a strong and intense band at 708 cm^{-1}, ascribed to the asymmetric Re–O–Re stretching mode [19]. The ν(Re=O) stretch is evidenced by a weak medium intensity band at 939 cm^{-1}. Absorption bands of medium intensity at 3059 and 3151 cm^{-1} in **1** and **2**, respectively, which are assigned to ν(N–H), verify that the amine nitrogen of mta has been deprotonated, and coordination of the amide is supported by the occurrence of Re–N stretching vibrations as strong bands at 522 (**1**) and 529 cm^{-1} (**2**). Coordination of the thioethereal sulfur is indicated by the lowering of the asymmetric C–S–C stretching mode from 1291 cm^{-1} in the free ligand to 1272 and 1271 cm^{-1} in the complexes. The Re–Cl stretch of **1** appears at 303 cm^{-1}, is typical of a chloride coordinated *trans* position to the oxo group [18].

Complexes **1** and **2** show sharp, well-resolved peaks in their ^{1}H NMR spectra, and illustrate that the two mta ligands in **1** are magnetically equivalent, as are the four mta chelates in **2**. Only four signals are produced for the protons of the chelates, and they occur in the form of a doublet (around δ 7.40 ppm), triplet ($\sim$7.20 ppm), doublet ($\sim$7.15 ppm) and triplet ($\sim$7.10 ppm). The amido protons in each complex appear as two broad singlets, downfield around δ 14.60 and 12.35 ppm.

3.3. *Description of the structure of 1*

An ORTEP view of the asymmetric unit along with the atom numbering scheme is given in figure 1. The rhenium atom lies at the centre of a distorted octahedron. Each mta ligand chelates to the oxorhenium core through the amido nitrogen and neutral thioethereal sulfur atom to form an equatorial N_2S_2 plane. The coordination site *trans* to the oxo group is occupied by a chloride, which completes the six-coordinate arrangement of donor atoms. The arrangement of the donor atoms in the equatorial plane is *cis-S* and *cis-N*.

The rhenium(V) atom deviates from the mean equatorial plane by 0.283 Å towards the oxo oxygen. The deviation of rhenium from this plane results in O–Re–N bond angles close to 105°, with O–Re–S angles close to orthogonality (table 2). The O–Re–Cl angle deviates considerably from linearity at 158.4(1)°, the smallest ever found for complexes of this type [18]. Bite angles of the bidentate mta chelates (average 81.3(1)°) contribute considerably to the distortion of the complex. The Re–Cl bond, *trans* to the oxo oxygen, at 2.473(1) Å, is significantly longer than in complexes with the chloride *cis* to the oxo group [7, 20]. In addition, the Re–O distance of 1.711(4) Å is considerably longer than the range of 1.67–1.69 Å that is normally found for monooxorhenium(V) complexes in distorted octahedral environment [5–11]. However, the Re–N (average 1.952(4) Å) and Re–S (average 2.500(1) Å) bond distances are notably shorter than normally found for these type of bonds in oxorhenium(V) complexes [18–20]. Bond distances in the phenyl rings are normal with an average C–C distance of 1.39(1) Å. The coordinated mta chelates show very little deviation from planarity. For example, S(1)C(1)C(2)C(3) and S(1)C(1)C(6)C(5) torsion angles are 179.2(4) and −179.8(4)°, respectively, with the S(2)C(8)C(9)N(2) torsion angle equal to −2.4(6)°.

Although oxorhenium(V) complexes like **1** and **2** (containing an amide and neutral thioethereal sulfur atom as donor atoms) are rare, many examples containing neutral amine and thiolato donor atoms exist [21, 22]. It was shown that the latter examples adopt a five-coordinate square-pyramidal geometry with *cis-N cis-S* configuration in the basal plane. Five-coordinate oxorhenium(V) complexes with a N_2S_2O donor set have also been prepared by using the bidentate *N*,*S*-thiolate

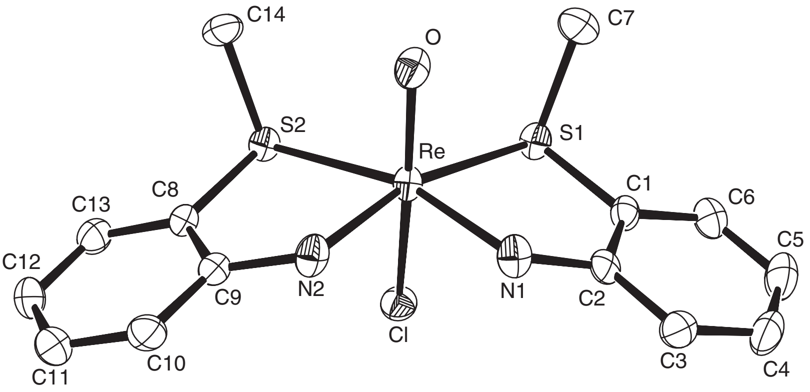

Figure 1. Molecular structure and atom numbering scheme for [ReO(mta)$_2$Cl] (**1**). Hydrogen atoms have been omitted for clarity.

ligands 1-(4′-methoxyphenyl)amino-2-methylpropane-2-thiolate and pyridine-2-methanethiolate; however, they form a basal plane with a *trans-N trans-S* configuration. Examples of six-coordinate oxorhenium(V) complexes with aminothiolate ligands are uncommon [23–24].

Supplementary data

CCDC-280121 contains crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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