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Note

# Synthesis and molecular structure of chloro(3-thiapentane-1,5-dithiolato)oxorhenium(V)

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# Abstract

Reaction of  $[BzEt_3N][ReOCl_4]$  (1) with 0.9 equiv. of 3-thiapentane-1,5-dithiol (HSSSH) in chloroform delivers [ReO(SSS)Cl] (2). The chloro ligand can be substituted by mercaptides when 2 is heated with an excess of a mercaptane, e.g.  $C_2H_5SH$ , in acetonitrile. Single crystal X-ray analysis of 2 shows square-pyramidal geometry.

Keywords: Rhenium complexes; Oxo complexes; Polydentate ligand complexes; Crystal structures

#### 1. Introduction

The '3+1' concept involves preparation of neutral technetium complexes with mixed tridentate dithiolate/ monodentate thiolate coordination [1,2] by common action of both types of thiol ligands on appropriate Tc(V) precursors. Recently we have applied this procedure to rhenium and used a large variety of monodentate ligands [3] as an access to neutral oxorhenium chelates with highly variable substituents. Using tetrachlorooxorhenate(V), [ReOCl<sub>4</sub>]<sup>-</sup>, as precursor and HS-CH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>2</sub>CH<sub>2</sub>-SH (HSSSH) as tridentate ligand in the reaction with monodentate thiols, formation of a light-blue by-product is observed. The same compound is obtained in high yields when the monodentate co-ligand is omitted and was found to be chloro(3-thiapentane-1,5-dithiolato)oxorhenium(V) [ReO(SSS)Cl]. We report on the formation and molecular structure of this compound as well as its reaction with ethanethiol.

#### 2. Experimental

# 2.1. General

3-Thiapentane-1,5-dithiol (Fluka) was used without further purification. Ammonium perrhenate was ob-

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tained from Aldrich.  $[BzEt_3N][ReOCl_4]$  was prepared according to Ref. [4] with some modifications.

# 2.2. Synthesis of $[BzEt_3N][ReOCl_4]$ (1)

Benzyltriethylammonium chloride (934 mg, 4.1 mmol; 1.1 equiv.) was added to a suspension of ammonium perrhenate (1 g, 3.73 mmol) in 50 ml ethanol. Dry HCl was passed through the suspension which changed into a clear deep orange solution. The addition of HCl was continued until the reaction mixture began to become turbid again. The solvent was removed by rotary evaporation and the residue dissolved in acetonitrile, filtered and the solvent removed again. The oily residue was dissolved in 5 ml ethanol. On slow addition of dry diethyl ether, the product was obtained as small lightorange needles. Yield 1.65 g (82.5%); m.p. 95–98 °C (dec.).

Anal. Calc. for  $C_{13}H_{22}NOCl_4Re: C, 29.11; H, 4.13;$ N, 2.61. Found: C, 29.30; H, 4.20; N, 2.39%. IR (KBr, cm<sup>-1</sup>): 1008 ( $\nu$ (Re=O)).

IR (KDI, CIII):  $1000 (\nu(Re=0))$ .

2.3. Synthesis of chloro(3-thiapentane-1,5dithiolato)oxorhenium(V) (2)

A solution of HSSSH (27.8 mg, 180  $\mu$ mol) in 5 ml chloroform was added over 15 min to a stirred and

cooled (0 °C) solution of 1 (107.3 mg, 200  $\mu$ mol) in 10 ml chloroform and 1 ml methanol. After stirring for a further 30 min, the solvent was removed by rotary evaporation. The residue was washed several times with chloroform giving a blue powder. The product was recrystallized from acetonitrile as dark-blue needles. Yield 48 mg (68% rel. to the ligand HSSSH); m.p. 221–223 °C (dec.).

Anal. Calc. for  $C_4H_8OS_3CIRe$ : C, 12.32; H, 2.07; S, 24.66; Cl, 9.09. Found: C, 12.40; H, 2.11; S, 24.43; Cl, 9.37%.

IR (KBr, cm<sup>-1</sup>): 968 ( $\nu$ (Re=O)).

UV–Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  (nm) (log  $\epsilon$ ): 572 (2.0), 348 (3.2), 258 (3.9), 232 (3.8).

<sup>1</sup>H NMR (CD<sub>3</sub>CN; ppm): 4.22 (m); 3.12–3.42 (m); 2.64 (m).

# 2.4. Synthesis of (ethanethiolato)(3-thiapentane-1,5-dithiolato)oxorhenium(V) (3)

400  $\mu$ l (5.4 mmol) ethanethiol were dropped into a refluxing solution of 33.9 mg (87  $\mu$ mol) of 2 in 5 ml acetonitrile. The mixture was refluxed for 10 min. The clear reddish-brown solution was evaporated to dryness and the residue was dissolved in chloroform and filtered. The product was purified by column chromatography onto silica gel 60 (0.063–0.1 mm) with chloroform as eluent. Only a small amount of material remained at the starting point. After addition of ethanol to the eluate and slow evaporation, brown needles were obtained. Yield 28.8 mg (80%); m.p. 163–165 °C (dec.).

*Anal* Calc. for C<sub>6</sub>H<sub>13</sub>OS<sub>4</sub>Re: C, 17.34; H, 3.15; S, 30.86. Found: C, 17.27; H, 3.11; S, 30.77%.

IR (KBr, cm<sup>-1</sup>): 962 ( $\nu$ (Re=O)).

# 2.5. Structure determination and crystal data

The X-ray data of 2 were collected at room temperature (294 K) on an Enraf-Nonius CAD 4 diffractometer, using graphite monochromatized Mo K $\alpha$ radiation ( $\lambda = 0.71069$  Å). A summary of the crystallographic data is given in Table 1. The positions of the non-hydrogen atoms were determined by the heavy atom technique. After anisotropic refinement of the positions of these, the hydrogen positions were calculated according to ideal geometries. Empirical absorption corrections with the program DIFABS [5] were made at two stages during structure refinement. Most of the calculations were carried out in the Enraf-Nonius SDP system with some local modifications. Selected bond lengths and angles are contained in Table 2. See also Section 5.

Table 1						
Crystallographic	data	for	[ReO	(SSS)	)CI]	(2)

Crystal data	
Empirical formula	C <sub>4</sub> H <sub>8</sub> ClOS <sub>3</sub> Re
Formula weight	389.95
Crystal system	orthorhombic
a (Å)	13.4244
b (Å)	6.3146
c (Å)	11.1339
α (°)	90
β (°)	90
γ (°)	90
V (Å <sup>3</sup> )	943.81
Space group, No.	Pca2 <sub>1</sub> ; 29
$Z; F(000); D_{calc}$	4, 720, 2.744
<i>T</i> (K)	294
Data collection	
Crystal size (mm)	$0.07 \times 0.18 \times 1.08$
λ (Mo Kα) (Å)	0.71069
$\mu  (\rm cm^{-1})$	139.13
Data sphere (°)	$1.5 \leq \theta \leq 28$
Scan mode	2 θ/ω
Scan rate (° min)	2.4-4.8 variable
Miller index range	h 0–14
	k 0-8
	1 0-17
Unique reflections measured	1345
Unique reflections used $(I_0 \ge 3\sigma(I))$	1117
Check reflections: intensity	4 0 4; 6 0 0
orientation	4 2 4; 4 0 6; 3 0 4
Absorption corrections	yes
$R = \Sigma[ F_{\rm o}  -  F_{\rm c} ] / \Sigma  F_{\rm o} $	0.04

Table 2

Selected bond lengths and angles for [ReO(SSS)Cl] (2)

Bond lengths	(Å)		
Re=O	1.74(2)	Re-S1	2.257(5)
ReCl	2.397(6)	Re-S2	2.269(5)
		Re-S3	2.245(5)
Bond angles (	°)		
O-Re-Cl	100.9(5)	Cl-Re-S2	157.7(2)
O-Re-S1	111.9(5)	Cl-Re-S3	84.5(2)
O-Re-S2	101.3(5)	S1-Re-S2	87.4(2)
O-Re-S3	115.0(5)	S1-Re-S3	132.9(2)
Cl-Re-S1	83.0(2)	S2–Re–S3	87.4(2)

#### 3. Results and discussion

When  $[\text{ReOCl}_4]^-$  (1) reacts with 0.9 equiv. HSSSH, a light-blue product 2 can be isolated (Fig. 1, reaction a). This compound was already observed [3] as a byproduct when a mixture of equivalent amounts of HSSSH and a monodentate co-ligand was dropped into a solution of  $[\text{ReOCl}_4]^-$  (reaction c). The yield of the by-product in the course of those reactions ranges up to 20% of the rhenium involved.

An excess of the tridentate ligand in the absence of the monothiol leads to a brown oily compound instead



Fig. 1. Reaction scheme for the preparation of complexes [ReO(SSS)CI] (2) and [ReO(SSS)(SR)] (3).

of 2. This should be a binuclear complex, the technetium analogue of which was described in Ref. [1]. However, the rhenium complex is not yet fully characterized.

The complex [ReO(SOS)Cl] derived from the oxygen analogous tridentate ligand HS- $CH_2CH_2-O-CH_2C$ - $H_2$ -SH, has not yet been isolated. Immediately after addition of the ligand to the precursor 1, a blue colour is observed but after about 10 s a chlorine-free reddishbrown precipitate is formed, which is insoluble in acetonitrile.

According to the elemental analysis, complex 2 was found to be chloro(3-thiapentane-1,5-dithiolato)oxorhenium(V) [ReO(SSS)Cl]. Its IR spectrum exhibits the known strong Re=O valence band at  $\nu = 968 \text{ cm}^{-1}$ . The electron impact mass spectrum shows the molecular peak at m/z = 390. Further peaks of interest are observed at m/z = 362 ( $M - (C_2H_4)$ ), m/z = 334 ( $M - 2 \times (C_2H_4)$ ), m/z = 302 and 270 ( $M - S(C_2H_4)_2$  and  $M - 2 \times (SC_2H_4)$ , respectively).

Compound 2 is soluble in acetonitrile, acetone and dimethyl sulfoxide and insoluble in non-polar solvents and water. Dark-blue needle-shaped crystals suitable for X-ray structure analysis were obtained on slow evaporation of its acetonitrile solution.

Whereas  $[\text{ReOCl}_4]^-$  is highly reactive and very sensitive to hydrolysis, the coordinated chlorine in 2 has a significantly lower tendency to undergo exchange reactions. The metal-chlorine bond is even stable to boiling water. However, the chlorine can be substituted by thiol ligands (RSH) as demonstrated for ethyl mercaptane (R = ethyl, reaction b in Fig. 1).

The exchange did not proceed upon standing for several days at room temperature in acetonitrile solution but was complete with clean conversion to [ReO(SSS)(SEt)] (3) (R = Et) after briefly heating of 1 with an excess of the mercaptane. Under these conditions, several thiol compounds react in an analogous manner to give the mixed ligand complexes [ReO(SSS)(SR)]. Since this ligand exchange is a more selective reaction, the overall yield of [ReO(SSS)(SR)], based on  $[ReOCl_4]^-$ , is generally higher than that in the 'one-pot' reaction [3].

Oxotechnetium(V) and oxorhenium(V) complexes of the general formula [MO(L)Cl] ( $H_2L=N$ -salicylidene-2-aminobenzenethiol) showing similar reactivities of the M-Cl bond have been described earlier [6]. Recently we found thioether complexes, [(MO(R-S-CH<sub>2</sub>-C-H<sub>2</sub>-S-R)Cl<sub>2</sub>)<sub>2</sub>O], (M=Tc, Re) with further enhanced stability of the M-Cl bond [7].

# 3.1. Crystal structure of chloro(3-thiapentane-1,5dithiolato)oxorhenium(V) (Fig. 2)

The X-ray crystal structure analysis of 2 shows squarepyramidal geometry. The structure consists of the tridentate HSSSH ligand coordinated through two thiolate sulfur atoms and a thioether sulfur in the equatorial positions, a chlorine ligand in the remaining equatorial position and the oxo ligand in the axial position. This is one of the rare examples of a tridentate ligand in the oxorhenium(V) series. Furthermore, it is one of the first reports [9] on the X-ray crystal structure of an oxorhenium(V) complex in which a thioether is involved in coordination. The Re=O bond length is found to be 1.74 Å. This value is remarkably longer than that observed for the fourfold sulfur-coordinated (ethanethiolato)(3-thiapentane-1,5-dithiolato)oxorhenium(V) (1.66 Å) containing the same tridentate ligand [8] and in  $[ReO(SOS)(SC_6H_4-OMe(p))]$  [3], but also than that in  $[ReOCl_4]^-$ , (1.63 [4a] and 1.65 [4b] Å for the AsPh<sub>4</sub> salt). The rhenium atom is situated 0.673 Å above the plane of the sulfur and chlorine atoms, while the corresponding value for  $[ReOCl_4]^-$  is 0.407 Å. The average Re– $S_{thiol}$  bond length is 2.251 Å, while the Re- $S_{\text{thioether}}$  bond is, as expected, longer (2.363 Å). Structural characteristics of further rhenium thioether complexes will be discussed in Ref. [8].



Fig. 2. ORTEP drawing of chloro(3-thiapentane-1,5-dithiolato)oxorhenium(V) (2). Ellipsoids correspond to 50% probability.

## 4. Conclusions

The stability of the easily accessible complex 2 enables transformation of the normal one-pot 3+1 reaction into a two-step one. This may become important when the reactivities of the tridentate and monodentate ligands differ too much to guarantee a simultaneous attack of the ligands on the precursor. 2 can serve as a precursor to bind a variety of less reactive and more complicated monodentate thiolate ligands to rhenium, thus offering promising potentials for designing new bifunctional rhenium tracers.

## 5. Supplementary material

Additional X-ray structure data (atomic positional parameters, thermal parameters, full lists of bond lengths and angles, and  $F_o/F_c$  values) can be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, quoting CSD No. 401490, the authors' names as well as the title of the paper.

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